CHIMIE ORGANIQUE

SOLUTIONS DÉTAILLÉES

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1 CARBON COMPOUNDS AND CHEMICAL BONDS

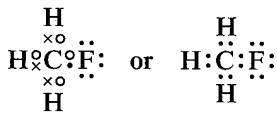
SOLUTIONS TO PROBLEMS

Another Approach to Writing Lewis Structures

When we write Lewis structures using this method, we assemble the molecule or ion from the constituent atoms showing only the valence electrons (i.e., the electrons of the outermost shell). By having the atoms share electrons, we try to give each atom the electronic structure of a noble gas. For example, we give hydrogen atoms two electrons because this gives them the structure of helium. We give carbon, nitrogen, oxygen, and fluorine atoms eight electrons because this gives them the electronic structure of neon. The number of valence electrons of an atom can be obtained from the periodic table because it is equal to the group number of the atom. Carbon, for example, is in group 4A and has four valence electrons; fluorine, in group 7A, has seven; hydrogen, in group 1A, has one. As an illustration, let us write the Lewis structure for CH_3F. In the example below, we will at first show a hydrogen's electron as x, carbon's electrons as o's, and fluorine's electrons as dots.

Example A

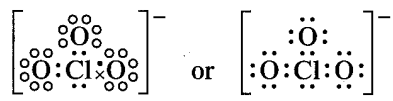
3 H×, ∘C∘, and ·F: are assembled as



If the structure is an ion, we add or subtract electrons to give it the proper charge. As an example, consider the chlorate ion, ClO_3^-.

Example B

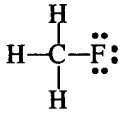
:Cl·, and O and an extra electron × are assembled as

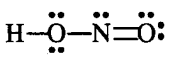


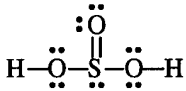
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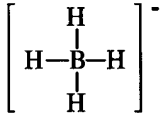
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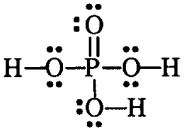
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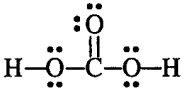
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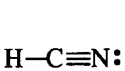
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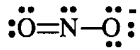
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(f) 

(g) 

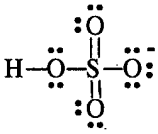
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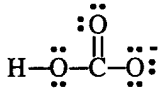
(i) 

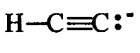
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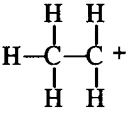
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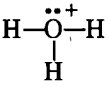
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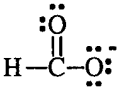
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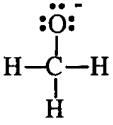
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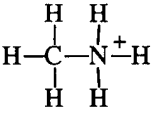
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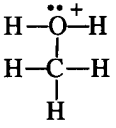
1.3 (a) 

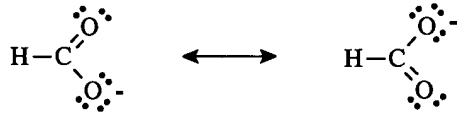
(b) 

(c) 

(d) 

(e) 

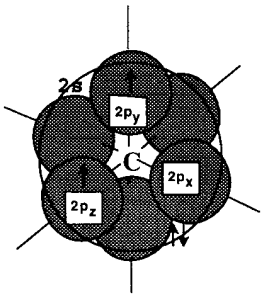
(f) 

1.4 (a) 

(b) and (c). Since the two resonance structures are equivalent, each should make an equal contribution to the overall hybrid. The C—O bonds should therefore be of equal length (they should be of bond order 1.5), and each oxygen atom should bear a 0.5 negative charge.

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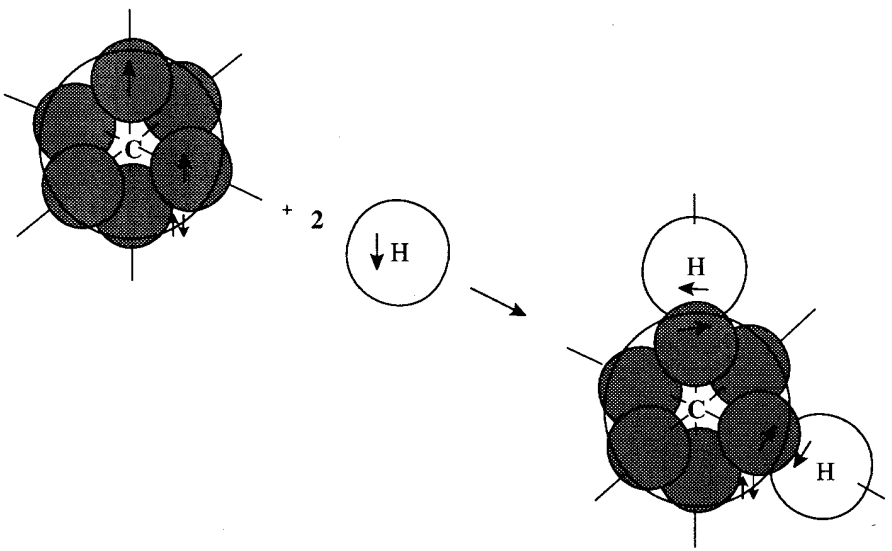
1.5 (a) In its ground state, the valence electrons of carbon might be disposed as shown in the following figure.



The electronic configuration of a ground state carbon atom. The p orbitals are designated $2p_x$, $2p_y$, and $2p_z$ to indicate their respective orientations along the x, y, and z axes. The assignment of the unpaired electrons to the $2p_y$ and $2p_x$ orbitals is arbitrary. They could also have been placed in the $2p_x$ and $2p_z$ or $2p_y$ and $2p_z$ orbitals. (To have placed them both in the same orbital would not have been correct, however, for this would have violated Hund's rule.) (Section 1.10.)

The formation of the covalent bonds of methane *from individual atoms* requires that the carbon atom overlap its orbitals containing *single electrons* with 1*s* orbitals of hydrogen atoms (which also contain a single electron). If a ground state carbon atom were to combine with hydrogen atoms in this way, the result would be that depicted below. *Only two carbon-hydrogen bonds would be formed, and these would be at right angles to each other.*

The hypothetical formation of CH_2 from a carbon atom in its ground state.



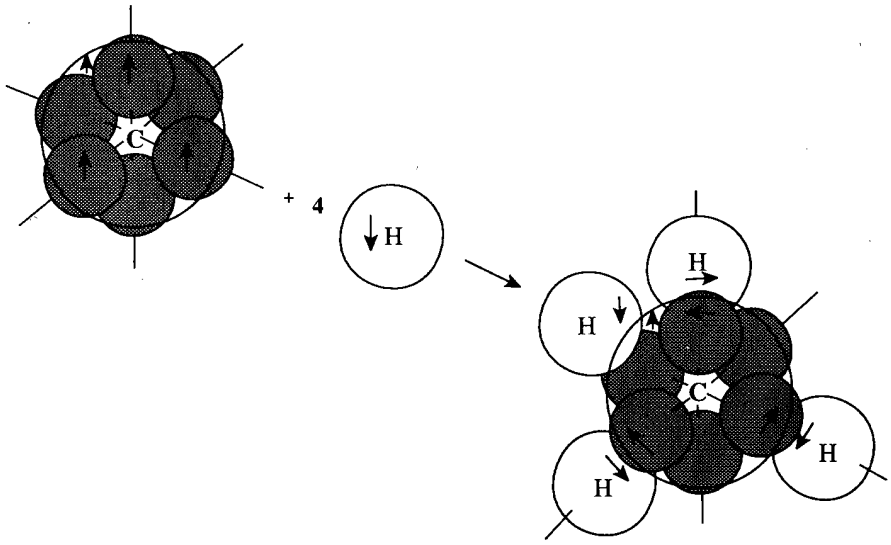
(b) An excited-state carbon atom might combine with four hydrogen atoms as shown in the figure above.

The promotion of an electron from the 2*s* orbital to the $2p_z$ orbital requires energy. The amount of energy required has been determined and is equal to 400 kJ mol^{-1}. This expenditure of energy can be rationalized by arguing that the energy released when two additional covalent bonds form would more than compensate for that required to excite the electron. No doubt this is true, but it solves only one problem. The problems that cannot be solved by using an excited-state carbon as a basis for a model of methane are the problems of the carbon-hydrogen bond angles and the apparent equivalence of

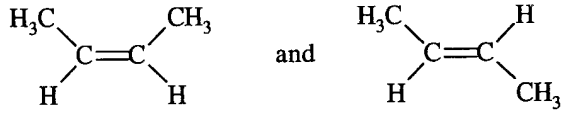
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all four carbon-hydrogen bonds. Three of the hydrogens—those overlapping their 1*s* orbitals with the three *p* orbitals—would, in this model, be at angles of 90° with respect to each other; the fourth hydrogen, the one overlapping its 1*s* orbital with the 2*s* orbital of carbon, would be at some other angle, probably as far from the other bonds as the confines of the molecule would allow. Basing our model of methane on this excited state of carbon gives us a carbon that is tetravalent *but one that is not tetrahedral,* and it predicts a structure for methane in which one carbon-hydrogen bond differs from the other three.

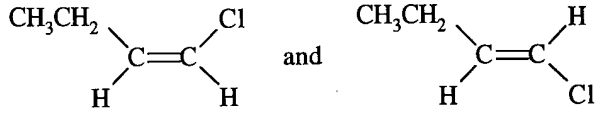
The hypothetical formation of CH_4 from an excited-state carbon atom.



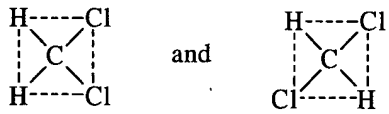
1.6 (a) Cis-trans isomers are not possible.

(b) 

(c) Cis-trans isomers are not possible.

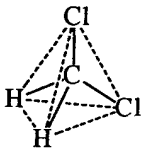
(d) 

1.7 If the geometry of the carbon atom were square planar, two isomeric compounds with the formula CH_2Cl_2 should exist.

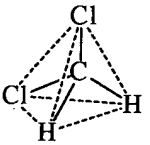


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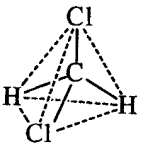
The fact that only one form of CH_2Cl_2 has ever been detected supports a tetrahedral geometry for carbon, because with a tetrahedral geometry only one compound with the formula CH_2Cl_2 is possible. All of the following structures are just different orientations of the same molecule.



is the same as



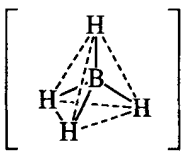
is the same as



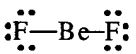
etc.

Make models to convince yourself of this fact.

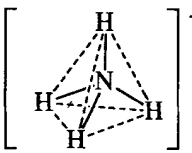
1.8 (a) There are four bonding pairs. The geometry is tetrahedral.



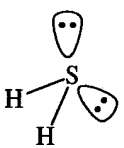
(b) There are two bonding pairs about the central atom. The geometry is linear.



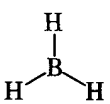
(c) There are four bonding pairs. The geometry is tetrahedral.



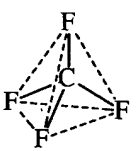
(d) There are two bonding pairs and two nonbonding pairs. The geometry is angular.



(e) There are three bonding pairs. The geometry is trigonal planar.

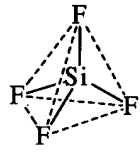


(f) There are four bonding pairs around the central atom. The geometry is tetrahedral.

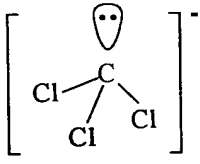


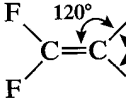
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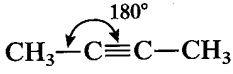
(g) There are four bonding pairs around the central atom. The geometry is tetrahedral.

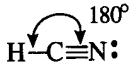


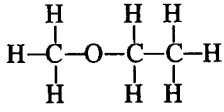
(h) There are three bonding pairs and one nonbonding pair around the central atom. The geometry is trigonal pyramidal.

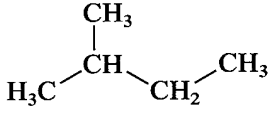
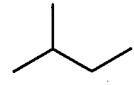


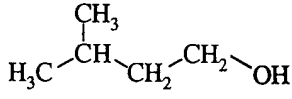
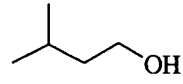
1.9 (a)  **, trigonal planar at each carbon atom.**

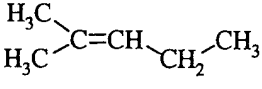
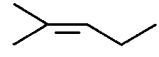
(b)  **linear**

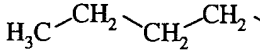
(c)  **linear**

1.10 

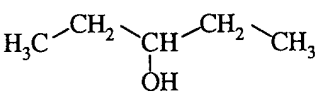
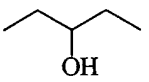
1.11 (a)  = 

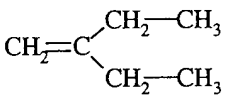
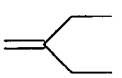
(b)  = 

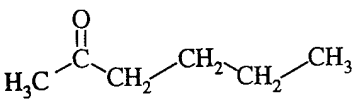
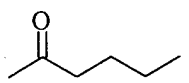
(c)  = 

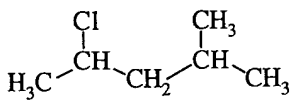
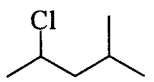
(d)  = 

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(e)  = 

(f)  = 

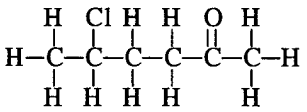
(g)  = 

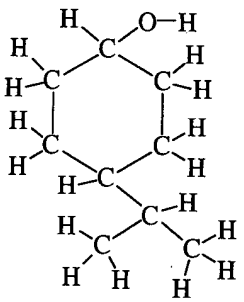
(h)  = 

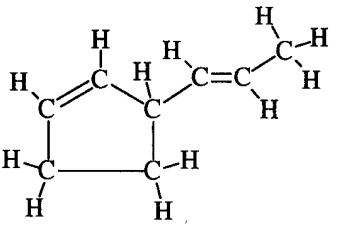
1.12 (a) and (d) are constitutional isomers with the molecular formula C_5H_{12}.

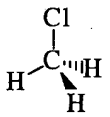
(b) and (e) are constitutional isomers with the molecular formula $C_5H_{12}O$.

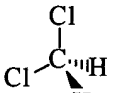
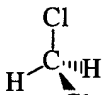
(c) and (f) are constitutional isomers with the molecular formula C_6H_{12}.

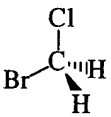
1.13 (a) 

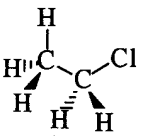
(b) 

(c) 

1.14 (a)  (Note that the **Cl** atom and the three **H** atoms may be written at any of the four positions.)

(b)  or  and so on

(c)  and others

(d)  and others

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1.15 (a) Na^+ has the electronic configuration, $1s^22s^22p^6$, of Ne.

(b) Cl^- has the electronic configuration, $1s^22s^22p^63s^23p^6$, of Ar.

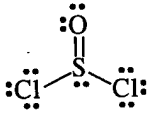
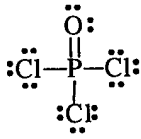
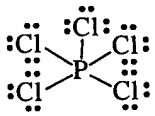
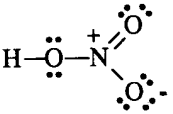
(c) F^+ and (h) Br^+ do not have the electronic configuration of a noble gas.

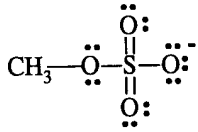
(d) H^- has the electronic configuration, $1s^2$, of He.

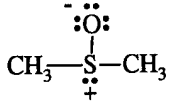
(e) Ca^{2+} has the electronic configuration, $1s^22s^22p^63s^23p^6$ of Ar.

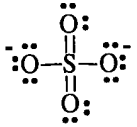
(f) S^{2-} has the electronic configuration, $1s^22s^22p^63s^23p^6$ of Ar.

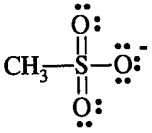
(g) O^{2-} has the electronic configuration, $1s^22s^22p^6$ of Ne.

1.16 (a)  (b)  (c)  (d) 

1.17 (a) 

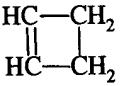
(b) 

(c) 

(d) 

1.18 (a) $(CH_3)_2CHCH_2OH$

(b) $(CH_3)_2CHC(=O)CH(CH_3)_2$

(c) 

(d) $(CH_3)_2CHCH_2CH_2OH$

1.19 (a) $C_4H_{10}0$

(b) $C_7H_{14}0$

(c) C_4H_6

(d) $C_5H_{12}0$

1.20 (a) Different compounds, not isomeric

(b) Constitutional isomers

(c) Same compound

(d) Same compound

(e) Same compound

(f) Constitutional isomers

(g) Different compounds, not isomeric

(h) Same compound

(i) Different compounds, not isomeric

(j) Same compound

(k) Constitutional isomers

(l) Different compounds, not isomeric

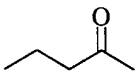
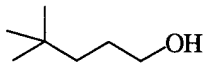
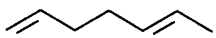
(m) Same compound

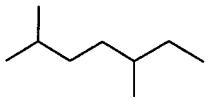
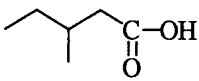
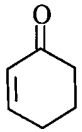
(n) Same compound

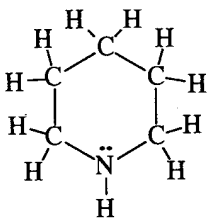
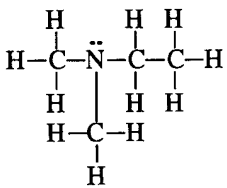
(o) Same compound

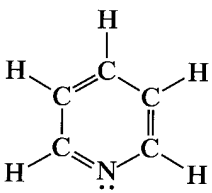
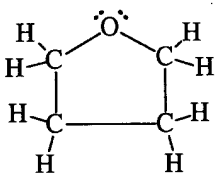
(p) Constitutional isomers

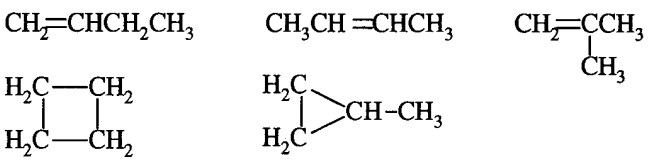
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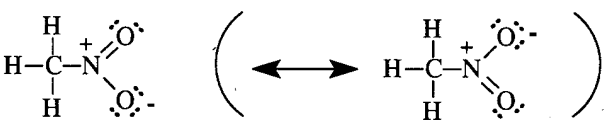
1.21 (a)  (c)  (e) 

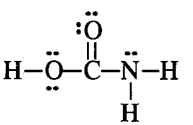
(b)  (d)  (f) 

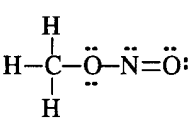
1.22 (a)  (c) 

(b)  (d) 

1.23 

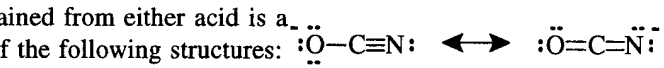
1.24 





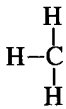
(Other structures are possible.)

*1.25 (a) While the structures differ in the position of their electrons, they also differ in the positions of their nuclei and thus *they are not resonance structures.* (In cyanic acid the hydrogen nucleus is bonded to oxygen; in isocyanic acid it is bonded to nitrogen.)

(b) The anion obtained from either acid is a resonance hybrid of the following structures: 

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1.26



(a) A + charge. ($F = 4 - \frac{1}{2} = +1$)

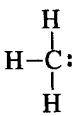
(b) A + charge. (It is called a methyl cation.)

(c) Trigonal planar, that is,



(d) sp^2

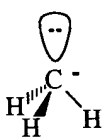
1.27



(a) A − charge. ($F = 4 - \frac{1}{2} - 2 = -1$)

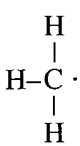
(b) A − charge. (It is called a methyl anion.)

(c) Trigonal pyramidal, that is



(d) sp^3

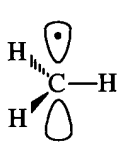
1.28



(a) No formal charge. ($F = 4 - \frac{1}{2} - 1 = 0$)

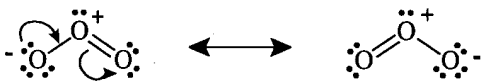
(b) No charge.

(c) sp^2, that is,



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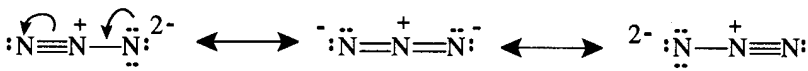
1.29 (a) and (b)



(c) Because the two resonance structures are equivalent, they should make equal contributions to the hybrid and, therefore, the bonds should be the same length.

(d) Yes. We consider the central atom to have two groups or units of bonding electrons and one unshared pair.

1.30

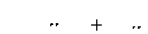


A **B** **C**

Structures **A** and **C** are equivalent and, therefore, make equal contributions to the hybrid. The bonds of the hybrid, therefore, have the same length.

***1.31** (a) constitutional isomers (b) the same
(c) resonance forms (d) constitutional isomers
(e) resonance forms (f) the same

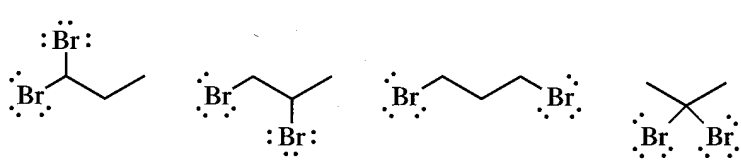
***1.32** (a)



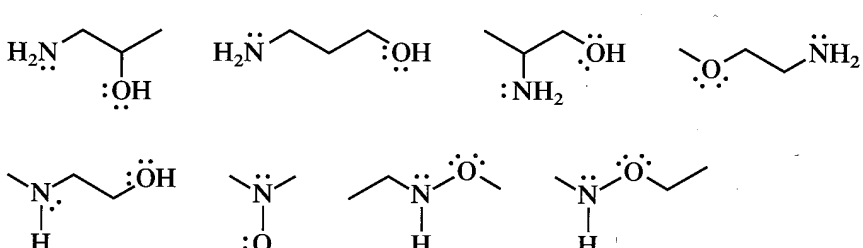
(b) Linear

(c) Carbon dioxide

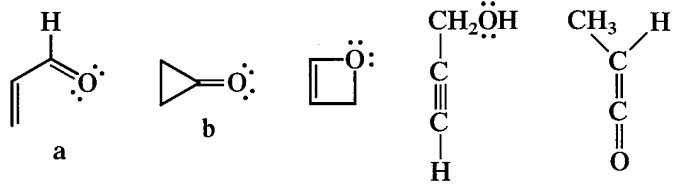
***1.33** Set A:



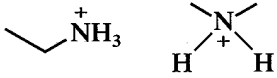
Set B:

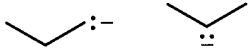


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Set C: 

[and unstable enol forms of a, b, and c]

Set D: 

Set E: 

(i.e., $CH_3CH_2\ddot{C}H_2^-$ and $CH_3\ddot{C}HCH_3$)

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2 REPRESENTATIVE CARBON COMPOUNDS: FUNCTIONAL GROUPS, INTERMOLECULAR FORCES, AND INFRARED (IR) SPECTROSCOPY

SOLUTIONS TO PROBLEMS

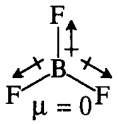
2.1 (a) H—F or $\overset{\delta+}{H}—\overset{\delta-}{F}$ (+ →)

(b) I—Br or $\overset{\delta+}{I}—\overset{\delta-}{Br}$ (+ →)

(c) Br—Br, $\mu = 0$

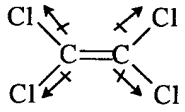
(d) F—F, $\mu = 0$

2.2 VSEPR theory predicts a planar structure for BF_3.

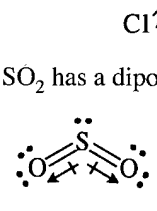


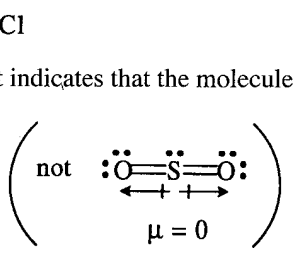
The vector sum of the bond moments of a trigonal planar structure would be zero, resulting in a prediction of $\mu = 0$ for BF_3. This correlates with the experimental observation and confirms the prediction of VSEPR theory.

2.3 The shape of $CCl_2{=}CCl_2$ (below is such that the vector sum of all of the C—Cl bond moments is zero.



2.4 The fact that SO_2 has a dipole moment indicates that the molecule is angular, not linear.

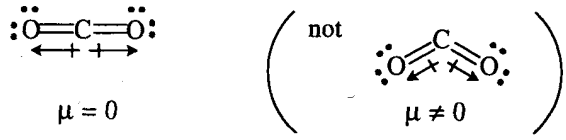




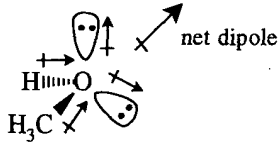
An angular shape is what we would expect from VSEPR theory, too.

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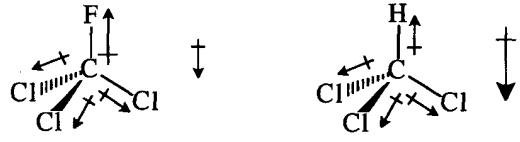
The fact that CO_2 has no dipole moment indicates that its shape is linear, not angular.

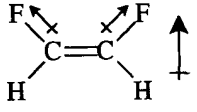
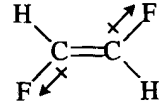


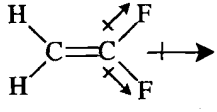
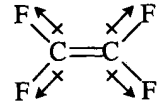
2.5 Again, this is what VSEPR theory predicts.

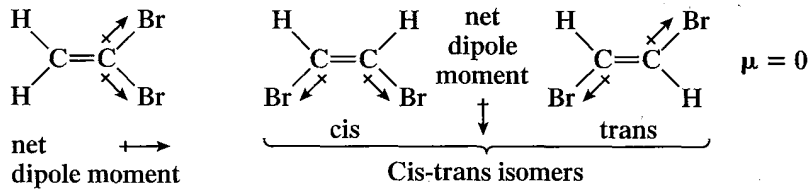


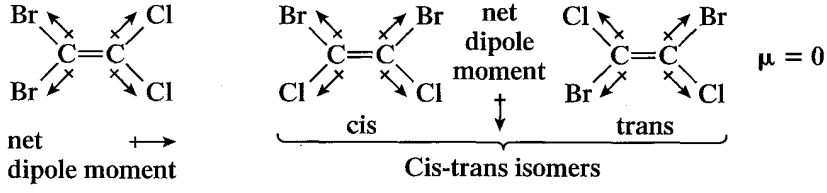
2.6 In $CFCl_3$ the large C–F bond moment opposes the C–Cl moments. Because hydrogen is much less electronegative than fluorine no such opposing effect occurs in $CHCl_3$; therefore, it has a larger net dipole moment.



2.7 (a)  net dipole moment (b)  μ = 0

(c)  net dipole moment (d)  μ = 0

2.8 (a) 

(b) 

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2.9 (a) $CH_3CH_2CH_2CH_2Br$ and CH_3CHCH_2Br (CH_3 on the CH)

(b) $CH_3CHCH_2CH_3$ (Br on the CH)

(c) $CH_3C(CH_3)_2Br$

2.10 (a) CH_3CH_2F

(b) CH_3CHCH_3 (Cl on the CH) or $(CH_3)_2CHCl$

(c) Propyl bromide

(d) Isopropyl fluoride

(e) Phenyl iodide

2.11 (a) $CH_3CH_2CH_2CH_2OH$ and CH_3CHCH_2OH (CH_3 on the CH)

(b) $CH_3CHCH_2CH_3$ (OH on the CH)

(c) $CH_3C(CH_3)_2OH$

2.12 (a) $CH_3CH_2CH_2OH$

(b) CH_3CHCH_3 (OH on the CH) or $CH_3CH(OH)CH_3$

2.13 (a) $CH_3CH_2-O-CH_2CH_3$

(b) $CH_3CH_2-O-CH_2CH_2CH_3$

(c) $CH_3CH_2-O-CHCH_3$ (CH_3 on the CH)

(d) Methyl propyl ether

(e) Diisopropyl ether

(f) Methyl phenyl ether

2.14 (a) $CH_3CH_2CH_2NH_2$

(b) $CH_3-N(CH_3)-CH_3$ or $(CH_3)_3N$

(c) $CH_3-N(CH_2CH_3)-CH(CH_3)_2$

(d) Isopropylpropylamine

(e) Tripropylamine

(f) Methylphenylamine

(g) Dimethylphenylamine

2.15 (a) (a) only (b) (d,f) (c) (b, c, e, g)

2.16 (a) $CH_3N(CH_3)CH_3 + H-Cl: \longrightarrow CH_3N^+H(CH_3)CH_3 + :Cl:^-$

(b) sp^3

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2.17 (a) $CH_3CH_2CH_2CH_2OH$ would boil higher because its molecules can form hydrogen bonds to each other through the $-\ddot{O}-H$ group.

(b) $CH_3CH_2NHCH_3$ would boil higher because its molecules can form hydrogen bonds to each other through the $-\ddot{N}(|)-H$ group.

(c) $HOCH_2CH_2CH_2OH$ because by having two $-\ddot{O}-H$ groups, it can form more hydrogen bonds.

2.18 Cyclopropane would have the higher melting point because its cyclic structure gives it a rigid compact shape that would permit stronger crystal lattice forces.

2.19 (a) Ketone (b) Alkyne (c) Alcohol (d) Aldehyde
(e) Alcohol (f) Alkene

2.20 (a) Three carbon-carbon double bonds (alkene) and a 2° alcohol
(b) Phenyl, carboxylic acid, amide, ester, and a 1° amine
(c) Phenyl and a 1° amine
(d) Carbon-carbon double bond and a 2° alcohol
(e) Phenyl, ester, and a 3° amine
(f) Carbon-carbon double bond and an aldehyde
(g) Carbon-carbon double bond and 2 ester groups

Le groupe fonctionnel « phenyl » ou phényle en français est incorrect. Le groupe fonctionnel s'appelle le cycle ou le groupe aromatique ou benzénique.

2.21

$CH_3CH_2CH_2CH_2Br$	$CH_3CH_2\underset{\displaystyle Br}{\underset{\vert}{C}}HCH_3$	$CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH_2Br$	$CH_3-\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle Br}{\underset{\vert}{C}}}}-CH_3$
1° Alkyl halide	2° Alkyl halide	1° Alkyl halide	3° Alkyl halide

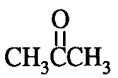
2.22

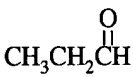
$CH_3CH_2CH_2CH_2OH$	$CH_3CH_2\underset{\displaystyle OH}{\underset{\vert}{C}}HCH_3$	$CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH_2OH$	$CH_3-\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle OH}{\underset{\vert}{C}}}}-CH_3$
1° Alcohol	2° Alcohol	1° Alcohol	3° Alcohol

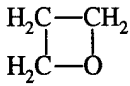
$CH_3OCH_2CH_2CH_3$	$CH_3O\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH_3$	$CH_3CH_2OCH_2CH_3$
Ether	Ether	Ether

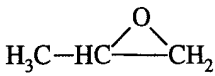
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2.23 Any four of the following:

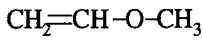

Ketone

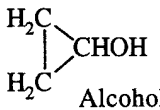

Aldehyde


Ether


Ether


Alkene, alcohol

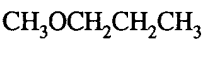

Alkene, ether

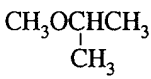

Alcohol

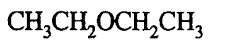
2.24 (a) 1° (b) 2° (c) 3° (d) 3° (e) 2°

2.25 (a) 2° (b) 1° (c) 3° (d) 2° (e) 2° (f) 3°

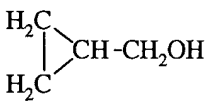
2.26 (a)

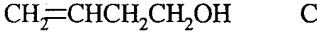


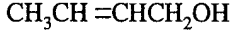




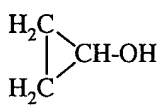
(b)



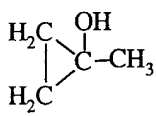




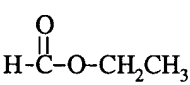
(c)

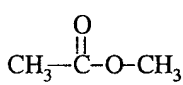


(d)

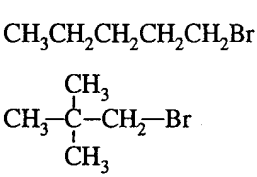


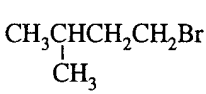
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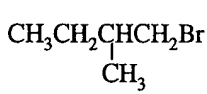




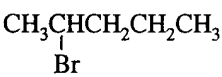
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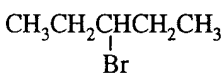


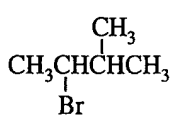




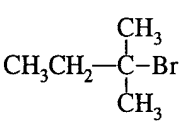
(g)



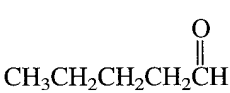


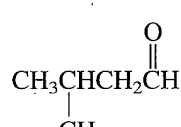


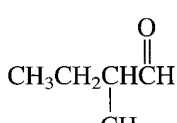
(h)



(i)







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(j) $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3$ $CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3$ $CH_3\overset{\overset{O}{\|}}{C}\underset{\underset{CH_3}{|}}{CH}CH_3$

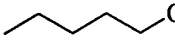
(k) $CH_3CH_2CH_2NH_2$ $CH_3\underset{\underset{CH_3}{|}}{C}HNH_2$

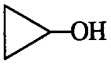
(l) $CH_3CH_2NHCH_3$ (m) $(CH_3)_3N$

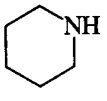
(n) $H\text{-}\overset{\overset{O}{\|}}{C}\text{-}NHCH_3$ $CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH_2$

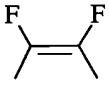
2.27 (a) $CH_3CH_2CH_2\ddot{O}H$ because its molecules can form hydrogen bonds to each other through its $-\ddot{O}-H$ group.

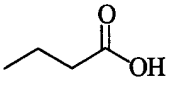
(b) $HOCH_2CH_2OH$ because with two $-\ddot{O}-H$ groups, its molecules can form more hydrogen bonds with each other.

(c)  because its molecules can form hydrogen bonds to each other.

(d)  [Same reason as (c)].

(e)  because its molecules can form hydrogen bonds to each other through its $-\ddot{N}-H$ group.

(f)  because its molecules will have a larger dipole moment. (The trans compound will have $\mu = 0$.)

(g)  [Same reason as (c)].

(h) Nonane, because of its larger molecular weight and larger size, will have larger van der Waals attractions.

(i) because its carbonyl group is far more polar than the double bond of  .

2.28 (a) The alcohol would have a broad absorption from the O—H group in the 3200 to 3500 cm^{-1} region of its IR spectrum. The ether would have no such absorption.

(c) The ketone would have a strong absorption from its carbonyl group near 1700 cm^{-1} in its IR spectrum. The alcohol would have a broad absorption due to its hydroxyl group in the 3200 to 3500 cm^{-1} region of its IR spectrum.

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(d) Same rationale as for (a)

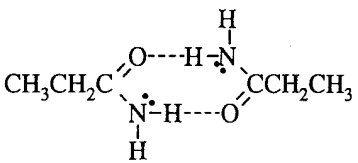
(e) The secondary amine would have an absorption near 3300 to 3500 cm^{-1} arising from N—H stretching. The tertiary amine would have no such absorption in this region since there is no N—H group present.

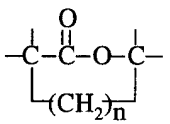
(g) Both compounds would exhibit absorptions near 1710 to 1780 cm^{-1} due to carbonyl stretching vibrations. The carboxylic acid would also have a broad absorption somewhere between 2500 and 3500 cm^{-1} due to its hydroxyl group. The ester would not have a hydroxyl absorption.

(i) The ketone would have a strong absorption from its carbonyl group near 1700 cm^{-1} in its IR spectrum. The alkene would have no such absorption but would have an absorption between 1620 and 1680 cm^{-1} due to C=C stretching.

2.29 (a) $CH_3CH_2\overset{\overset{O}{\|}}{C}NH_2$ $CH_3\overset{\overset{O}{\|}}{C}N(H)CH_3$ $H\overset{\overset{O}{\|}}{C}NHCH_2CH_3$ $H\overset{\overset{O}{\|}}{C}-N(CH_3)_2$

(b) The last one given above [i.e., $H\overset{\overset{O}{\|}}{C}N(CH_3)_3$] because it does not have a hydrogen that is covalently bonded to nitrogen and, therefore, its molecules cannot form hydrogen bonds to each other. The other molecules all have a hydrogen covalently bonded to nitrogen and, therefore, hydrogen-bond formation is possible. With the first molecule, for example, hydrogen bonds could form in the following way:



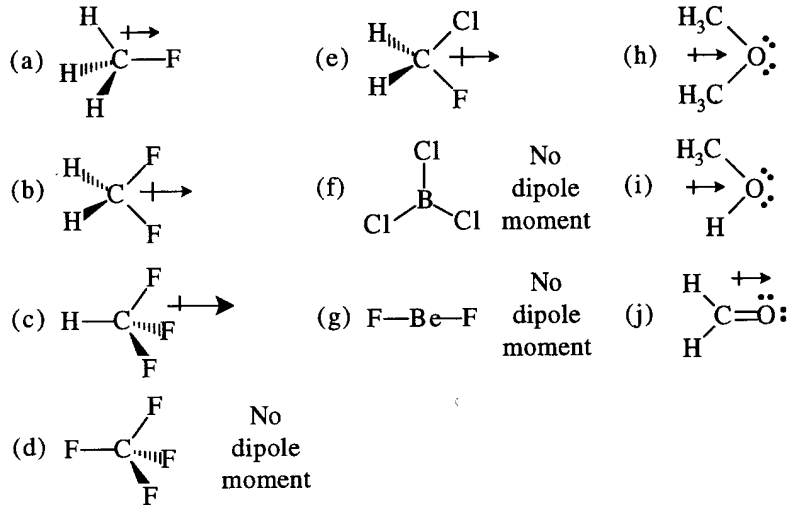
2.30 An ester group, 

2.31 The attractive forces between hydrogen fluoride molecules are the very strong dipole–dipole attractions that we call *hydrogen bonds*. (The partial positive charge of a hydrogen fluoride molecule is relatively exposed because it resides on the hydrogen nucleus. By contrast, the positive charge of an ethyl fluoride molecule is buried in the ethyl group and is shielded by the surrounding electrons. Thus the positive end of one hydrogen fluoride molecule can approach the negative end of another hydrogen fluoride molecule much more closely, with the result that the attractive force between them is much stronger.)

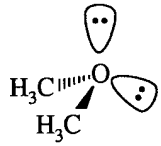
2.32 (a) and (b) are polar and hence are able to dissolve ionic compounds. (c) and (d) are nonpolar and will not dissolve ionic compounds.

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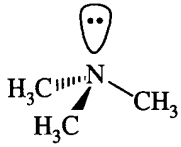
2.33



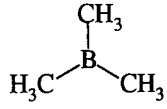
2.34 (a) Dimethyl ether: There are four electron pairs around the central oxygen: two bonding pairs and two nonbonding pairs. We would expect sp^3 hybridization of the oxygen with a bond angle of approximately 109.5° between the methyl groups.



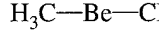
(b) Trimethylamine: There are four electron pairs around the central nitrogen: three bonding pairs and one nonbonding pair. We would expect sp^3 hybridization of the nitrogen with a bond angle of approximately 109.5° between the methyl groups.



(c) Trimethylboron: There are only three bonding electron pairs around the central boron. We would expect sp^2 hybridization of the boron with a bond angle of 120° between the methyl groups.



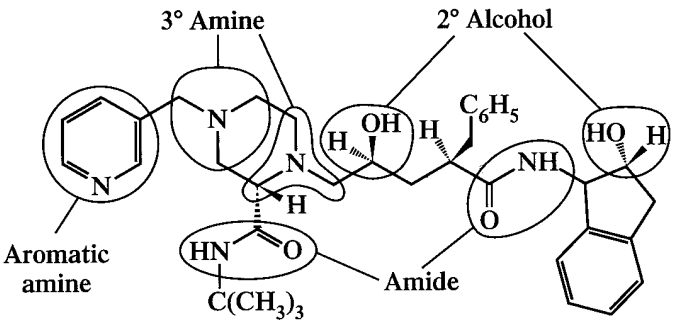
(d) Dimethylberyllium: There are only two bonding electron pairs around the central beryllium atom. We would expect *sp* hybridization of the beryllium atom with a bond angle of 180° between the methyl groups.



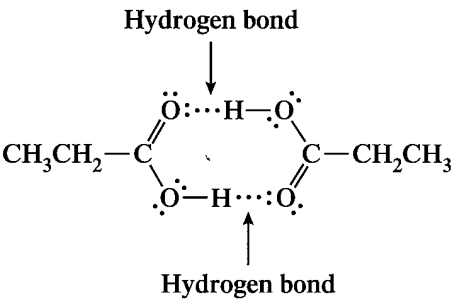
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2.35 Without one (or more) polar bonds, a molecule cannot possess a dipole moment and, therefore, it cannot be polar. If the bonds are directed so that the bond moments cancel, however, the molecule will not be polar even though it has polar bonds.

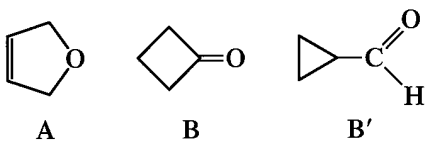
2.36 Crixivan has the following functional groups:



2.37

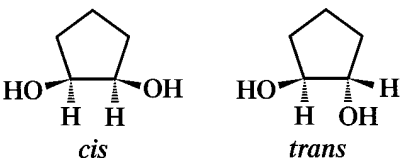


*2.38



The 1780-cm^{-1} band is in the general range for C=O stretching so structure B′ is considered one of the possible answers, but only B would have its C=O stretch at this high frequency (B′ would be at about 1730 cm^{-1}).

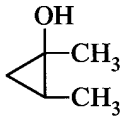
*2.39 (a)



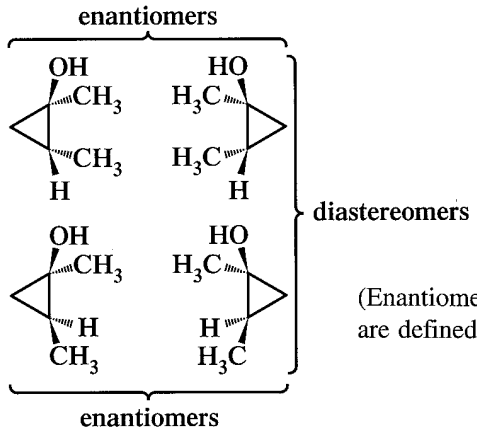
(b) The *cis* isomer will have the 3572-cm^{-1} band because only in it are the two hydroxyl groups close enough to permit intramolecular hydrogen-bonding. (Intermolecular hydrogen-bonding is not possible at high dilution in a non-polar solvent like CCl_4.)

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*2.40 (a)



(b)



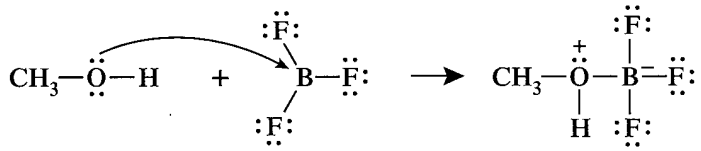
(Enantiomers and diastereomers are defined in Chapter 5.)

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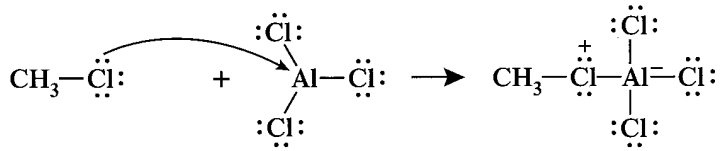
3 AN INTRODUCTION TO ORGANIC REACTIONS: ACIDS AND BASES

SOLUTIONS TO PROBLEMS

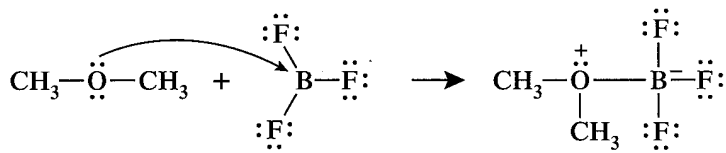
3.1 (a)



(b)



(c)

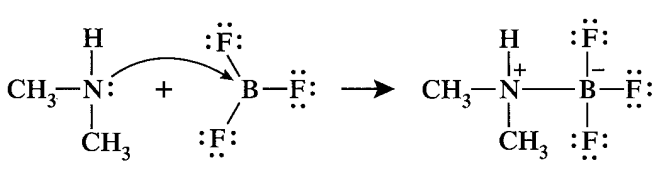


3.2 (a) Lewis base (b) Lewis acid

(c) Lewis base (d) Lewis base

(e) Lewis acid (f) Lewis base

3.3



Lewis base Lewis acid

3.4 (a) $K_a = \dfrac{[H_3O^+]\,[HCO_2^-]}{[HCO_2H]} = 1.77 \times 10^{-4}$

Let $x = [H_3O^+] = [HCO_2^-]$ at equilibrium

then, $0.1 - x = [HCO_2H]$ at equilibrium

but, since the K_a is very small, x will be very small and $0.1 - x \simeq 0.1$

Therefore,

$$\frac{(x)\,(x)}{0.1} = 1.77 \times 10^{-4}$$

$$x^2 = 1.77 \times 10^{-5}$$

$$x = 0.0042 = [H_3O^+] = [HCO_2^-]$$

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(b) % Ionized $= \dfrac{[H_3O^+]}{0.1} \times 100$ or $\dfrac{[HCO_2^-]}{0.1} \times 100$

$= \dfrac{.0042}{0.1} \times 100 = 4.2\%$

3.5 (a) $pK_a = -\log 10^{-7} = -(-7) = 7$

(b) $pK_a = -\log 5.0 = -0.699$

(c) Since the acid with a $K_a = 5$ has a larger K_a, it is the stronger acid.

3.6 When H_3O^+ acts as an acid in aqueous solution, the equation is

$$H_3O^+ + H_2O \leftrightarrows H_2O + H_3O^+$$

and K_a is

$$K_a = \frac{[H_2O][H_3O^+]}{[H_3O^+]} = [H_2O]$$

The molar concentration of H_2O in pure H_2O, that is, $[H_2O] = 55.5$; therefore, $K_a = 55.5$

The pK_a is

$pK_a = -\log 55.5 = -1.74$

3.7 The pK_a of the methylaminium ion is equal to 10.6 (Section 3.5C). Since the pK_a of the anilinium ion is equal to 4.6, the anilinium ion is a stronger acid than the methylaminium ion, and aniline ($C_6H_5NH_2$) is a weaker base than methylamine (CH_3NH_2).

3.8 (a) Negative. Because the atoms are constrained to one molecule in the product, they have to become more ordered.

(b) Approximately zero.

(c) Positive. Because the atoms are in two separate product molecules, they become more disordered.

3.9 (a) If $K_{eq} = 1$

then,

$\log K_{eq} = 0 = \dfrac{-\Delta G^\circ}{2.303RT}$

$\Delta G^\circ = 0$

(b) If $K_{eq} = 10$

then,

$\log K_{eq} = 1 = \dfrac{-\Delta G^\circ}{2.303RT}$

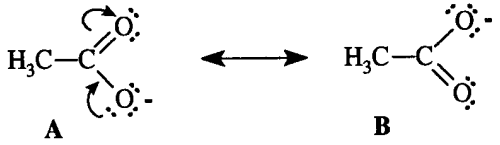
$\Delta G^\circ = -(2.303)(0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1})(298 \text{ K}) = -5.71 \text{ kJ mol}^{-1}$

(c) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta G^\circ = \Delta H^\circ = -5.71 \text{ kJ mol}^{-1}$ if $\Delta S^\circ = 0$

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3.10 Structures **A** and **B** make equal contributions to the overall hybrid. This means that the carbon-oxygen bonds should be the same length and that the oxygens should bear equal positive charges.



A **B**

3.11 (a) $CHCl_2CO_2H$ would be the stronger acid because the electron-withdrawing inductive effect of *two chlorine atoms* would make its hydroxyl proton more positive. The electron-withdrawing effect of the two chlorine atoms would also stabilize the dichloroacetate ion more effectively by dispersing its negative charge more extensively.

(b) CCl_3CO_2H would be the stronger acid for reasons similar to those given in (a), except here there are three versus two electron-withdrawing chlorine atoms involved.

(c) CH_2FCO_2H would be the stronger acid because the electron-withdrawing effect of a fluorine atom is greater than that of a bromine atom (fluorine is more electronegative).

(d) CH_2FCO_2H is the stronger acid because the fluorine atom is nearer the carboxyl group and is, therefore, better able to exert its electron-withdrawing inductive effect. (*Remember:* Inductive effects weaken steadily as the distance between the substituent and the group increases.)

3.12 All compounds containing oxygen and most compounds containing nitrogen will have an unshared electron pair on their oxygen or nitrogen atom. These compounds can, therefore, act as bases and accept a proton from concentrated sulfuric acid. When they accept a proton, these compounds become either oxonium ions or ammonium ions, and having become ionic, they are soluble in the polar medium of sulfuric acid. The only nitrogen compounds that do not have an electron pair on their nitrogen atom are quaternary ammonium compounds, and these, already being ionic, also dissolve in the polar medium of concentrated sulfuric acid.

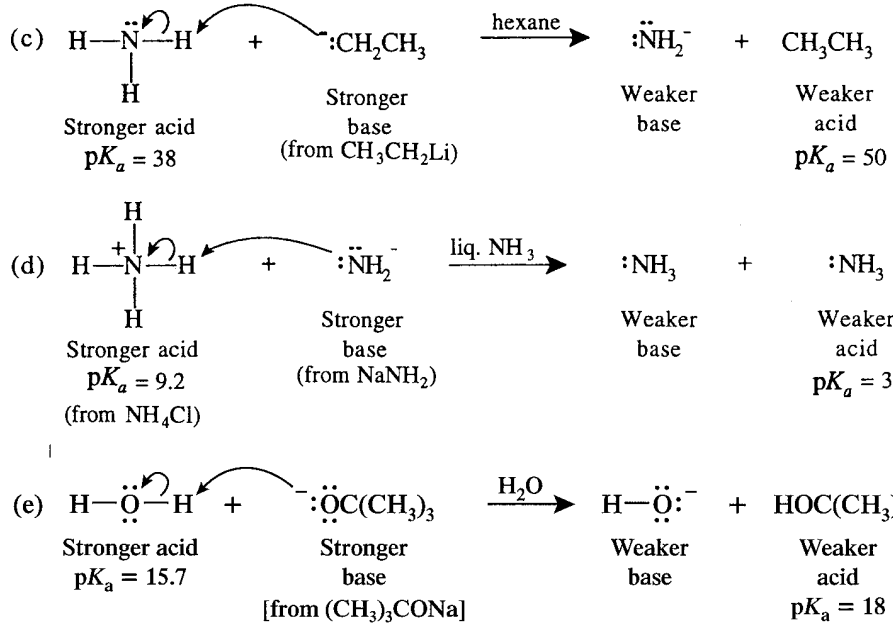
3.13 (a) $CH_3\ddot{O}-H + :H^- \xrightarrow{\text{methanol}} CH_3\ddot{O}:^- + H_2$

Stronger acid	Stronger base (from NaH)	Weaker base	Weaker acid
$pK_a = -16$			$pK_a = 35$

(b) $CH_3CH_2\ddot{O}-H + :\ddot{N}H_2^- \xrightarrow{\text{ethanol}} CH_3CH_2\ddot{O}:^- + :NH_3$

Stronger acid	Stronger base (from $NaNH_2$)	Weaker base	Weaker acid
$pK_a = 16$			$pK_a = 38$

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(f) No appreciable acid-base reaction would occur because NaOH is not a strong enough base to remove a proton from $(CH_3)_3COH$.

3.14 (a) $HC{\equiv}CH + NaH \xrightarrow{\text{hexane}} HC{\equiv}CNa + H_2$

(b) $HC{\equiv}CNa + D_2O \xrightarrow{\text{hexane}} HC{\equiv}CD + NaOD$

(c) $CH_3CH_2Li + D_2O \xrightarrow{\text{hexane}} CH_3CH_2D + LiOD$

(d) $CH_3CH_2OH + NaH \xrightarrow{\text{hexane}} CH_3CH_2ONa + H_2$

(e) $CH_3CH_2ONa + T_2O \xrightarrow{\text{hexane}} CH_3CH_2OT + NaOT$

(f) $CH_3CH_2CH_2Li + D_2O \xrightarrow{\text{hexane}} CH_3CH_2CH_2D + LiOD$

3.15 (a) $:\ddot{N}H_2^-$ (the amide ion)

(b) $H-\ddot{O}:^-$ (the hydroxide ion)

(c) $:H^-$ (the hydride ion)

(d) $H-C{\equiv}C:^-$ (the ethynide ion)

(e) $CH_3\ddot{O}:^-$ (the methoxide ion)

(f) H_2O (water)

3.16 $:\ddot{N}H_2^- > :H^- > H-C{\equiv}C:^- > CH_3\ddot{O}:^- \approx H-\ddot{O}:^- > H_2O$

3.17 (a) H_2SO_4

(b) H_3O^+

(c) $CH_3NH_3^+$

(d) NH_3

(e) CH_3CH_3

(f) CH_3CO_2H

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3.18 $H_2SO_4 > H_3O^+ > CH_3CO_2H > CH_3NH_3^+ > NH_3 > CH_3CH_3$

3.19 (a) $CH_3CH_2\text{—}\ddot{Cl}: + AlCl_3 \longrightarrow CH_3CH_2\text{—}\overset{+}{\ddot{Cl}}\text{—}Al^{-}(\ddot{Cl}:)_3\text{—}\ddot{Cl}:$

Lewis base — Lewis acid

(b) $CH_3\text{—}\ddot{O}H + BF_3 \longrightarrow CH_3\text{—}\overset{+}{\ddot{O}}(H)\text{—}B^{-}(\ddot{F}:)_3$

Lewis base — Lewis acid

(c) $(CH_3)_3C^+ + H_2\ddot{O}: \longrightarrow (CH_3)_3C\text{—}\overset{+}{\ddot{O}}H_2$

Lewis acid — Lewis base

3.20 (a) $CH_3\text{—}\ddot{O}H + H\text{—}\ddot{I}: \longrightarrow CH_3\text{—}\overset{+}{\ddot{O}}(H)\text{—}H + :\ddot{I}:^-$

(b) $CH_3\text{—}\ddot{N}H_2 + H\text{—}\ddot{Cl}: \longrightarrow CH_3\text{—}\overset{+}{N}H_2\text{—}H + :\ddot{Cl}:^-$

(c) $H_2C{=}CH_2 + H\text{—}\ddot{F}: \longrightarrow H\text{—}\overset{+}{C}H_2\text{—}CH_2\text{—}H + :\ddot{F}:^-$

3.21 Because the proton attached to the highly electronegative oxygen atom of CH_3OH is much more acidic than the protons attached to the much less electronegative carbon atom.

3.22 $CH_3CH_2\text{—}\ddot{O}\text{—}H + {}^-:C{\equiv}C\text{—}H \xrightarrow{\text{liq. } NH_3} CH_3CH_2\text{—}\ddot{O}:^- + H\text{—}C{\equiv}C\text{—}H$

3.23 (a) $pK_a = -\log 1.77 \times 10^{-4} = 4 - 0.248 = 3.752$

(b) $K_a = 10^{-13}$

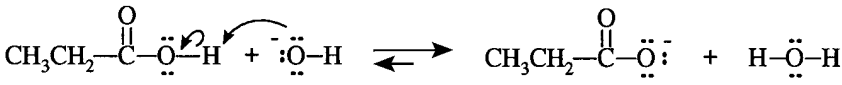
3.24 (a) HB is the stronger acid because it has the smaller pK_a.

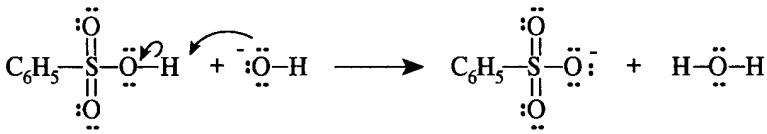
(b) Yes. Since A^- is the stronger base and HB is the stronger acid, the following acid-base reaction will take place.

$A:^- + H\text{—}B \longrightarrow A\text{—}H + B:^-$

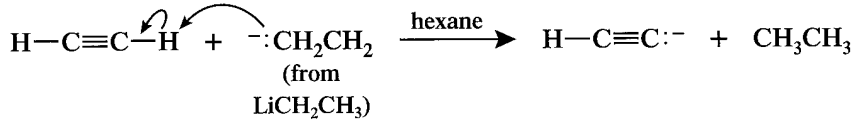
Stronger base	Stronger acid	Weaker acid	Weaker base
	$pK_a = 10$	$pK_a = 20$	

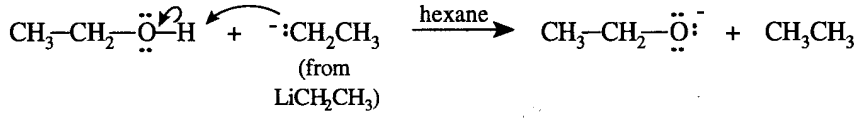
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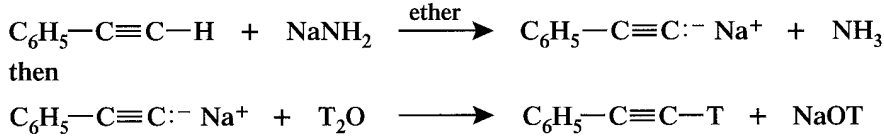
3.25 (a) 

(b) 

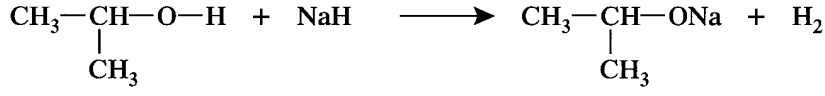
(c) No appreciable acid-base reaction takes place because CH_3CH_2ONa is too weak a base to remove a proton from ethyne.

(d) 

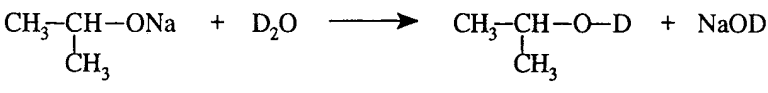
(e) 

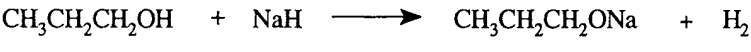
3.26 (a) 

then

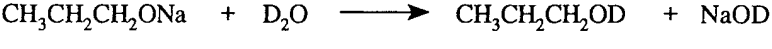
(b) 

then



(c) 

then



3.27 (a) $CH_3CH_2OH > CH_3CH_2NH_2 > CH_3CH_2CH_3$

Oxygen is more electronegative than nitrogen, which is more electronegative than carbon. The O-H bond is most polarized, the N-H bond is next, and the C-H bond is least polarized.

(b) $CH_3CH_2O^- < CH_3CH_2NH^- < CH_3CH_2CH_2^-$

The weaker the acid, the stronger the conjugate base.

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3.28 (a) $CH_3C{\equiv}CH > CH_3CH{=}CH_2 > CH_3CH_2CH_3$

(b) $CH_3CHClCO_2H > CH_3CH_2CO_2H > CH_3CH_2CH_2OH$

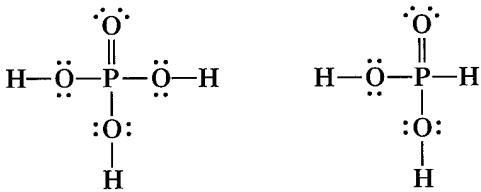
(c) $CH_3CH_2OH_2^+ > CH_3CH_2OH > CH_3OCH_3$

3.29 (a) $CH_3NH_3^+ < CH_3NH_2 < CH_3NH^-$

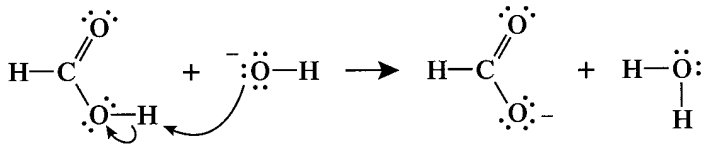
(b) $CH_3O^- < CH_3NH^- < CH_3CH_2^-$

(c) $CH_3C{\equiv}C^- < CH_3CH{=}CH^- < CH_3CH_2CH_2^-$

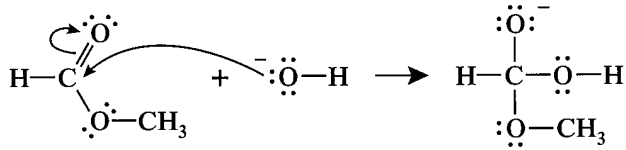
3.30 The acidic hydrogens must be attached to oxygen atoms. In H_3PO_3, one hydrogen is bonded to a phosphorus atom:



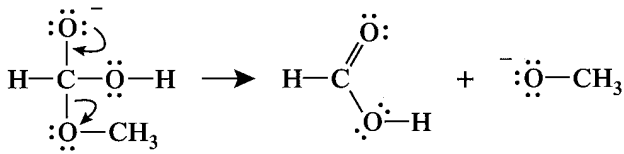
3.31 (a)



(b)



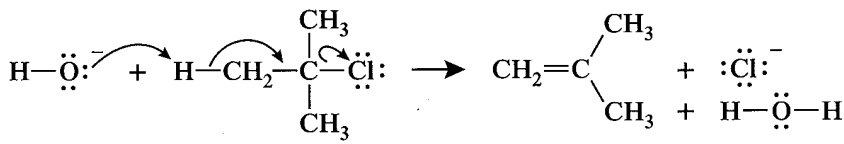
(c)



(d)

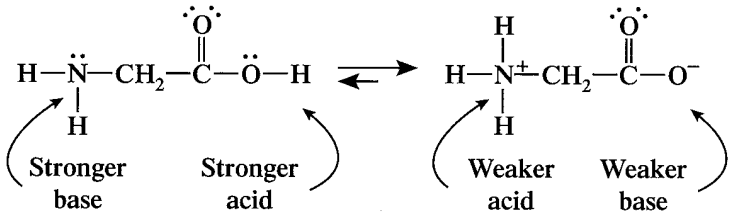


(e)



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3.32 (a) Assume that the acidic and basic groups of glycine in its two forms have acidities and basicities similar to those of acetic acid and methylamine. Then consider the equilibrium between the two forms:



We see that the ionic form contains the groups that are the weaker acid and weaker base. The equilibrium, therefore, will favor this form.

(b) The high melting point shows that the ionic structure better represents glycine.

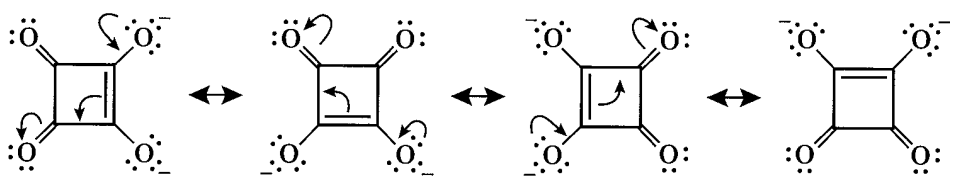
3.33 (a) The second carboxyl group of malonic acid acts as an electron-withdrawing group and stabilizes the conjugate base formed (i.e., $HO_2CCH_2CO_2^-$) when malonic acid loses a proton. [Any factor that stabilizes the conjugate base of an acid always increases the strength of the acid (Section 3.10C).] An important factor here may be an entropy effect as explained in Section 3.9.

(b) When $^-O_2CCH_2CO_2H$ loses a proton, it forms a dianion, $^-O_2CCH_2CO_2^-$. This dianion is destabilized by having two negative charges in close proximity.

3.34 HB is the stronger acid.

3.35
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$= 6.3 \text{ kJ mol}^{-1} - (298 \text{ K})(0.0084 \text{ kJ mol}^{-1}\text{K}^{-1})$$
$$= 3.8 \text{ kJ mol}^{-1}$$
$$\log K_{eq} = \log K_a = -\text{p}K_a = -\frac{\Delta G^\circ}{2.303RT}$$
$$\text{p}K_a = \frac{\Delta G^\circ}{2.303RT}$$
$$\text{p}K_a = \frac{3.8 \text{ kJ mol}^{-1}}{(2.303)(0.008314 \text{ kJ mol}^{-1}\text{K}^{-1})(298 \text{ K})}$$
$$\text{p}K_a = 0.66$$

3.36 The dianion is a hybrid of the following resonance structures:



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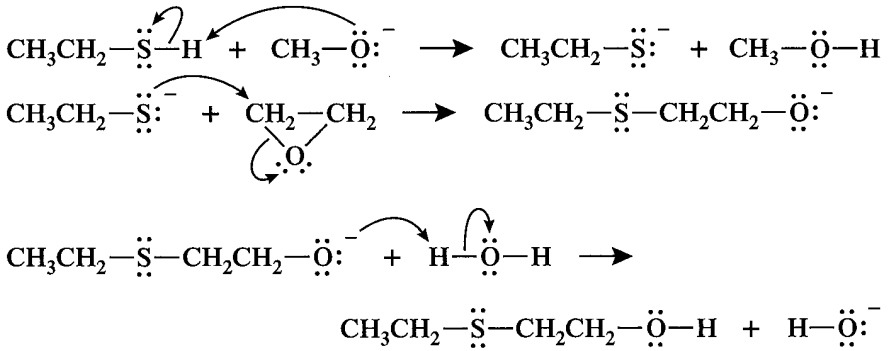
If we mentally fashion a hybrid of these structures, we see that each carbon-carbon bond is a single bond in three structures and a double bond in one. Each carbon-oxygen bond is a double bond in two structures and a single bond in two structures. Therefore, we would expect all of the carbon-carbon bonds to be equivalent and of the same length, and exactly the same can be said for the carbon-oxygen bonds.

*3.37 (a) *A* is $CH_3CH_2S^-$ *B* is CH_3OH

C is $CH_3CH_2SCH_2CH_2O^-$ *D* is $CH_3CH_2SCH_2CH_2OH$

E is OH^-

(b)



*3.38 (a) $CH_3(CH_2)_8OD + CH_3(CH_2)_8Li \longrightarrow CH_3(CH_2)_8O^-Li^+ + CH_3(CH_2)_8D$

Hexane could be used as solvent. Liquid ammonia and ethanol could not because they would compete with $CH_3(CH_2)_8OD$ and generate mostly non-deuterio-labelled $CH_3(CH_2)_7CH_3$.

(b) $NH_2^- + CH_3C{\equiv}CH \longrightarrow NH_3 + CH_3C{\equiv}C:^-$

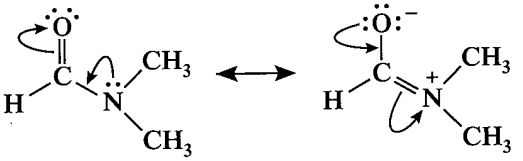
Hexane or liquid ammonia could be used; ethanol is too acidic and would lead to $CH_3CH_2O^-$ (ethoxide ion) instead of the desired alkynide ion.

(c)



Hexane or ethanol could be used; liquid ammonia is too strong a base and would lead to NH_4^+ instead of the desired anilinium ion.

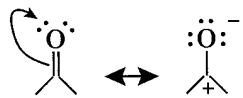
*3.39 (a,b)



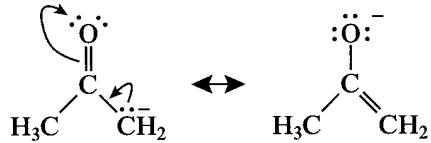
(c) Since DMF does not bind with (solvate) anions, their electron density remains high and their size small, both of which make nucleophiles more reactive.

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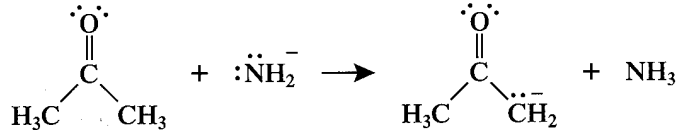
*3.40 (a)

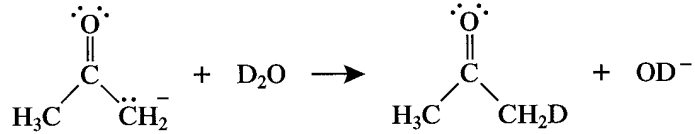


(b)



(c)



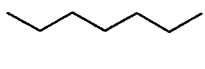


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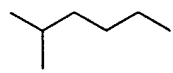
4 ALKANES: NOMENCLATURE, CONFORMATIONAL ANALYSIS, AND AN INTRODUCTION TO SYNTHESIS

SOLUTIONS TO PROBLEMS

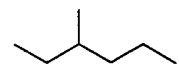
4.1



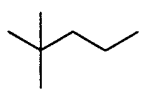
Heptane



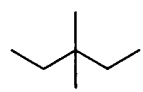
2-Methylhexane



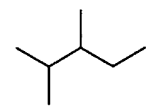
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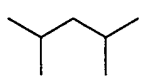
2,2-Dimethylpentane



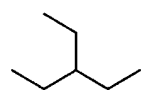
3,3-Dimethylpentane



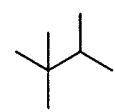
2,3-Dimethylpentane



2,4-Dimethylpentane



3-Ethylpentane



2,2,3-Trimethylbutane

4.2 (a) $CH_3CH_2CH_2CH_2CH_2-$ 1-Pentyl

$CH_3CH_2CH_2\underset{|}{C}HCH_3$ 2-Pentyl

$CH_3CH_2\underset{|}{C}HCH_2CH_3$ 3-Pentyl

$CH_3CH_2CH(CH_3)CH_2-$ 2-Methyl-1-butyl

$CH_3CH(CH_3)CH_2CH_2-$ 3-Methyl-1-butyl

$CH_3\underset{|}{C}HCH(CH_3)CH_3$ 3-Methyl-2-butyl

$CH_3\underset{|}{C}(CH_3)CH_2CH_3$ 2-Methyl-2-butyl

(b) See the answer to Problem 4.1 for the names of C_7H_{16} isomers.

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4.3 (a) $CH_3CH_2CH_2CH_2Cl$

1-Chlorobutane

$CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$

2-Chlorobutane

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Cl$

1-Chloro-2-methylpropane

$CH_3-\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$

2-Chloro-2-methylpropane

(b) $CH_3CH_2CH_2CH_2CH_2Br$

1-Bromopentane

$CH_3CH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

2-Bromopentane

$CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_3$

3-Bromopentane

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Br$

1-Bromo-3-methylbutane

$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Br$

1-Bromo-2-methylbutane

$CH_3\underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}HCH_3$

2-Bromo-3-methylbutane

$CH_3\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}CH_2Br$

1-Bromo-2,2-dimethylpropane

$CH_3CH_2\underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}CH_3$

2-Bromo-2-methylbutane

4.4 (a) $CH_3CH_2CH_2CH_2OH$

1-Butanol

$CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$

2-Butanol

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH$

2-Methyl-1-propanol

$CH_3\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}OH$

2-Methyl-2-propanol

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(b) $CH_3CH_2CH_2CH_2CH_2OH$

1-Pentanol

$CH_3CHCH_2CH_2OH$ (CH$_3$ branch)

3-Methyl-1-butanol

$CH_3CH_2CH_2CHCH_3$ (OH)

2-Pentanol

$CH_3CH_2CHCH_2OH$ (CH$_3$ branch)

2-Methyl-1-butanol

$CH_3CH_2CHCH_2CH_3$ (OH)

3-Pentanol

$CH_3CHCHCH_3$ (CH$_3$ and OH)

3-Methyl-2-butanol

CH_3CCH_2OH (CH$_3$ and CH$_3$)

2,2-Dimethyl-1-propanol

$CH_3CH_2CCH_3$ (CH$_3$ and OH)

2-Methyl-2-butanol

4.5 (a) 1-(1-Methylethyl)-2-(1,1-dimethylethyl)cyclopentane or 1-*tert*-butyl-2-isopropylcyclopentane

(b) 1-Methyl-2-(2-methylpropyl)cyclohexane or 1-isobutyl-2-methylcyclohexane

(c) Butylcyclohexane

(d) 1-Chloro-2,4-dimethylcyclohexane

(e) 2-Chlorocyclopentanol

(f) 3-(1,1-Dimethylethyl)cyclohexanol or 3-*tert*-butylcyclohexanol

4.6 (a) 2-Chlorobicyclo[1.1.0]butane

(b) Bicyclo[3.2.1]octane

(c) Bicyclo[2.1.1]hexane

(d) 9-Chlorobicyclo[3.3.1]nonane

(e) 2-Methylbicyclo[2.2.2]octane

(f)  Bicyclo[3.1.0]hexane or  bicyclo[2.1.1]hexane

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4.7 (a) *trans*-3-Heptene

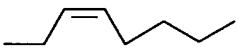
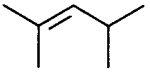
(b) 2,5-Dimethyl-2-octene

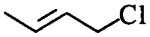
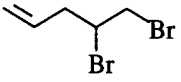
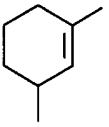
(c) 4-Ethyl-2-methyl-1-hexene

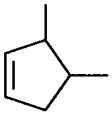
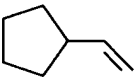
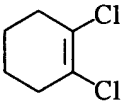
(d) 3,5-Dimethylcyclohexene

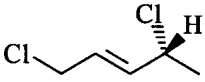
(e) 4-Methyl-4-penten-2-ol

(f) 2-Chloro-3-methyl-3-cyclohexen-1-ol

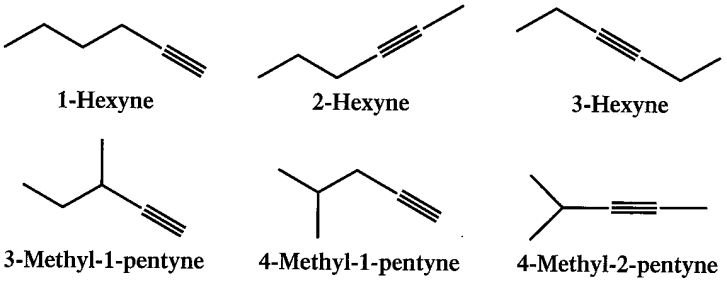
4.8 (a)  (b)  (c) 

(d)  (e)  (f) 

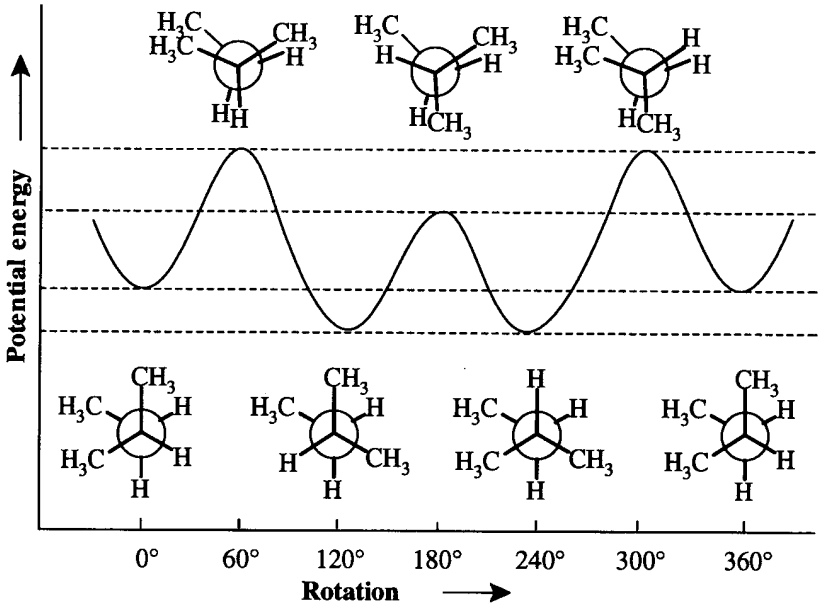
(g)  (h)  (i) 

(j) 

4.9



4.10



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4.11

$$\log K_{eq} = \frac{\Delta G^\circ}{-2.303RT} = \frac{-7600\ \text{J}}{(-2.303)(8.314\ \text{J K}^{-1})(298\ \text{K})} = 1.32$$

$K_{eq} = 21.38$

Let e = amount of equatorial form

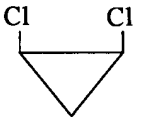
and a = amount of axial form

then, $K_{eq} = \frac{e}{a} = 21.38$

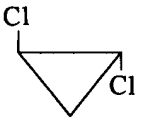
$e = 21.38a$

$$\%e = \frac{21.38a}{a + 21.38a} \times 100 = 95.5\%$$

4.12 (a)

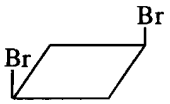


(cis)

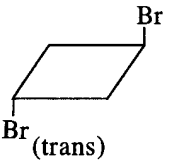


(trans)

(b)

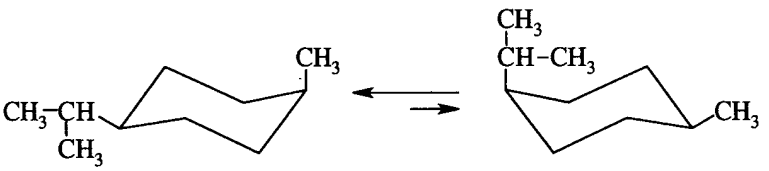


(cis)



(trans)

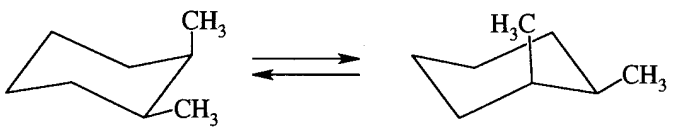
4.13 (a-d)



More stable because larger group is equatorial

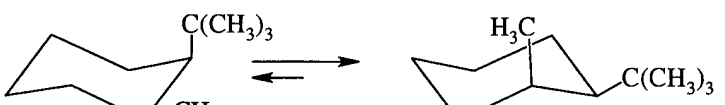
Less stable because larger group is axial

4.14 (a)



(b) Yes

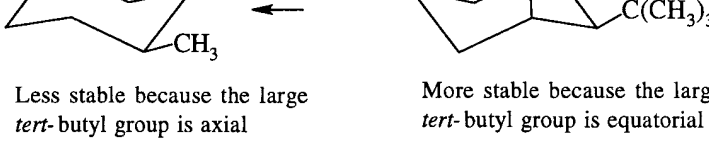
(c)



Less stable because the large *tert*-butyl group is axial

More stable because the large *tert*-butyl group is equatorial

(d)

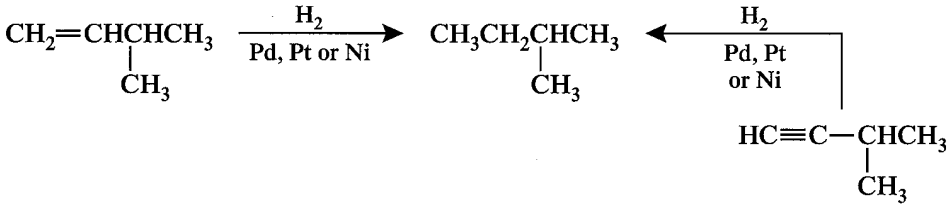


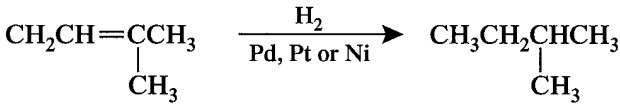
More stable because both methyl groups are equatorial

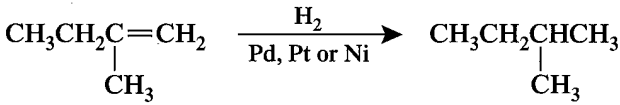
Less stable because both methyl groups are axial

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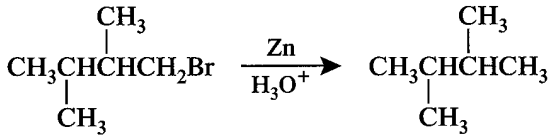
4.15

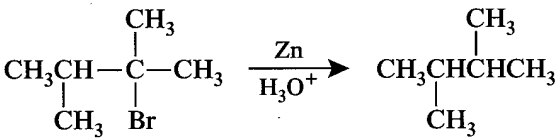




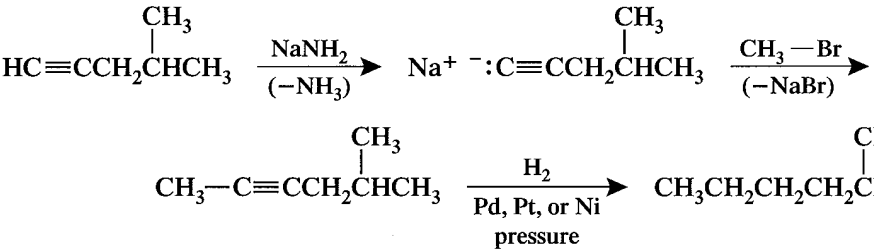


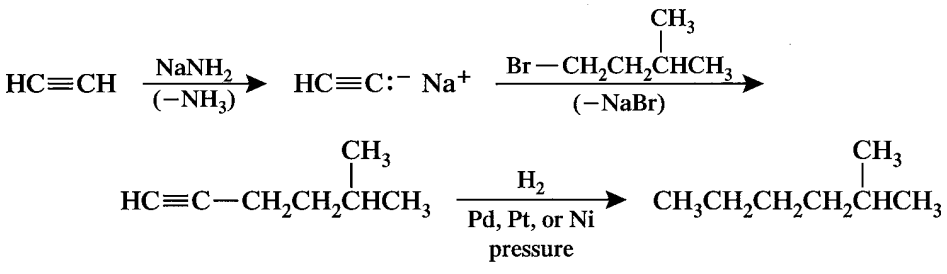
4.16

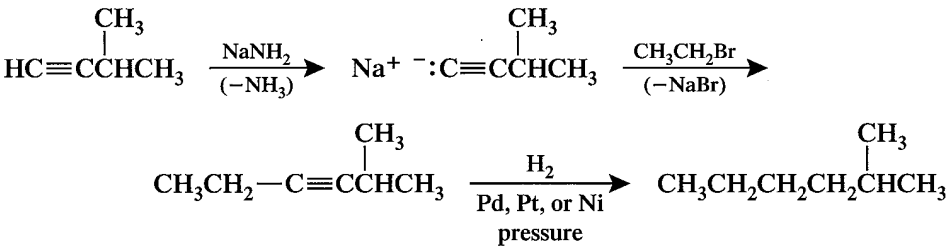




4.17

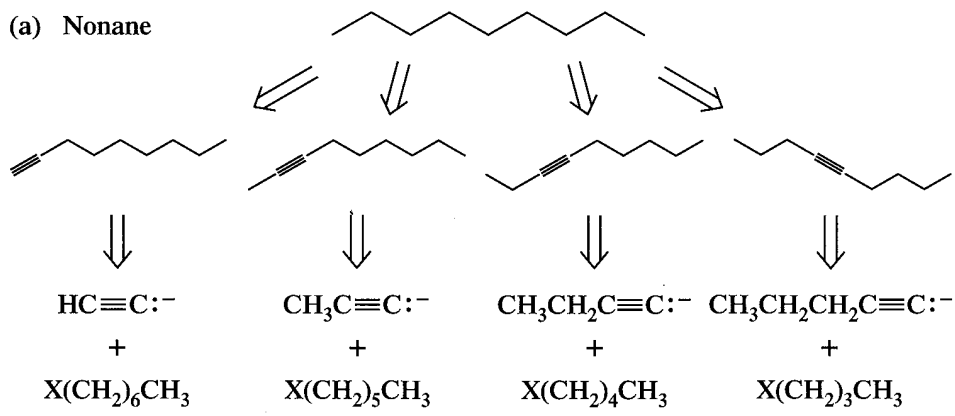




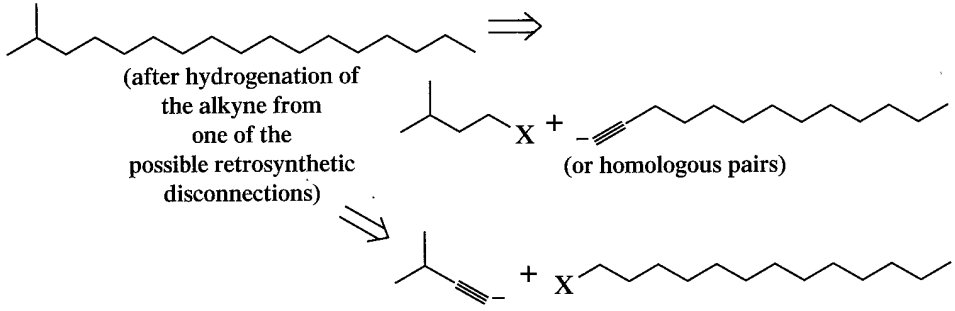


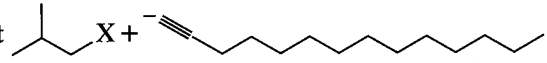
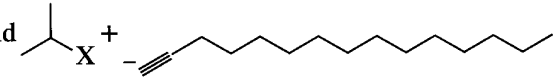
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4.18 (a) Nonane

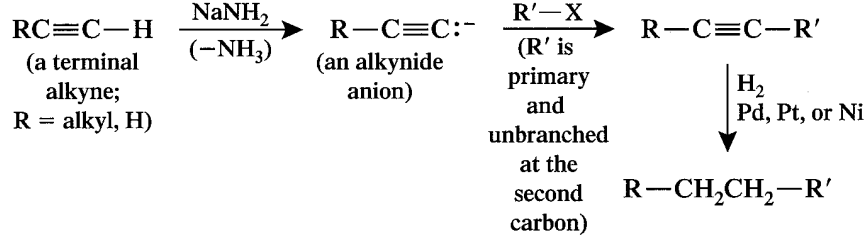


2-Methylheptadecane



(Note that  is not a good choice because the alkyl halide is branched at the carbon adjacent to the halogen. Neither would  work because the alkyl halide is secondary.)

(b) For any pair of reactants above that is a feasible retrosynthetic disconnection, the steps for the synthesis would be



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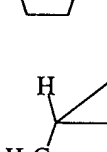
4.19 (a) $ClCH_2CH_2CH_2CHCH_3$ (Cl)

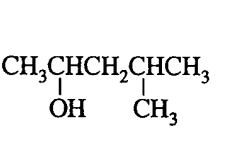
(b) $CH_3CH_2CHCH_3$ (Br)

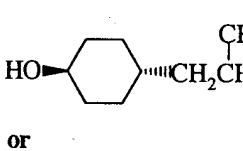
(c) $CH_3CH_2CH_2CHCH_2CH_2CH_3$ ($CHCH_3$, CH_3)

(d) $CH_3C(CH_3)(CH_3)CHCH_2CH_3$

(e) $CH_3CHCHCH_2CH_2CH_3$ (CH_3, CH_2CH_3)

(f) 

(g) 

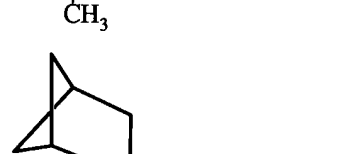
(h) 

(i) $CH_3CHCH_2CHCH_3$ (OH, CH_3)

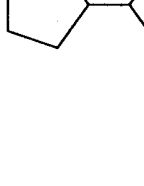
(j) 

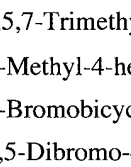
or



(k) 

(l) $CH_3C(CH_3)(CH_3)CH_2OH$

(m) 

(n) 

(o)

4.20 (a) 3,3,4-Trimethylhexane

(b) 2,2-Dimethyl-1-butanol

(c) 3,5,7-Trimethylnonane

(d) 3-Methyl-4-heptanol

(e) 2-Bromobicyclo[3.3.1]nonane

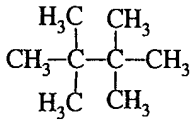
(f) 2,5-Dibromo-4-ethyloctane

(g) Cyclobutylcyclopentane

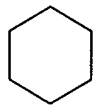
(h) 7-Chlorobicyclo[2.2.1]heptane

4.21 The two secondary carbon atoms in *sec*-butyl alcohol are equivalent; however, there are three five-carbon alcohols (pentyl alcohols) that contain a secondary carbon atom.

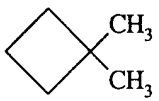
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4.22 (a) 

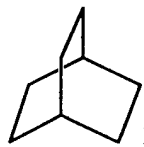
2,2,3,3 -Tetramethylbutane

(b) 

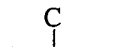
Cyclohexane

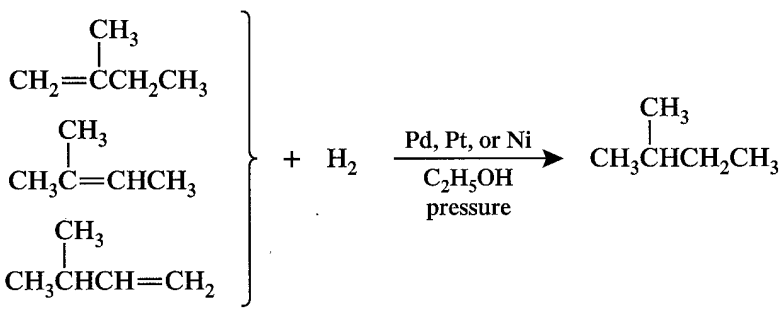
(c) 

1,1-Dimethylcyclobutane

(d) 

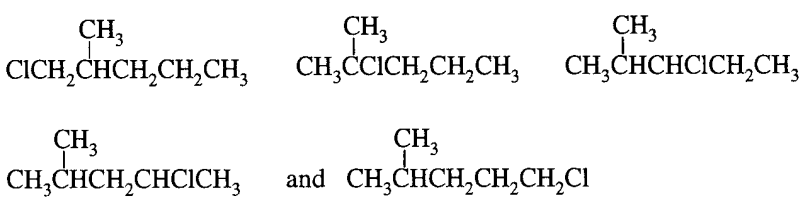
Bicyclo [2.2.2] octane

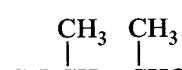
4.23 Each of the desired alkenes must have the same carbon skeleton as 2-methylbutane,  ; they are therefore



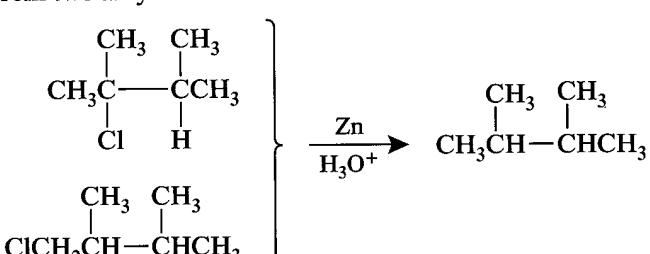
4.24 Only one isomer of C_6H_{14} can be produced from five isomeric hexyl chlorides ($C_6H_{13}Cl$).

The alkane is 2-methylpentane, $CH_3CHCH_2CH_2CH_3$ (CH₃ on the second carbon). The five alkyl chlorides are



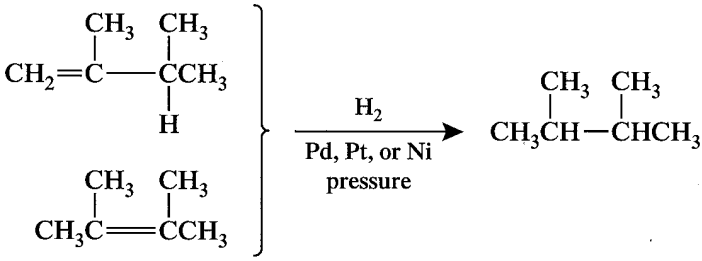
4.25  2,3-Dimethylbutane

From two alkyl chlorides

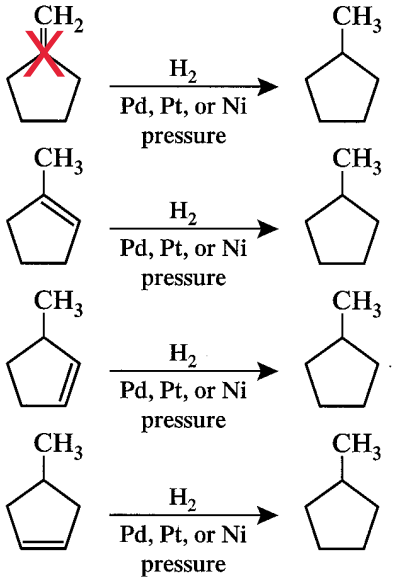


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From two alkenes

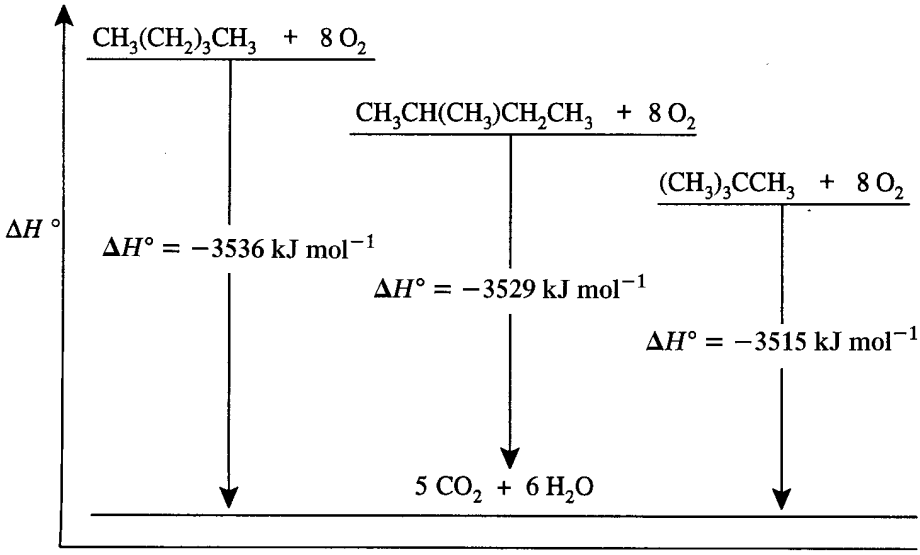


4.26



La liaison double à l'extérieur de la structure cyclique n'est pas vraiment stable. Donc, il existe 3 alcènes différents qui se transforment en méthylcyclopentane : 1-méthylcyclopentène, 3-méthylcyclopentène et 4-méthylcyclopentène.

4.27 $(CH_3)_3CCH_3$ is the most stable isomer (i.e., it is the isomer with the lowest potential energy) because it evolves the least amount of heat on a molar basis when subjected to complete combustion.

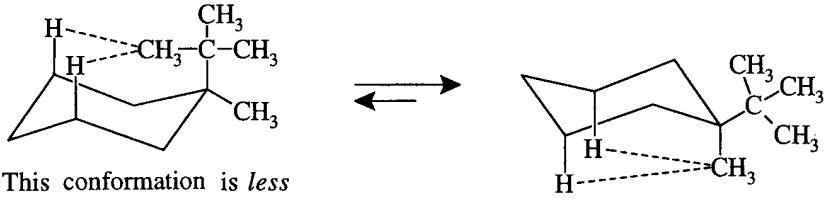


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4.28 A homologous series is one in which each member of the series differs from the one preceding it by a constant amount, usually a CH_2 group. A homologous series of alkyl halides would be the following:

CH_3X
CH_3CH_2X
$CH_3(CH_2)_2X$
$CH_3(CH_2)_3X$
$CH_3(CH_2)_4X$
etc.

4.29



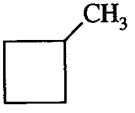
This conformation is *less stable* because 1,3-diaxial interactions with the large *tert*-butyl group cause considerable repulsion.

This conformation is *more stable* because 1,3-diaxial interactions with the smaller methyl group are less repulsive.

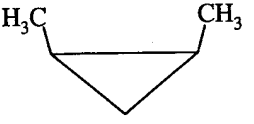
4.30



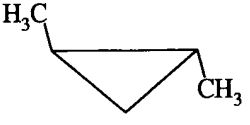
Cyclopentane



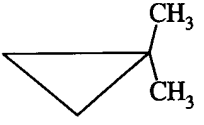
Methylcyclobutane



cis-1,2-Dimethylcyclopropane



trans-1,2-Dimethylcyclopropane

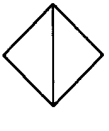


1,1-Dimethylcyclopropane

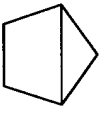


Ethylcyclopropane

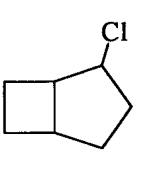
4.31 (a)



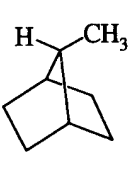
(b)



(c)



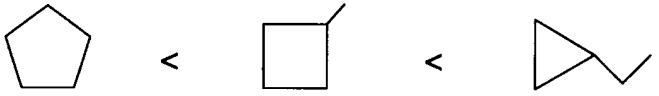
(d)



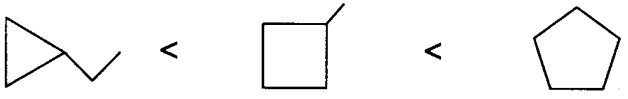
4.32 $S - A + 1 = N$

For cubane, S = 12 and A = 8. Thus $12 - 8 + 1 = N$; N = 5 rings in cubane.

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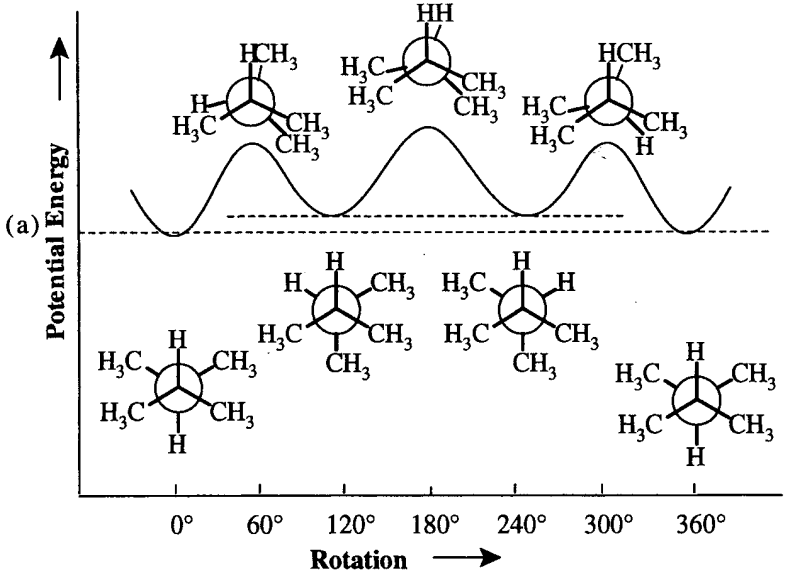
4.33 (a) 

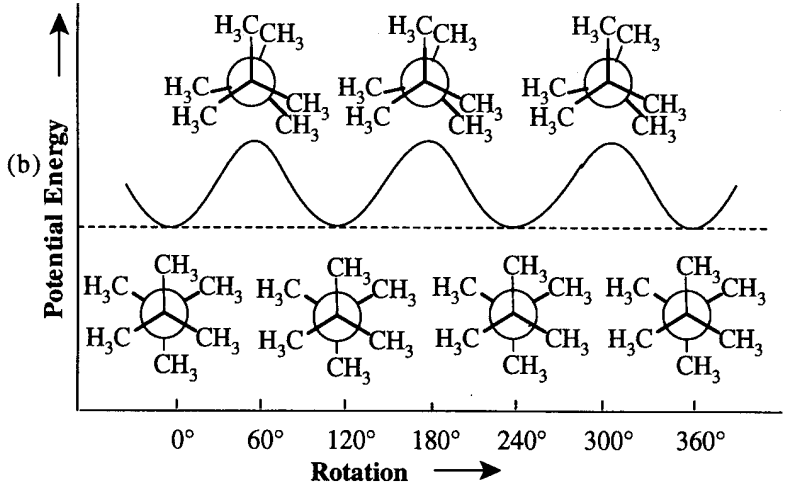
Smallest heat of combustion — Largest heat of combustion

(b) 

Least stable — Most stable

4.34





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4.35 (a) Pentane would boil higher because its chain is unbranched. Chain-branching lowers the boiling point.

(b) Heptane would boil higher because it has the larger molecular weight and would, because of its larger surface area, have larger van der Waals attractions.

(c) 2-Chloropropane because it is more polar and because it has a larger molecular weight.

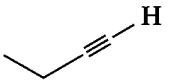
(d) 1-Propanol would boil higher because its molecules would be associated with each other through hydrogen-bond formation.

(e) Propanone (CH_3COCH_3) would boil higher because its molecules are more polar.

4.36 C_4H_6



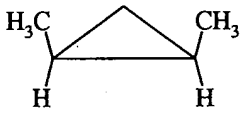
Bicyclo[1.1.0]butane



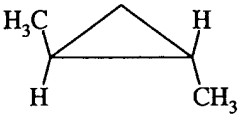
1-Butyne

The IR stretch at ~2250 cm^{-1} for the terminal alkyne *sp* C—H bond distinguishes these two compounds.

4.37 *trans*-1,2-Dimethylcyclopropane would be more stable because there is less crowding between its methyl groups.



Less stable



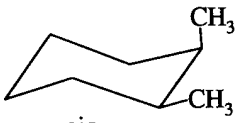
More stable

4.38 (a)



trans

More stable because both methyl groups are equatorial in the most stable conformation



cis

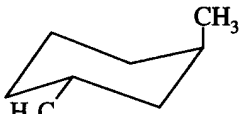
Less stable because one methyl group must be axial and so has the larger heat of combustion

(b)



cis

More stable because both methyl groups are equatorial in the most stable conformation

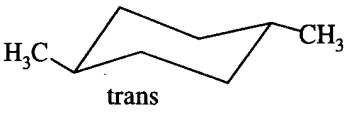


trans

Less stable because one methyl group must be axial and so has the larger heat of combustion

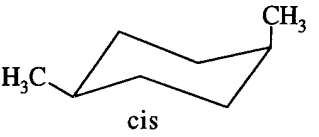
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(c)



trans

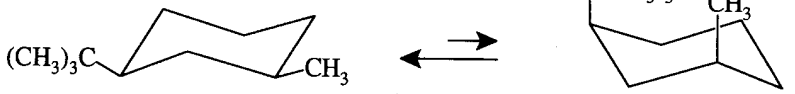
More stable because both methyl groups are equatorial in the most stable conformation



cis

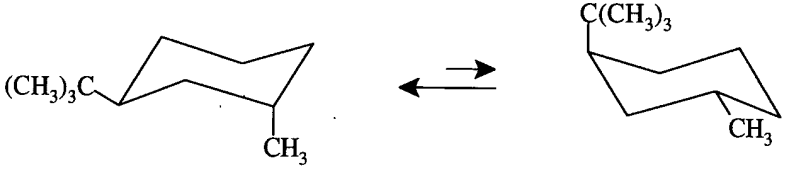
Less stable because one methyl group must be axial and so has the larger heat of combustion

4.39 (a)



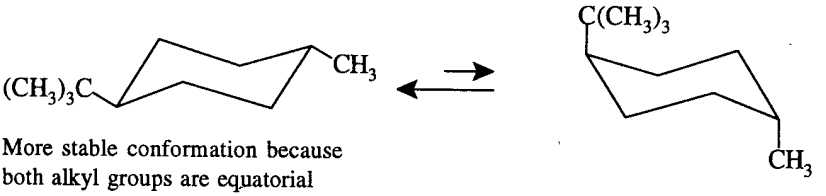
More stable conformation because both alkyl groups are equatorial

(b)



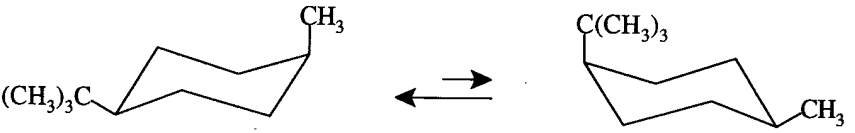
More stable because larger group is equatorial

(c)



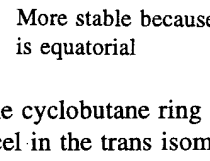
More stable conformation because both alkyl groups are equatorial

(d)

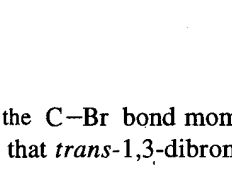


More stable because larger group is equatorial

4.40 If the cyclobutane ring were planar, the C−Br bond moments would exactly cancel in the trans isomer. The fact that *trans*-1,3-dibromocyclobutane has a dipole moment shows the ring is not planar.



Planar form
$\mu = 0$

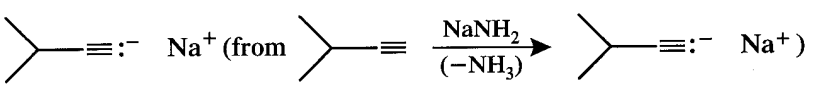


Bent form
$\mu \neq 0$

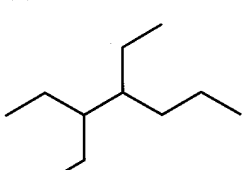
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4.41 (a) H_2, Pd, Pt, or Ni catalyst, pressure

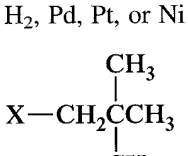
(b) (1) $NaNH_2$ (2) $BrCH_2CH_2CH_2CH_3$

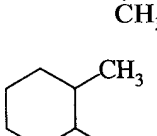
(c) (1) 

(2) H_2, Pd, Pt, or Ni catalyst, pressure

(d) 

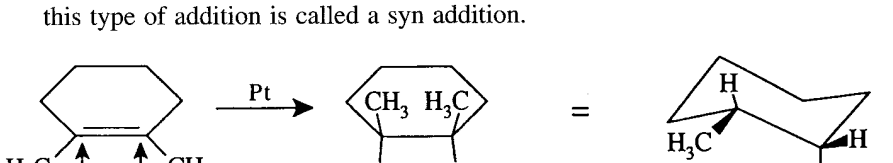
(e) H_2, Pd, Pt, or Ni catalyst, pressure

(f) 

*4.42 (a) 

(b) From Table 4.8 we find that this is *cis*-1,2-dimethylcyclohexane.

(c) Since catalytic hydrogenation produces the cis isomer, both hydrogen atoms must have added from the same side of the double bond. (As we shall see in Section 7.14, this type of addition is called a syn addition.

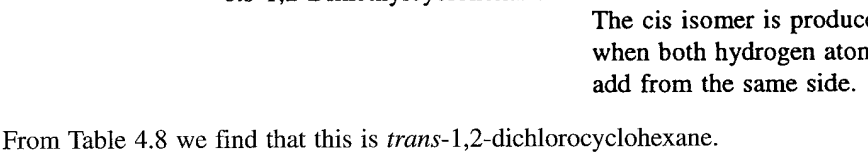


cis-1,2-Dimethylcyclohexane

The cis isomer is produced when both hydrogen atoms add from the same side.

*4.43 (a) From Table 4.8 we find that this is *trans*-1,2-dichlorocyclohexane.

(b) Since the product is the trans isomer, we can conclude that the chlorine atoms have added from opposite sides of the double bond.

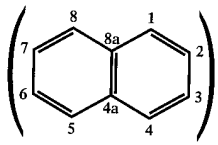


trans-1,2-Dichlorocyclohexane

The trans isomer is produced when the chlorine atoms add from opposite sides of the double bond.

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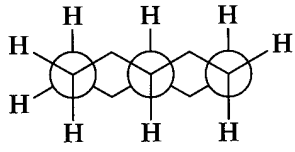
4.44 If *trans*-1,3-di-*tert*-butylcyclohexane were to adopt a chair conformation, one *tert*-butyl group would have to be axial. It is, therefore, more energetically favorable for the molecule to adopt a twist boat conformation.

***4.45** (a) More rules are needed (see Chapter 7) to indicate relative stereochemistry for these 1-bromo-2-chloro-1-fluoroethenes.
(b) Bicyclo[4.4.0]decane (or decalin)
(c) Bicyclo[4.4.0]dec-2-ene (or Δ^1-octalin)
(d) Bicyclo[4.4.0]dec-1-ene (or $\Delta^{1(8a)}$-octalin)
NOTE: The common name decalin comes from decahydronaphthalene, the derivative of naphthalene  that has had all of its five double bonds converted to single bonds by addition of 10 atoms of hydrogen. Octalin similarly comes from octahydronaphthalene and contains one surviving double bond. When using these common names derived from naphthalene, their skeletons are usually numbered like that of naphthalene. When, as in case (d), a double bond does not lie between the indicated carbon and the next higher numbered carbon, its location is specified as shown.

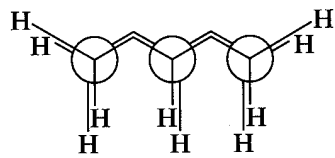
Also, the symbol Δ is one that has been used with commom names to indicate the presence of a double bond at the position specified by the accompanying superscript number(s).

***4.46** D-Glucose has all of its attached groups equatorial in the lowest energy chair conformation. Other sugars have at least one group axial in their lowest energy chair conformation.

***4.47** Because if the configuration of stereocenters is changed, not all of the ring substituents can simultaneously be in the preferred equatorial position, as they are in glucose.



trans



cis

The *trans* isomer would be more stable because it can have both of its rings in the favored chair conformation, avoiding the many eclipsing interactions found in the doubly boat conformation of the *cis* isomer (which would increase its stability slightly by twisting).

***4.48**

$$H{-}C{\equiv}C{-}C{\equiv}C{-}H \xrightarrow[2\text{ mol equiv. } CH_3(CH_2)_3Br]{2\text{ mol equiv. } LiNH_2}$$

$$CH_3(CH_2)_3{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_3CH_3 \xrightarrow[\text{Pt catalyst}]{H_2} CH_3(CH_2)_{10}CH_3$$

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5 STEREOCHEMISTRY: CHIRAL MOLECULES

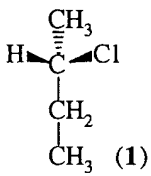
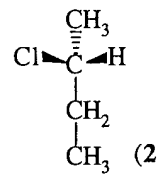
SOLUTIONS TO PROBLEMS

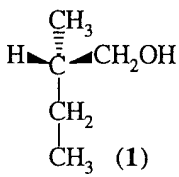
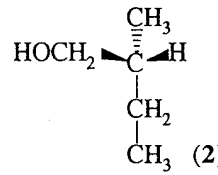
5.1 (a) Achiral (c) Chiral (e) Chiral (g) Chiral
(b) Achiral (d) Chiral (f) Chiral (h) Achiral

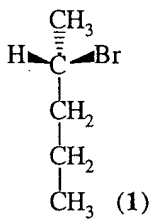
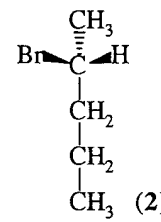
5.2 (a) Yes (b) No (c) No

5.3 (a) They are the same molecule. (b) They are enantiomers.

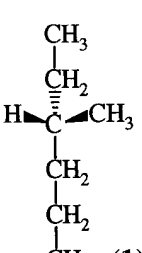
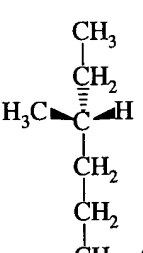
5.4 (a), (b), and (f) do not have stereocenters.

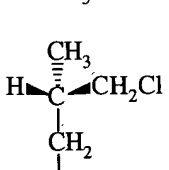
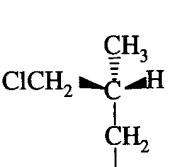
(c)  (1)  (2)

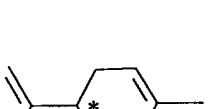
(d)  (1)  (2)

(e)  (1)  (2)

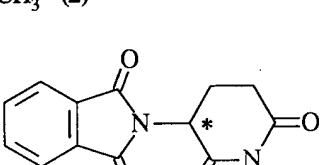
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(g)  (1)  (2)

(h)  (1)  (2)

5.5 (a) 

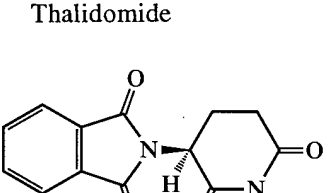
Limonene

(b) 

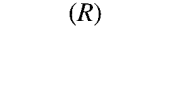
Thalidomide



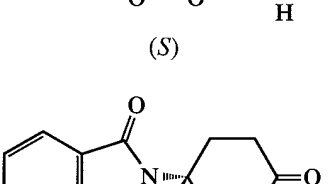
(*R*)



(*S*)



(*S*)



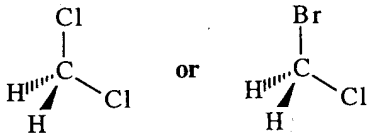
(*R*)

5.6 (a) Two in each instance.



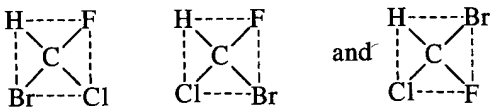
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(b) Only one in each instance.

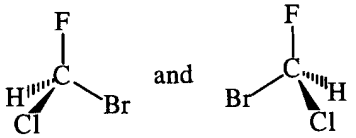


Any other tetrahedral arrangements will be superposable on one or the other of the above.

(c) Three:



(d) Two:



5.7 The following items possess a plane of symmetry, and are, therefore, achiral.

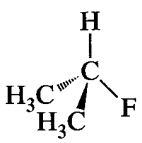
(a) A screwdriver

(b) A baseball bat (ignoring any writing on it)

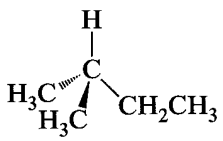
(h) A hammer

5.8 In each instance below, the plane defined by the page is a plane of symmetry.

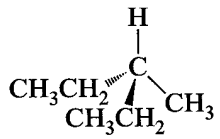
(a)



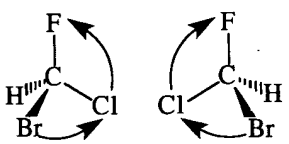
(b)



(f)



5.9



(*S*) (*R*)

5.10 (c) (1) is (*S*)
(2) is (*R*)

(d) (1) is (*S*)
(2) is (*R*)

(e) (1) is (*S*)
(2) is (*R*)

(g) (1) is (*S*)
(2) is (*R*)

(h) (1) is (*S*)
(2) is (*R*)

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5.11 (a) $-Cl > -SH > -OH > -H$

(b) $-CH_2Br > -CH_2Cl > -CH_2OH > -CH_3$

(c) $-OH > -CHO > -CH_3 > -H$

(d) $-C(CH_3)_3 > -CH{=}CH_2 > -CH(CH_3)_2 > -H$

(e) $-OCH_3 > -N(CH_3)_2 > -CH_3 > -H$

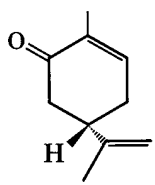
5.12 (a) (*S*) (b) (*R*) (c) (*S*)

5.13 (a) Enantiomers

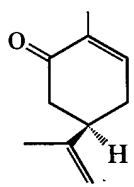
(b) Two molecules of the same compound

(c) Enantiomers

5.14



(*S*)-(+)-Carvone



(*R*)-(−)-Carvone

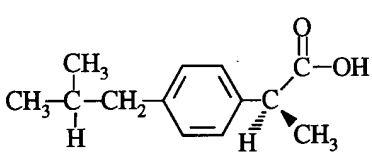
5.15 (a) Enant. Excess $= \dfrac{\text{observed rotation}}{\text{specific rotation of pure enantiomer}} \times 100$

$= \dfrac{+1.151°}{+5.756°} \times 100$

$= 20.00\%$

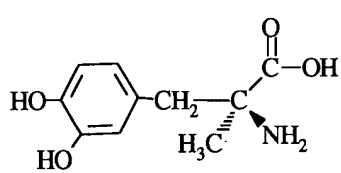
(b) since the (*R*) enantiomer (see Section 5.7C) is +, the (*R*) enantiomer is present in excess.

5.16 (a)



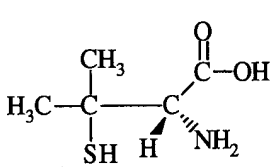
(*S*)-Ibuprofen

(b)



(*S*)-Methyldopa

(c)



(*S*)-Penicillamine

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5.17 (a) Diastereomers.

(b) Diastereomers in each instance.

(c) No, diastereomers have different melting points.

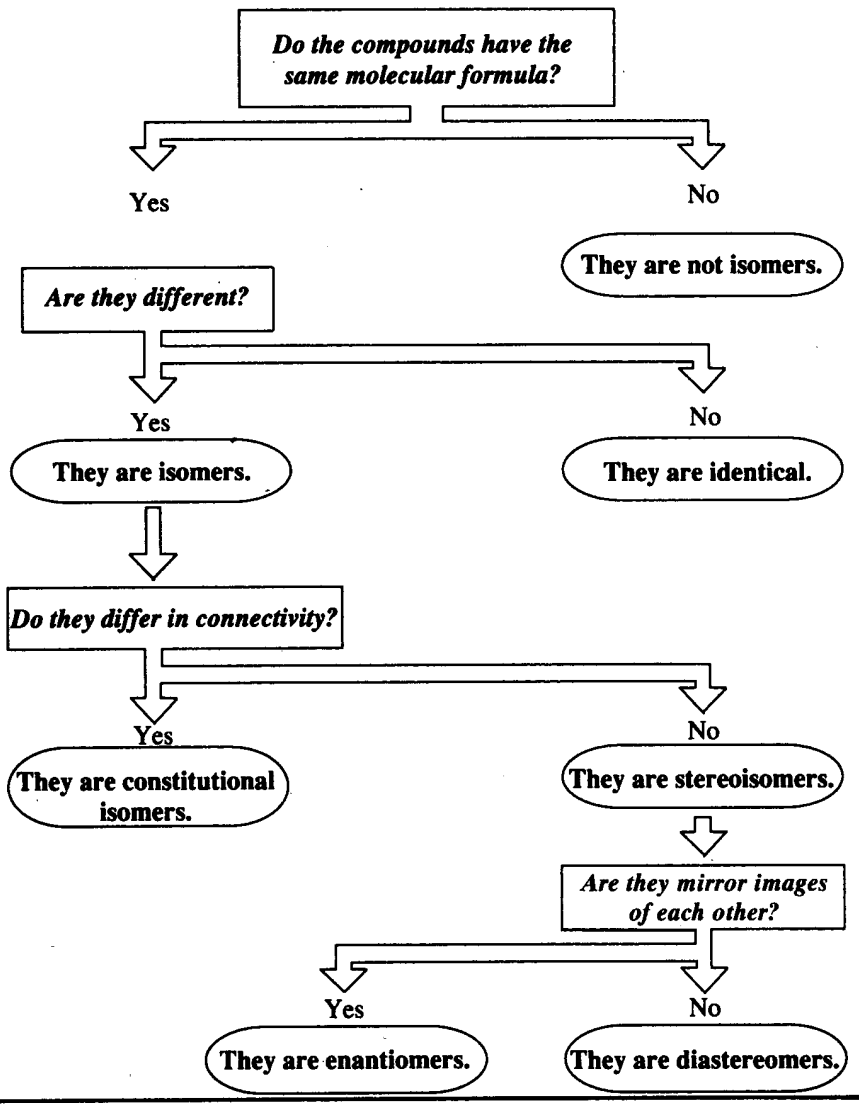
(d) No, diastereomers have different boiling points.

(e) No, diastereomers have different vapor pressures.

STUDY AID

An Approach to the Classification of Isomers

We can classify isomers by asking and answering a series of questions:



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5.18 (a) It would be optically active.

(b) It would be optically active.

(c) No, because it is a meso compound.

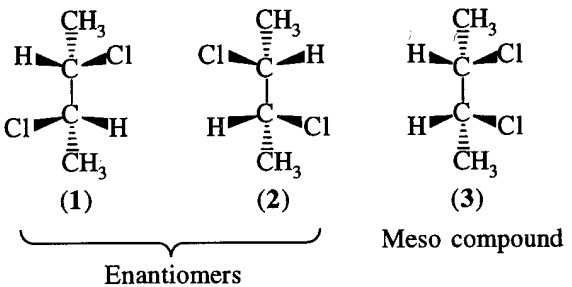
(d) No, because it would be a racemic form.

5.19 (a) Represents **A**

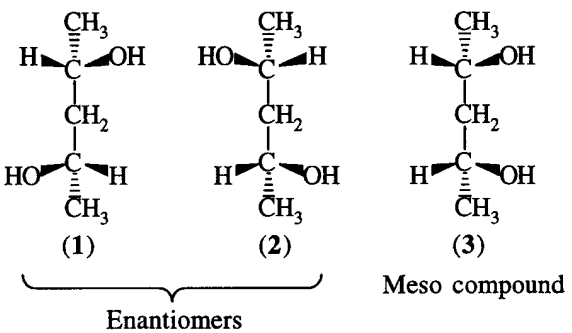
(b) Represents **C**

(c) Represents **B**

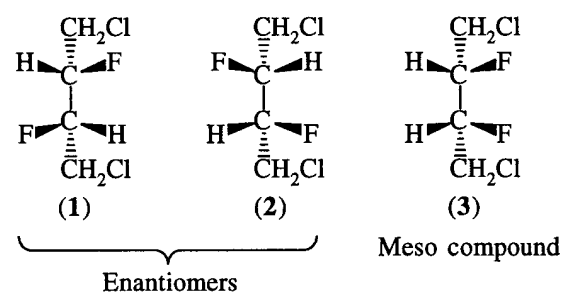
5.20 (a)



(b)

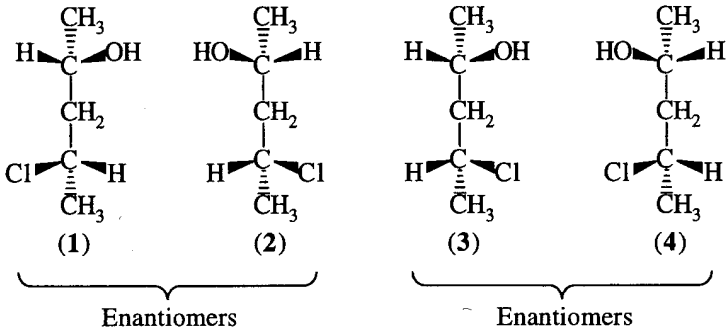


(c)

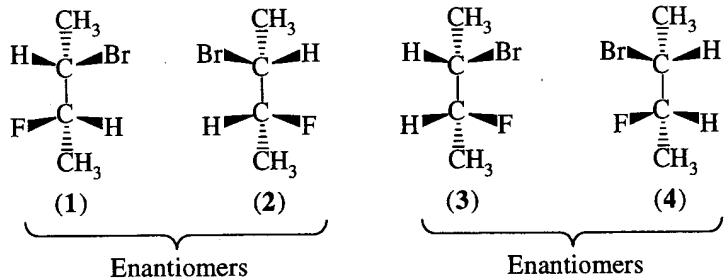


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(d)



(e)



5.21 **B** is (2*S*,3*S*)-2,3-Dibromobutane
C is (2*R*,3*S*)-2,3-Dibromobutane

5.22 (a) (**1**) is (2*S*,3*S*)-2,3-Dichlorobutane
(**2**) is (2*R*,3*R*)-2,3-Dichlorobutane
(**3**) is (2*R*,3*S*)-2,3-Dichlorobutane

(b) (**1**) is (2*S*,4*S*)-2,4-Pentanediol
(**2**) is (2*R*,4*R*)-2,4-Pentanediol
(**3**) is (2*R*,4*S*)-2,4-Pentanediol

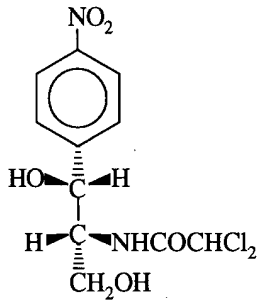
(c) (**1**) is (2*R*,3*R*)-1,4-Dichloro-2,3-difluorobutane
(**2**) is (2*S*,3*S*)-1,4-Dichloro-2,3-difluorobutane
(**3**) is (2*R*,3*S*)-1,4-Dichloro-2,3-difluorobutane

(d) (**1**) is (2*S*,4*S*)-4-Chloro-2-pentanol
(**2**) is (2*R*,4*R*)-4-Chloro-2-pentanol
(**3**) is (2*S*,4*R*)-4-Chloro-2-pentanol
(**4**) is (2*R*,4*S*)-4-Chloro-2-pentanol

(e) (**1**) is (2*S*,3*S*)-2-Bromo-3-fluorobutane
(**2**) is (2*R*,3*R*)-2-Bromo-3-fluorobutane
(**3**) is (2*S*,3*R*)-2-Bromo-3-fluorobutane
(**4**) is (2*R*,3*S*)-2-Bromo-3-fluorobutane

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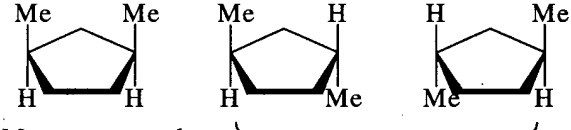
5.23



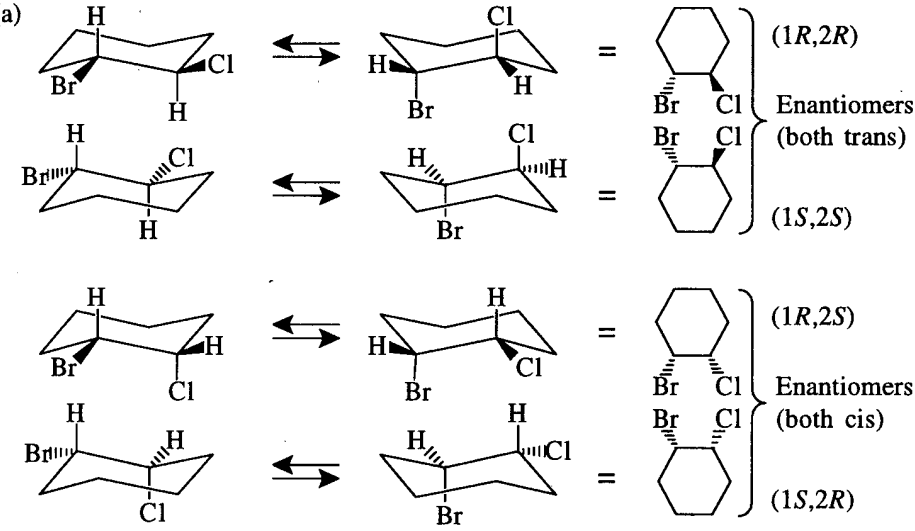
Chloramphenicol

5.24 (a) No (b) Yes (c) No (d) No (e) Diastereomers (f) Diastereomers

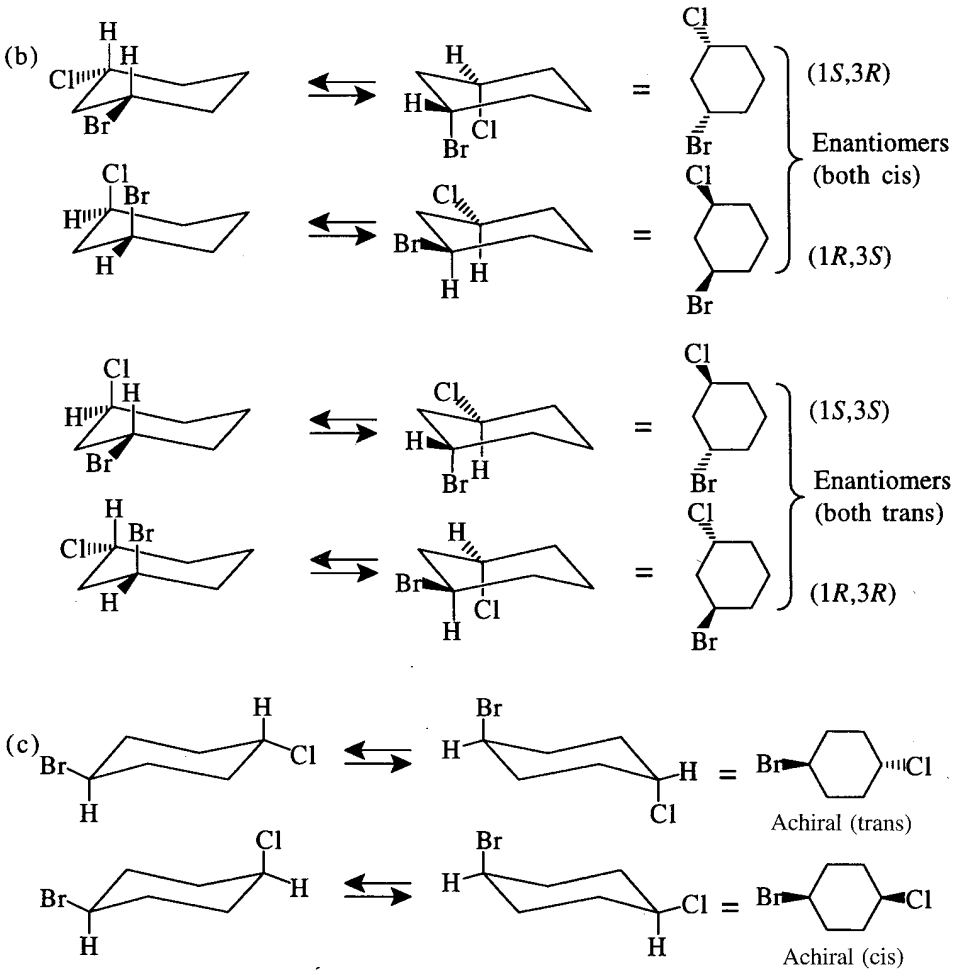
5.25



5.26 (a)

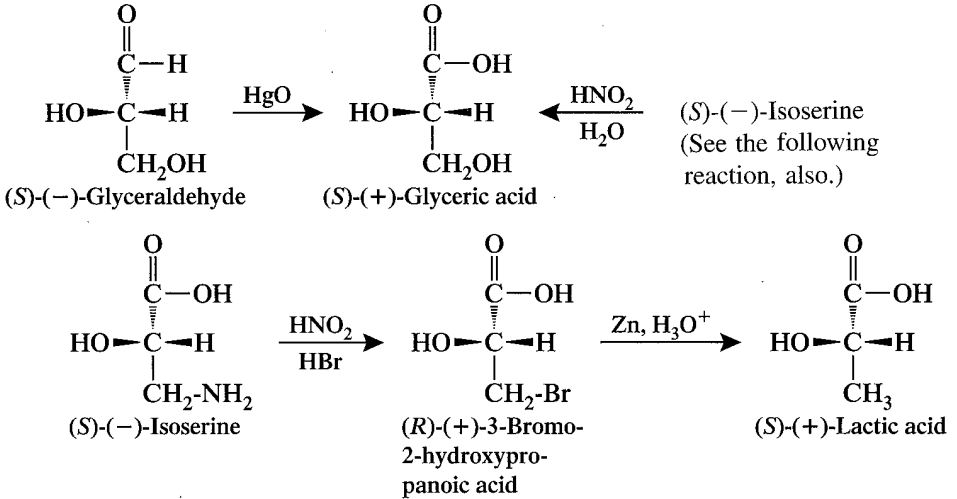


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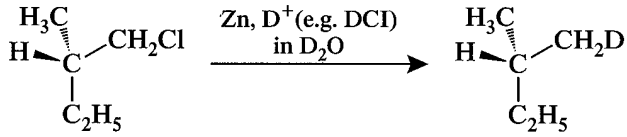
5.27 See Problem 5.26. The molecules in (c) are achiral, so they have no (*R*-*S*) designation.

5.28



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5.29



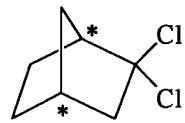
(*S*)-(+)-1-Chloro-2-methylbutane (*R*)-1-Deuterio-2-methylbutane

5.30 (a), (b), (f) and (g) only

5.31 (a) Seven.

(b) (*R*)- and (*S*)-3-Methylhexane and (*R*)- and (*S*)-2,3-dimethylpentane.

5.32 (a) and (b)



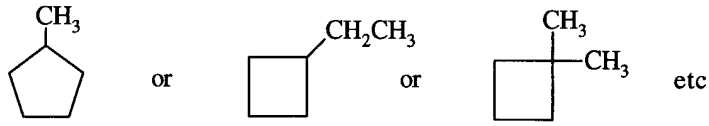
(c) Four

(d) Because a trans arrangement of the one carbon bridge is structurally impossible. Such a molecule would have too much strain.

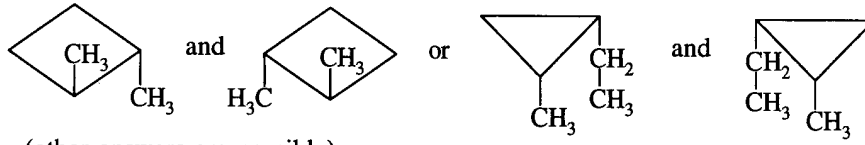
5.33 (a) **A** is (*R,S*)-2,3-dichlorobutane; **B** is (*S,S*)-2,3-dichlorobutane; **C** is (*R,R*)-2,3-dichlorobutane.

(b) **A**

5.34 (a)

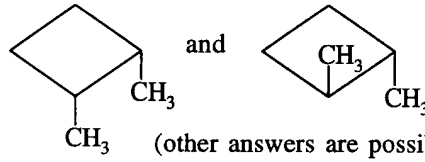


(b)



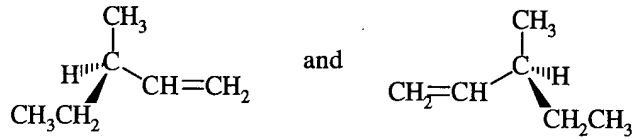
(other answers are possible)

(c)

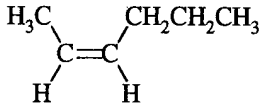
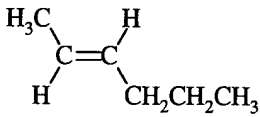


(other answers are possible)

(d)



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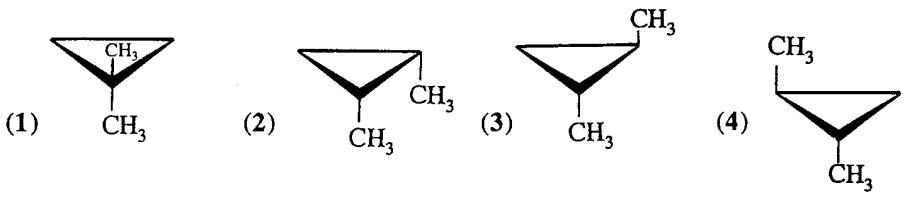
(e)  and 

(other answers are possible)

5.35 (a) Same
(b) Enantiomers
(c) Diastereomers
(d) Same
(e) Same
(f) Constitutional isomers
(g) Diastereomers
(h) Enantiomers
(i) Same
(j) Enantiomers that are interconvertible by a ring flip
(k) Diastereomers
(l) Same
(m) Diastereomers
(n) Constitutional isomers
(o) Diastereomers
(p) Same
(q) Same

5.36 All of these molecules are expected to be planar. Their stereochemistry is identical to that of the corresponding chloroethenes. (a) can exist as cis and trans isomers. Only one compound exists in the case of (b) and (c).

5.37 (a)

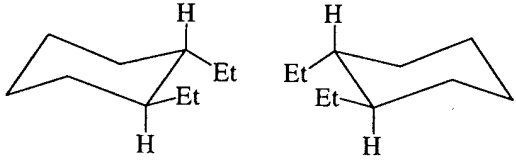


(b) (**3**) and (**4**) are chiral and are enantiomers of each other.

(c) Three fractions: a fraction containing (**1**), a fraction containing (**2**), and a fraction containing (**3**) and (**4**) [because, being enantiomers, (**3**) and (**4**) would have the same vapor pressure].

(d) None

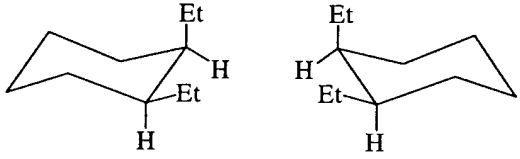
5.38 (a)



(b) No, they are not superposable.

(c) No, and they are, therefore, enantiomers of each other.

(d)

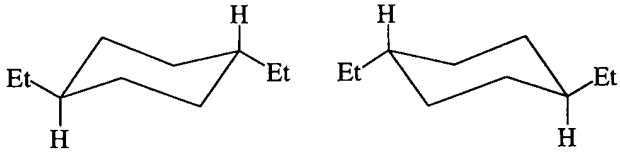


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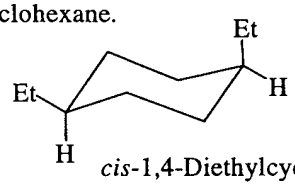
(e) No, they are not superposable.

(f) Yes, and they are, therefore, just different conformations of the same molecule.

5.39 (a)



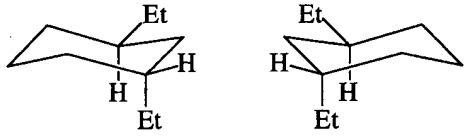
(b) Yes, and therefore *trans*-1.4-diethylcyclohexane is achiral.
(c) No, they are different orientations of the same molecule.
(d) Yes, *cis*-1,4-diethylcyclohexane is a stereoisomer (a diastereomer) of *trans*-1.4-diethylcyclohexane.



cis-1,4-Diethylcyclohexane

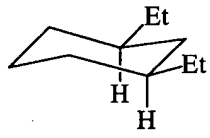
(e) No, it, too, is superposable on its mirror image. (Notice, too, that the plane of the page constitutes a plane of symmetry for both *cis*-1,4-diethylcyclohexane and for *trans*-1,4-diethylcyclohexane as we have drawn them.)

5.40 *trans*-1,3-Diethylcyclohexane can exist in the following enantiomeric forms.



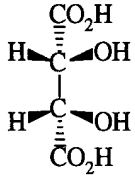
trans-1,3-Diethylcyclohexane enantiomers

cis-1,3-Diethylcyclohexane consists of achiral molecules because they have a plane of symmetry. [The plane of the page (below) is a plane of symmetry.]



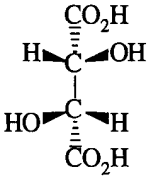
cis-1,3-Diethylcyclohexane

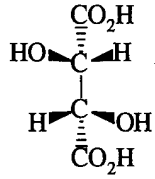
***5.41** (a) Since it is optically active and not resolvable, it must be the meso form:



(meso)

(b)





(c) No (d) A racemic modification

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***5.42** (a) $[\alpha]_D = \dfrac{-30°}{(0.10\ \text{g/mL})(1.0\ \text{dm})} = -300°$

(b) $[\alpha]_D = \dfrac{+165°}{(0.05\ \text{g/mL})(1.0\ \text{dm})} = +3300°$

The two rotation values can be explained by recognizing that this is a powerfully optically active substance and that the first reading, assumed to be $-30°$, was really $+330°$. Making this change the $[\alpha]_D$ becomes $+3300°$ in both cases.

(c) No, the apparent 0° rotation could actually be + or $-360°$ (or an integral multiple of these values).

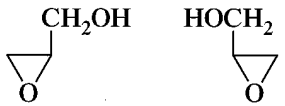
***5.43** Yes, it could be a *meso* form or an enantiomer whose stereocenters, by rare coincidence, happen to cancel each others activities.

***5.44** A compound $C_3H_6O_2$ has an index of hydrogen deficiency of 1. Thus, it could possess a carbon-carbon double bond, a carbon-oxygen double bond, or a ring.

The IR spectral data rule out a carbonyl group but indicate the presence of an —OH group.

No stable structure having molecular formula $C_3H_6O_2$ with a C=C bond can exist in stereoisomeric forms and 1,2-cyclopropanediol can exist in three stereoisomeric forms.

Only ethylene oxide (oxirane) derivatives are possible for Y:



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6 IONIC REACTIONS— NUCLEOPHILIC SUBSTITUTION AND ELIMINATION REACTIONS OF ALKYL HALIDES

SOLUTIONS TO PROBLEMS

6.1 (a) $CH_3-\ddot{I}: + CH_3CH_2-\ddot{O}:^- \longrightarrow CH_3-\ddot{O}-CH_2CH_3 + :\ddot{I}:^-$

Substrate; Nucleophile; Leaving group

(b) $:\ddot{I}:^- + CH_3CH_2-\ddot{Br}: \longrightarrow CH_3CH_2-\ddot{I}: + :\ddot{Br}:^-$

Nucleophile; Substrate; Leaving group

(c) $CH_3\ddot{O}H + (CH_3)_3C-\ddot{Cl}: \longrightarrow (CH_3)_3C-\ddot{O}-CH_3 + :\ddot{Cl}:^- + H^+$

Nucleophile; Substrate; Leaving group

(d) $CH_3CH_2CH_2-\ddot{Br}: + :C\equiv N:^- \longrightarrow CH_3CH_2CH_2-CN + :\ddot{Br}:^-$

Substrate; Nucleophile; Leaving group

(e) $C_6H_5CH_2-\ddot{Br}: + :NH_3 \longrightarrow C_6H_5CH_2-\ddot{N}H_2 + :\ddot{Br}:^- + H^+$

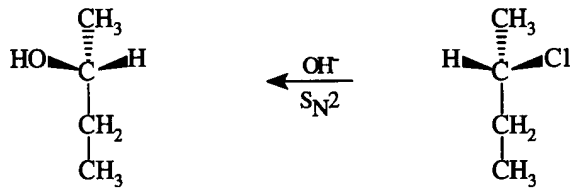
Substrate; Nucleophile; Leaving group

6.2



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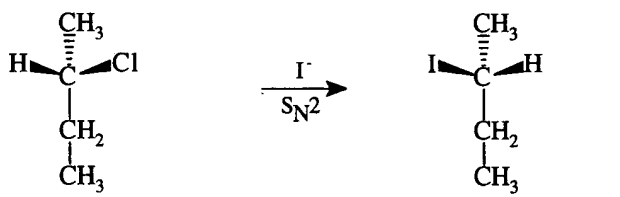
6.3 (a) We know that when a secondary alkyl halide reacts with hydroxide ion by substitution, the reaction occurs with *inversion of configuration* because the reaction is S_N2. If we know that the configuration of (−)-2-butanol (from Section 5.7C) is that shown here, then we can conclude that (+)-2-chlorobutane has the opposite configuration.



(*R*)-(-)-2-Butanol
$[\alpha]_D^{25°} = -13.52°$

(*S*)-(+)-2-Chlorobutane
$[\alpha]_D^{25°} = +36.00°$

(b) Again the reaction is S_N2. Because we now know the configuration of (+)-2-chlorobutane to be (*S*) [cf., part (a)], we can conclude that the configuration of (−)-2-iodobutane is (*R*).

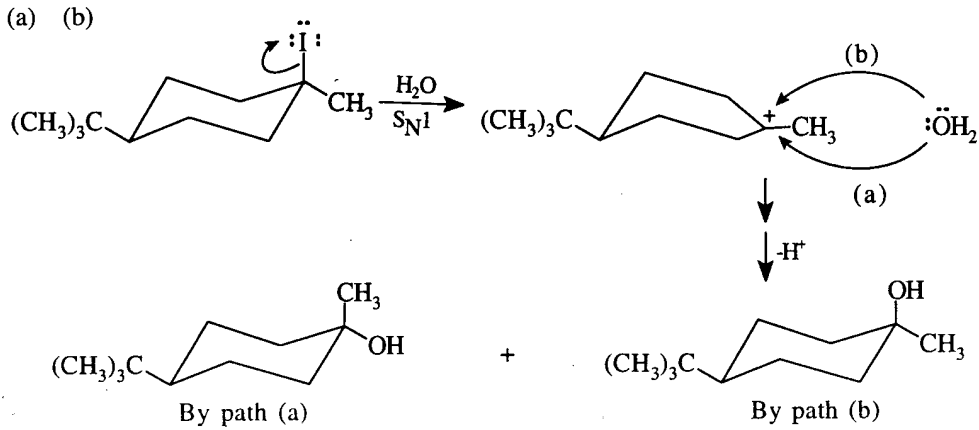


(*S*)-(+)-2-Chlorobutane

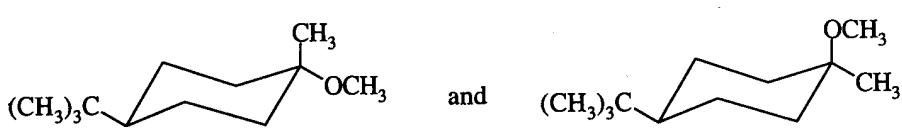
(*R*)-(-)-2-Iodobutane

(+)-2-Iodobutane has the (*S*) configuration

6.4 (a) (b)



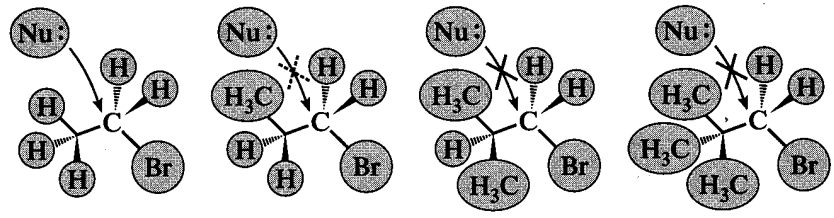
6.5



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6.6 (a) Being primary halides, the reactions are most likely to be S_N2, with the nucleophile in each instance being a molecule of the solvent (i.e., a molecule of ethanol).

(b) Steric hindrance is provided by the substituent or substituents on the carbon β to the carbon bearing the leaving group. With each addition of a methyl group at the β carbon (below), the number of pathways open to the attacking nucleophile becomes fewer.



6.7 **Protic solvents** are those that have an H bonded to an oxygen or nitrogen (or to another strongly electronegative atom). Therefore, the protic solvents are formic acid, HCOH (O double-bonded); formamide, $\mathrm{HCNH_2}$ (O double-bonded): ammonia, NH_3; and ethylene glycol, $HOCH_2CH_2OH$

Aprotic solvents lack an H bonded to a strongly electronegative element. Aprotic solvents in this list are acetone, $\mathrm{CH_3CCH_3}$ (O double-bonded); acetonitrile, $CH_3C{\equiv}N$; sulfur dioxide, SO_2; and trimethylamine, $N(CH_3)_3$.

6.8 The reaction is an S_N2 reaction. In the polar aprotic solvent (DMF), the nucleophile (CN^-) will be relatively unencumbered by solvent molecules, and, therefore, it will be more reactive than in ethanol. As a result, the reaction will occur faster in *N,N*-dimethylformamide.

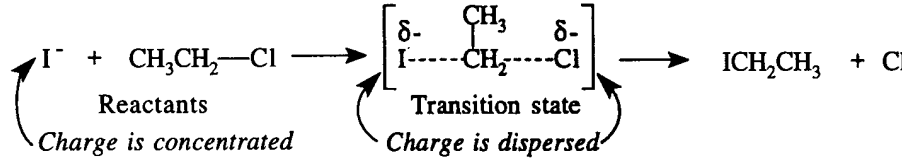
6.9 (a) CH_3O^-

(b) H_2S

(c) $(CH_3)_3P$

6.10 (a) Increasing the percentage of water in the mixture increases the polarity of the solvent. (Water is more polar than methanol.) Increasing the polarity of the solvent increases the rate of the solvolysis because separated charges develop in the transition state. The more polar the solvent, the more the transition state is stabilized (Section 6.14D).

(b) In an S_N2 reaction of this type, the charge becomes dispersed in the transition state:

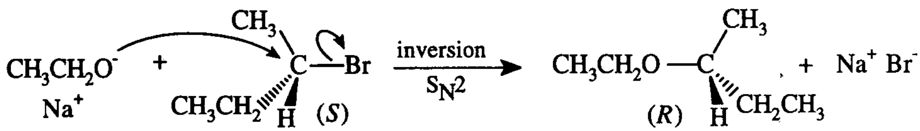


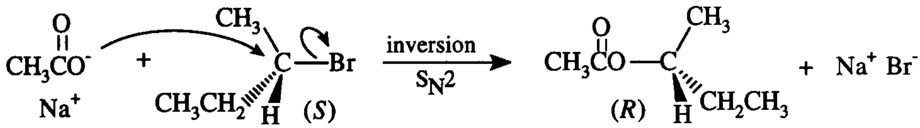
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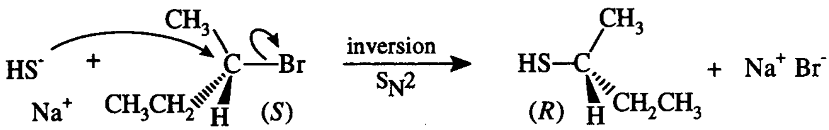
Increasing the polarity of the solvent increases the stabilization of the reactant I^- more than the stabilization of the transition state, and thereby increases the free energy of activation, thus decreasing the rate of reaction.

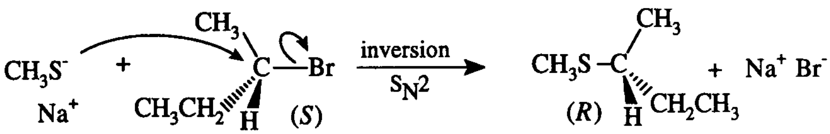
6.11 $CH_3OSO_2CF_3 > CH_3I > CH_3Br > CH_3Cl > CH_3F > {}^{14}CH_3OH$

(Most reactive) (Least reactive)

6.12 (a) 

(b) 

(c) 

(d) 

6.13 (a) $CH_3CH_2CH_2Br + NaOH \longrightarrow CH_3CH_2CH_2OH + NaBr$

(b) $CH_3CH_2CH_2Br + NaI \longrightarrow CH_3CH_2CH_2I + NaBr$

(c) $CH_3CH_2CH_2Br + CH_3CH_2ONa \longrightarrow CH_3CH_2CH_2OCH_2CH_3 + NaBr$

(d) $CH_3CH_2CH_2Br + CH_3SNa \longrightarrow CH_3CH_2CH_2SCH_3 + NaBr$

(e) $CH_3CH_2CH_2Br + CH_3\overset{O}{\overset{\|}{C}}-ONa \longrightarrow CH_3CH_2CH_2O\overset{O}{\overset{\|}{C}}CH_3 + NaBr$

(f) $CH_3CH_2CH_2Br + NaN_3 \longrightarrow CH_3CH_2CH_2N_3 + NaBr$

(g) $CH_3CH_2CH_2Br + :N(CH_3)_3 \longrightarrow CH_3CH_2CH_2-\overset{+}{N}(CH_3)_3\ Br^-$

(h) $CH_3CH_2CH_2Br + NaCN \longrightarrow CH_3CH_2CH_2CN + NaBr$

(i) $CH_3CH_2CH_2Br + NaSH \longrightarrow CH_3CH_2CH_2SH + NaBr$

6.14 (a) 1-Bromopropane would react more rapidly because, being a primary halide, it is less hindered.

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(b) 1-Iodobutane, because iodide ion is a better leaving group than chloride ion.

(c) 1-Chlorobutane, because the carbon bearing the leaving group is less hindered than in 1-chloro-2-methylpropane.

(d) 1-Chloro-3-methylbutane, because the carbon bearing the leaving group is less hindered than in 1-chloro-2-methylbutane.

(e) 1-Chlorohexane because it is a primary halide. Phenyl halides are unreactive in S_N2 reactions.

6.15 (a) Reaction (1) because ethoxide ion is a stronger nucleophile than ethanol.

(b) Reaction (2) because the ethyl sulfide ion is a stronger nucleophile than the ethoxide ion in a protic solvent. (Because sulfur is larger than oxygen, the ethyl sulfide ion is less solvated and it is more polarizable.)

(c) Reaction (2) because triphenylphosphine $[(C_6H_5)_3P]$ is a stronger nucleophile than triphenylamine. (Phosphorus atoms are larger than nitrogen atoms.)

(d) Reaction (2) because in an S_N2 reaction the rate depends on the concentration of the substrate and the nucleophile. In reaction (2) the concentration of the nucleophile is twice that of the reaction (1).

6.16 (a) Reaction (2) because bromide ion is a better leaving group than chloride ion.

(b) Reaction (1) because water is a more polar solvent than methanol, and S_N1 reactions take place faster in more polar solvents.

(c) Reaction (2) because the concentration of the substrate is twice that of reaction (1). (The major reaction would be E2. However, the problem asks us to consider that small portion of the overall reaction that proceeds by an S_N1 pathway.)

(d) Both reactions would take place at the same rate because, being S_N1 reactions, they are independent of the concentration of the nucleophile.
(The major reaction would be E2. However, the problem asks us to consider that small portion of the overall reaction that proceeds by an S_N1 pathway.)

(e) Reaction (1) because the substrate is a tertiary halide. Phenyl halides are unreactive in S_N1 reactions.

6.17 Possible methods are given here.

(a) $CH_3Cl \xrightarrow[S_N2]{I^- / CH_3OH} CH_3I$

(b) $CH_3CH_2Cl \xrightarrow[S_N2]{I^- / CH_3OH} CH_3CH_2I$

(c) $CH_3Cl \xrightarrow[S_N2]{OH^- / CH_3OH/H_2O} CH_3OH$

(d) $CH_3CH_2Cl \xrightarrow[S_N2]{OH^- / CH_3OH/H_2O} CH_3CH_2OH$

(e) $CH_3Cl \xrightarrow[S_N2]{SH^- / CH_3OH} CH_3SH$

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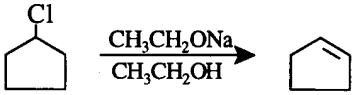
(f) $CH_3CH_2Cl \xrightarrow[S_N2]{SH^- \atop CH_3OH} CH_3CH_2SH$

(g) $CH_3Cl \xrightarrow[DMF]{CN^-} CH_3CN$

(h) $CH_3CH_2Cl \xrightarrow[DMF]{CN^-} CH_3CH_2CN$

(i) $CH_3OH \xrightarrow[(-H_2)]{NaH} CH_3ONa \xrightarrow[CH_3OH]{CH_3I} CH_3OCH_3$

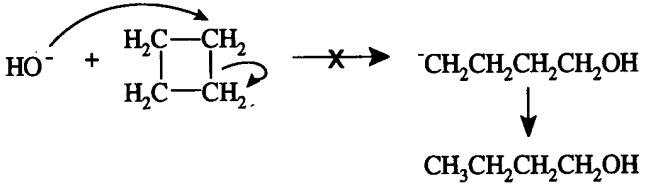
(j) $CH_3CH_2OH \xrightarrow[(-H_2)]{NaH} CH_3CH_2ONa \xrightarrow{CH_3I} CH_3CH_2OCH_3$

(k) 

6.18 (a) The reaction will not take place because the leaving group would have to be a methyl anion, a very powerful base, and a very poor leaving group.

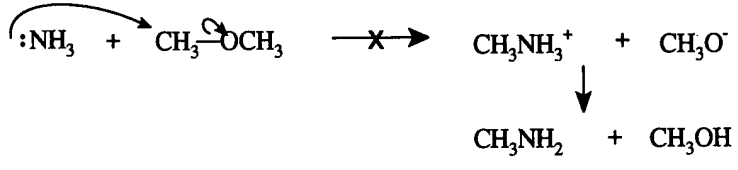
(b) The reaction will not take place because the leaving group would have to be a hydride ion, a very powerful base, and a very poor leaving group.

(c) The reaction will not take place because the leaving group would have to be a carbanion, a very powerful base, and a very poor leaving group.



(d) The reaction will not take place by an S_N2 mechanism because the substrate is a tertiary halide, and is, therefore, not susceptible to S_N2 attack because of the steric hindrance. (A very small amount of S_N1 reaction may take place, but the main reaction will be E2 to produce an alkene.)

(e) The reaction will not take place because the leaving group would have to be a CH_3O^- ion, a strong base, and a very poor leaving group.



(f) The reaction will not take place because the first reaction that would take place would be an acid-base reaction that would convert the ammonia to an ammonium ion. An ammonium ion, because it lacks an electron pair, is not nucleophilic.

$$NH_3 + CH_3OH_2^+ \rightleftharpoons NH_4^+ + CH_3OH$$

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6.19 The better yield will be obtained by using the secondary halide, 1-bromo-1-phenylethane, because the desired reaction is E2. Using the primary halide will result in substantial S_N2 reaction as well, producing the alcohol instead of the desired alkene.

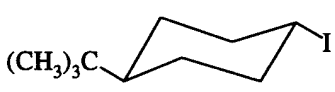
6.20 Reaction (2) would give the better yield because the desired reaction is an S_N2 reaction, and the substrate is a methyl halide. Use of reaction (1) would, because the substrate is a secondary halide, result in considerable elimination by an E2 pathway.

6.21 (a) The major product would be $CH_3CH_2CH_2CH_2CH_2OCH_2CH_3$ (by an S_N2 mechanism) because the substrate is primary and the nucleophile-base is not hindered. Some $CH_3CH_2CH_2CH{=}CH_2$ would be produced by an E2 mechanism.

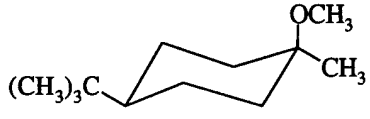
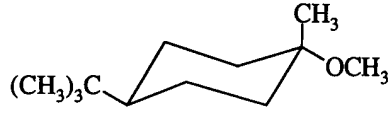
(b) The major product would be $CH_3CH_2CH_2CH{=}CH_2$ (by an E2 mechanism), even though the substrate is primary because the base is a hindered strong base. Some $CH_3CH_2CH_2CH_2CH_2OC(CH_3)_3$ would be produced by an S_N2 mechanism.

(c) For all practical purposes, $(CH_3)_2C{=}CH_2$ (by an E2 mechanism) would be the only product because the substrate is tertiary and the base is strong.

(d) Same answer as (c) above.

(e)  (formed by an S_N2 mechanism) would, for all practical purposes, be the only product. Iodide ion is a very weak base and a good nucleophile.

(f) Because the substrate is tertiary and the only nucleophile is the solvent, the mechanism is E1. The two products that follow would be formed.

 and 

(g) $CH_3CH{=}CHCH_2CH_3$ (by an E2 mechanism) would be the major product because the substrate is secondary and the base/nucleophile is a strong base. Some of the ether, $CH_3CH_2CH(OCH_3)CH_2CH_3$, would be formed by an S_N2 pathway.

(h) The major product would be $CH_3CH_2CH(O_2CCH_3)CH_2CH_3$ (by an S_N2 mechanism) because the acetate ion is a weak base. Some $CH_3CH{=}CHCH_2CH_2CH_3$ might be formed by an E2 pathway.

(i) $CH_3CH{=}CHCH_3$ and $CH_2{=}CHCH_2CH_3$ (by E2) would be major products, and (*S*)-$CH_3CH(OH)CH_2CH_3$ (by S_N2) would be the minor product.

(j) (±)-$CH_3CH_2\underset{\displaystyle OCH_3}{\underset{|}{C}}(CH_3)CH_2CH_2CH_3$ (by S_N1) would be the major product.

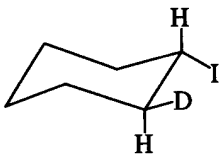
$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_2CH_3$, $CH_3CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}CH_2CH_2CH_3$, and

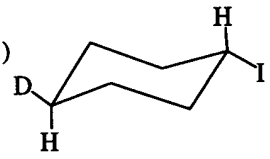
$CH_3CH_2\underset{\displaystyle CH_2}{\underset{\|}{C}}CH_2CH_2CH_3$ (by E1) would be minor products.

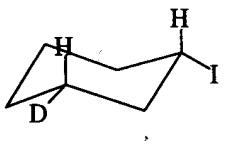
(k) (*R*)-$CH_3CHIC_6H_{13}$ (by S_N2) would be the only product.

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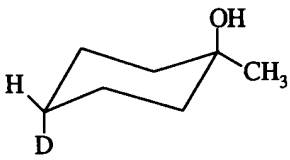
6.22 (a), (b), and (c) are all S_N2 reactions and, therefore, proceed with inversion of configuration. The products are

(a) 

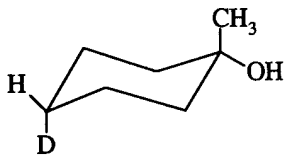
(b) 

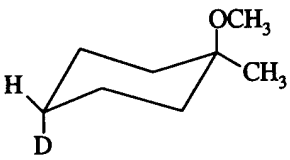
(c) 

(d) is an S_N1 reaction. The carbocation that forms can react with either nucleophile (H_2O or CH_3OH) from either the top or bottom side of the molecule. Four substitution products (below) would be obtained. (Considerable elimination by an E1 path would also occur.)

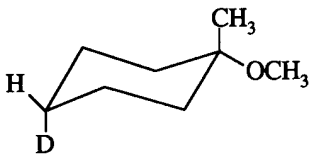


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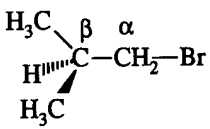




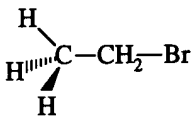
and



6.23 Isobutyl bromide is more sterically hindered than ethyl bromide because of the methyl groups on the β carbon atom.



Isobutyl bromide



Ethyl bromide

This steric hindrance causes isobutyl bromide to react more slowly in S_N2 reactions and to give relatively more elimination (by an E2 path) when a strong base is used.

6.24 (a) S_N2 because the substrate is a 1° halide.

(b) Rate = k [CH_3CH_2Cl][I^-]

$= 5 \times 10^{-5}$ L mol^{-1}s^{-1} $\times$ 0.1 mol L^{-1} $\times$ 0.1 mol L^{-1}

Rate = 5×10^{-7} mol L^{-1}s^{-1}

(c) 1×10^{-6} mol L^{-1}s^{-1}

(d) 1×10^{-6} mol L^{-1}s^{-1}

(e) 2×10^{-6} mol L^{-1}s^{-1}

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6.25 (a) CH_3NH^- because it is the stronger base.

(b) CH_3O^- because it is the stronger base.

(c) CH_3SH because sulfur atoms are larger and more polarizable than oxygen atoms.

(d) $(C_6H_5)_3P$ because phosphorus atoms are larger and more polarizable than nitrogen atoms.

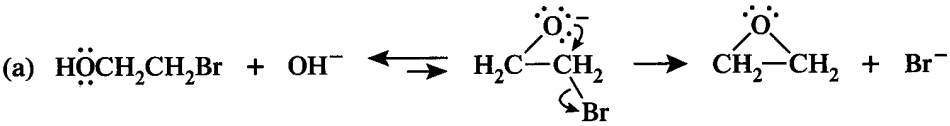
(e) H_2O because it is the stronger base.

(f) NH_3 because it is the stronger base.

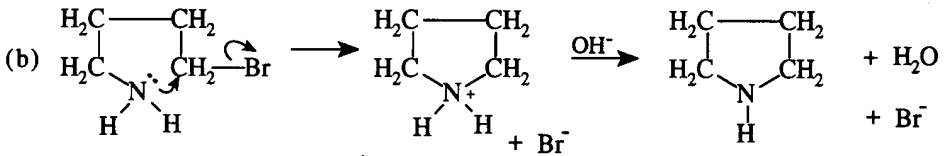
(g) HS^- because it is the stronger base.

(h) OH^- because it is the stronger base.

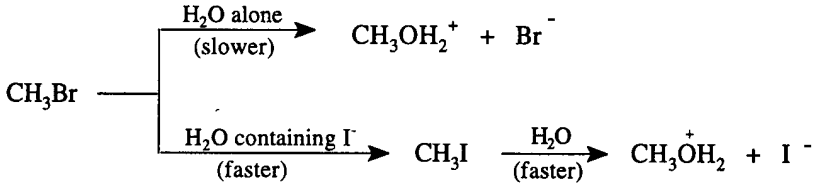
6.26 (a)



(b)



6.27 Iodide ion is a good nucleophile and a good leaving group; it can rapidly convert an alkyl chloride or alkyl bromide into an alkyl iodide, and the alkyl iodide can then react rapidly with another nucleophile. With methyl bromide in water, for example, the following reaction can take place:



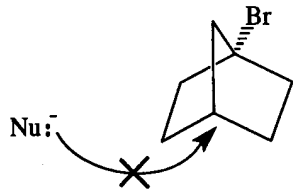
6.28 *tert*-Butyl alcohol and *tert*-butyl methyl ether are formed via an S_N1 mechanism. The rate of the reaction is independent of the concentration of methoxide ion (from sodium methoxide). This, however, is only one reaction that causes *tert*-butyl bromide to disappear. A competing reaction that also causes *tert*-butyl bromide to disappear is an E2 reaction in which methoxide ion reacts with *tert*-butyl bromide. This reaction is dependent on the concentration of methoxide ion; therefore, increasing the methoxide ion concentration causes an increase in the rate of disappearance of *tert*-butyl bromide.

6.29 (a) You should use a strong base, such as RO^-, at a higher temperature to bring about an E2 reaction.

(b) Here we want an S_N1 reaction. We use ethanol as the solvent *and as the nucleophile,* and we carry out the reaction at a low temperature so that elimination will be minimized.

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6.30 1-Bromobicyclo[2.2.1]heptane is unreactive in an S_N2 reaction because it is a tertiary halide and its ring structure makes the backside of the carbon bearing the leaving group completely inaccessible to attack by a nucleophile.

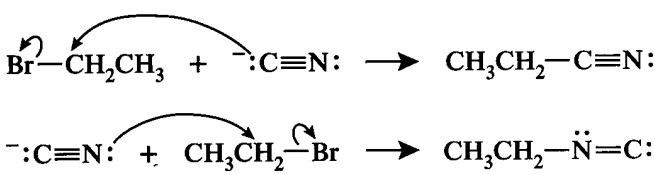


1-Bromobicyclo[2.2.1]heptane is unreactive in an S_N1 reaction because the ring structure makes it impossible for the carbocation that must be formed to assume the required trigonal planar geometry around the positively charged carbon. Any carbocation formed from 1-bromobicyclo[2.2.1]heptane would have a trigonal pyramidal arrangement of the $-CH_2-$ groups attached to the positively charged carbon (make a model). Such a structure does not allow stabilization of the carbocation by overlap of sp^3 orbitals from the alkyl groups (see Fig. 6.9).

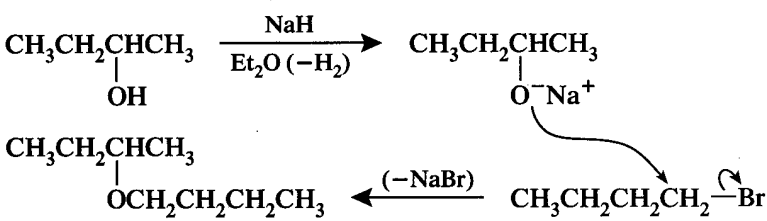
6.31 The cyanide ion has two nucleophilic atoms; it is what is called an ambident nucleophile.

$$\cdot\cdot\ddot{C}\equiv N:$$

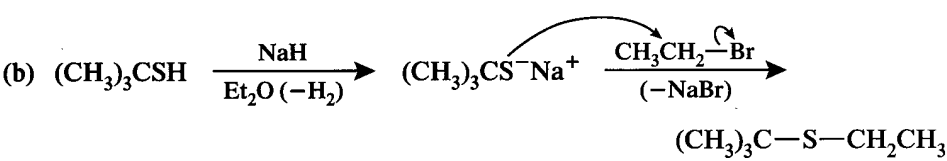
It can react with a substrate using either atom, although the carbon atom is more nucleophilic.



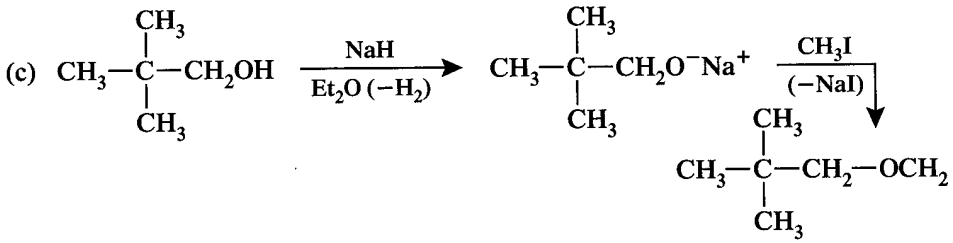
6.32 (a)

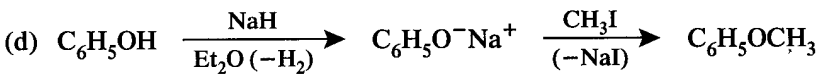


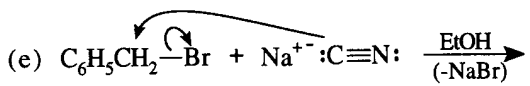
(b)

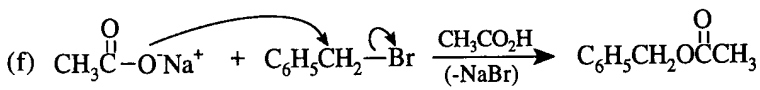


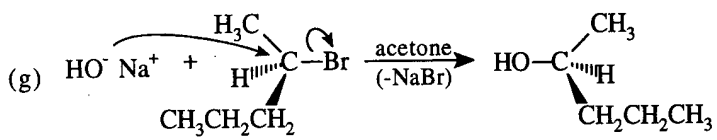
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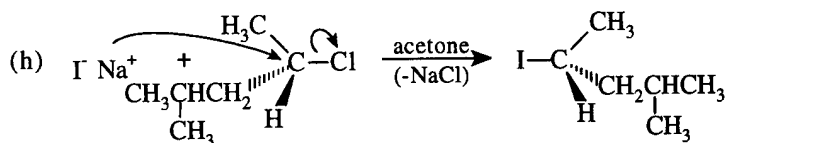
(c) 

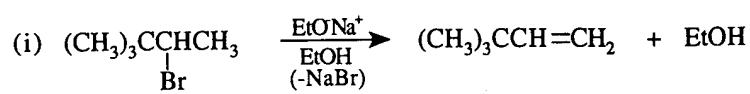
(d) 

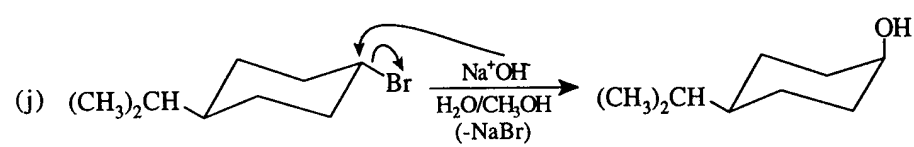
(e) 

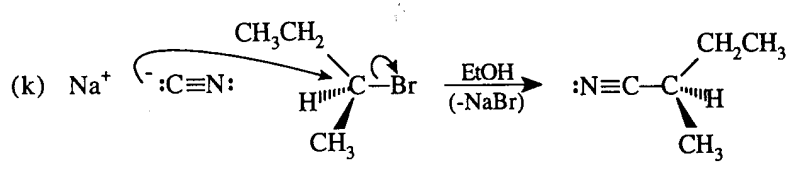
(f) 

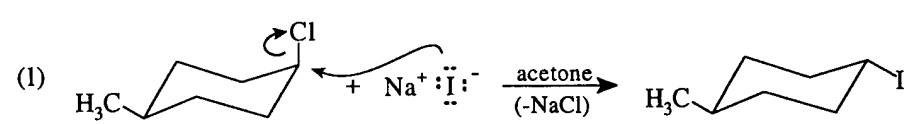
(g) 
(*R*)-2-Bromopentane (*S*)-2-Pentanol

(h) 
(*S*)-2-Chloro-4-methylpentane (*R*)-2-Iodo-4-methylpentane

(i) 

(j) 

(k) 
(*S*)-2-Bromobutane

(l) 

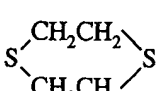
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6.33 (a) 

(Formation of this product depends on the fact that bromide ion is a much better leaving group than fluoride ion.)

(b) $CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_2CH_2-I$

(Formation of this product depends on the greater reactivity of 1° substrates in S_N2 reactions.)

(c) 

(Here two S_N2 reactions produce a cyclic molecule.)

(d) $Cl\text{-}CH_2CH_2CH_2CH_2OH + NaH \xrightarrow[Et_2O]{-H_2} Cl\text{-}CH_2CH_2CH_2CH_2O^-$



(e) $CH_3C{\equiv}CH + NaNH_2 \xrightarrow[\text{liq. } NH_3]{} CH_3C{\equiv}C{:}^-Na^+ \xrightarrow{CH_3-I} CH_3C{\equiv}CCH_3 + NaI$

6.34 The rate-determining step in the S_N1 reaction of *tert*-butyl bromide is the following:

$$(CH_3)_3C\text{—}Br \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} (CH_3)_3C^+ + Br^- \xrightarrow{H_2O} (CH_3)_3COH_2^+$$

$(CH_3)_3C^+$ is so unstable that it reacts almost immediately with one of the surrounding water molecules, and, for all practical purposes, no reverse reaction with Br^- takes place. Adding a common ion (Br^- from NaBr), therefore, has no effect on the rate.

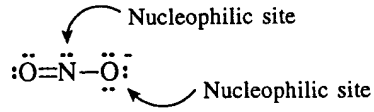
Because the $(C_6H_5)_2CH^+$ cation is more stable, a reversible first step occurs and adding a common ion (Br^-) slows the overall reaction by increasing the rate at which $(C_6H_5)_2CH^+$ is converted back to $(C_6H_5)_2CHBr$.

$$(C_6H_5)_2CHBr \rightleftharpoons (C_6H_5)_2CH^+ + Br^- \xrightarrow{H_2O} (C_6H_5)_2CHOH_2^+$$

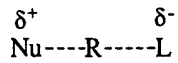
6.35 Two different mechanisms are involved. $(CH_3)_3CBr$ reacts by an S_N1 mechanism, and apparently this reaction takes place faster. The other three alkyl halids react by an S_N2 mechanism, and their reactions are slower because the nucleophile (H_2O) is weak. The reaction rates of CH_3Br, CH_3CH_2Br, and $(CH_3)_2CHBr$ are affected by the steric hindrance, and thus their order of reactivity is $CH_3Br > CH_3CH_2Br > (CH_3)_2CHBr$.

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6.36 The nitrite ion is an *ambident nucleophile;* that is, it is an ion with two nucleophilic sites. The equivalent oxygen atoms and the nitrogen atom are nucleophilic.

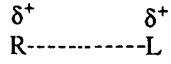


6.37 (a) The transition state has the form:



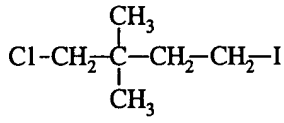
in which charges are developing. The more polar the solvent, the better it can solvate the transition state, thus lowering the free energy of activation and increasing the reaction rate.

(b) The transition state has the form:

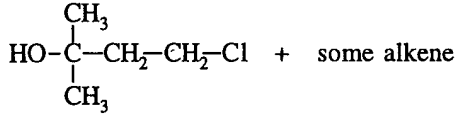


in which the charge is becoming dispersed. A polar solvent is less able to solvate this transition state than it is to solvate the reactant. The free energy of activation, therefore, will become somewhat larger as the solvent polarity increases, and the rate will be slower.

6.38 (a)



(b)



6.39 (a) In an S_N1 reaction the carbocation intermediate reacts rapidly with any nucleophile it encounters in a Lewis acid–Lewis base reaction. In the case of the S_N2 reaction, the leaving group departs only when "pushed out" by the attacking nucleophile, and some nucleophiles are better than others.

(b) CN^- is a much better nucleophile than ethanol and hence the nitrile is formed in the S_N2 reaction of $CH_3CH_2CH_2CH_2Cl$. In the case of $(CH_3)_3CCl$ the *tert*-butyl cation reacts chiefly with the nucleophile present in higher concentration, here the ethanol solvent.

***6.40**

	$\Delta H°$, kJ mol^{-1}	
$(CH_3)_3C{-}Cl \longrightarrow (CH_3)_3C\cdot + Cl\cdot$	+328	Homolytic bond dissoc. energy
$(CH_3)_3C\cdot \longrightarrow (CH_3)_3C^+ + e^-$	+715	Ionization potential
$Cl\cdot + e^- \longrightarrow Cl^-$	−330	Electron affinity
$(CH_3)_3C{-}Cl \longrightarrow (CH_3)_3C^+ + Cl^-$	+713	Heterolytic bond dissoc. energy

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***6.41** (a) The entropy term is slightly favorable. (The enthalpy term is highly unfavorable.)

(b) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$= 26.6 \text{ kJ mol}^{-1} - (298)(0.00481 \text{ kJ mol}^{-1})$

$= 25.2 \text{ kJ mol}^{-1}$

(c) $\log K_{eq} = \dfrac{-\Delta G^\circ}{2.303RT}$

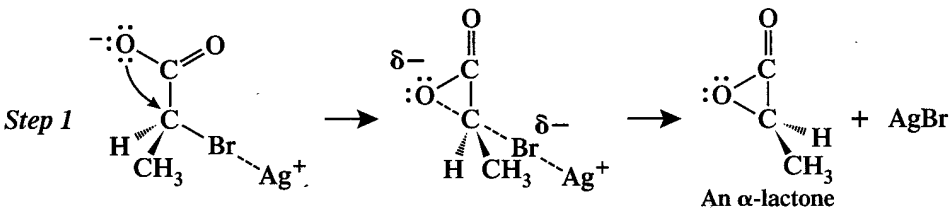
$= \dfrac{-25.2 \text{ kJ mol}^{-1}}{(2.303)(0.008315 \text{ kJ mol}^{-1} \text{ K}^{-1})(298 \text{ K})}$

$= -4.4160$

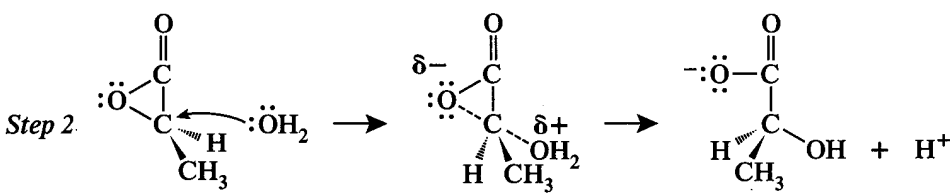
$K_{eq} = 10^{-4.4160} = 3.84 \times 10^{-5}$

(d) The equilibrium is very much more favorable in aqueous solution because solvation of the products (ethanol, hydronium ions, and chloride ions) takes place and thereby stabilizes them.

***6.42** The mechanism for the reaction involves the participation of the carboxylate group. In step 1 (see following reaction) an oxygen of the carboxylate group attacks the stereocenter from the backside and displaces bromide ion. (Silver ion aids in this process in much the same way that protonation assists the ionization of an alcohol.) The configuration of the stereocenter inverts in step 1, and a cyclic ester called an α-lactone forms.



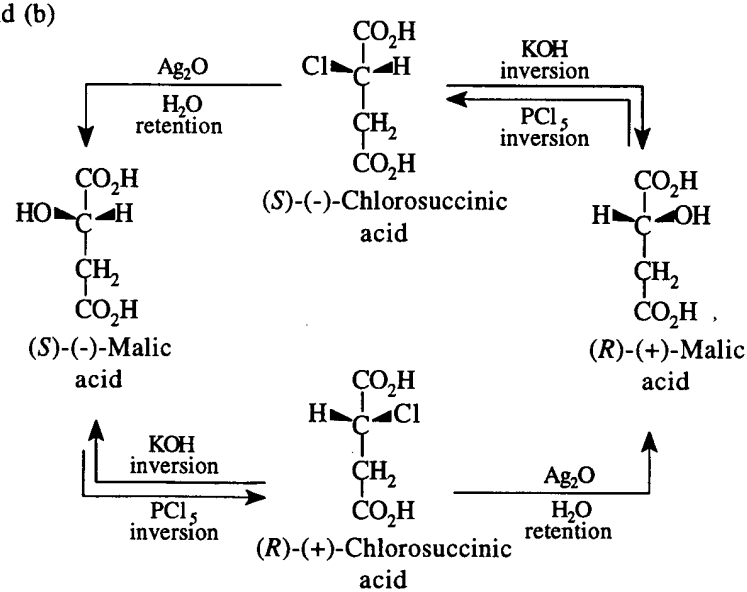
The highly strained three-membered ring of the α-lactone opens when it is attacked by a water molecule in step 2. *This step also takes place with an inversion of configuration.*



The net result of two inversions (in steps 1 and 2) is an overall *retention of configuration.*

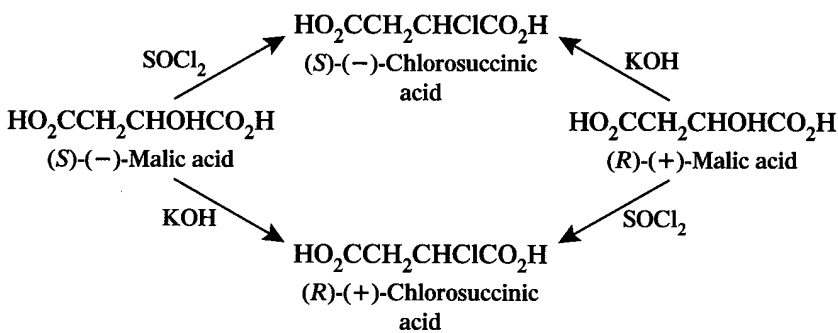
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***6.43** (a) and (b)

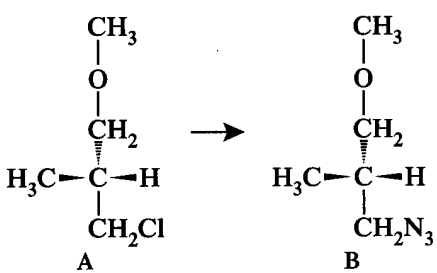


(c) The reaction takes place with retention of configuration.

(d)



***6.44**

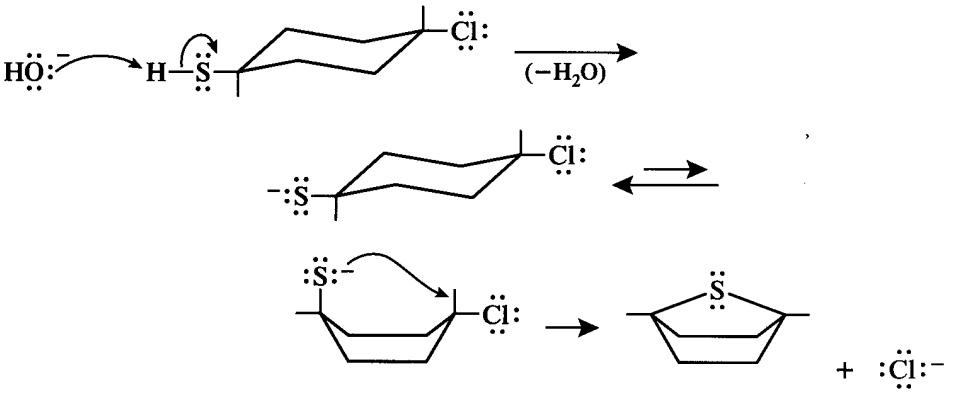


No change of configuration occurs, just a change in the relative priority of a group at the stereocenter.

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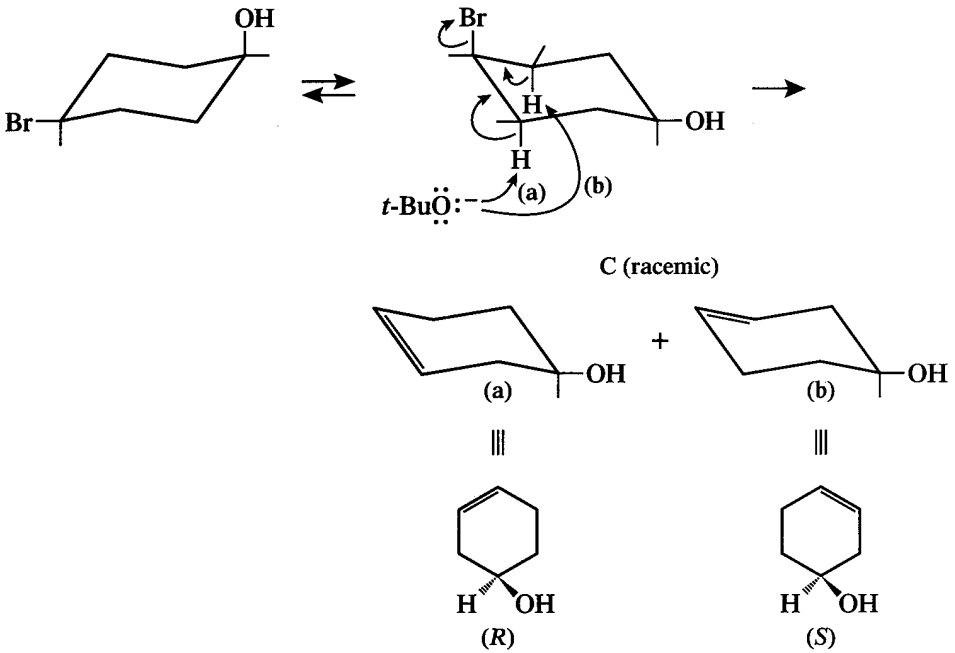
***6.45** Comparison of the molecular formulas of starting material and product indicates a loss of HCl. The absence of IR bands in the 1620–1680 cm^{-1} region rules out the presence of the alkene function.

A nucleophilic substitution agrees with the evidence:



***6.46** The IR evidence indicates that C possesses both an alkene function and a hydroxyl group.

An E2 reaction on this substrate produces enantiomeric unsaturated alcohols.



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7 ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS

SOLUTIONS TO PROBLEMS

7.1 (a) (*E*)-1-Bromo-1-chloro-1-pentene

(b) (*E*)-2-Bromo-1-chloro-1-iodo-1-butene

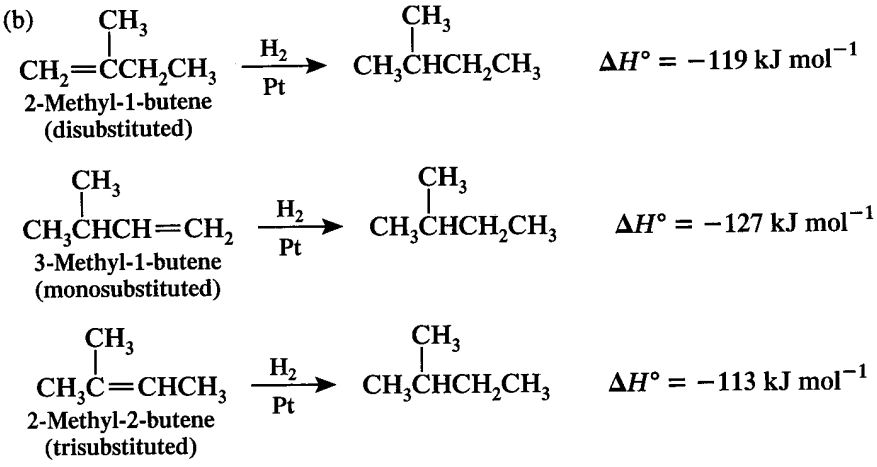
(c) (*Z*)-3,5-Dimethyl-2-hexene

(d) (*Z*)-1-Chloro-1-iodo-2-methyl-1-butene

(e) (*Z*,4*S*)-3,4-Dimethyl-2-hexene

(f) (*Z*,3*S*)-1-Bromo-2-chloro-3-methyl-1-hexene

7.2 (a), (b)



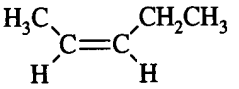
(c) Yes, because hydrogenation converts each alkene into the same product.

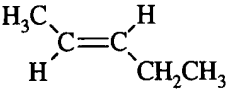
(d) $CH_3C(CH_3)=CHCH_3$ (trisubstituted) > $CH_2=C(CH_3)CH_2CH_3$ (disubstituted) > $CH_3CH(CH_3)CH=CH_2$ (monosubstituted)

Notice that this predicted order of stability is confirmed by the heats of hydrogenation. 2-Methyl-2-butene evolves the least heat; therefore, it is the most stable. 3-Methyl-1-butene evolves the most heat; therefore, it is the least stable.

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(e) $CH_2{=}CHCH_2CH_2CH_3$
1-Pentene


cis-2-Pentene


trans-2-Pentene

(f) Heats of combustion, because complete combustion would convert all of the alkenes to the same products. (All of the alkenes have the formula C_5H_{10}.)

$$C_5H_{10} + 7\,1/2\ O_2 \longrightarrow 5\ CO_2 + 5\ H_2O$$

7.3 (a) 2,3-Dimethyl-2-butene would be the more stable because the double bond is tetrasubstituted. 2-Methyl-2-pentene has a trisubstituted double bond.

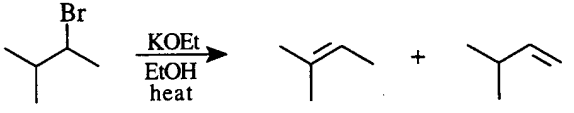
(b) *trans*-3-Hexene would be the more stable because alkenes with trans double bonds are more stable than those with cis double bonds.

(c) *cis*-3-Hexene would be more stable because its double bond is disubstituted. The double bond of 1-hexene is monosubstituted.

(d) 2-Methyl-2-pentene would be the more stable because its double bond is trisubstituted. The double bond of *trans*-2-hexene is disubstituted.

7.4 The relative stabilities of the pairs of alkenes in parts (b) and (c) in Problem 7.3 could be determined by measuring heats of hydrogenation, because in each instance the two alkenes would yield the same product. Heats of combustion could be used to determine the relative stabilities of the alkene pairs in parts (a) and (d) [and also those in parts (b) and (c)] because on complete combustion the alkenes produce the same number of molar equivalents of CO_2 and H_2O.

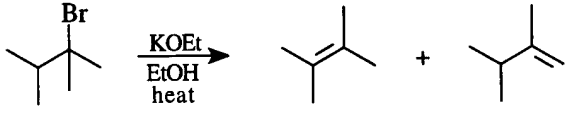
7.5 (a)



(trisubstituted, more stable) Major product

(monosubstituted, less stable) Minor product

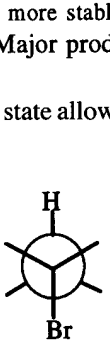
(b)



(tetrasubstituted, more stable) Major product

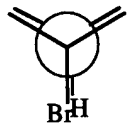
(disubstituted, less stable) Minor product

7.6 An anti periplanar transition state allows the molecule to assume the more stable staggered conformation,

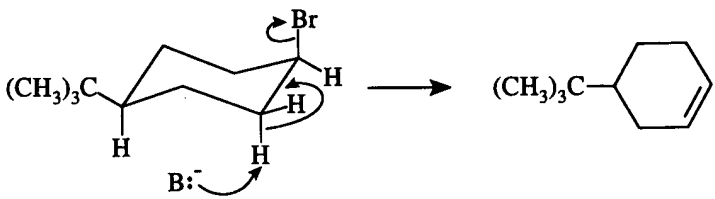


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whereas a syn periplanar transition state requires the molecule to assume the less stable eclipsed conformation:

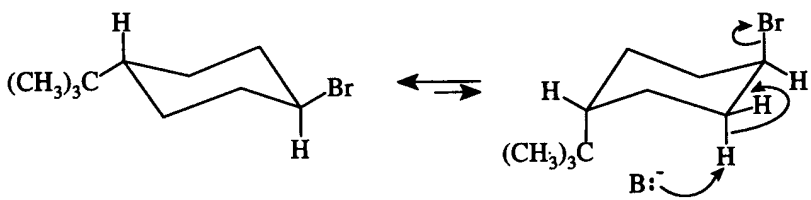


7.7 *cis*-1-Bromo-4-*tert*-butylcyclohexane can assume an anti periplanar transition state in which the bulky *tert*-butyl group is equatorial:



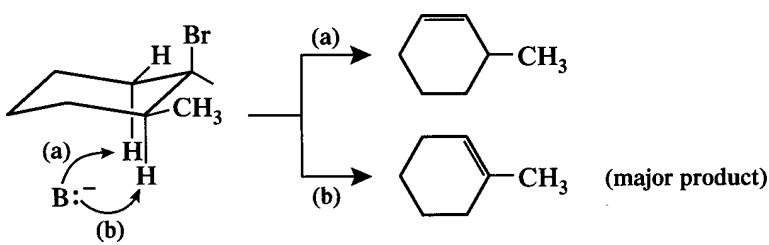
The conformation (above), because it is relatively stable, is assumed by most of the molecules present, and, therefore, the reaction is rapid.

On the other hand, for *trans*-1-bromo-4-*tert*-butylcyclohexane to assume an anti periplanar transition state, the molecule must assume a conformation in which the large *tert*-butyl group is axial:



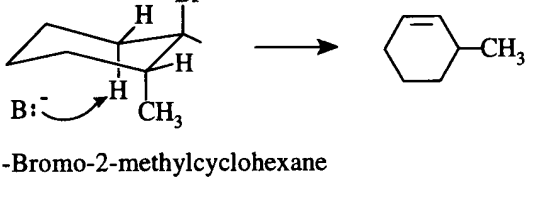
Such a conformation is of high energy; therefore, very few molecules assume this conformation. The reaction, consequently, is very slow.

7.8 (a) Anti periplanar elimination can occur in two ways with the cis isomer.



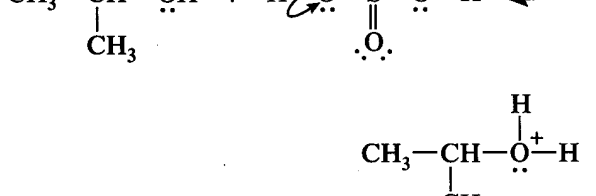
cis-1-Bromo-2-methylcyclohexane

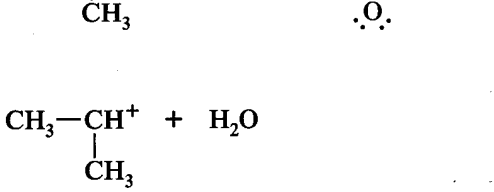
(b) Anti periplanar elimination can occur in only one way with the trans isomer.



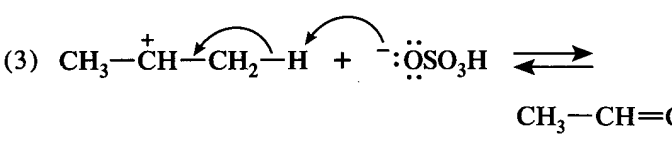
trans-1-Bromo-2-methylcyclohexane

7.9 (a) (1)

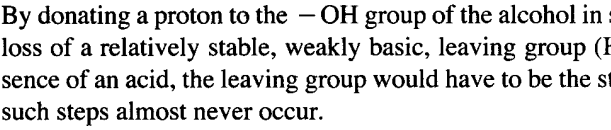




(2)

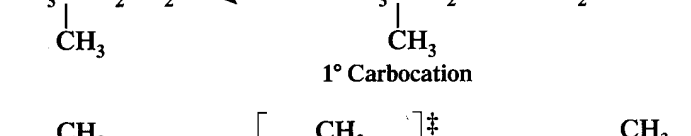


(3)

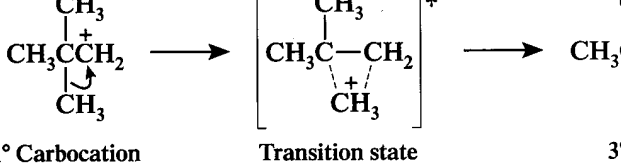


(b) By donating a proton to the $-OH$ group of the alcohol in step (1), the acid allows the loss of a relatively stable, weakly basic, leaving group (H_2O) in step (2). In the absence of an acid, the leaving group would have to be the strongly basic OH^- ion, and such steps almost never occur.

7.10 (1)

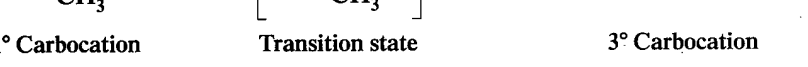


(2)



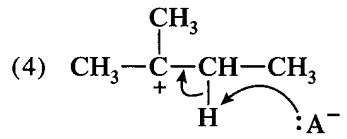
1° Carbocation

(3)

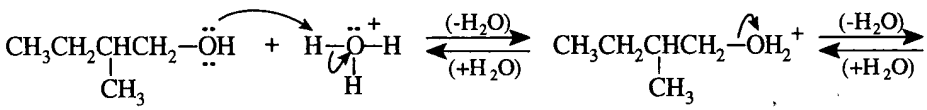


1° Carbocation Transition state 3° Carbocation

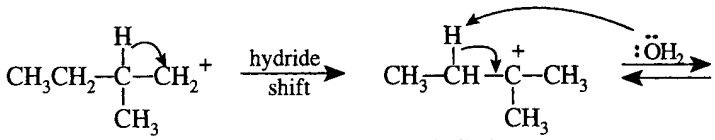
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(4) 

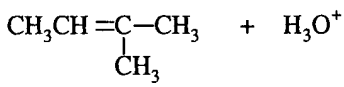
2-Methyl-2-butene

7.11 

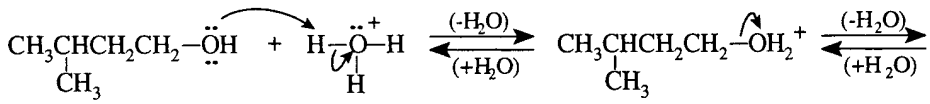
2-Methyl-1-butanol



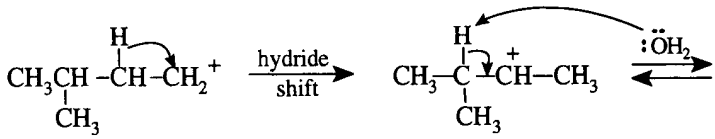
1° Cation 3° Cation

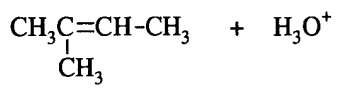


2-Methyl-2-butene

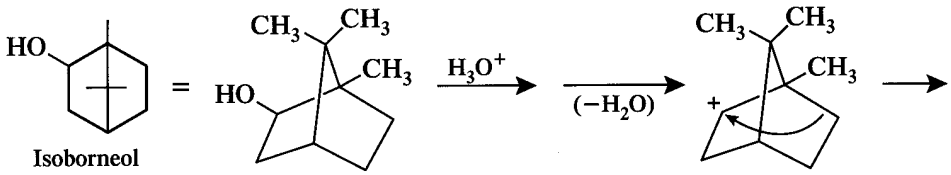


3-Methyl-1-butanol

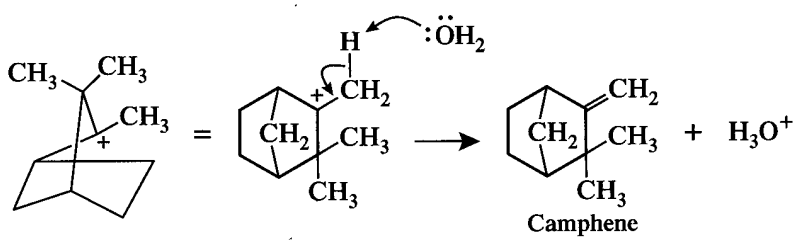




2-Methyl-2-butene

7.12 

Isoborneol



Camphene

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7.13 (a) $CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[0°C]{PCl_5} CH_3CCl_2CH_3 \xrightarrow[\text{mineral oil, heat}]{\text{(1) 3 } NaNH_2,\ \text{(2) } NH_4^+} CH_3C{\equiv}CH$

(b) $CH_3CH_2CHBr_2 \xrightarrow[\text{mineral oil, heat}]{\text{(1) 3 } NaNH_2,\ \text{(2) } NH_4^+} CH_3C{\equiv}CH$

(c) $CH_3CHBrCH_2Br \xrightarrow{\text{[same as (b)]}} CH_3C{\equiv}CH$

(d) $CH_3CH{=}CH_2 \xrightarrow[CCl_4]{Br_2} CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_2Br \xrightarrow{\text{[same as (b)]}} CH_3C{\equiv}CH$

7.14 (a) $CH_3CH{=}CH_2 + NaNH_2 \longrightarrow$ No reaction

(b) $CH_3C{\equiv}C{-}H + Na^+\ {}^-{:}\ddot{N}H_2 \longrightarrow CH_3C{\equiv}C{:}^-\ Na^+ + {:}NH_3$

Stronger acid; Stronger base; Weaker base; Weaker acid

(c) $CH_3CH_2CH_3 + NaNH_2 \longrightarrow$ No reaction

(d) $CH_3C{\equiv}C{:}^- + H{-}\ddot{O}CH_2CH_3 \longrightarrow CH_3C{\equiv}CH + {:}\ddot{O}CH_2CH_3$

Stronger base; Stronger acid; Weaker acid; Weaker base

(e) $CH_3C{\equiv}C{:}^- + H{-}\overset{+}{N}H_3 \longrightarrow CH_3C{\equiv}CH + {:}NH_3$

Stronger base; Stronger acid; Weaker acid; Weaker base

7.15 $CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}C{\equiv}C{-}H + Na^+\ {}^-{:}\ddot{N}H_2 \xrightarrow{(-NH_3)} CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}C{\equiv}C{:}^-\ Na^+$

$CH_3{-}I$

$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}C{\equiv}C{-}CH_3$

7.16 (a) C_6H_{14} = formula of alkane
C_6H_{12} = formula of 2-hexene
H_2 = difference = 1 pair of hydrogen atoms
Index of hydrogen deficiency = 1

(b) C_6H_{14} = formula of alkane
C_6H_{12} = formula of methylcyclopentane
H_2 = difference = 1 pair of hydrogen atoms
Index of hydrogen deficiency = 1

(c) No, all isomers of C_6H_{12}, for example, have the same index of hydrogen deficiency.

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(d) No

(e) C_6H_{14} = formula of alkane
C_6H_{10} = formula of 2-hexyne
H_4 = difference = 2 pairs of hydrogen atoms

Index of hydrogen deficiency = 2

(f) $C_{10}H_{22}$ (alkane)
$C_{10}H_{16}$ (compound)
H_6 = difference = 3 pairs of hydrogen atoms

Index of hydrogen deficiency = 3

The structural possibilities are thus

3 double bonds
1 double bond and one triple bond
2 double bonds and 1 ring
1 double bond and 2 rings
3 rings
1 triple bond and one ring

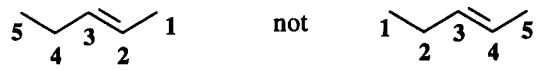
7.17 (a) $C_{15}H_{32}$ = formula of alkane
$C_{15}H_{24}$ = formula of zingiberene
H_8 = difference = 4 pairs of hydrogen atoms

Index of hydrogen deficiency = 4

(b) Since 1 mol of zingiberene absorbs 3 mol of hydrogen, one molecule of zingiberene must contain three double bonds. (We are told that molecules of zingiberene do not contain any triple bonds.)

(c) If a molecule of zingiberene has three double bonds and an index of hydrogen deficiency equal to 4, it must have one ring. (The structural formula for zingiberene can be found in Problem 23.2.)

7.18 (a) We designate the position of the double bond by using the *lower* number of the two numbers of the doubly bonded carbon atoms, and the chain is numbered from the end nearer the double bond. The correct name is *trans*-2-pentene

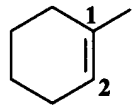


(b) We must choose the longest chain for the base name. The correct name is 2-methylpropene.

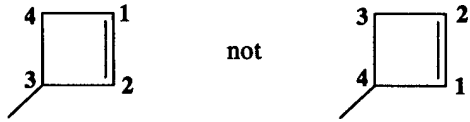


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(c) We use the lower number of the two doubly bonded carbon atoms to designate the position of the double bond. The correct name is 1-methylcyclohexene.



(d) We must number the ring starting with the double bond in the direction that gives the substituent the lower number. The correct name is 3-methylcyclobutene.



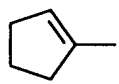
(e) We number in the way that gives the double bond *and the substituent* the lower number. The correct name is (*Z*)-2-chloro-2-butene.

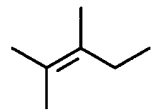


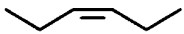
(f) We number the ring starting with the double bond so as to give the substituents the lower numbers. The correct name is 3,4-dichlorocyclohexene.

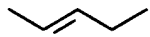


7.19 (a) 

(b) 

(c) 

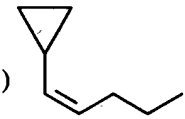
(d) 

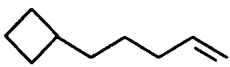
(e) 

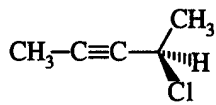
(f) $CH_2{=}CHCBr_3$

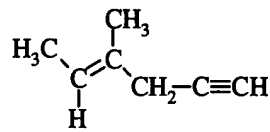
(g) 

(h) 

(i) 

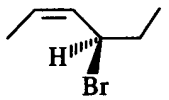
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(k) 

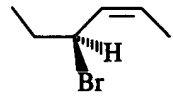
(l) 

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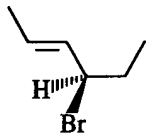
7.20 (a)



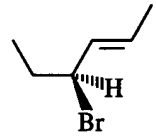
(*Z*,*4R*)-4-Bromo-2-hexene



(*Z*,*4S*)-4-Bromo-2-hexene

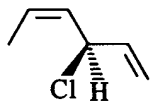


(*E*,*4R*)-4-Bromo-2-hexene

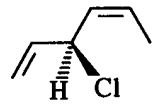


(*E*,*4S*)-4-Bromo-2-hexene

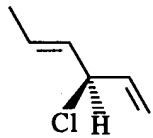
(b)



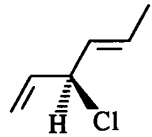
(*3R*,*4Z*)-3-Chloro-1,4-hexadiene



(*3S*,*4Z*)-3-Chloro-1,4-hexadiene

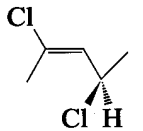


(*3R*,*4E*)-3-Chloro-1,4-hexadiene

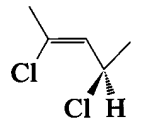


(*3S*,*4E*)-3-Chloro-1,4-hexadiene

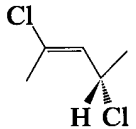
(c)



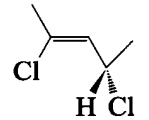
(*2E*,*4R*)-2,4-Dichloro-2-pentene



(*2Z*,*4R*)-2,4-Dichloro-2-pentene

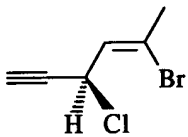


(*2E*,*4S*)-2,4-Dichloro-2-pentene

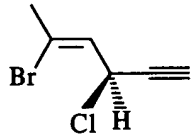


(*2Z*,*4S*)-2,4-Dichloro-2-pentene

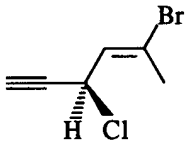
(d)



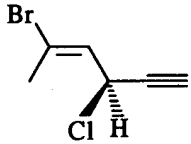
(*3R*,*4Z*)-5-Bromo-3-chloro-4-hexen-1-yne



(*3S*,*4Z*)-5-Bromo-3-chloro-4-hexen-1-yne



(*3R*,*4E*)-5-Bromo-3-chloro-4-hexen-1-yne



(*3S*,*4E*)-5-Bromo-3-chloro-4-hexen-1-yne

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7.21 (a) (*E*)-3,5-Dimethyl-2-hexene

(b) 4-Chloro-3-methylcyclopentene

(c) 6-Methyl-3-heptyne

(d) 1-*sec*-Butyl-2-methylcyclohexene or 1-methyl-2-(1-methylpropyl)cyclohexene

(e) (Z,5*R*)-5-Chloro-3-hepten-6-yne

(f) 2-Pentyl-1-heptene

7.22 (a) $CH_3CH_2CH_2Cl \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_3CH=CH_2$

(b) $CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3 \xrightarrow[CH_3CH_2OH]{CH_3CH_2ONa} CH_3CH=CH_2$

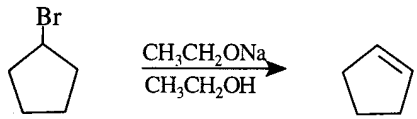
(c) $CH_3CH_2CH_2OH \xrightarrow{H^+,\ heat} CH_3CH=CH_2$

(d) $CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 \xrightarrow{H^+,\ heat} CH_3CH=CH_2$

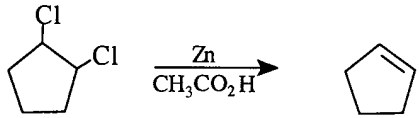
(e) $CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_2Br \xrightarrow[\text{or NaI/acetone}]{Zn,\ CH_3CO_2H} CH_3CH=CH_2$

(f) $CH_3C\equiv CH \xrightarrow[Ni_2B\ (P\text{-}2)]{H_2} CH_3CH=CH_2$

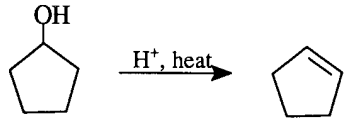
7.23 (a)



(b)



(c)

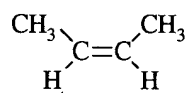


7.24 (a) $HC\equiv CH \xrightarrow[liq.\ NH_3]{NaNH_2} HC\equiv C{:}^-Na^+ \xrightarrow[(-NaI)]{CH_3{-}I} HC\equiv C{-}CH_3$

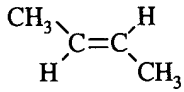
(b) $HC\equiv CH \xrightarrow[liq.\ NH_3]{NaNH_2} HC\equiv C{:}^-Na^+ \xrightarrow[(-NaBr)]{CH_3CH_2{-}Br} HC\equiv C{-}CH_2CH_3$

(c) $CH_3C\equiv CH$ [from(a)] $\xrightarrow[liq.\ NH_3]{NaNH_2} CH_3C\equiv C{:}^-Na^+ \xrightarrow[(-NaI)]{CH_3{-}I} CH_3{-}C\equiv C{-}CH_3$

(d) $CH_3{-}C\equiv C{-}CH_3$ [from(c)] $\xrightarrow[Ni_2B\ (P\text{-}2)]{H_2}$

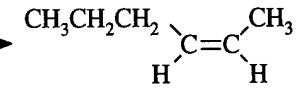


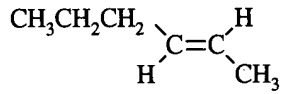
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(e) $CH_3—C\equiv C—CH_3$ [from(c)] $\xrightarrow[(2)\ NH_4Cl]{(1)\ Li,\ CH_3CH_2NH_2}$ 

(f) $HC\equiv C^-\ Na^+$ [from(a)] $\xrightarrow[(-NaBr)]{CH_3CH_2CH_2—Br}$ $HC\equiv C—CH_2CH_2CH_3$

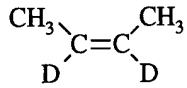
(g) $CH_3CH_2CH_2C\equiv CH$ [from(f)] $\xrightarrow[liq.\ NH_3]{NaNH_2}$ $CH_3CH_2CH_2C\equiv C^-\ Na^+$ $\xrightarrow[(-NaI)]{CH_3—I}$ $CH_3CH_2CH_2C\equiv CCH_3$

(h) $CH_3CH_2CH_2C\equiv CCH_3$ [from(g)] $\xrightarrow[Ni_2B\ (P\text{-}2)]{H_2}$ 

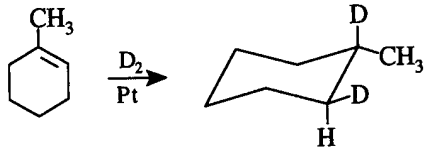
(i) $CH_3CH_2CH_2C\equiv CCH_3$ [from(g)] $\xrightarrow[(2)\ NH_4Cl]{(1)\ Li,\ CH_3CH_2NH_2}$ 

(j) $HC\equiv C^-\ Na^+$ [from(a)] $\xrightarrow[(-NaBr)]{CH_3CH_2—Br}$ $HC\equiv CCH_2CH_3$ $\xrightarrow[liq.\ NH_3]{NaNH_2}$ $CH_3CH_2C\equiv C^-\ Na^+$ $\xrightarrow{CH_3CH_2—Br}$ $CH_3CH_2C\equiv CCH_2CH_3$

(k) $CH_3CH_2C\equiv C^-\ Na^+$ [from(j)] $\xrightarrow{D_2O}$ $CH_3CH_2C\equiv CD$

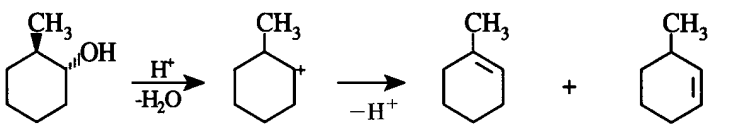
(l) $CH_3C\equiv CCH_3$ [from(c)] $\xrightarrow[Ni_2B\ (P\text{-}2)]{D_2}$ 

7.25 We notice that the deuterium atoms are cis to each other, and we conclude, therefore, that we need to choose a method that will cause a syn addition of deuterium. One way would be to use D_2 and a metal catalyst (Section 7.13)



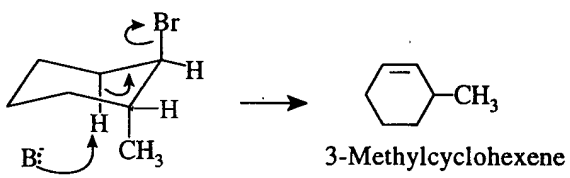
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7.26 Dehydration of *trans*-2-methylcyclohexanol proceeds through the formation of a carbocation (through an E1 reaction of the protonated alcohol) and leads preferentially to the more stable alkene. 1-Methylcyclohexene (below) is more stable than 3-methylcyclohexene (the minor product of the dehydration) because its double bond is more highly substituted.



(major) Trisubstituted double bond (minor) Disubstituted double bond

Dehydrohalogenation of *trans*-1-bromo-2-methylcyclohexane is an E2 reaction and must proceed through an anti periplanar transition state. Such a transition state is possible only for the elimination leading to 3-methylcyclohexene (cf. Problem 7.8).



3-Methylcyclohexene

7.27 (a) $C_6H_5-\underset{\displaystyle Br}{\overset{\displaystyle Br}{\underset{|}{\overset{|}{C}}}}-CH_3 \xrightarrow[\text{mineral oil, heat}]{3\,NaNH_2} C_6H_5-C\equiv C^{-}\,Na^{+} \xrightarrow{NH_4Cl} C_6H_5-C\equiv CH$

(b) $C_6H_5CH_2-CHBr_2 \xrightarrow[\text{mineral oil, heat}]{3\,NaNH_2} C_6H_5C\equiv C^{-}\,Na^{+} \xrightarrow{NH_4Cl} C_6H_5-C\equiv CH$

(c) $C_6H_5CH=CH_2 \xrightarrow[CCl_4]{Br_2} C_6H_5-\underset{\displaystyle Br}{CH}-\underset{\displaystyle Br}{CH_2} \xrightarrow[\text{mineral oil, heat}]{3\,NaNH_2} C_6H_5C\equiv C^{-}\,Na^{+} \xrightarrow{NH_4Cl} C_6H_5-C\equiv CH$

(d) $C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 \xrightarrow{PCl_5} C_6H_5-\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{\underset{|}{\overset{|}{C}}}}-CH_3 \xrightarrow[\text{mineral oil, heat}]{3\,NaNH_2} C_6H_5C\equiv C^{-}\,Na^{+} \xrightarrow{NH_4Cl} C_6H_5-C\equiv CH$

7.28 Cyclobutane is less stable than any of the butene isomers.

7.29 1-Pentene, 3375 kJ mol^{-1}

cis-2-Pentene, 3369 kJ mol^{-1}

trans-2-Pentene, 3365 kJ mol^{-1}

2-Methyl-1-butene, 3361 kJ mol^{-1}

2-Methyl-2-butene, 3355 kJ mol^{-1}

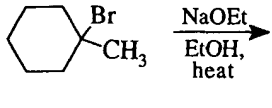
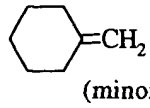
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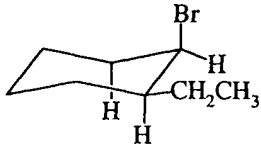
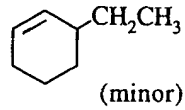
7.30 1-Pentanol > 1-pentyne > 1-pentene > pentane
(See Section 3.7 for the explanation.)

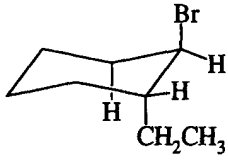
7.31 (a) $CH_3CH(Br)CHCH_3$ $\xrightarrow[EtOH,\ heat]{NaOEt}$ $CH_3C(H)=C(CH_3)CH_3$ (major) + $CH_2=CHCH(CH_3)CH_3$ (minor)

(b) $CH_3C(CH_3)(CH_3)CH(Br)CH_3$ $\xrightarrow[EtOH,\ heat]{NaOEt}$ $CH_3C(CH_3)(CH_3)CH=CH_2$

(c) $CH_3CH_2C(Br)(CH_3)CH_2CH_3$ $\xrightarrow[EtOH,\ heat]{NaOEt}$ $CH_3CH=C(CH_3)CH_2CH_3$ (major) + $CH_2=C(CH_2CH_3)_2$ (minor)

(d)  (major) +  (minor)

(e)  (major) +  (minor)

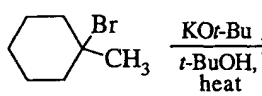
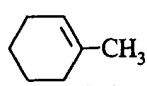
(f) 

7.32 (a) $CH_3CH(Br)CHCH_3$ $\xrightarrow[t\text{-}BuOH,\ heat]{KO\text{-}t\text{-}Bu}$ $CH_2=CHCH(CH_3)CH_3$ (major) + $CH_3CH=C(CH_3)CH_3$ (minor)

(b) $CH_3C(CH_3)(CH_3)CH_2CH_2Br$ $\xrightarrow[t\text{-}BuOH,\ heat]{KO\text{-}t\text{-}Bu}$ $CH_3C(CH_3)(CH_3)CH=CH_2$ (only)

(c) $CH_3CH_2C(Br)(CH_3)CH_2CH_3$ $\xrightarrow[t\text{-}BuOH,\ heat]{KO\text{-}t\text{-}Bu}$ $CH_3CH_2C(=CH_2)CH_2CH_3$ (major) + $CH_3CH=C(CH_3)CH_2CH_3$ (minor)

(d) $CH_3C(CH_3)(CH_3)CH_2CH(Br)CH_3$ $\xrightarrow[t\text{-}BuOH,\ heat]{KO\text{-}t\text{-}Bu}$ $CH_3C(CH_3)(CH_3)CH_2CH=CH_2$ (major) + $CH_3C(CH_3)(CH_3)CH=CHCH_3$ (minor)

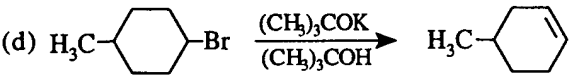
(e)  (major) +  (minor)

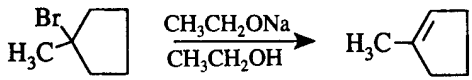
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7.33 (a) $CH_3CH_2CH_2CH_2CH_2Br \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_3CH_2CH_2CH{=}CH_2$

(b) $CH_3CH(CH_3)CH_2CH_2Br \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_3CH(CH_3)CH{=}CH_2$

(c) $CH_3CH(CH_3)CH(CH_3)CH_2Br \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_3CH(CH_3)C{=}CH_2$ (CH_3)

(d) 

(e) 

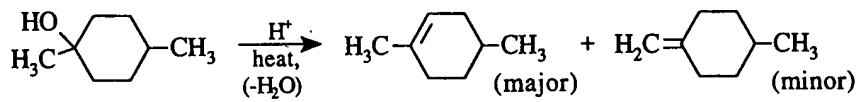
7.34 $CH_3CH(OH)CH_2CH_3$ (3°) > $CH_3CH(OH)CHCH_3$ (2°) > $CH_3CH_2CH_2CH_2CH_2OH$ (1°)

7.35 (a) $CH_3C(OH)CH_3 \xrightarrow[(-H_2O)]{H^+,\ heat} CH_2{=}CCH_3$

(b) $CH_3CH(OH)CHCH_3 \xrightarrow[(-H_2O)]{H^+,\ heat} CH_2{=}CHCCH_3$ (minor) + $CH_3CH{=}CCH_3$ (major)

(c) $CH_3CH_2C(OH)CH_2CH_3 \xrightarrow[(-H_2O)]{H^+,\ heat} CH_3CH{=}CCH_2CH_3$ (major) + $CH_3CH_2C(=CH_2)CH_2CH_3$ (minor)

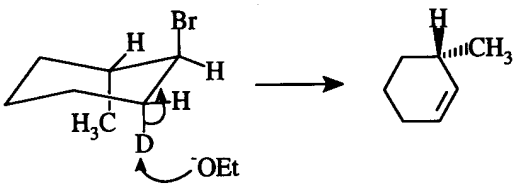
(d) $CH_3C(CH_3)(OH)CH_2OH \xrightarrow[(-H_2O)\ \text{rearrangement}]{H^+,\ heat} CH_3C(CH_3){=}CHCH_3$ (major) + $CH_2{=}CCH_2CH_3$ (CH_3) (minor)

(e) 

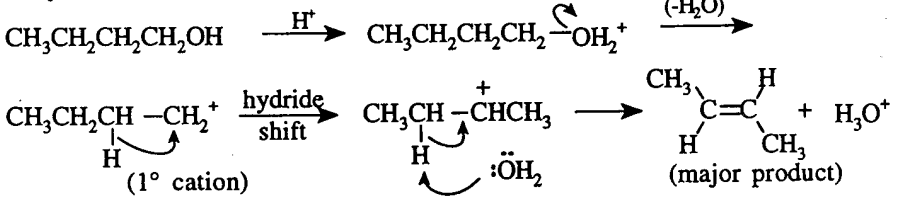
7.36 The alkene cannot be formed because the double bond in the product is too highly strained. Recall that the atoms at each carbon of a double bond prefer to be in the same plane.

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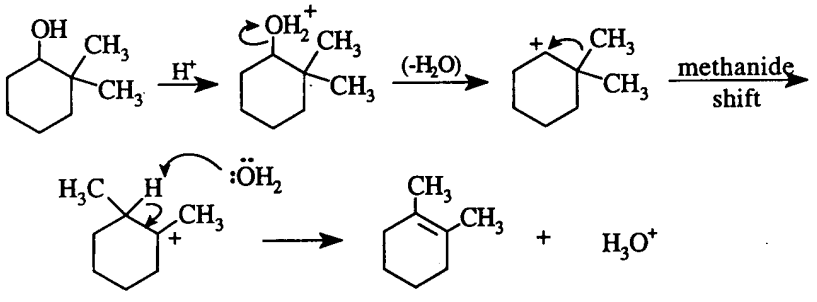
7.37 Only the deuterium atom can assume the anti periplanar orientation necessary for an E2 reaction to occur.



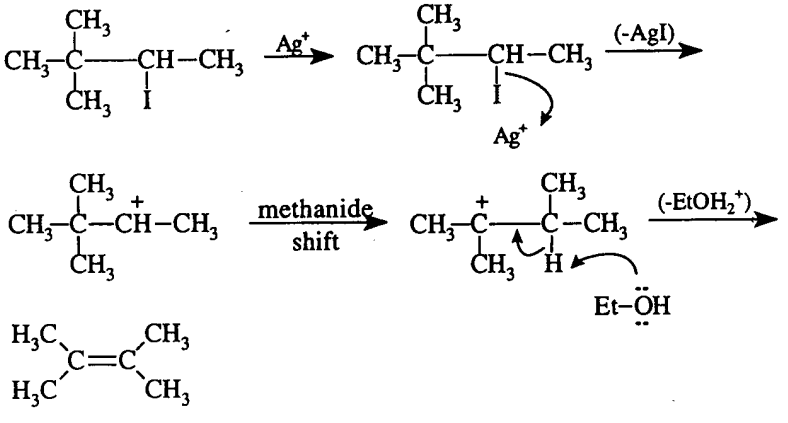
7.38 (a) A hydride shift occurs.



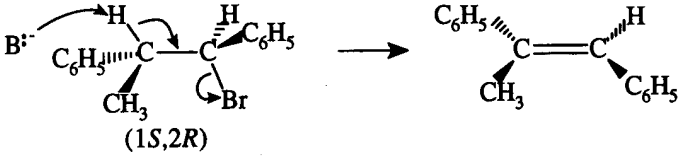
(b) A methanide shift occurs.



(c) A methanide shift occurs.

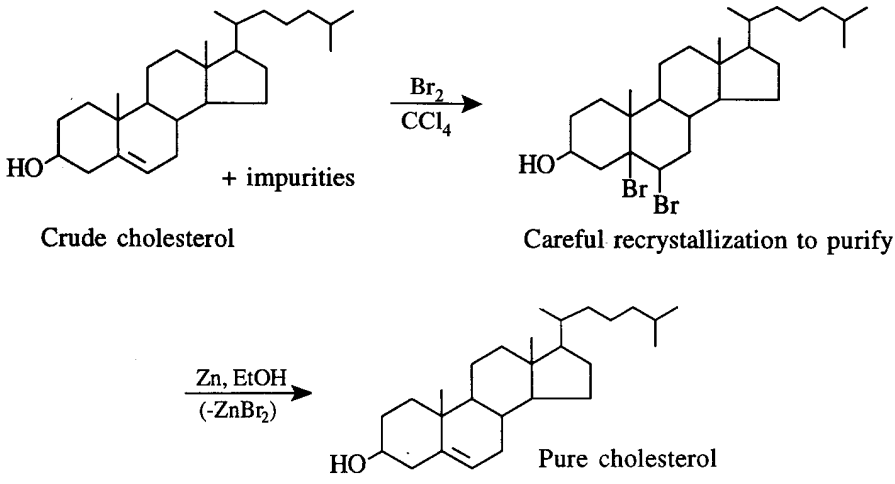


(d) The required anti periplanar transtition state leads only to (*E*) alkene:



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7.39 In the first step, cholesterol reacts with bromine to form the *vic*-dibromide. This product is then purified by crystallization, and then treatment with zinc in ethanol converts the pure *vic*-dibromide back to cholesterol. (Recrystallization of the *vic*-dibromide is especially easy because it has a higher melting point than cholesterol.)



7.40 (a) Caryophyllene has the same molecular formula as zingiberene (Problem 7.17); thus it, too, has an index of hydrogen deficiency equal to 4. That 1 mol of caryophyllene absorbs 2 mol of hydrogen on catalytic hydrogenation indicates the presence of two double bonds per molecule.

(b) Caryophyllene molecules must also have two rings. (See Problem 23.2 for the structure of caryophyllene.)

7.41 (a) $C_{30}H_{62}$ = formula of alkane
$C_{30}H_{50}$ = formula of squalene
H_{12} = difference = 6 pairs of hydrogen atoms

Index of hydrogen deficiency = 6

(b) Molecules of squalene contain six double bonds.

(c) Squalene molecules contain no rings. (See Problem 23.2 for the structural formula of squalene.)

7.42 (a) We are given (Section 7.3A) the following heats of hydrogenation:

$$\textit{cis}\text{-2-Butene} + H_2 \xrightarrow{Pt} \text{butane} \qquad \Delta H^\circ = -120 \text{ kJ mol}^{-1}$$

$$\textit{trans}\text{-2-Butene} + H_2 \xrightarrow{Pt} \text{butane} \qquad \Delta H^\circ = -115 \text{ kJ mol}^{-1}$$

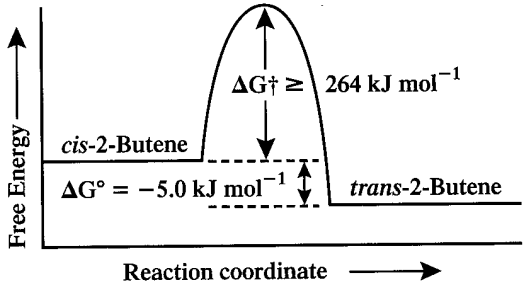
Thus, for

$$\textit{cis}\text{-2-Butene} \longrightarrow \textit{trans}\text{-2-butene} \qquad \Delta H^\circ = -5.0 \text{ kJ mol}^{-1}$$

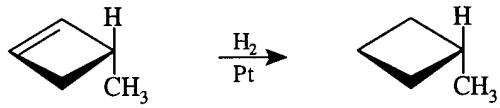
(b) Converting *cis*-2-butene into *trans*-2-butene involves breaking the π bond. Therefore, we would expect the energy of activation to be at least as large as the π-bond strength, that is, at least 264 kJ mol^{-1}.

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(c)



7.43 (a)

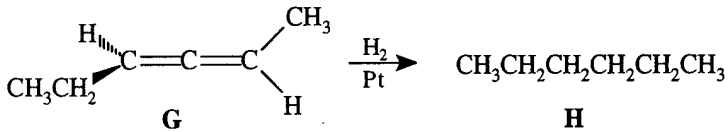


E **F**

Optically active (the enantiomeric form is an equally valid answer)

Optically inactive and nonresolvable

(b)

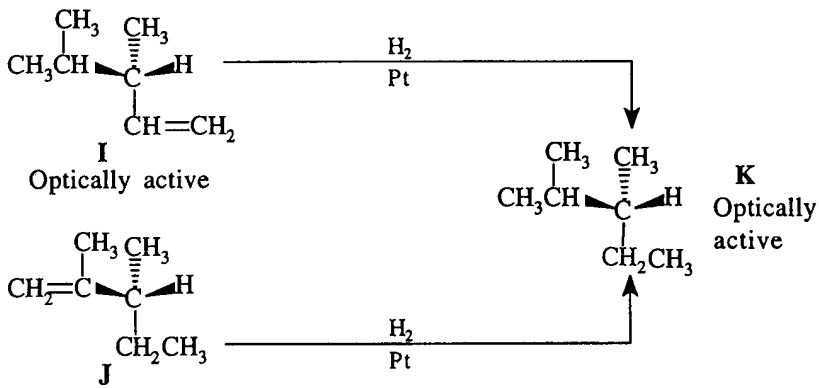


G **H**

Optically active (the enantiomeric form is an equally valid answer)

Optically inactive and nonresolvable

7.44 That **I** and **J** rotate plane-polarized light in the same direction tells us that **I** and **J** are not enantiomers of each other. Thus, the following are possible structures for **I, J,** and **K.** (The enantiomers of **I, J,** and **K** would form another set of structures, and other answers are possible as well.)



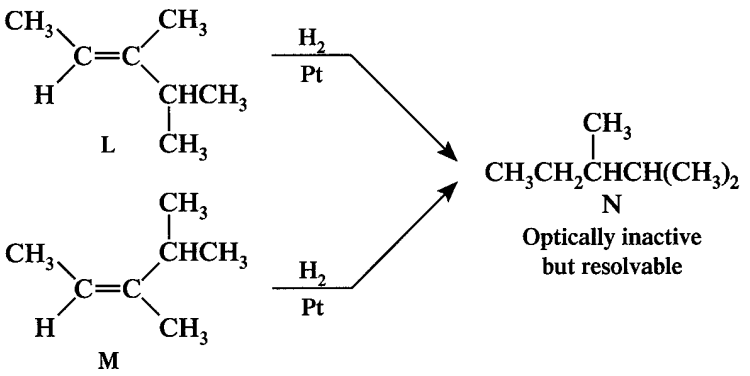
I Optically active

J Optically active

K Optically active

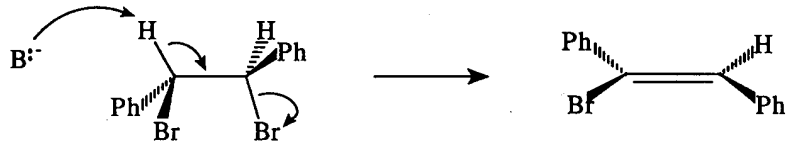
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7.45 The following are possible structures:



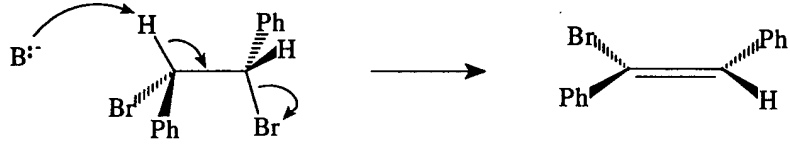
(other answers are possible as well)

7.46 (a) With either the (1*R*,2*R*)- or the (1*S*,2*S*)-1,2-dibromo-1,2-diphenylethane, only one conformation will allow an anti periplanar arrangement of the H- and Br-. In either case, the elimination leads only to (*Z*)-1-bromo-1,2-diphenylethene:



(1*R*,2*R*)-1,2-Dibromo-1,2-diphenylethane
(anti periplanar orientation of H- and -Br)

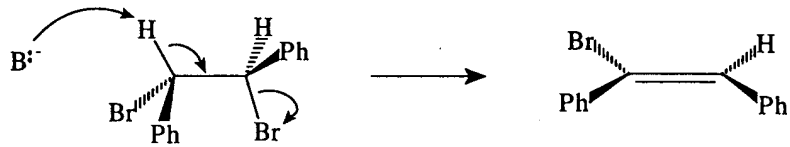
(*Z*)-1-Bromo-1,2-diphenylethene



(1*S*,2*S*)-1,2-Dibromo-1,2-diphenylethane
(anti periplanar orientation of H- and -Br)

(*Z*)-1-Bromo-1,2-diphenylethene

(b) With (1*R*,2*S*)-1,2-dibromo-1,2-diphenylethane, only one conformation will allow an anti periplanar arrangement of the H- and Br-. In this case, the elimination leads only to (*E*)-1-bromo-1,2-diphenylethene:



(1*R*,2*S*)-1,2-Dibromo-1,2-diphenylethane
(anti periplanar orientation of H- and -Br)

(*E*)-1-Bromo-1,2-diphenylethene

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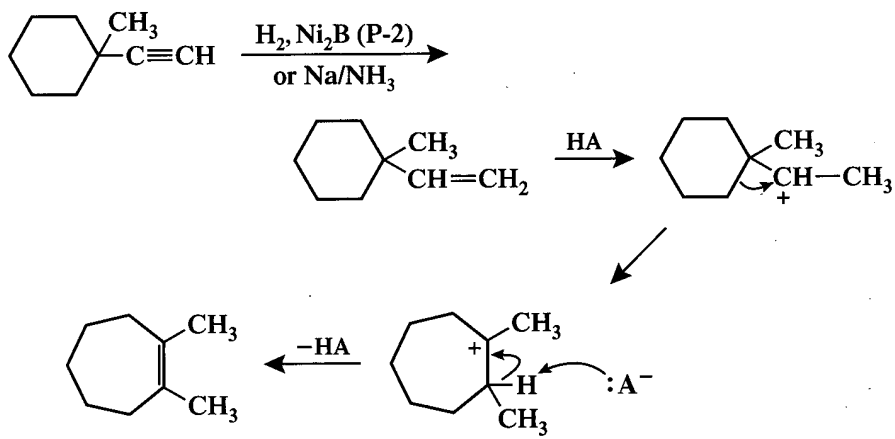
(c) With (1*R*,2*S*)-1,2-dibromo-1,2-diphenylethane, only one conformation will allow an anti periplanar arrangement of both bromine atoms. In this case, the elimination leads only to (*E*)-1,2-diphenylethene:



(1*R*,2*S*)-1,2-Dibromo-1,2-diphenylethane (anti periplanar orientation of both -Br atoms)

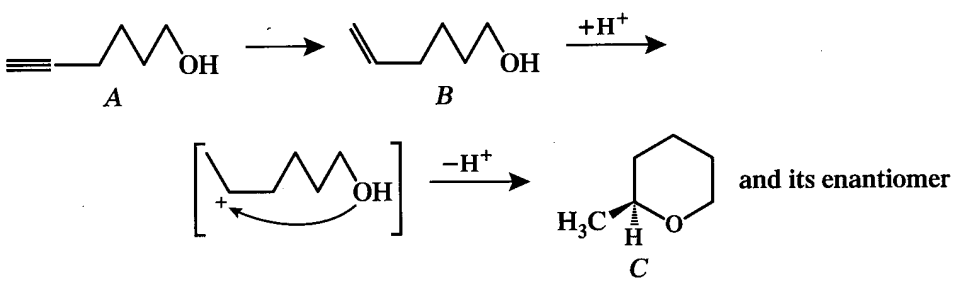
(*E*)-1,2-Diphenylethene

***7.47** (a)



(b) No, tetrasubstituted double bonds usually show no C=C stretching absorption in their infrared spectra.

***7.48**



and its enantiomer

***7.49** (a) Three
(b) Six

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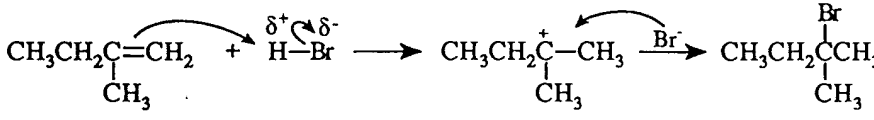
8 ALKENES AND ALKYNES II: ADDITION REACTIONS

SOLUTIONS TO PROBLEMS

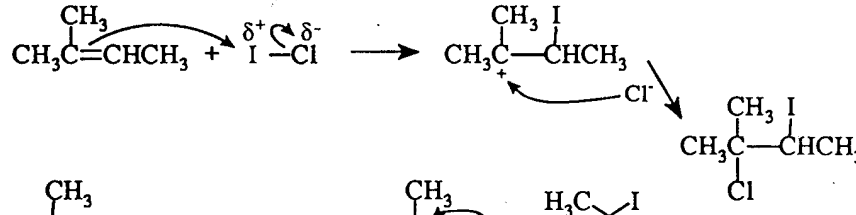
8.1 CH_3CHCH_2I (Br on the middle carbon)

2-Bromo-1-iodopropane

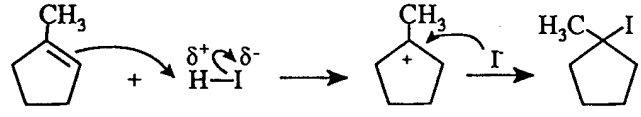
8.2 (a)



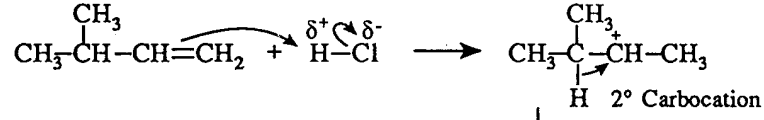
(b)

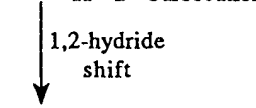


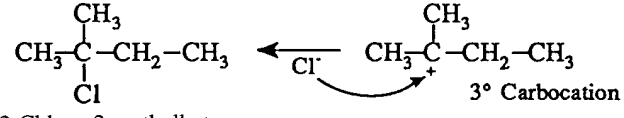
(c)



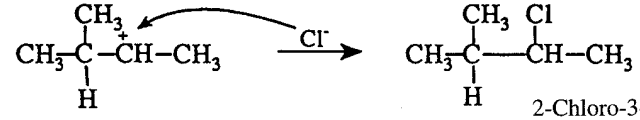
8.3 (a)







2-Chloro-2-methylbutane
(from rearranged carbocation)

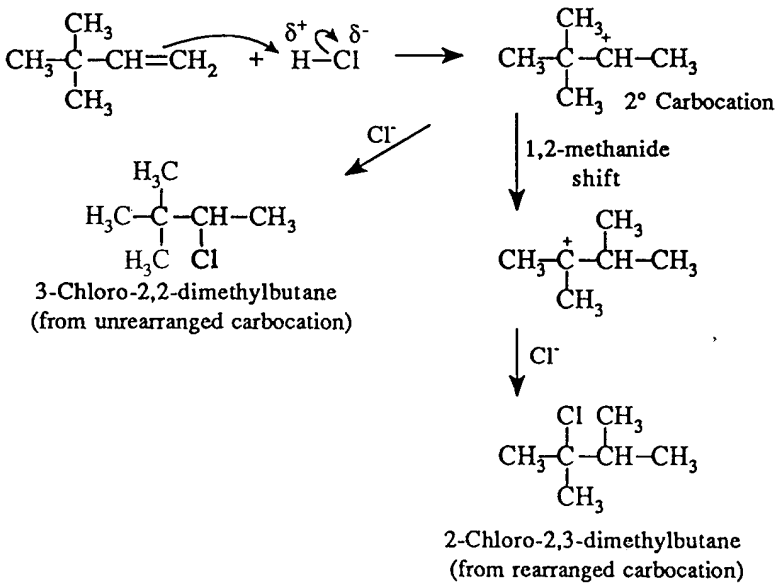


Unrearranged 2° carbocation

2-Chloro-3-methylbutane
(from unrearranged carbocation)

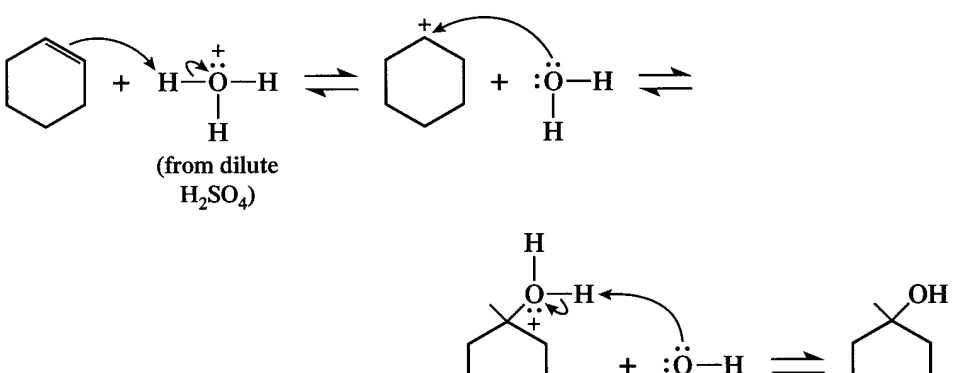
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(b)



8.4 $CH_2{=}CH_2 + H_2SO_4 \longrightarrow CH_3CH_2OSO_3H \xrightarrow[\text{heat}]{H_2O} CH_3CH_2OH + H_2SO_4$

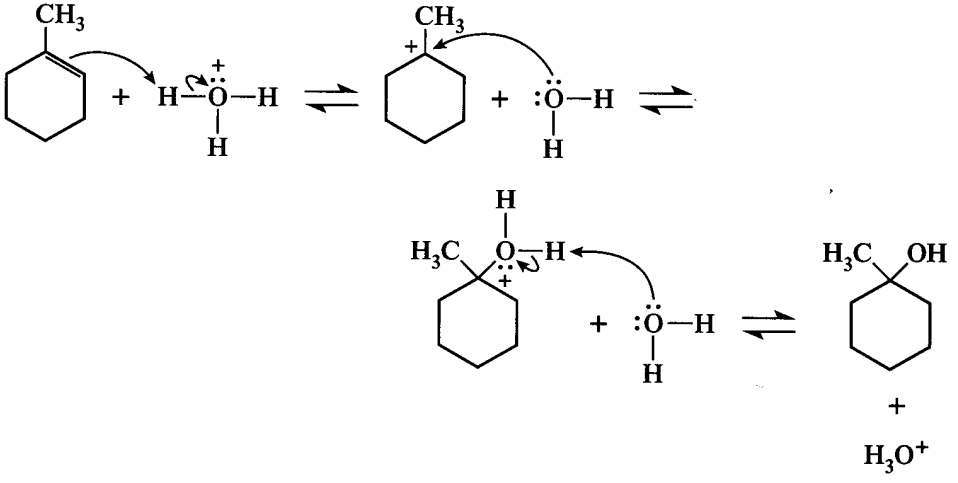
8.5 (a) Use a high concentration of water because we want the carbocation produced to react with water. And use a strong acid whose conjugate base is a very weak nucleophile. (For this reason we would not use HI, HBr, or HCl.) An excellent method, therefore, is to use dilute sulfuric acid.



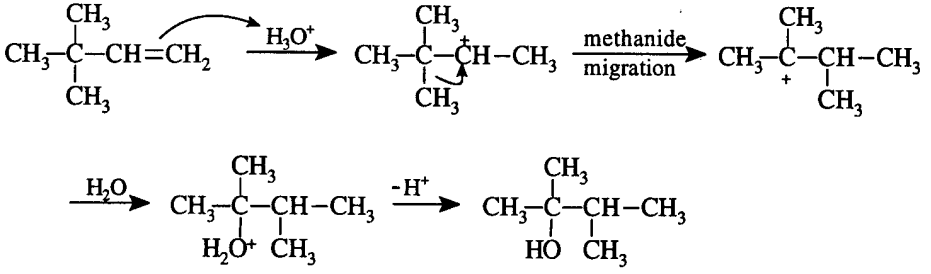
(b) Use a low concentration of water (i.e., use concentrated H_2SO_4) and use a higher temperature to encourage elimination.

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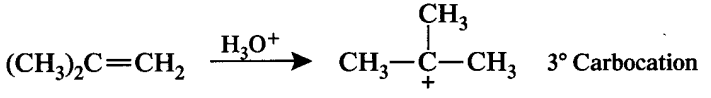
(c) 1-Methylcyclohexanol would be the product because a 3° carbocation would be formed as the intermediate.



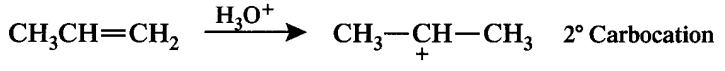
8.6



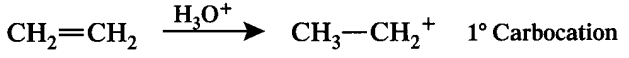
8.7 The order reflects the relative ease with which these alkenes accept a proton and form a carbocation. $(CH_3)_2C{=}CH_2$ reacts faster because it leads to a tertiary cation,



$CH_3CH{=}CH_2$ leads to a secondary cation,



and $CH_2{=}CH_2$ reacts most slowly because it leads to a primary carbocation.

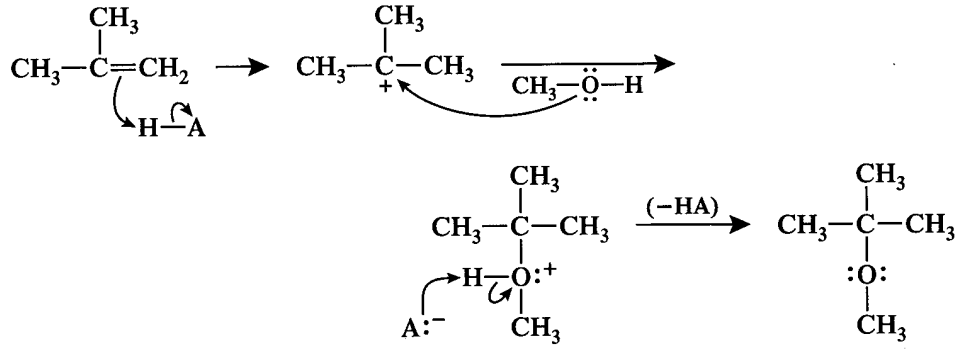


Recall that formation of the carbocation is the rate-determining step in acid-catalyzed hydration and that the order of stabilities of carbocations is the following:

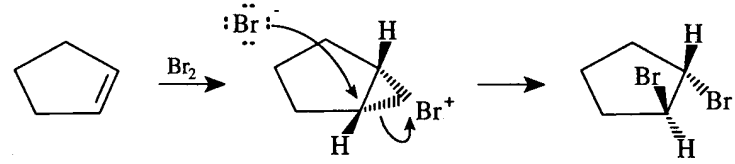
$$3° > 2° > 1° > {}^+CH_3$$

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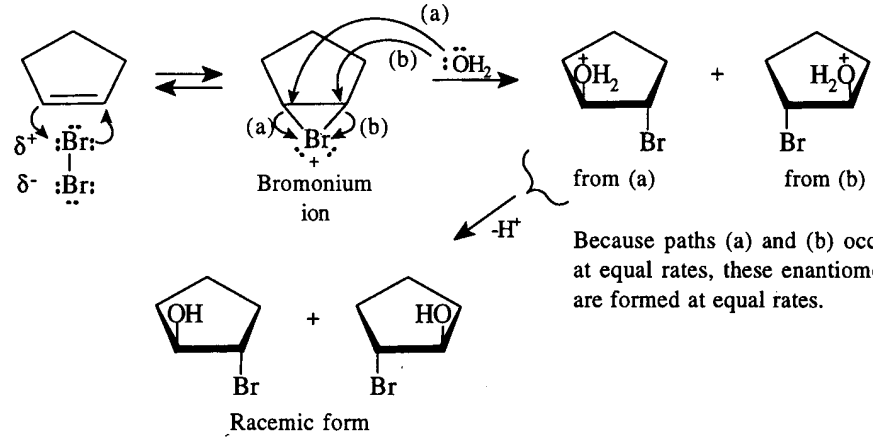
8.8



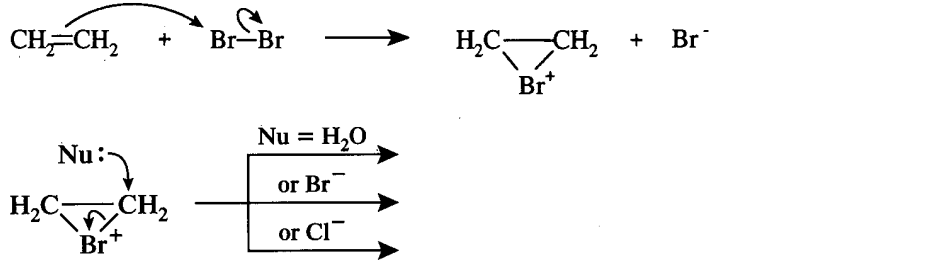
8.9



8.10



8.11

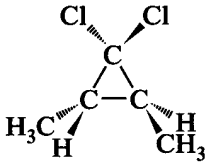
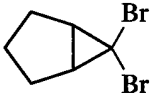


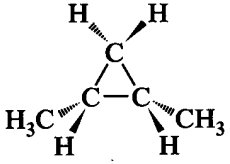
$$Br{-}CH_2CH_2{-}\overset{+}{O}H_2 \xrightarrow{-H^+} Br{-}CH_2CH_2{-}OH$$

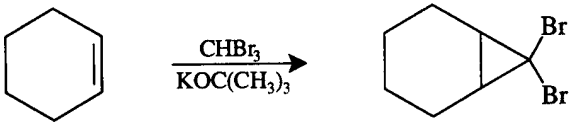
$$Br{-}CH_2CH_2{-}Br$$

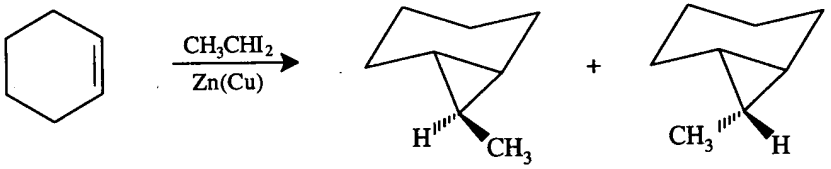
$$Br{-}CH_2CH_2{-}Cl$$

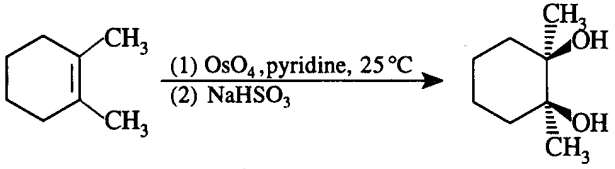
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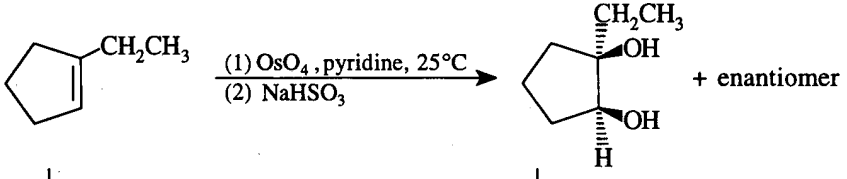
8.12 (a)  + enantiomer (b) 

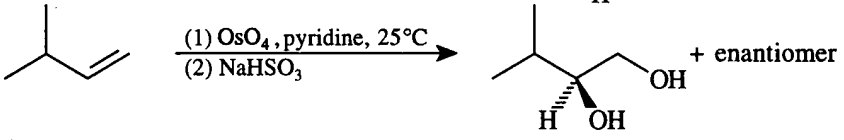
(c) 

8.13 

8.14 

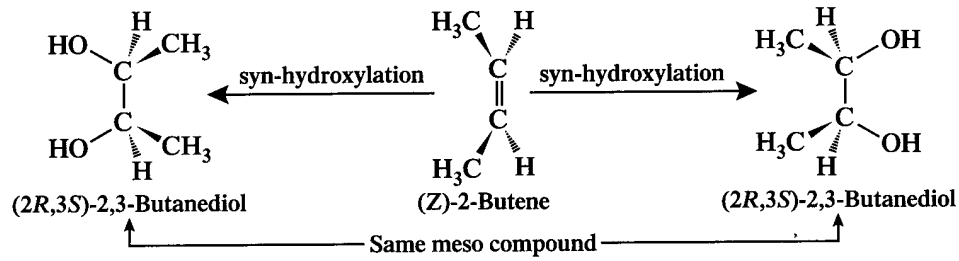
8.15 (a) 

(b) 

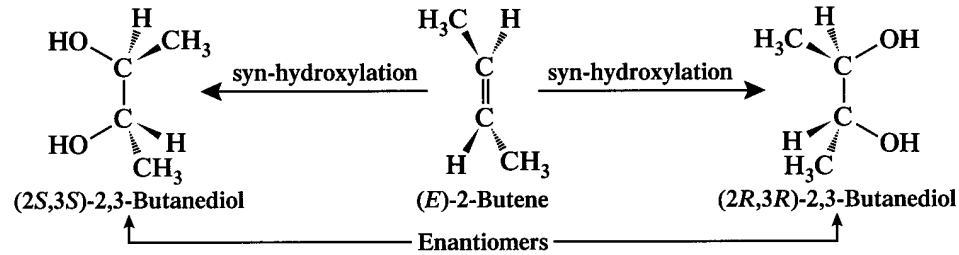
(c) 

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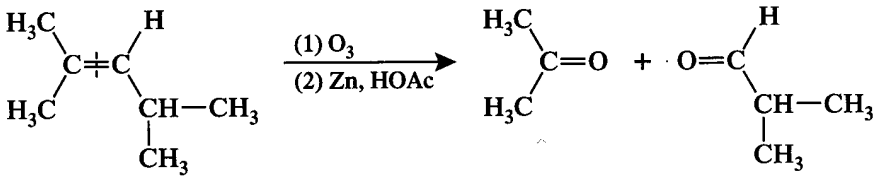
8.16 (a) Syn-hydroxylation at either face of (*Z*)- or cis-alkene leads to the meso compound (2*R*,3*S*)-2,3-butanediol.



(b) Syn-hydroxylation at one face of the (*E*)- or trans-alkene leads to the (2*R*,3*R*)-enantiomer; at the other face, which is equally likely, it leads to the (2*S*,3*S*)-enantiomer.

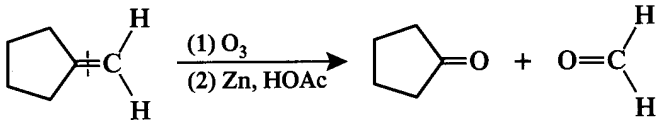


8.17 (a)

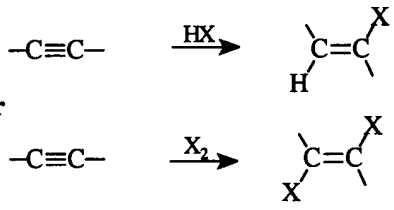


(b) $CH_3CH_2CH{=}CHCH_2CH_3 \xrightarrow[(2)\ Zn,\ HOAc]{(1)\ O_3} CH_3CH_2CH{=}O$

(c)



8.18 Ordinary alkenes *are* more reactive toward electrophilic reagents. But the alkenes obtained from the addition of an electrophilic reagent to an alkyne have at least one electronegative atom (Cl, Br, etc.) attached to a carbon atom of the double bond.



These alkenes are less reactive than alkynes toward electrophilic addition because the electronegative group makes the double bond "electron poor."

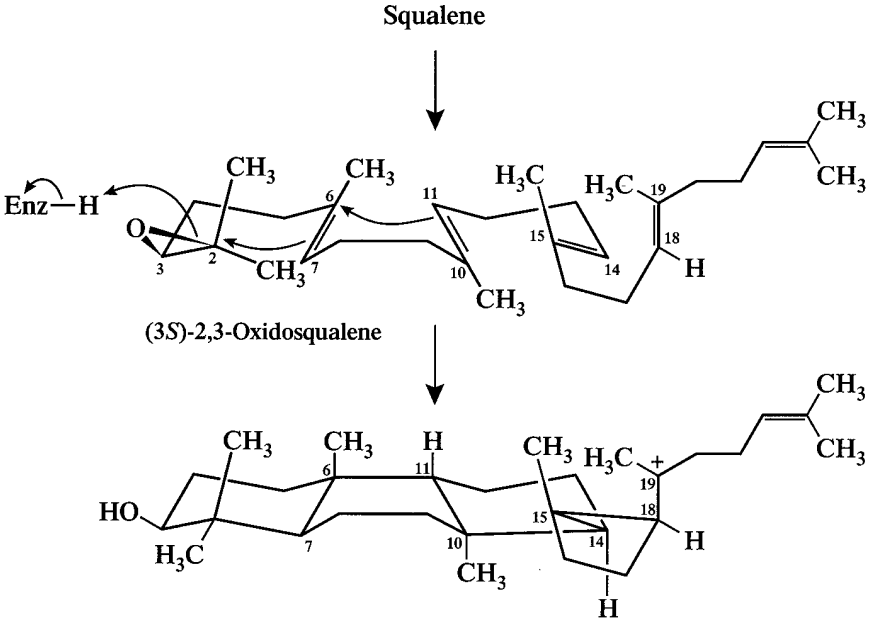
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8.19 The molecular formula and the formation of octane from **A** and **B** indicate that both compounds are unbranched octynes. Since **A** yields only $CH_3CH_2CH_2CO_2H$ on ozonolysis, **A** must be the symmetrical octyne $CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_3$. The IR absorption for **B** shows the presence of a terminal triple bond. Hence **B** is $CH_3(CH_2)_5C{\equiv}CH$.

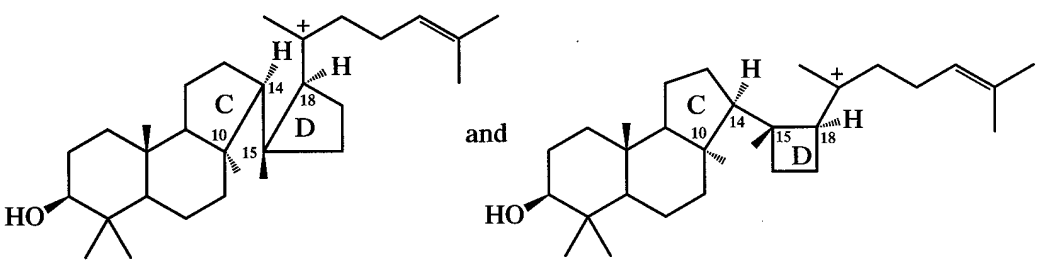
Since **C** (C_8H_{12}) gives $HO_2C(CH_2)_6CO_2H$ on ozonolysis, **C** must be cyclooctyne. This is supported by the molecular formula of **C** and the fact that it is converted to C_8H_{16} (cyclooctane) on catalytic hydrogenation.

Answer to the Study Problem related to cholesterol biosynthesis, page 355.

In cholesterol biosynthesis an anti-Markovnikov addition occurs between C10 (once it becomes like a tertiary carbocation) and C15, forming the six-membered "C" ring of cholesterol (see the reactions in the text, page 355). This process results in a developing *secondary* carbocation at C14, which adds to C18 to form the five-membered "D" ring of cholesterol. If, on the other hand, Markovnikov addition occurred between C10 and C14 instead of anti-Markovnikov addition between C10 and C15, as shown in the following scheme, a developing *tertiary* carbocation would result at C15, along with formation of a five-membered "C" ring. Then, Markovnikov addition of C15 (as it becomes like a tertiary carbocation) to C18 would lead to a four-membered "D" ring and a tertiary carbocation at C19.

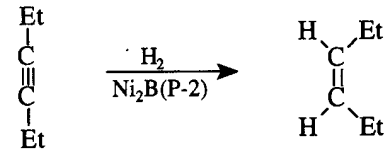


which is the same as:

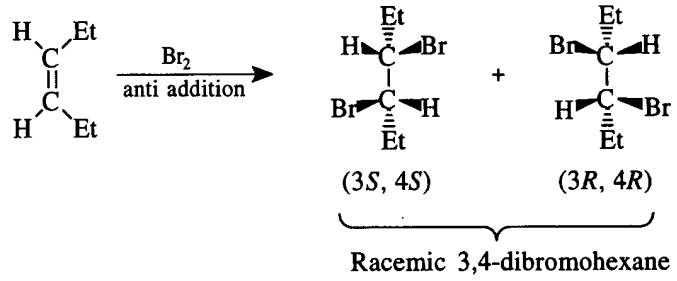


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8.20 By converting the 3-hexyne to *cis*-3-hexene using H_2/Ni_2B (P-2).



Then, addition of bromine to *cis*-3-hexene will yield (3*R*,4*R*), and (3*S*,4*S*)-3,4-dibromohexane as a racemic form.



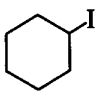
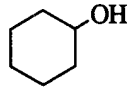
8.21 (a) $CH_3CH_2\underset{\displaystyle I}{\underset{|}{C}}HCH_3$ (b) $CH_3CH_2CH_2CH_3$ (c) $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$

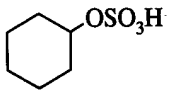
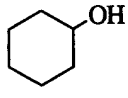
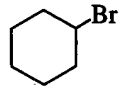
(d) $CH_3CH_2\underset{\displaystyle OSO_3H}{\underset{|}{C}}HCH_3$ (e) $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$ (f) $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

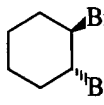
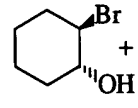
(g) $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_2Br$ (h) $CH_3CH_2CH{=}CH_2$ (i) $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2Br$

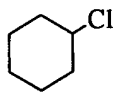
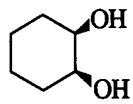
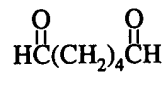
(j) $CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$ (k) $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2OH$ (l) $CH_3CH_2\overset{\displaystyle O}{\overset{\|}{C}}H + H\overset{\displaystyle O}{\overset{\|}{C}}H$

(m) $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2OH$ (n) $CH_3CH_2CO_2H + CO_2$

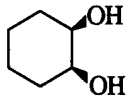
8.22 (a)  (b)  (c) 

(d)  (e)  (f) 

(g)  + enantiomer (h)  (i)  + enantiomer

(j)  (k)  (l) 

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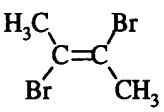
(m) 

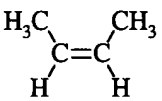
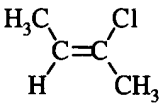
(n) $HOC(CH_2)_4COH$ (O, O)

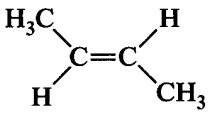
8.23 (a) $CH_3CH_2C(Br)=CHBr$ (b) $CH_3CH_2C(Br)=CH_2$ (c) $CH_3CH_2CBr_2CH_3$

(d) $CH_3CH_2CH_2CH_3$ (e) $CH_3CH_2CH=CH_2$ (f) $CH_3CH_2C\equiv CCH_3$

(g) $CH_3CH_2C\equiv CH$ and $CH_2=C(CH_3)CH_3$ [An E2 reaction would take place when $CH_3CH_2C\equiv CNa$ is treated with $(CH_3)_3CBr$.]

8.24 (a) $CH_3C(Br)=CHCH_3$ (b) $CH_3CBr_2CH_2CH_3$ (c) 

(d) $CH_3CBr_2CBr_2CH_3$ (e)  (f) 

(g)  (h) $CH_3CH_2CH_2CH_3$ (i) $CH_3CH_2CH_2CH_3$

(j) CH_3CO_2H (2 molar equivalents) (k) CH_3CO_2H (2 molar equivalents)

(l) no reaction

8.25 (a) $CH_3CH_2CH=CH_2 \xrightarrow[CCl_4]{Br_2} CH_3CH_2CH(Br)-CH_2(Br) \xrightarrow[\text{mineral oil, heat}]{3NaNH_2}$

$CH_3CH_2C\equiv CNa \xrightarrow{NH_4Cl} CH_3CH_2C\equiv CH$

(b) $CH_3CH_2CH_2CH_2Cl \xrightarrow[t\text{-BuOH, heat}]{t\text{-BuOK}} CH_3CH_2CH=CH_2$ Then as in (a)

(c) $CH_3CH_2CH=CHCl \xrightarrow[\text{mineral oil, heat}]{2NaNH_2} CH_3CH_2C\equiv CNa \xrightarrow{NH_4Cl} CH_3CH_2C\equiv CH$

(d) $CH_3CH_2CH_2CH(Cl)-Cl \xrightarrow[\text{mineral oil, heat}]{3NaNH_2} CH_3CH_2C\equiv CNa \xrightarrow{NH_4Cl} CH_3CH_2C\equiv CH$

(e) $H-C\equiv C-H \xrightarrow[liq.\,NH_3]{NaNH_2} H-C\equiv CNa \xrightarrow{CH_3CH_2-Br} CH_3CH_2C\equiv CH$

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8.26 (a) $CH_3C(CH_3)=CH_2 \xrightarrow{H_3O^+, H_2O} CH_3C(CH_3)(OH)CH_3$

(b) $CH_3C(CH_3)=CH_2 \xrightarrow{HCl} CH_3C(CH_3)(Cl)CH_3$

(c) $CH_3C(CH_3)=CH_2 \xrightarrow[\text{(no peroxides)}]{HBr} CH_3C(CH_3)(Br)CH_3$

(d) $CH_3C(CH_3)=CH_2 \xrightarrow{HF} CH_3C(CH_3)(F)CH_3$

(e) $CH_3C(CH_3)=CH_2 \xrightarrow{Cl_2, H_2O} CH_3C(CH_3)(OH)CH_2Cl$

8.27 (a) $C_{10}H_{22}$ (saturated alkane)
$C_{10}H_{16}$ (formula of myrcene)
H_6 = 3 pairs of hydrogen atoms

Index of hydrogen deficiency (IHD) = 3

(b) Myrcene contains no rings because complete hydrogenation gives $C_{10}H_{22}$, which corresponds to an alkane.

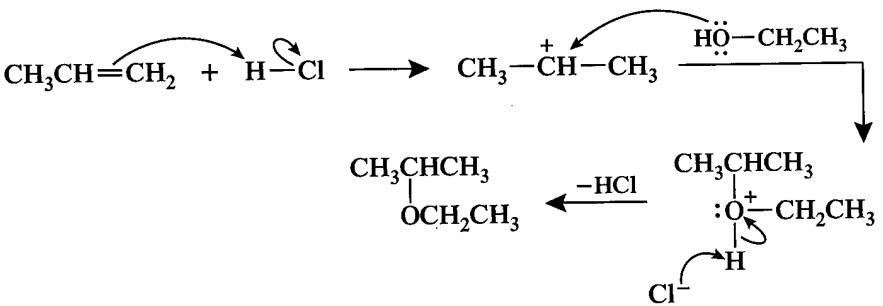
(c) That myrcene absorbs three molar equivalents of H_2 on hydrogenation indicates that it contains three double bonds.

(d) Three structures are possible; however, only one gives 2,6-dimethyloctane on complete hydrogenation. Myrcene is therefore

$$CH_3C(CH_3)=CHCH_2CH_2C(=CH_2)CH=CH_2$$

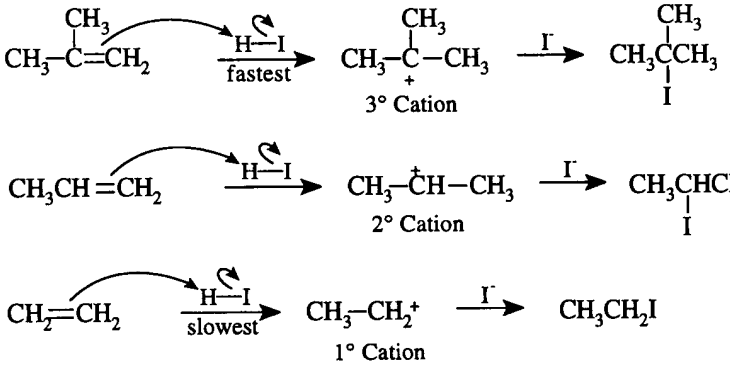
(e) $O=CHCH_2CH_2C(=O)CH=O$

8.28



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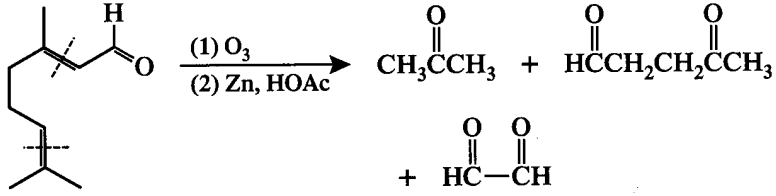
8.29 The rate-determining step in each reaction is the formation of a carbocation when the alkene accepts a proton from HI. When 2-methylpropene reacts, it forms a 3° carbocation (the most stable); therefore, it reacts fastest. When ethene reacts, it forms a 1° carbocation (the least stable); therefore, it reacts the slowest.



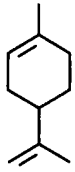
8.30 $CH_3CHCH_2CH_2CH_2CHCH_2CH_2CH_2CHCH_2CH_3$ (CH₃ groups at positions 2, 6, and 10)

2,6,10-Trimethyldodecane

8.31

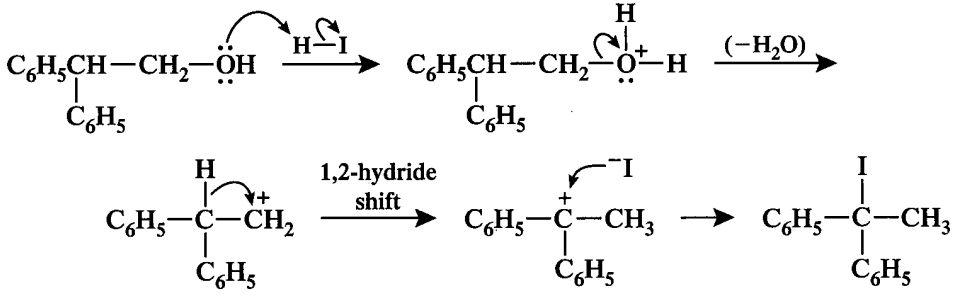


8.32



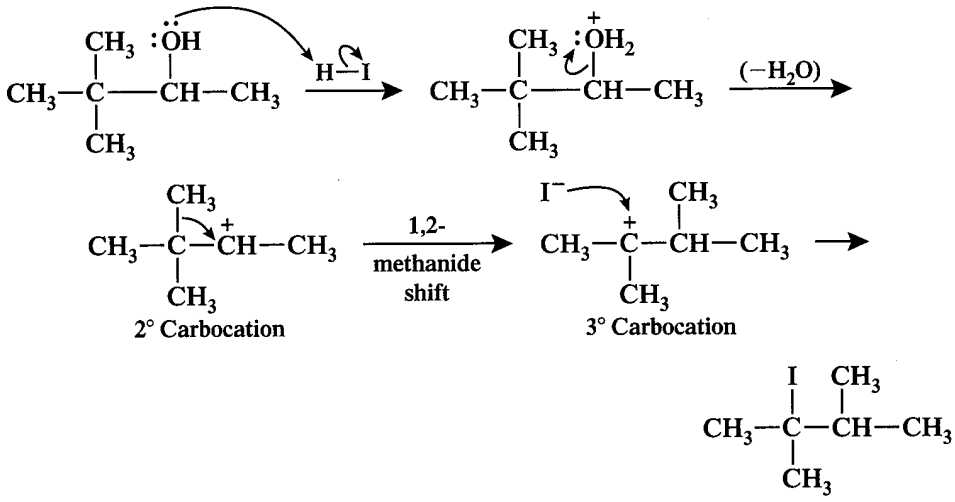
Limonene

8.33

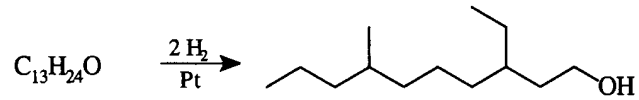


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8.34



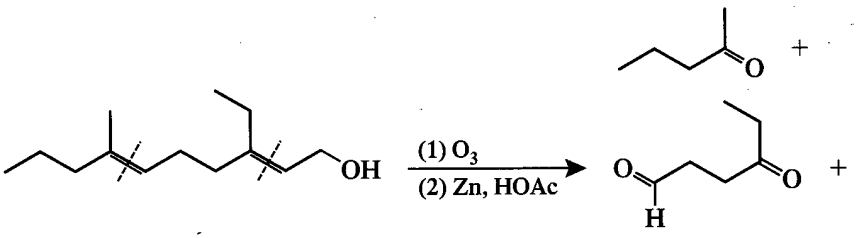
8.35 (a) The hydrogenation experiment discloses the carbon skeleton of the pheromone.



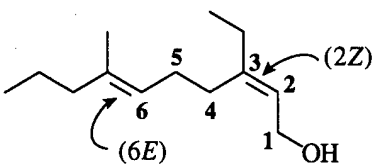
Codling moth pheromone

3-Ethyl-7-methyl-1-decanol

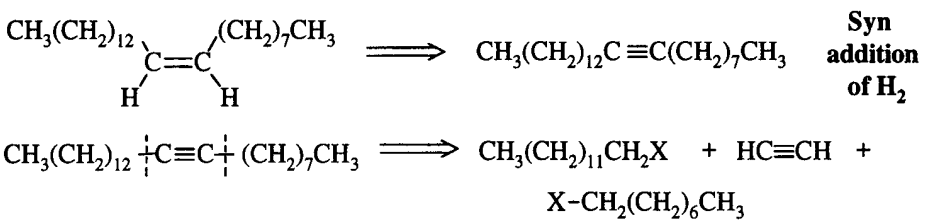
The ozonolysis experiment allows us to locate the position of the double bonds.



(b)



8.36 ***Retrosynthetic analysis***



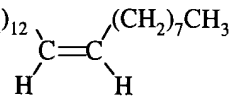
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Synthesis

$$HC{\equiv}CH \xrightarrow[\text{liq.}NH_3]{NaNH_2} HC{\equiv}C^{-}\,Na^{+} \xrightarrow[(\text{-NaBr})]{CH_3(CH_2)_6CH_2{-}Br}$$

$$HC{\equiv}C(CH_2)_7CH_3 \xrightarrow[\text{liq.}NH_3]{NaNH_2} Na^{+}\,{}^{-}C{\equiv}C(CH_2)_7CH_3 \xrightarrow[(\text{-NaBr})]{CH_3(CH_2)_{11}CH_2{-}Br}$$

$$CH_3(CH_2)_{12}C{\equiv}C(CH_2)_7CH_3 \xrightarrow[Ni_2B\ (P\text{-}2)]{H_2}$$



Muscalure

8.37** ***Retrosynthetic analysis

$$CH_3CBr_2CH_2CH_2CH_2CH_2CH_3 \xrightarrow[\text{addition}]{\text{Markov-nikov}} CH_2{=}CBrCH_2CH_2CH_2CH_2CH_3 + HBr$$

$$\xrightarrow[\text{addition}]{\text{Markov-nikov}} HC{\equiv}CCH_2CH_2CH_2CH_2CH_3 + HBr \Longrightarrow HC{\equiv}CH + BrCH_2CH_2CH_2CH_2CH_3$$

Synthesis

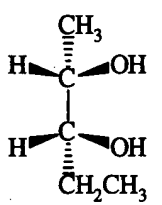
$$HC{\equiv}CH \xrightarrow[\text{liq.}NH_3]{NaNH_2} HC{\equiv}C^{-}\,Na^{+} \xrightarrow[(\text{-NaBr})]{CH_3CH_2CH_2CH_2CH_2{-}Br}$$

$$HC{\equiv}CCH_2CH_2CH_2CH_2CH_3 \xrightarrow[CH_3COBr/alumina]{\text{"HBr"}} HC(Br){=}CHCH_2CH_2CH_2CH_2CH_3$$

$$\xrightarrow[CH_3COBr/alumina]{\text{"HBr"}} CH_3CBr_2CH_2CH_2CH_2CH_2CH_3$$

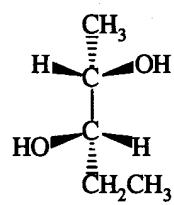
8.38 Syn hydrogenation of the triple bond is required. So use H_2 and Ni_2B(P-2) or H_2 and Lindlar's catalyst.

8.39 (a)



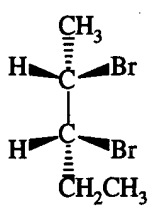
and enantiomer through syn addition

(b)



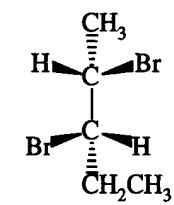
and enantiomer through syn addition

(c)



and enantiomer through anti addition

(d)



and enantiomer through anti addition

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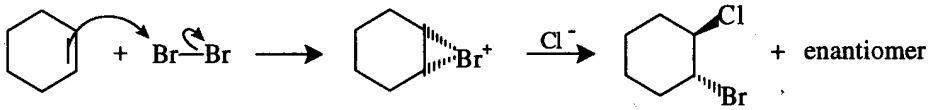
8.40 (a) (2*S*,3*R*)- [the enantiomer is (2*R*,3*S*)-]

(b) (2*S*,3*S*)- [the enantiomer is (2*R*,3*R*)-]

(c) (2*S*,3*R*)- [the enantiomer is (2*R*,3*S*)-]

(d) (2*S*,3*S*)- [the enantiomer is (2*R*,3*R*)-]

8.41



Bromonium ion

The bromonium ion reacts with a chloride ion to produce the *trans*-1-bromo-2-chlorocyclohexane enantiomers.

8.42 (a) 1-Pentyne has IR absorption at about 3300 cm^{-1} due to its terminal triple bond. Pentane does not absorb in that region.

(b) 1-Pentene absorbs in the 1620–1680 cm^{-1} region due to the alkene function. Pentane does not exhibit absorption in that region.

(c) See parts (a) and (b).

(d) 1-Bromopentane shows C-Br absorption in the 690-515 cm^{-1} region while pentane does not.

(e) For 1-pentyne, see (a). The interior triple bond of 2-pentyne gives relatively weak absorption in the 2100–2260 cm^{-1} region.

(f) For 1-pentene, see (b). 1-Pentanol has a broad absorption band in the 3200–3550 cm^{-1} region.

(g) See (f)

(h) 1-Bromo-2-pentene has double bond absorption in the 1620–1680 cm^{-1} region which 1-bromopentane lacks.

(i) 2-Penten-1-ol has double bond absorption in the 1620–1680 cm^{-1} region not found in 1-pentanol.

8.43 Because of the electron-withdrawing nature of chlorine, the electron density at the double bond is greatly reduced and attack by the electrophilic bromine does not occur.

***8.44** The index of hydrogen deficiency of **A, B,** and **C** is two.

$$\begin{array}{r} C_6H_{14} \\ \underline{C_6H_{10}} \\ H_4 \end{array} \quad = \quad 2 \text{ pairs of hydrogen atoms}$$

This result suggests the presence of a triple bond, two double bonds, a double bond and a ring, or two rings. The fact that **A, B,** and **C** all decolorize Br_2/CCl_4 and dissolve in concd. H_2SO_4 suggests they all have a carbon-carbon multiple bond.

A must be a terminal alkyne, because of IR absorption at about 3300 cm^{-1}.

Since **A** gives hexane on catalytic hydrogenation, **A** must be 1-hexyne.

$$\underset{\textbf{A}}{CH_3(CH_2)_3C{\equiv}CH} \xrightarrow[Pt]{2H_2} CH_3(CH_2)_4CH_3$$

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This is confirmed by the oxidation experiment

$$CH_3(CH_2)_3C{\equiv}CH \xrightarrow[(2)\ H_3O^+]{(1)\ KMnO_4,\ OH^-,\ heat} CH_3(CH_2)_3CO_2H + CO_2\uparrow$$

Hydrogenation of **B** to hexane shows that its chain is unbranched, and the oxidation experiment shows that **B** is 3-hexyne.

$$\underset{\mathbf{B}}{CH_3CH_2C{\equiv}CCH_2CH_3} \xrightarrow[(2)\ H_3O^+]{(1)\ KMnO_4,\ OH^-,\ heat} 2\ CH_3CH_2CO_2H$$

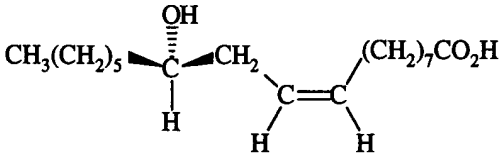
Oxidation of **C** shows that it is cyclohexene.

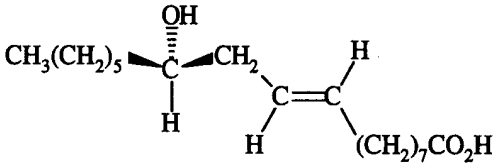


$$\xrightarrow[(2)\ H_3O^+]{(1)\ KMnO_4,\ OH^-,\ heat} HO_2C(CH_2)_4CO_2H$$

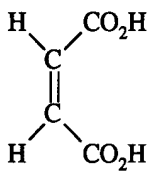
C

8.45 (a) Four

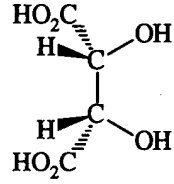
(b)  + enantiomer

 + enantiomer

8.46 Hydroxylations by $KMnO_4$ are syn hydroxylations (cf. Section 8.9). Thus, maleic acid must be the *cis*-dicarboxylic acid:

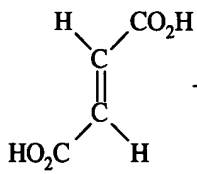


$$\xrightarrow[\text{syn hydroxylation}]{KMnO_4}$$

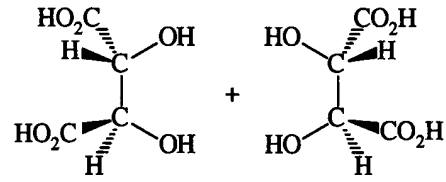


Maleic acid *meso*-Tartaric acid

Fumaric acid must be the *trans*-dicarboxylic acid:



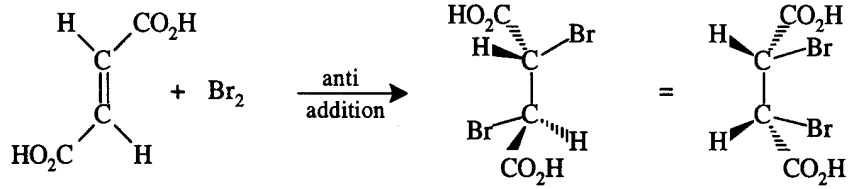
$$\xrightarrow[\text{syn hydroxylation}]{KMnO_4}$$



Fumaric acid (±)-Tartaric acid

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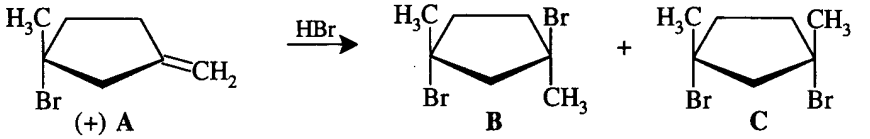
8.47 (a) The addition of bromine is an anti addition. Thus, fumaric acid yields a meso compound.



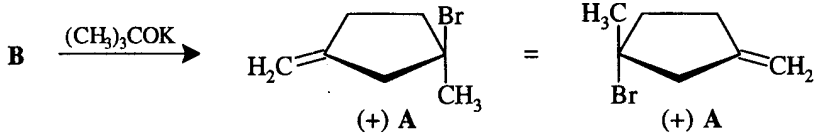
A meso compound

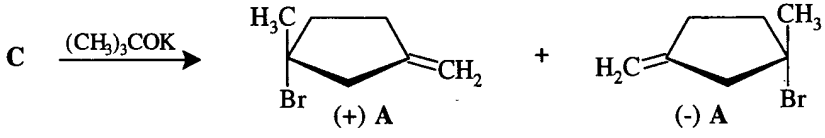
(b) Maleic acid adds bromine to yield a racemic modification.

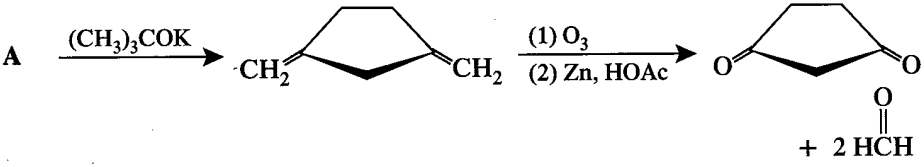
***8.48**



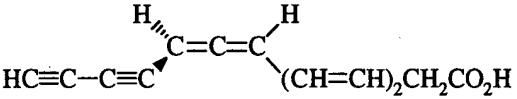
(optically active) (a meso compound)

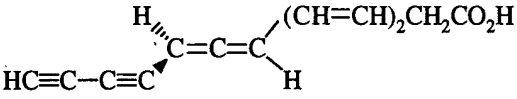






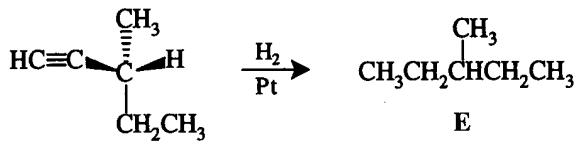
8.49





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8.50



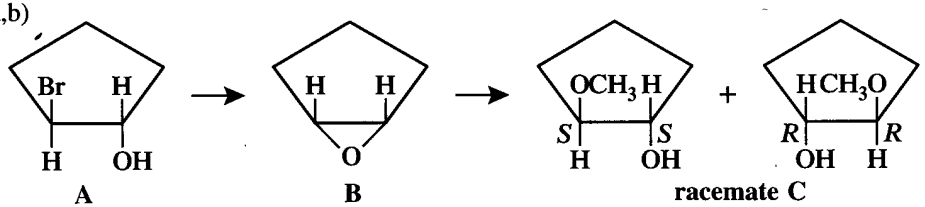
D

E

Optically active (the other enantiomer is an equally valid answer)

Optically inactive (nonresolvable)

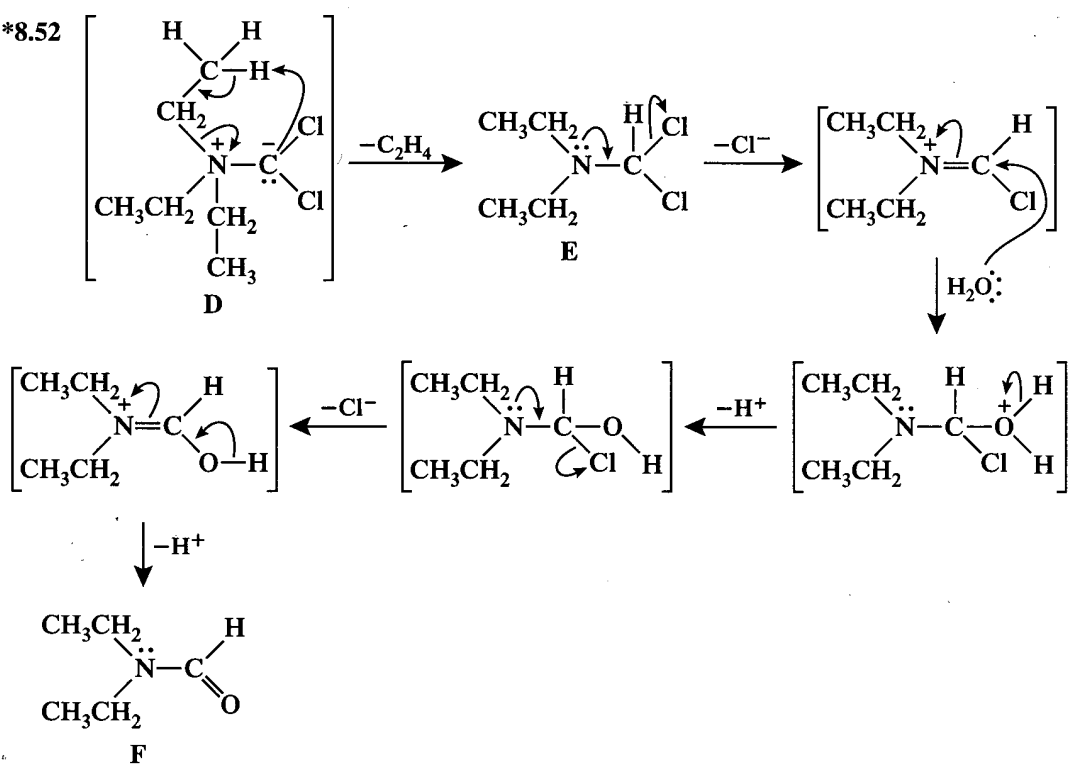
***8.51** (a,b)



A B racemate C

(c) **C**, in contrast to its *cis* isomer, would exhibit no intramolecular hydrogen-bonding. This would be proven by the absence of infrared absorption in the 3500- to 3600-cm^{-1} region when studied as a very dilute solution in CCl_4. **C** would only show free O—H stretch at about 3625 cm^{-1}

***8.52**



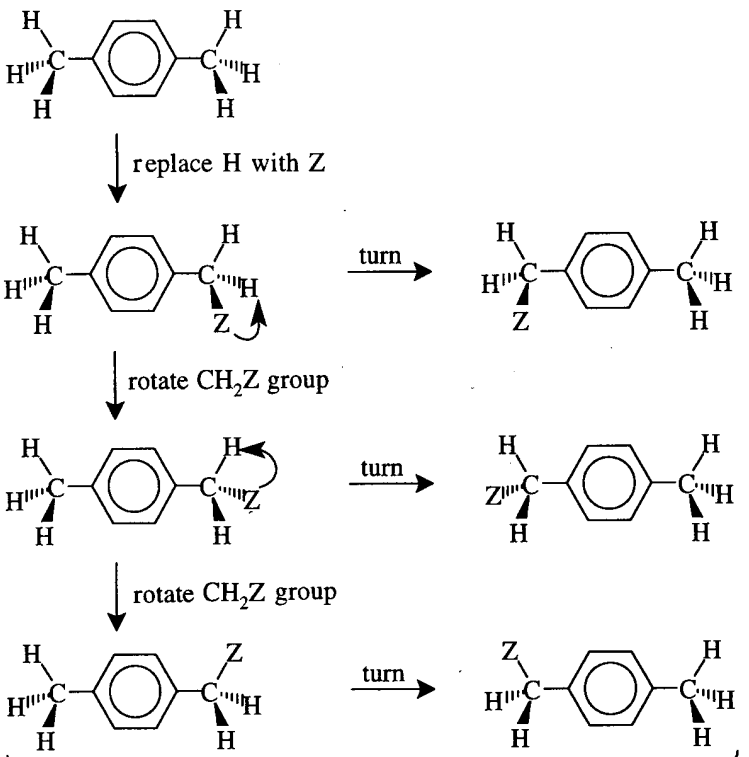
D E F

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9 NUCLEAR MAGNETIC RESONANCE AND MASS SPECTROMETRY: TOOLS FOR STRUCTURE DETERMINATION

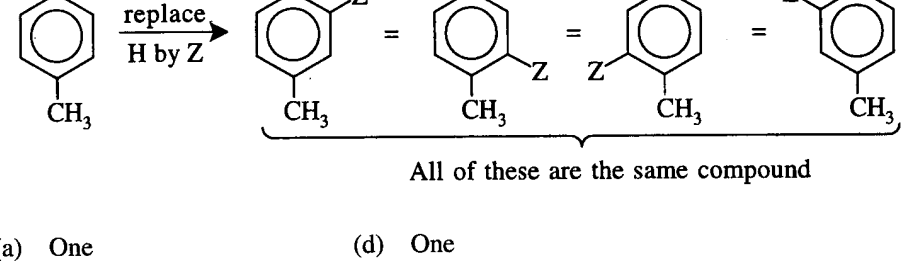
SOLUTIONS TO PROBLEMS

9.1 We see below that if we replace a methyl hydrogen by some group Z, then rotation of the methyl group or turning the whole molecule end-for-end gives structures that represent the same compound. This means that all of the methyl hydrogens are equivalent.



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Replacing a ring hydrogen by Z gives another compound, but replacing each ring hydrogen in turn gives the same compound. This shows that all four ring hydrogens are equivalent and that 1,4-dimethylbenzene has only two sets of chemical shift equivalent protons.

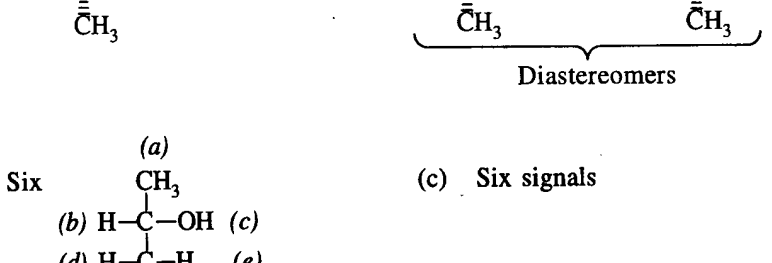


9.2 (a) One (d) One

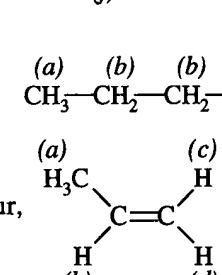
(b) Two (e) Two

(c) Two (f) Two

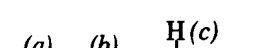
9.3 (a)



(b) Six

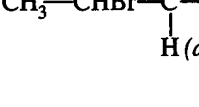


(c) Six signals

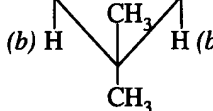
9.4 (a) Two, 

(b) Three, 

(c) Four,

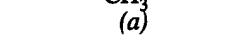


(d) Two,



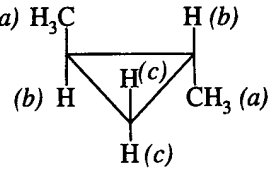
(e) Four,

(f) Two,

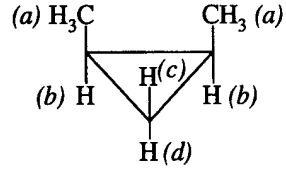


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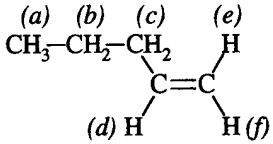
(g) Three,



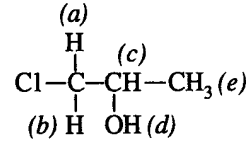
(h) Four,



(i) Six,



(j) Five,



9.5 The ^1H NMR spectrum of $CHBr_2CHCl_2$ consists of two doublets. The doublet from the proton of the $-CHCl_2$ group should occur at lower magnetic field strength because the greater electronegativity of chlorine reduces the electron density in the vicinity of the $-CHCl_2$ proton, and consequently, reduces its shielding relative to $-CHBr_2$.

9.6 The determining factors here are the number of chlorine atoms attached to the carbon atoms bearing protons and the deshielding that results from chlorine's electronegativity. In 1,1,2-trichloroethane the proton that gives rise to the triplet is on a carbon atom that bears two chlorines, and the signal from this proton is downfield. In 1,1,2,3,3-pentachloropropane, the proton that gives rise to the triplet is on a carbon atom that bears only one chlorine; the signal from this proton is upfield.

9.7 The signal from the three equivalent protons designated *(a)* should be split into a doublet by the proton *(b)*. This doublet, because of the electronegativity of the attached chlorines, should occur downfield.

$$\overset{(a)}{(Cl_2CH)_3}\!-\!\overset{(b)}{CH}$$

The signal for the proton designated *(b)* should be split into a quartet by the three equivalent protons *(a)*. The quartet should occur upfield.

9.8

A C_3H_7I is $\overset{(a)}{CH_3}\!-\!\overset{(b)}{\underset{\displaystyle I}{CH}}\!-\!\overset{(a)}{CH_3}$

(*a*) doublet δ 1.9
(*b*) septet δ 4.35

B $C_2H_4Cl_2$ is $\overset{(a)}{CH_3}\!-\!\overset{(b)}{\underset{\displaystyle Cl}{CH}}\!-Cl$

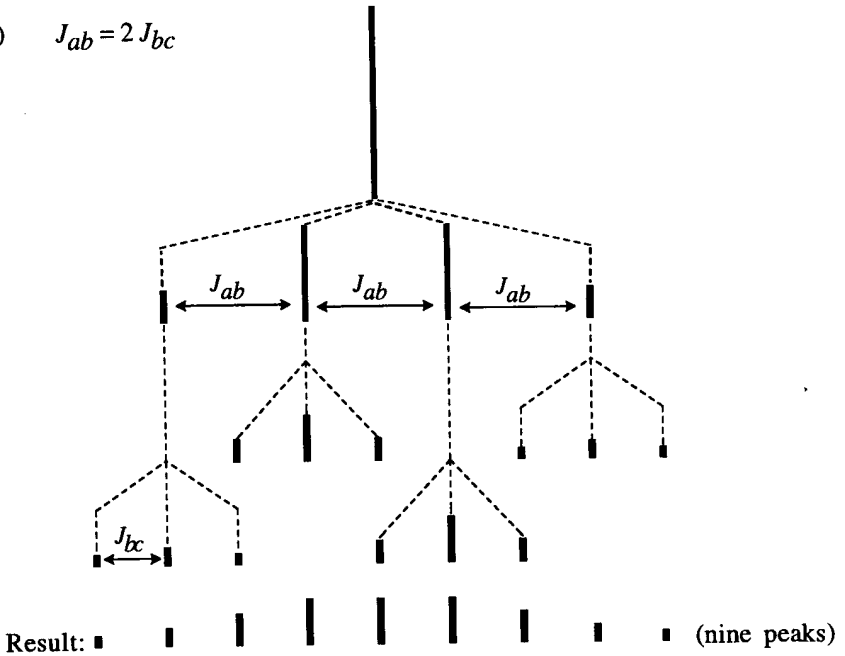
(*a*) doublet δ 2.08
(*b*) quartet δ 5.9

C $C_3H_6Cl_2$ is $\overset{(a)}{Cl\!-\!CH_2}\!-\!\overset{(b)}{CH_2}\!-\!\overset{(a)}{CH_2}\!-Cl$

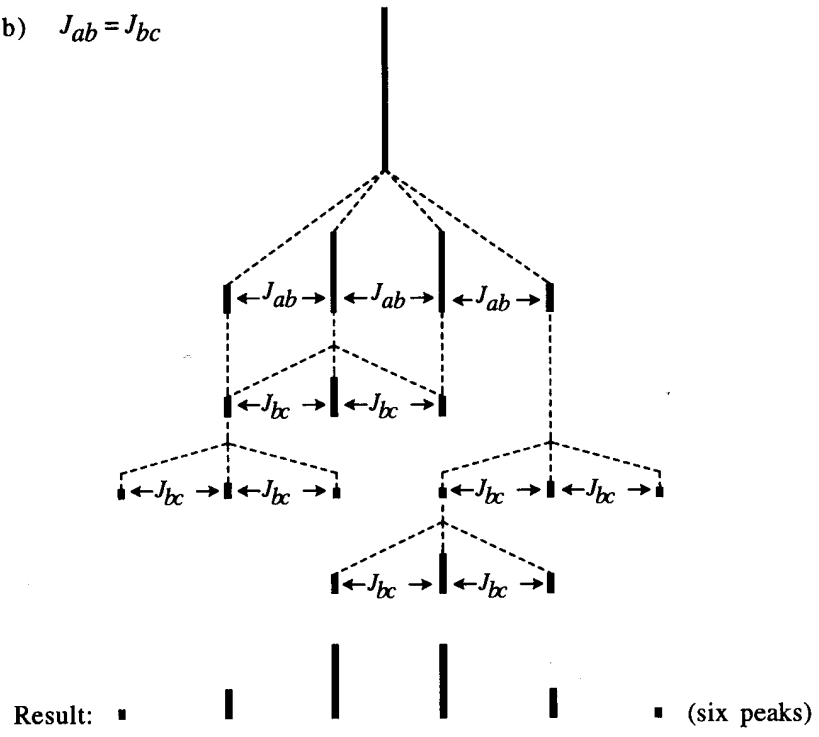
(*a*) triplet δ 3.7
(*b*) quintet δ 2.2

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9.9 (a) $J_{ab} = 2\,J_{bc}$



(b) $J_{ab} = J_{bc}$



9.10 A single unsplit signal, because the proton is rapidly shifted from axial to equatorial positions.

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9.11 **A** is 1-bromo-3-methylbutane. The following are the signal assignments:

(d) (c) (b) (a)
$BrCH_2CH_2CH(CH_3)_2$

(a) δ 23
(b) δ 27
(c) δ 32
(d) δ 42

B is 2-bromo-2-methylbutane. The following are the signal assignments:

(a) (c) Br *(b)*
$CH_3CH_2C(CH_3)_2$
(d)

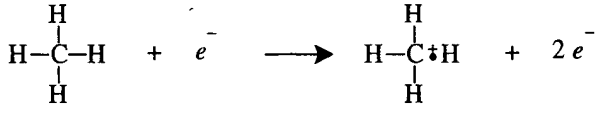
(a) δ 11
(b) δ 33
(c) δ 40
(d) δ 68

C is 1-bromopentane. The following are the signal assignments.

(e) (d) (c) (b) (a)
$BrCH_2CH_2CH_2CH_2CH_3$

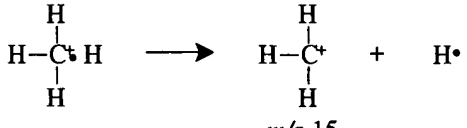
(a) δ 14
(b) δ 23
(c) δ 30
(d) δ 33
(e) δ 34

9.12 The compound is methane, CH_4. The molecular ion is at *m/z* 16. (This peak also happens to be the base peak.)

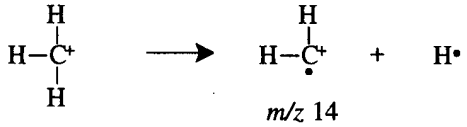


m/z 16
$M^{+\cdot}$

The peaks at *m/z* 15, 14, 13, and 12 are caused by successive losses of hydrogen atoms.

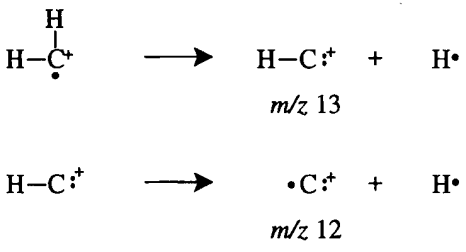


m/z 15

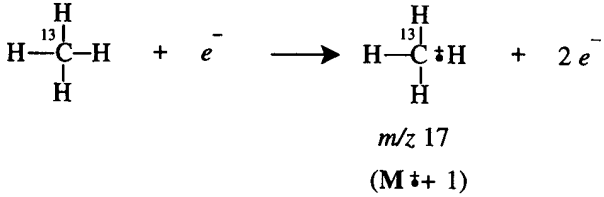


m/z 14

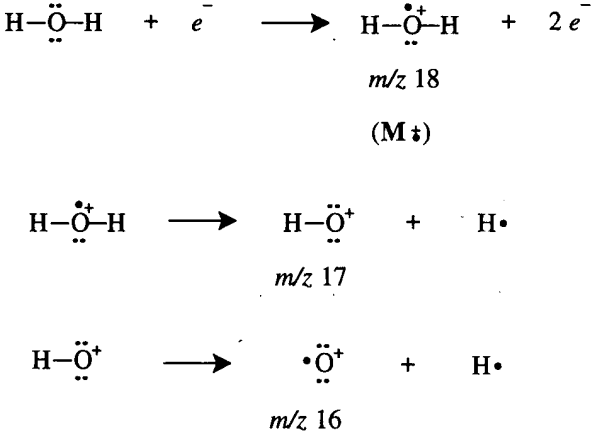
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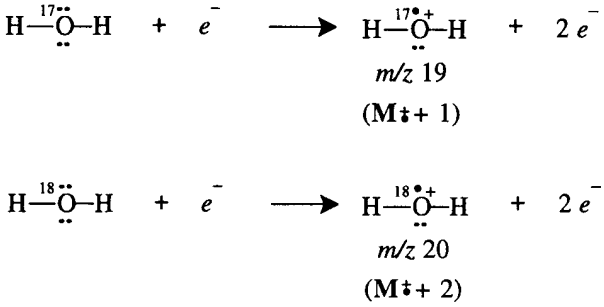
The small peak at *m/z* 17 ($\mathbf{M}^{+\cdot} + \mathbf{1}$) comes mainly from methane molecules that contain ^{13}C.



9.13 The compound is water.



The peaks at *m/z* 19 and *m/z* 20 are due (primarily) to naturally occurring oxygen isotopes.



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9.14 The compound is methyl fluoride, CH_3F.

$$CH_3{-}F + e^- \longrightarrow [CH_3{-}F]^{+\bullet} + 2e^-$$

m/z 34
(**M**$^{+\bullet}$)

$$[CH_3F]^{+\bullet} \longrightarrow [CH_2F]^+ + H^\bullet$$
m/z 33

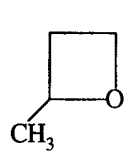
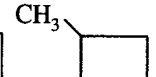
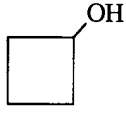
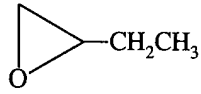
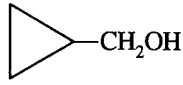
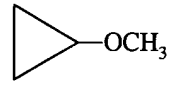
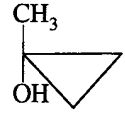
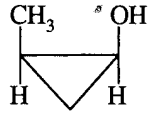
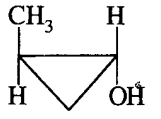
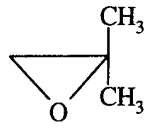
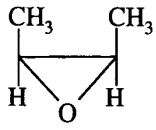
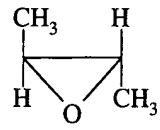
$$[CH_2F]^+ \longrightarrow [CHF]^{+\bullet} + H^\bullet$$
m/z 32

$$[CHF]^{+\bullet} \longrightarrow [CF]^+ + H^\bullet$$
m/z 31

$$[CH_3F]^{+\bullet} \longrightarrow [F]^+ + CH_3^\bullet$$
m/z 19

$$[CH_3F]^{+\bullet} \longrightarrow [CH_3]^+ + F^\bullet$$
m/z 15

$$[CH_3]^+ \longrightarrow [CH_2]^{+\bullet} + H^\bullet$$
m/z 14

9.15 (a) $CH_3CCH_2CH_3$ (O), $CH_3CH_2CH_2CH$ (O), CH_3CHCH (O, CH_3), $CH_2{=}CHCH_2OCH_3$, $CH_3CH{=}CHCH_2OH$, $CH_2{=}C(CH_3){-}CH_2OH$,  ,  ,  ,  ,  ,  ,  ,  ,  ,  ,  ,  , 

(b) Only the first three. (The peak at 1730 cm^{-1} is due to a C=O group.)

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9.16 First, we recalculate the intensities of the peaks so as to base them on the M^+ peak:

m/z		INTENSITY % of M^+
86 M^+	10.0/10.0 × 100 =	100
87	0.56/10.0 × 100 =	5.6
88	0.04/10.0 × 100 =	0.4

1. Since M^+ is even, the compound must contain an even number of nitrogen atoms (i.e., 0, 2, 4, etc.).

2. The value of the $M^+ + 1$ peak gives the number of carbon atoms.

$$\text{Number of carbon atoms} = 5.6/1.1 \simeq 5$$

The compound must contain no nitrogen atoms because $C_5N_2 = (5 \times 12) + (2 \times 14) = 88$, and the molecular weight of the compound (from the M^+ peak) is only 86.

3. The very low value of the $M^+ + 2$ peak (0.4%) tells us that the compound does not contain S, Cl, or Br.

4. If the compound were composed only of C and H, it would have to be C_5H_{26}:

$$H = 86 - (5 \times 12) = 26$$

But C_5H_{26} is impossible.

However, a formula with one oxygen gives a reasonable number of hydrogen atoms,

$$H = 86 - (5 \times 12) - 16 = 10$$

and thus our compound has the formula $C_5H_{10}O$.

9.17 (a) The $M^+ + 2$ peak due to CH_3–^{37}Cl (at *m/z* 52) should be almost one-third (32.5%) as large as the M^+ peak at *m/z* 50.

(b) The peaks due to CH_3–^{79}Br and CH_3–^{81}Br (at *m/z* 94 and *m/z* 96, respectively) should be of nearly equal intensity.

(c) That the M^+ and $M^+ + 2$ peaks are of nearly equal intensity tells us that the compound contains bromine. C_3H_7Br is therefore a likely molecular formula.

$C_3 = 36$	$C_3 = 36$
$H_7 = 7$	$H_7 = 7$
$^{79}Br = \underline{79}$	$^{81}Br = \underline{81}$
m/z = 122	*m/z* = 124

9.18 Recalculating the intensities to base on M^+

PEAK	*m/z*	% of BASE PEAK	% of M^+
M^+	73	86.1	100
$M^+ + 1$	74	3.2	3.72
$M^+ + 2$	75	0.2	0.23

These data best fit the formula C_3H_7NO.

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9.19 (a) First recalculating the intensities so as to base them on the $M^{+\cdot}$ peak:

m/z		INTENSITY % of $M^{+\cdot}$
78 $M^{+\cdot}$	24/24 × 100 =	100
79	0.8/24 × 100 =	3.3
80	8/24 × 100 =	33

1. Since $M^{+\cdot}$ is even, the compound contains an even number of nitrogen atoms.

2. Number of carbon atoms = $(M^{+\cdot} + 1)/1.1 = 3.3/1.1 = 3$.

3. The intensity of the $M^{+\cdot} + 2$ peak (33%) tells us that the compound contains one chlorine atom.

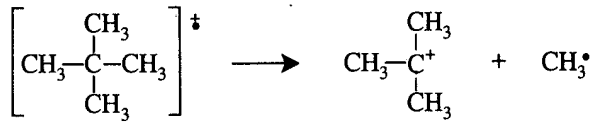
4. We use the molecular weight (from the $M^{+\cdot}$ peak) to calculate the number of hydrogen atoms.

$$H = 78 - (3 \times 12) - 35 = 7$$

Thus, the formula for the compound is C_3H_7Cl.

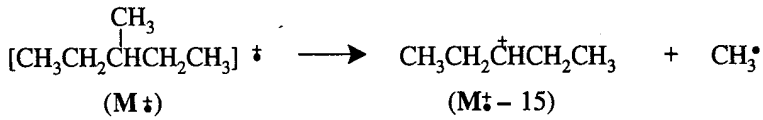
(b) CH_3CHCH_3 (Cl on the CH)

9.20 (a) A *tert*-butyl cation, $(CH_3)_3C^+$.

(b) 

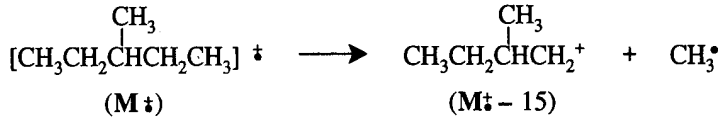
m/z 57

9.21 A peak at $M^{+\cdot}$ - 15 involves the loss of a methyl radical and the formation of a 1° or 2° carbocation.



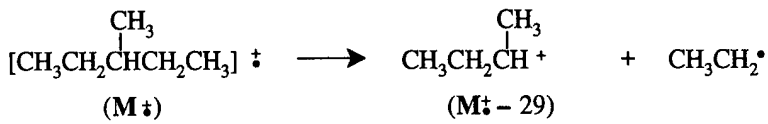
(**M**$^{+\cdot}$) (**M**$^{+\cdot}$ – 15)

or



(**M**$^{+\cdot}$) (**M**$^{+\cdot}$ – 15)

A peak at $M^{+\cdot}$ - 29 arises from the loss of an ethyl radical and the formation of a 2° carbocation.

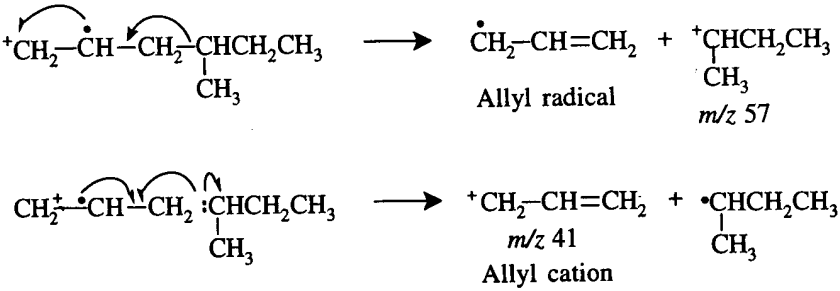


(**M**$^{+\cdot}$) (**M**$^{+\cdot}$ – 29)

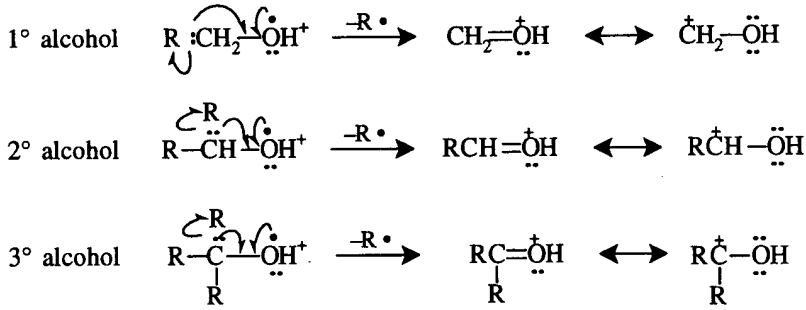
Since a 2° carbocation is more stable, the peak at $M^{+\cdot}$ - 29 is more intense.

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9.22 Both peaks arise from allylic fragmentations:



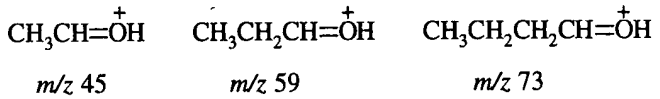
9.23 (a) Alcohols undergo rapid cleavage of a carbon-carbon bond next to oxygen because this leads to a resonance-stabilized cation.



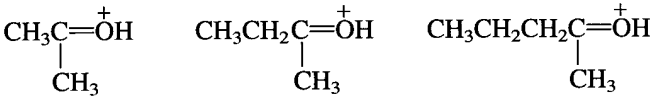
The cation obtained from a tertiary alcohol is the most stable (because of the electron-releasing R groups).

(b) Primary alcohols give a peak at *m/z* 31 due to $CH_2{=}\overset{+}{O}H$.

(c) Secondary alcohols give peaks at *m/z* 45, 59, 73, and so forth, because ions like the following are produced.

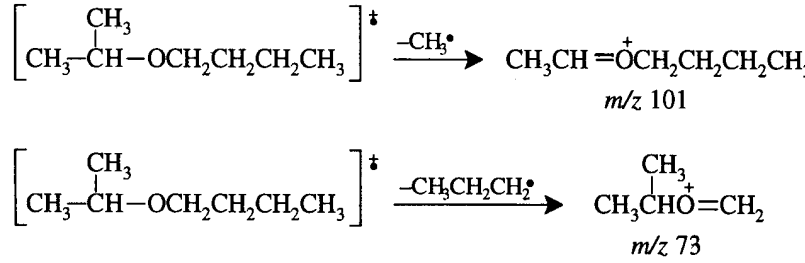


(d) Tertiary alcohols give peaks at *m/z* 59, 73, 87, and so forth, because ions like the following are produced.

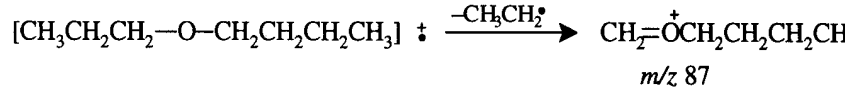


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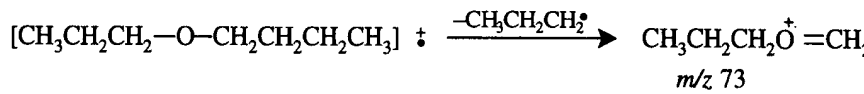
9.24 The spectrum given in Fig. 9.41 is that of butyl isopropyl ether. The main clues are the peaks at *m/z* 101 and *m/z* 73 due to the following fragmentations.



Butyl propyl ether (Fig. 9.42) has no peak at *m/z* 101 but has a peak at *m/z* 87 instead.

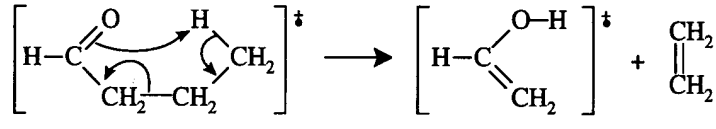


Butyl propyl ether also has a peak at *m/z* 73.

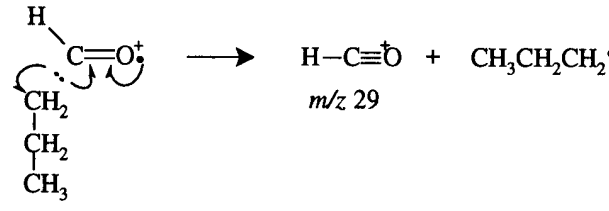


[Although the observation does not help us decide, it is interesting to notice that both spectra have intense peaks at *m/z* 43 and *m/z* 57 corresponding to propyl (or isopropyl) and butyl cations formed by carbon-oxygen bond cleavage.]

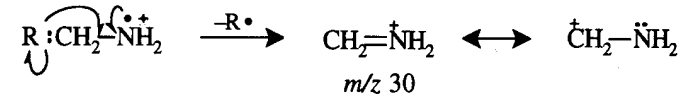
9.25 The compound is butanal. The peak at *m/z* 44 arises from a McLafferty rearrangement.



The peak at *m/z* 29 arises from a fragmentation producing an acylium ion.

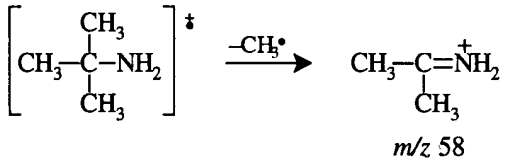


9.26 The ion, $CH_2{=}\overset{+}{N}H_2$, produced by the following fragmentation.



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9.27 Compound **A** is *tert*-butylamine. Our first clue is the molecular ion at *m/z* 73 (an odd-numbered mass unit) indicating the presence of an odd number of nitrogen atoms. The base peak at *m/z* 58 is our second important clue. It arises from the following fragmentation.



The ^{1}H NMR spectrum confirms the structure

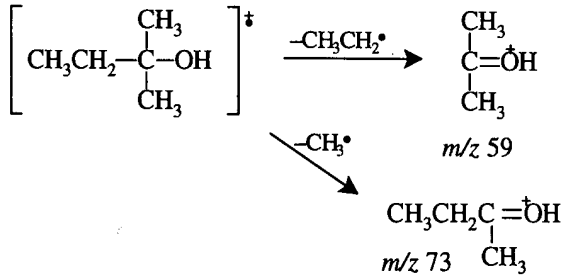
$$\overset{(a)}{(CH_3)_3}\overset{(b)}{C-NH_2}$$

(a) Singlet δ 1.2 (9H)
(b) Singlet δ 1.3 (2H)

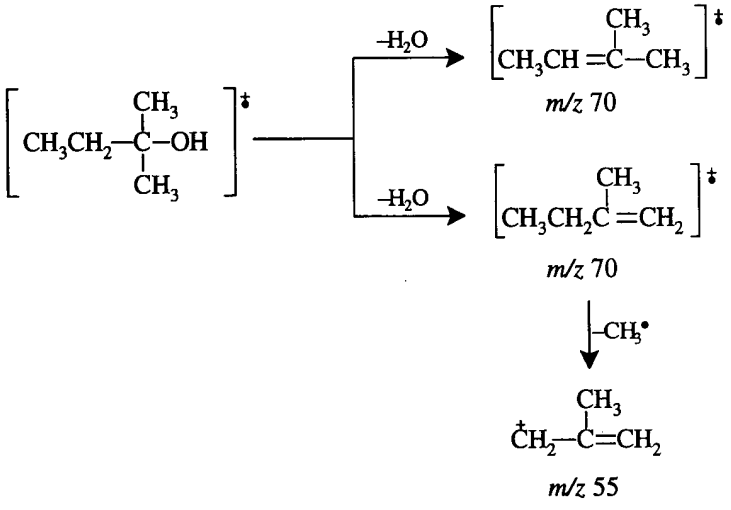
9.28 The compound is 2-methyl-2-butanol. Although the molecular ion is not discernible, we are given that it is at *m/z* 88. This information gives us the molecular weight of **B** and rules out the possibility of a structure with an odd number of nitrogen atoms.

The IR absorption (3200–3550 cm^{-1}) suggests the presence of an —OH group.

Two important peaks in the mass spectrum are the intense peaks at *m/z* 59 and *m/z* 73. These peaks correspond to fragmentation reactions that produce resonance-stabilized oxonium ions and strongly suggest that we have a tertiary alcohol [see Problem 9.23, part (d)].

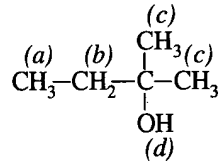


The peak at *m/z* 70 corresponds to the loss of a molecule of water from the molecular ion, and the peak at *m/z* 55 probably arises from a subsequent allylic cleavage.



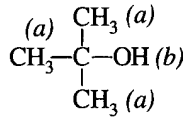
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The ^1H NMR spectrum of **B** confirms that it is 2-methyl-2-butanol.



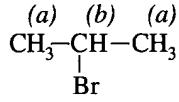
(a) Triplet, δ 0.9 (3H)
(b) Quartet, δ 1.6 (2H)
(c) and *(d)* Overlapping singlets, δ 1.1 (7H)

9.29 (a)



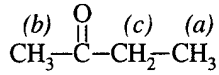
(a) Singlet, δ 1.28 (9H)
(b) Singlet, δ 1.35 (1H)

(b)



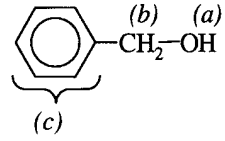
(a) Doublet, δ 1.71 (6H)
(b) Septet, δ 4.32 (1H)

(c)



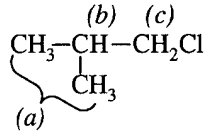
(a) Triplet, δ 1.05 (3H) C=O, 1720 cm^{-1}
(b) Singlet, δ 2.13 (3H)
(c) Quartet, δ 2.47 (2H)

(d)



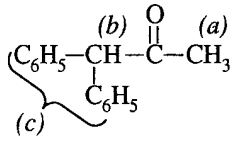
(a) Singlet, δ 2.43 (1H) O–H, 3200-3550 cm^{-1}
(b) Singlet, δ 4.58 (2H)
(c) Multiplet, δ 7.28 (5H)

(e)



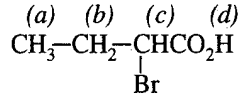
(a) Doublet, δ 1.04 (6H)
(b) Multiplet, δ 1.95 (1H)
(c) Doublet, δ 3.35 (2H)

(f)



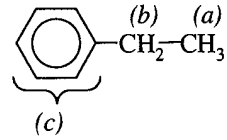
(a) Singlet, δ 2.20 (3H) C=O, near 1720 cm^{-1}
(b) Singlet, δ 5.08 (1H)
(c) Multiplet, δ 7.25 (10H)

(g)



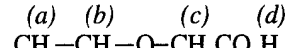
(a) Triplet, δ 1.08 (3H) C=O (acid) 1715 cm^{-1}
(b) Multiplet, δ 2.07 (2H) O–H, 2500-3000 cm^{-1}
(c) Triplet, δ 4.23 (1H)
(d) Singlet, δ 10.97 (1H)

(h)



(a) Triplet, δ 1.25 (3H)
(b) Quartet, δ 2.68 (2H)
(c) Multiplet, δ 7.23 (5H)

(i)



(a) Triplet, δ 1.27 (3H) C=O (acid) 1715 cm^{-1}
(b) Quartet, δ 3.66 (2H) O–H, 2500-3000 cm^{-1}
(c) Singlet, δ 4.13 (2H)
(d) Singlet, δ 10.95 (1H)

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(j) $CH_3-\underset{\displaystyle NO_2}{\overset{\displaystyle (b)}{CH}}-\overset{\displaystyle (a)}{CH_3}$

(a) Doublet, δ 1.55 (6H)
(b) Septet, δ 4.67 (1H)

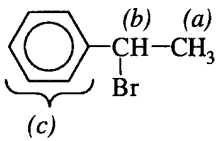
(k) $CH_3O-CH_2CH_2-OCH_3$ (a) (b) (b) (a)

(a) Singlet, δ 3.25 (6H)
(b) Singlet, δ 3.45 (4H)

(l) $CH_3-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-\underset{\displaystyle CH_3}{\overset{\displaystyle (c)}{CH}}-CH_3$ (b) (a)

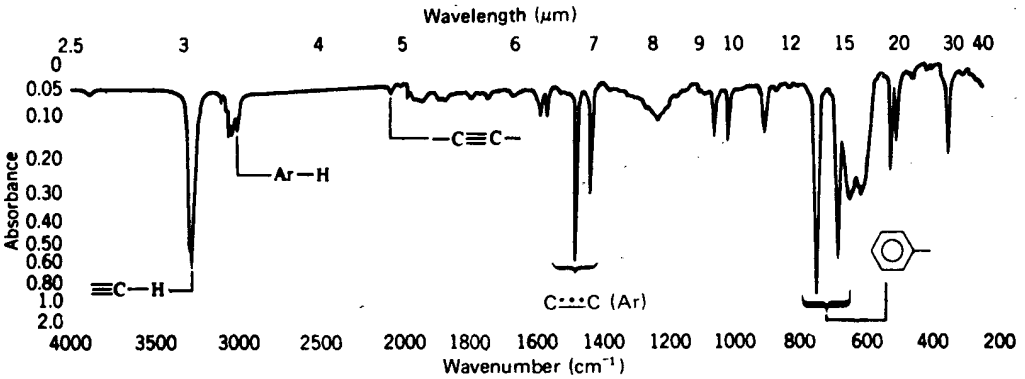
(a) Doublet, δ 1.10 (6H)
(b) Singlet, δ 2.10 (3H)
(c) Septet, δ 2.50 (1H)

C=O, near 1720 cm^{-1}

(m) 

(a) Doublet, δ 2.00 (3H)
(b) Quartet, δ 5.15 (1H)
(c) Multiplet, δ 7.35 (5H)

9.30 Compound **E** is phenylacetylene, $C_6H_5C{\equiv}CH$. We can make the following assignments in the IR spectrum:



The IR spectrum of compound **E** (Problem 9.30). (Spectrum courtesy of Sadtler Research Laboratories Inc., Philadelphia.)

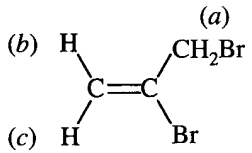
9.31 Compound **G** is 2-bromobutane. Assignments are as follows:

$CH_3-CH_2-\underset{\displaystyle Br}{\overset{\displaystyle (d)}{CH}}-\overset{\displaystyle (c)}{CH_3}$ (a) (b)

(a) triplet δ 1.05
(b) multiplet δ 1.82
(c) doublet δ 1.7
(d) multiplet δ 4.1

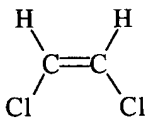
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Compound **H** is 2,3-dibromopropene. Assignments are as follows:



(*a*) δ 4.2
(*b*) δ 6.05
(*c*) δ 5.64

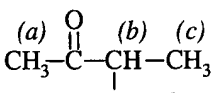
9.32 Compound **J** is *cis*-1,2-dichloroethene.



We can make the following IR assignments:

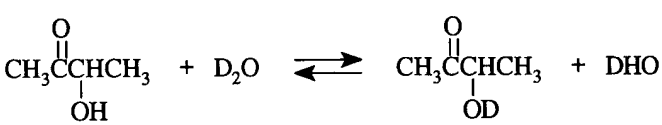
3125 cm^{-1}, alkene C—H stretching
1625 cm^{-1}, C=C stretching
695 cm^{-1}, out-of-plane bending of cis double bond

9.33 (a) Compound **K** is,



(*a*) Singlet, δ 2.15 C=O, 1720 cm^{-1}
(*b*) Quartet, δ 4.25
(*c*) Doublet, δ 1.35
(*d*) Singlet, δ 3.75

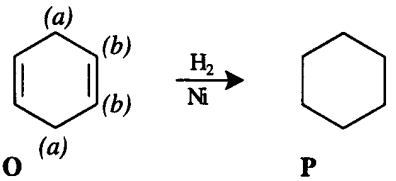
(b) When the compound is dissolved in D_2O, the —OH proton (*d*) is replaced by a deuteron, and thus the ^1H NMR absorption peak disappears.



***9.34** Run the spectrum with the spectrometer operating at a different magnetic field strength (i.e., at 30 or at 100 MHz). If the peaks are two singlets the distance between them—*when measured in hertz*—will change because chemical shifts *expressed in hertz* are proportional to the strength of the applied field (Section 9.6). If, however, the two peaks represent a doublet, then the distance that separates them, expressed in hertz, will not change because this distance represents the magnitude of the coupling constant and coupling constants are independent of the applied magnetic field (Section 9.8).

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9.35 Compound **O** is 1,4-cyclohexadiene and **P** is cyclohexane.

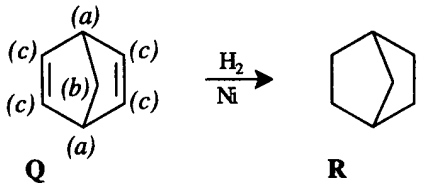


O **P**

(a) δ 26.0
(b) δ 124.5

***9.36** The molecular formula of **Q** (C_7H_8) indicates an index of hydrogen deficiency (Section 7.8) of four. The hydrogenation experiment suggests that **Q** contains two double bonds (or one triple bond). Compound **Q,** therefore, must contain two rings.

Bicyclo[2.2.1]hepta-2,5-diene. The following reasoning shows one way to arrive at this conclusion: There is only one signal (δ 143) in the region for a doubly bonded carbon. This fact indicates that the doubly bonded carbon atoms are all equivalent. That the signal at δ 143 is a CH group in the DEPT spectra indicates that each of the doubly bonded carbon atoms bears one hydrogen atom. Information from the DEPT spectra tells us that the signal at δ 75 is a $—CH_2—$ group and the signal at δ 50 is a $>C—H$ group. The molecular formula tells us that the compound must contain two $>C—H$ groups, and since only one signal occurs in the ^{13}C spectrum, these $>C—H$ groups must be equivalent. Putting this all together, we get the following:

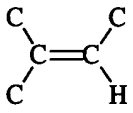


Q **R**

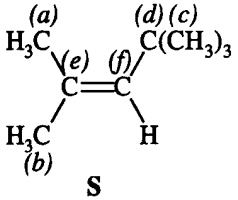
(a) δ 50
(b) δ 75
(c) δ 143

***9.37** That S decolorizes bromine indicates that it is unsaturated. The molecular formula of **S** allows us to calculate an index of hydrogen deficiency equal to 1. Therefore, we can conclude that **S** has one double bond.

The ^{13}C spectrum shows the doubly bonded carbon atoms at δ 130 and δ 135. In the DEPT spectra, one of these signals (δ 130) is a carbon that bears no hydrogen atoms; the other (δ 135) is a carbon that bears one hydrogen atom. We can now arrive at the following partial structure.



The three most upfield signals (δ 19, δ 28, and δ 31) all arise from methyl groups. The signal at δ 32 is a carbon atom with no hydrogen atoms. Putting these facts together allows us to arrive at the following structure.

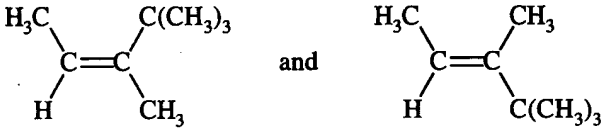


S

(a) δ 19
(b) δ 28
(c) δ 31
(d) δ 32
(e) δ 130
(f) δ 135

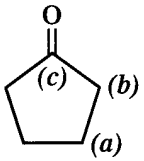
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Although the structure just given is the actual compound, other reasonable structures that one might be led to are



9.38 The IR absorption band at 1745 cm^{-1} indicates the presence of a $\rangle C{=}O$ group in a five-member ring, and the signal at δ 218.2 can be assigned to the carbon of the carbonyl group.

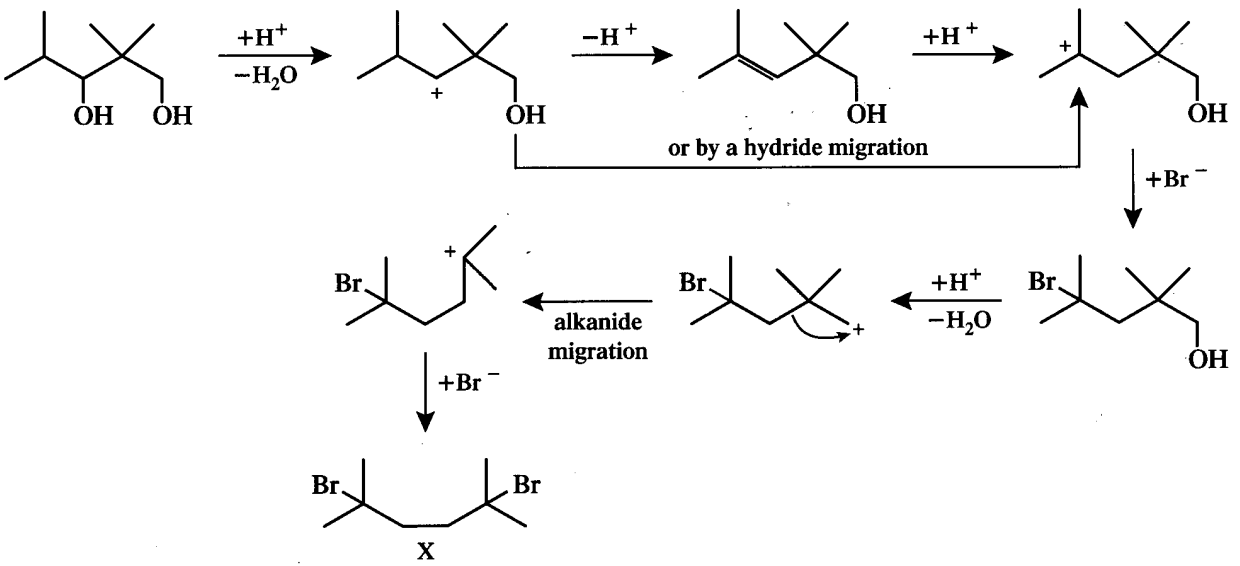
There are only two other signals in the ^{13}C spectrum; the DEPT spectra suggest two equivalent sets of two $-CH_2-$ groups each. Putting these facts together, we arrive at cyclopentanone as the structure for **T.**



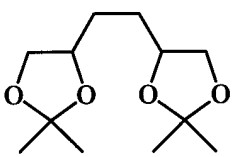
T

(a) δ 23.5
(b) δ 38.0
(c) δ 218.2

***9.39**



***9.40**



Y

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10 RADICAL REACTIONS

SOLUTIONS TO PROBLEMS

10.1 (a) $\underset{(DH^\circ = 435)}{H{-}H} + \underset{(DH^\circ = 159)}{F{-}F} \longrightarrow \underset{2(DH^\circ = 569)}{2\,H{-}F}$

$+594$ kJ mol^{-1} is required for bond cleavage

-1138 kJ mol^{-1} is evolved in bond formation

$$\Delta H^\circ = +594 - 1138 = -544 \text{ kJ mol}^{-1}$$

(b) $\underset{(DH^\circ = 435)}{CH_3{-}H} + \underset{(DH^\circ = 159)}{F{-}F} \longrightarrow \underset{(DH^\circ = 452)}{CH_3{-}F} + \underset{(DH^\circ = 569)}{H{-}F}$

$+594$ kJ mol^{-1} is required for bond cleavage

-1021 kJ mol^{-1} is evolved in bond formation

$$\Delta H^\circ = +594 - 1021 = -427 \text{ kJ mol}^{-1}$$

(c) $\underset{(DH^\circ = 435)}{CH_3{-}H} + \underset{(DH^\circ = 243)}{Cl{-}Cl} \longrightarrow \underset{(DH^\circ = 349)}{CH_3{-}Cl} + \underset{(DH^\circ = 431)}{H{-}Cl}$

$+678$ kJ mol^{-1} is required for bond cleavage

-780 kJ mol^{-1} is evolved in bond formation

$$\Delta H^\circ = +678 - 780 = -102 \text{ kJ mol}^{-1}$$

(d) $\underset{(DH^\circ = 435)}{CH_3{-}H} + \underset{(DH^\circ = 192)}{Br{-}Br} \longrightarrow \underset{(DH^\circ = 293)}{CH_3{-}Br} + \underset{(DH^\circ = 366)}{H{-}Br}$

$+627$ kJ mol^{-1} is required for bond cleavage

-659 kJ mol^{-1} is evolved in bond formation

$$\Delta H^\circ = +627 - 659 = -32 \text{ kJ mol}^{-1}$$

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(e) $CH_3—H$ ($DH° = 435$) + $I—I$ ($DH° = 151$) ⟶ $CH_3—I$ ($DH° = 234$) + $H—I$ ($DH° = 297$)

$+586$ kJ mol^{-1} is required for bond cleavage

-531 kJ mol^{-1} is evolved in bond formation

$$\Delta H° = +586 - 531$$
$$= +55 \text{ kJ mol}^{-1}$$

(f) $CH_3CH_2—H$ ($DH° = 410$) + $Cl—Cl$ ($DH° = 243$) ⟶ $CH_3CH_2—Cl$ ($DH° = 341$) + $H—Cl$ ($DH° = 431$)

$+653$ kJ mol^{-1} is required for bond cleavage

-772 kJ mol^{-1} is evolved in bond formation

$$\Delta H° = +653 - 772$$
$$= -119 \text{ kJ mol}^{-1}$$

(g) $(CH_3)_2CH—H$ ($DH° = 395$) + $Cl—Cl$ ($DH° = 243$) ⟶ $(CH_3)_2CH—Cl$ ($DH° = 339$) + $H—Cl$ ($DH° = 431$)

$+638$ kJ mol^{-1} is required for bond cleavage

-770 kJ mol^{-1} is evolved in bond formation

$$\Delta H° = +638 - 770$$
$$= -132 \text{ kJ mol}^{-1}$$

(h) $(CH_3)_3C—H$ ($DH° = 381$) + $Cl—Cl$ ($DH° = 243$) ⟶ $(CH_3)_3C—Cl$ ($DH° = 328$) + $H—Cl$ ($DH° = 431$)

$+624$ kJ mol^{-1} is required for bond cleavage

-759 kJ mol^{-1} is evolved in bond formation

$$\Delta H° = +624 - 759$$
$$= -135 \text{ kJ mol}^{-1}$$

10.2 $CH_3CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\bullet$ > $CH_3CH_2\underset{\displaystyle CH_3}{\overset{|}{CH}}\bullet$ > $(CH_3)_2CHCH_2\bullet$ > $CH_3\bullet$

3° > 2° > 1° > **Methyl**

10.3 The compounds all have different boiling points. They could, therefore, be separated by careful fractional distillation. Or, because the compounds have different vapor pressures, they could easily be separated by gas chromatography. GC/MS (gas chromatography/mass spectrometry) could be used to separate the compounds as well as provide structural information from their mass spectra. Their mass spectra would show contributions from the naturally occurring ^{35}Cl and ^{37}Cl isotopes. The natural abundance of

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^{35}Cl is approximately 75% and that of ^{37}Cl is approximately 25%. Thus, for CH_3Cl, containing only one chlorine atom, there will be an $M^{+\cdot}$ peak and an $M^{+\cdot}$ +2 peak in roughly a 3:1 (0.75:0.25) ratio of intensities. For CH_2Cl_2 there will be $M^{+\cdot}$, $M^{+\cdot}$ +2, and $M^{+\cdot}$ +4 peaks in roughly a 9:6:1 ratio, respectively. [The probability of a molecular ion $M^{+\cdot}$ with both chlorine atoms as ^{35}Cl is (.75)(.75) = .56, the probability of an $M^{+\cdot}$ +2 ion from one ^{35}Cl and one ^{37}Cl is 2(.75)(.25) = .38, and the probability of an $M^{+\cdot}$ +4 ion peak from both chlorine atoms as ^{37}Cl is (.25)(.25) = 0.06; thus, their ratio is 9:6:1.] For $CHCl_3$ there will be $M^{+\cdot}$, $M^{+\cdot}$ +2, and $M^{+\cdot}$ +4, and $M^{+\cdot}$ +6 peaks in approximately a 27:27:9:1 ratio, respectively (based on a calculation by the same method). (This calculation does not take into account the contribution of ^{13}C, ^{2}H, and other isotopes, but these are much less abundant.)

10.4 A small amount of ethane is formed by the combination of two methyl radicals:

$$2CH_3\cdot \longrightarrow CH_3 : CH_3$$

This ethane then reacts with chlorine in a substitution reaction (see Section 10.6) to form chloroethane.

The significance of this observation is that it is evidence for the proposal that the combination of methyl radicals is one of the chain-terminating steps in the chlorination of methane.

10.5 The use of a large excess of chlorine allows all of the chlorinated methanes (CH_3Cl, CH_2Cl_2, and $CHCl_3$) to react with chlorine.

10.6 ***Chain Initiation***

Step 1 $\underset{(DH^\circ = 159)}{F{-}F} \longrightarrow 2\,F\cdot \quad \Delta H^\circ = +159\ \text{kJ mol}^{-1}$

Chain Propagation

Step 2 $\underset{(DH^\circ = 435)}{CH_3{-}H} + F\cdot \longrightarrow CH_3\cdot + \underset{(DH^\circ = 569)}{H{-}F} \quad \Delta H^\circ = -134\ \text{kJ mol}^{-1}$

Step 3 $CH_3\cdot + \underset{(DH^\circ = 159)}{F{-}F} \longrightarrow \underset{(DH^\circ = 452)}{CH_3{-}F} + F\cdot \quad \Delta H^\circ = -293\ \text{kJ mol}^{-1}$

Chain Termination

$$CH_3\cdot + F\cdot \longrightarrow \underset{(DH^\circ = 452)}{CH_3{-}F} \quad \Delta H^\circ = -452\ \text{kJ mol}^{-1}$$

$$CH_3\cdot + CH_3\cdot \longrightarrow \underset{(DH^\circ = 368)}{CH_3{-}CH_3} \quad \Delta H^\circ = -368\ \text{kJ mol}^{-1}$$

$$F\cdot + F\cdot \longrightarrow \underset{(DH^\circ = 159)}{F{-}F} \quad \Delta H^\circ = -159\ \text{kJ mol}^{-1}$$

10.7

$$CH_3{-}H + \cancel{F\cdot} \longrightarrow \cancel{CH_3\cdot} + H{-}F \quad \Delta H^\circ = -134\ \text{kJ mol}^{-1}$$

$$\cancel{CH_3\cdot} + F{-}F \longrightarrow CH_3{-}F + \cancel{F\cdot} \quad \Delta H^\circ = -293\ \text{kJ mol}^{-1}$$

$$\overline{CH_3{-}H + F{-}F \longrightarrow CH_3{-}F + H{-}F \quad \Delta H^\circ = -427\ \text{kJ mol}^{-1}}$$

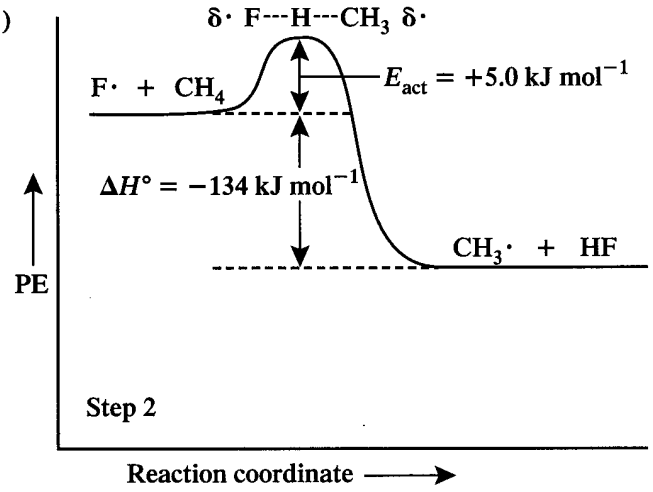
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10.8 (a) Reactions (3), (5), and (6) should have $E_{act} = 0$ because these are gas-phase reactions in which small radicals combine to form molecules.

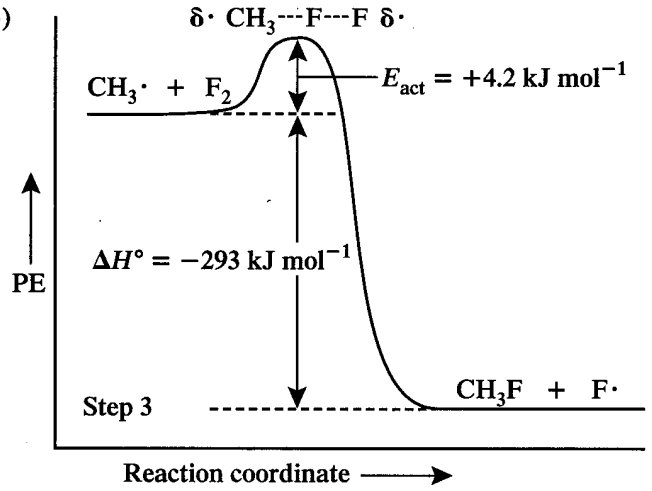
(b) Reactions (1), (2), and (4) should have $E_{act} > 0$ because in them covalent bonds are broken.

(c) Reactions (1) and (2) should have $E_{act} = \Delta H°$ because in them bonds are broken homolytically but no bonds are formed.

10.9 (a)

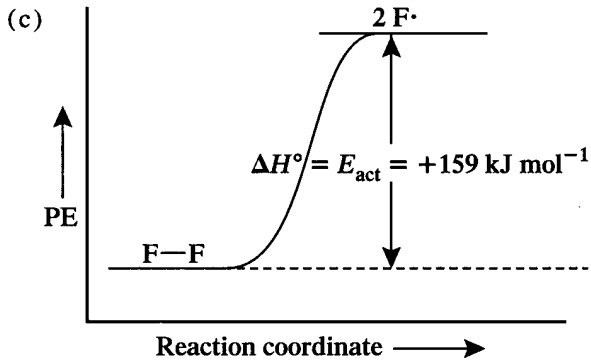


(b)

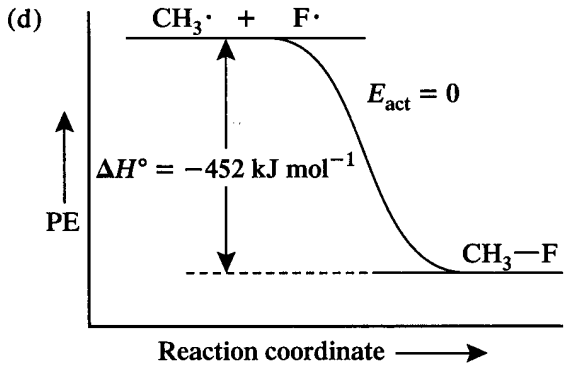


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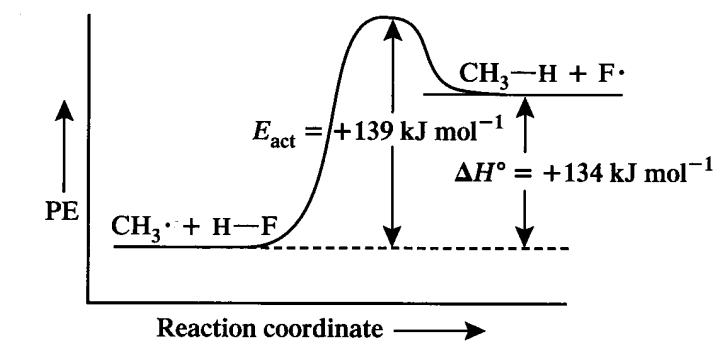
(c)



(d)



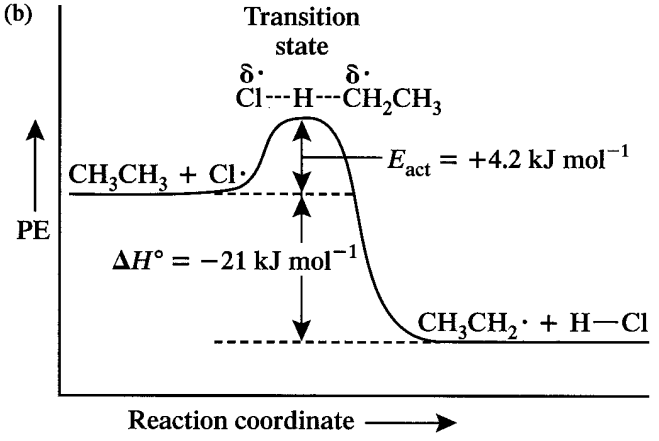
(e) Notice that this is the reverse of Step (2) in part (a)



10.10 (a) $CH_3CH_2—H + Cl\cdot \longrightarrow CH_3CH_2\cdot + H—Cl$
($DH° = 410$) ($DH° = 431$)

$\Delta H° = -431 + 410 = -21$ kJ mol^{-1}

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(c) The hydrogen abstraction step for ethane,

$$CH_3CH_2{-}H + Cl\bullet \longrightarrow CH_3CH_2\bullet + HCl \quad (E_{act} = 4.2 \text{ kJ mol}^{-1})$$

has a much lower energy of activation than the corresponding step for methane:

$$CH_3{-}H + Cl\bullet \longrightarrow CH_3\bullet + HCl \quad (E_{act} = 15.9 \text{ kJ mol}^{-1})$$

Therefore, ethyl radicals form much more rapidly in the mixture than methyl radicals, and this leads to the more rapid formation of ethyl chloride.

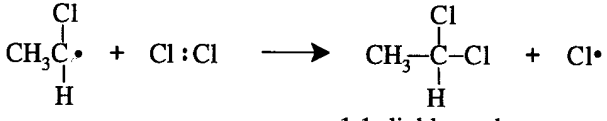
10.11

$$Cl_2 \xrightarrow[\text{or heat}]{h\nu} 2\,Cl\cdot$$

Step 2a



Step 3a



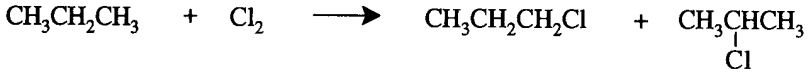
1,1-dichloroethane

Step 2b $Cl\bullet + H{-}CH_2CH_2Cl \longrightarrow H{:}Cl + \bullet CH_2CH_2Cl$

Step 3b $\bullet CH_2CH_2Cl + Cl{:}Cl \longrightarrow ClCH_2CH_2Cl + Cl\bullet$

1,2-dichloroethane

10.12 (a) There is a total of eight hydrogen atoms in propane. There are six equivalent 1° hydrogen atoms, replacement of any one of which leads to propyl chloride, and there are two equivalent 2° hydrogen atoms, replacement of any one of which leads to isopropyl chloride.



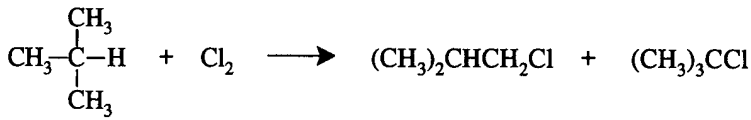
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If all the hydrogen atoms were equally reactive, we would expect to obtain 75% propyl chloride and 25% isopropyl chloride:

$$\%\ \text{Propyl chloride} = \tfrac{6}{8} \times 100 = 75\%$$

$$\%\ \text{Isopropyl chloride} = \tfrac{2}{8} \times 100 = 25\%$$

(b) Reasoning in the same way as in part (a), we would expect 90% isobutyl chloride and 10% *tert*-butyl chloride, if the hydrogen atoms were equally reactive.



$$\%\ \text{Isobutyl chloride} = \tfrac{9}{10} \times 100 = 90\%$$

$$\%\ \textit{tert}\text{-Butyl chloride} = \tfrac{1}{10} \times 100 = 10\%$$

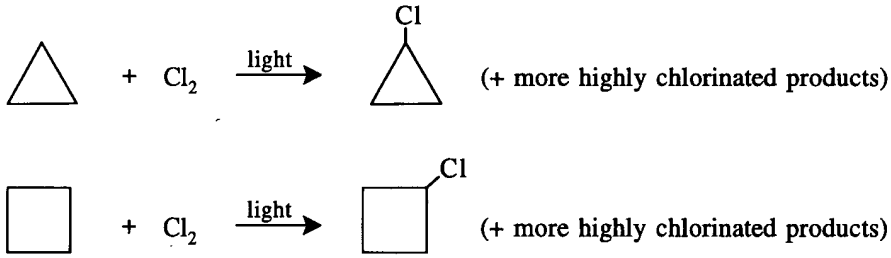
(c) In the case of propane (see Section 10.6), we actually get more than twice as much isopropyl chloride (55%) than we would expect if the 1° and 2° hydrogen atoms were equally reactive (25%). Clearly, then, 2° hydrogen atoms are more than twice as reactive as 1° hydrogen atoms.

In the case of isobutane, we get almost four times as much *tert*-butyl chloride (37%) as we would get (10%) if the 1° and 3° hydrogen atoms were equally reactive.

The order of reactivity of the hydrogens then must be

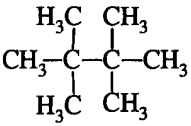
$$3° > 2° > 1°$$

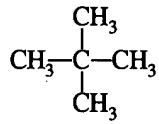
10.13 The hydrogen atoms of these molecules are all equivalent. Replacing any one of them yields the same product.



We can minimize the amounts of more highly chlorinated products formed by using a large excess of the cyclopropane or cyclobutane. (And we can recover the unreacted cyclopropane or cyclobutane after the reaction is over.)

10.14 (a) 

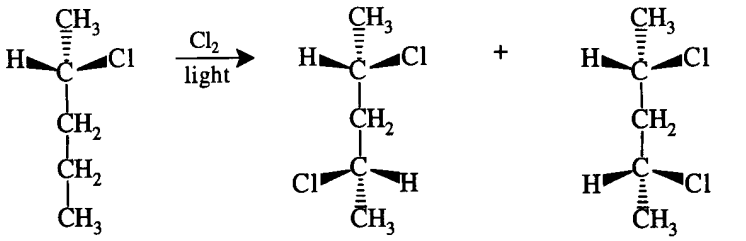
(b) 

(c) 

10.15 At lower temperatures, isomer distribution accurately reflects the inherent reactivities of the hydrogens of the alkanes. As the temperature is raised, chlorine atoms become more reactive, and hence less discriminating. If the temperature is high enough, hydrogens are replaced by chlorine on a purely statistical basis.

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10.16 (a)



(2*S*,4*S*)-2,4-Dichloropentane

(2*R*,4*S*)-2,4-Dichloropentane

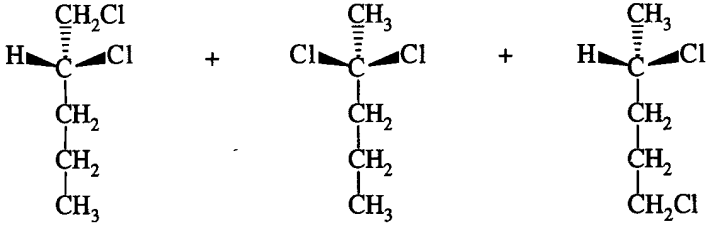
(b) They are diastereomers. (They are stereoisomers, but they are not mirror images of each other.)

(c) No, (2*R*,4*S*)-2,4-dichloropentane is achiral because it is a meso compound. (It has a plane of symmetry passing through C3.)

(d) No, the achiral meso compound would not be optically active.

(e) Yes, by fractional distillation or by gas chromatography. (Diastereomers have different physical properties. Therefore, the two isomers would have different vapor pressures.)

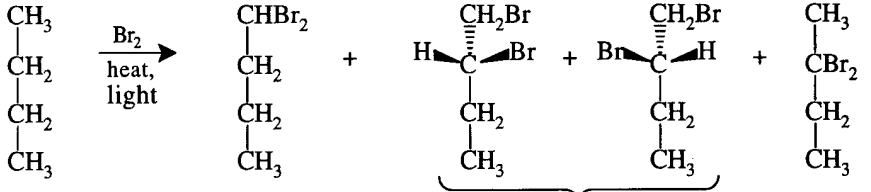
(f and g) In addition to the (2*S*,4*S*)-2,4-dichloropentane and (2*R*,4*S*)-2,4-dichloropentane isomers described previously, we would also get (2*S*,3*S*)-2,3-dichloropentane, (2*S*,3*R*)-2,3-dichloropentane and the following:



(optically active) (optically inactive) (optically active)

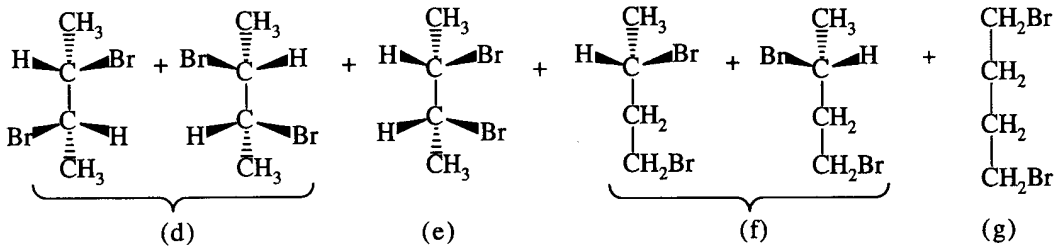
10.17 (a) Seven (see below)

(b)



(a) (b) (c)

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(c) None of the fractions would show optical activity. Fractions (b), (d), and (f) are racemic forms; all others contain achiral molecules.

(d) Ions likely to be formed are the molecular ion ($M^{+\cdot}$), $M^{+\cdot}$-Br, and others. The $M^{+\cdot}$ peak would be accompanied by $M^{+\cdot}+2$ and $M^{+\cdot}+4$ peaks due to the isotopes of bromine. The natural abundance of ^{79}Br is 50.5% and the natural abundance of ^{81}Br is 49.5%. Thus, the $M^{+\cdot}$ peak (where both bromines are ^{79}Br) has probability (.505)(.505) = .255, the $M^{+\cdot}+2$ peak (one ^{79}Br and one ^{81}Br) has probability 2(.495)(.505) = .500, and the probability of the $M^{+\cdot}+4$ peak (where both bromine atoms are ^{81}Br) is (.495)(.495) = .245. Thus, the $M^{+\cdot}$, $M^{+\cdot}+2$, and $M^{+\cdot}+4$ peaks will have an intensity ratio of approximately 1:2:1, respectively. (This calculation does not take into account the contribution of ^{13}C, ^{2}H, and other isotopes.) The $M^{+\cdot}$-Br peak would also be accompanied by an $M^{+\cdot}$-Br+2 peak.

10.18 (a) No, the only fractions that would contain chiral molecules (as enantiomers) would be those containing 1-chloro-2-methylbutane and the one containing 2-chloro-3-methylbutane. These fractions would not show optical activity, however, because they would contain racemic forms of the enantiomers.

(b) Yes, the fractions containing 1-chloro-2-methylbutane and the one containing 2-chloro-3-methylbutane.

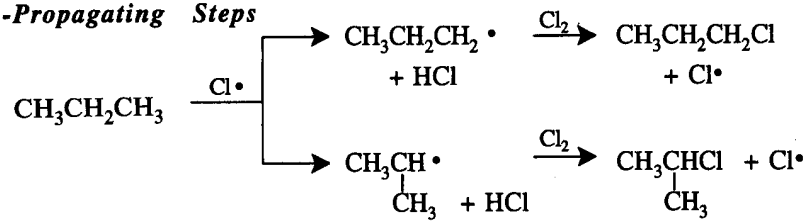
(c) Yes, each fraction from the distillation could be identified on the basis of ^{1}H NMR spectroscopy. The signals related to the carbons where the chlorine atom is bonded would be sufficient to distinguish them. The protons at C1 of 1-chloro-2-methyl butane would be a doublet due to splitting from the single hydrogen at C2. There would be no proton signal for C2 of 2-chloro-2-methylbutane since there are no hydrogens bonded at C2 in this compound; however, there would be a strong singlet for the six hydrogens of the geminal methyl groups. The protons at C2 of 2-chloro-3-methylbutane would approximately be a pentet, due to combined splitting from the three hydrogens at C1 and the single hydrogen at C3. The protons at C1 of 1-chloro-3-methylbutane would be a triplet due to splitting by the two hydrogens at C2.

10.19 ***Chain-Initiating Step***

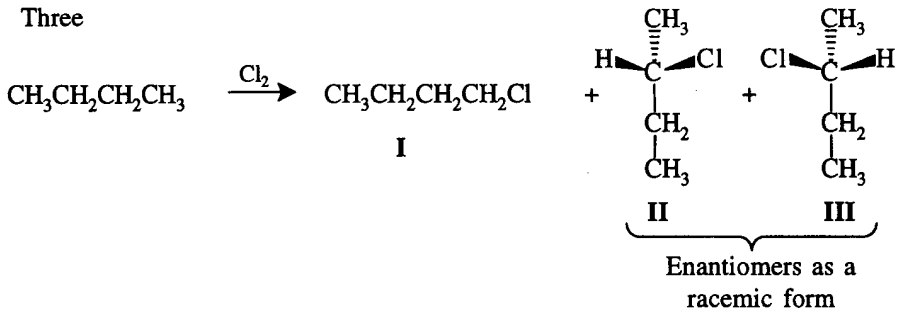
$$Cl_2 \xrightarrow[\text{light}]{\text{heat},h\nu} 2\ Cl^{\bullet}$$

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Chain-Propagating Steps



***10.20** (a) Three



(b) Only two: one fraction containing I, and another fraction containing the enantiomers II and III as a racemic form. (The enantiomers, having the same boiling points, would distill in the same fraction.)

(c) Both of them.

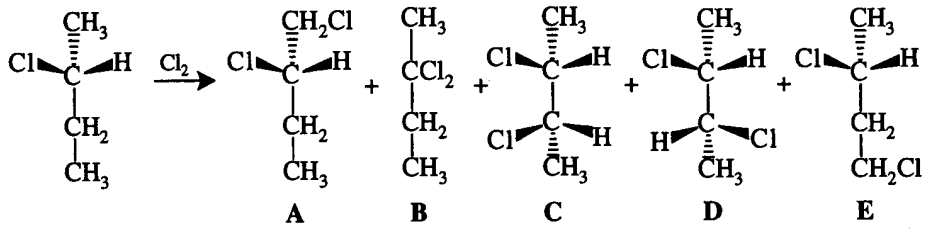
(d) The fraction containing the enantiomers.

(e) The ^1H spectrum for 1-chlorobutane would show a triplet at approximately δ3.6-3.8, whereas the hydrogens at C2 of 2-chlorobutane (either enantiomer) would approximately be a pentet at δ3.6-3.8. The DEPT spectra for 1-chlorobutane would have three positive signals corresponding to the carbons of the three CH_2 groups and one negative signal corresponding to the CH_3. The DEPT spectra for the 2-chlorobutane enantiomers would have only one positive signal corresponding to the single CH_2 carbon, and three negative signals corresponding to the two CH_3 groups and the CH carbon.

(f) Molecular ions from both 1-chlorobutane and the 2-chlorobutane enantiomers would be present (but probably of different intensities). $M^{+\cdot}$ +2 peaks would also be present. Both compounds would likely undergo C-Cl bond cleavage to yield $C_4H_9^+$ cations. The mass spectrum of 1-chlorobutane would probably show loss of a propyl radical by C-C bond cleavage adjacent to the chlorine, resulting in an m/z 49 peak for CH_2Cl^+ (and m/z 51 from ^{37}Cl). Similar fragmentation in 2-chlorobutane would produce an m/z 63 peak for CH_3CHCl^+ (and m/z 65).

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10.21 (a) Five



(b) Five. None of the fractions would be a racemic form.

(c) The fractions containing **A, D,** and **E.** The fraction containing **B** and **C** would be optically inactive. (**B** contains no stereocenter and **C** is a meso compound.)

10.22 (a) Oxygen-oxygen bonds are especially weak, that is,

$$\text{HO—OH} \qquad DH° = 213 \text{ kJ mol}^{-1}$$
$$\text{CH}_3\text{CH}_2\text{O—OCH}_3 \qquad DH° = 184 \text{ kJ mol}^{-1}$$

This means that a peroxide will dissociate into radicals at a relatively low temperature.

$$\text{RO—OR} \xrightarrow{100\text{-}200°\text{C}} 2\ \text{RO}\bullet$$

Oxygen-hydrogen single bonds, on the other hand, are very strong. (For HO-H, $DH°$ = 498 kJ mol^{-1}.) This means that reactions like the following will be highly exothermic.

$$\text{RO}\bullet + \text{R—H} \longrightarrow \text{RO—H} + \text{R}\bullet$$

(b) *Step 1* $(\text{CH}_3)_3\text{CO—OC}(\text{CH}_3)_3 \xrightarrow{\text{heat}} 2\ (\text{CH}_3)_3\text{CO}\bullet$

Step 2 $(\text{CH}_3)_3\text{CO}\bullet + \text{R—H} \longrightarrow (\text{CH}_3)_3\text{COH} + \text{R}\bullet$ } Chain Initiation

Step 3 $\text{R}\bullet + \text{Cl—Cl} \longrightarrow \text{R—Cl} + \text{Cl}\bullet$

Step 4 $\text{Cl}\bullet + \text{R—H} \longrightarrow \text{H—Cl} + \text{R}\bullet$ } Chain Propagation

10.23 $\underset{(3°)}{\text{CH}_3\overset{\bullet}{\text{C}}\text{CH}_2\text{CH}_3} > \underset{(2°)}{\text{CH}_3\text{CH}\overset{\bullet}{\text{C}}\text{HCH}_3} > \underset{(1°)}{\text{CH}_3\text{CHCH}_2\text{CH}_2\bullet} \sim \underset{(1°)}{\text{CH}_3\text{CHCH}_2\text{CH}_3}$

10.24 (1) $\text{Cl}_2 \longrightarrow 2\ \text{Cl}\bullet \qquad \Delta H° = +243 \text{ kJ mol}^{-1}$

(2) $\text{Cl}\bullet + \text{CH}_4 \longrightarrow \text{CH}_3\text{Cl} + \text{H}\bullet \qquad \Delta H° = +85.8 \text{ kJ mol}^{-1}$

(3) $\text{H}\bullet + \text{Cl}_2 \longrightarrow \text{HCl} + \text{Cl}\bullet \qquad \Delta H° = -188 \text{ kJ mol}^{-1}$

This mechanism is highly unlikely to compete with one given in Section 10.4 because step (2) of this mechanism is highly endothermic ($\Delta H° = +85.8$ kJ mol^{-1}). This means that the energy of activation for this step, a chain-propagating step, will have to be larger than +85.8 kJ mol^{-1}. Notice in Section 10.5B that neither of the chain-propagating steps for the mechanism given in Section 10.4 has an energy of activation greater than +15.9

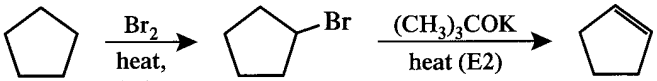
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kJ mol^{-1}. The alternative mechanism given in this problem, consequently, will proceed at a rate that is very much slower than the one given in Section 10.4 and will, for all practical purposes, not compete with it at all.

10.25 (a) $CH_3CH_3 \xrightarrow[\text{heat, light}]{Br_2} CH_3CH_2Br \xrightarrow[(S_N2)]{NaI} CH_3CH_2I$

(b) CH_3CH_2Br [from part (a)] $\xrightarrow[(S_N2)]{NaOH} CH_3CH_2OH \xrightarrow[(-H_2)]{Na} CH_3CH_2O^- Na^+$

$CH_3CH_2O^- Na^+ \xrightarrow{CH_3CH_2Br} CH_3CH_2OCH_2CH_3$

(c)  $\xrightarrow[\text{heat, light}]{Br_2}$ $\xrightarrow[\text{heat (E2)}]{(CH_3)_3COK}$

(d) $CH_3CH(CH_3)CH_2CH_3 \xrightarrow[\text{heat, light}]{Br_2} CH_3C(Br)(CH_3)CH_2CH_3 \xrightarrow[\text{EtOH, heat (E2)}]{NaOEt} CH_3C(CH_3)=CHCH_3$

$CH_3C(CH_3)=CHCH_3 \xrightarrow[\text{ROOR, heat, light}]{HBr} CH_3C(CH_3)(H)CH(Br)CH_3$ (by anti-Markovnikov addition)

(e) $CH_4 \xrightarrow[\text{heat, light}]{Br_2} CH_3Br$

$HC{\equiv}CH \xrightarrow[2)\ CH_3Br]{1)\ NaNH_2} HC{\equiv}C{-}CH_3 \xrightarrow[2)\ CH_3Br]{1)\ NaNH_2} CH_3{-}C{\equiv}C{-}CH_3$

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(f) $HC{\equiv}CH \xrightarrow[\text{2) } CH_3CH_2Br \text{ [from part (a)]}]{\text{1) } NaNH_2} CH_3CH_2C{\equiv}CH \xrightarrow[\text{or } H_2\text{, Lindlar's catalyst}]{H_2,\ Ni_2B}$

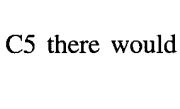
$CH_3CH_2CH{=}CH_2 \xrightarrow{HA,\ H_2O}$

$CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$

(g) $CH_3CH_2Br + Na^+\ {}^-N{=}\overset{+}{N}{=}N^- \xrightarrow[S_N2]{} CH_3CH_2{-}N{=}\overset{+}{N}{=}N^-$

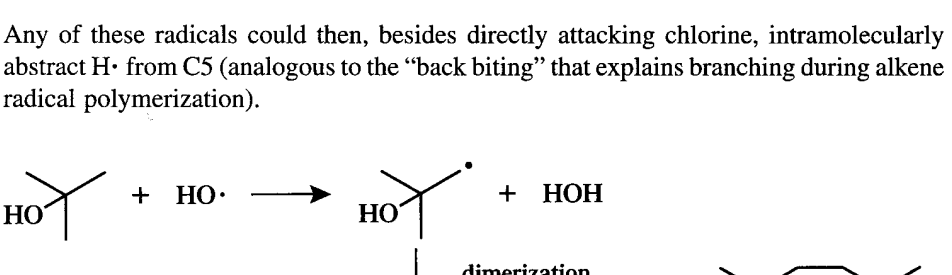
10.26 Chlorine atoms are electronegative and abstract hydrogens according to their "electron richness." The electronegative fluorine atom reduces electron density in proportion to its proximity to the different CH_2 groups. The CH_3 group is the least reactive site because the bond dissociation energy for a CH_3 group is greater than that for a CH_2 group.

***10.27** Besides direct H· abstraction from C5 there would be many H· abstractions from the three methyl groups, leading to:



Any of these radicals could then, besides directly attacking chlorine, intramolecularly abstract H· from C5 (analogous to the "back biting" that explains branching during alkene radical polymerization).

***10.28**



X

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Use the single-bond dissociation energies of Table 10.1:

Table 10.1 Single-bond homolytic dissociation energies DH° at 25°C

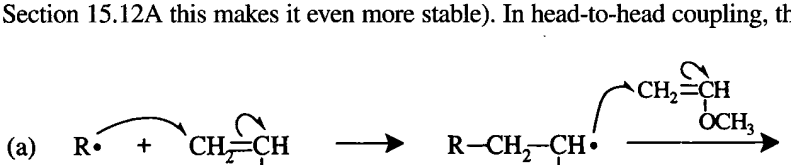
Compound	A : B ⟶ A· + B· kJ mol^{-1}	Compound	kJ mol^{-1}
H–H	435	$(CH_3)_2CH$–Br	285
D–D	444	$(CH_3)_2CH$–I	222
F–F	159	$(CH_3)_2CH$–OH	385
Cl–Cl	243	$(CH_3)_2CH$–OCH_3	337
Br–Br	192	$(CH_3)_2CHCH_2$–H	410
I–I	151	$(CH_3)_3C$–H	381
H–F	569	$(CH_3)_3C$–Cl	328
H–Cl	431	$(CH_3)_3C$–Br	264
H–Br	366	$(CH_3)_3C$–I	207
H–I	297	$(CH_3)_3C$–OH	379
CH_3–H	435	$(CH_3)_3C$–OCH_3	326
CH_3–F	452	$C_6H_5CH_2$–H	356
CH_3–Cl	349	CH_2=$CHCH_2$–H	356
CH_3–Br	293	CH_2=CH–H	452
CH_3–I	234	C_6H_5–H	460
CH_3–OH	383	HC≡C–H	523
CH_3–OCH_3	335	CH_3–CH_3	368
CH_3CH_2–H	410	CH_3CH_2–CH_3	356
CH_3CH_2–F	444	$CH_3CH_2CH_2$–CH_3	356
CH_3CH_2–Cl	341	CH_3CH_2–CH_2CH_3	343
CH_3CH_2–Br	289	$(CH_3)_2CH$–CH_3	351
CH_3CH_2–I	224	$(CH_3)_3C$–CH_3	335
CH_3CH_2–OH	383	HO–H	498
CH_3CH_2–OCH_3	335	HOO–H	377
$CH_3CH_2CH_2$–H	410	HO–OH	213
$CH_3CH_2CH_2$–F	444	$(CH_3)_3CO$—$OC(CH_3)_3$	157
$CH_3CH_2CH_2$–Cl	341		
$CH_3CH_2CH_2$–Br	289		
$CH_3CH_2CH_2$–I	224	C_6H_5CO—OCC_6H_5	139
$CH_3CH_2CH_2$–OH	383	CH_3CH_2O–OCH_3	184
$CH_3CH_2CH_2$–OCH_3	335	CH_3CH_2O–H	431
$(CH_3)_2CH$–H	395		
$(CH_3)_2CH$–F	439	CH_3C–H	364
$(CH_3)_2CH$–Cl	339		

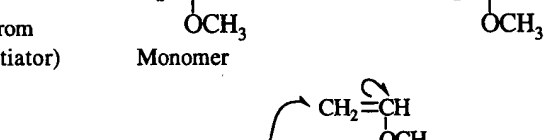
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A SPECIAL TOPIC
Chain-Growth Polymers

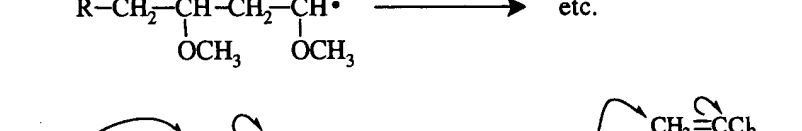
A.1 Head-to-tail polymerization leads to a more stable radical on the growing polymer chain. In head-to-tail coupling, the radical is 2° (actually 2° benzylic, and as we shall see in Section 15.12A this makes it even more stable). In head-to-head coupling, the radical is 1°.

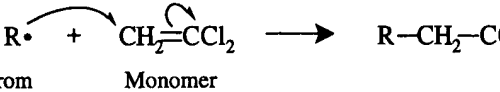
A.2 (a)



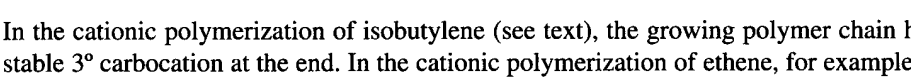


(b)

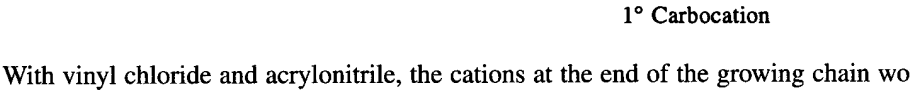


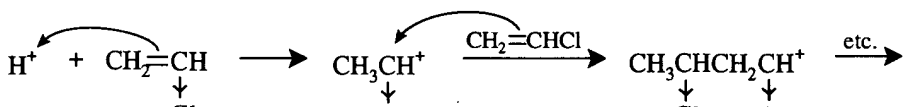


A.3 In the cationic polymerization of isobutylene (see text), the growing polymer chain has a stable 3° carbocation at the end. In the cationic polymerization of ethene, for example, the intermediates would be much less stable 1° cations.



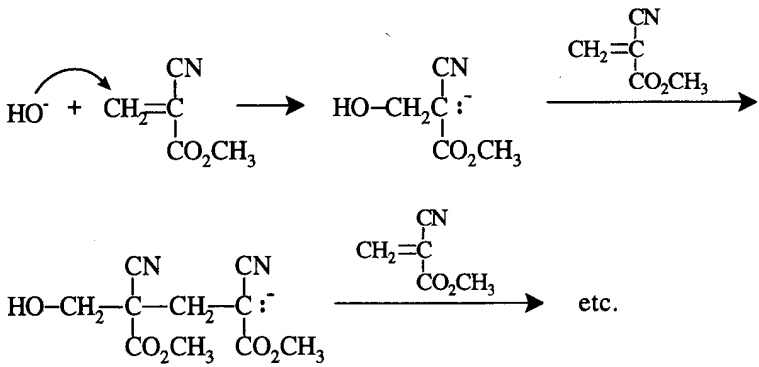
With vinyl chloride and acrylonitrile, the cations at the end of the growing chain would be destabilized by electron-withdrawing groups.



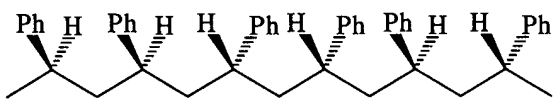


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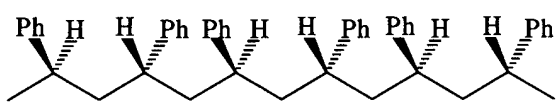
A.4



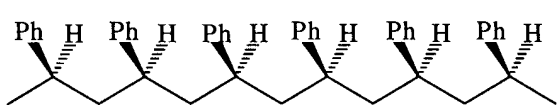
A.5 (a)



Atactic polystyrene
(Ph = C_6H_5)



Syndiotactic polystyrene
(Ph = C_6H_5)



Isotactic polystyrene
(Ph = C_6H_5)

(b) The solution of isotactic polystyrene.

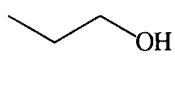
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11 ALCOHOLS AND ETHERS

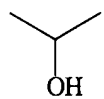
SOLUTIONS TO PROBLEMS

11.1 These names mix two systems of nomenclature (radicofunctional and substitutive; see Section 4.3F). The proper names are: isopropyl alcohol (radicofunctional) or 2-propanol (substitutive), and *tert*-butyl alcohol (radicofunctional) and 2-methyl-2-propanol (substitutive). Names with mixed systems of nomenclature should not be used.

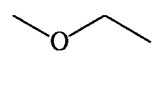
11.2 (a)



1-Propanol (Propyl alcohol)

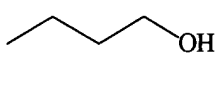


2-Propanol (Isopropyl alcohol)

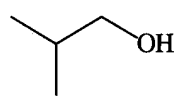


Methoxyethane (Ethyl methyl ether)

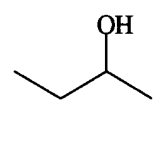
(b)



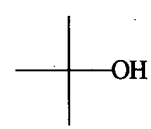
1-Butanol (Butyl alcohol)



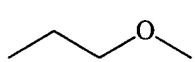
2-Methyl-1-propanol (Isobutyl alcohol)



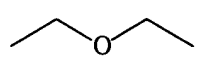
2-Butanol (*sec*-Butyl alcohol)



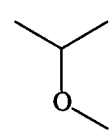
2-Methyl-2-propanol (*tert*-Butyl alcohol)



1-Methoxypropane (Methyl propyl ether)



Ethoxyethane (Diethyl ether)



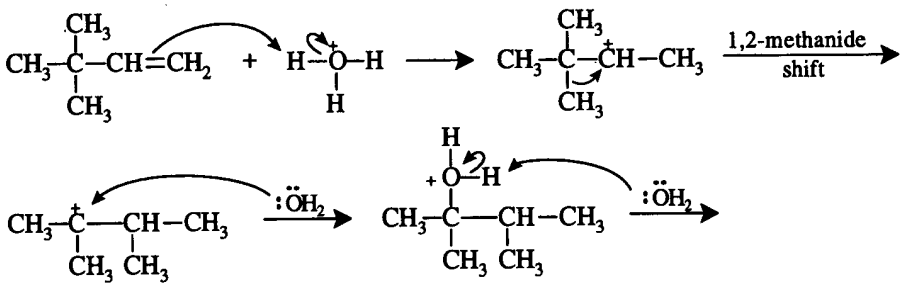
2-Methoxypropane (Isopropyl methyl ether)

11.3 The presence of two $-OH$ groups in each molecule of 1,2-propanediol and 1,3-propanediol allows their molecules to form more hydrogen bonds. Greater hydrogen-bond formation means that the molecules of 1,2-propanediol and 1,3-propanediol are more highly associated, and, consequently, their boiling points are higher.

11.4 (a) CH_3CH_2OH (b) $CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$ (c) $CH_3\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH$ (d) $CH_3\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}CH_2CH_3$

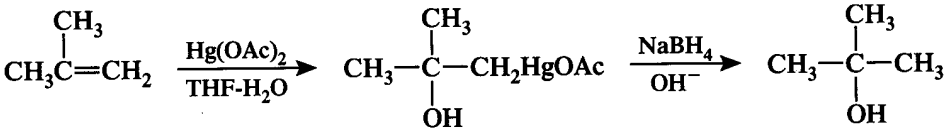
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11.5 A rearrangement takes place.

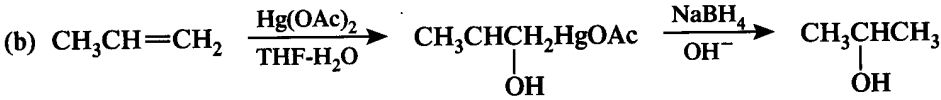


2,3-Dimethyl-2-butanol (major product)

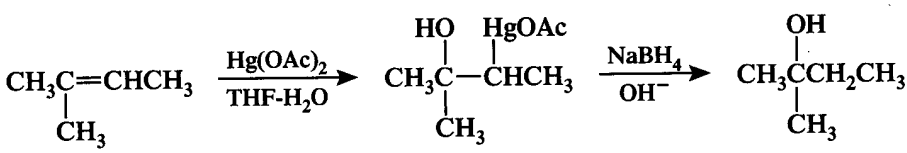
11.6 (a)



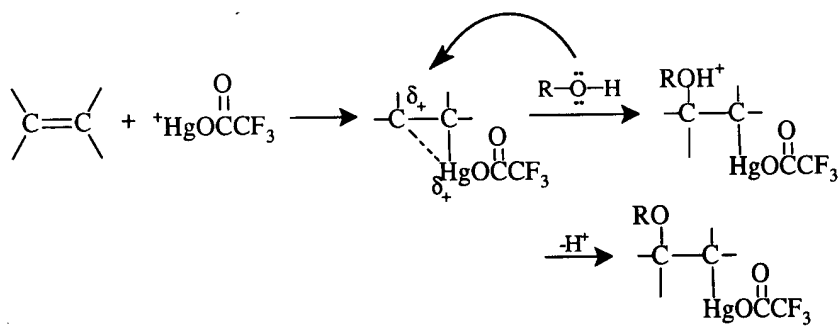
(b)



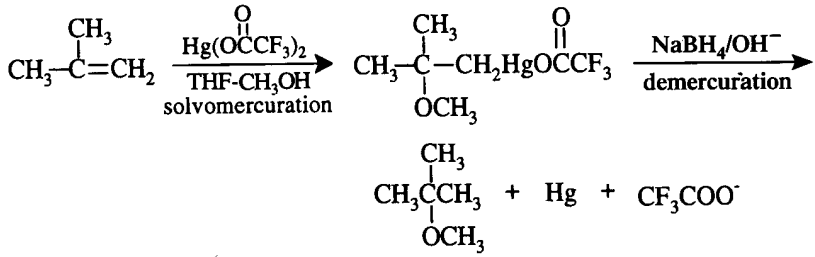
(c)



11.7 (a)



(b)

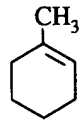
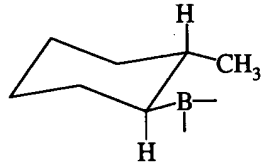


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11.8 (a) $3\ CH_3CH_2CH{=}CH_2 \xrightarrow{THF:\ BH_3} (CH_3CH_2CH_2CH_2)_3B$

(b) $3\ CH_3C(CH_3){=}CH_2 \xrightarrow{THF:\ BH_3} (CH_3CH(CH_3)CH_2)_3B$

(c) $3\ CH_3CH{=}CHCH_3 \xrightarrow{THF:\ BH_3} (CH_3CH_2CH(CH_3))_3B$

(d) 3  $\xrightarrow[\text{syn addition}]{THF:\ BH_3}$  + enantiomer

anti Markovnikov

11.9 $CH_3C(CH_3){=}CHCH_3 \xrightarrow{THF:\ BH_3} [CH_3CH(CH_3)CH(CH_3)]_2BH$

Disiamylborane

11.10 (a) $CH_3CH_2CH_2CH{=}CH_2 \xrightarrow[(2)\ H_2O_2,\ OH]{(1)\ THF:BH_3} CH_3CH_2CH_2CH_2CH_2OH$

1-Pentene

(b) $CH_3CH_2CH_2C(CH_3){=}CH_2 \xrightarrow[(2)\ H_2O_2,\ OH]{(1)\ THF:BH_3} CH_3CH_2CH_2CH(CH_3)CH_2OH$

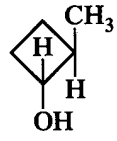
2-Methyl-1-pentene

(c) $CH_3CH_2C(CH_3){=}CHCH_3 \xrightarrow[(2)\ H_2O_2,\ OH]{(1)\ THF:BH_3} CH_3CH_2CH(OH)CH(CH_3)CH_3$

3-Methyl-2-pentene

(d) $CH_3C(CH_3){=}CHCH_2CH_3 \xrightarrow[(2)\ H_2O_2,\ OH]{(1)\ THF:BH_3} CH_3CH(OH)CH(CH_3)CH_2CH_3$

2-Methyl-2-pentene

(e)  $\xrightarrow[(2)\ H_2O_2,\ OH]{(1)\ THF:BH_3}$  + enantiomer

1-Methylcyclobutene

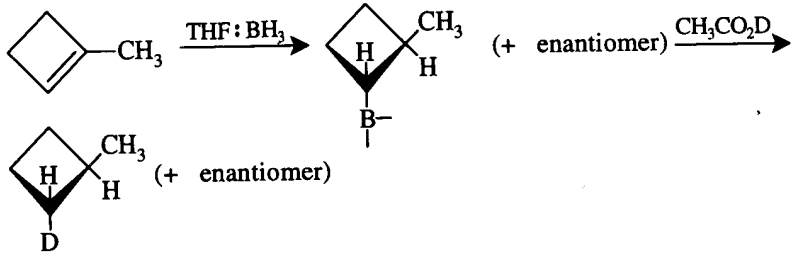
11.11 (a) $3\ CH_3CH(CH_3)CH{=}CH_2 \xrightarrow{THF:BH_3} [CH_3CH(CH_3)CH_2CH_2]_3B \xrightarrow{CH_3CO_2D}$

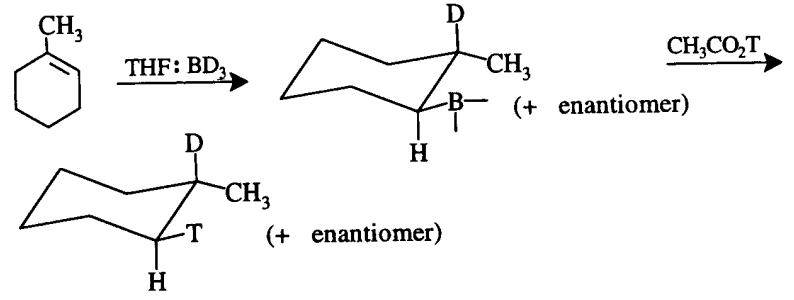
$3\ CH_3CH(CH_3)CH_2CH_2D$

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(b) $CH_3C(CH_3)=CHCH_3 \xrightarrow{THF:BH_3} CH_3CH(CH_3)-CH(-B-)-CH_3 \xrightarrow{CH_3CO_2D}$

$CH_3CH(CH_3)CHDCH_3$

(c) 

(d) 

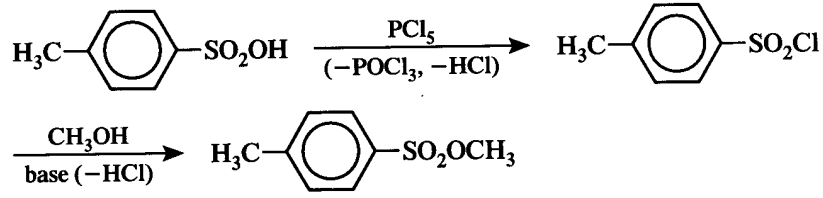
11.12 (a) CH_3CH_2OH (Stronger acid) + $NaNH_2$ (Stronger base) $\longrightarrow$ CH_3CH_2ONa (Weaker base) + NH_3 (Weaker acid)

(b) $CH_3CH_2OH + HC{\equiv}CNa \longrightarrow CH_3CH_2ONa + HC{\equiv}CH$

(c) CH_3CH_2OH (Weaker acid) + $NaOAc$ (Weaker base) $\not\longrightarrow$ CH_3CH_2ONa (Stronger base) + $HOAc$ (Stronger acid)

11.13 Use an alcohol containing labeled oxygen. If all of the label appears in the sulfonate ester, then one can conclude that the alcohol C–O bond does not break during the reaction:

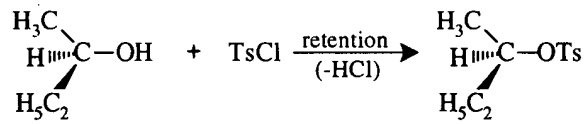
$$R-{}^{18}O-H + R'-SO_2Cl \xrightarrow[(-HCl)]{\text{base}} R-{}^{18}O-SO_2-R'$$

11.14 (a) 

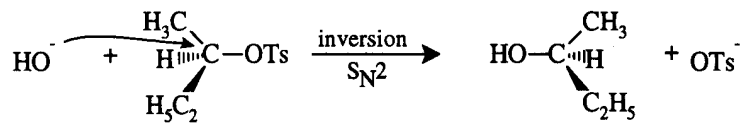
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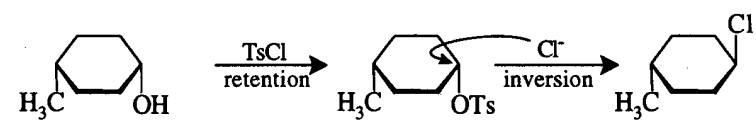
(b) $CH_3SO_2OH \xrightarrow[(-POCl_3,\ -HCl)]{PCl_5} CH_3SO_2Cl \xrightarrow[\text{base } (-HCl)]{(CH_3)_2CHCH_2OH} CH_3SO_2OCH_2CH(CH_3)_2$

(c) $CH_3SO_2Cl \xrightarrow[\text{base (-HCl)}]{(CH_3)_3COH} CH_3SO_2OC(CH_3)_3$

11.15 (a) 

(*R*)-2-Butanol

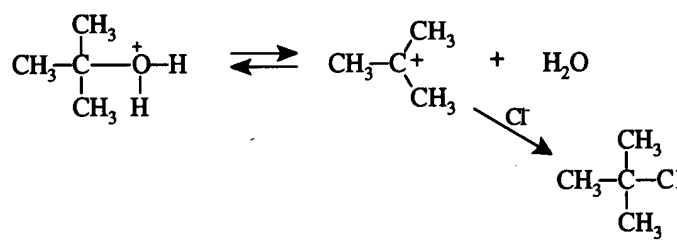
(b) 

(c) 

cis-4-Methyl-cyclohexanol

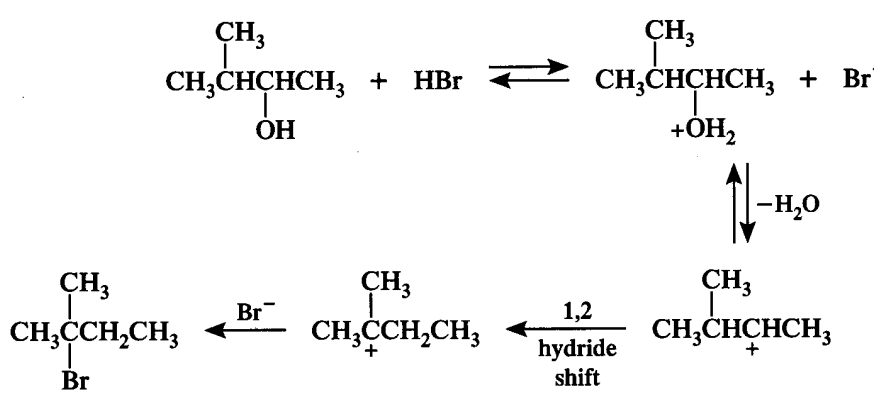
trans-1-Chloro-4-methylcyclohexane

11.16 (a) Tertiary alcohols react faster than secondary alcohols because they form more stable carbocations; that is, 3° rather than 2°:



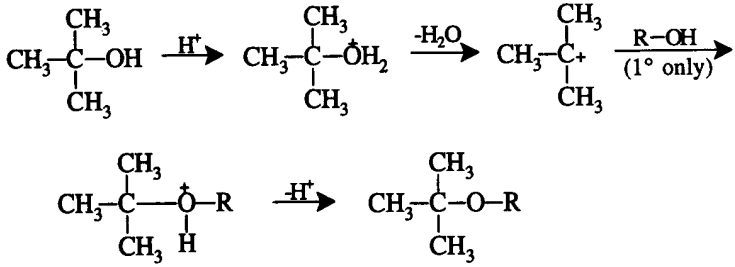
(b) CH_3OH reacts faster than 1° alcohols because it offers less hindrance to S_N2 attack. (Recall that CH_3OH and 1° alcohols must react through an S_N2 mechanism.)

11.17



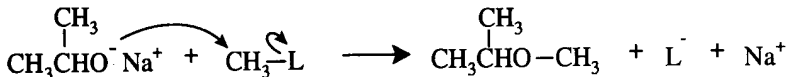
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11.18 (a)



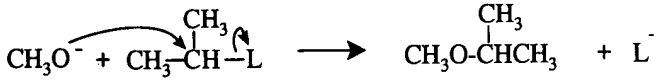
This reaction succeeds because a 3° carbocation is much more stable than a 1° carbocation. Consequently, mixing the 1° alcohol and H_2SO_4 does not lead to formation of appreciable amounts of a 1° carbocation. However, when the 3° alcohol is added, it is rapidly converted to a 3° carbocation, which then reacts with the 1° alcohol that is present in the mixture.

11.19 (a) (1)



(L = X, OSO_2R, or OSO_2OR)

(2)



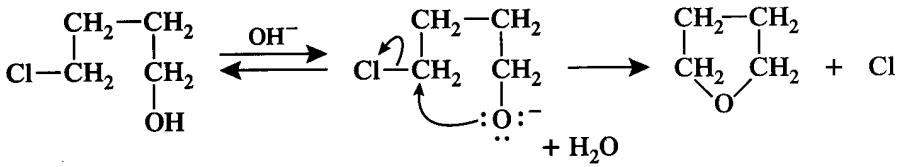
(L = X, OSO_2R, or OSO_2OR)

(b) Both methods involve S_N2 reactions. Therefore, method (1) is better because substitution takes place at an unhindered methyl carbon atom. In method (2) where substitution must take place at a relatively hindered secondary carbon atom, the reaction would be accompanied by considerable elimination.

11.20 Reaction of the alcohol with K and then of the resulting salt with C_2H_5Br does not break bonds to the stereocenter, and these reactions therefore occur with retention of configuration at the stereocenter.

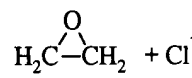
Reaction of the tosylate, $C_6H_5CH_2\underset{\displaystyle OTs}{\underset{|}{C}}HCH_3$, with C_2H_5OH in K_2CO_3 solution, however, is an S_N2 reaction that takes place at the stereocenter and thus it occurs with inversion at the stereocenter.

11.21

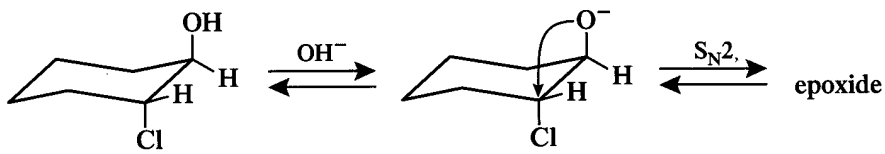


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11.22 (a) $HO^- + HOCH_2{-}CH_2{-}Cl \rightleftharpoons H_2O + {}^-O{-}CH_2{-}CH_2{-}Cl \longrightarrow$

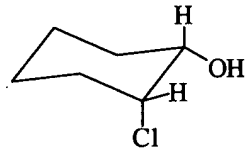


(b) The $-\ddot{\underset{\cdot\cdot}{O}}:^-$ group must displace the Cl^- from the backside,



trans-2-Chlorocyclohexanol

Backside attack is not possible with the cis isomer (below); therefore, it does not form an epoxide.



cis-2-Chlorocyclohexanol

11.23 (a) $CH_2{=}C(CH_3)_2 \xrightarrow{H^+} CH_3{-}C^+(CH_3)_2 \xrightarrow{R{-}OH} CH_3{-}C(CH_3)_2{-}\overset{+}{O}(H)R \xrightarrow{-H^+} CH_3{-}C(CH_3)_2{-}OR$

(b) The *tert*-butyl group is easily removed because, in acid, it is easily converted to a relatively stable, tertiary carbocation.

(c) $CH_3{-}C(CH_3)_2{-}O{-}R \xrightarrow{H^+} CH_3{-}C(CH_3)_2{-}\overset{+}{O}(H){-}R \longrightarrow CH_3{-}C^+(CH_3)_2 + HOR$

$CH_3{-}C(CH_3)_2{-}OH \xleftarrow{-H^+} CH_3{-}C(CH_3)_2{-}OH_2^+ \xleftarrow{H_2O} CH_3{-}C^+(CH_3)_2 \xrightarrow{-H^+} CH_2{=}C(CH_3)_2$

11.24 (a) $CH_3O{-}C(H)(CH_3)(CH_2CH_3) + HI \longrightarrow I^- + CH_3{-}\overset{+}{O}(H){-}C(H)(CH_3)(CH_2CH_3) \longrightarrow$

$ICH_3 + HO{-}C(H)(CH_3)(CH_2CH_3)$

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S_N2 attack of I^- occurs at the methyl carbon atom because it is less hindered; therefore, the bond between the *sec*-butyl group and the oxygen is not broken.

(b) $CH_3{-}O{-}C(CH_3)_3 + HI \longrightarrow CH_3{-}\overset{+}{O}(H){-}C(CH_3)_3 + I^-$

$CH_3OH + CH_3{-}\overset{+}{C}(CH_3)_2 \xrightarrow{I^-} CH_3{-}C(CH_3)_2{-}I$

In this reaction the much more stable *tert*-butyl cation is produced. It then combines with I^- to form *tert*-butyl iodide.

11.25 (a) $H_2C{-}CH_2$ (O) $\xrightarrow{HA}$ $H_2C{-}CH_2$ (O, H) $\xrightarrow{CH_3{-}\ddot{O}H}$ $CH_2(OH){-}CH_2{-}\overset{+}{O}H{-}CH_3$

$\xrightarrow[A^-]{}$ $HOCH_2CH_2OCH_3$ Methyl Cellosolve

(b) An analogous reaction yields ethyl cellosolve, $HOCH_2CH_2OCH_2CH_3$.

(c) $H_2C{-}CH_2$ (O) $\xrightarrow{I^-}$ $CH_2(I){-}CH_2{-}O^-$ $\xrightarrow{H_2O}$ $HOCH_2CH_2I + OH^-$

(d) $H_2C{-}CH_2$ (O) $\xrightarrow{:NH_3}$ $CH_2(NH_3^+){-}CH_2{-}O^-$ $\longrightarrow$ $HOCH_2CH_2NH_2$

(e) $H_2C{-}CH_2$ (O) $\xrightarrow{CH_3O^-}$ $CH_2(OCH_3){-}CH_2{-}O^-$ $\xrightarrow{CH_3OH}$ $HOCH_2CH_2OCH_3 + CH_3O^-$

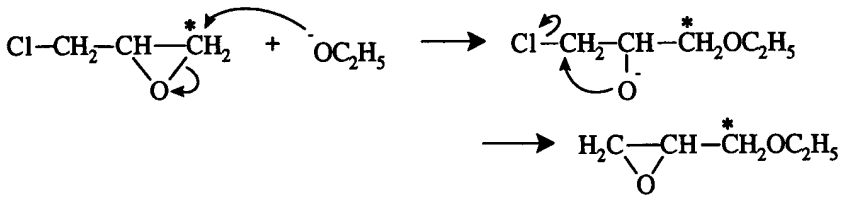
11.26 The reaction is an S_N2 reaction, and thus nucleophilic attack takes place much more rapidly at the primary carbon atom than at the more hindered secondary carbon atom.

$CH_3{-}C(CH_3){-}CH_2$ (O) $+ CH_3O^- \xrightarrow[CH_3OH]{\text{fast}}$ $CH_3{-}C(CH_3)(OH){-}CH_2{-}OCH_3$ Major product

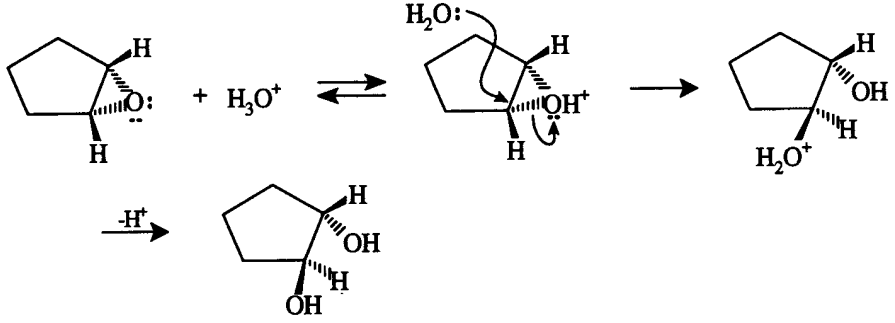
$CH_3{-}C(CH_3){-}CH_2$ (O) $+ CH_3O^- \xrightarrow[CH_3OH]{\text{slow}}$ $CH_3{-}C(CH_3)(OCH_3){-}CH_2{-}OH$ Minor product

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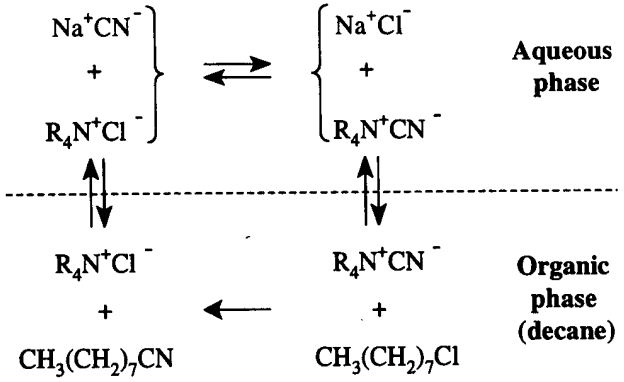
11.27 Ethoxide ion attacks the epoxide ring at the primary carbon because it is less hindered, and the following reactions take place.



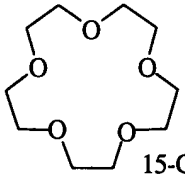
11.28



11.29

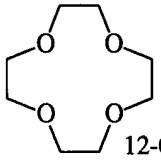


11.30 (a)



15-Crown-5

(b)



12-Crown-4

11.31 (a) 3,3-Dimethyl-1-butanol

(b) 4-Penten-2-ol

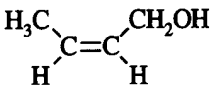
(c) 2-Methyl-1,4-butanediol

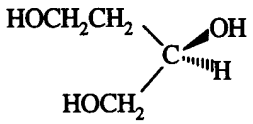
(d) 2-Phenylethanol

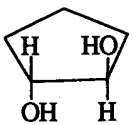
(e) 1-Methyl-2-cyclopenten-1-ol

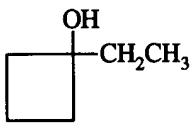
(f) *cis*-3-Methylcyclohexanol

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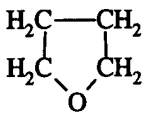
11.32 (a) 

(b) 

(c) 

(d) 

(e) $CH_3CH_2C{\equiv}CCHCH_2OH$ (Cl)

(f) 

(g) $CH_3CHCH_2CH_2CH_3$ (OCH_2CH_3)

(h) $CH_3CH_2-O-C_6H_5$

(i) $CH_3CH(CH_3)-O-CH(CH_3)CH_3$

(j) $CH_3CH_2-O-CH_2CH_2OH$

11.33 (a) $CH_3CH_2CH{=}CH_2 \xrightarrow[\text{(hydroboration)}]{THF:BH_3} (CH_3CH_2CH_2CH_2)_3B$

$\xrightarrow[\text{(oxidation)}]{H_2O_2/OH^-} CH_3CH_2CH_2CH_2OH$

(b) $CH_3CH_2CH_2CH_2Cl \xrightarrow{OH^-} CH_3CH_2CH_2CH_2OH$

(c) $CH_3CH_2CHCH_3$ (Cl) $\xrightarrow{(CH_3)_3COK/(CH_3)_3COH} CH_3CH_2CH{=}CH_2$

$\xrightarrow[ROOR]{HBr} CH_3CH_2CH_2CH_2Br \xrightarrow{OH^-} CH_3CH_2CH_2CH_2OH$

(d) $CH_3CH_2C{\equiv}CH \xrightarrow[Ni_2B\ (P\text{-}2)]{H_2} CH_3CH_2CH{=}CH_2$

$\xrightarrow{[\text{as in (a)}]} CH_3CH_2CH_2CH_2OH$

11.34 (a) $3\ CH_3CH_2CHCH_3$ (OH) $+\ PBr_3 \longrightarrow 3\ CH_3CH_2CHCH_3$ (Br) $+\ H_3PO_3$

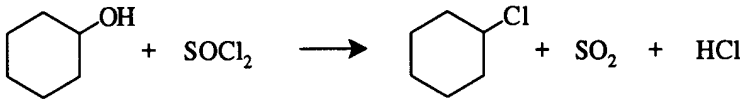
(b) $CH_3CH_2CH_2CH_2OH \xrightarrow{PBr_3} CH_3CH_2CH_2CH_2Br \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK}$

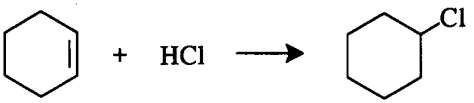
$CH_3CH_2CH{=}CH_2 \xrightarrow[\text{(no peroxides)}]{HBr} CH_3CH_2CHCH_3$ (Br)

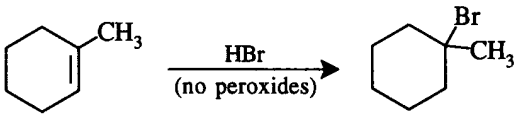
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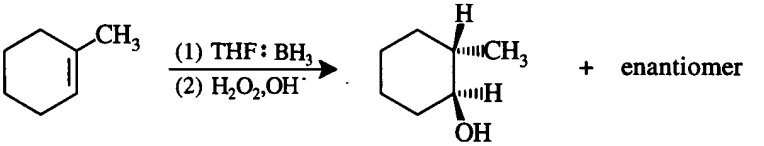
(c) See (b) above.

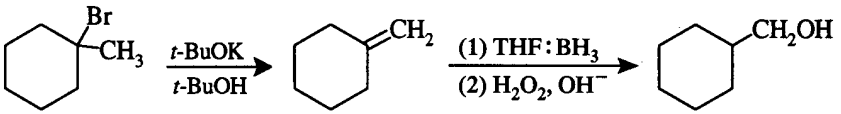
(d) $CH_3CH_2C{\equiv}CH \xrightarrow[Ni_2B\ (P\text{-}2)]{H_2} CH_3CH_2CH{=}CH_2 \xrightarrow[(no\ peroxides)]{HBr} CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

11.35 (a) 

(b) 

(c) 

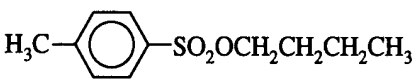
(d) 

(e) 

11.36 (a) $CH_3CH_2CH_2CH_2ONa$ Sodium butoxide

(b) $CH_3CH_2CH_2CH_2OCH_2CH_2CH_3$ Butyl propyl ether

(c) $CH_3SO_2OCH_2CH_2CH_2CH_3$ Butyl mesylate

(d)  Butyl tosylate

(e) $CH_3OCH_2CH_2CH_2CH_3$ 1-Methoxybutane

(f) $CH_3CH_2CH_2CH_2I$ Butyl iodide

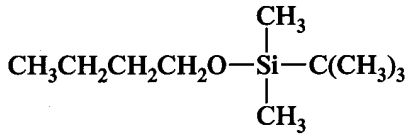
(g) $CH_3CH_2CH_2CH_2Cl$ Butyl chloride

(h) same as (g)

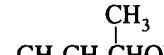
(i) $CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_3$ Dibutyl ether

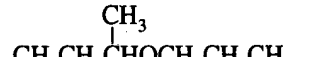
(j) $CH_3CH_2CH_2CH_2Br$ Butyl bromide

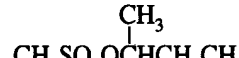
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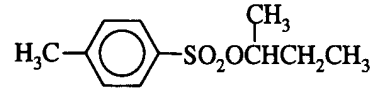
(k)  Butyl *tert*-butyldimethylsilyl ether

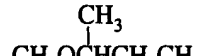
(l) $CH_3CH_2CH_2CH_2OH$ 1-Butanol

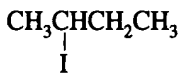
11.37 (a)  Sodium *sec*-butoxide

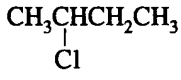
(b)  *sec*-Butyl propyl ether

(c)  *sec*-Butyl mesylate

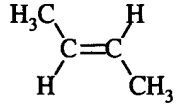
(d)  *sec*-Butyl tosylate

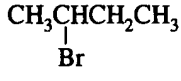
(e)  2-Methoxybutane

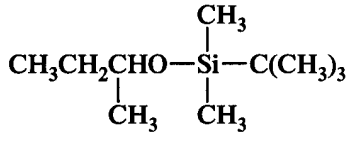
(f)  *sec*-Butyl iodide

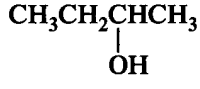
(g)  *sec*-Butyl chloride

(h) same as (g)

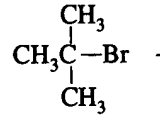
(i)  mainly, *trans*-2-Butene

(j)  *sec*-Butyl bromide

(k)  *sec*-Butyl *tert*-butyldimethylsilyl ether

(l)  2-Butanol

11.38 (a) $CH_3Br + CH_3CH_2Br$

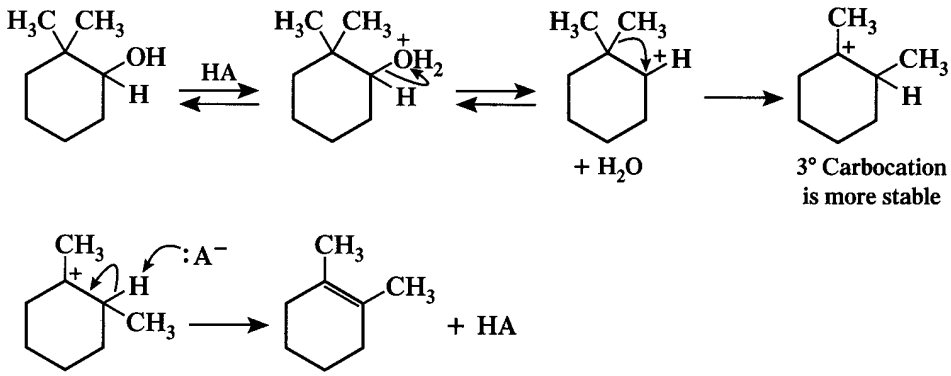
(b) 

(c) $Br{-}CH_2CH_2CH_2CH_2{-}Br$

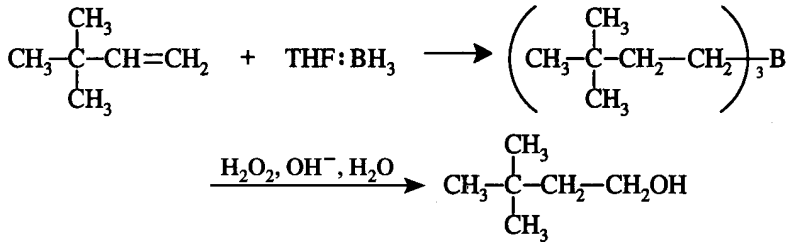
(d) $Br{-}CH_2CH_2{-}Br$ (2 molar equivalents)

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11.39

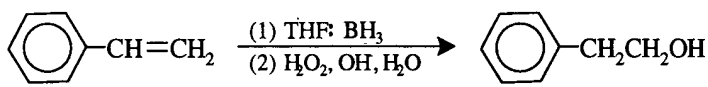


11.40 (a)

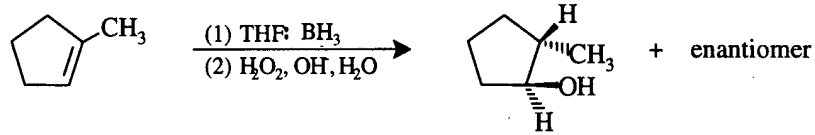


(b) $CH_3CH_2CH_2CH_2CH{=}CH_2 \xrightarrow[(2)\ H_2O_2,\ OH,\ H_2O]{(1)\ THF:\ BH_3} CH_3CH_2CH_2CH_2CH_2CH_2OH$

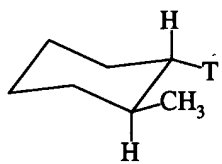
(c)



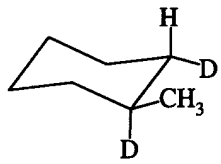
(d)



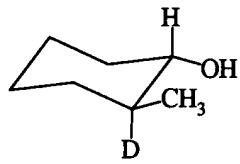
11.41 (a)



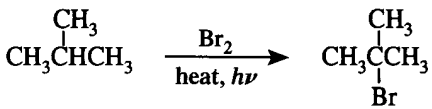
(b)



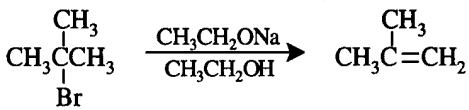
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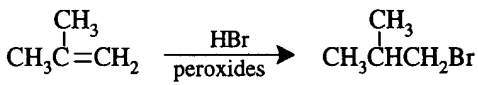
11.42 (a)



(b)



(c)



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(d) $CH_3CH(CH_3)CH_2Br \xrightarrow[\text{acetone}]{KI} CH_3CH(CH_3)CH_2I$

(e) $CH_3CH(CH_3)CH_2Br \xrightarrow[H_2O]{OH^-} CH_3CH(CH_3)CH_2OH$

or $CH_3C(CH_3)=CH_2 \xrightarrow[(2)\ H_2O_2,OH^-]{(1)\ (BH_3)_2} CH_3CH(CH_3)CH_2OH$

(f) $CH_3C(CH_3)=CH_2 \xrightarrow[\text{heat}]{H_3O^+,\ H_2O} CH_3C(CH_3)(OH)CH_3$

(g) $CH_3CH(CH_3)CH_2Br \xrightarrow[CH_3OH]{CH_3ONa} CH_3CH(CH_3)CH_2OCH_3$

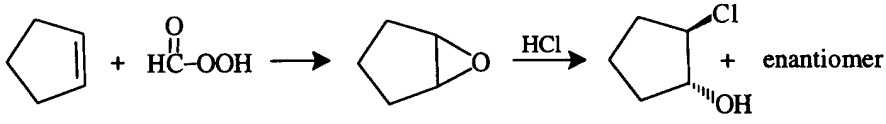
(h) $CH_3CH(CH_3)CH_2Br \xrightarrow[CH_3COH]{CH_3CONa} CH_3CH(CH_3)CH_2OCCH_3$

(i) $CH_3CH(CH_3)CH_2Br \xrightarrow{NaCN} CH_3CH(CH_3)CH_2CN$

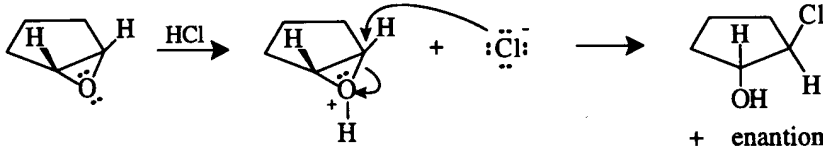
(j) $CH_3CH(CH_3)CH_2Br \xrightarrow{CH_3SNa} CH_3CH(CH_3)CH_2SCH_3$

or $CH_3C(CH_3)=CH_2 \xrightarrow[\text{peroxides}]{CH_3SH} CH_3CH(CH_3)CH_2SCH_3$

(k) $CH_3C(CH_3)=CH_2 \xrightarrow[\text{peroxides}]{CBr_4} CH_3C(Br)CH_2CBr_3$

11.43 (a) 

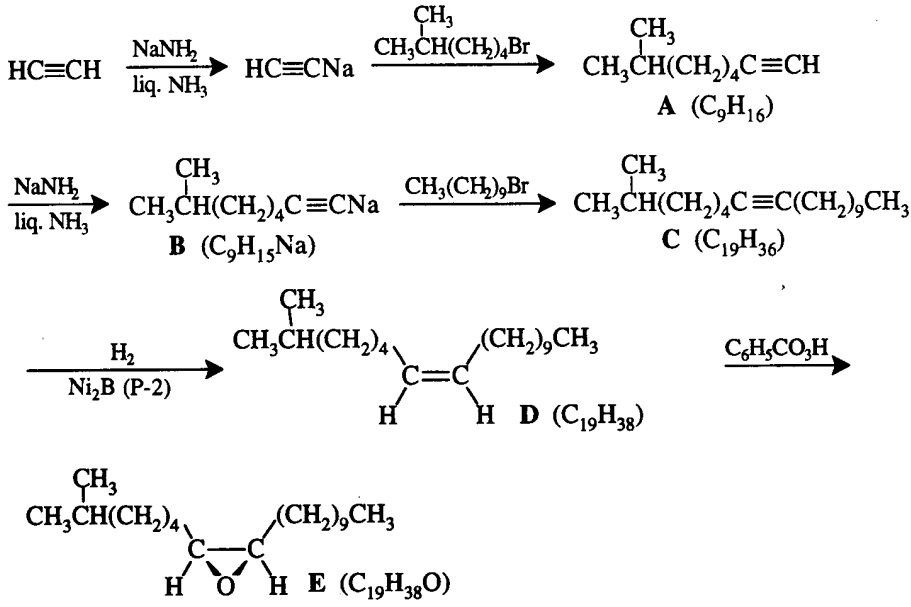
(b) The trans product because the Cl^- attacks anti to the epoxide and an inversion of configuration occurs.



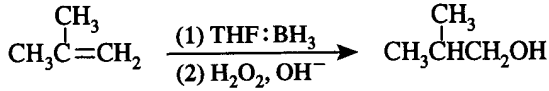
+ enantiomer

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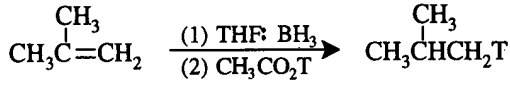
11.44



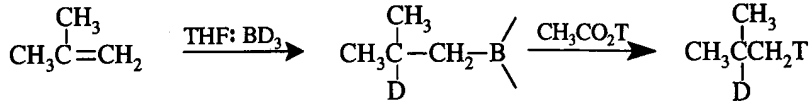
11.45 (a)



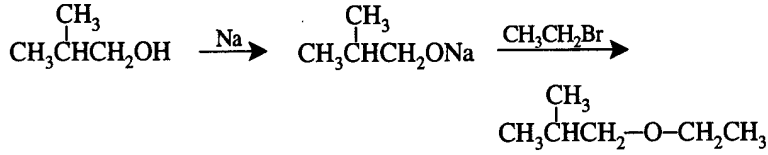
(b)



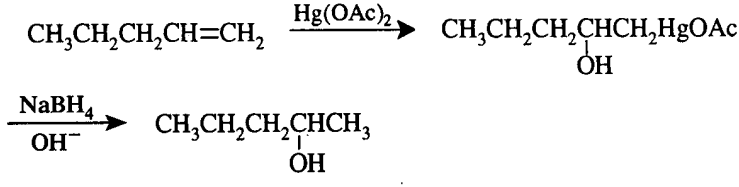
(c)



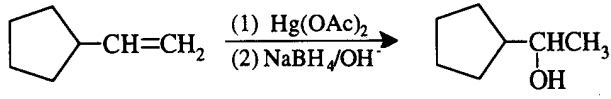
(d)



11.46 (a)

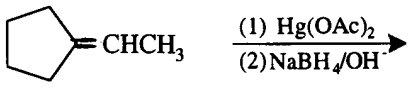


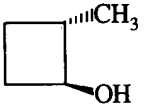
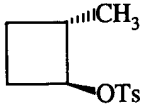
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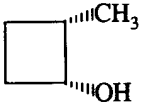


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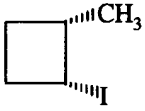
(c) $CH_3CH{=}\overset{CH_3}{\overset{|}{C}}CH_2CH_3 \xrightarrow[(2)\,NaBH_4/OH^-]{(1)\,Hg(OAc)_2} CH_3CH_2\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}CH_2CH_3$

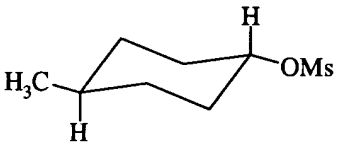
(d) 

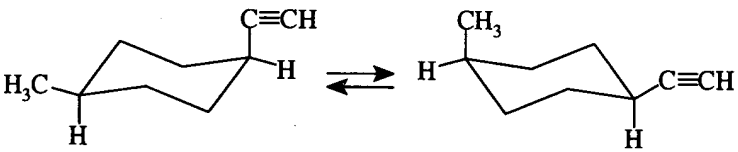
*11.47 (a) **A** =  + enantiomer **B** =  + enantiomer

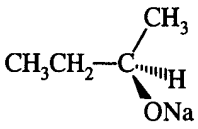
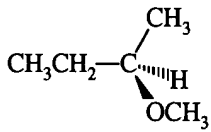
C =  + enantiomer

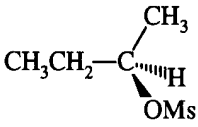
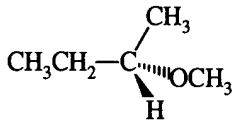
(b) Diastereomers

(c) **D** =  + enantiomer

(d) **E** = 

F = 

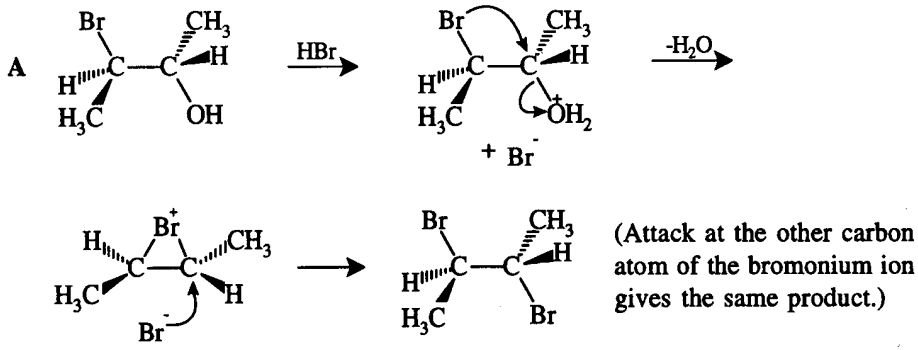
(e) **H** =  **J** = 

(f) **K** =  **L** = 

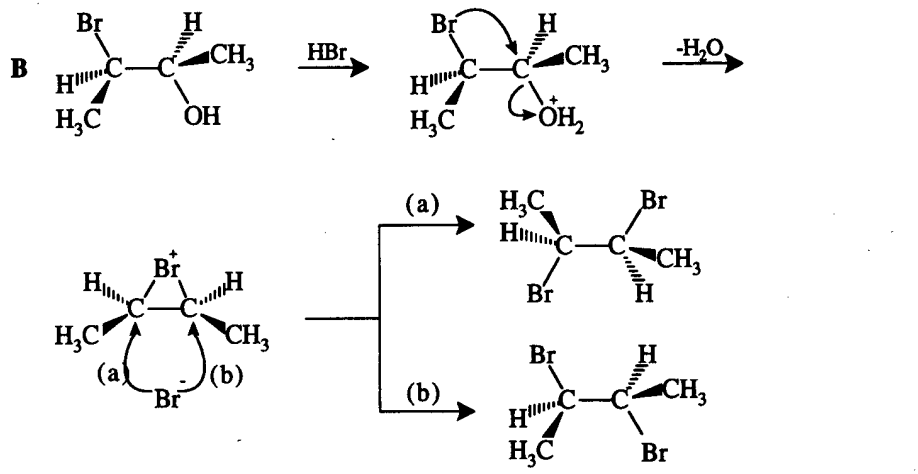
(g) Enantiomers

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***11.48** The reactions proceed through the formation of bromonium ions identical to those formed in the bromination of *trans*- and *cis*-2-butene (see Section 8.7A).

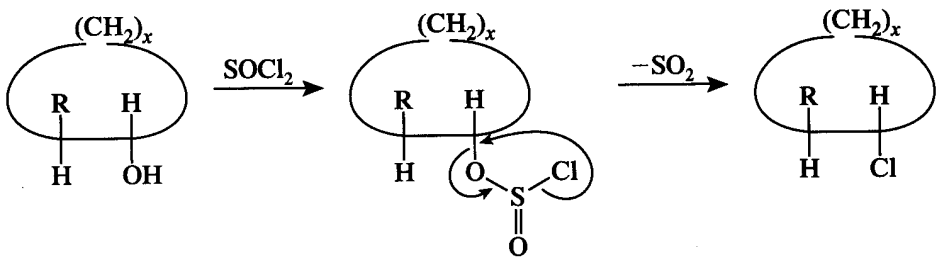


meso-2,3-Dibromobutane



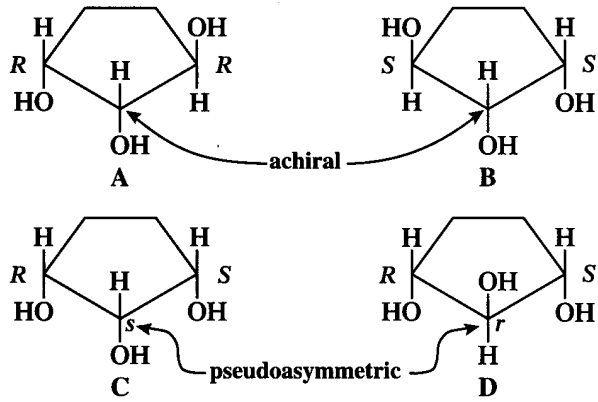
(±)-2,3-Dibromobutane

***11.49**



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*11.50



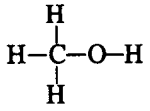
A and **B** are enantiomers
A, C, and **D** are all diastereomers
B, C, and **D** are all diastereomers
C is meso
D is meso

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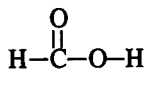
12 ALCOHOLS FROM CARBONYL COMPOUNDS: OXIDATION–REDUCTION AND ORGANOMETALLIC COMPOUNDS

SOLUTIONS TO PROBLEMS

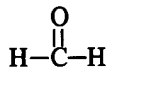
12.1 (a)



3 **H** = -3
1 **O** = +1
Total = -2 = oxidation state of C



1 **H** = -1
3 **O** = +3
Total = +2 = oxidation state of C



2 **H** = -2
2 **O** = +2
Total = 0 = oxidation state of C

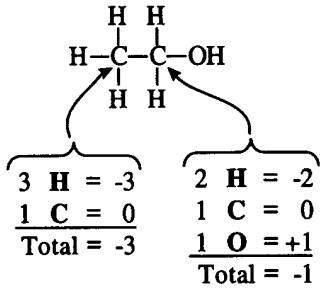
(b) CH_4 (-4) CH_3OH (-2)  (0)  (+2) CO_2 (+4)

(c) A change from -2 to 0

(d) An oxidation, since the oxidation state increases

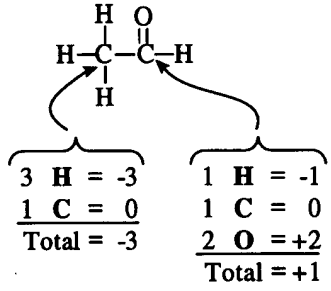
(e) A reduction from +6 to +3

12.2 (a)



3 **H** = -3
1 **C** = 0
Total = -3

2 **H** = -2
1 **C** = 0
1 **O** = +1
Total = -1



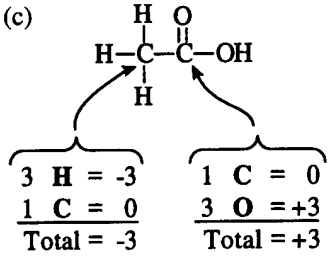
3 **H** = -3
1 **C** = 0
Total = -3

1 **H** = -1
1 **C** = 0
2 **O** = +2
Total = +1

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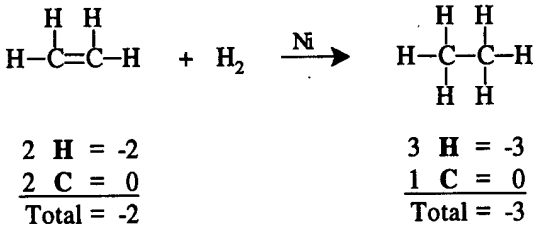
(b) Only the carbon atom of the $-CH_2OH$ group of ethanol undergoes a change in oxidation state. The oxidation state of the carbon atom in the CH_3- group remains unchanged.

(c)



The oxygen-bearing carbon atom increases its oxidation state from +1 (in acetaldehyde) to +3 (in acetic acid).

12.3 (a) If we consider the hydrogenation of ethene as an example, we find that the oxidation state of carbon decreases. Thus, because the reaction involves the *addition* of *hydrogen,* it is both an *addition reaction* and a *reduction.*



(b) The hydrogenation of acetaldehyde is not only an addition reaction, but it is also a *reduction* because the carbon atom of the C=O group goes from a + 1 to a − 1 oxidation state. The reverse reaction (the *dehydrogenation* of ethanol) is not only an *elimination* reaction, but also an *oxidation.*

Ion-Electron Half-Reaction Method for Balancing Organic Oxidation–Reduction Equations

Only two simple rules are needed:

Rule 1 Electrons (e^-) together with protons (H^+) are arbitrarily considered the reducing agents in the half-reaction for the reduction of the oxidizing agent. Ion charges are balanced by *adding electrons to the left-hand side.* (If the reaction is run in neutral or basic solution, add an equal number of OH^- ions to both sides of the balanced half-reaction to neutralize the H^+, and show the resulting $H^+ + OH^-$ as H_2O.)

Rule 2 Water (H_2O) is arbitrarily taken as the formal source of oxygen for the oxidation of the organic compound, producing *product, protons,* and *electrons* on the right-hand side. (Again, use OH^- to neutralize H^+ in the *balanced* half-reaction in neutral or basic media.)

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EXAMPLE 1

Write a balanced equation for the oxidation of RCH_2OH to RCO_2H by $Cr_2O_7^{2-}$ in acid solution.

Reduction half-reaction:

$$Cr_2O_7^{2-} + H^+ + e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

Balancing atoms and charges:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$$

Oxidation half-reaction:

$$RCH_2OH + H_2O = RCO_2H + 4H^+ + 4e^-$$

The least common multiple of a 6-electron uptake in the reduction step and a 4-electron loss in the oxidation step is 12, so we multiply the first half-reaction by 2 and the second by 3, and add:

$$3RCH_2OH + 3H_2O + 2Cr_2O_7^{2-} + 28H^+ = 3RCO_2H + 12H^+ + 4Cr^{3+} + 14H_2O$$

Canceling common terms, we get:

$$3RCH_2OH + 2Cr_2O_7^{2-} + 16H^+ = 3RCO_2H + 4Cr^{3+} + 11H_2O$$

This shows that the oxidation of 3 mol of a primary alcohol to a carboxylic acid requires 2 mol of dichromate.

EXAMPLE 2

Write a balanced equation for the oxidation of styrene to benzoate ion and carbonate ion by MnO_4^- in alkaline solution.

Reduction:

$$MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O \text{ (in acid)}$$

Since this reaction is carried out in basic solution, we must add 4 OH^- to neutralize the $4H^+$ on the left side, and, of course, 4 OH^- to the right side to maintain a balanced equation.

$$MnO_4^- + 4H^+ + 4\,OH^- + 3e^- = MnO_2 + 2H_2O + 4\,OH^-$$

or, $MnO_4^- + 2H_2O + 3e^- = MnO_2 + 4\,OH^-$

Oxidation:

$$ArCH{=}CH_2 + 5H_2O = ArCO_2^- + CO_3^{2-} + 13H^+ + 10e^-$$

We add 13 OH^- to each side to neutralize the H^+ on the right side,

$$ArCH{=}CH_2 + 5H_2O + 13\,OH^- = ArCO_2^- + CO_3^{2-} + 13H_2O + 10e^-$$

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The least common multiple is 30, so we multiply the reduction half-reaction by 10 and the oxidation half-reaction by 3 and add:

$$3ArCH{=}CH_2 + 39\,OH^- + 10MnO_4^- + 20H_2O = 3ArCO_2^- + 3CO_3^{2-} + 24H_2O + 10MnO_2 + 40\,OH^-$$

Canceling:

$$3ArCH{=}CH_2 + 10MnO_4^- = 3ArCO_2^- + 3CO_3^{2-} + 4H_2O + 10MnO_2 + OH^-$$

SAMPLE PROBLEMS

Using the ion–electron half-reaction method, write balanced equations for the following oxidation reactions.

(a) Cyclohexene + MnO_4^- + H^+ $\xrightarrow{\text{(hot)}}$ $HO_2C(CH_2)_4CO_2H + Mn^{2+} + H_2O$

(b) Cyclopentene + MnO_4^- + H_2O $\xrightarrow{\text{(cold)}}$ *cis*-1,2-cyclopentanediol + MnO_2 + OH^-

(c) Cyclopentanol + HNO_3 $\xrightarrow{\text{(hot)}}$ $HO_2C(CH_2)_3CO_2H + NO_2 + H_2O$

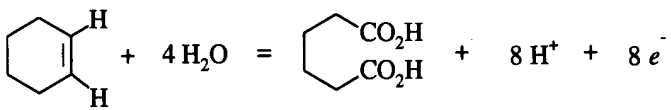
(d) 1,2,3-Cyclohexanetriol + HIO_4 $\xrightarrow{\text{(cold)}}$ $OCH(CH_2)_3CHO + HCO_2H + HIO_3$

SOLUTIONS TO SAMPLE PROBLEMS

(a) Reduction:

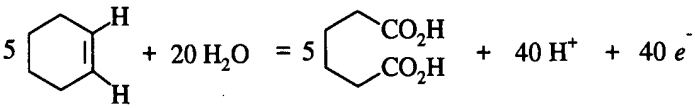
$$MnO_4^- + 8\,H^+ + 5\,e^- = Mn^{2+} + 4\,H_2O$$

Oxidation:

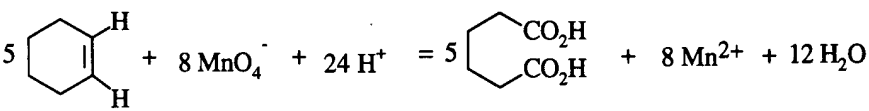


The least common multiple is 40:

$$8\,MnO_4^- + 64\,H^+ + 40\,e^- = 8\,Mn^{2+} + 32\,H_2O$$



Adding and canceling:

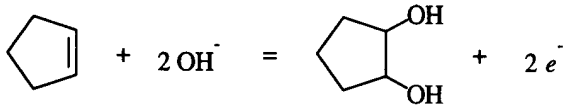


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(b) Reduction:

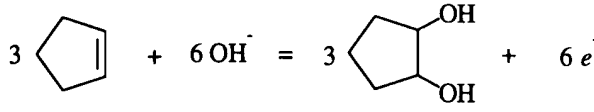
$$MnO_4^- + 2\,H_2O + 3\,e^- = MnO_2 + 4\,OH^-$$

Oxidation:

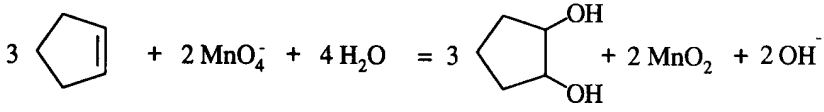


The least common multiple is 6:

$$2\,MnO_4^- + 4\,H_2O + 6\,e^- = 2\,MnO_2 + 8\,OH^-$$



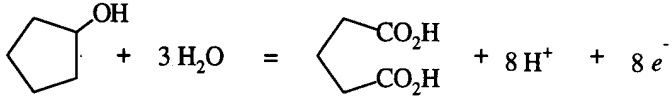
Adding and cancelling:



(c) Reduction:

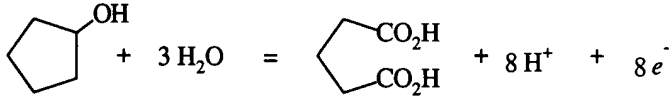
$$HNO_3 + H^+ + e^- = NO_2 + H_2O$$

Oxidation:

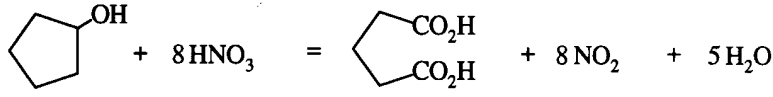


The least common multiple is 8:

$$8\,HNO_3 + 8\,H^+ + 8\,e^- = 8\,NO_2 + 8\,H_2O$$



Adding and cancelling:

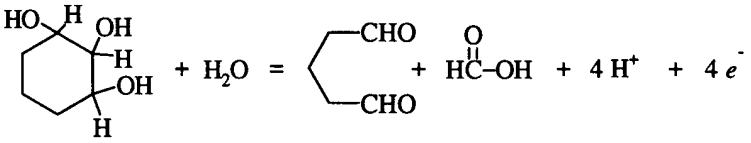


(d) Reduction:

$$HIO_4 + 2\,H^+ + 2\,e^- = HIO_3 + H_2O$$

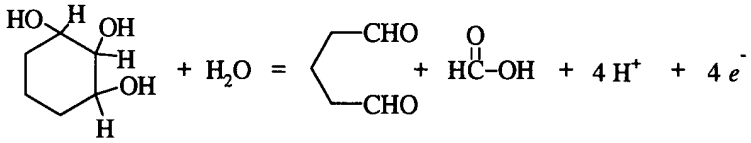
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Oxidation:

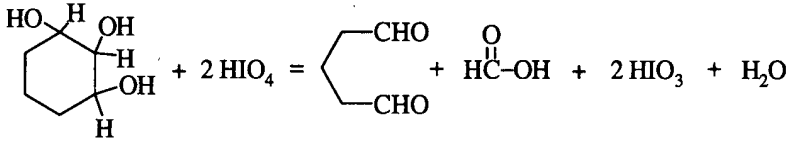


The least common multiple is 4:

$$2\,HIO_4 + 4\,H^+ + 4\,e^- = 2\,HIO_3 + 2\,H_2O$$



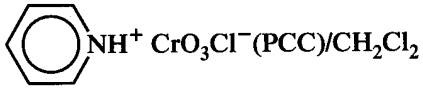
Adding and cancelling:



12.4 (a) $LiAlH_4$

(b) $LiAlH_4$

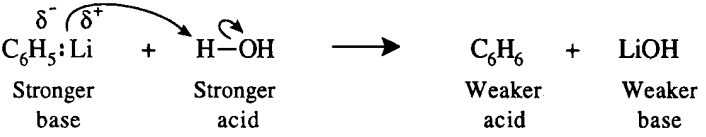
(c) $NaBH_4$

12.5 (a) 

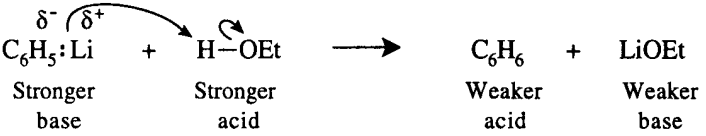
(b) $KMnO_4$, OH^-, H_2O, heat; then H_3O^+

(c) H_2CrO_4/acetone

(d) (1) O_3 (2) Zn, HOAc

12.6 (a) 

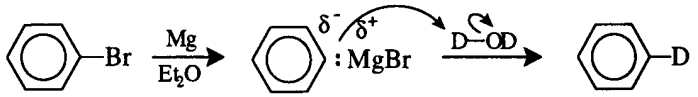
Stronger base	Stronger acid		Weaker acid	Weaker base

(b) 

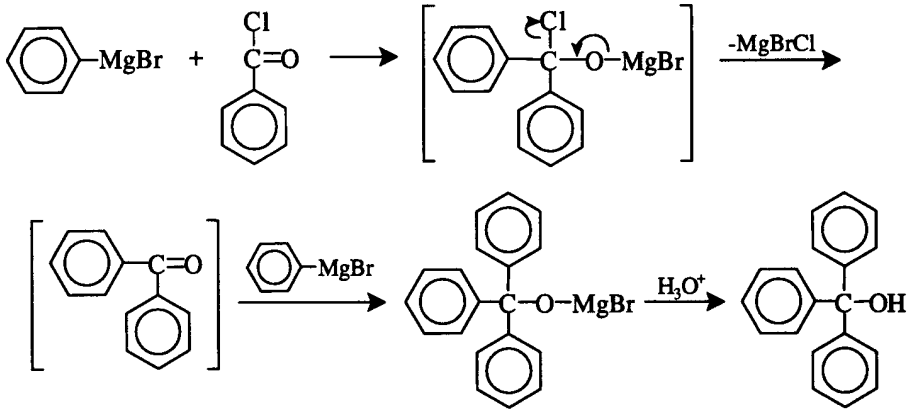
Stronger base	Stronger acid		Weaker acid	Weaker base

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12.7



12.8



12.9 (a) (1) $CH_3CCH_2CH_3 + CH_3MgI \xrightarrow[(2)\ NH_4^+]{(1)\ \text{ether}} CH_3C(OH)(CH_3)CH_2CH_3$

(2) $CH_3CCH_3 + CH_3CH_2MgBr \xrightarrow[(2)\ NH_4^+]{(1)\ \text{ether}} CH_3C(OH)(CH_3)CH_2CH_3$

(3) $CH_3CH_2COCH_2CH_3 + 2\,CH_3MgI \xrightarrow[(2)\ NH_4^+]{(1)\ \text{ether}} CH_3C(OH)(CH_3)CH_2CH_3$

(b) (1) $CH_3CH_2CCH_2CH_3 + CH_3MgI \xrightarrow[(2)\ NH_4^+]{(1)\ \text{ether}} CH_3CH_2C(OH)(CH_3)CH_2CH_3$

(2) $CH_3CH_2CCH_3 + CH_3CH_2MgBr \xrightarrow[(2)\ NH_4^+]{(1)\ \text{ether}} CH_3CH_2C(OH)(CH_3)CH_2CH_3$

(3) $CH_3COCH_3 + 2\,CH_3CH_2MgBr \xrightarrow[(2)\ NH_4^+]{(1)\ \text{ether}} CH_3CH_2C(OH)(CH_3)CH_2CH_3$

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(c) (1) CH_3CH (O) + $BrMgCHCH_2CH_3$ (CH_2CH_3) $\xrightarrow[(2)\ H_3O^+]{(1)\ \text{ether}}$ $CH_3CHCHCH_2CH_3$ (OH; CH_2CH_3)

(2) CH_3MgI + $HCCHCH_2CH_3$ (O; CH_2CH_3) $\xrightarrow[(2)\ H_3O^+]{(1)\ \text{ether}}$ $CH_3CHCHCH_2CH_3$ (OH; CH_2CH_3)

(d) (1) $C_6H_5CCH_3$ (O) + $CH_3CH_2CH_2MgBr$ $\xrightarrow[(2)\ NH_4^+]{(1)\ \text{ether}}$ $C_6H_5C(OH)(CH_3)CH_2CH_2CH_3$

(2) $C_6H_5CCH_2CH_2CH_3$ (O) + CH_3MgI $\xrightarrow[(2)\ NH_4^+]{(1)\ \text{ether}}$ $C_6H_5C(OH)(CH_3)CH_2CH_2CH_3$

(3) $CH_3CCH_2CH_2CH_3$ (O) + C_6H_5MgBr $\xrightarrow[(2)\ NH_4^+]{(1)\ \text{ether}}$ $C_6H_5C(OH)(CH_3)CH_2CH_2CH_3$

(e) (1) C_6H_5COEt (O) + $2\ C_6H_5MgBr$ $\xrightarrow[(2)\ NH_4^+]{(1)\ \text{ether}}$ $(C_6H_5)_3COH$

(2) $C_6H_5CC_6H_5$ (O) + C_6H_5MgBr $\xrightarrow[(2)\ NH_4^+]{(1)\ \text{ether}}$ $(C_6H_5)_3COH$

12.10 (a) $CH_3CH_2CH_2OH$ $\xrightarrow[CH_2Cl_2]{PCC}$ CH_3CH_2CH (O) $\xrightarrow[\text{ether}]{C_6H_5MgBr}$ $CH_3CH_2CHC_6H_5$ (OMgBr)

$\xrightarrow[H_2O]{H_3O^+}$ $CH_3CH_2CHC_6H_5$ (OH)

(b) C_6H_5MgBr $\xrightarrow[(2)\ H_3O^+]{(1)\ HCH\ (O),\ \text{ether}}$ $C_6H_5CH_2OH$ $\xrightarrow[CH_2Cl_2]{PCC}$ C_6H_5CH (O)

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(c) $CH_3CH_2\overset{O}{\overset{\|}{C}}OCH_3 \xrightarrow[\text{ether}]{2\ C_6H_5MgBr} C_6H_5\overset{OMgBr}{\overset{|}{C}}CH_2CH_3 \xrightarrow[H_2O]{NH_4^+} C_6H_5\overset{OH}{\overset{|}{C}}CH_2CH_3$

(d) $CH_3\overset{CH_3}{\overset{|}{C}}HCH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3\overset{CH_3}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}H \xrightarrow[\text{ether}]{C_6H_5MgBr} CH_3\overset{CH_3}{\overset{|}{C}}HCHC_6H_5$

$\xrightarrow[H_2O]{H_3O^+} CH_3\overset{CH_3}{\overset{|}{C}}HCHC_6H_5$ (OH)

12.11 (a) $(CH_3)_2CHCH_2OH + (CH_3)_2C{=}CH_2$

(b) $(CH_3)_2CHCH_2CN$

(c) $(CH_3)_2C{=}CH_2$

(d) $CH_3\overset{CH_3}{\overset{|}{C}}HCH_2OCH_3 + (CH_3)_2C{=}CH_2$

(e) $(CH_3)_2CHCH_2\overset{OH}{\overset{|}{C}}(CH_3)CH_3$

(f) $(CH_3)_2CHCH_2\overset{OH}{\overset{|}{C}}HCH_3$

(g) $(CH_3)_2CHCH_2\overset{OH}{\overset{|}{C}}(CH_3)CH_2CH(CH_3)_2$

(h) $(CH_3)_2CHCH_2CH_2CH_2OH$

(i) $(CH_3)_2CHCH_2CH_2OH$

(j) $(CH_3)_2CHCH_3$

(k) $(CH_3)_2CHCH_3 + CH_3C{\equiv}CLi$

12.12 (a) CH_3CH_3

(b) CH_3CH_2D

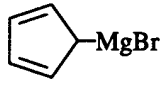
(c) $C_6H_5\overset{OH}{\overset{|}{C}}HCH_2CH_3$

(d) $C_6H_5\overset{OH}{\overset{|}{C}}(CH_2CH_3)C_6H_5$

(e) $C_6H_5\overset{OH}{\overset{|}{C}}(CH_2CH_3)CH_2CH_3$

(f) $C_6H_5\overset{OH}{\overset{|}{C}}(CH_3)CH_2CH_3$

(g) $CH_3CH_3 + CH_3CH_2C{\equiv}C\overset{OH}{\overset{|}{C}}HCH_3$

(h) CH_3CH_3 + 

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12.13 (a) $(CH_3)_2CHCHCH_2CH_2CH_3$ (OH)

(b) $(CH_3)_2CHCCH_2CH_2CH_3$ (OH, CH_3)

(c) $CH_3CH_2CH_3$ + $CH_3CH_2CH_2C{\equiv}C{-}C{-}CH_3$ (OH, CH_3)

(d) $CH_3CH_2CH_3$

(e) $CH_3CH_2CH_2CH_2CH{=}CH_2$

(f) $CH_3CH_2CH_2$–cyclopentane

(g) $CH_3CH_2CH_2$, CH_3, H, H

(h) $CH_3CH_2CH_2CH_3$

Note: This variation of the Corey-Posner, Whitesides-House synthesis is stereospecific.

(i) $CH_3CH_2CH_2D$

12.14 (a) $LiAlH_4$

(b) $NaBH_4$

(c) $LiAlH_4$

(d) (1) $KMnO_4$, OH^-, heat, (2) H_3O^+

(e) PCC/CH_2Cl_2

12.15 (a) $3\,(CH_3)_2CHOH + PBr_3 \longrightarrow (CH_3)_2CHBr + H_3PO_3$

$(CH_3)_2CHBr + Mg \xrightarrow{\text{ether}} (CH_3)_2CHMgBr$

$(CH_3)_2CHMgBr + CH_3CH(O) \xrightarrow[(2)\ H_3O^+]{(1)\ \text{ether}} (CH_3)_2CHCHCH_3$ (OH)

(b) $(CH_3)_2CHMgBr$ [from part (a)] + $HCH(O) \xrightarrow[(2)\ H_3O^+]{(1)\ \text{ether}} (CH_3)_2CHCH_2OH$

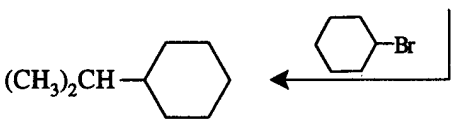
(c) $(CH_3)_2CHMgBr$ [from part (a)] + $H_2C(O)CH_2 \xrightarrow[(2)\ H_3O^+]{(1)\ \text{ether}} (CH_3)_2CHCH_2CH_2OH \xrightarrow{SOCl_2} (CH_3)_2CHCH_2CH_2Cl$

(d) $(CH_3)_2CHMgBr$ [from part (a)] + $HCCH(CH_3)_2$ (O) $\xrightarrow[(2)\ H_3O^+]{(1)\ \text{ether}} (CH_3)_2CHCHCH(CH_3)_2$ (OH)

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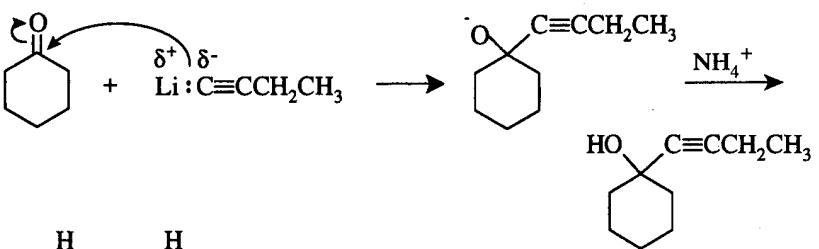
(e) $(CH_3)_2CHMgBr + D_2O \longrightarrow (CH_3)_2CHD$
[from part (a)]

(f) $(CH_3)_2CHBr + Li \longrightarrow (CH_3)_2CHLi \xrightarrow{CuI} [(CH_3)_2CH]_2CuLi$
[from part (a)]

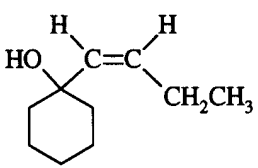


12.16 (a) $CH_3{:}Li + H{-}C{\equiv}C{-}CH_2CH_3 \longrightarrow CH_4 + Li{:}C{\equiv}CCH_2CH_3$

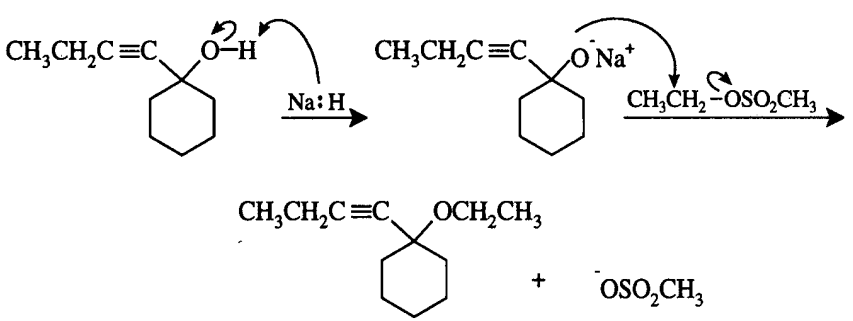
(b)



(c)



(d)



(e) $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$

(f) $CH_3CH_2\underset{\displaystyle OSO_2CH_3}{\underset{|}{C}}HCH_3$

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(g) $CH_3CH_2\underset{\underset{OSO_2CH_3}{|}}{CH}CH_3 + Na^+ {}^-O\overset{\overset{O}{\|}}{C}CH_3 \longrightarrow CH_3CH_2\underset{\underset{O}{\|}}{\overset{\overset{OCCH_3}{|}}{CH}}CH_3 + Na^+ {}^-OSO_2CH_3$

(h) $CH_3CH_2\underset{\underset{OH}{|}}{CH}CH_3 + CH_3CH_2OH$

12.17 (a) $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow{PBr_3} CH_3CH_2CH_2CH_2CH_2Br$

(b) $CH_3CH_2CH_2CH_2CH_2Br$ [from (a)] $\xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_3CH_2CH_2CH{=}CH_2$

(c) $CH_3CH_2CH_2CH{=}CH_2$ [from (b)] $\xrightarrow[(2)\ NaBH_4/OH^-]{(1)\ Hg(OAc)_2/THF\text{-}H_2O} CH_3CH_2CH_2\underset{\underset{OH}{|}}{CH}CH_3$

(d) $CH_3CH_2CH_2\underset{\underset{OH}{|}}{CH}CH_3$ [from (c)] $\xrightarrow[acetone,\ H_2O]{H_2CrO_4} CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$

(e) $CH_3CH_2CH_2\underset{\underset{OH}{|}}{CH}CH_3$ [from (c)] $\xrightarrow{PBr_3} CH_3CH_2CH_2\underset{\underset{Br}{|}}{CH}CH_3$

(f) $CH_3CH_2CH_2CH_2CH_2Br$ [from (a)] $\xrightarrow[Et_2O]{Mg} CH_3CH_2CH_2CH_2CH_2MgBr \xrightarrow[(2)\ H_3O^+]{(1)\ \overset{\overset{O}{\|}}{HCH}} CH_3CH_2CH_2CH_2CH_2CH_2OH$

(g) $CH_3CH_2CH_2CH_2CH_2MgBr$ [from (f)] $\xrightarrow[(2)\ H_3O^+]{(1)\ H_2C\overset{\overset{O}{/\backslash}}{-}CH_2} CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$

(h) $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}H$

(i) $CH_3CH_2CH_2\underset{\underset{OH}{|}}{CH}CH_3$ [from (c)] $\xrightarrow[acetone,\ H_2O]{H_2CrO_4} CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$

(j) $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[(2)\ H_3O^+]{(1)\ KMnO_4,\ OH^-,\ heat} CH_3CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}OH$

(k) (1) $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[140^\circ C]{H_2SO_4} (CH_3CH_2CH_2CH_2CH_2)_2O$

(2) $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[(-H_2)]{NaH} CH_3CH_2CH_2CH_2CH_2ONa$

$\xrightarrow[\text{[from (a)]}]{CH_3CH_2CH_2CH_2CH_2Br} (CH_3CH_2CH_2CH_2CH_2)_2O$

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(l) $CH_3CH_2CH_2CH{=}CH_2 \xrightarrow[CCl_4]{Br_2} CH_3CH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_2Br \xrightarrow[heat]{3\ NaNH_2}$
[from (b)]

$$CH_3CH_2CH_2C{\equiv}CNa \xrightarrow{H^+} CH_3CH_2CH_2C{\equiv}CH$$

(m) $CH_3CH_2CH_2C{\equiv}CH \xrightarrow{HBr} CH_3CH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}{=}CH_2$
[from (l)]

(n) $CH_3CH_2CH_2CH_2CH_2Br \xrightarrow[Et_2O]{Li} CH_3CH_2CH_2CH_2CH_2Li$
[from (a)]

(o) $CH_3CH_2CH_2CH_2CH_2Li \xrightarrow{CuI} (CH_3CH_2CH_2CH_2CH_2)_2CuLi$
[from (n)]

$$\xrightarrow[\text{[from (a)]}]{CH_3CH_2CH_2CH_2CH_2Br} CH_3(CH_2)_8CH_3$$

(p) $CH_3CH_2CH_2CH_2CH_2MgBr \xrightarrow[(2)\ NH_4^+]{(1)\ CH_3(CH_2)_2\overset{\displaystyle O}{\overset{\|}{C}}CH_3\text{[from (d)]}}$
[from (f)]

$$CH_3(CH_2)_4\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}(CH_2)_2CH_3$$

12.18 (a) $C_6H_5C{\equiv}CH \xrightarrow[\text{ether } (-CH_4)]{CH_3MgBr} C_6H_5C{\equiv}CMgBr \xrightarrow[(2)\ NH_4^+]{(1)\ CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_3}$

$$C_6H_5C{\equiv}CC(OH)(CH_3)_2$$

(b) $C_6H_5COCH_3 \xrightarrow[OH]{NaBH_4} C_6H_5\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$

(c) $C_6H_5C{\equiv}CH \xrightarrow[Ni_2B\ (P\text{-}2)]{H_2} C_6H_5CH{=}CH_2$

(d) $C_6H_5CH{=}CH_2 \xrightarrow[(2)\ H_2O_2,\ OH]{(1)\ THF{:}\ BH_3} C_6H_5CH_2CH_2OH$

(e) $C_6H_5CH_2CH_2OH \xrightarrow[(2)\ Mg,\ Et_2O]{(1)\ PBr_3} C_6H_5CH_2CH_2MgBr \xrightarrow[(2)\ H_3O^+]{(1)\ H_2C\overset{\displaystyle O}{\overset{\diagup\diagdown}{}}CH_2}$

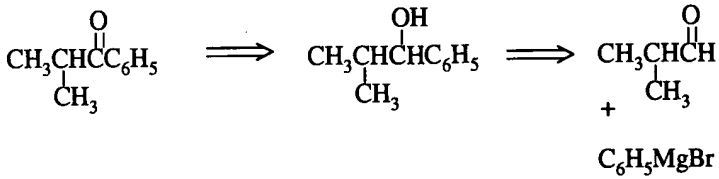
$$C_6H_5CH_2CH_2CH_2CH_2OH$$

(f) $C_6H_5CH_2CH_2OH \xrightarrow[(-H_2)]{NaH} C_6H_5CH_2CH_2ONa \xrightarrow{CH_3I}$

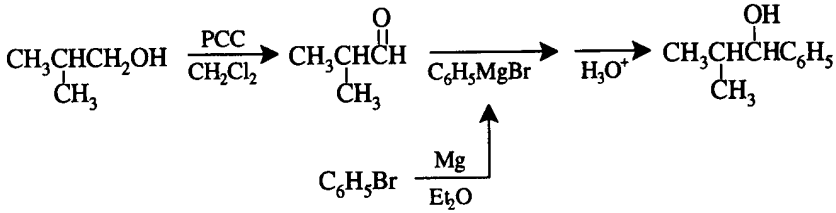
$$C_6H_5CH_2CH_2OCH_3$$

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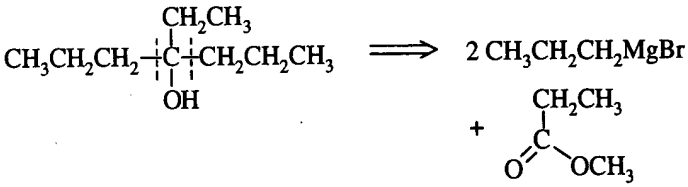
12.19 (a) ***Partial Analysis***



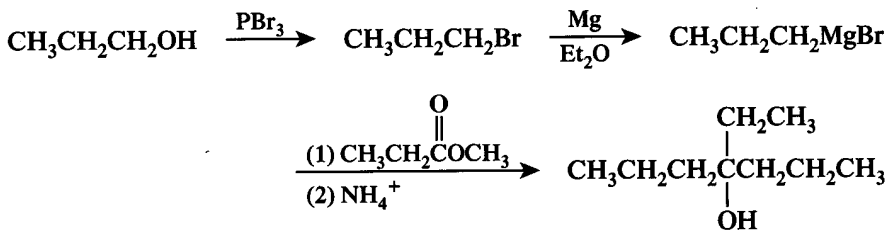
Synthesis



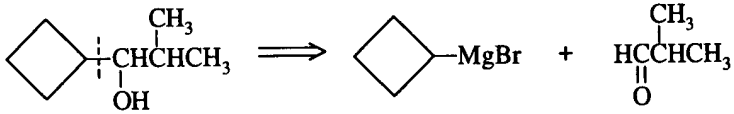
(b) ***Partial Analysis***



Synthesis

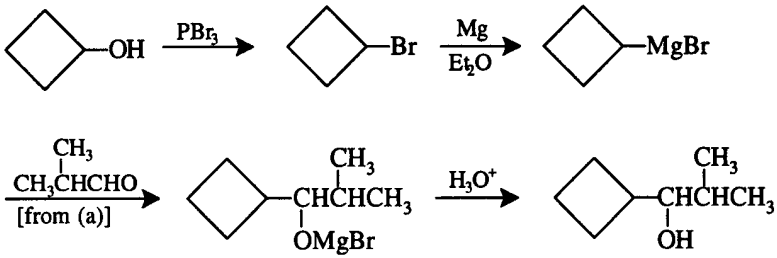


(c) ***Partial Analysis***

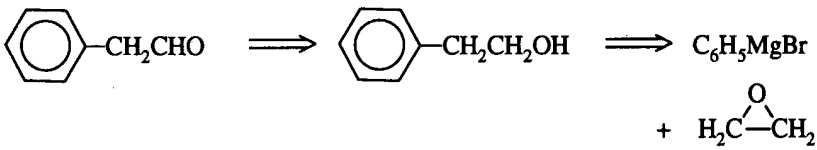


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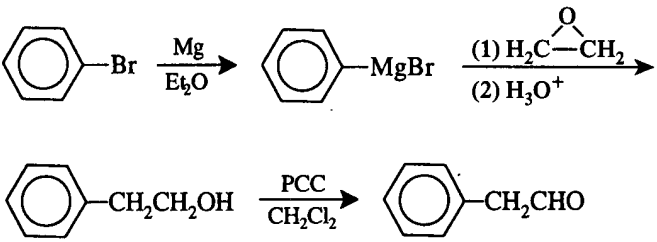
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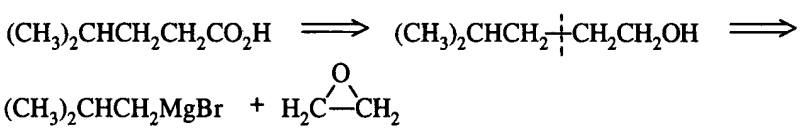
(d) ***Partial Analysis***



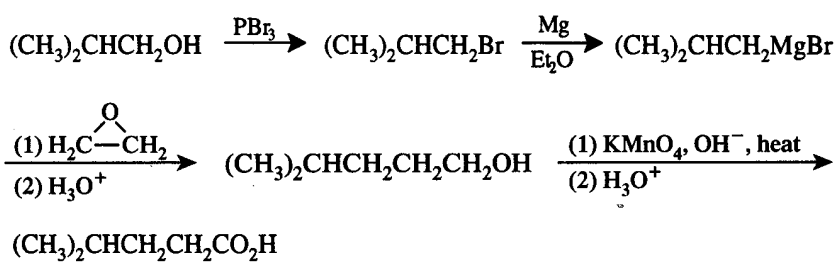
Synthesis



(e) ***Partial Analysis***

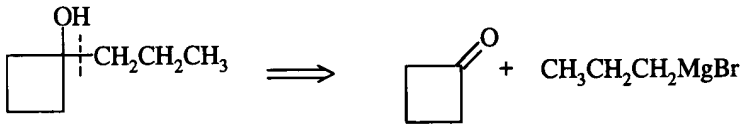


Synthesis

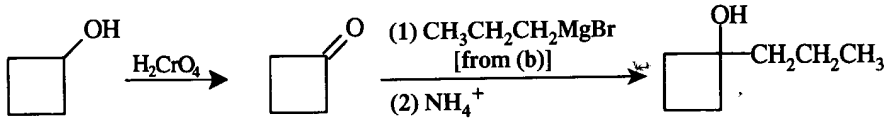


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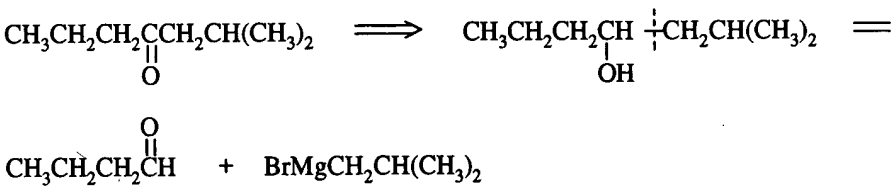
(f) ***Partial Analysis***



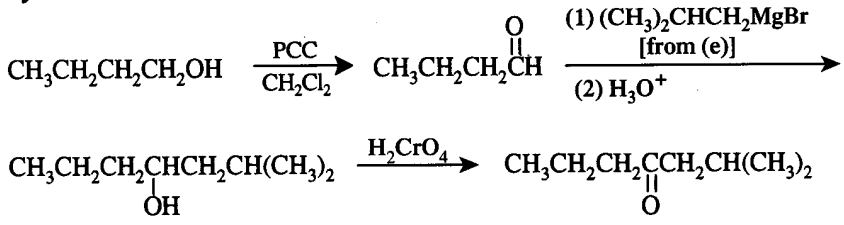
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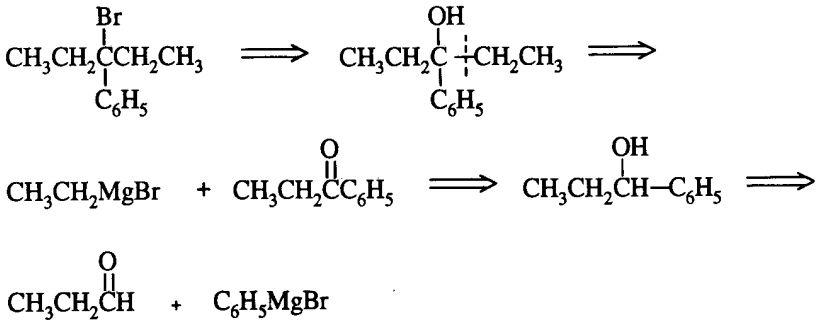
(g) ***Partial Analysis***



Synthesis

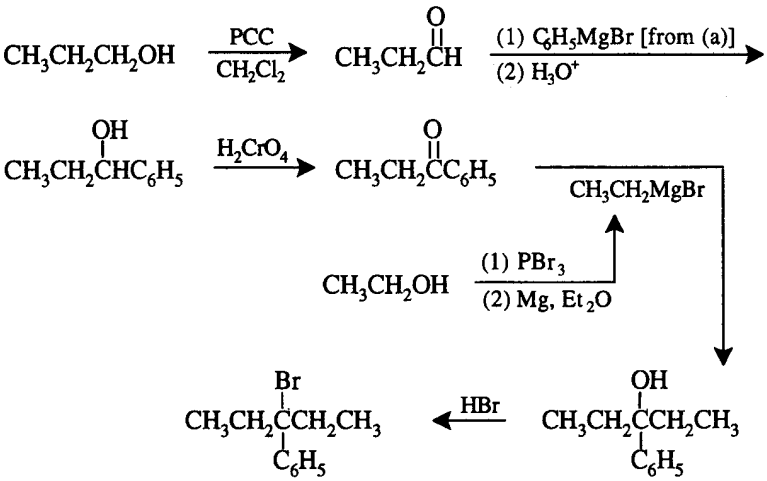


(h) ***Partial Analysis***

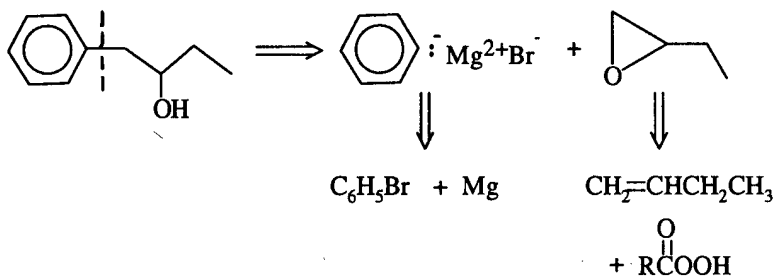


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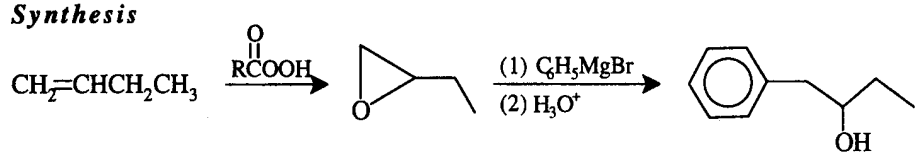
Synthesis



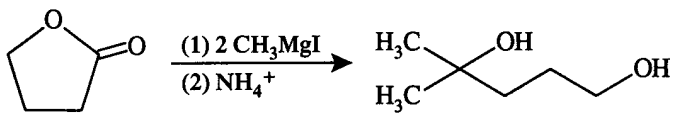
12.20 ***Analysis***



Synthesis

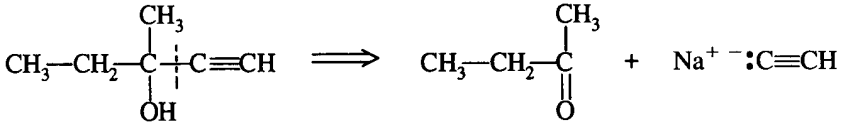


12.21 The starting compound is a cyclic ester. Addition of two molar equivalents of CH_3MgI will (after acidification) furnish the desired product.

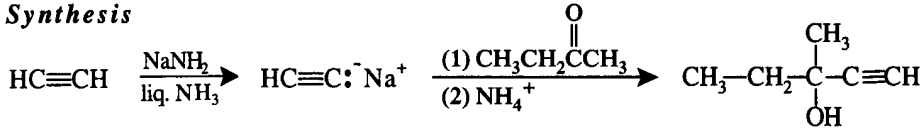


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12.22 *Analysis*

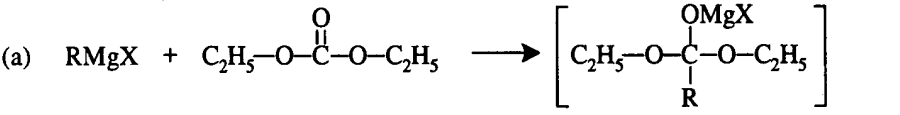


Synthesis

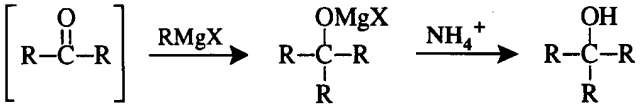


12.23 The three- and four-membered rings are strained, and so they open on reaction with RMgX or RLi. THF possesses an essentially unstrained ring and hence is far more resistant to attack by an organometallic compound.

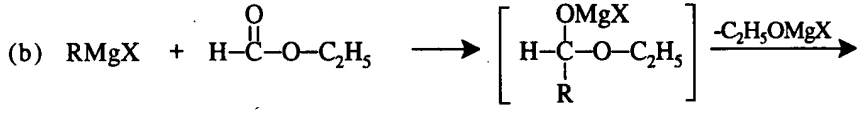
12.24 (a)

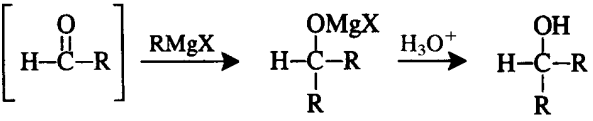






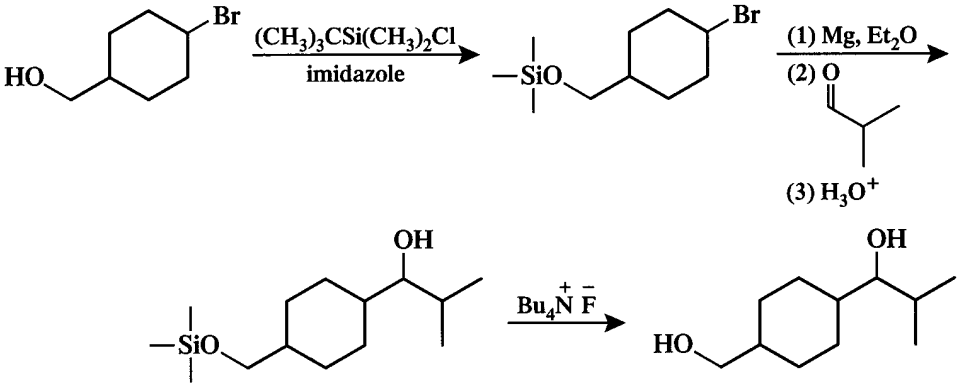
(b)





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*12.25



Before converting the reactant to a Grignard reagent it is first necessary to mask the alcohol, such as by converting it to a *tert*-butyldimethylsilyl ether. After the Grignard reaction is over the protecting group is removed.

*12.26 2-Phenylethanol, 1,2-diphenylethanol, and 1,1-diphenylethanol are distinct from diphenylacetic acid and benzyl phenylacetate in that they do not have carbonyl groups. IR spectroscopy can be used to segregate these compounds into two groups according to those that do or do not exhibit carbonyl absorptions.

^{1}H NMR can differentiate among all of the compounds. In the case of the alcohols, in the ^{1}H NMR spectrum of 2-phenylethanol there will be two triplets of equal integral value, whereas for 1,2-diphenylethanol there will be a doublet and a triplet in a 2:1 area ratio. The triplet will be downfield of the doublet. 1,1-Diphenylethanol will exhibit a singlet for the unsplit methyl hydrogens.

The broadband proton-decoupled ^{13}C NMR spectrum of 2-phenylethanol should show 6 signals (assuming no overlap), four of which are in the chemical shift region for aromatic carbons. 1,2-Diphenylethanol should exhibit 10 signals (assuming no overlap), 8 of which are in the aromatic region. 1,1-Diphenylethanol should show 6 signals (assuming no overlap), four of which would be in the aromatic region. The DEPT ^{13}C NMR spectra would give direct evidence as to the number of attached hydrogens on each carbon.

Regarding the carbonyl compounds, both diphenylacetic acid and benzyl 2-phenylacetate will show carbonyl absorptions in the IR, but only the former will also have a hydroxyl absorption. The ^{1}H NMR spectrum of diphenylacetic acid should show a broad absorption for the carboxylic acid hydrogen and a sharp singlet for the unsplit hydrogen at C2. Their integral values should be the same, and approximately one tenth the integral value of the signals in the aromatic region. Benzyl phenylacetate will exhibit two singlets, one for each of the unsplit CH_2 groups. These signals will have an area ratio of 1:5 with respect to the signal for the 10 aromatic hydrogens. The broadband ^{1}H decoupled ^{13}C NMR spectrum for diphenylacetic acid should show four aromatic carbon signals, whereas that for benzyl phenylacetate (assuming no overlapping signals) would show 10 signals in the aromatic carbon region. Aside from the carbonyl and aromatic carbon signals, benzyl phenylacetate would show two additional signals, whereas diphenylacetic acid would show only one. DEPT ^{13}C NMR spectra for these two compounds would also distinguish them directly.

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***12.27** It makes it impossible to distinguish between aldehyde and ketone type sugars (aldoses and ketoses) that had been components of the saccharide. Also, because the R groups of these sugars contain stereocenters, reduction of the ketone carbonyl will be stereoselective. This will complicate the determination of the ratio of sugars differing in configuration at C2.

***12.28** The IR indicates the presence of OH and absence of C=C and C=O. The MS indicates a molecular weight of 116 amu and confirms the presence of hydroxyl. The reaction data indicate X contains 2 protons per molecule that are acidic enough to react with a Grignard reagent, meaning two hydroxyl groups per molecule. (This analytical procedure, the Zerewitinoff determination, was routinely done before the advent of NMR.)

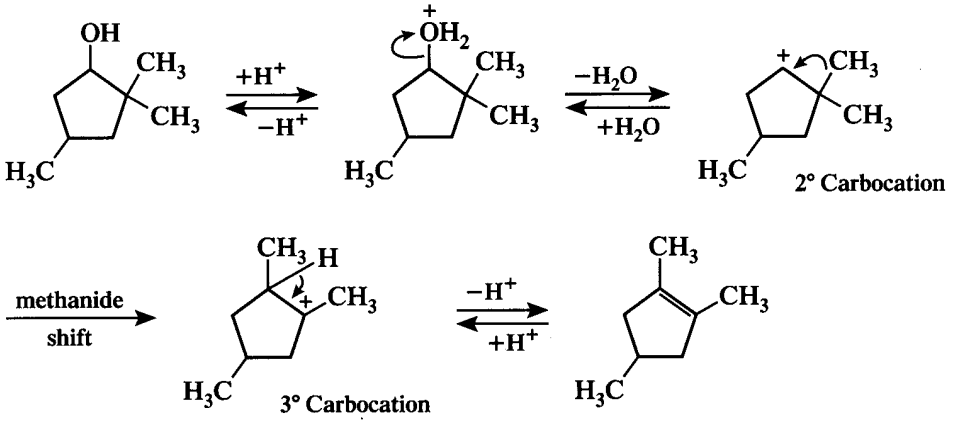
Thus X has a partial structure like:

$C_6H_{10}(OH)_2$ with one ring, or
$C_5H_6O(OH)_2$ with two rings, or (less likely)
$C_4H_2O_2(OH)_2$ with three rings.

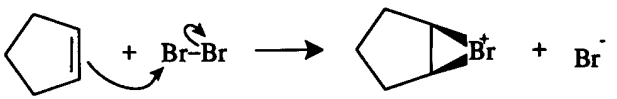
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ANSWERS TO FIRST REVIEW PROBLEM SET

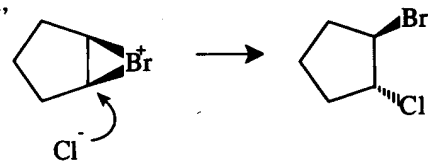
1 (a)



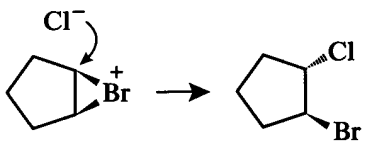
(b)



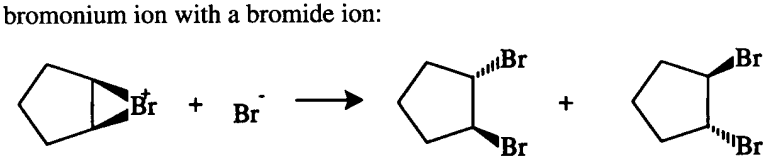
then,



(c) The enantiomer of the product given would be formed in an equimolar amount via the following reaction:



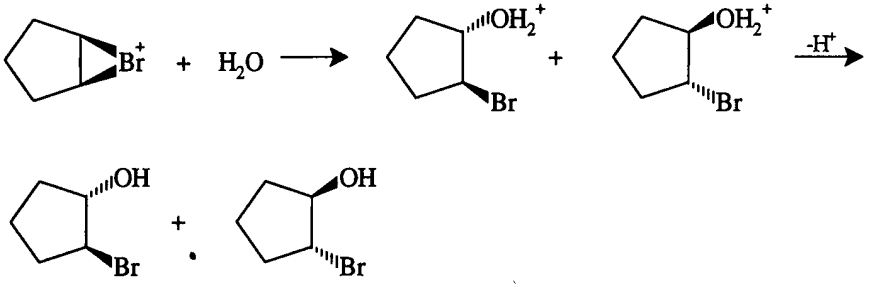
The *trans*-1, 2-dibromocyclopentane would be formed as a racemic form via the reaction of the bromonium ion with a bromide ion:



Racemic *trans*-1,2-dibromocyclopentane

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And, *trans*-2-bromocyclopentanol (the bromohydrin) would be formed (as a racemic form) via the reaction of the bromonium ion with water.



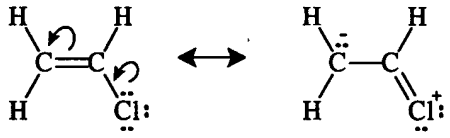
Racemic *trans*-2-bromocyclopentanol

2 (a) $CHCl_3$ (b) The cis isomer (c) CH_3Cl

3 This indicates that the bonds in BF_3 are geometrically arranged so as to cancel each others' polarities in contrast to the case of NF_3. This, together with other evidence, indicates that BF_3 has trigonal planar structure and NF_3 has trigonal pyramidal structure.

4 (a) sp^3
(b) They are much smaller (60°) than the expected 109.5°.
(c) That the bent bonds in cyclopropane, like compressed springs, contain stored energy that is available to assist in reactions that open the 3-membered ring.

5 All of these differences can be explained by the contribution to the CH_2=CHCl molecule made by the following **A** and **B** resonance structures.

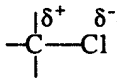


A **B**

(a) Because of the contribution made to the hybrid by **B,** the C–Cl bond of CH_2=CH–Cl has some double-bond character and is, therefore, shorter than the "pure" single bond of CH_3CH_2–Cl.

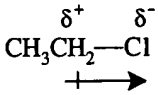
(b) The contribution made to the hybrid by **B** imparts some single-bond character to the carbon-carbon double bond of CH_2=CH–Cl, causing it to be longer than the "pure" double bond of CH_2=CH_2.

(c) Electronegativity differences would cause a carbon-chlorine bond to be polarized as follows:



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And this effect accounts, almost entirely, for the dipole moment of CH_3CH_2Cl.



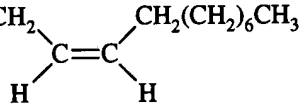
$\mu = 2.05$ D

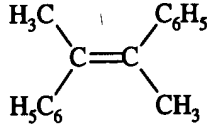
With CH_2=CH–Cl, however, the resonance contribution of **B** tends to oppose the polarization of the C–Cl bond caused by electronegativity differences. That is, the resonance effect partially cancels the electronegativity effect, causing the dipole moment to be smaller.

6 **A** = $CH_3(CH_2)_{11}CH_2C{\equiv}CH$

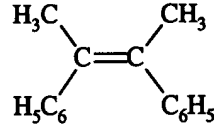
B = $CH_3(CH_2)_{11}CH_2C{\equiv}CNa$

C = $CH_3(CH_2)_{11}CH_2C{\equiv}CCH_2(CH_2)_6CH_3$

Muscalure = 

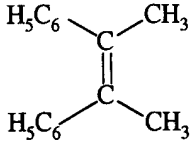
7 

(*E*)-2,3-Diphenyl-2-butene

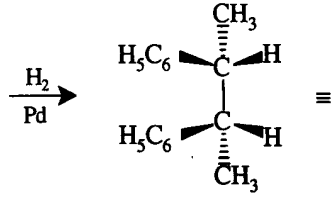


(*Z*)-2,3-Diphenyl-2-butene

Because catalytic hydrogenation is a syn addition, catalytic hydrogenation of the (*Z*) isomer would yield a meso compound.



(*Z*)

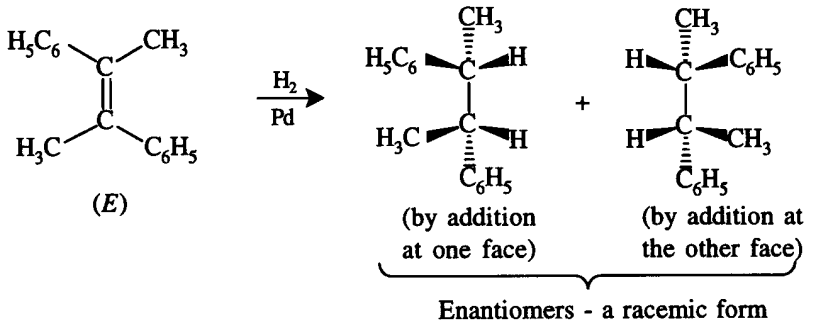


(by addition at one face)
A meso compound

(by addition at the other face)

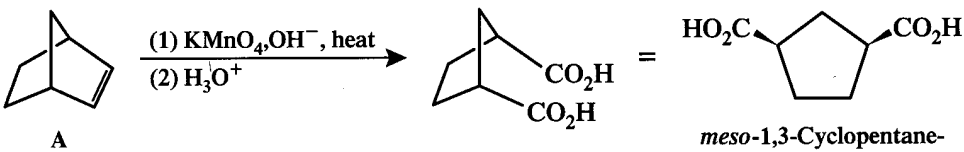
Syn addition of hydrogen to the (*E*) isomer would yield a racemic form:

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8 From the molecular formula of **A** and of its hydrogenation product **B,** we can conclude that **A** has two rings and a double bond. (**B** has two rings.)

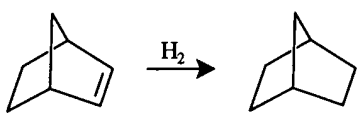
From the product of strong oxidation with $KMnO_4$ and its stereochemistry (i.e., compound **C**), we can deduce the structure of **A**.



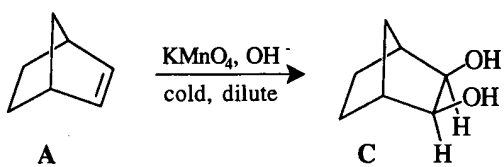
A

meso-1,3-Cyclopentane-dicarboxylic acid

Compound **B** is bicyclo[2.2.1]heptane and **C** is a glycol.



A **B**

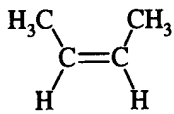


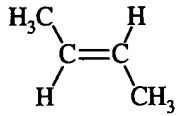
A **C**

Notice that **C** is also a meso compound.

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9 (a) $CH_3C{\equiv}CH \xrightarrow[\text{liq. } NH_3]{NaNH_2} CH_3C{\equiv}CNa \xrightarrow{CH_3I} CH_3C{\equiv}CCH_3$

(b) $CH_3C{\equiv}CCH_3$ [from (a)] $\xrightarrow[Ni_2B\ (P\text{-}2)]{H_2}$ 

(c) $CH_3C{\equiv}CCH_3$ [from (a)] $\xrightarrow[NH_3]{Li}$ 

(d) $CH_3C{\equiv}CH \xrightarrow[Ni_2B\ (P2)]{H_2} CH_3CH{=}CH_2 \xrightarrow[\text{light}\ 25°]{NBS} BrCH_2CH{=}CH_2$

$+$

$CH_3I \xrightarrow[Et_2O]{Li} CH_3Li \xrightarrow{CuI} (CH_3)_2CuLi$

$\longrightarrow CH_3CH_2CH{=}CH_2$

or

$CH_3C{\equiv}CH \xrightarrow[(2)\ CH_3Br]{(1)\ NaNH_2} CH_3C{\equiv}CCH_3 \xrightarrow[\text{or (1) Na, liq. } NH_3\ \ (2)\ NH_4Cl]{H_2\ \ Ni_2B\ (P2)} CH_3CH{=}CHCH_3$

$CH_3CH{=}CHCH_3 \xrightarrow{HBr} CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

$CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow[\text{heat}]{\textit{tert}\text{-BuOK},\ \textit{tert}\text{-BuOH},} CH_3CH_2CH{=}CH_2$

(e) $CH_3CH_2CH{=}CH_2$ [from (d)] $\xrightarrow[CCl_4]{NBS}$ $CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_2{=}CH_2 + CH_3CH{=}CHCH_2Br \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_2{=}CH{-}CH{=}CH_2$

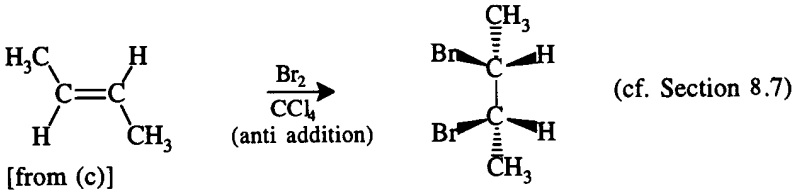
(f) $CH_3CH_2CH{=}CH_2$ [from (d)] $\xrightarrow[ROOR]{HBr} CH_3CH_2CH_2CH_2Br$

(g) $CH_3CH{=}CHCH_3$ [from (b) or (c)] $\xrightarrow[\text{no peroxides}]{HBr} CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

or

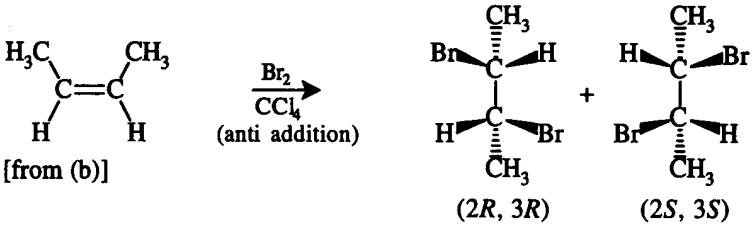
$CH_3CH_2CH{=}CH_2$ [from (d)] $\xrightarrow[\text{no peroxides}]{HBr} CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

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(h) 

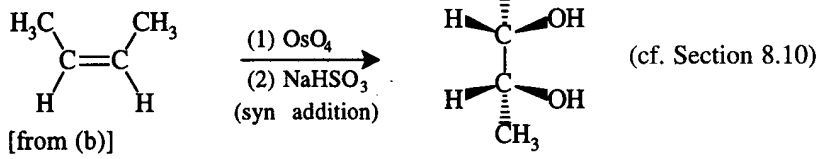
(cf. Section 8.7)

(2*R*, 3*S*)
A meso compound

(i) 

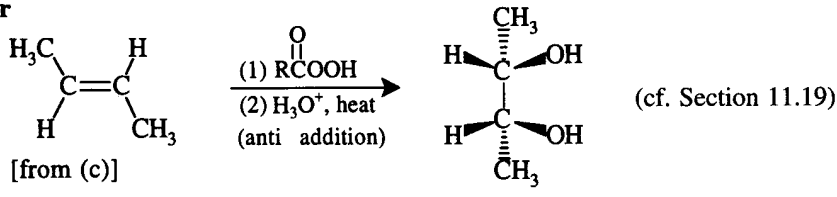
(2*R*, 3*R*) (2*S*, 3*S*)

A racemic form

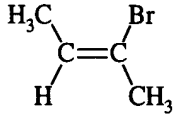
(j) 

(cf. Section 8.10)

or



(cf. Section 11.19)

(k) $CH_3C{\equiv}CCH_3$ $\xrightarrow[CH_3CO_2H]{HBr,Br^-}$ 

(cf. Section 8.13)

10 $CH_3\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}HCH_2CH_3$ $\xrightarrow[h\nu,\text{heat}]{Br_2}$ $CH_3\underset{\displaystyle CH_3}{\overset{\displaystyle Br}{\overset{|}{\underset{|}{C}}}}CH_2CH_3$ (cf. Section 10.6)

(a) $CH_3\underset{\displaystyle CH_3}{\overset{\displaystyle Br}{\overset{|}{\underset{|}{C}}}}CH_2CH_3$ $\xrightarrow[CH_3CH_2OH,\ \text{heat}]{CH_3CH_2ONa}$ $CH_3\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{=}CHCH_3$

(b) $CH_3\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{=}CHCH_3$ $\xrightarrow[H_2O]{H_3O^+}$ $CH_3\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}CH_2CH_3$

[from (a)]

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(c) $CH_3C(CH_3)=CHCH_3$ [from (a)] $\xrightarrow[(2)H_2O_2,\ OH^-]{(1)\ THF:\ BH_3}$ $CH_3CH(OH)CH_3$

(CH3)

(d) $CH_3CH(CH_3)CH=CH_2 \xrightarrow[CCl_4]{Br_2} CH_3CH(CH_3)CHBrCH_2Br \xrightarrow[heat]{3\ NaNH_2}$

$CH_3CH(CH_3)C\equiv CNa \xrightarrow{H_3O^+} CH_3CH(CH_3)C\equiv CH$

(e) $CH_3CH(CH_3)CH=CH_2 \xrightarrow[ROOR,\ heat]{HBr} CH_3CH(CH_3)CH_2CH_2Br$

(f) $CH_3CH(CH_3)CH=CH_2 \xrightarrow{HCl} CH_3CH(CH_3)CHClCH_3$

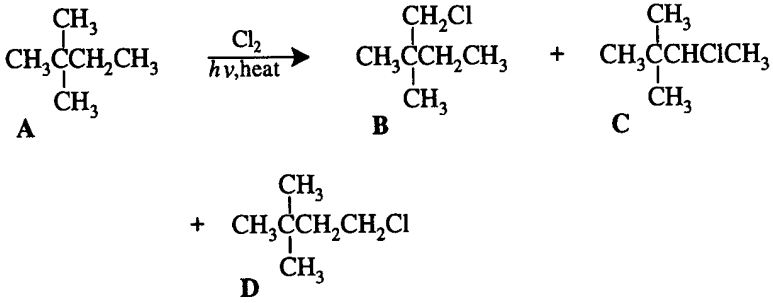
(g) $CH_3C(CH_3)=CHCH_3$ [from (a)] $\xrightarrow{HCl} CH_3CCl(CH_3)CH_2CH_3$

(h) $CH_3CH(CH_3)CH_2CH_2Br$ [from (e)] $\xrightarrow[acetone,\ S_N2]{NaI} CH_3CH(CH_3)CH_2CH_2I$

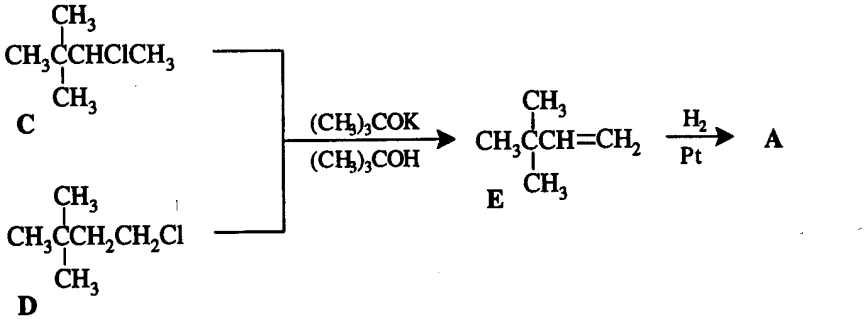
(i) $CH_3C(CH_3)=CHCH_3$ [from (a)] $\xrightarrow[(2)\ Zn,\ HOAc]{(1)\ O_3} CH_3CCH_3 + CH_3CH$

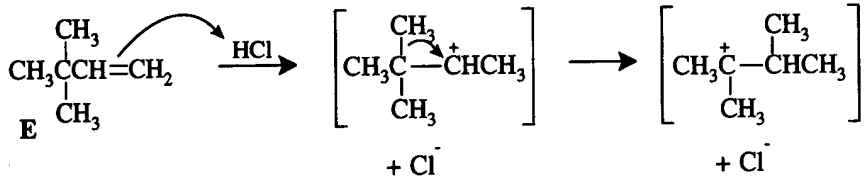
(j) $CH_3CH(CH_3)CH=CH_2 \xrightarrow[(2)\ Zn,\ HOAc]{(1)\ O_3} CH_3CH(CH_3)CH + HCH$

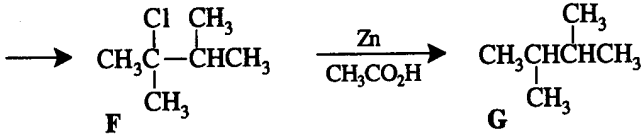
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11 

B cannot undergo dehydrohalogenation because it has no β hydrogen; however, **C** and **D** can, as shown next.





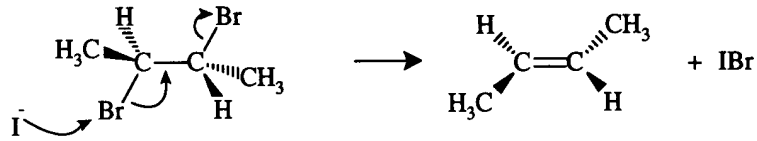


12

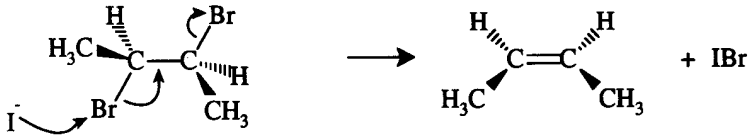
(a meso compound)

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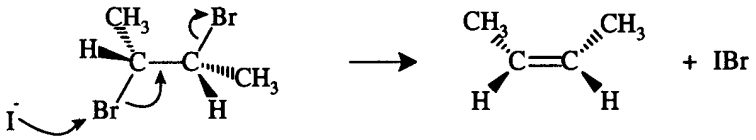
13 The eliminations are anti eliminations, requiring an anti periplanar arrangement of the bromine atoms.



meso-2,3-Dibromobutane → *trans*-2-Butene + IBr

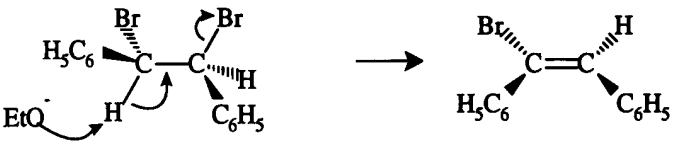


(2*S*,3*S*)-2,3-Dibromobutane → *cis*-2-Butene + IBr

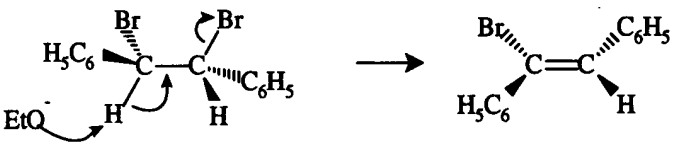


(2*R*,3*R*)-2,3-Dibromobutane → *cis*-2-Butene + IBr

14 The eliminations are anti eliminations, requiring an anti periplanar arrangement of the −H and −Br.



meso-1,2-Dibromo-1,2-diphenylethane → (*E*) -1-Bromo-1,2-diphenylethene

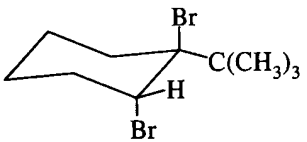


(2*R*,3*R*)-1,2-Dibromo-1,2-diphenylethane → (*Z*) -1-Bromo-1,2-diphenylethene

(2*S*,3*S*)-1,2-Dibromo-1,2-diphenylethane will also give (*Z*)-1-bromo-1,2-diphenylethene in an anti elimination.

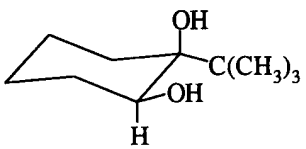
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15 In all the following structures, notice that the large *tert*-butyl group is equatorial.

(a) 

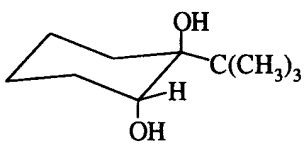
+ enantiomer
as a racemic form

(bromine addition is anti; cf. Section 8.7)

(b) 

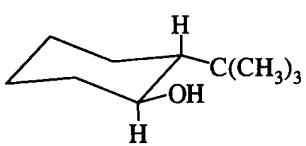
+ enantiomer
as a racemic form

(syn hydroxylation; cf. Section 8.10)

(c) 

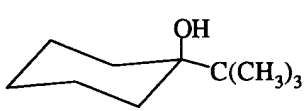
+ enantiomer
as a racemic form

(anti hydroxylation; cf. Section 11.19)

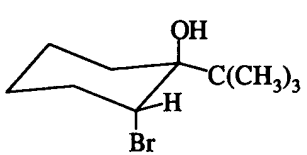
(d) 

+ enantiomer
as a racemic form

(syn and anti Markovnikov addition of —H and —OH; cf. Section 11.7)

(e) 

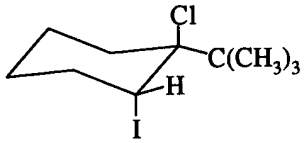
(Markovnikov addition of —H and —OH; cf. Section 11.4)

(f) 

+ enantiomer
as a racemic form

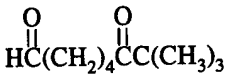
(anti addition of –Br and –OH, with –Br and –OH placement resulting from the more stable partial carbocation in the intermediate bromonium ion; cf. Section 8.8)

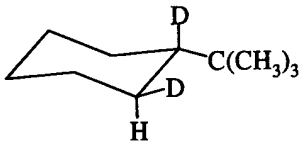
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(g) 

+ enantiomer
as a racemic form

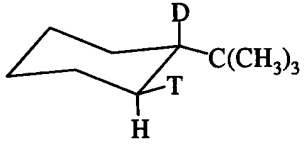
(anti addition of –I and –Cl, following Markovnikov's rule; cf. Section 8.2)

(h) 

(i) 

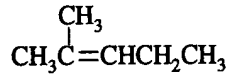
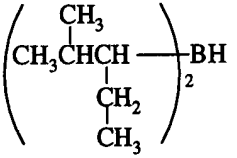
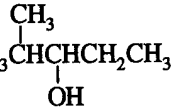
+ enantiomer
as a racemic form

(syn addition of deuterium; cf. Section 7.14)

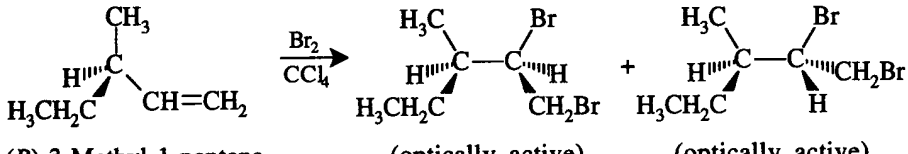
(j) 

+ enantiomer
as a racemic form

(syn, anti Markovnikov addition of −D and $-\underset{|}{B}-$, with $-\underset{|}{B}-$ being replaced by -T where it stands; cf. Section 11.7)

16 **A** =  **B** =  **C** = 

17 (a) The following products are diastereomers. They would have different boiling points and would be in separate fractions. Each fraction would be optically active.



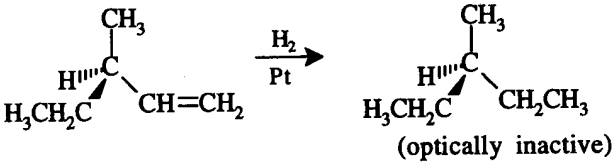
(*R*)-3-Methyl-1-pentene

(optically active) (optically active)

Diastereomers

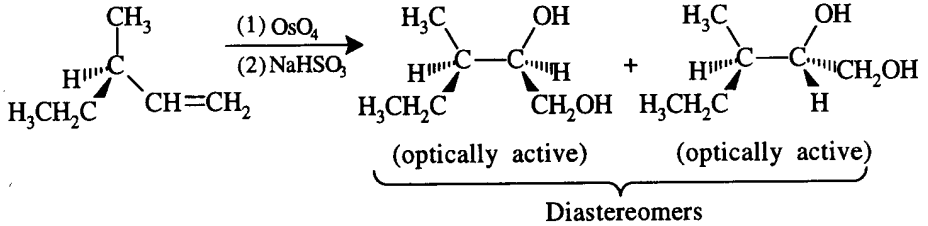
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(b) Only one product is formed. It is achiral, and, therefore, it would not be optically active.



(optically inactive)

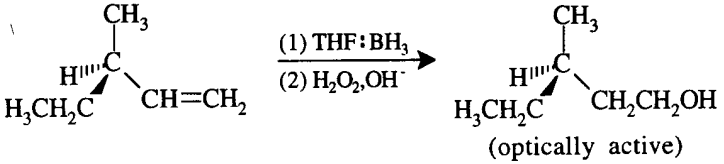
(c) Two diastereomeric products are formed. Two fractions would be obtained. Each fraction would be optically active.



(optically active) (optically active)

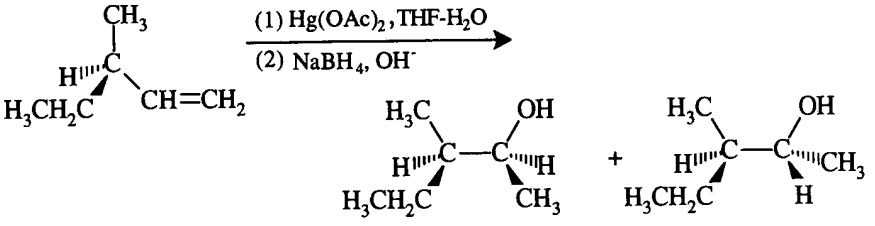
Diastereomers

(d) One optically active compound is produced.



(optically active)

(e) Two diastereomeric products are formed. Two fractions would be obtained. Each fraction would be optically active.

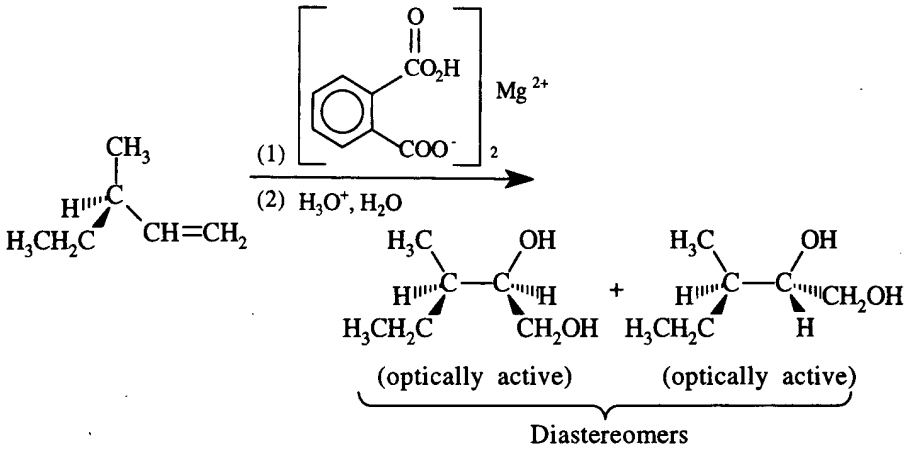


(optically active) (optically active)

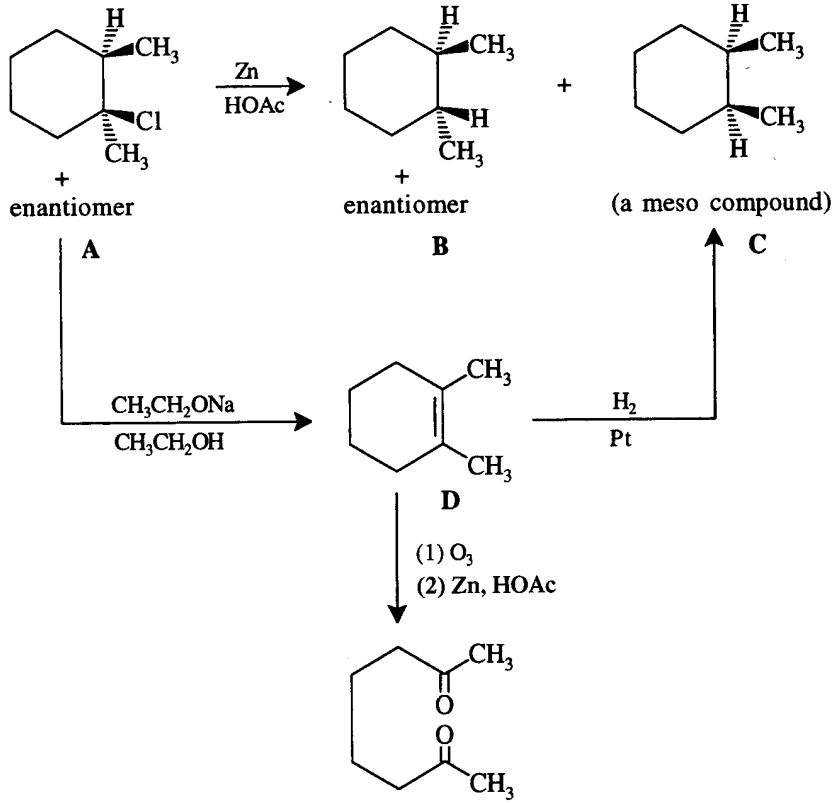
Diastereomers

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(f) Two diastereomeric products are formed. Two fractions would be obtained. Each fraction would be optically active.

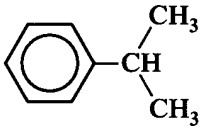


18



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19



m/z 120 = $M^{+\cdot}$

105 = $M^{+\cdot} - 15(CH_3\cdot) = C_6H_5{-}\overset{+}{C}HCH_3$

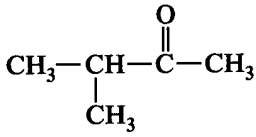
77 = $M^{+\cdot} - 43(i\text{-}Pr\cdot) = C_6H_5^+$

δ 7.2–7.6	5 ring protons
2.95	CH of isopropyl group
1.29	equivalent CH_3s of isopropyl group

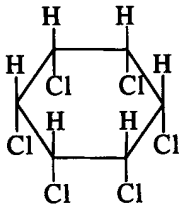
20 $C_5H_{10}O$ has IHD = 2

IR absorption indicates C=O

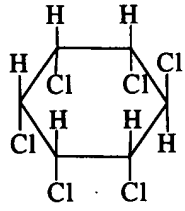
^{13}C NMR spectrum for **X** is consistent with structure



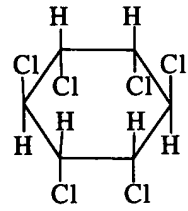
21 (a)



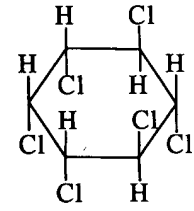
1 all *cis* meso



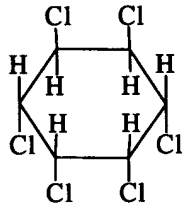
2 1-*trans* meso



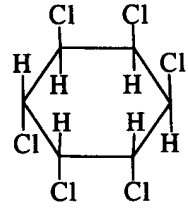
3 1,4-*trans* meso



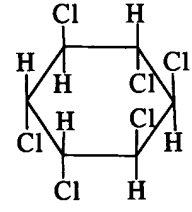
4 1,3-*trans* meso



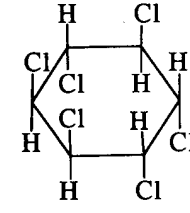
5 1,2-*trans* meso



6 1,2,3-*trans* meso

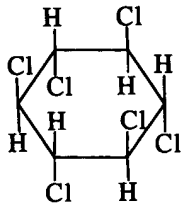


7



8

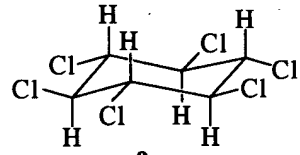
1,2,4-*trans* Enantiomers



9 1,3,5-*trans* meso

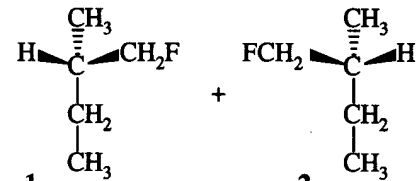
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(b) Isomer **9** is slow to react in an E2 reaction because in its more stable conformation (see following structure) all the chlorine atoms are equatorial and an anti periplanar transition state cannot be achieved. All other isomers **1-8** can have a −Cl axial and thus achieve an anti periplanar transition state.



9

22 (a) $CH_3CHCH_2CH_3$ (CH$_3$ on the CH) $\xrightarrow{F_2}$



1 + **2**

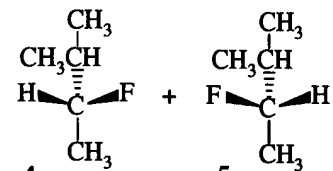
Enantiomers (obtained in one fraction as an optically inactive racemic form)

+ $CH_3CCH_2CH_3$ (F and CH$_3$ on the C; CH$_3$ on the CH)

3

(achiral and, therefore, optically inactive)

+



4 + **5**

Enantiomers (obtained in one fraction as an optically inactive racemic form)

+ $CH_3CHCH_2CH_2F$ (CH$_3$ on the CH)

6

(achiral and, therefore, optically inactive)

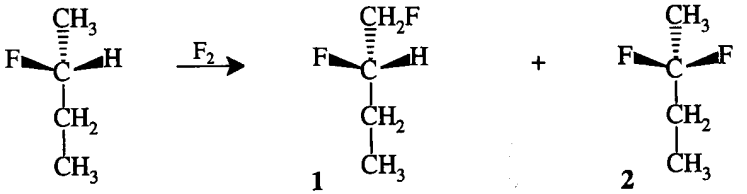
(b) Four fractions. The enantiomeric pairs would not be separated by fractional distillation because enantiomers have the same boiling points.

(c) All of the fractions would be optically inactive.

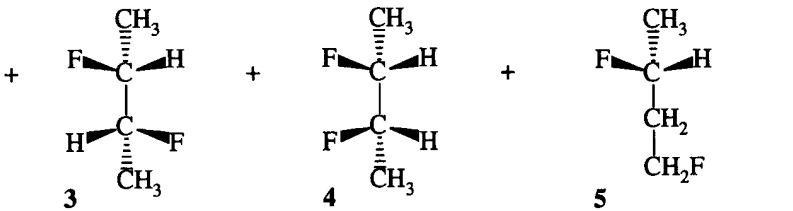
(d) The fraction containing **1** and **2** and the fraction containing **4** and **5.**

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23



(*R*)-2-Fluorobutane (optically active) (achiral and, therefore, optically inactive)

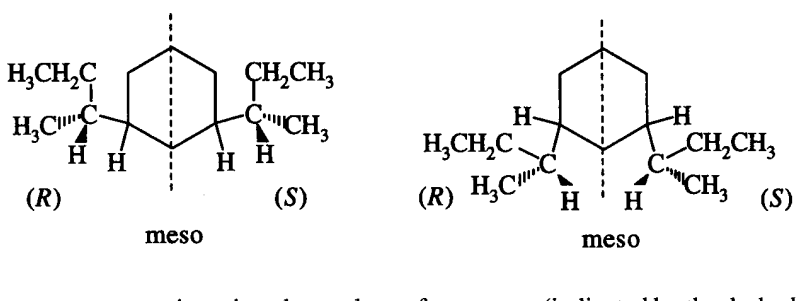


(optically active) meso compound (optically inactive) (optically active)

(b) Five. Compounds **3** and **4** are diastereomers. All others are constitutional isomers of each other.

(c) See above.

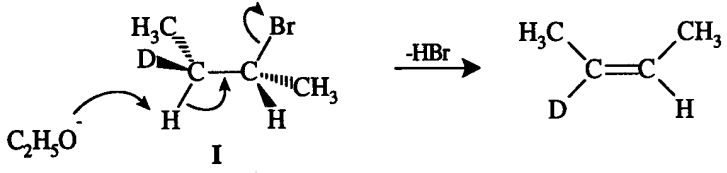
24



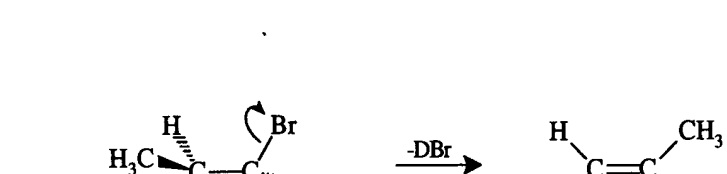
Each of the two structures just given has a plane of symmetry (indicated by the dashed line), and, therefore, each is a meso compound. The two structures are not superposable one on the other; therefore, they represent molecules of different compounds and are diastereomers.

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25 Only a proton or deuteron anti to the bromine can be eliminated; that is, the two groups undergoing elimination (H and Br or D and Br) must lie in an anti periplanar arrangement. The two conformations of *erythro*-2-bromobutane-3-*d* in which a proton or deuteron is anti periplanar to the bromine are **I** and **II.**



I



II

Conformation **I** can undergo loss of HBr to yield *cis*-2-butene-2-*d*. Conformation **II** can undergo loss of DBr to yield *trans*-2-butene.

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13 CONJUGATED UNSATURATED SYSTEMS

SOLUTIONS TO PROBLEMS

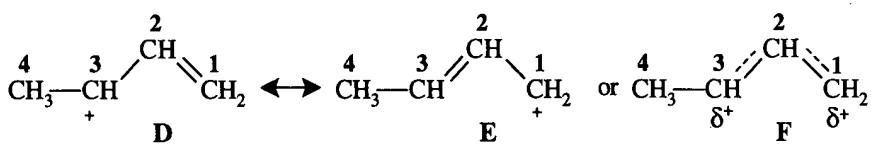
13.1 (a) $^{14}CH_2{=}CHCH_2X$ and $CH_2{=}CH{-}\overset{14}{C}H_2X$

(b) The reaction proceeds through the resonance-stabilized radical.

$$^{14}CH_2{=}CH{-}\dot{C}H_2 \longleftrightarrow {}^{14}\dot{C}H_2{-}CH{=}CH_2 \quad \text{or} \quad {}^{14}\overset{\delta\bullet}{C}H_2{\cdots}CH{\cdots}\overset{\delta\bullet}{C}H_2$$

Thus, attack on X_2 can occur by the carbon atom at either end of the chain since these atoms are equivalent.

(c) 50:50 because attack at the two ends of the chain is equally probable.

13.2 (a) 

(b) We know that the allylic cation is almost as stable as a tertiary carbocation. Here we find not only the resonance stabilization of an allylic cation but also the additional stabilization that arises from contributor **D** in which the plus charge is on a secondary carbon atom.

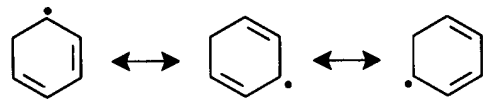
(c) $CH_3{-}\overset{Cl}{\overset{|}{C}}H{-}CH{=}CH_2$ and $CH_3{-}CH{=}CH{-}CH_2{-}Cl$, because the Cl will attack the chain at the two positive centers shown in structure **F**.

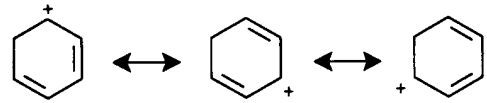
13.3 (a) $CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2^{\bullet} \longleftrightarrow {}^{\bullet}CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2$

(b) $CH_2{=}CH{-}\underset{+}{C}H{-}CH{=}CH_2 \longleftrightarrow {}^{+}CH_2{-}CH{=}CH{-}CH{=}CH_2 \longleftrightarrow$

$CH_2{=}CH{-}CH{=}CH{-}\overset{+}{C}H_2$

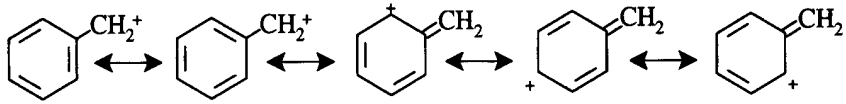
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(c) 

(d) 

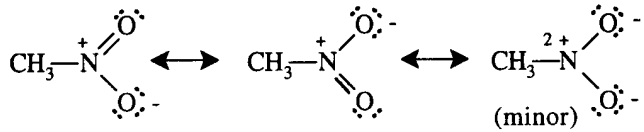
(e) $CH_3CH{=}CH{-}CH{=}\overset{+}{\underset{\cdot\cdot}{O}}H \longleftrightarrow CH_3CH{=}CH{-}\overset{+}{C}H{-}\underset{\cdot\cdot}{O}H \longleftrightarrow CH_3\overset{+}{C}H{-}CH{=}CH{-}\underset{\cdot\cdot}{O}H$

(f) $CH_2{=}CH{-}\ddot{B}r: \longleftrightarrow :CH_2{-}CH{=}\overset{+}{B}r:$

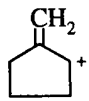
(g) 

(h) $:\overset{-}{C}H_2{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}{-}CH_3 \longleftrightarrow CH_2{=}\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}{-}CH_3$

(i) $CH_3{-}\ddot{S}{-}CH_2^+ \longleftrightarrow CH_3{-}\overset{+}{S}{=}CH_2$

(j) 

13.4 (a) $CH_3CH_2\overset{CH_3}{\overset{|}{\overset{+}{C}}}{-}CH{=}CH_2$ because the positive charge is on a tertiary carbon atom rather than a primary one (rule 8).

(b)  because the positive charge is on a secondary carbon atom rather than a primary one (rule 8).

(c) $CH_2{=}\overset{+}{N}(CH_3)_2$ because all atoms have a complete octet (rule 8b), and there are more covalent bonds (rule 8a).

(d) $CH_3{-}\overset{O}{\overset{\|}{C}}{-}OH$ because it has no charge separation (rule 8c).

(e) $CH_2{=}CH\dot{C}HCH{=}CH_2$ because the radical is on a secondary carbon atom rather than a primary one (rule 8).

(f) $:NH_2{-}C{\equiv}N:$ because it has no charge separation (rule 8c).

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13.5 In resonance structures, the positions of the nuclei must remain the same for all structures (rule 2). The keto and enol forms shown differ not only in the positions of their electrons, but also in the position of one of the hydrogen atoms. In the enol form, it is attached to an oxygen atom; in the keto form, it has been moved so that it is attached to a carbon atom.

13.6 (a) *cis*-1,3-Pentadiene, *trans,trans*-2,4-hexadiene, *cis,trans*-2,4-hexadiene, and 1,3-cyclohexadiene are conjugated dienes.

(b) 1,4-Cyclohexadiene and 1,4-pentadiene are isolated dienes.

(c) 1-Penten-4-yne is an isolated enyne.

13.7 The formula, C_6H_8, tells us that **A** and **B** have six hydrogen atoms less than an alkane. This unsaturation may be due to three double bonds, one triple bond and one double bond, or combinations of two double bonds and a ring, or one triple bond and a ring. Since both **A** and **B** react with 2 mol of H_2 to yield cyclohexane, they are either cyclohexyne or cyclohexadienes. The absorption maximum of 256 nm for **A** tells us that it is conjugated. Compound **B,** with no absorption maximum beyond 200 nm, possesses isolated double bonds. We can rule out cyclohexyne because of ring strain caused by the requirement of linearity of the —C≡C— system. Therefore, **A** is 1,3-cyclohexadiene; **B** is 1,4-cyclohexadiene.

13.8 All three compounds have an unbranched five-carbon chain, because the product of hydrogenation is unbranched pentane. The formula, C_5H_6, suggests that they have one double bond and one triple bond. Compounds **D, E,** and **F** must differ, therefore, in the way the multiple bonds are distributed in the chain. Compounds **E** and **F** have a terminal —C≡CH [IR absorption at ~3300 cm^{-1}]. The UV absorption maximum near 230 nm for **D** and **E** suggests that in these compounds, the multiple bonds are conjugated. The structures are

$CH_3—C{\equiv}C—CH{=}CH_2$ **D** $\quad HC{\equiv}C—CH{=}CH—CH_3$ **E** $\quad HC{\equiv}C—CH_2—CH{=}CH_2$ **F**

13.9 (a) Recall that 1,2 and 1,4 addition refer to the conjugated system itself and not the entire carbon chain. $CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH{=}CHCH_3$ and $CH_3CH_2CH{=}\underset{\displaystyle Cl}{\underset{|}{C}}HCHCH_3$

(b) The most stable cation is a hybrid of equivalent forms:

$$CH_3\overset{+}{C}HCH{=}CHCH_3 \longleftrightarrow CH_3CH{=}CH\overset{+}{C}HCH_3$$

Thus, 1,4 and 1,2 addition yield the same product.

$$CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH{=}CHCH_3$$

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13.10 Addition of the proton gives the resonance hybrid.

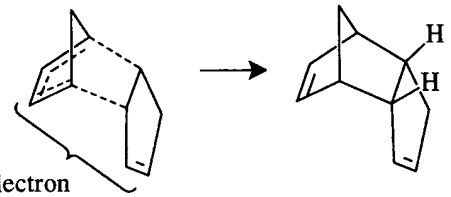
(a) $CH_3-\overset{+}{C}H-CH=CH_2 \longleftrightarrow CH_3-CH=CH-\overset{+}{C}H_2$

I **II**

The inductive effect of the methyl group in **I** stabilizes the positive charge on the adjacent carbon. Such stabilization of the positive charge does not occur in **II.** Because **I** contributes more heavily to the resonance hybrid than does **II,** C2 bears a greater positive charge and reacts faster with the bromide ion.

(b) In the 1,4-addition product, the double bond is more highly substituted than in the 1,2-addition product; hence it is the more stable alkene.

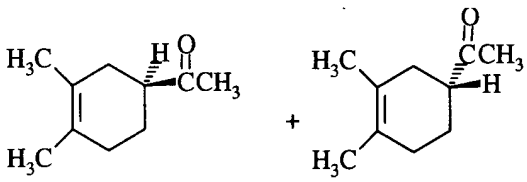
13.11 (a), (c)



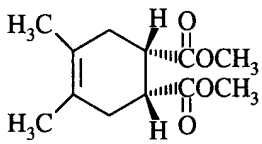
(b) π-Electron interaction occurs here.

Endo adduct

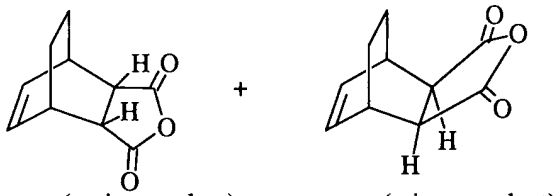
13.12 (a)



(b)

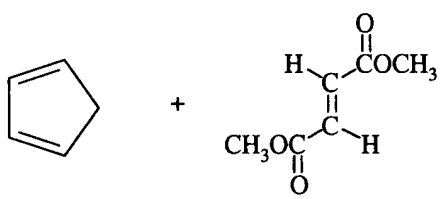


(c)



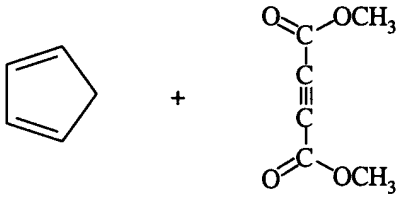
(major product) (minor product)

13.13 Use the trans diester because the stereochemistry is retained in the adduct.

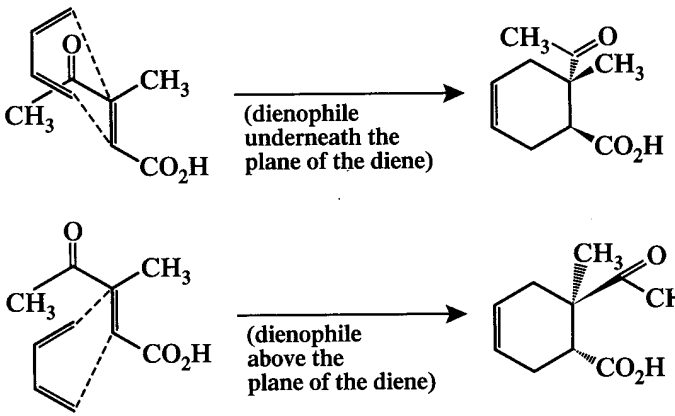


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13.14



13.15



(Or, in each case, the other face of the dienophile could present itself to the diene, resulting in the respective enantiomer.)

13.16 (a) $BrCH_2CH_2CH_2CH_2Br \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_2{=}CH{-}CH{=}CH_2$

(b) $HOCH_2CH_2CH_2CH_2OH \xrightarrow[\text{heat}]{\text{concd } H_2SO_4} CH_2{=}CH{-}CH{=}CH_2$

(c) $CH_2{=}CH{-}CH_2CH_2{-}OH \xrightarrow[\text{heat}]{\text{concd } H_2SO_4} CH_2{=}CH{-}CH{=}CH_2$

(d) $CH_2{=}CH{-}CH_2CH_2{-}Cl \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_2{=}CH{-}CH{=}CH_2$

(e) $CH_2{=}CH{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_3 \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_2{=}CH{-}CH{=}CH_2$

(f) $CH_2{=}CH{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3 \xrightarrow[\text{heat}]{\text{concd. } H_2SO_4} CH_2{=}CH{-}CH{=}CH_2$

(g) $CH_2{=}CH{-}C{\equiv}CH + H_2 \xrightarrow{Ni_2B\ (P\text{-}2)} CH_2{=}CH{-}CH{=}CH_2$

13.17 $CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$

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13.18 (a) $Cl-CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH=CH_2$ + $Cl-CH_2-CH=CH-CH_2-Cl$

(b) $CH_2(Cl)-CH(Cl)-CH(Cl)-CH_2(Cl)$ (c) $CH_2(Br)-CH(Br)-CH(Br)-CH_2(Br)$

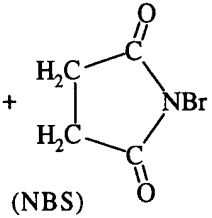
(d) $CH_3-CH_2-CH_2-CH_3$

(e) $Cl-CH_2-\underset{\displaystyle OH}{\underset{|}{C}}H-CH=CH_2$ + $Cl-CH_2-CH=CH-CH_2-OH$

[+ $ClCH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH=CH_2$ + $ClCH_2CH=CHCH_2Cl$]

(f) 4 CO_2 (*Note:* $KMnO_4$ oxidizes HO_2C-CO_2H to 2 CO_2)

(g) $CH_3-\underset{\displaystyle OH}{\underset{|}{C}}H-CH=CH_2$ + $CH_3-CH=CH-CH_2-OH$

13.19 (a) $CH_2=CH-CH_2-CH_3$ +  (NBS) $\xrightarrow{CCl_4}$ $CH_2=CH-\underset{\displaystyle Br}{\underset{|}{C}}H-CH_3$

(+ $CH_2(Br)-CH=CH-CH_3$)

$\xrightarrow[(CH_3)_3COH]{(CH_3)_3COK}$ $CH_2=CH-CH=CH_2$

Note: In the second step, both allylic halides undergo elimination of **HBr** to yield 1,3-butadiene; therefore, separating the mixture produced in the first step is unnecessary. The $BrCH_2CH=CHCH_3$ undergoes a 1,4 elimination (the opposite of a 1,4 addition).

(b) $CH_2=CH-CH_2-CH_2-CH_3$ + NBS $\xrightarrow{CCl_4}$ $CH_2=CH-\underset{\displaystyle Br}{\underset{|}{C}}H-CH_2-CH_3$

(+ $CH_2(Br)-CH=CH-CH_2-CH_3$) $\xrightarrow[(CH_3)_3COH]{(CH_3)_3COK}$ $CH_2=CH-CH=CH-CH_3$

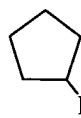
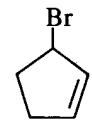
Here again both products undergo elimination of **HBr** to yield 1,3-pentadiene.

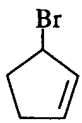
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(c) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{heat}]{\text{concd } H_2SO_4} CH_3CH{=}CHCH_3$ (+ $CH_3CH_2CH{=}CH_2$) [as in (a)]

$CH_2{-}CH{=}CH{-}CH_2$ (Br, Br) $\xleftarrow[\text{heat}]{Br_2} CH_2{=}CH{-}CH{=}CH_2$

(d) $CH_3{-}CH{=}CH{-}CH_3 + NBS \xrightarrow{CCl_4} CH_3{-}CH{=}CH{-}CH_2Br + CH_2{=}CH{-}CHBr{-}CH_3$

(e)  (excess) + $Br_2 \xrightarrow[\text{heat}]{\text{light}}$  $\xrightarrow[(CH_3)_3COH]{(CH_3)_3COK}$  $\xrightarrow[CCl_4]{NBS}$ 

(f)  $\xrightarrow[(CH_3)_3COH]{(CH_3)_3COK}$  (same as )

13.20 $R{-}\ddot{O}{-}\ddot{O}{-}R \xrightarrow[\text{or light}]{\text{heat}} 2\ R{-}\ddot{O}\cdot$

$R{-}\ddot{O}\cdot + H{-}\ddot{B}r: \longrightarrow R{-}\ddot{O}{-}H + \cdot\ddot{B}r:$

$CH_2{=}CH{-}CH{=}CH_2 + \cdot\ddot{B}r: \longrightarrow \left[CH_2{=}CH{-}\dot{C}H{-}CH_2 (Br) \longleftrightarrow \dot{C}H_2{-}CH{=}CH{-}CH_2 (Br)\right]$

$\xrightarrow{HBr} CH_2{=}CH{-}CH(H){-}CH_2(Br) + CH_2{-}CH{=}CH{-}CH_2(H,Br) + \cdot\ddot{B}r:$

(*E* and *Z*)

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13.21 Various IR, ^1H NMR, ^{13}C NMR, and MS features could be used to differentiate the members of any of these pairs. IR absorptions can be used to indicate whether double or triple bonds are present in a given molecule, or whether a hydroxyl group or halogen is present. Chemical shifts in the proton and carbon NMR spectra indicated can also be used to indicate the hybridization state of carbon atoms. The number of signals in the proton or carbon NMR spectrum for a given compound can suggest whether there is symmetry to the structure or not. Splitting patterns in the proton spectra can give detailed information about the connectivity of atoms. Mass spectra will indicate molecular weight differences when the molecular ions are present. Fragmentation patterns can indicate specific aspects of molecular structure characteristic to one member of a pair or another. UV would distinguish members of a pair where one is conjugated and the other is not. Consult tables with representative spectral information to predict specific aspects of the spectra for each compound.

13.22 (a) Because a highly resonance-stabilized radical is formed:

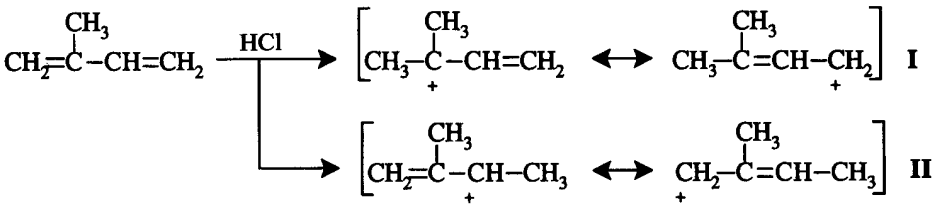
$$CH_2{=}CH{-}\dot{C}H{-}CH{=}CH_2 \longleftrightarrow CH_2{=}CH{-}CH{=}CH{-}\dot{C}H_2 \longleftrightarrow \dot{C}H_2{-}CH{=}CH{-}CH{=}CH_2$$

(b) Because the carbanion is more stable:

$$CH_2{=}CH{-}\ddot{C}H^-{-}CH{=}CH_2 \longleftrightarrow CH_2{=}CH{-}CH{=}CH{-}\ddot{C}H_2^- \longleftrightarrow \ddot{C}H_2^-{-}CH{=}CH{-}CH{=}CH_2$$

That is, we can write more reasonance structures of nearly equal energies.

13.23

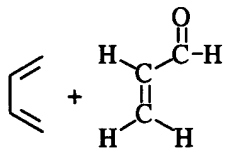


The resonance hybrid, **I,** has the positive charge, in part, on the tertiary carbon atom; in **II,** the positive charge is on primary and secondary carbon atoms only. Therefore, hybrid **I** is more stable and will be the intermediate carbocation. A 1,4 addition to **I** gives

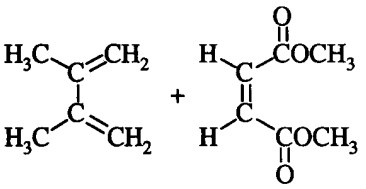
$$CH_3{-}\underset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH_2{-}Cl$$

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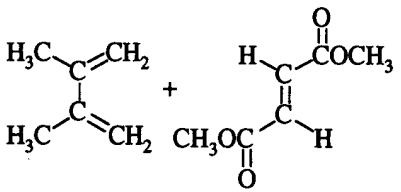
13.24 (a)



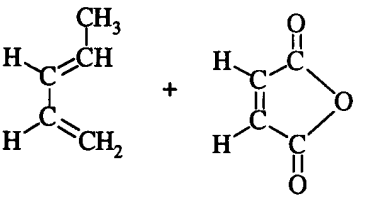
(b)



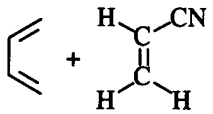
(c)



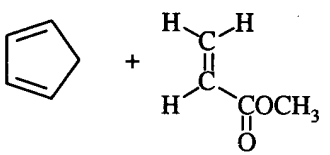
(d)



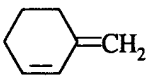
(e)



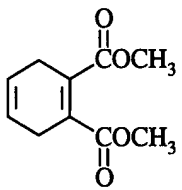
(f)



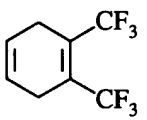
13.25 Neither compound can assume the s-cis conformation. 1,3-Butadiyne is linear, and

 is held in an s-trans conformation by the requirements of the ring.

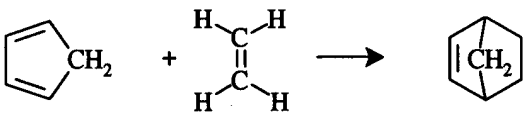
13.26 (a)



(b)



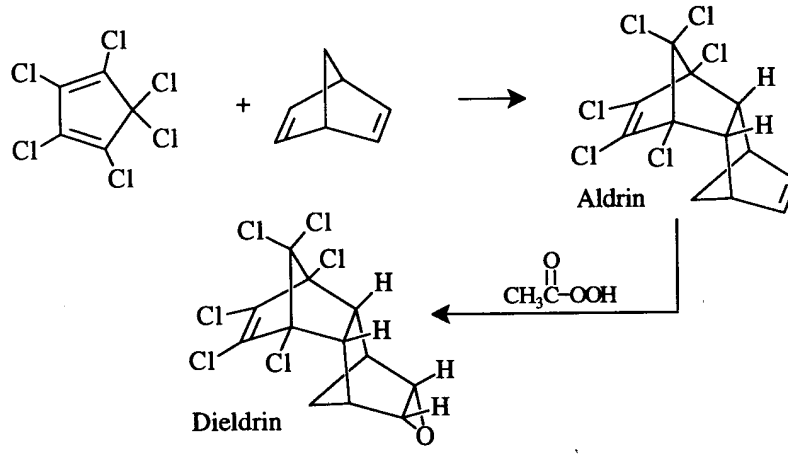
13.27



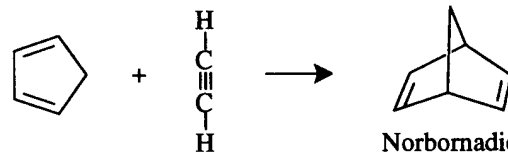
13.28 The endo adduct is less stable than the exo, but is produced at a faster rate at 25°C. At 90°C the Diels-Alder reaction becomes reversible; an equilibrium is established, and the more stable exo adduct predominates.

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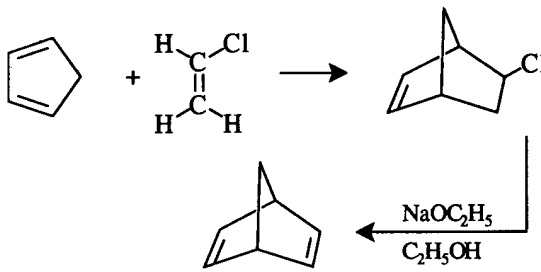
13.29



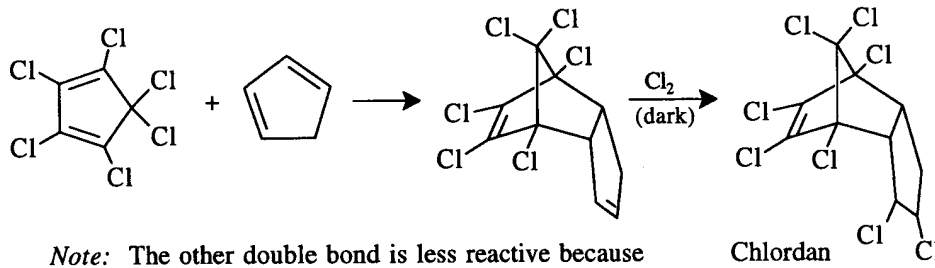
13.30 (a)



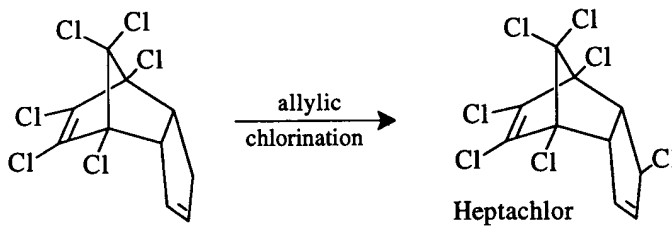
(b)



13.31

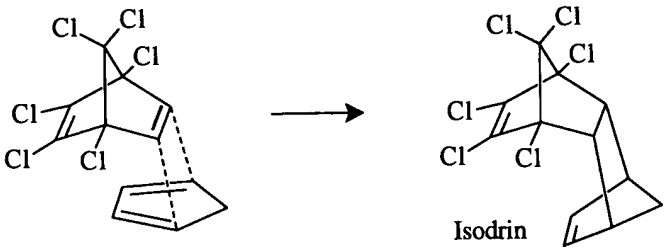


Note: The other double bond is less reactive because of the presence of the two chlorine substituents.



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13.32



13.33 Protonation of the alcohol and loss of water lead to an allylic cation that can react with a chloride ion at either C1 or C3.

$$CH_3CH{=}CHCH_2OH \xrightarrow{H^+} CH_3CH{=}CHCH_2{-}\overset{+}{O}(H){-}H \xrightarrow{-H_2O}$$

$$CH_3CH{=}\overset{+}{C}HCH_2 \longleftrightarrow CH_3\overset{+}{C}HCH{=}CH_2 \xrightarrow{Cl^-}$$

$$CH_3CH{=}CHCH_2Cl \quad + \quad CH_3\underset{Cl}{C}HCH{=}CH_2$$

13.34 (1) $CH_2{=}CH{-}CH{=}CH_2 + Cl_2 \longrightarrow ClCH_2{-}\overset{+}{C}H{-}CH{=}CH_2$

$$ClCH_2{-}CH{=}CH{-}\overset{+}{C}H_2$$

$$ClCH_2{-}CH{=}CH{-}\overset{+}{C}H_2$$

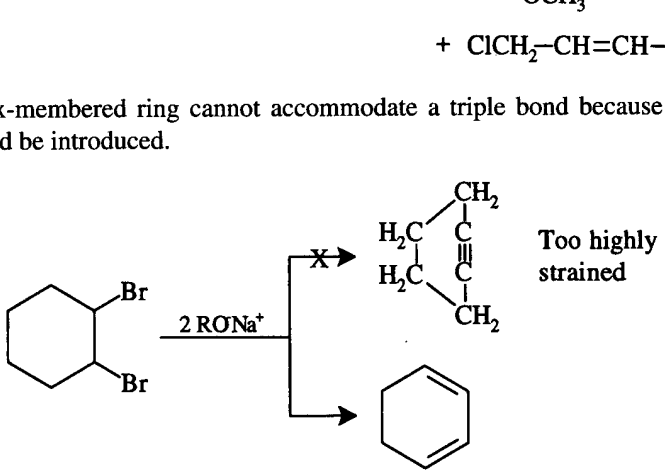
$$\delta^+ \qquad \delta^+$$

$$ClCH_2{-}CH{=}CH{=}CH_2$$

(2) $ClCH_2{-}CH{=}CH{=}CH_2 \xrightarrow[(-H^+)]{CH_3OH} ClCH_2{-}\underset{OCH_3}{CH}{-}CH{=}CH_2$

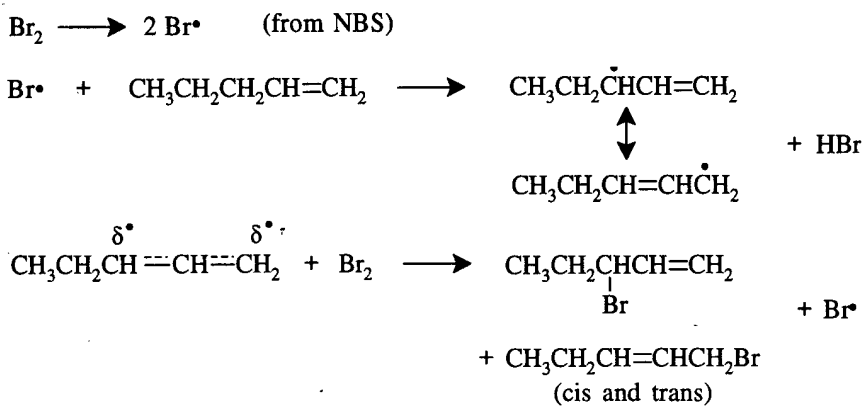
$$+ \quad ClCH_2{-}CH{=}CH{-}CH_2OCH_3$$

13.35 A six-membered ring cannot accommodate a triple bond because of the strain that would be introduced.

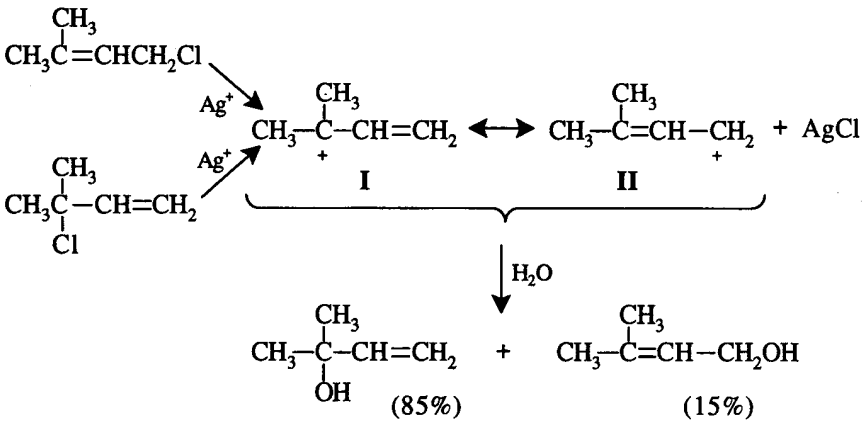


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13.36 The products are $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH=CH_2$ and $CH_3CH_2CH=CHCH_2Br$ (cis and trans). They are formed from an allylic radical in the following way:

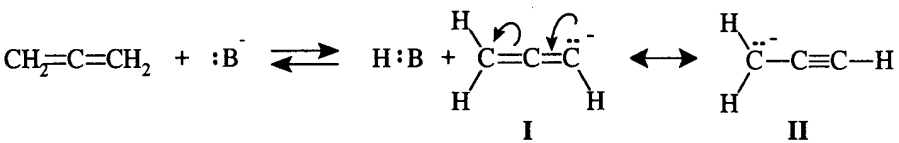


13.37 (a) The same carbocation (a resonance hybrid) is produced in the dissociation step:



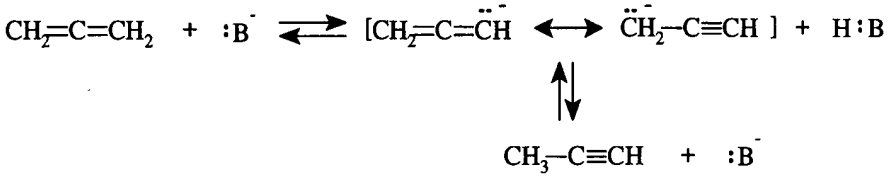
(b) Structure **I** contributes more than **II** to the resonance hybrid of the carbocation (rule 8). Therefore, the hybrid carbocation has a larger partial positive charge on the tertiary carbon atom than on the primary carbon atom. Reaction of the carbocation with water will therefore occur more frequently at the tertiary carbon atom.

13.38 (a) Propyne. (b) Base (: B^-) removes a proton, leaving the anion whose resonance structures are shown:

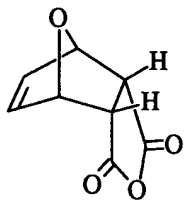


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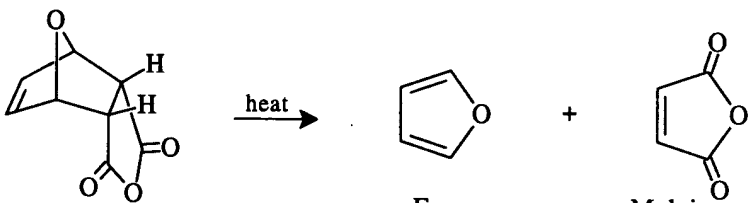
Reaction with H:B may then occur at the CH_2 carbanion. The overall reaction is



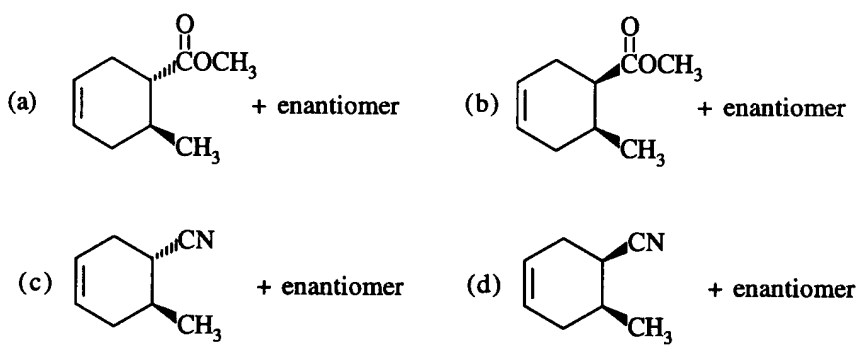
13.39 The first crystalline solid is the Diels-Alder adduct below, mp 125°C,



On melting, this adduct undergoes a reverse Diels-Alder reaction, yielding furan (which vaporizes) and maleic anhydride, mp 56°C,



13.40

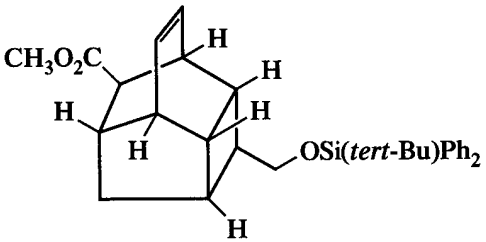


13.41 The product formed when butyl bromide undergoes elimination is 1-butene, a simple monosubstituted alkene. When 4-bromo-1-butene undergoes elimination, the product is 1,3-butadiene, a conjugated diene, and therefore, a more stable product. The transition states leading to the products reflect the relative stabilities of the products. Since the transition state leading to 1,3-butadiene has the lower free energy of activation of the two, the elimination reaction of 4-bromo-1-butene will occur more rapidly.

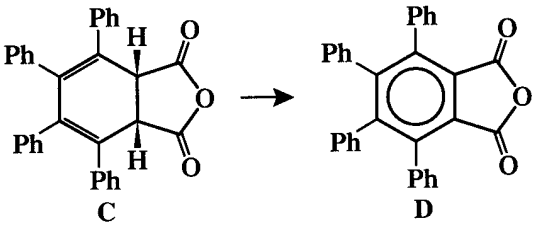
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13.42 The diene portion of the molecule is locked into an s-trans conformation. It cannot, therefore, achieve the s-cis conformation necessary for a Diels-Alder reaction.

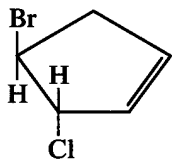
13.43



***13.44**

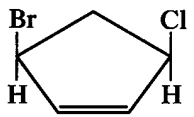


***13.45** (a)



(isomer *2*)

(b)



(isomer *1*)

(c) See above

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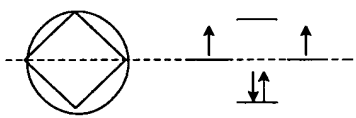
14 AROMATIC COMPOUNDS

SOLUTIONS TO PROBLEMS

14.1 Compounds (a) and (b) would yield only one monosubstitution product.

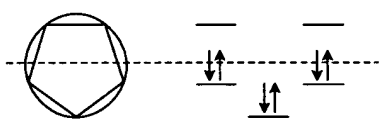
14.2 Resonance structures are defined as being structures that differ *only* in the positions of the electrons. In the two 1,3,5-cyclohexatrienes shown, the carbon atoms are in different positions; therefore, they cannot be resonance structures.

14.3 Inscribing a square in a circle with one corner at the bottom gives the following results:

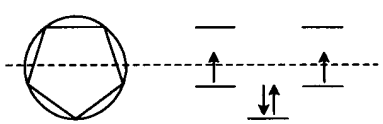


We see, therefore, that cyclobutadiene would be a diradical and would not be aromatic.

14.4 (a)



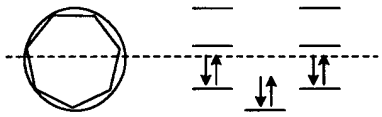
The cyclopentadienyl anion (above) should be aromatic because it has a closed bonding shell of delocalized π electrons.
(b) and (c) The cyclopentadienyl cation (below) would be a diradical. We would not expect it to be aromatic.



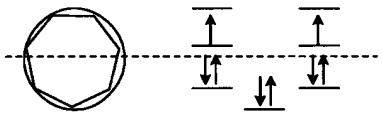
(d) No, 4 is not a Hückel number.

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14.5 (a) The cycloheptatrienyl cation (below) would be aromatic because it would have a closed bonding shell of delocalized π electrons.



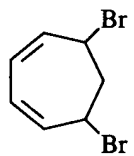
(b) No, the cycloheptatrienyl anion (below) would be a diradical.



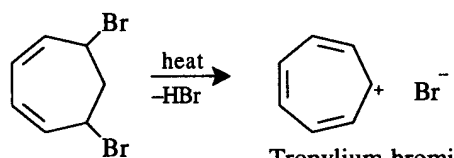
(c) No, 8 is not a Hückel number.

14.6 If the 1,3,5-cycloheptatrienyl anion *were* aromatic, we would expect it to be unusually stable. This would mean that 1,3,5-cycloheptatriene should be unusually acidic. The fact that 1,3,5-cycloheptatriene is not unusually acidic (it is less acidic than 1,3,5-heptatriene) confirms the prediction made in the previous problem, that the 1,3,5-cycloheptatrienyl anion should not be aromatic.

14.7 (a)



(b)

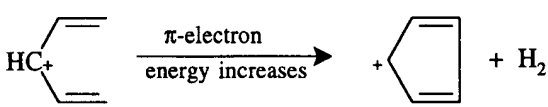


Tropylium bromide

These results suggest that the bonding in tropylium bromide is ionic; that is, it consists of a positive tropylium ion and a negative bromide ion.

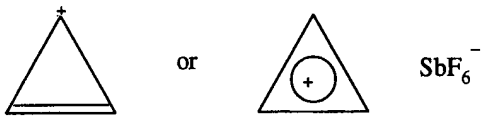
14.8 It suggests that the cyclopropenyl cation should be aromatic.

14.9 The fact that the cyclopentadienyl cation is antiaromatic means that the following hypothetical transformation would occur with an increase in π-electron energy.



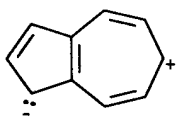
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14.10 The cyclopropenyl cation (below).

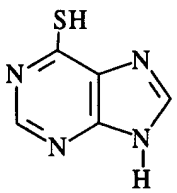


14.11 The high field signal arises from the six methyl protons of *trans*-15,16-dimethyldihydropyrene, which by virtue of their location are strongly shielded by the magnetic field created by the aromatic ring current (see Figure 14.8).

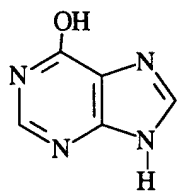
14.12 Major contributors to the hybrid must be ones that involve separated charges. Contributors like the following would have separated charges, and would have aromatic five- and seven-membered rings.



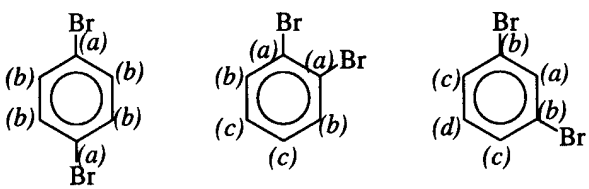
14.13 (a)



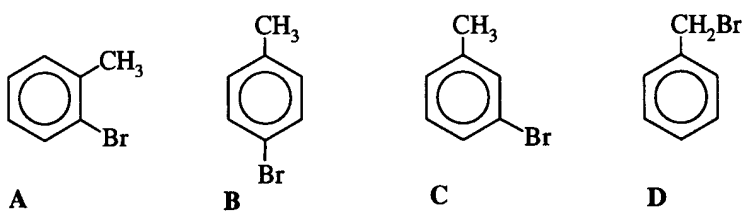
(b)



14.14 Because of their symmetries, *p*-dibromobenzene would give two ^{13}C signals, *o*-dibromobenzene would give three, and *m*-dibromobenzene would give four.



14.15



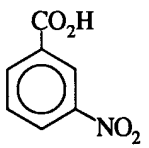
A. Strong absorption at 740 cm^{-1} is characteristic of ortho substitution.

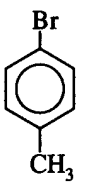
B. A very strong absorption peak at 800 cm^{-1} is characteristic of para substitution.

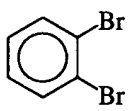
C. Strong absorption peaks at 680 and 760 cm^{-1} are characteristic of meta substitution.

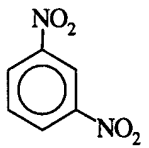
D. Strong absorption peaks at 693 and 765 cm^{-1} are characteristic of a monosubstituted benzene ring.

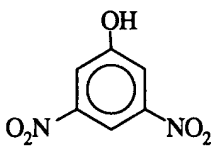
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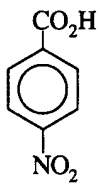
14.16 (a) 

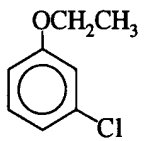
(b) 

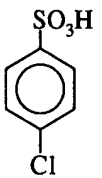
(c) 

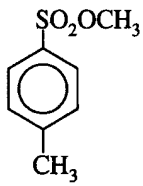
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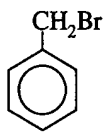
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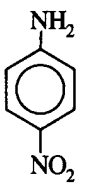
(f) 

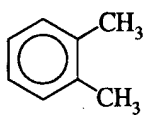
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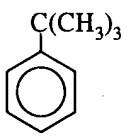
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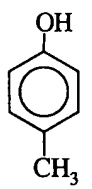
(i) 

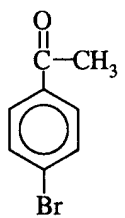
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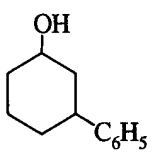
(k) 

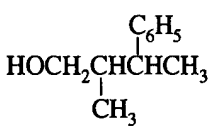
(l) 

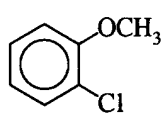
(m) 

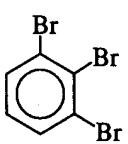
(n) 

(o) 

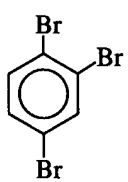
(p) 

(q) 

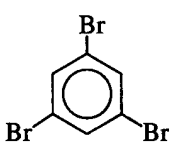
(r) 

14.17 (a) 

1,2,3-Tribromobenzene



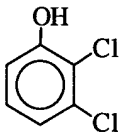
1,2,4-Tribromobenzene



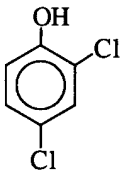
1,3,5-Tribromobenzene

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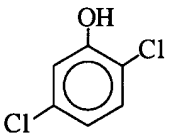
(b)



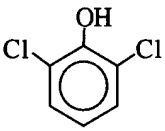
2,3-Dichlorophenol



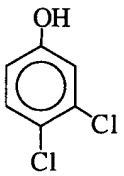
2,4-Dichlorophenol



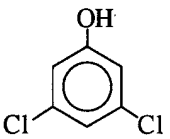
2,5-Dichlorophenol



2,6-Dichlorophenol

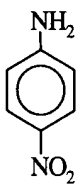


3,4-Dichlorophenol

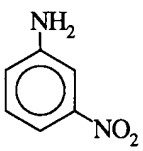


3,5-Dichlorophenol

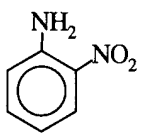
(c)



4-Nitroaniline (*p*-nitroaniline)

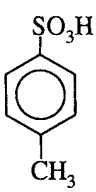


3-Nitroaniline (*m*-nitroaniline)

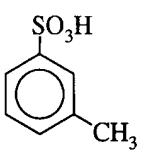


2-Nitroaniline (*o*-nitroaniline)

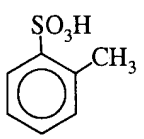
(d)



4-Methylbenzenesulfonic acid (*p*-toluenesulfonic acid)

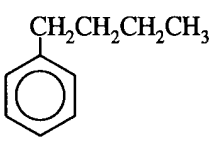


3-Methylbenzenesulfonic acid (*m*-toluenesulfonic acid)

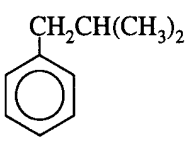


2-Methylbenzenesulfonic acid (*o*-toluenesulfonic acid)

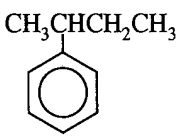
(e)



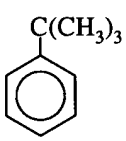
Butylbenzene



Isobutylbenzene



sec-Butylbenzene



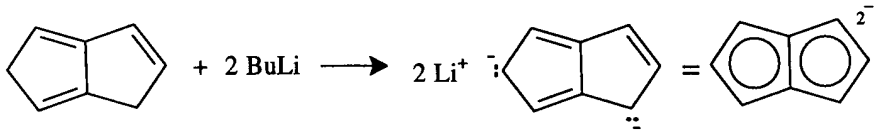
tert-Butylbenzene

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14.18 Hückel's rule should apply to both pentalene and heptalene. Pentalene's antiaromaticity can be attributed to its having 8 π electrons. Heptalene's lack of aromaticity can be attributed to its having 12 π electrons. Neither 8 nor 12 is a Hückel number.

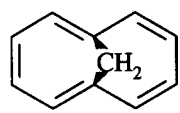
14.19 (a) The extra two electrons go into the two partly filled (nonbonding) molecular orbitals (Fig. 14.6), causing them to become filled. The dianion, therefore, is not a diradical. Moreover, the cyclooctatetraene dianion has 10 π electrons (a Hückel number), and this apparently gives it the stability of an aromatic compound. (The highest occupied molecular orbitals may become slightly lower in energy and become bonding molecular orbitals.) The stability gained by becoming aromatic is apparently large enough to overcome the extra strain involved in having the ring of the dianion become planar.

(b) The strong base (butyllithium) removes two protons from the compound on the left. This acid-base reaction leads to the formation of the 10 π electron pentalene dianion, an aromatic dianion.

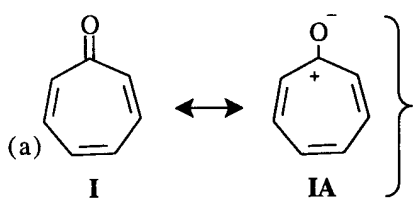


Pentalene dianion

14.20 The bridging $-CH_2-$group causes the 10 π electron ring system (below) to become planar. This allows the ring to become aromatic.

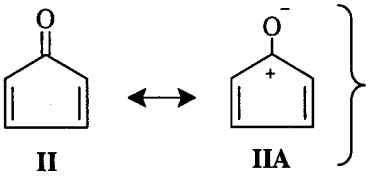


14.21 (a) Resonance contributors that involve the carbonyl group of **I** resemble the *aromatic* cycloheptatrienyl cation and thus stabilize **I.** Similar contributors to the hybrid of **II** resemble the *antiaromatic* cyclopentadienyl cation (see Problem 14.9) and thus destabilize **II.**



Contributors like **IA** are exceptionally stable because they resemble an aromatic compound. They therefore make large stabilizing contributions to the hybrid.

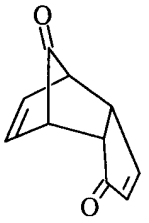
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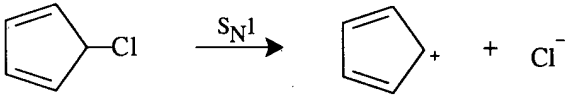
II IIA

Contributors like **IIA** are exceptionally unstable because they resemble an antiaromatic compound. Any contribution they make to the hybrid is destabilizing.

(b)

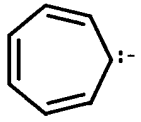


14.22 Ionization of 5-chloro-1,3-cyclopentadiene would produce a cyclopentadienyl cation, and the cyclopentadienyl cation (see Problem 14.9) would be highly unstable because it would be antiaromatic.

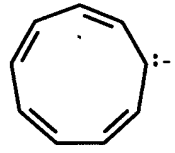


Antiaromatic ion
(highly unstable)

14.23 (a) The cycloheptatrienyl anion has 8 π electrons and does not obey Hückel's rule; the cyclononatetraenyl anion with 10 π electrons obeys Hückel's rule.



Cycloheptatrienyl anion
8 π-electrons
Antiaromatic



Cyclononatetraenyl anion
10 π-electrons
Aromatic

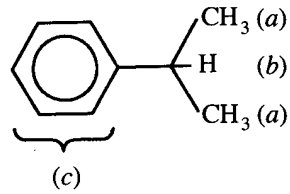
(b) By adding 2 π electrons, [16]annulene becomes an 18 π electron system and therefore obeys Hückel's rule.

14.24 As noted in Problem 13.28, furan can serve as the diene component of Diels-Alder reactions, readily losing all aromatic character in the process. Benzene, on the other hand, is so unreactive in a Diels-Alder reaction that it can be used as a nonreactive solvent for Diels-Alder reactions.

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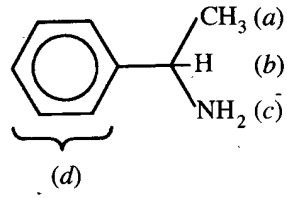
14.25

A



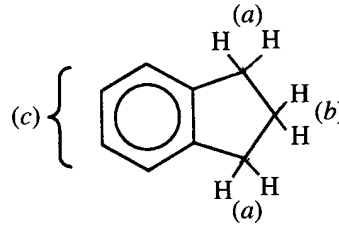
(*a*) doublet δ 1.25
(*b*) septet δ 2.9
(*c*) multiplet δ 7.3

B



(*a*) doublet δ 1.35
(*b*) quartet δ 4.1
(*c*) singlet δ 1.8
(*d*) multiplet δ 7.3

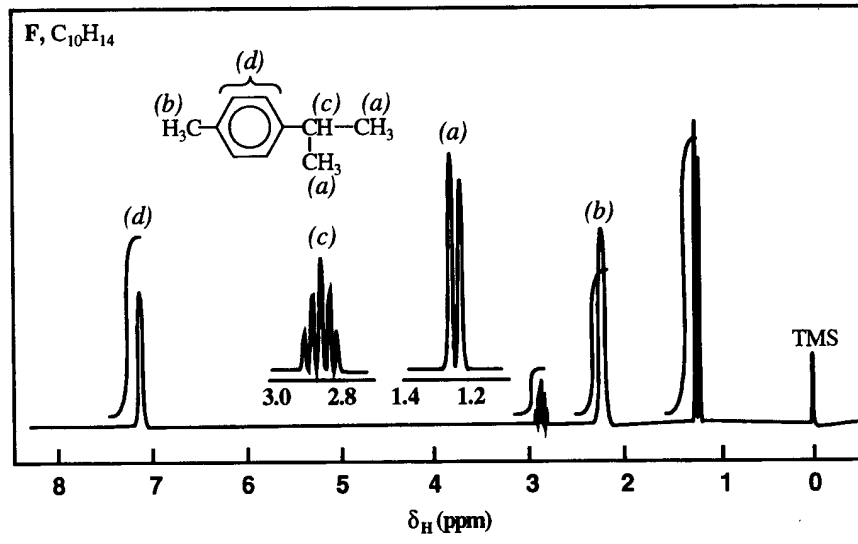
C



(*a*) triplet δ 2.9
(*b*) quintet δ 2.1
(*c*) multiplet δ 7.1

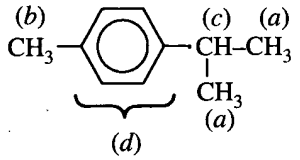
14.26 A ^{1}H NMR signal this far upfield indicates that cyclooctatetraene is a cyclic polyene and is not aromatic.

14.27 Compound F is *p*-isopropyltoluene. ^{1}H NMR assignments are shown in the following spectrum.



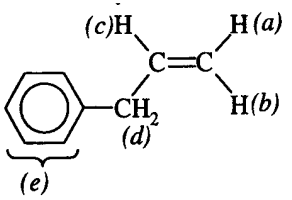
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We can make the following ^1H NMR assignments:



(a) doublet δ 1.25
(b) singlet δ 2.3
(c) septet δ 2.85
(d) multiplet δ 7.1

14.28 Compound **L** is allylbenzene,



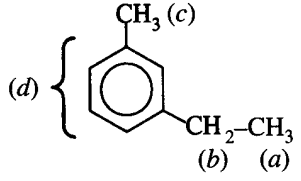
(d) Doublet, δ 3.1 (2H)
(a) or *(b)* Multiplet, δ 4.8
(a) or *(b)* Multiplet, δ 5.1
(c) Multiplet, δ 5.8
(e) Multiplet, δ 7.1 (5H)

The following IR assignments can be made.

3035 cm^{-1}, C–H stretching of benzene ring
3020 cm^{-1}, C–H stretching of $-CH=CH_2$ group
2925 cm^{-1} and 2853 cm^{-1}, C–H stretching of $-CH_2-$group
1640 cm^{-1}, C=C stretching
990 cm^{-1} and 915 cm^{-1}, C–H bendings of $-CH=CH_2$ group
740 cm^{-1} and 695 cm^{-1}, C–H bendings of $-C_6H_5$ group

The UV absorbance maximum at 255 nm is indicative of a benzene ring that is not conjugated with a double bond.

14.29 Compound **M** is *m*-ethyltoluene. We can make the following assignments in the spectra.



(*a*) triplet δ 1.4
(*b*) quartet δ 2.6
(*c*) singlet δ 2.4
(*d*) multiplet δ 7.05

Meta substitution is indicated by the very strong peaks at 690 and 780 cm^{-1} in the IR spectrum.

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14.30 Compound **N** is $C_6H_5CH{=}CHOCH_3$. The absence of absorption peaks due to O–H or C=O stretching in the IR spectrum of **N** suggests that the oxygen atom is present as part of an ether linkage. The (5H) ^{1}H NMR multiplet between δ 7.1–7.6 strongly suggests the presence of a monosubstituted benzene ring; this is confirmed by the strong peaks at ~690 and ~770 cm^{-1} in the IR spectrum.

We can make the following assignments in the ^{1}H NMR spectrum:

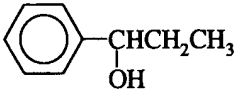
$$\underset{}{C_6H_5}\text{–}\underset{(a)}{CH}{=}\underset{(b)}{CH}\text{–}\underset{(c)}{OCH_3}$$

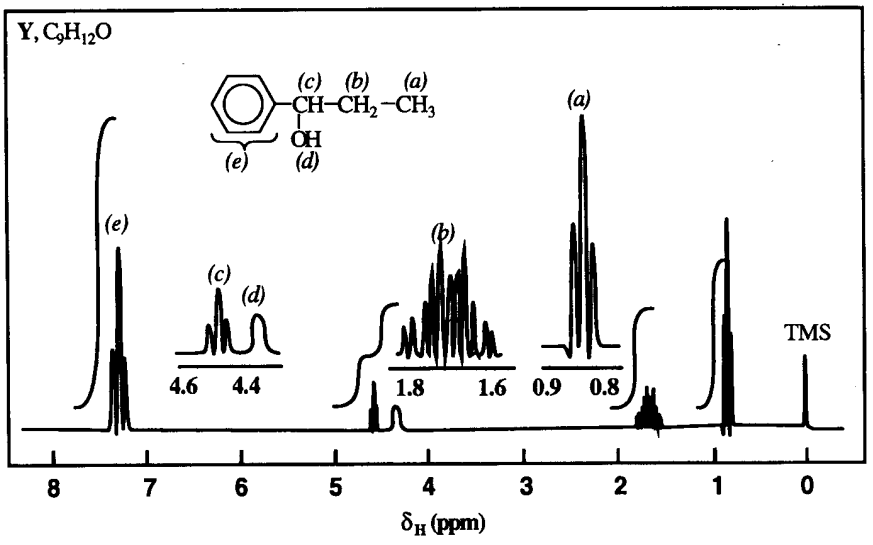
(d)

(a) Multiplet δ 7.1–7.6
(b) Doublet δ 6.1
(c) Doublet δ 5.2
(d) Singlet δ 3.7

14.31 Compound **X** is *meta*-xylene. The upfield signal at δ 2.3 arises from the two equivalent methyl groups. The downfield signals at δ 6.9 and 7.1 arise from the protons of the benzene ring. Meta substitution is indicated by the strong IR peak at 680 cm^{-1} and very strong IR peak at 760 cm^{-1}.

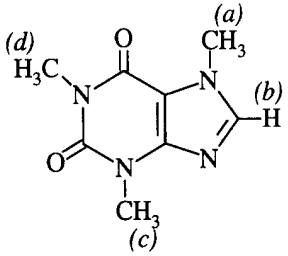
14.32 The broad IR peak at 3400 cm^{-1} indicates a hydroxy group, and the two bands at 720 and 770 cm^{-1} suggest a monosubstituted benzene ring. The presence of these groups is also indicated by the peaks at δ 4.4 and δ 7.2 in the ^{1}H NMR spectrum. The ^{1}H NMR spectrum also shows a triplet at δ 0.85 indicating a $-CH_3$ group coupled with an adjacent $-CH_2-$group. There is a complex multiplet at δ 1.7 and there is also a triplet at δ 4.5 (1H). Putting these pieces together in the only way possible gives us the following structure for **Y.**





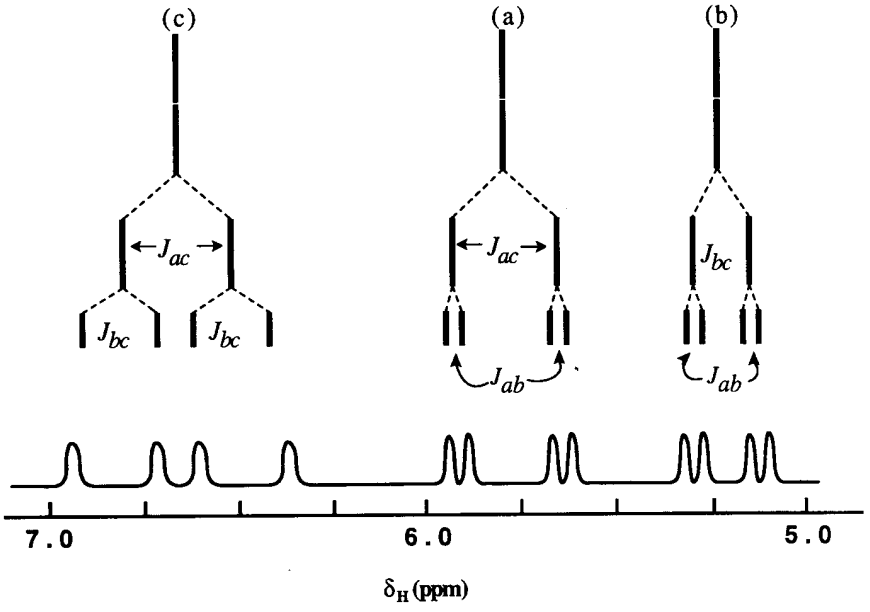
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14.33 (a) Four unsplit signals,

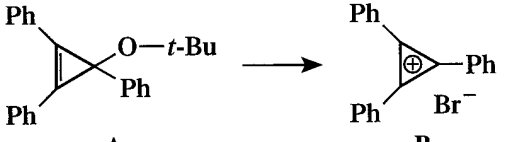


(b) Absorptions arising from: =C–H, CH_3, and C=O groups.

***14.34** The vinylic protons of *p*-chlorostyrene should give a spectrum approximately like the following:

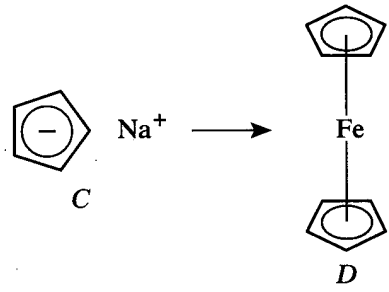


***14.35**



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*14.36



C *D* (a "sandwich compound")

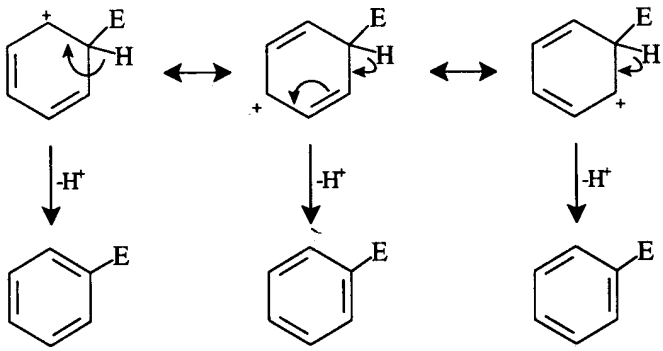
*14.37 Ph—C≡C—C≡C—Ph

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15 REACTIONS OF AROMATIC COMPOUNDS

SOLUTIONS TO PROBLEMS

15.1



15.2 The rate is dependent on the concentration of NO_2^+ ion formed from protonated nitric acid.

$$H{-}\overset{+}{O}(H){-}NO_2 + HA \longrightarrow NO_2^+ + H_3O^+ + A^-$$

(where HA = HNO_3 or $HOSO_3H$)

Because H_2SO_4 ($HOSO_3H$) is a stronger acid, a mixture of it and HNO_3 will contain a higher concentration of protonated nitric acid than will nitric acid alone.

That is, the reaction,

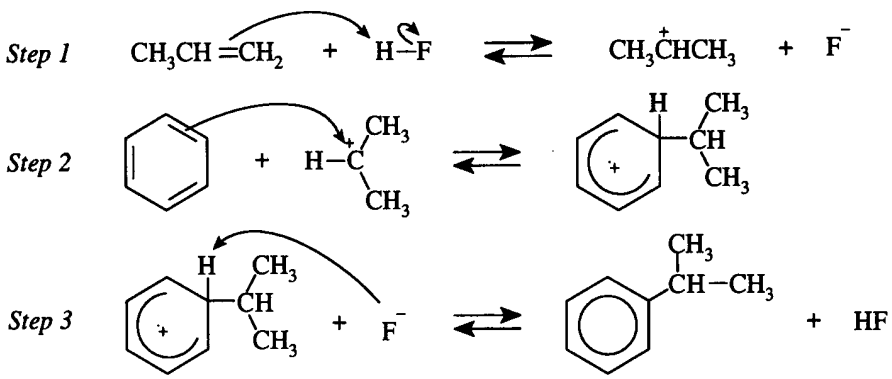
$$H{-}O{-}NO_2 + HOSO_3H \rightleftharpoons \underset{\text{Protonated nitric acid}}{H{-}\overset{+}{O}(H){-}NO_2} + HSO_4^-$$

produces more protonated nitric acid than the reaction,

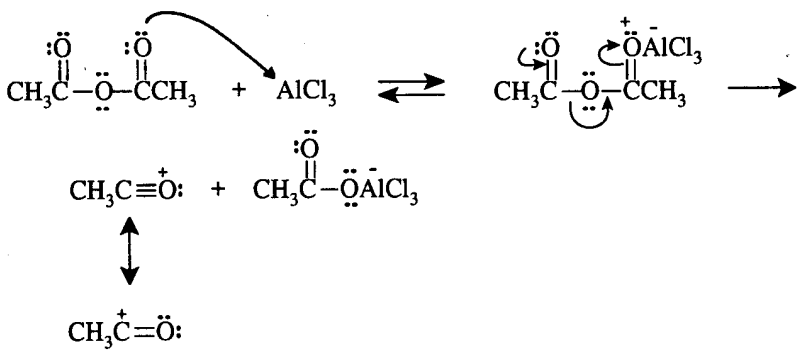
$$H{-}O{-}NO_2 + H{-}O{-}NO_2 \rightleftharpoons H{-}\overset{+}{O}(H){-}NO_2 + NO_3^-$$

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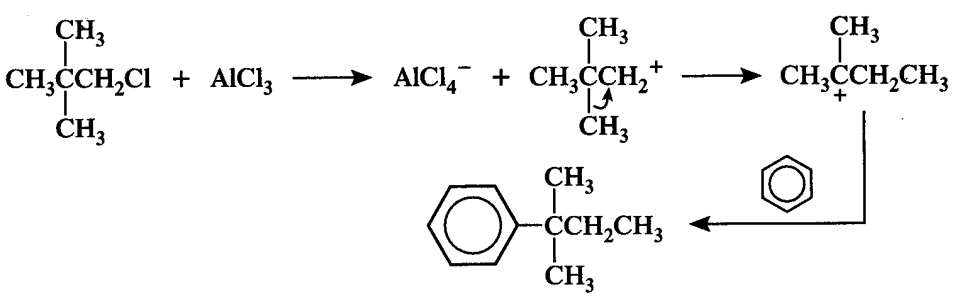
15.3



15.4



15.5 The carbocation formed by the action of $AlCl_3$ on neopentyl chloride is primary. This carbocation rearranges to the more stable tertiary carbocation before it can react with the benzene ring:



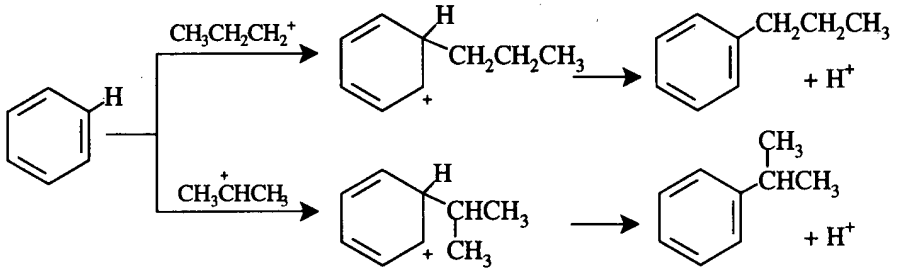
15.6 $CH_3CH_2CH_2{-}OH + BF_3 \rightleftharpoons CH_3CH_2CH_2^+ + HOBF_3$

The propyl cation can rearrange into an isopropyl cation:

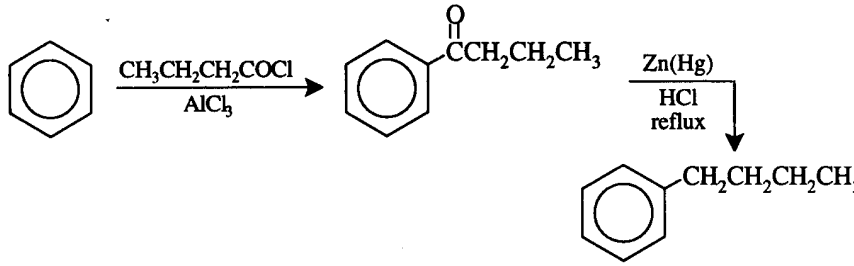
$$CH_3CH_2CH_2^+ \xrightarrow[\text{shift}]{\text{hydride}} CH_3\overset{+}{C}HCH_3$$

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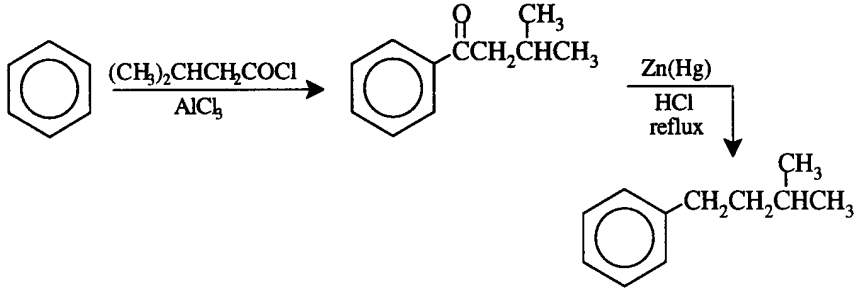
Both carbocations can then attack the ring.



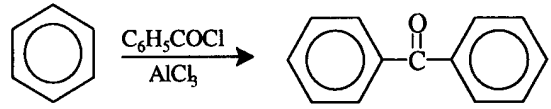
15.7 (a)



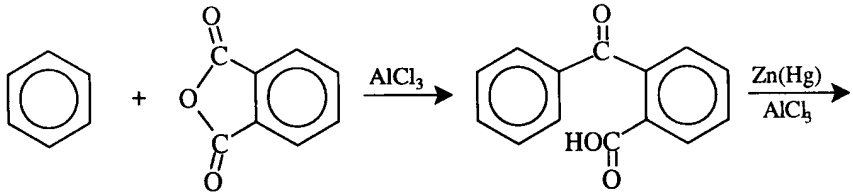
(b)



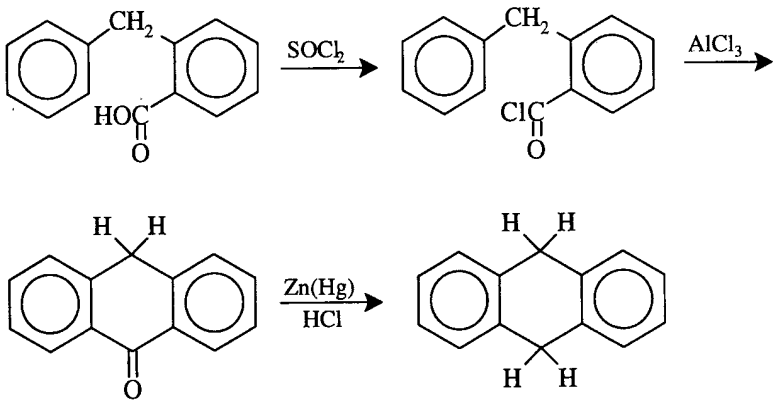
(c)



(d)

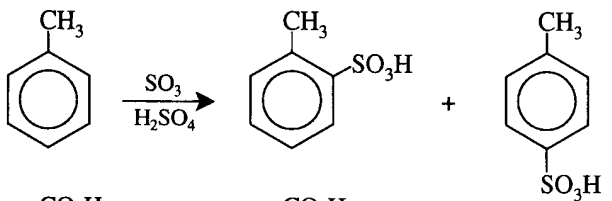


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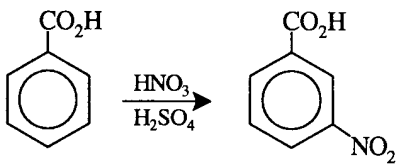


15.8 If the methyl group had no directive effect on the incoming electrophile, we would expect to obtain the products in purely statistical amounts. Since there are two ortho hydrogen atoms, two meta hydrogen atoms, and one para hydrogen, we would expect to get 40% ortho (2/5), 40% meta (2/5), and 20% para (1/5). Thus, we would expect that only 60% of the mixture of mononitrotoluenes would have the nitro group in the ortho or para position. And we would expect to obtain 40% of *m*-nitrotoluene. In actuality, we get 96% of combined *o*- and *p*-nitrotoluene and only 4% *m*-nitrotoluene. This shows the ortho-para directive effect of the methyl group.

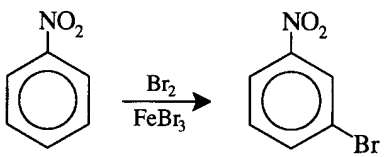
15.9 (a)



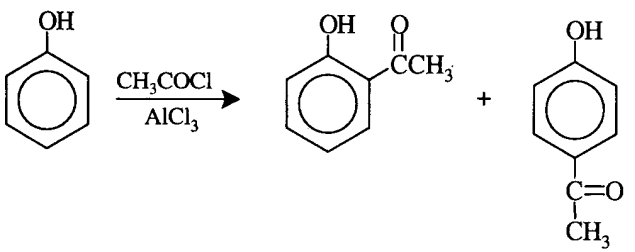
(b)



(c)



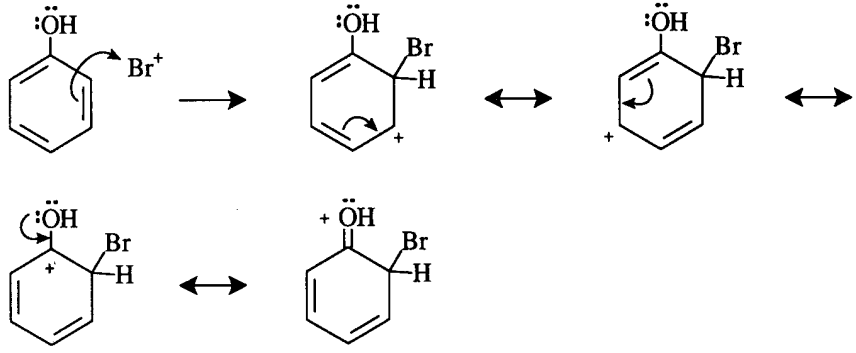
(d)



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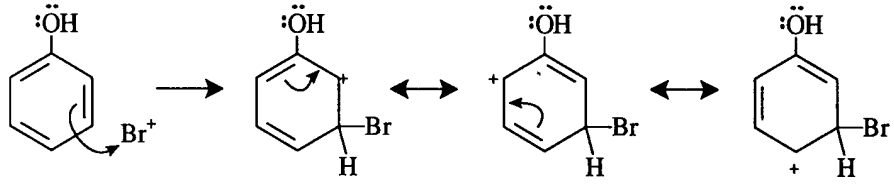
15.10 As the following structures show, attack at the ortho and para positions of phenol leads to arenium ions that are more stable (than the one resulting from meta attack) because they are hybrids of four resonance structures, one of which is relatively stable. Only three resonance structures are possible for the meta arenium ion, and none is relatively stable.

Ortho attack

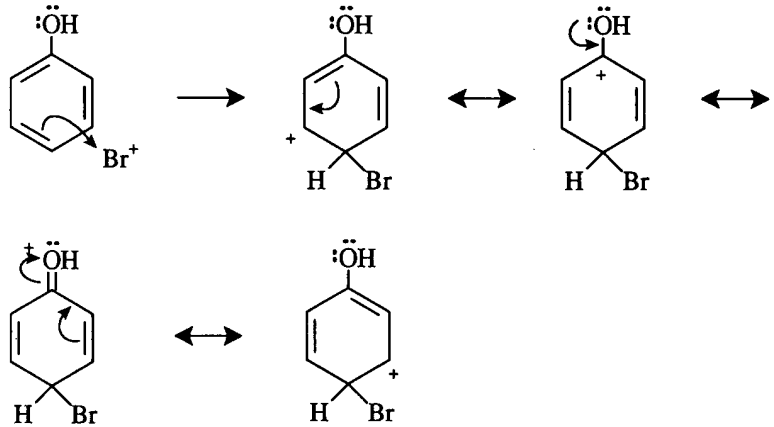


Relatively stable

Meta attack



Para attack

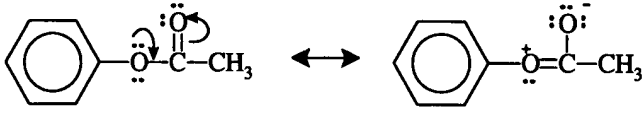


Relatively stable

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15.11 (a) The atom (an oxygen atom) attached to the benzene ring has an unshared electron pair that it can donate to the arenium ions formed from ortho and para attack stabilizing them. (The arenium ions are analogous to the previous answer with a $-COCH_3$ group replacing the –H).

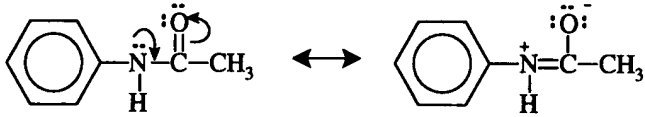
(b) Structures such as the following compete with the benzene ring for the oxygen electrons, making them less available to the benzene ring.



This effect makes the benzene ring of phenyl acetate less electron rich and, therefore, less reactive.

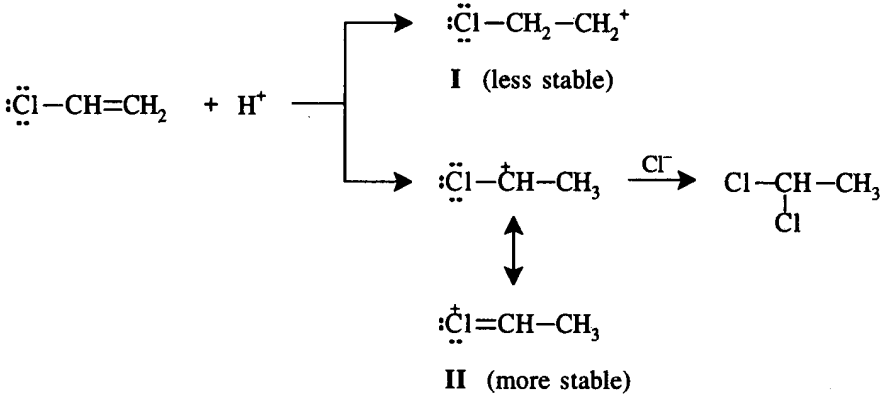
(c) Because the acetamido group has an unshared electron pair on the nitrogen atom that it can donate to the benzene ring it is an ortho-para director.

(d) Structures such as the following compete with the benzene ring for the nitrogen electrons, making them less available to the benzene ring.



15.12 The electron-withdrawing inductive effect of the chlorine of chloroethene makes its double bond less electron rich than that of ethene. This causes the rate of reaction of chloroethene with an electrophile (i.e., a proton) to be slower than the corresponding reaction of ethene.

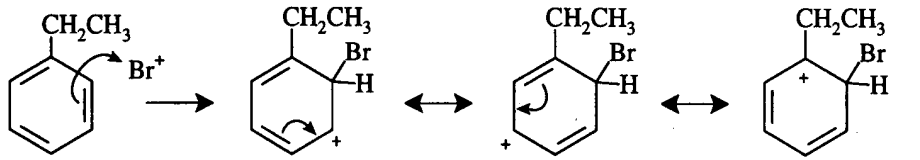
When chloroethene adds a proton, the orientation is governed by a resonance effect. In theory, two carbocations can form:



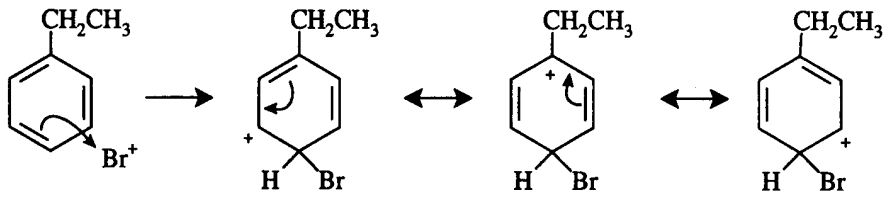
Carbocation **II** is more stable than **I** because of the resonance contribution of the extra structure just shown in which the chlorine atom donates an electron pair (see Section 15.11D).

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15.13 *Ortho attack*

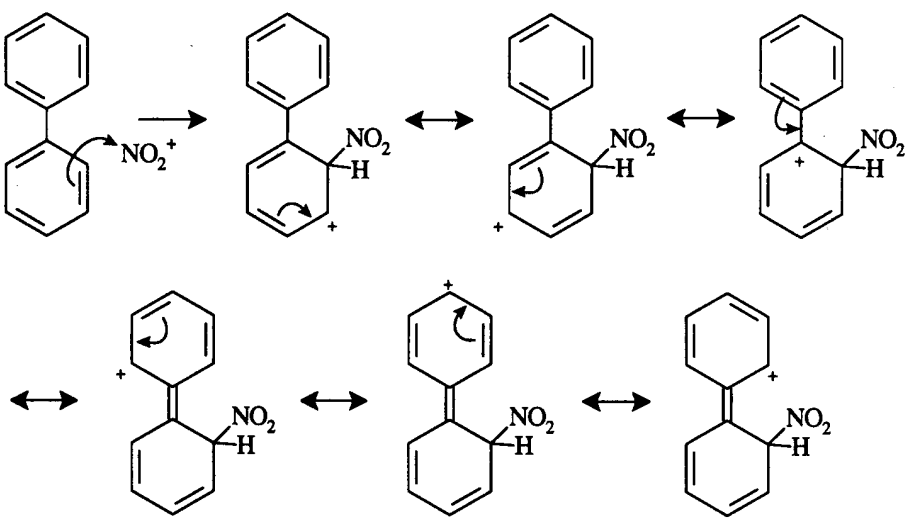


Para attack



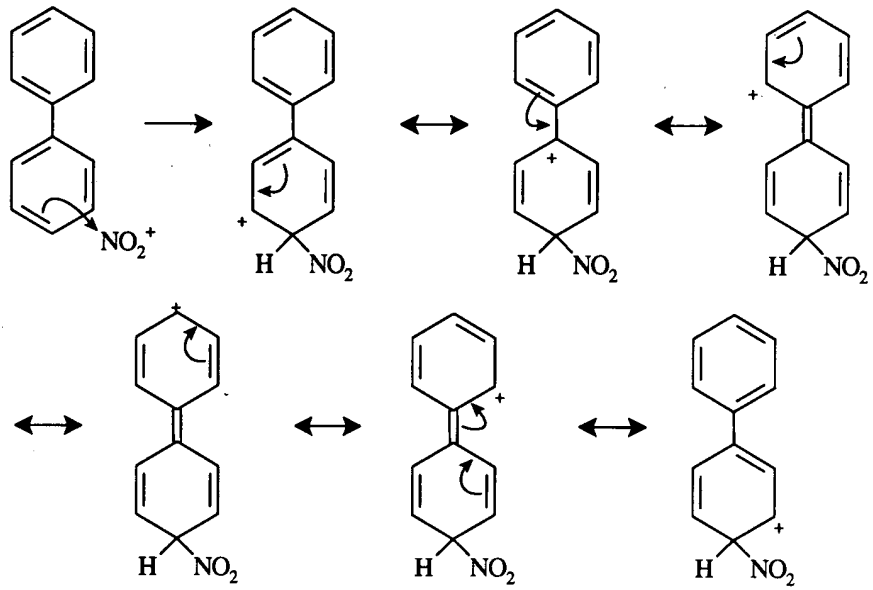
15.14 The phenyl group, as the following resonance structures show, can act as an electron-releasing group and can stabilize the arenium ions formed from ortho and para attack.

Ortho attack

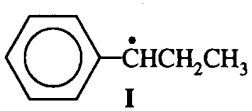


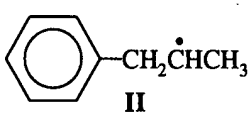
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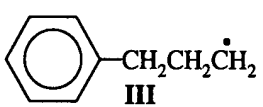
Para attack



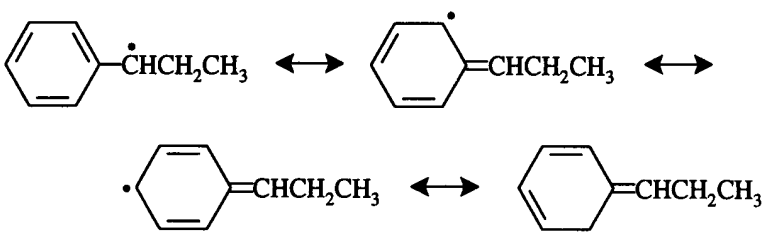
15.15


I leads to 1-chloro-1-phenylpropane

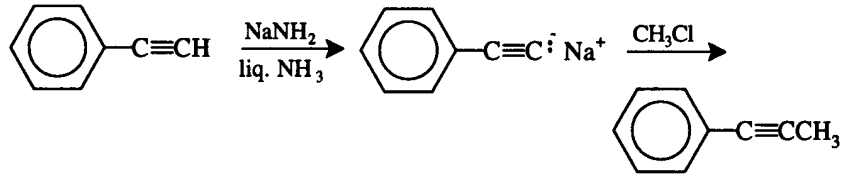

II leads to 2-chloro-1-phenylpropane

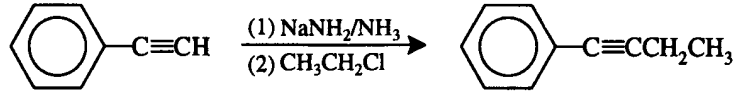

III leads to 1-chloro-3-phenylpropane

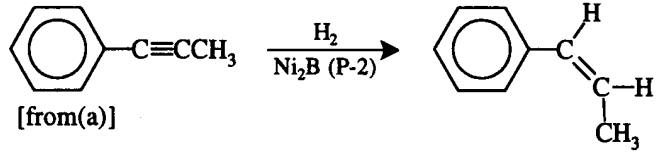
The major product is 1-chloro-1-phenylpropane because **I** is the most stable radical. It is a benzylic radical and therefore is stabilized by resonance.



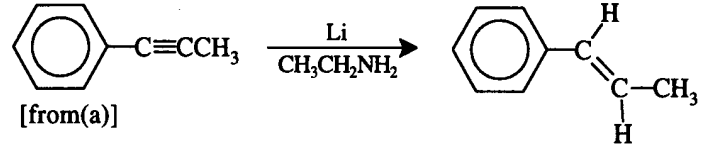
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15.16 (a) 

(b) 

(c) 

[from(a)]

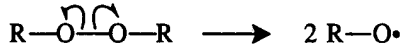
(d) 

[from(a)]

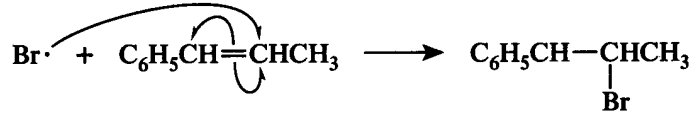
15.17 The addition of hydrogen bromide to 1-phenylpropene proceeds through a benzylic radical in the presence of peroxides, and through a benzylic cation in their absence (cf., a and b as follows).

(a) Hydrogen bromide addition in the presence of peroxides.

Chain Initiation

Step 1 

Step 2 

Step 3 

A benzylic radical

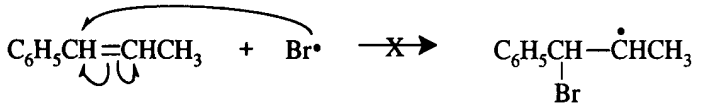
Chain Propagation

Step 4 

2-Bromo-1-phenylpropane

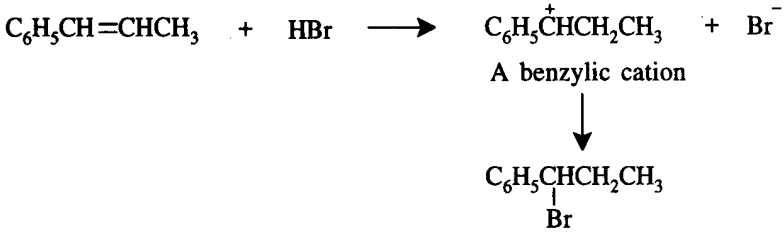
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The mechanism for the addition of hydrogen bromide to 1-phenylpropene in the presence of peroxides is a chain mechanism analogous to the one we discussed when we described anti-Markovnikov addition in Section 10.9. The step that determines the orientation of the reaction is the first chain-propagating step. Bromine attacks the second carbon atom of the chain because by doing so the reaction produces a more stable benzylic radical. Had the bromine atom attacked the double bond in the opposite way, a less stable secondary radical would have been formed.



A secondary radical

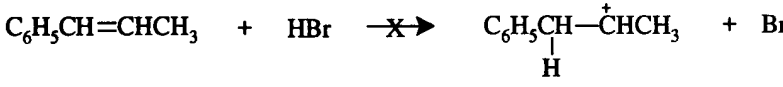
(b) Hydrogen bromide addition in the absence of peroxides.



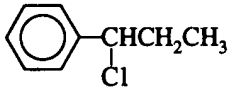
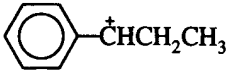
A benzylic cation

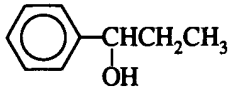
1-Bromo-1-phenylpropane

In the absence of peroxides, hydrogen bromide adds through an ionic mechanism. The step that determines the orientation in the ionic mechanism is the first, where the proton attacks the double bond to give the more stable benzylic cation. Had the proton attacked the double bond in the opposite way, a less stable secondary cation would have been formed.



A secondary cation

15.18 (a)  because the more stable carbocation intermediate is the benzylic carbocation,  , which then reacts with a chloride ion.

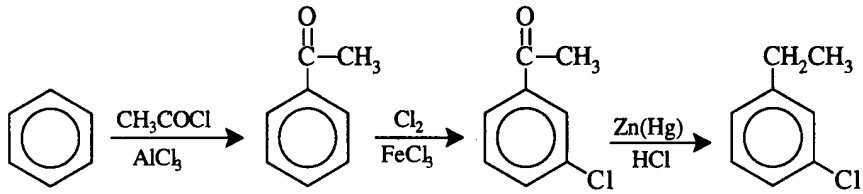
(b)  because the more stable intermediate is a benzylic cation, which then reacts with H_2O.

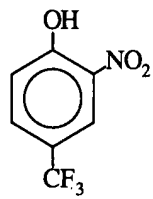
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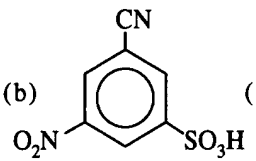
15.19 (a) The first method would fail because introducing the chlorine substituent first would introduce an ortho-para directing group. Consequently, the subsequent Friedel-Crafts reaction would not then take place at the desired meta position.

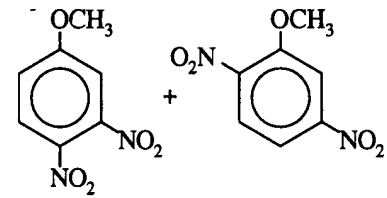
The second method would fail for essentially the same reasons. Introducing the ethyl group first would introduce an ortho-para director, and subsequent ring chlorination would not take place at the desired meta position.

(b) If we introduce an acetyl group first, which we later convert to an ethyl group, we install a meta director. This allows us to put the chlorine atom in the desired position. Conversion of the acetyl group to an ethyl group is then carried out using the Clemmensen reduction.



15.20 (a) 

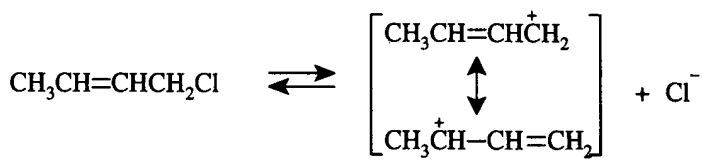
(b) 

(c) 

15.21 (a) In concentrated base and ethanol (a relatively nonpolar solvent), the S_N2 reaction is favored. Thus, the rate depends on the concentration of both the alkyl halide and $NaOC_2H_5$. Since no carbocation is formed, the only product is

$$CH_3CH{=}CHCH_2OCH_2CH_3$$

(b) When the concentration of $C_2H_5O^-$ ion is small or zero, the reaction occurs through the S_N1 mechanism. The carbocation that is produced in the first step of the S_N1 mechanism is a resonance hybrid.

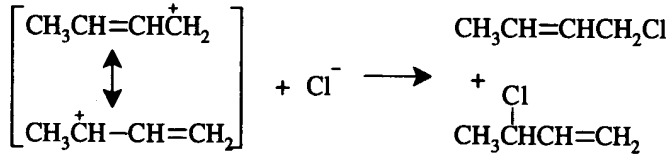


This ion reacts with the nucleophile ($C_2H_5O^-$ or C_2H_5OH) to produce two isomeric ethers

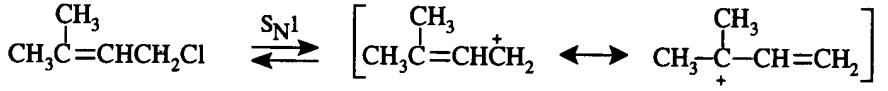


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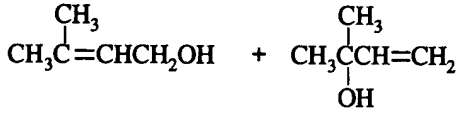
(c) In the presence of water, the first step of the S_N1 reaction occurs. The reverse of this reaction produces two compounds because the positive charge on the carbocation is distributed over carbon atoms one and three



15.22 (a) The carbocation that is produced in the S_N1 reaction is exceptionally stable because one resonance contributor is not only allylic but also tertiary.



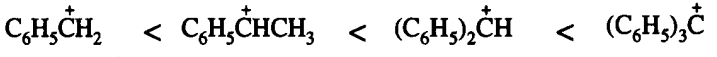
A 3° allylic carbocation

(b) 

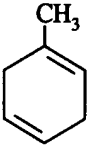
15.23 Compounds that undergo reactions by an S_N1 path must be capable of forming relatively stable carbocations. Primary halides of the type $ROCH_2X$ form carbocations that are stabilized by resonance:

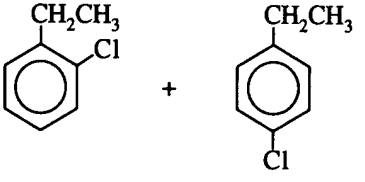
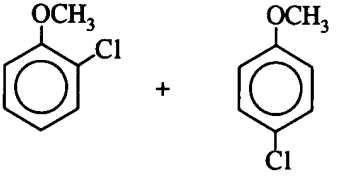


15.24 The relative rates are in the order of the relative stabilities of the carbocations:

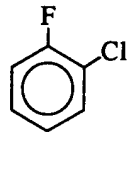
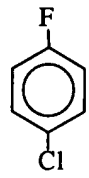


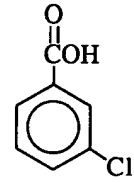
The solvolysis reaction involves a carbocation intermediate.

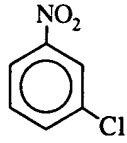
15.25 

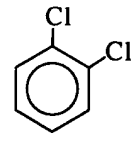
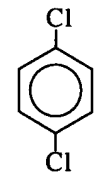
15.26 (a)  (b) 

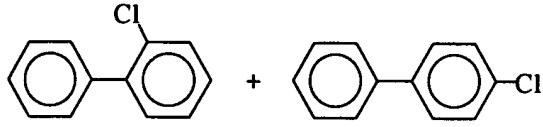
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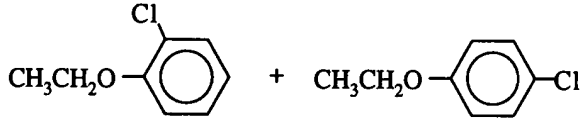
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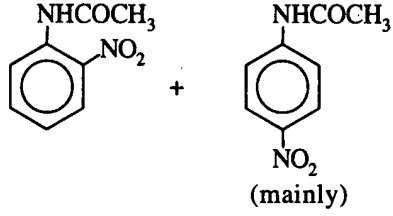
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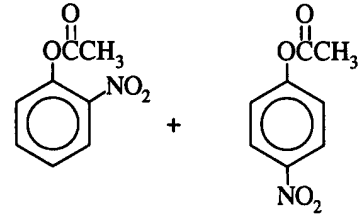
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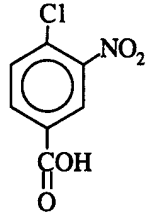
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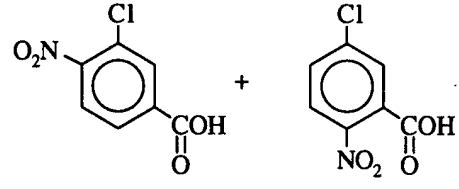
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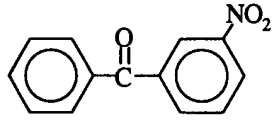
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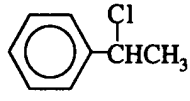
15.27 (a) 
(mainly)

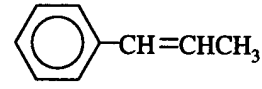
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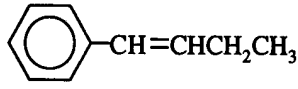
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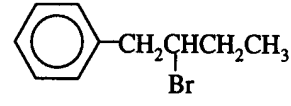
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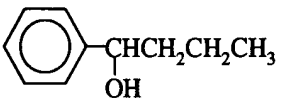
15.28 (a) 

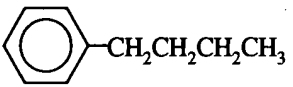
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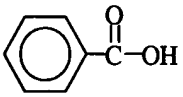
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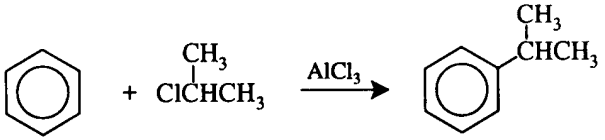
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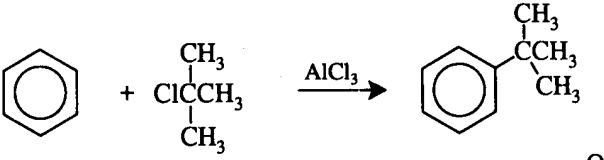
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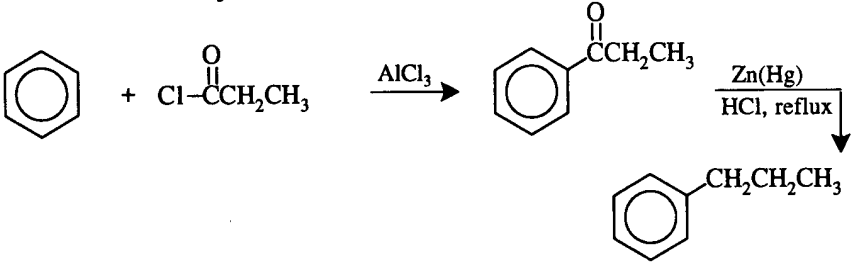
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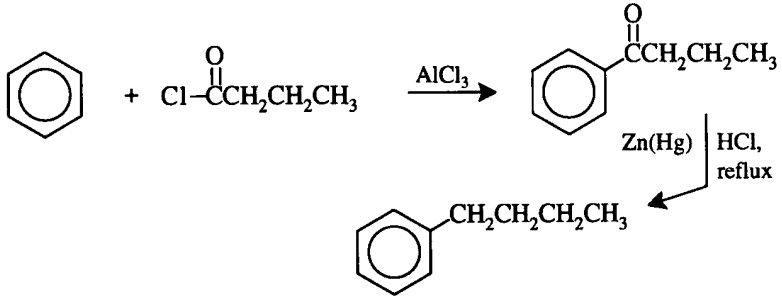
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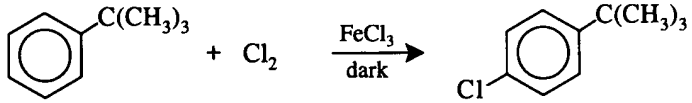
15.29 (a) 

(b) 

(c) 

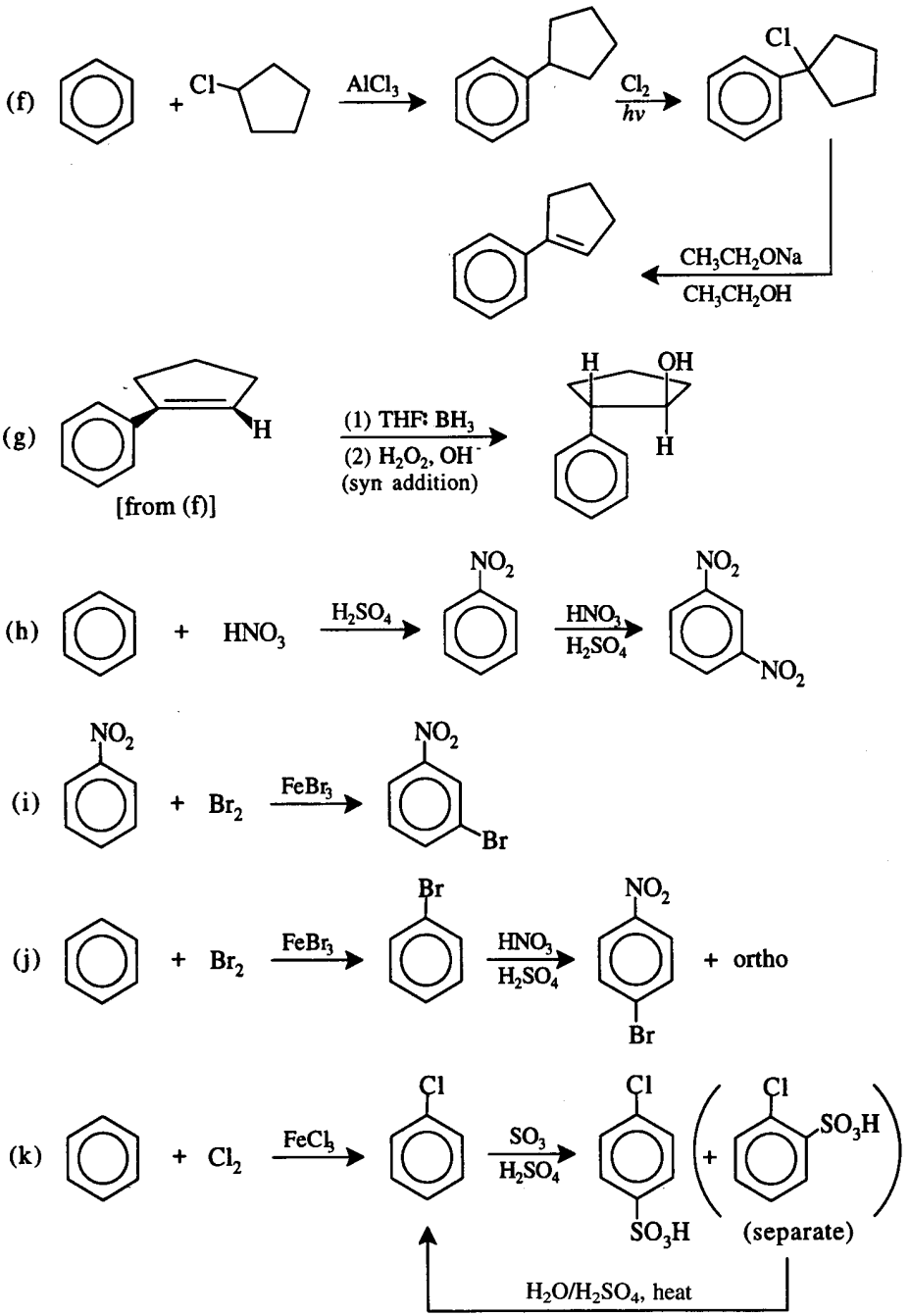
(*Note:* The use of Cl-$CH_2CH_2CH_3$ in a Friedel-Crafts synthesis gives mainly the rearranged product, isopropylbenzene.)

(d) 

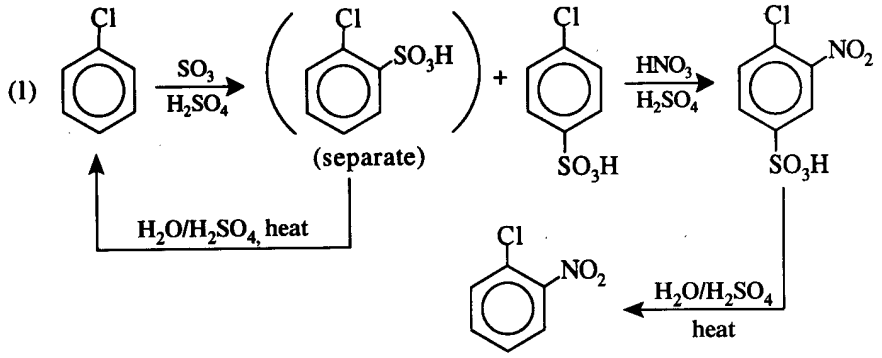
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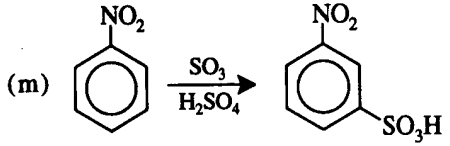
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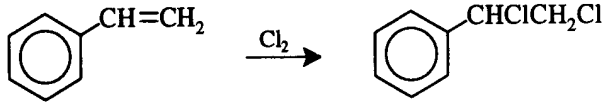
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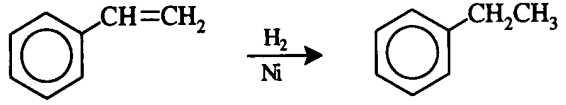


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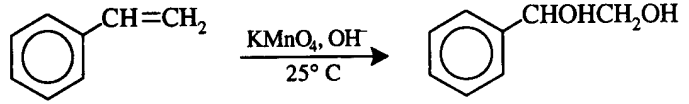
15.30 (a)



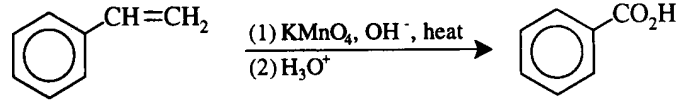
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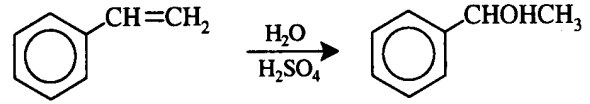
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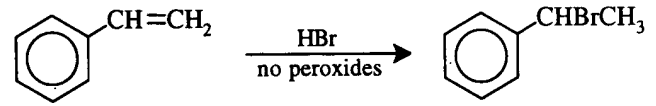
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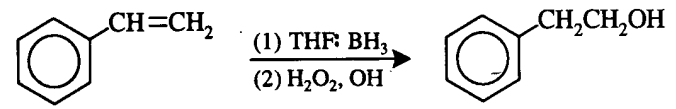
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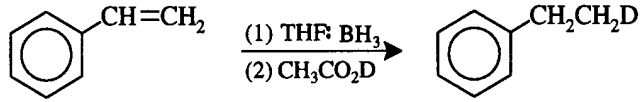
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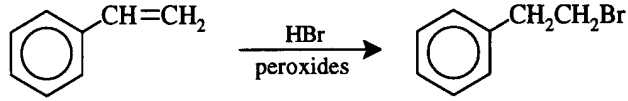


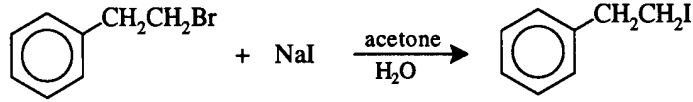
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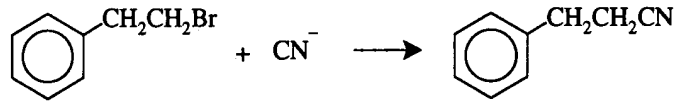
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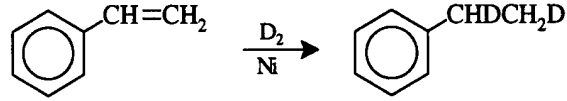
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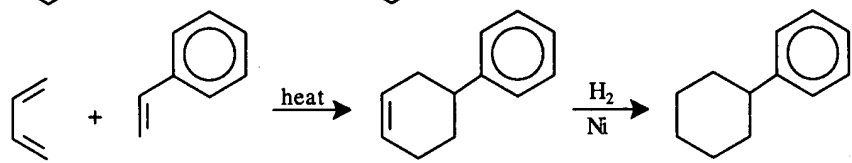
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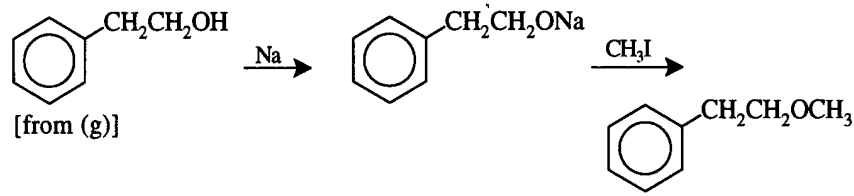
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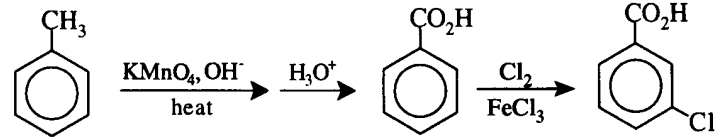
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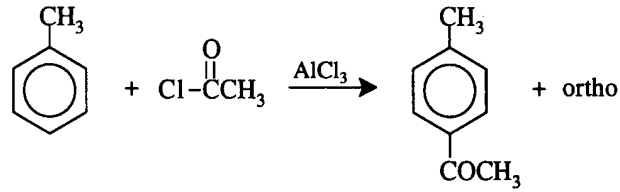
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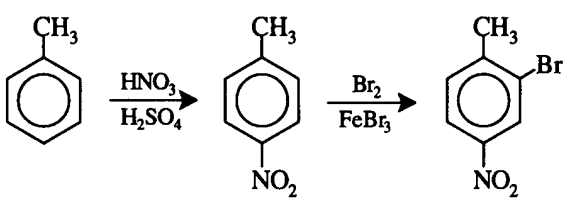
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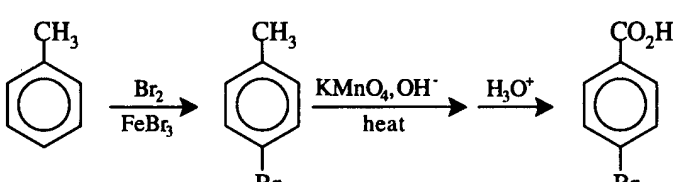
15.31 (a) 

(b) 

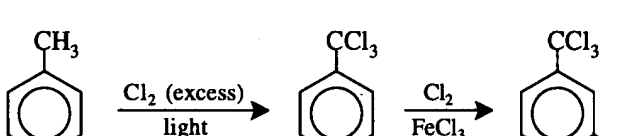
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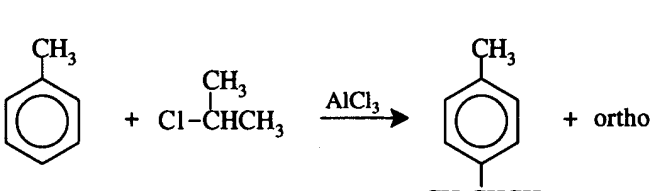
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(+ ortho)

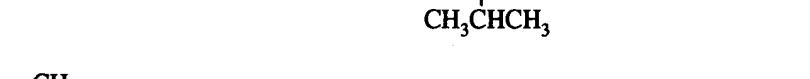
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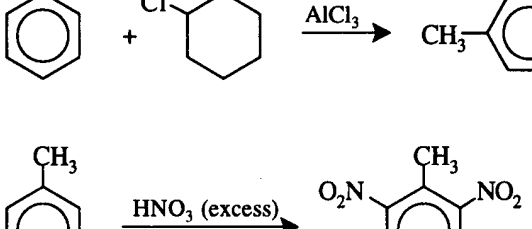
(e) 

(f) 

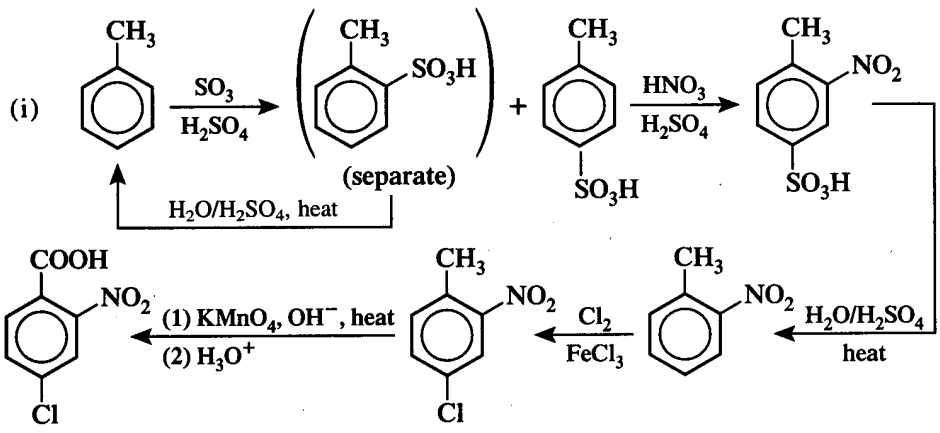
+ ortho

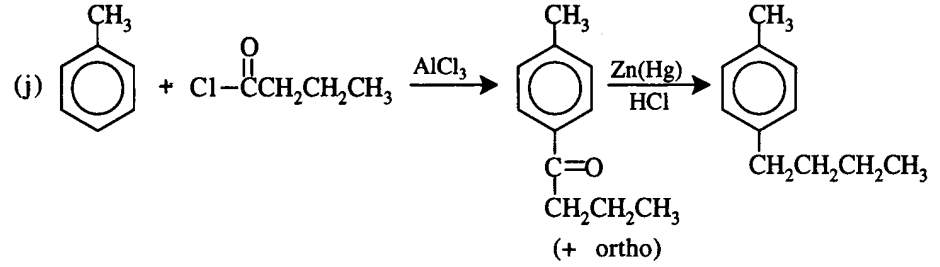
(g) 

+ ortho

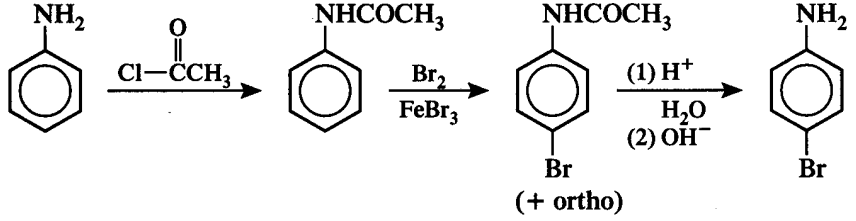
(h) 

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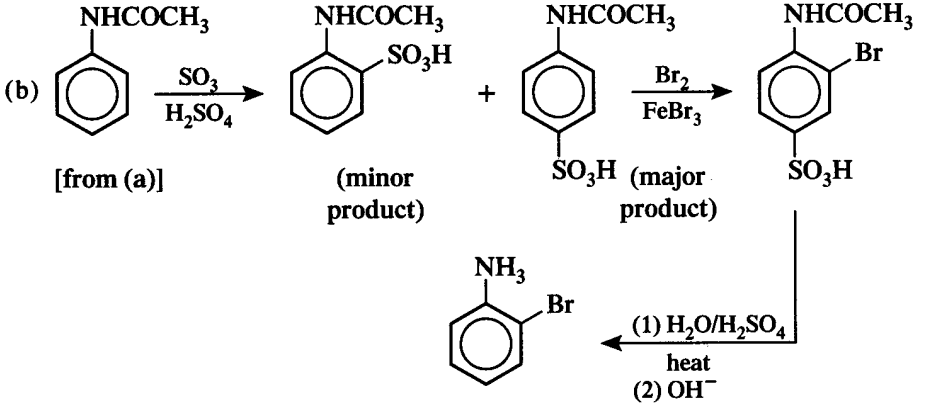




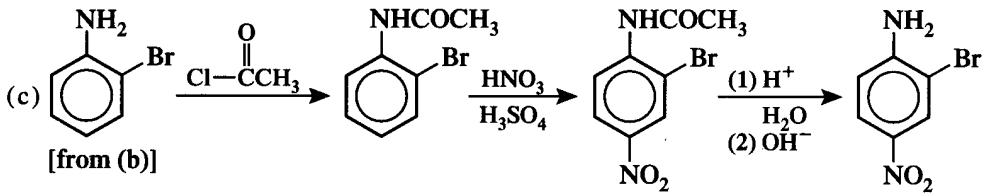
15.32 (a)

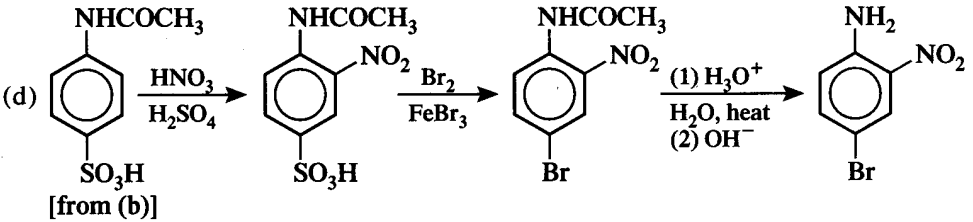


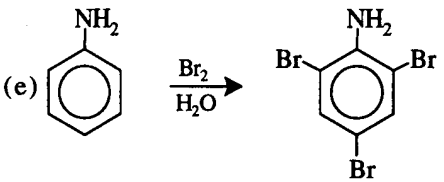
(b)



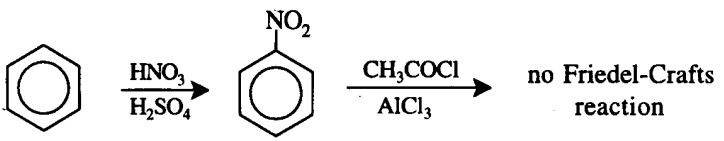
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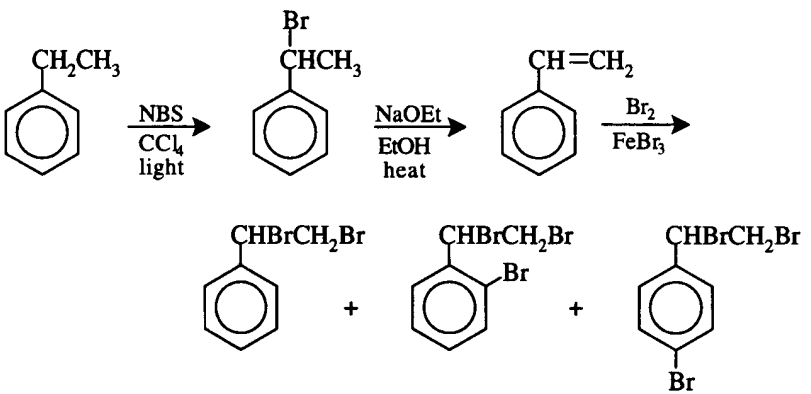




15.33 (a) Step (2) will fail because a Friedel-Crafts reaction will not take place on a ring that bears an $-NO_2$ group (or any meta director).

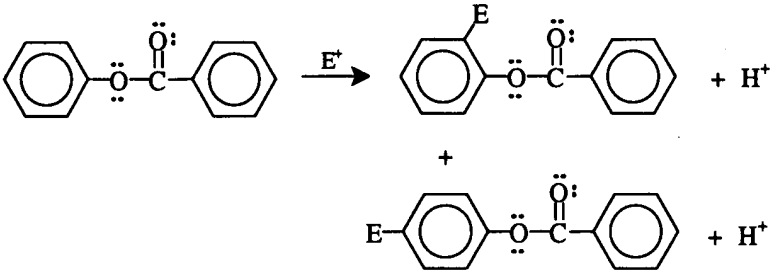


(b) The last step will first brominate the double bond.



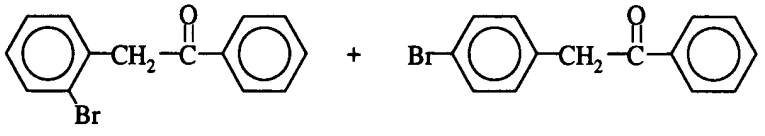
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15.34 (a) Electrophilic aromatic substitution will take place as follows:

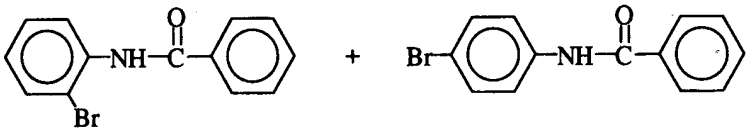


(b) The ring directly attached to the oxygen atom is activated toward electrophilic attack because the oxygen atom can donate an unshared electron pair to it and stabilize the intermediate arenium ion when attack occurs at the ortho or para position.

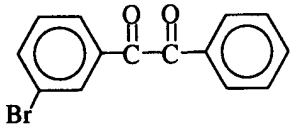
15.35 (a)



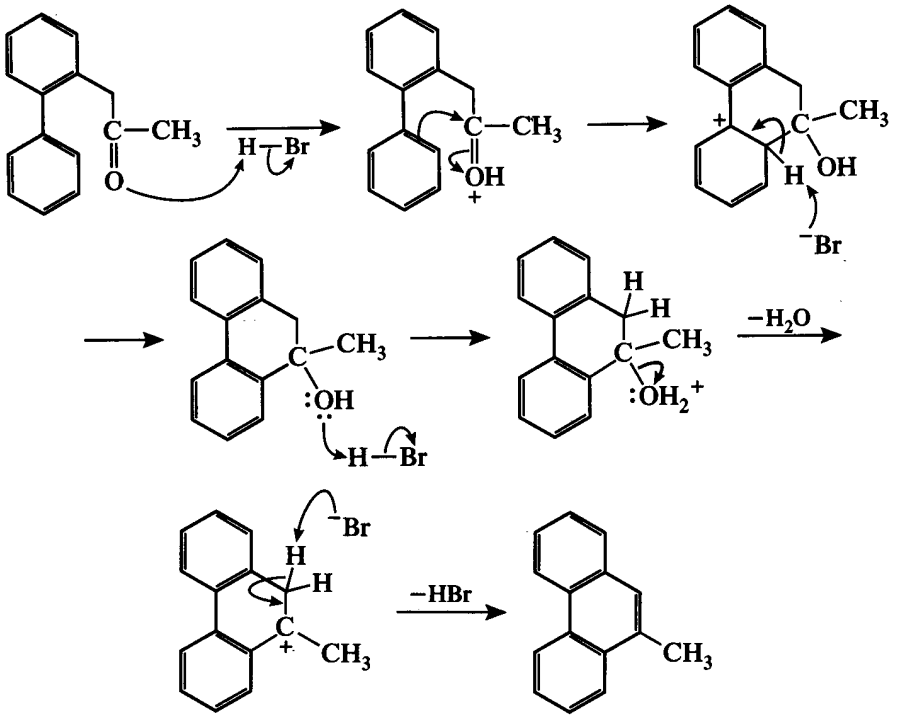
(b)



(c)

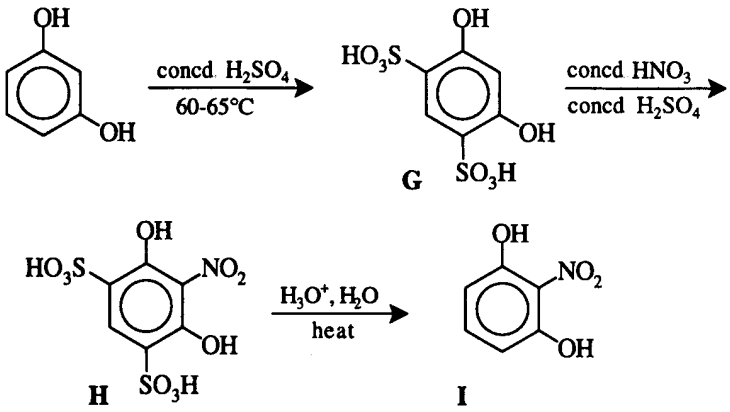


15.36

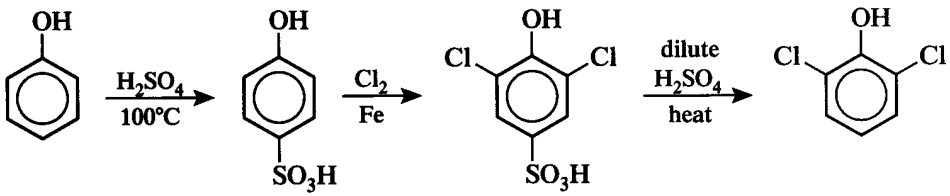


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15.37 This problem serves as another illustration of the use of a sulfonic acid group as a blocking group in a synthetic sequence. Here we are able to bring about nitration between two meta substituents.



15.38



15.39 (a) (1) $C_6H_5CH{=}CH{-}CH{=}CH_2 \xrightarrow{H^+}$ $C_6H_5CH{=}CH{-}\overset{+}{C}H{-}CH_3 \leftrightarrow C_6H_5\overset{+}{C}H{-}CH{=}CH{-}CH_3$

$C_6H_5\overset{\delta+}{C}H{=}CH{=}\overset{\delta+}{C}H{-}CH_3$

(2) $C_6H_5\overset{\delta+}{C}H{=}CH{=}\overset{\delta+}{C}H{-}CH_3 \xrightarrow{X^-} C_6H_5CH{=}CH{-}\underset{X}{CH}{-}CH_3$

(b) 1,2 Addition.

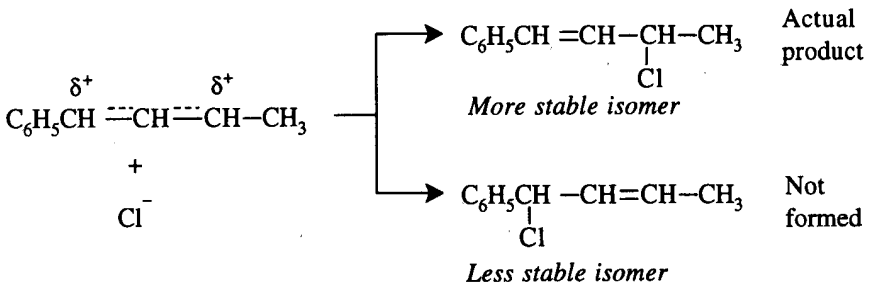
(c) Yes. The carbocation given in (a) is a hybrid of *secondary allylic and benzylic* contributors and is therefore more stable than any other possibility; for example,

$C_6H_5CH{=}CH{-}CH{=}CH_2 \xrightarrow{H^+} C_6H_5CH_2{-}\overset{+}{C}H{-}CH{=}CH_2 \leftrightarrow C_6H_5CH_2{-}CH{=}CH{-}\overset{+}{C}H_2$

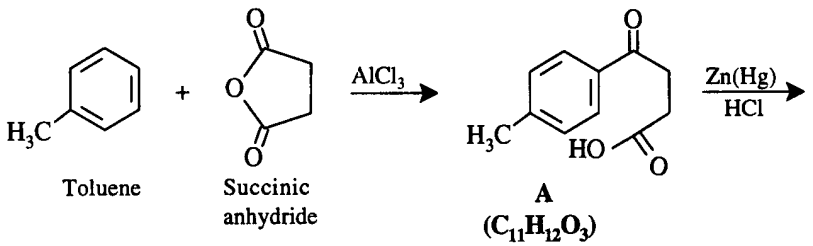
A hybrid of allylic contributors only

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(d) Since the reaction produces only *the more stable isomer*—that is, the one in which the double bond is conjugated with the benzene ring—the reaction is likely to be under equilibrium control:

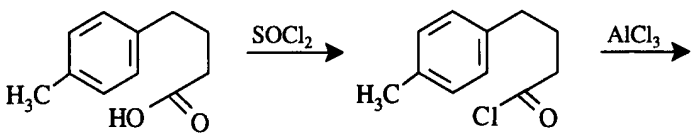


15.40

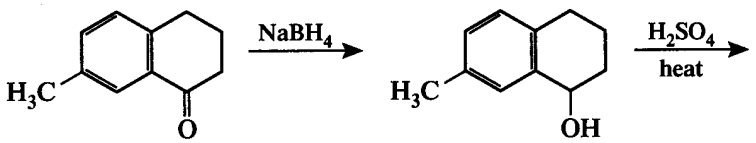


Toluene — Succinic anhydride

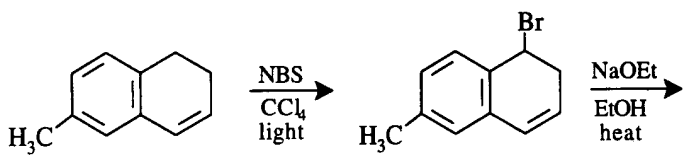
A ($C_{11}H_{12}O_3$)



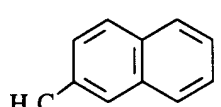
B ($C_{11}H_{14}O_2$) — **C** ($C_{11}H_{13}ClO$)



D ($C_{11}H_{12}O$) — **E** ($C_{11}H_{14}O$)



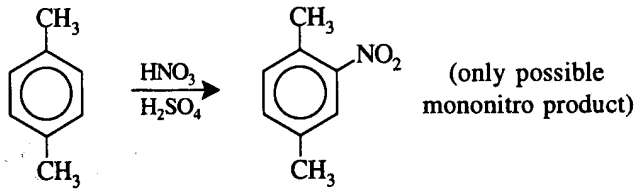
F ($C_{11}H_{12}$) — **G** ($C_{11}H_{11}Br$)



2-Methylnaphthalene

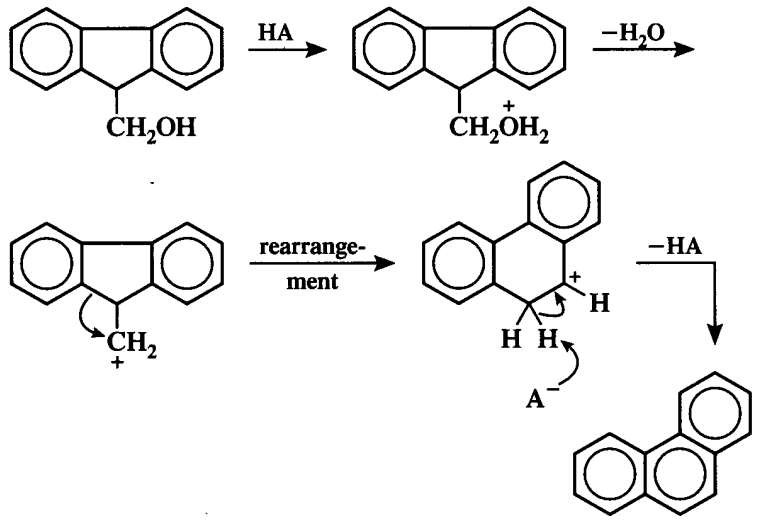
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15.41

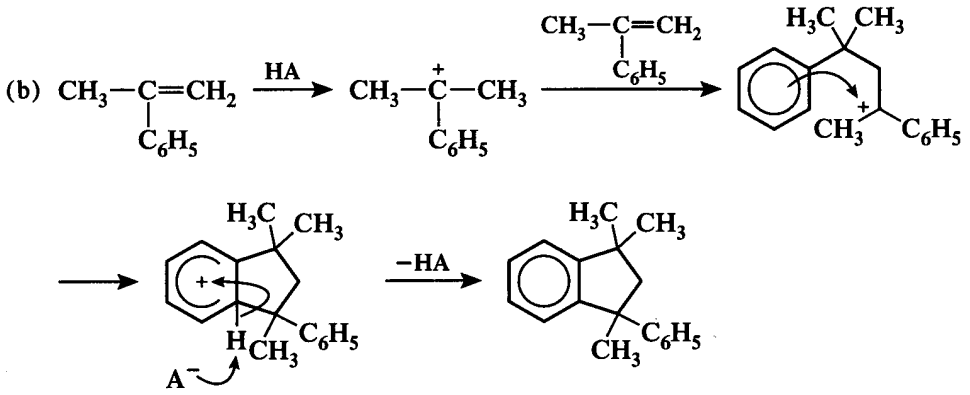


(only possible mononitro product)

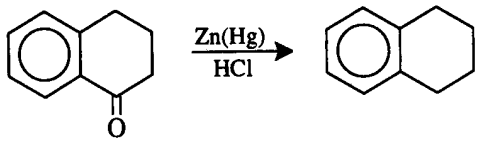
15.42 (a)



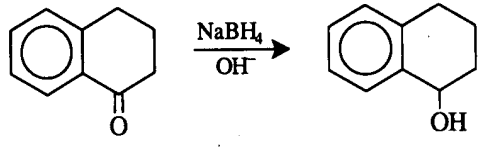
(b)



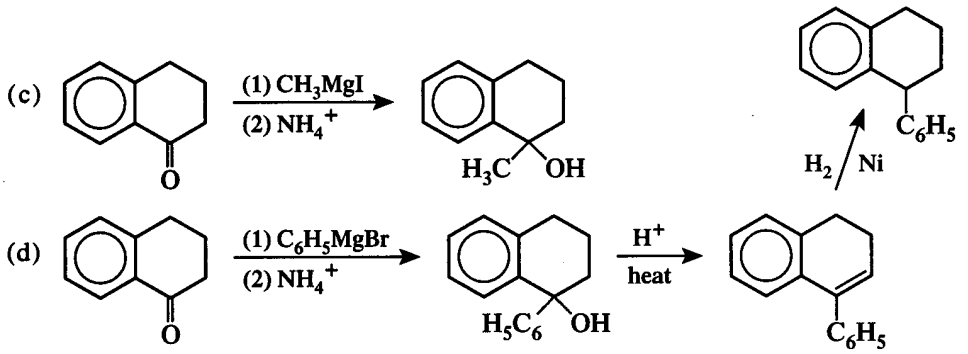
15.43 (a)



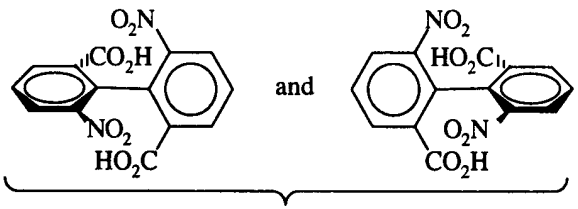
(b)



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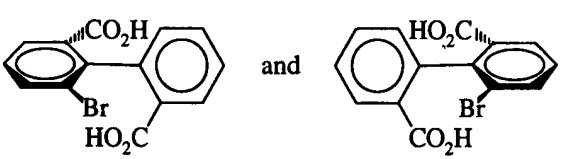


15.44 (a) Large ortho substituents prevent the two rings from becoming coplanar and prevent rotation about the single bond that connects them. If the correct substitution patterns are present, the molecule as a whole will be chiral. Thus, enantiomeric forms are possible even though the molecules do not have a stereocenter. The compound with 2-NO_2, 6-CO_2H, 2′-NO_2, 6′-CO_2H is an example,

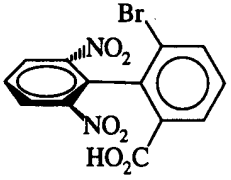


These molecules are nonsuperposable mirror images and, thus, are enantiomers.

(b) Yes

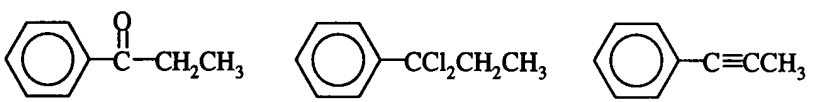


(c) This molecule has a plane of symmetry.



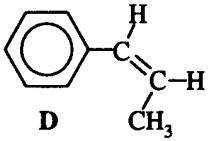
The plane of the page is a plane of symmetry.

15.45 (a)



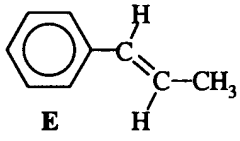
A B C

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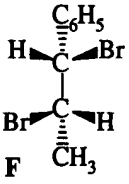
D

(b)



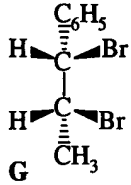
E

(c)



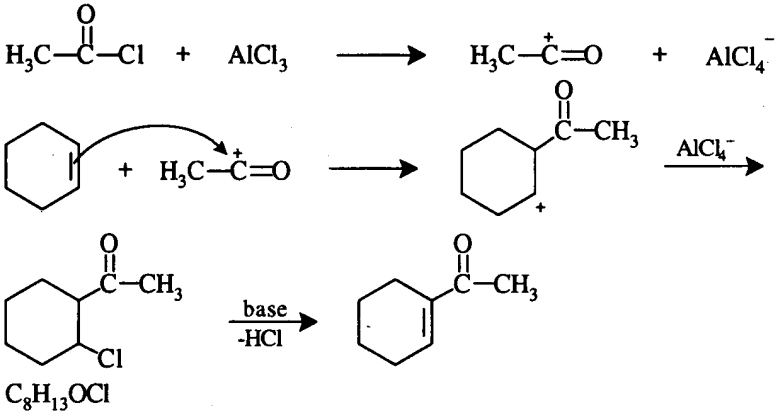
F

(d)



G

15.46



$C_8H_{13}OCl$

15.47 (a and b) The *tert*-butyl group is easily introduced by any of the variations of the Friedel-Crafts alkylation reaction, and, because of the stability of the *tert*-butyl cation, it is easily removed under acidic conditions.

(c) In contrast to the $-SO_3H$ group often used as a blocking group, $-C(CH_3)_3$ activates the ring to further electrophilic substitution.

15.48 At the lower temperature, the reaction is kinetically controlled, and the usual o/p directive effects of the $-CH_3$ group are observed. At higher temperatures, the reaction is thermodynamically controlled. At reaction times long enough for equilibrium to be reached, the most stable isomer, *m*-toluenesulfonic acid, is the principal product.

15.49 The evidence indicates that the mechanistic step in which the C–H bond is broken is *not* rate determining. (In the case cited, it makes no difference kinetically if a C–H or C–D bond is broken in electrophilic aromatic substitution.) This evidence is consistent with the two-step mechanism given in Section 15.2. The step in which the aromatic compound reacts with the electrophile (NO_2^+) is the slow rate-determining step. Proton (or deuteron) loss from the arenium ion to return to an aromatic system is a rapid step and has no effect on the overall rate.

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15.50 (a) $C_6H_5CH_2Br \xrightarrow[\text{DMF}]{\text{NaCN}} C_6H_5CH_2CN$ (-NaBr)

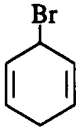
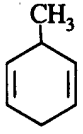
(b) $C_6H_5CH_2Br \xrightarrow[CH_3OH]{CH_3ONa} C_6H_5CH_2OCH_3$ (-NaBr)

(c) $C_6H_5CH_2Br \xrightarrow[CH_3CO_2H]{CH_3CO_2Na} C_6H_5CH_2O_2CCH_3$ (-NaBr)

(d) $C_6H_5CH_2Br \xrightarrow[\text{acetone}]{\text{NaI}} C_6H_5CH_2I$ (-NaBr)

(e) $CH_2{=}CHCH_2Br \xrightarrow[\text{acetone}]{NaN_3} CH_2{=}CHCH_2N_3$ (-NaBr)

(f) $CH_2{=}CHCH_2Br \xrightarrow[(CH_3)_2CHCH_2OH]{NaOCH_2CH(CH_3)_2} CH_2{=}CHCH_2OCH_2CH(CH_3)_2$ (-NaBr)

15.51 A =  B =  C = 

15.52 $(C_6H_5)_3C{-}O{-}H \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} (C_6H_5)_3C{-}\overset{+}{O}H_2 \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} (C_6H_5)_3C^+$ (Very stable carbocation) $\underset{-EtOH}{\overset{+EtOH}{\rightleftharpoons}}$

$(C_6H_5)_3C{-}\overset{+}{O}(H){-}Et \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} (C_6H_5)_3C{-}O{-}Et$

15.53 (a) $CH_3CH_2CH{=}CHCH_2Br$ would be the most reactive in an S_N2 reaction because it is a 1° allylic halide. There would, therefore, be less steric hindrance to the attacking nucleophile.

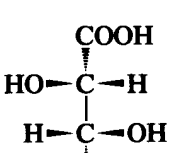
(b) $CH_2{=}CHCBr(CH_3)_2$ would be the most reactive in an S_N1 reaction because it is a 3° allylic halide. The carbocation formed in the rate-determining step, being both 3° and allylic, would be the most stable.

15.54 The final product is *o*-nitroaniline. (The reactions are given in Section 15.14.) The presence of six signals in the ^{13}C NMR spectrum confirms that the substitution in the final product is *ortho* and not *para*. A final product with para substitution (i.e., *p*-nitroaniline) would have given only four signals in the ^{13}C NMR spectrum.

***15.55** $CH_2OHCHOHCH_2OH$ (Glycerol) After sodium borohydride reduction of the aldehyde, ozonolysis oxidatevely degrades the aromatic ring, leaving only the polyhydroxy side chain. Water is an alternative to HOAc sometimes used to work up ozonolysis reactions.

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***15.56**



(Threonic acid)

Ozonolysis oxidatively degrades the aromatic rings, leaving only the carboxyl carbon as a remnant of the alkyl substituted benzene ring. Water is an alternative to HOAc used to work up the ozonolysis reaction.

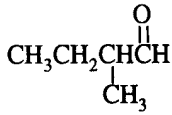
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16 ALDEHYDES AND KETONES I. NUCLEOPHILIC ADDITION TO THE CARBONYL GROUP

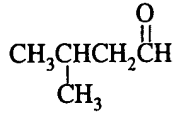
SOLUTIONS TO PROBLEMS

16.1 (a) 

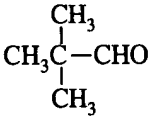
Pentanal



2-Methylbutanal



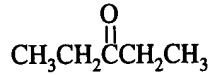
3-Methylbutanal



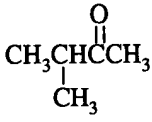
2,2-Dimethylpropanal



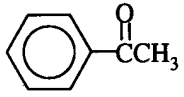
2-Pentanone



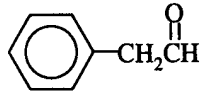
3-Pentanone



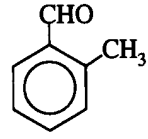
3-Methyl-2-butanone

(b) 

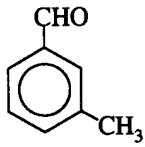
Acetophenone or
methyl phenyl ketone



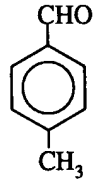
Phenylethanal or
phenylacetaldehyde



2-Methylbenzaldehyde
(*o*-tolualdehyde)



3-Methylbenzaldehyde
(*m*-tolualdehyde)



4-Methylbenzaldehyde
(*p*-tolualdehyde)

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16.2 (a) 1-Pentanol, because its molecules form hydrogen bonds to each other.

(b) 2-Pentanol, because its molecules form hydrogen bonds to each other.

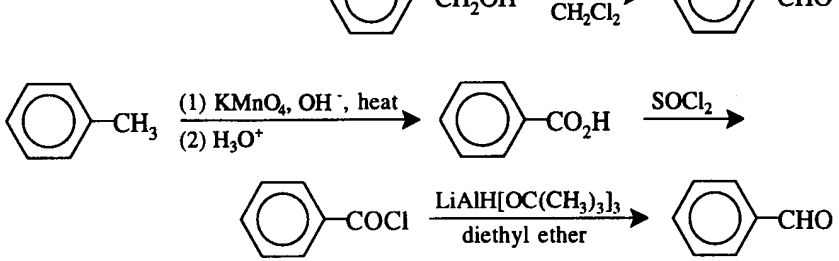
(c) Pentanal, because its molecules are more polar.

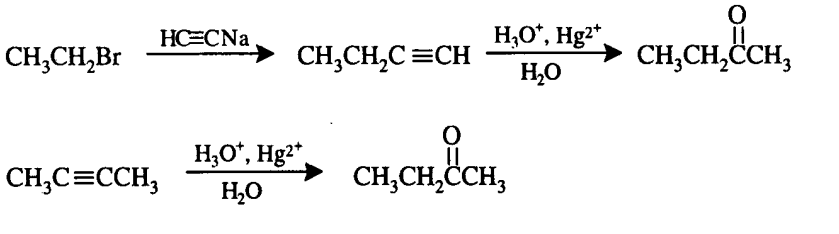
(d) 2-Phenylethanol, because its molecules form hydrogen bonds to each other.

(e) Benzyl alcohol because its molecules form hydrogen bonds to each other.

16.3 (a) $CH_3CH_2CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3CH_2\overset{O}{\overset{\|}{C}}H$

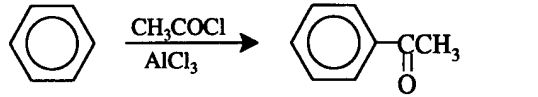
(b) $CH_3CH_2CO_2H \xrightarrow{SOCl_2} CH_3CH_2\overset{O}{\overset{\|}{C}}Cl \xrightarrow[\text{diethyl ether}]{LiAlH[OC(CH_3)_3]_3} CH_3CH_2\overset{O}{\overset{\|}{C}}H$

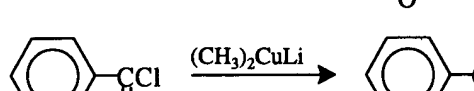
16.4 (a) 

(b) 

(c) $CH_3CH_2Br \xrightarrow{HC{\equiv}CNa} CH_3CH_2C{\equiv}CH \xrightarrow[H_2O]{H_3O^+,\ Hg^{2+}} CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$

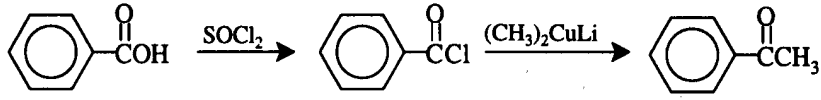
(d) $CH_3C{\equiv}CCH_3 \xrightarrow[H_2O]{H_3O^+,\ Hg^{2+}} CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$

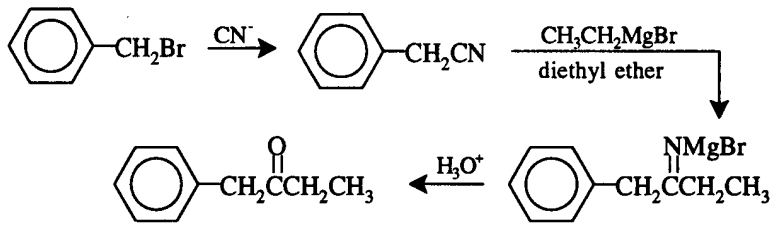
(e) 

(f) 

(g) 

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(h) 

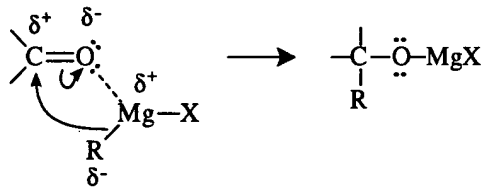
(i) 

(j) $C_6H_5CH_2CN \xrightarrow[(2)\ H_3O^+]{(1)\ i\text{-}Bu_2AlH} C_6H_5CH_2\overset{O}{\overset{\|}{C}}H$

(k) $CH_3(CH_2)_4CO_2CH_3 \xrightarrow[(2)\ H_3O^+]{(1) i\text{-}Bu_2AlH} CH_3(CH_2)_4\overset{O}{\overset{\|}{C}}H$

16.5 (a) The nucleophile is the negatively charged carbon of the Grignard reagent *acting as a carbanion.*

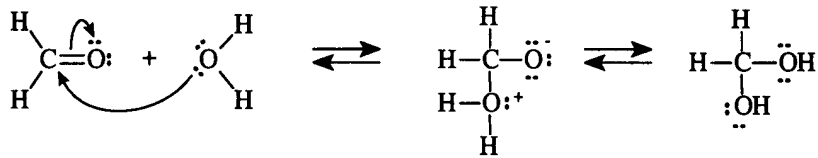
(b) The magnesium portion of the Grignard reagent acts as a Lewis acid and accepts an electron pair of the carbonyl oxygen. This acid-base interaction makes the carbonyl carbon even more positive and, therefore, even more susceptible to nucleophilic attack.



(c) The product that forms initially (above) is a magnesium derivative of an alcohol.

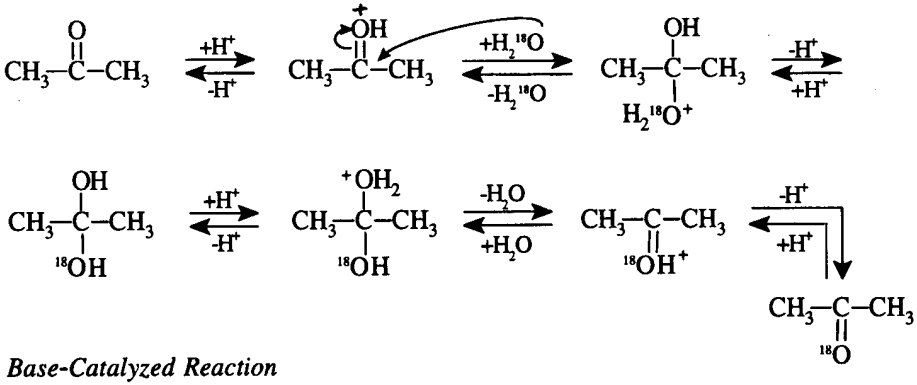
(d) On addition of water, the organic product that forms is an alcohol.

16.6 The nucleophile is a hydride ion.

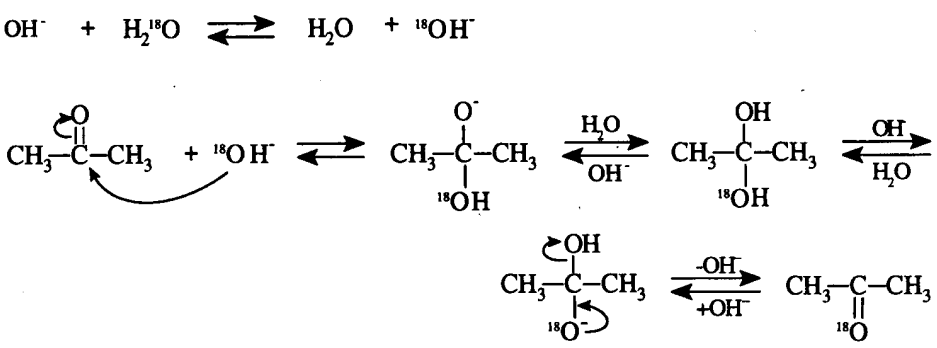
16.7 

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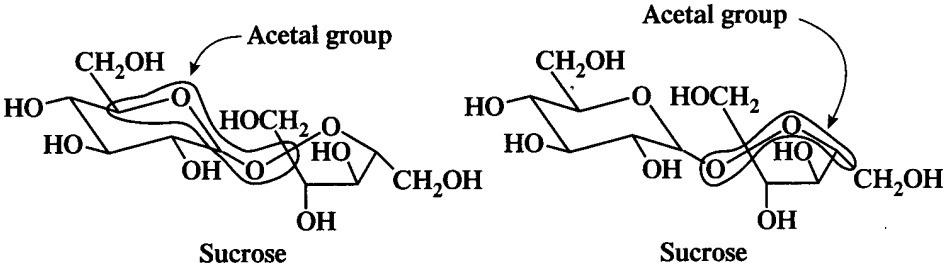
16.8 *Acid-Catalyzed Reaction*



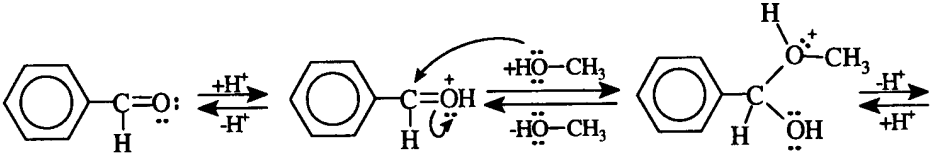
Base-Catalyzed Reaction



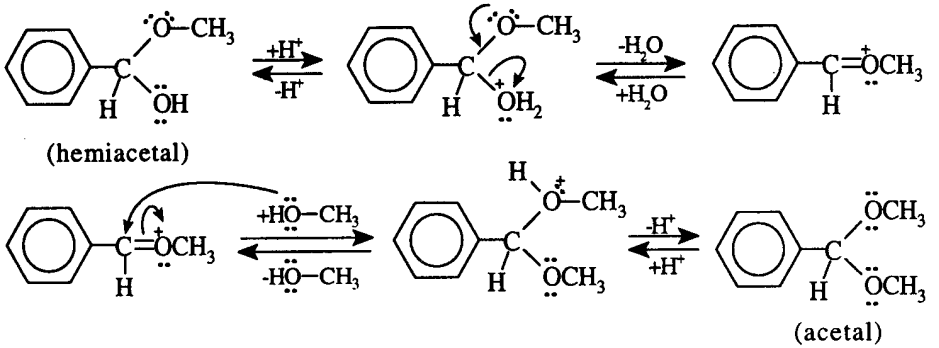
16.9



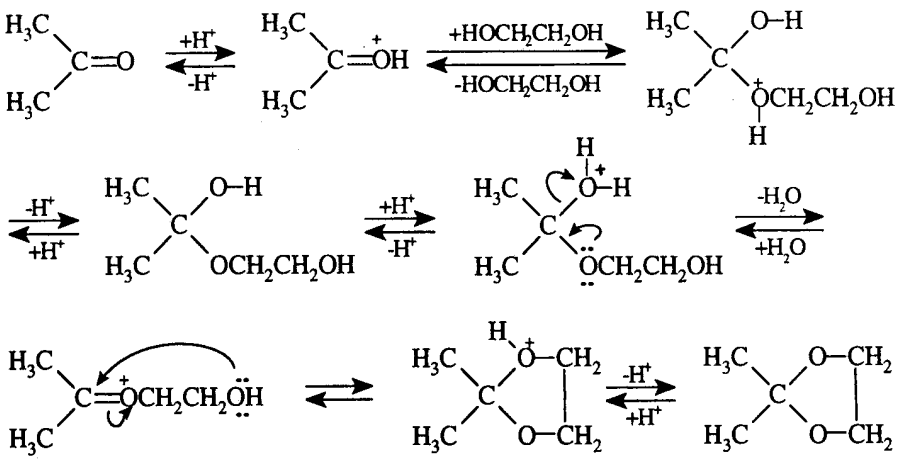
16.10



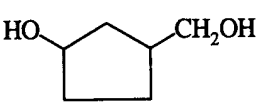
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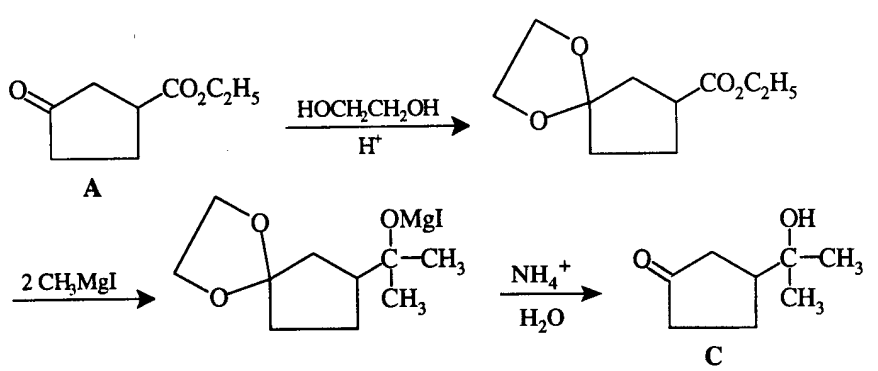
16.11



16.12

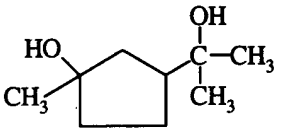


16.13 (a)

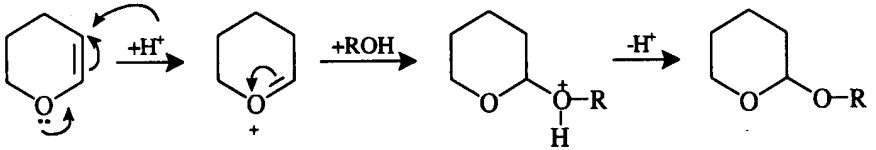


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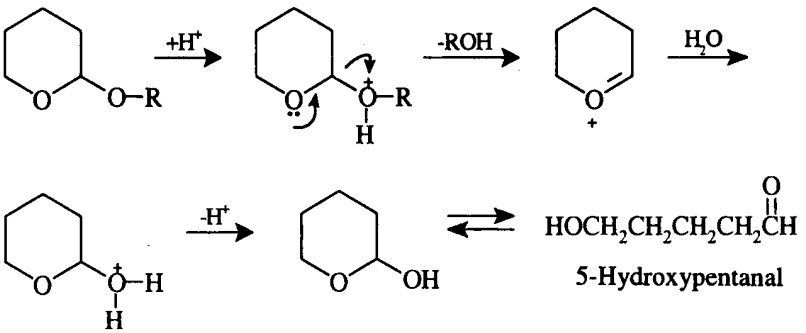
(b) Addition would take place at the ketone group as well as at the ester group. The product (after hydrolysis) would be.



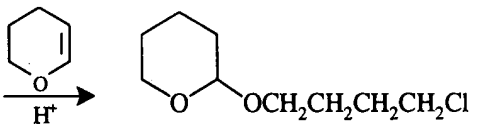
16.14 (a)

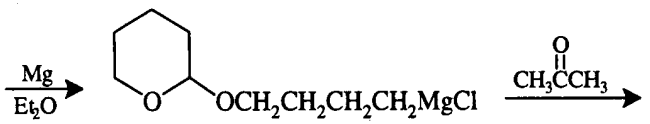


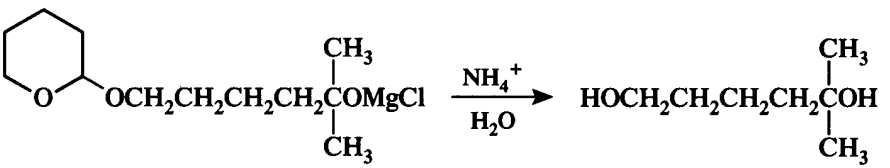
(b) Tetrahydropyranyl ethers are acetals; thus, they are stable in aqueous base and hydrolyze readily in aqueous acid.



(c) $HOCH_2CH_2CH_2CH_2Cl$

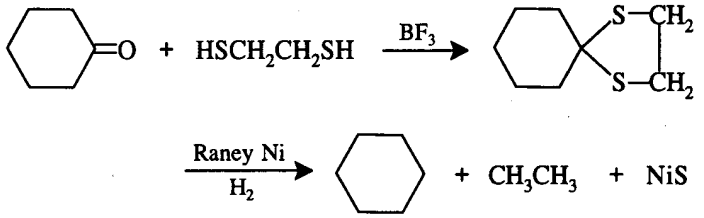




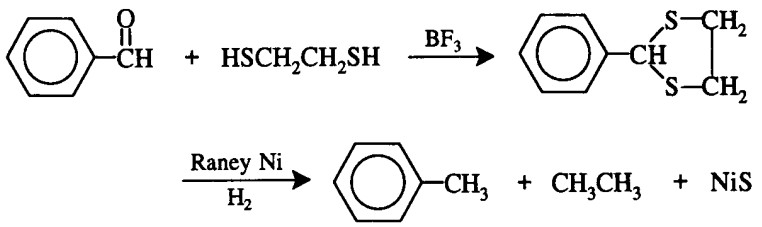


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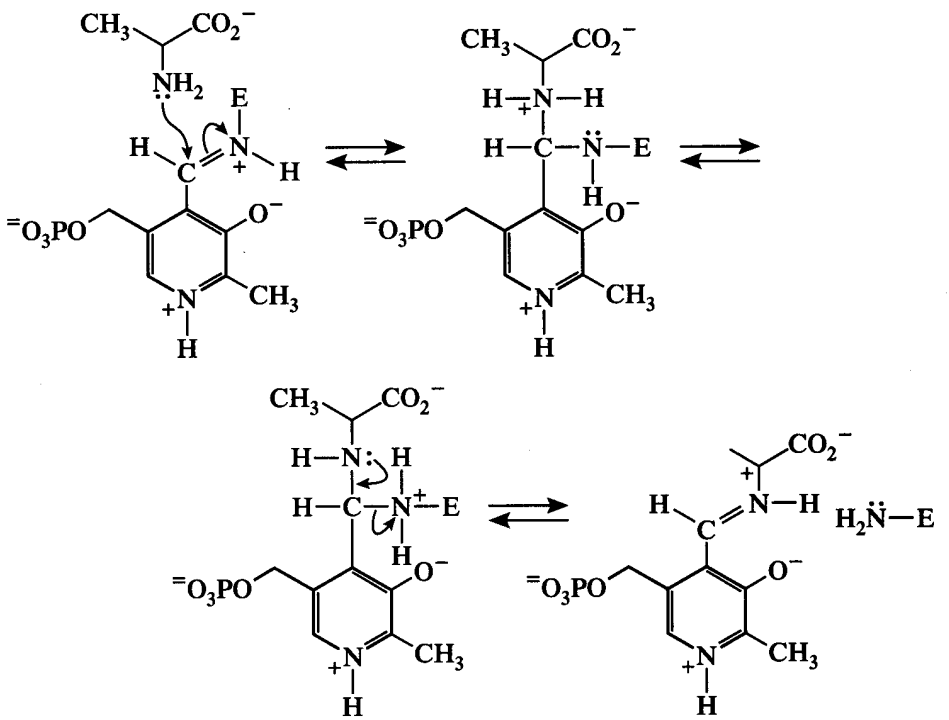
16.15 (a)



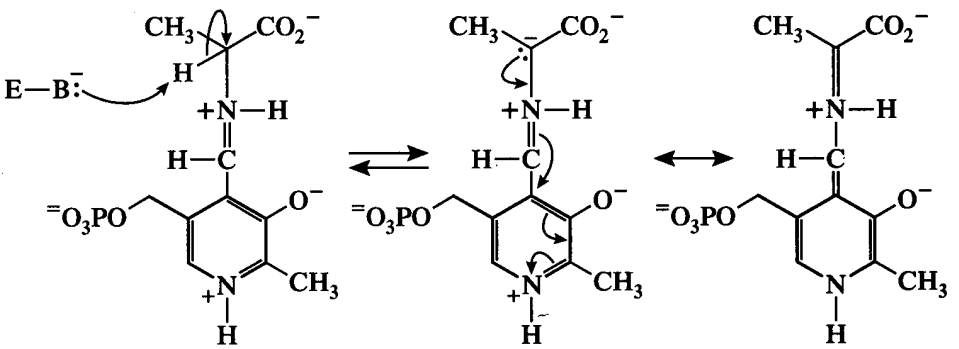
(b)



16.B1



16.B2



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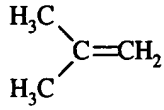
16.16 (a) $CH_3\overset{O}{\overset{\|}{C}}H \xrightarrow{HCN} CH_3\overset{OH}{\overset{|}{C}}HCN \xrightarrow[\text{reflux}]{HCl,\ H_2O} CH_3\overset{OH}{\overset{|}{C}}HCO_2H$

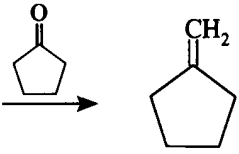
Lactic acid

(b) A racemic form

16.17 (a) $CH_3I \xrightarrow[(2)\ RLi]{(1)\ (C_6H_5)_3P} {:}\overset{-}{C}H_2{-}\overset{+}{P}(C_6H_5)_3 \xrightarrow{C_6H_5\overset{O}{\overset{\|}{C}}CH_3} C_6H_5\overset{CH_2}{\overset{|}{C}}{=}CH_2$ (CH$_3$ on C)

(b) $CH_3CH_2Br \xrightarrow[(2)\ RLi]{(1)\ (C_6H_5)_3P} CH_3\overset{-}{\underset{\cdot\cdot}{C}}H{-}\overset{+}{P}(C_6H_5)_3 \xrightarrow{C_6H_5\overset{O}{\overset{\|}{C}}CH_3} C_6H_5\overset{CH_3}{\overset{|}{C}}{=}CHCH_3$

(c) ${:}\overset{-}{C}H_2{-}\overset{+}{P}(C_6H_5)_3$ [from part (a)] $\xrightarrow{CH_3\overset{O}{\overset{\|}{C}}CH_3}$ 

(d) ${:}\overset{-}{C}H_2{-}\overset{+}{P}(C_6H_5)_3$ [from part (a)] $\longrightarrow$ 

(e) $CH_3CH_2CH_2Br \xrightarrow[(2)\ RLi]{(1)\ (C_6H_5)_3P} CH_3CH_2\overset{-}{\underset{\cdot\cdot}{C}}H{-}\overset{+}{P}(C_6H_5)_3 \xrightarrow{CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3}$

$CH_3CH_2CH{=}\overset{CH_3}{\overset{|}{C}}CH_2CH_3$

(f) $CH_2{=}CHCH_2Br \xrightarrow[(2)\ RLi]{(1)\ (C_6H_5)_3P} CH_2{=}CH\overset{-}{\underset{\cdot\cdot}{C}}H{-}\overset{+}{P}(C_6H_5)_3 \xrightarrow{C_6H_5\overset{O}{\overset{\|}{C}}H}$

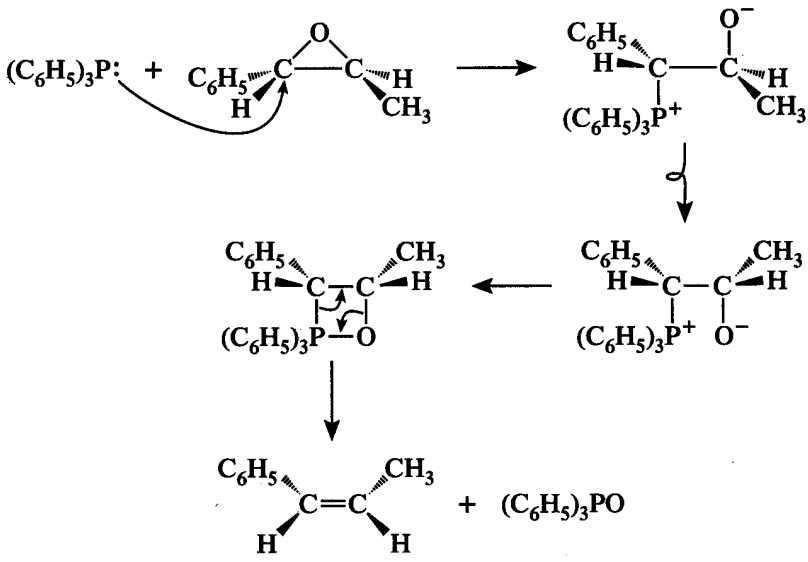
$C_6H_5CH{=}CHCH{=}CH_2$

(g) $C_6H_5CH_2Br \xrightarrow[(2)\ RLi]{(1)\ (C_6H_5)_3P} C_6H_5\overset{-}{\underset{\cdot\cdot}{C}}H{-}\overset{+}{P}(C_6H_5)_3 \xrightarrow{C_6H_5\overset{O}{\overset{\|}{C}}H}$

$C_6H_5CH{=}CHC_6H_5$

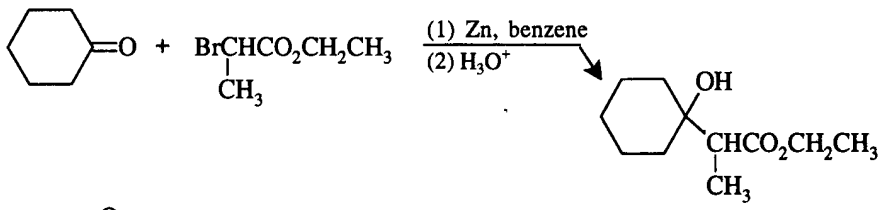
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16.18



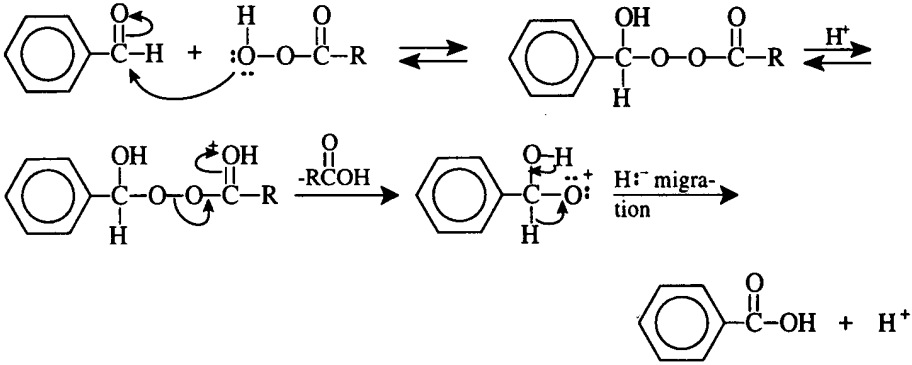
16.19 (a) $(CH_3)_2C{=}O + BrCH_2CO_2CH_2CH_3 \xrightarrow[\text{benzene}]{Zn} (CH_3)_2C(OZnBr)CH_2CO_2CH_2CH_3 \xrightarrow{H_3O^+} (CH_3)_2C(OH)CH_2CO_2CH_2CH_3$

(b)



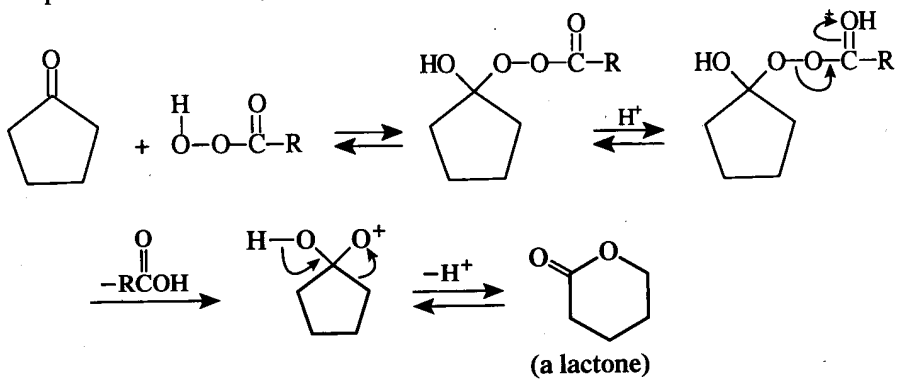
(c) $CH_3CH_2CHO + BrCH_2CO_2CH_2CH_3 \xrightarrow[(2)\ H_3O^+,\ \text{heat}]{(1)\ Zn,\ \text{benzene}} CH_3CH_2CH{=}CHCO_2CH_2CH_3 \xrightarrow[Pt]{H_2} CH_3CH_2CH_2CH_2CO_2CH_2CH_3$

16.20

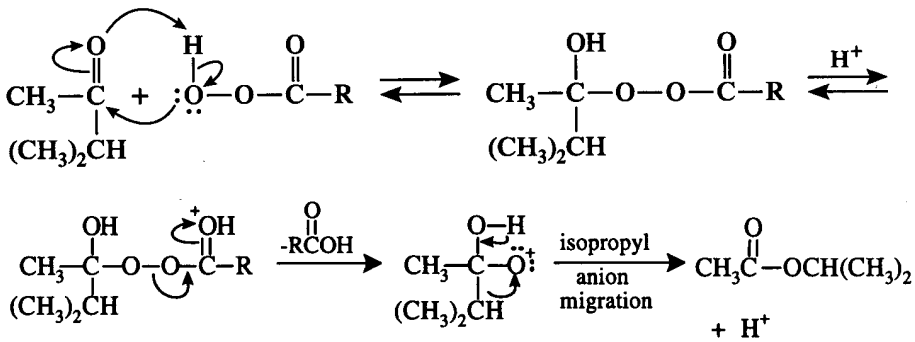


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16.21 The product is a lactone, formed as follows:



16.22 $CH_3C(=O)-O-CH(CH_3)_2$ The isopropyl group has a greater migratory aptitude than the methyl group. The mechanism is as follows:



16.23

(a) HCHO — Methanal

(b) CH_3CHO — Ethanal

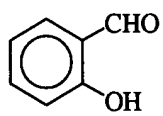
(c) $C_6H_5CH_2CHO$ — Phenylethanal

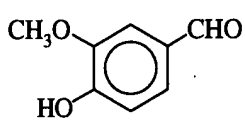
(d) CH_3COCH_3 — Propanone

(e) $CH_3COCH_2CH_3$ — Butanone

(f) $CH_3COC_6H_5$ — 1-Phenylethanone or methyl phenyl ketone

(g) $C_6H_5COC_6H_5$ — Diphenylmethanone or diphenyl ketone

(h)  — 2-Hydroxybenzaldehyde or *o*-hydroxybenzaldehyde

(i)  — 4-Hydroxy-3-methoxybenzaldehyde

(j) $CH_3CH_2COCH_2CH_3$ — 3-Pentanone

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(k) $CH_3CH_2COCH(CH_3)_2$ 2-Methyl-3-pentanone

(l) $(CH_3)_2CHCOCH(CH_3)_2$ 2,4-Dimethyl-3-pentanone

(m) $CH_3(CH_2)_3CO(CH_2)_3CH_3$ 5-Nonanone

(n) $CH_3(CH_2)_2CO(CH_2)_2CH_3$ 4-Heptanone

(o) $C_6H_5CH{=}CHCHO$ 3-Phenyl-2-propenal

16.24 (a) $CH_3CH_2CH_2OH$

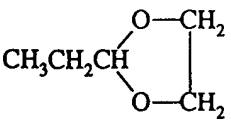
(b) $CH_3CH_2CHOHC_6H_5$

(c) $CH_3CH_2CH_2OH$

(d) $CH_3CH_2\overset{\overset{O}{\|}}{C}-O^-$

(e) $CH_3CH_2CH{=}CH_2$

(f) $CH_3CH_2CH_2OH$

(g) 

(h) $CH_3CH_2CH{=}CHCH_3$

(i) $CH_3CH_2CHOHCH_2CO_2C_2H_5$

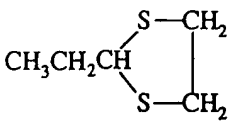
(j) $CH_3CH_2CO_2^-\,NH_4^+ + Ag\downarrow$

(k) $CH_3CH_2CH{=}NOH$

(l) $CH_3CH_2CH{=}NNHCONH_2$

(m) $CH_3CH_2CH{=}NNHC_6H_5$

(n) $CH_3CH_2CO_2H$

(o) 

(p) $CH_3CH_2CH_3 + CH_3CH_3 + NiS$

16.25 (a) $CH_3CHOHCH_3$

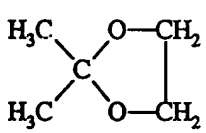
(b) $C_6H_5\underset{\underset{CH_3}{|}}{C}OHCH_3$

(c) $CH_3CHOHCH_3$

(d) No reaction

(e) $CH_3\underset{\underset{CH_3}{|}}{C}{=}CH_2$

(f) $CH_3CHOHCH_3$

(g) 

(h) $CH_3CH{=}C(CH_3)_2$

(i) $CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}CH_2CO_2C_2H_5$

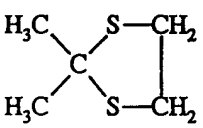
(j) No reaction

(k) $CH_3\underset{\underset{CH_3}{|}}{C}{=}NOH$

(l) $CH_3\underset{\underset{CH_3}{|}}{C}{=}NNHCONH_2$

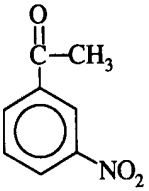
(m) $CH_3\underset{\underset{CH_3}{|}}{C}{=}NNHC_6H_5$

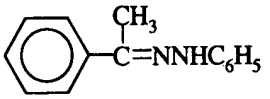
(n) No reaction

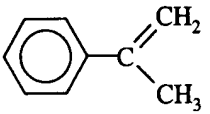
(o) 

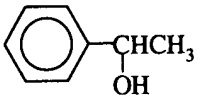
(p) $CH_3CH_2CH_3 + CH_3CH_3 + NiS$

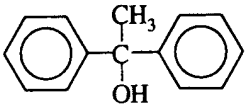
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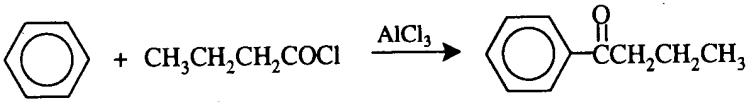
16.26 (a) 

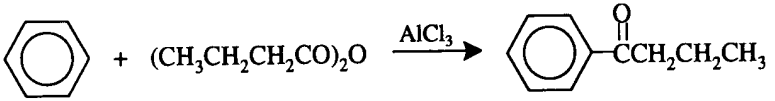
(b) 

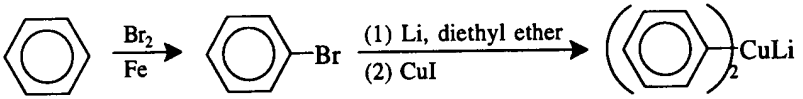
(c) 

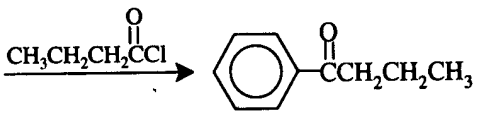
(d) 

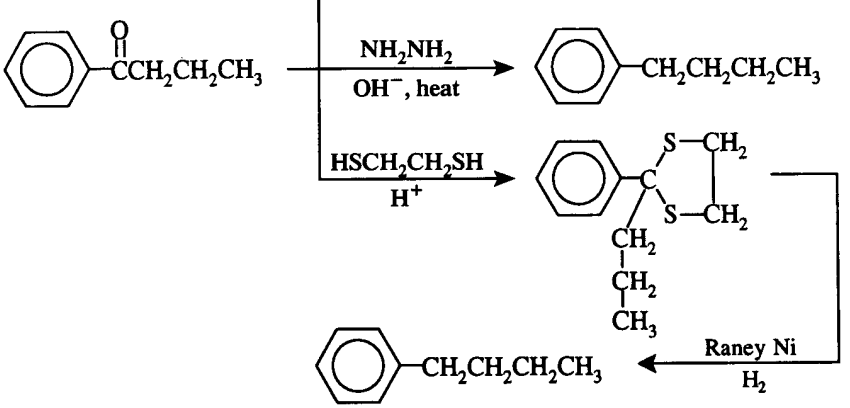
(e) 

16.27 (a) 

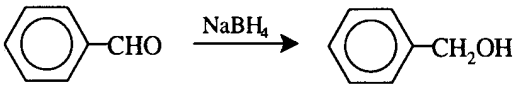


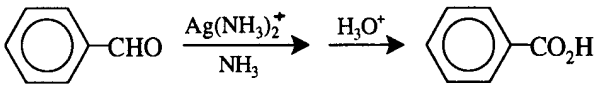


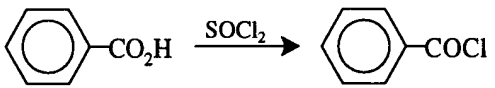


(b) 

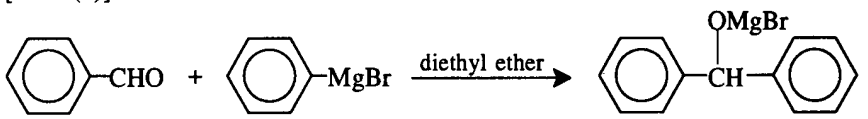
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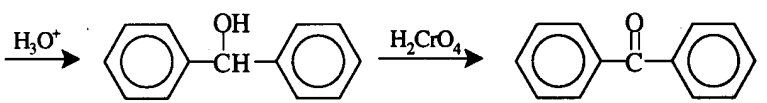
16.28 (a) 

(b) 

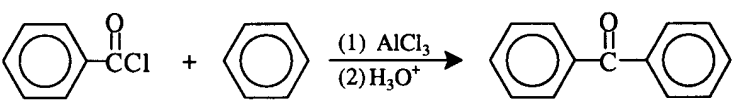
(c) 

[from (b)]

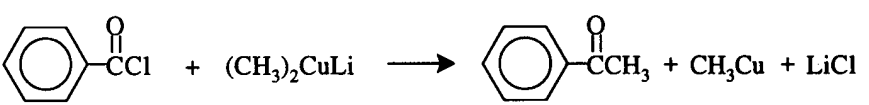
(d) 



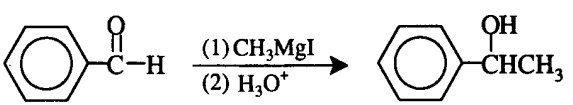
or

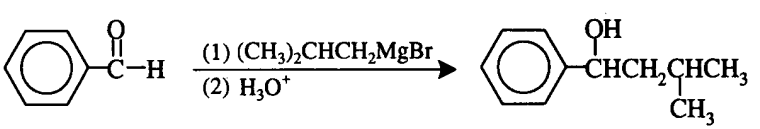


[from (c)]

(e) 

[from (c)]

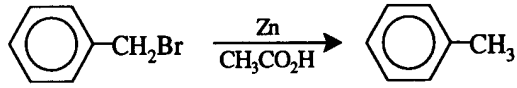
(f) 

(g) 

(h)

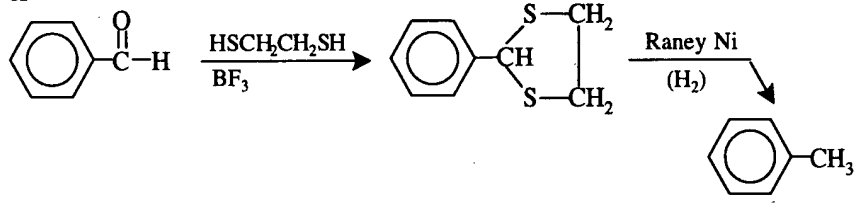
[from (a)]

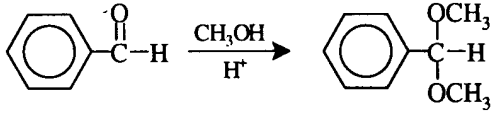
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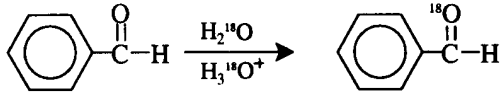
(i) 

[from (h)]

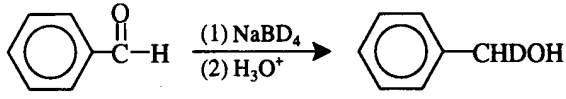
or



(j) 

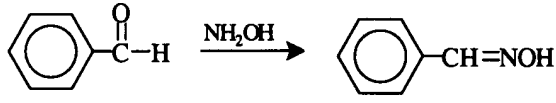
(k) 

(See problem 16.8 for the mechanism)

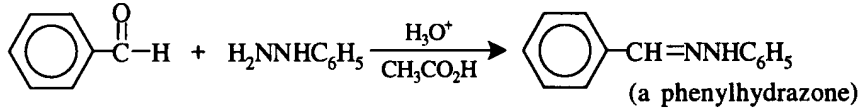
(l) 

(m) 

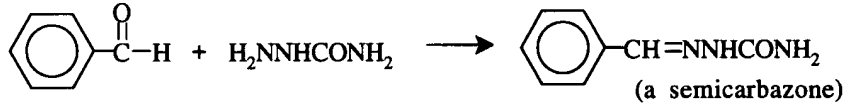
(a cyanohydrin)

(n) 

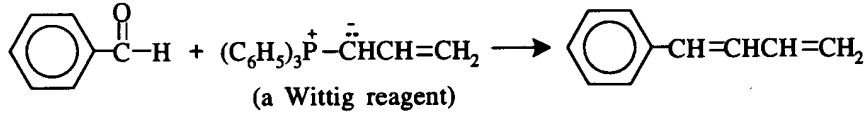
(an oxime)

(o) 

(a phenylhydrazone)

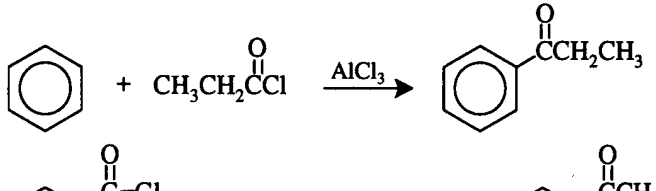
(p) 

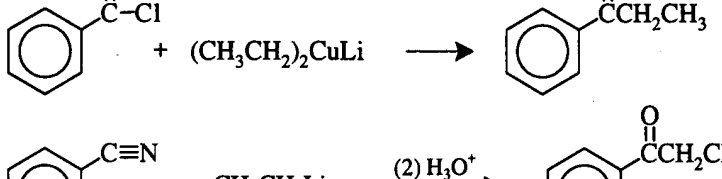
(a semicarbazone)

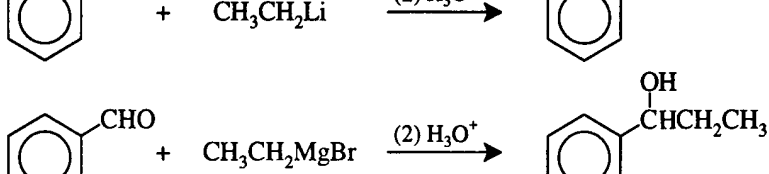
(q) 

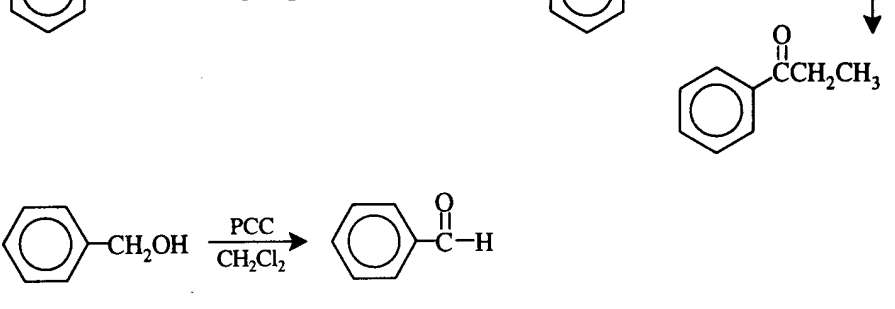
(a Wittig reagent)

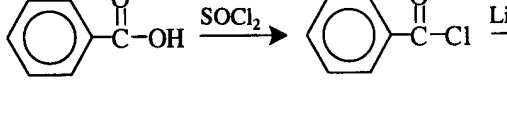
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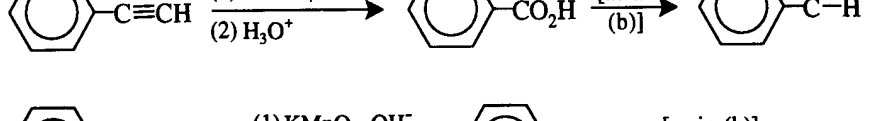
16.29 (a) 

(b) 

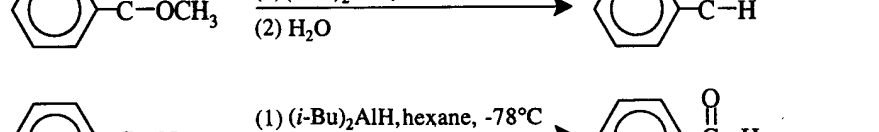
(c) 

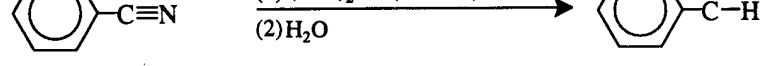
(d) 

16.30 (a) 

(b) 

(c) 

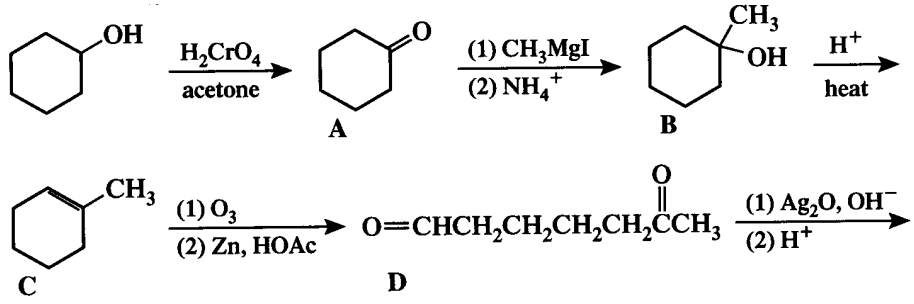
(d) 

(e) 

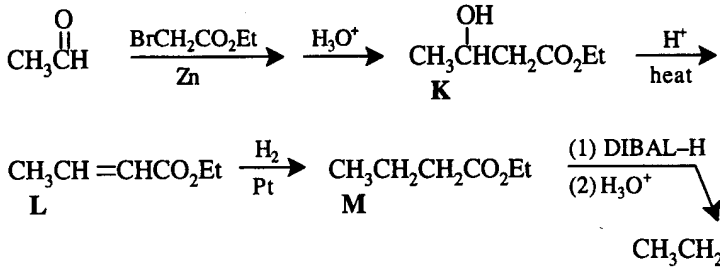
(f)

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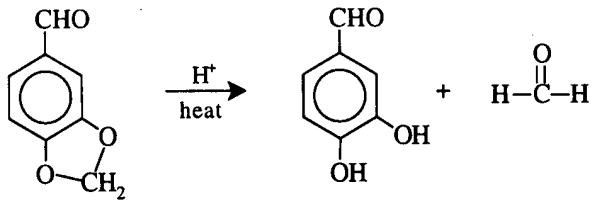
16.31



16.32

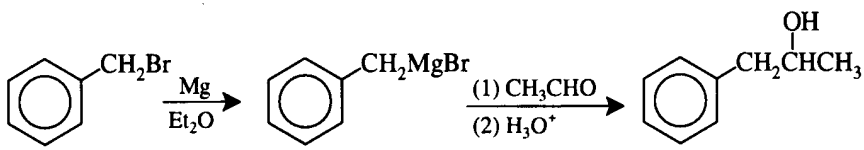


16.33

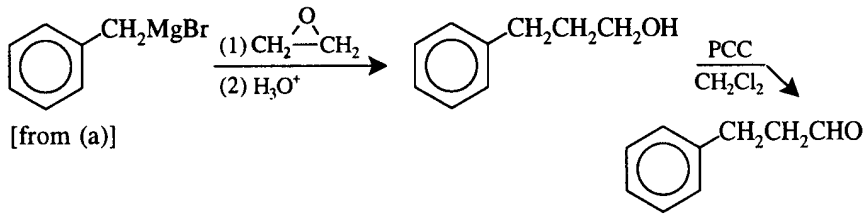


The compound $C_7H_6O_3$ is 3,4-dihydroxybenzaldehyde. The reaction involves hydrolysis of the acetal of formaldehyde.

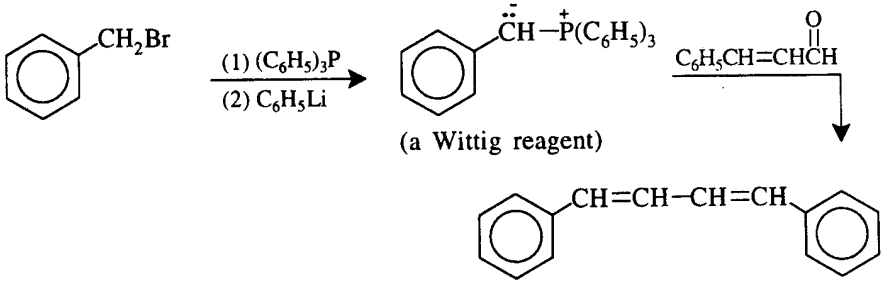
16.34 (a)

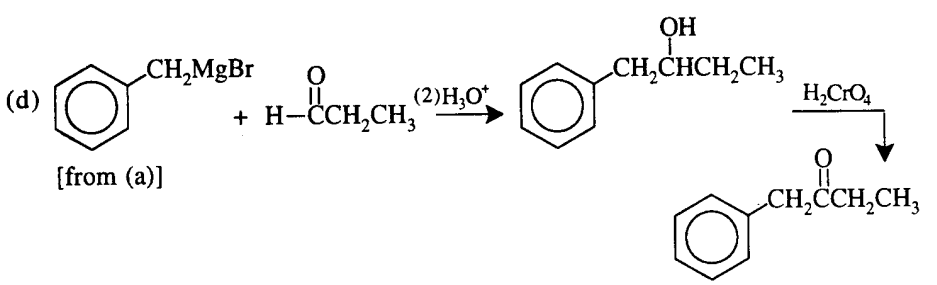


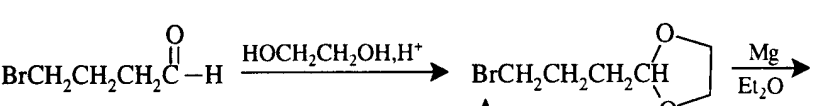
(b)

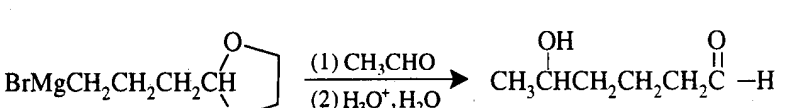


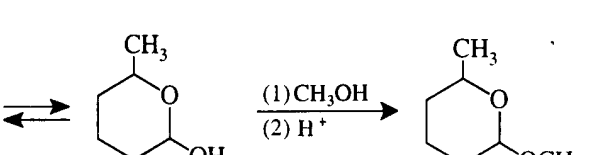
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(c) 

(d) 

16.35 



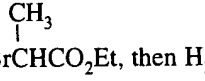


16.36 (a) $(CH_3)_2SO_4$, NaOH, or CH_3I, NaOH

(b) PCC/CH_2Cl_2

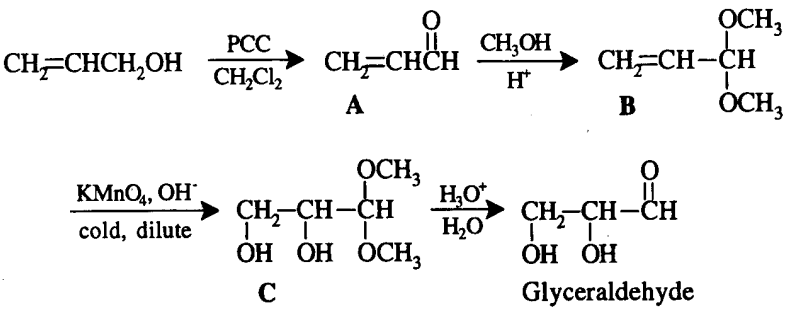
(c) Zn, $BrCHCO_2Et$, then H_3O^+

(d) $LiAlH_4$, then H_2O

Intermediate is 

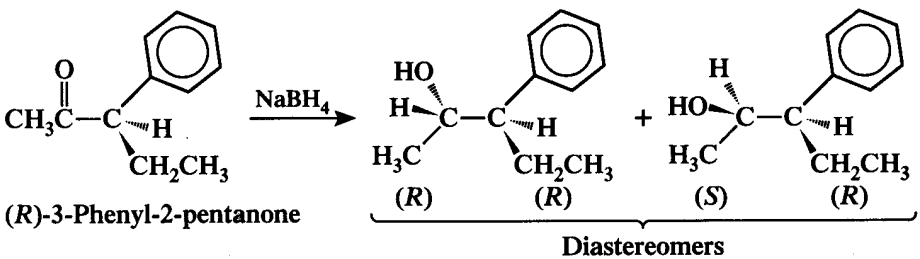
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16.37

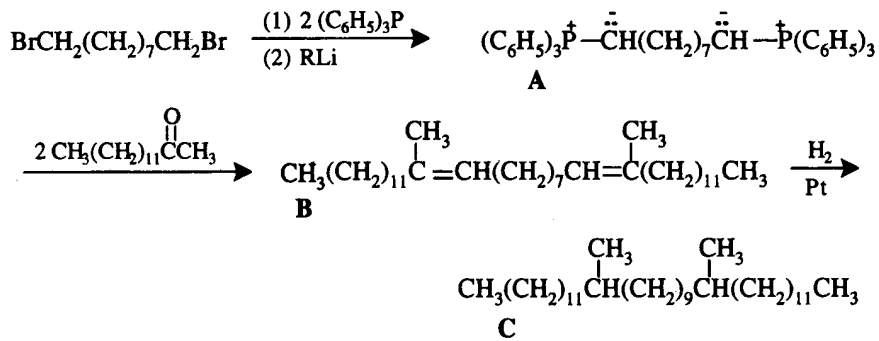


The product would be racemic as no chiral reagents were used.

16.38



16.39



16.40 (a) $Ag(NH_3)_2^+OH^-$ (positive test with benzaldehyde)

(b) $Ag(NH_3)_2^+OH^-$ (positive test with hexanal)

(c) Concentrated H_2SO_4 (2-hexanone is soluble)

(d) CrO_3 in H_2SO_4 (positive test with 2-hexanol)

(e) Br_2 in CCl_4 (decolorization with $C_6H_5CH{=}CHCOC_6H_5$)

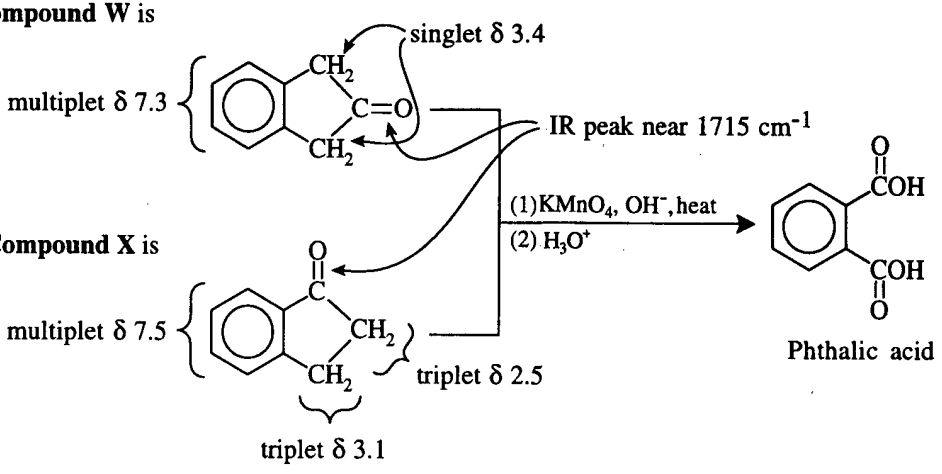
(f) $Ag(NH_3)_2^+OH^-$ (positive test with pentanal)

(g) Br_2 in CCl_4 (immediate decolorization occurs with enol form)

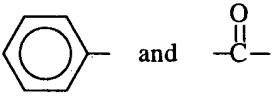
(h) $Ag(NH_3)_2^+OH^-$ (positive test with cyclic hemiacetal)

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16.41 **Compound W** is



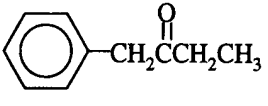
16.42 Each ^{1}H NMR spectrum (Figs. 16.4 and 16.5) has a five-hydrogen peak near δ 7.2, suggesting the **Y** and **Z** each has a C_6H_5-group. The IR spectrum of each compound shows a strong peak near 1710 cm^{-1}. This absorption indicates that each compound has a C=O group not adjacent to the phenyl group. We have, therefore, the following pieces,



If we subtract the atoms of these pieces from the molecular formula,

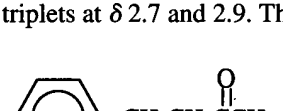
$$\begin{array}{ll} & C_{10}H_{12}O \\ -) & \underline{C_7H_5O} \quad (C_6H_5 + C{=}O) \\ \text{We are left with,} & C_3H_7 \end{array}$$

In the ^{1}H NMR spectrum of **Y**, we see an ethyl group [triplet, δ 1.0 (3H) and quartet, δ 2.45 (2H)] and an unsplit $-CH_2-$group [singlet, δ 3.7 (2H)]. This means that **Y** must be



1-Phenyl-2-butanone

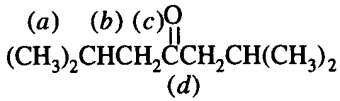
In the ^{1}H NMR spectrum of **Z**, we see an unsplit $-CH_3$ group [singlet, δ 2.1 (3H)] and two triplets at δ 2.7 and 2.9. This means **Z** must be



4-Phenyl-2-butanone

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16.43 That compound **A** forms a phenylhydrazone, gives a negative Tollens' test, and gives an IR band near 1710 cm^{-1} indicates that **A** is a ketone. The ^{13}C spectrum of **A** contains only four signals indicating that A has a high degree of symmetry. The information from the DEPT ^{13}C NMR spectra enables us to conclude that **A** is diisobutyl ketone:



Assignments:

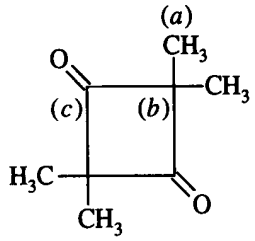
(a) δ 22.6

(b) δ 24.4

(c) δ 52.3

(d) δ 210.0

16.44 That the ^{13}C spectrum of **B** contains only three signals indicates that **B** has a highly symmetrical structure. The information from DEPT spectra indicates the presence of equivalent methyl groups (CH_3 at δ 18.8), equivalent $-\overset{|}{C}-$ groups (at δ 70.4), and equivalent $\rangle C{=}O$ groups (at δ 215.0). These features allow only one possible structure for **B:**



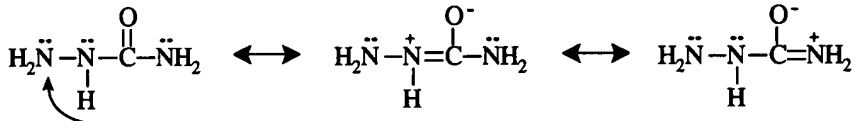
Assignments:

(a) δ 18.8

(b) δ 70.4

(c) δ 215.0

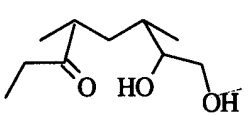
16.45 The two nitrogen atoms of semicarbazide that are adjacent to the C=O group bear partial positive charges because of resonance contributions made by the second and third structures below.



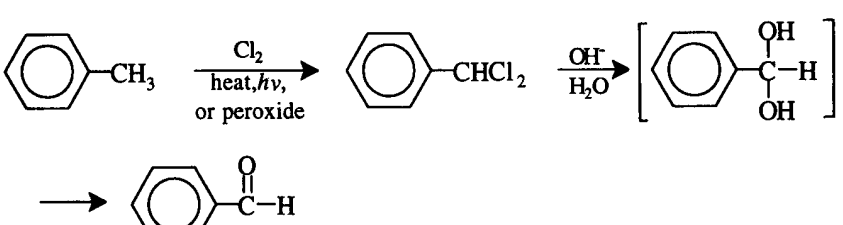
Only this nitrogen is nucleophilic.

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16.46 Hydrolysis of the acetal linkage of multistriatin produces the ketodiol below.

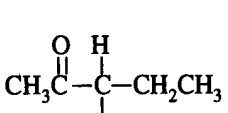


16.47



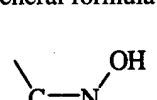
The *gem*-diol formed in the alkaline hydrolysis step readily loses water to form the aldehyde.

16.48

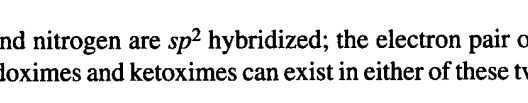


or its enantiomer

16.49 The general formula for an oxime is



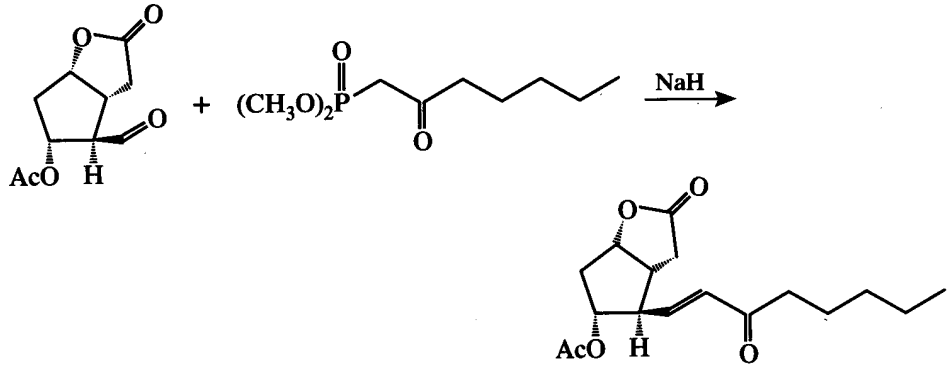
Both carbon and nitrogen are sp^2 hybridized; the electron pair on nitrogen occupies one sp^2 orbital. Aldoximes and ketoximes can exist in either of these two stereoisomeric forms:



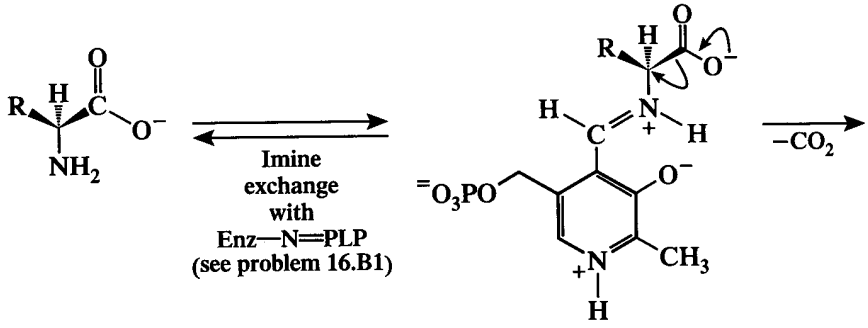
This type of stereoisomerism is also observed in the case of other compounds that possess the C=N group, for example, phenylhydrazones and semicarbazones.

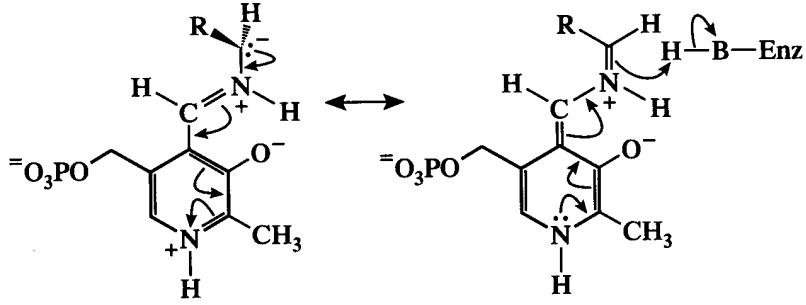
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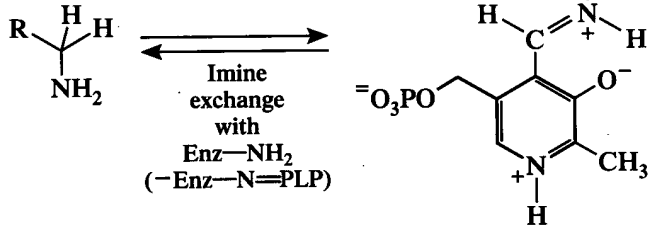
16.50



*16.51

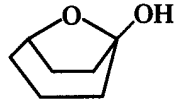




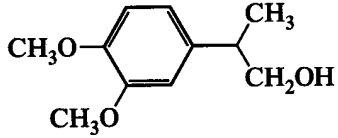


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***16.52** (a) O—H stretch at about 3300 cm^{-1}; C=O stretch at about 1710 cm^{-1}

(b) 

(Intramolecular hemiacetal from *A*)

***16.53** 

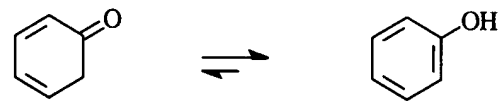
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17 ALDEHYDES AND KETONES II. ALDOL REACTIONS

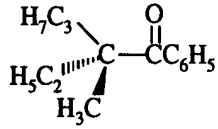
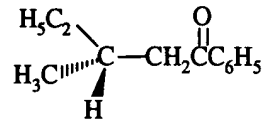
SOLUTIONS TO PROBLEMS

17.1

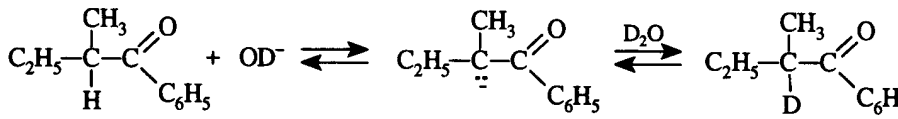


2,4-Cyclohexadien-1-one (keto form) ⇌ Phenol (enol form)

The enol form is aromatic, and it is therefore stabilized by the resonance energy of the benzene ring.

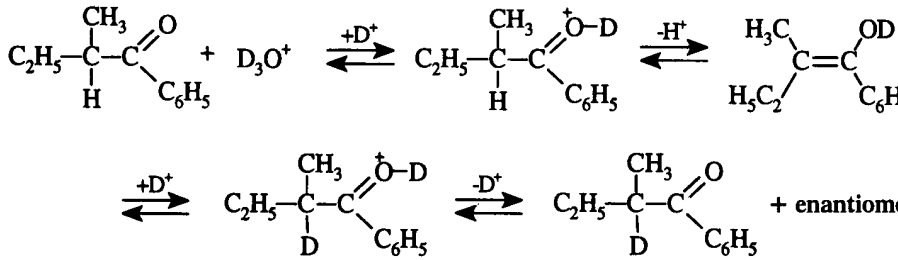
17.2 No.  does not have a hydrogen attached to its α-carbon atom (which is a stereocenter) and thus enol formation involving the stereocenter is not possible. With  the stereocenter is a β carbon and thus enol formation does not affect it.

17.3 In OD^-/D_2O:



+ enantiomer

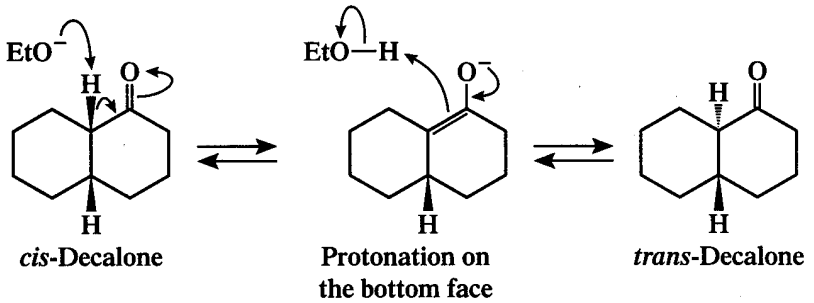
In D_3O^+/D_2O:

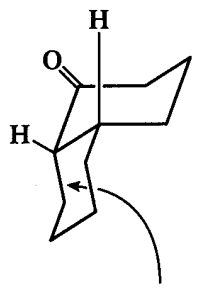


+ enantiomer

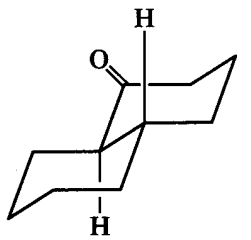
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17.4





A large group is axial in *cis*-decalone.



No bulky groups are axial in *trans*-decalone.

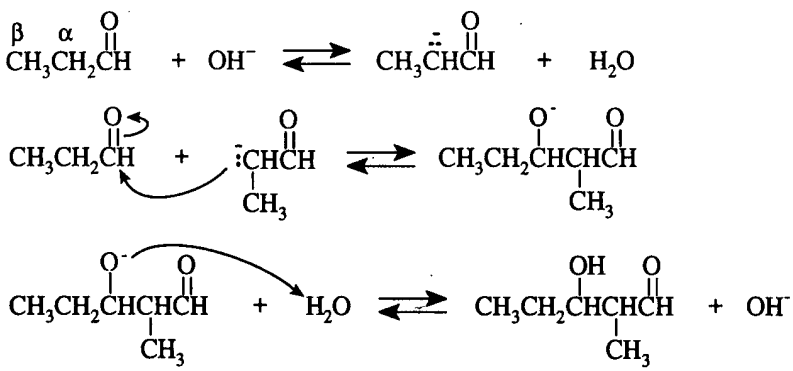
17.5 The reaction is said to be "base promoted" because base is consumed as the reaction takes place. A catalyst is, by definition, not consumed.

17.6 (a) The slow step in base-catalyzed racemization is the same as that in base-promoted halogenation—*the formation of an enolate ion.* (Formation of an enolate ion from *sec*-butyl phenyl ketone leads to racemization because the enolate ion is achiral. When it accepts a proton, it yields a racemic form.) The slow step in acid-catalyzed racemization is also the same as that in acid-catalyzed halogenation—*the formation of an enol.* (The enol, like the enolate ion, is achiral and tautomerizes to yield a racemic form of the ketone.)

(b) According to the mechanism given, the slow step for acid-catalyzed iodination (formation of the enol) is the same as that for acid-catalyzed bromination. Thus, we would expect both reactions to occur at the same rate.

(c) Again, the slow step for both reactions (formation of the enolate ion) is the same, and consequently, both reactions take place at the same rate.

17.7 (a)

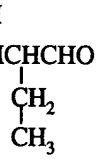


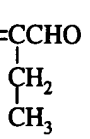
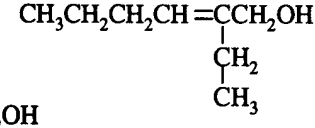
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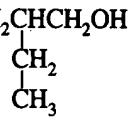
(b) For $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}H$ to form, a hydroxide ion would have to remove a β proton in the first step. This does not happen because the anion that would be produced, that is, $\ddot{:}CH_2CH_2CHO$, cannot be stabilized by resonance.

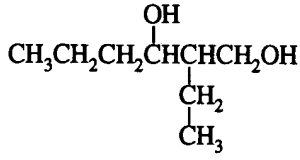
(c) $CH_3CH_2CH{=}\overset{\displaystyle O}{\overset{\|}{C}}\overset{\displaystyle CH_3}{\overset{|}{C}}H$

17.8 $CH_3CHO \xrightarrow[5°C]{10\%\ NaOH} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CHO$ (aldol) $\xrightarrow{heat} CH_3CH{=}CHCHO \xrightarrow[Ni]{H_2} CH_3CH_2CH_2CH_2OH$

17.9 (a) $2\,CH_3CH_2CH_2CHO \xrightarrow[H_2O]{OH^-}$ 

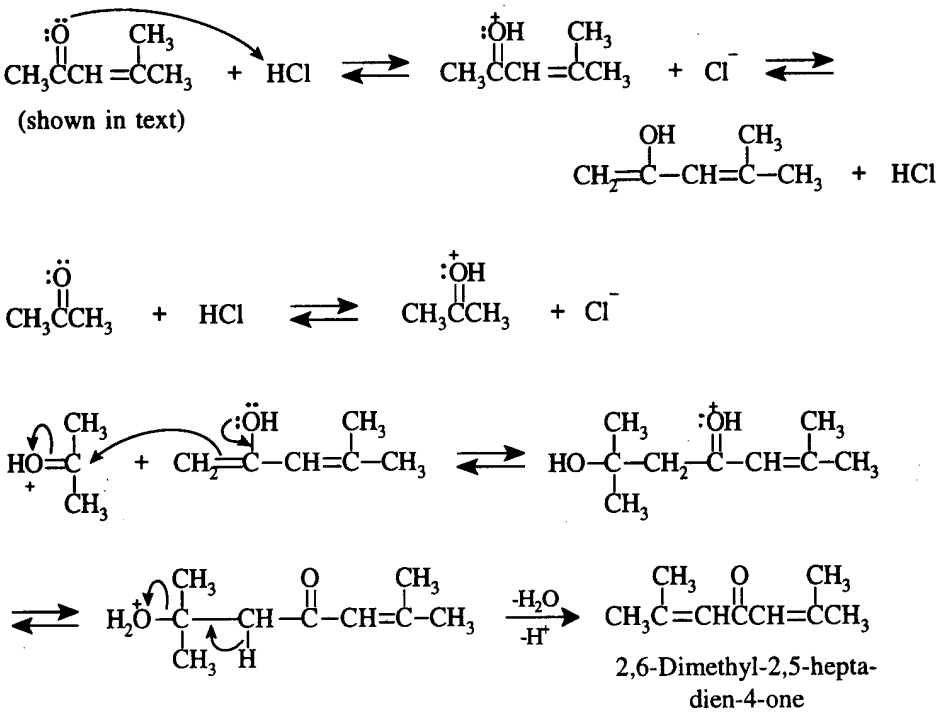
(b) Product of (a) $\xrightarrow[-H_2O]{H^+}$  $\xrightarrow[(2)\ H_2O]{(1)\ LiAlH_4,\ Et_2O}$ 

(c) Product of (b) $\xrightarrow[Pt]{H_2}$ 

(d) Product of (a) $\xrightarrow{NaBH_4}$ 

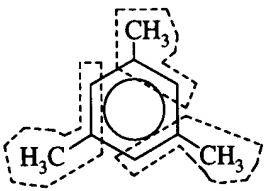
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17.10 (shown in text)



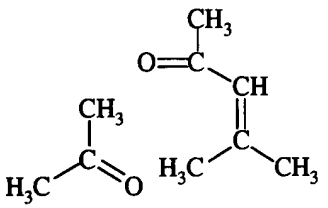
2,6-Dimethyl-2,5-hepta-dien-4-one

17.11 Drawing the molecules as they will appear in the final product helps to visualize the necessary steps:



Mesitylene

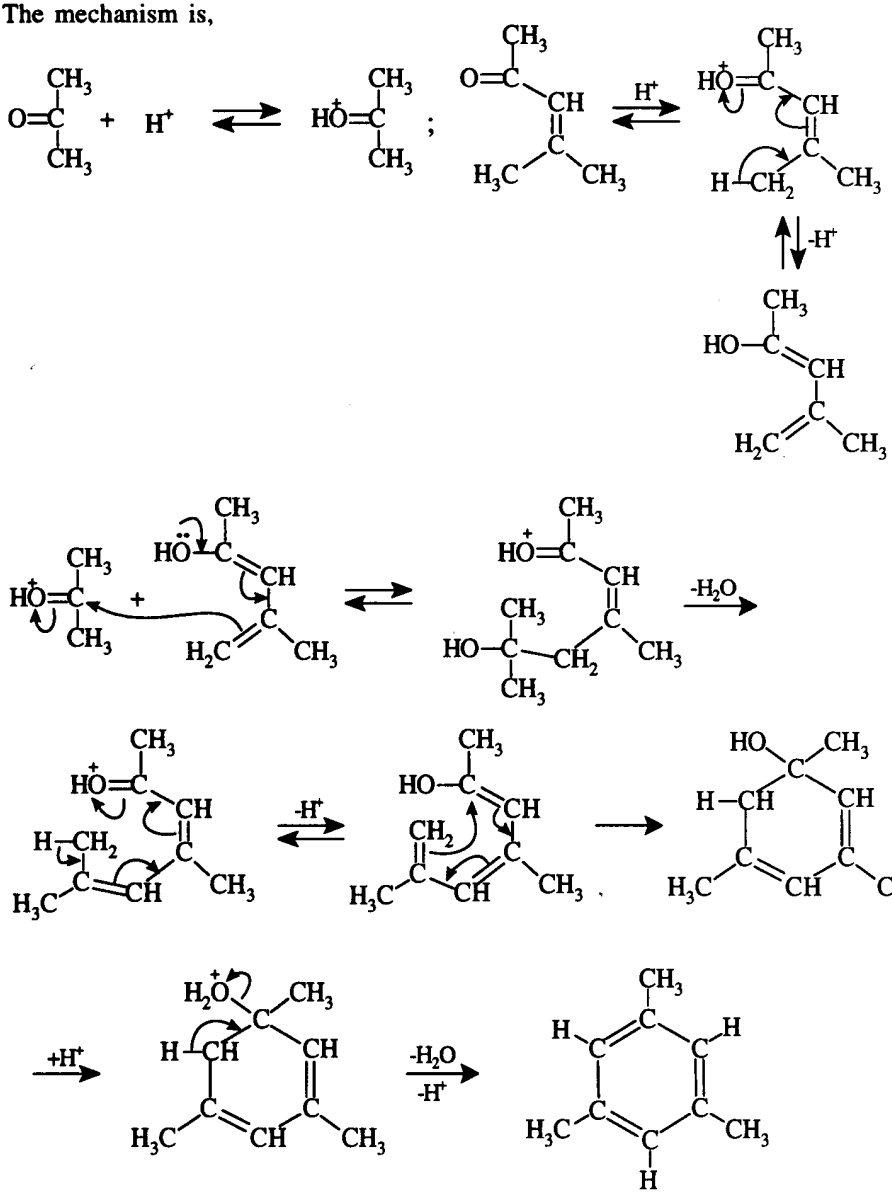
The two molecules that lead to mesitylene are shown as follows:



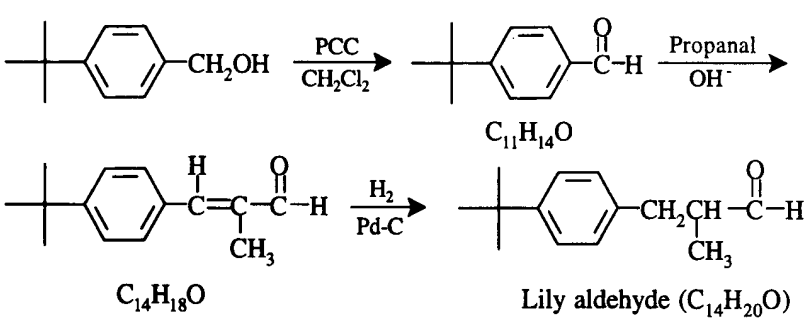
This molecule (4-methyl-3-penten-2-one) is formed by an acid-catalyzed condensation between two molecules of acetone as shown in the text.

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The mechanism is,

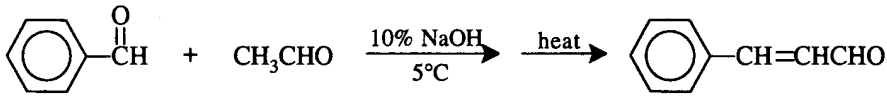


17.12



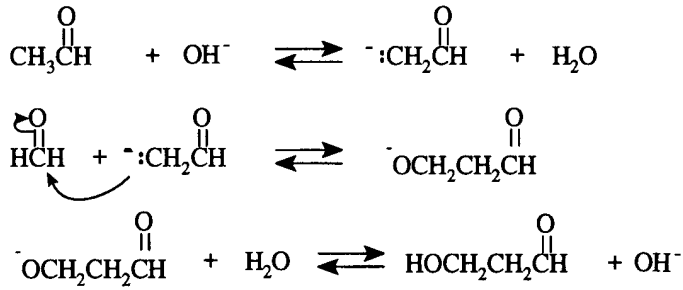
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17.13

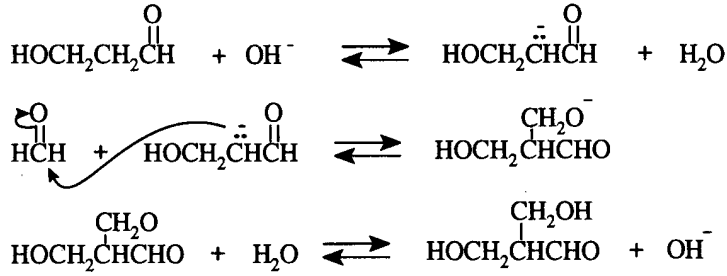


17.14 Three successive aldol additions occur.

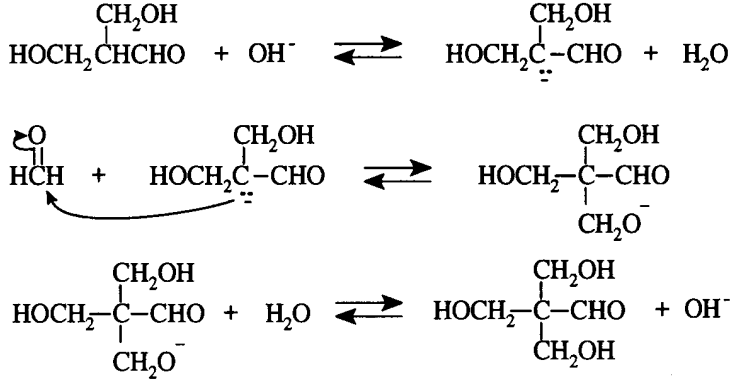
First Aldol Addition



Second Aldol Addition

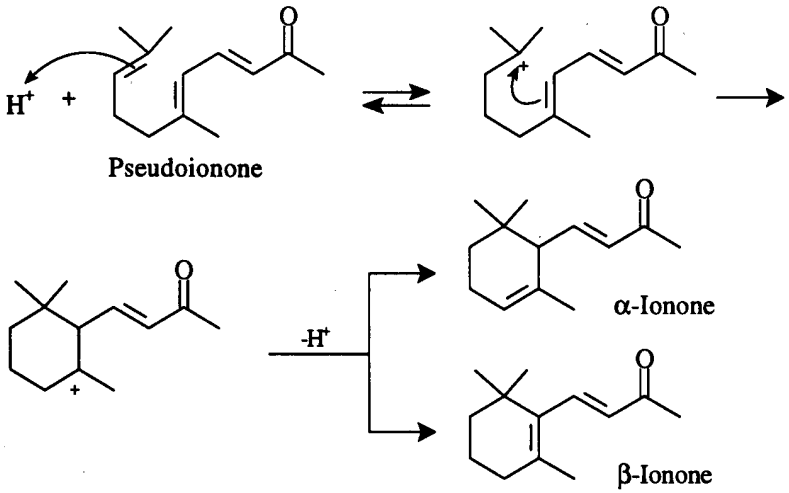


Third Aldol Addition



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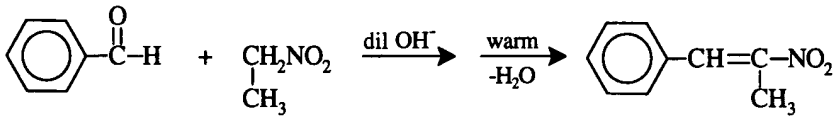
17.15 (a) $CH_3CO_2H + BF_3 \rightleftharpoons CH_3CO_2BF_3^- + H^+$



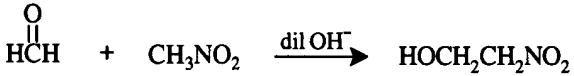
(b) In β-ionone both double bonds and the carbonyl group are conjugated; thus it is more stable.

(c) β-Ionone, because it is a fully conjugated unsaturated system.

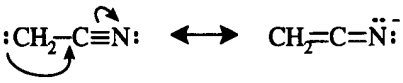
17.16 (a)



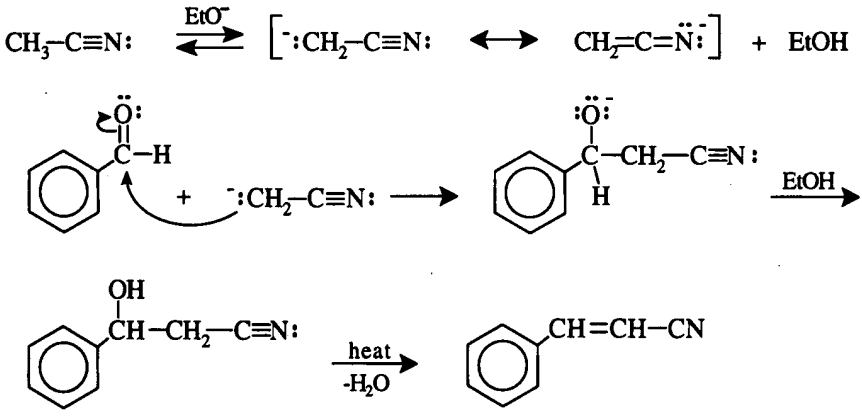
(b)



17.17 (a)

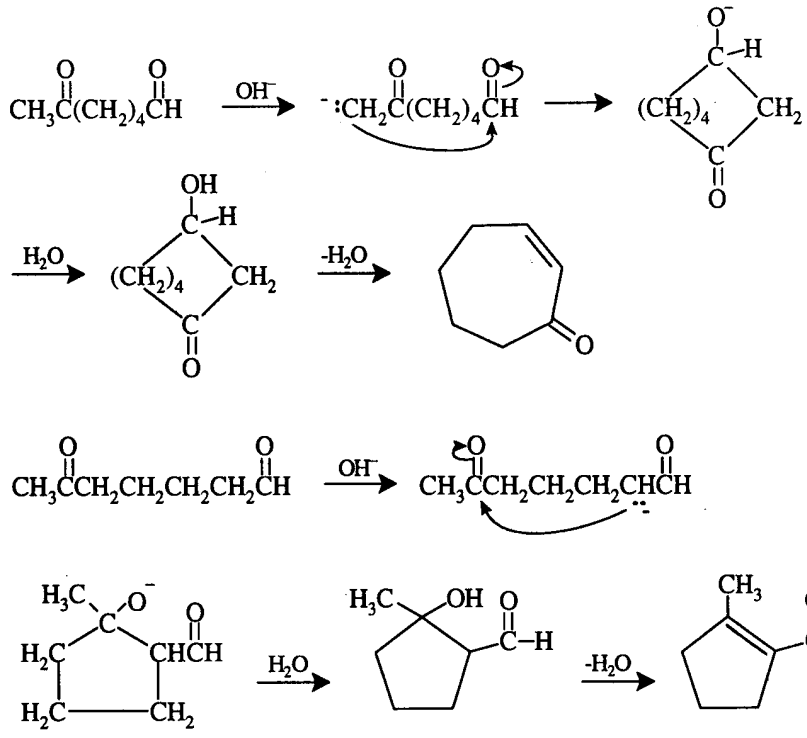


(b)

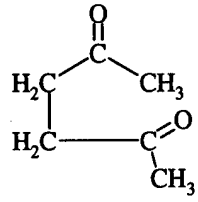


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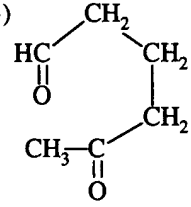
17.18



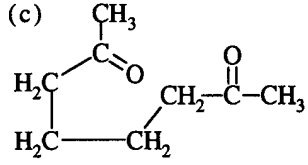
17.19 (a)



(b)



(c)

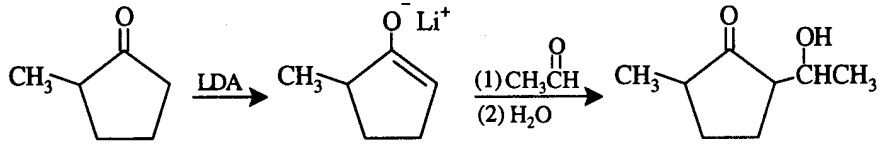


Notice that starting compounds are drawn so as to indicate which atoms are involved in the cyclization reaction.

17.20 It is necessary for conditions to favor the intramolecular reaction rather than the intermolecular one. One way to create these conditions is to use very dilute solutions when we carry out the reaction. When the concentration of the compound to be cyclized is very low (i.e., when we use what we call a "high dilution technique"), the probability is greater that one end of a molecule will react with the other end of that same molecule rather than with a different molecule.

17.21

(a)



Kinetic enolate

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(b) $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{LDA} CH_3CH_2\overset{O^- Li^+}{\overset{|}{C}}=CH_2 \xrightarrow[(2)\ H_2O]{(1)\ C_6H_5\overset{O}{\overset{\|}{C}}H} CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2\overset{OH}{\overset{|}{C}}HC_6H_5$

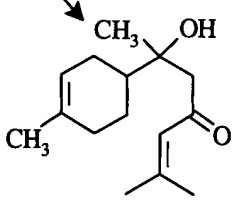
Kinetic enolate

(c) $CH_3\overset{CH_3}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{LDA} CH_3\overset{CH_3}{\overset{|}{C}}H\overset{O^- Li^+}{\overset{|}{C}}=CH_2 \xrightarrow[(2)\ H_2O]{(1)\ CH_3CH_2\overset{O}{\overset{\|}{C}}H} CH_3\overset{CH_3}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}CH_2\overset{OH}{\overset{|}{C}}HCH_2CH_3$

Kinetic enolate

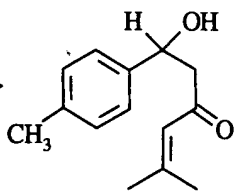
(d) $CH_3CH{=}CH\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{LDA} CH_3CH{=}CH\overset{O^- Li^+}{\overset{|}{C}}{=}CH_2 \xrightarrow[(2)\ H_2O]{(1)\ CH_3\overset{O}{\overset{\|}{C}}H} CH_3CH{=}CH\overset{O}{\overset{\|}{C}}CH_2\overset{OH}{\overset{|}{C}}HCH_3$

17.22 (a) $CH_3C(CH_3){=}CH\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{LDA} CH_3C(CH_3){=}CH\overset{O^- Li^+}{\overset{|}{C}}{=}CH_2 \xrightarrow[(2)\ H_2O]{(1)\ CH_3\text{-}C_6H_4\text{-}\overset{O}{\overset{\|}{C}}CH_3}$



α-Bisabolanone

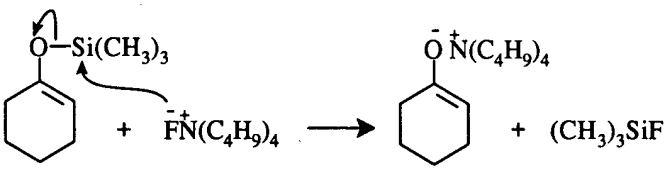
(b) $CH_3C(CH_3){=}CH\overset{O^- Li^+}{\overset{|}{C}}{=}CH_2$ [prepared in (a)] $\xrightarrow[(2)\ H_2O]{(1)\ CH_3\text{-}C_6H_4\text{-}\overset{O}{\overset{\|}{C}}H}$



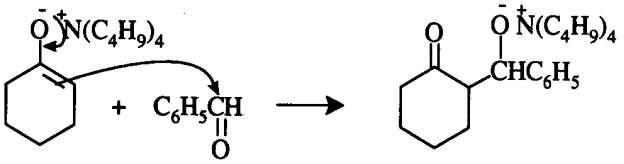
Ocimenone

17.B1

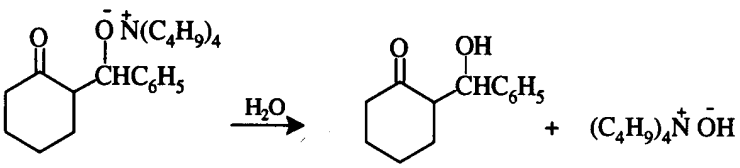
Step 1



Step 2

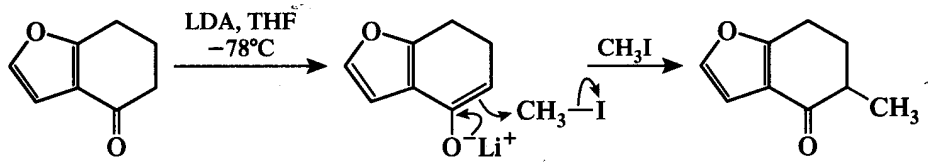


Step 3

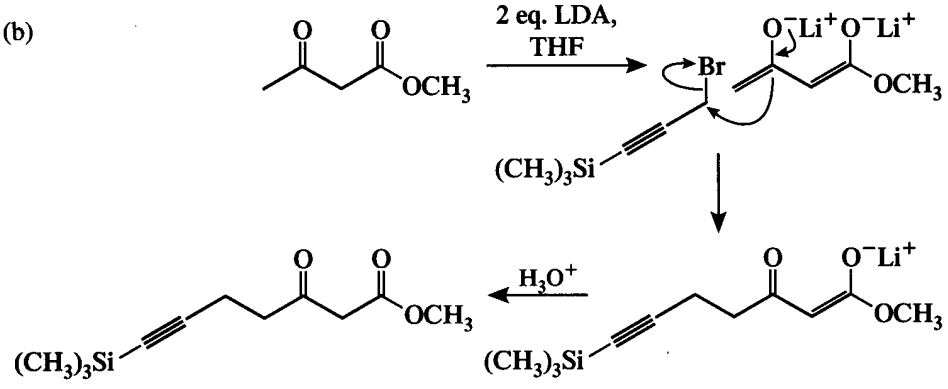


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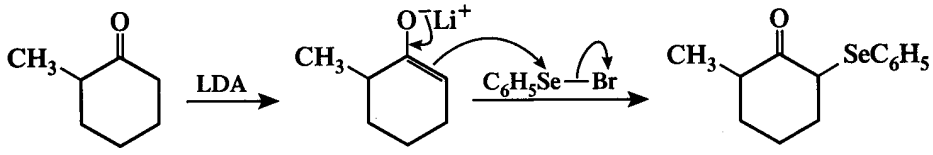
17.23 (a)



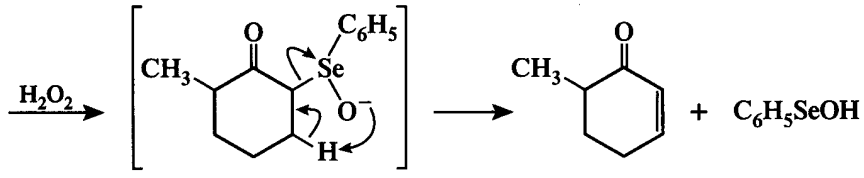
(b)



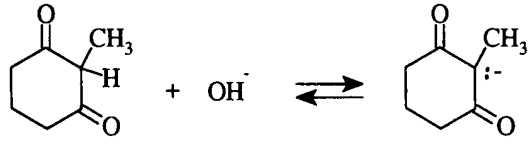
17.24

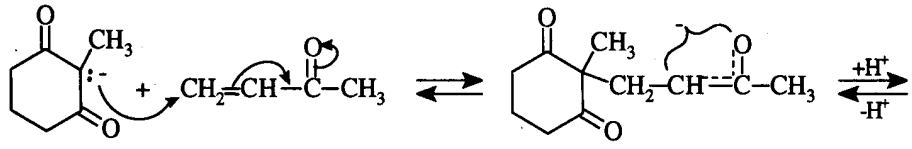


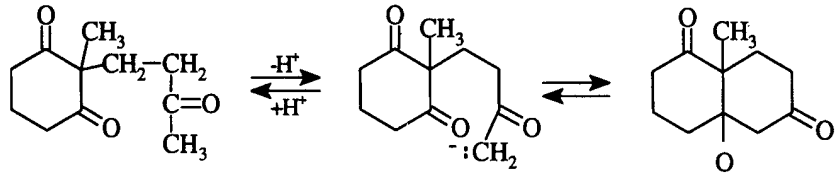
Kinetic enolate



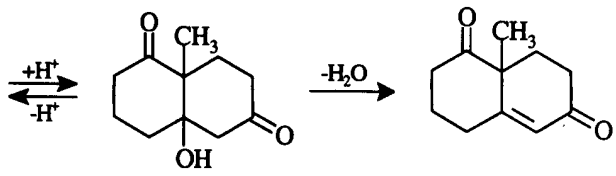
17.25 (a)



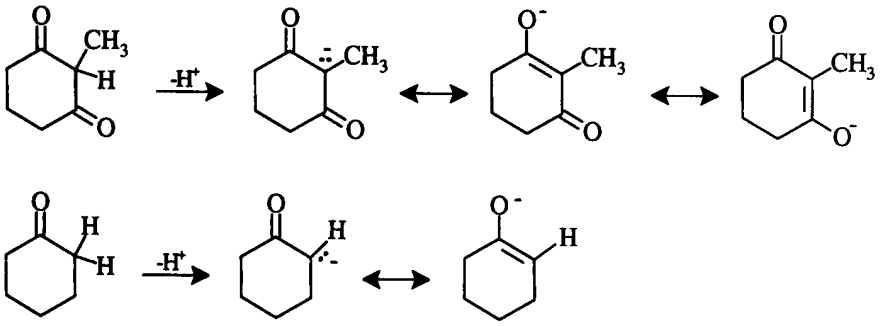




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(b) 2-Methyl-1,3-cyclohexanedione is more acidic because its enolate ion is stabilized by an additional resonance structure.



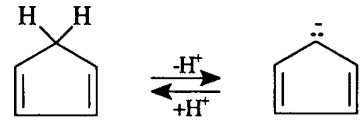
17.26 (a) $C_6H_5CCH_3 \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} C_6H_5\overset{\overset{O}{\|}}{C}CH_2:^-$

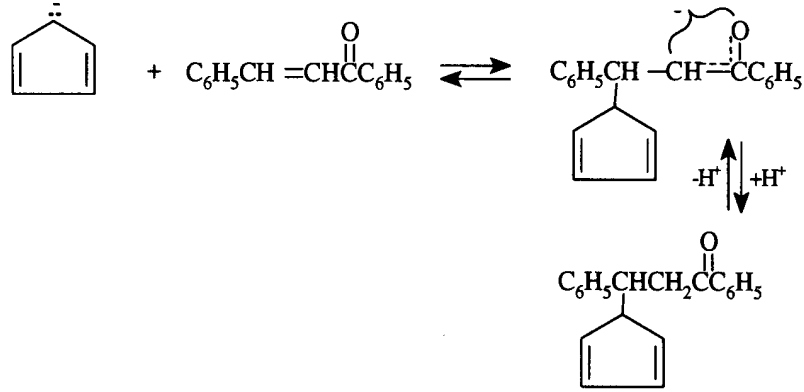
$C_6H_5\overset{\overset{O}{\|}}{C}CH_2:^- + C_6H_5CH{=}CH\overset{\overset{O}{\|}}{C}C_6H_5 \rightleftharpoons C_6H_5CH(CH_2\overset{\overset{O}{\|}}{C}C_6H_5)CH{=}\overset{\overset{O}{\|}}{C}C_6H_5$

$C_6H_5CH(CH_2\overset{\overset{O}{\|}}{C}C_6H_5)CH{=}\overset{\overset{O}{\|}}{C}C_6H_5 \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} C_6H_5CH(CH_2\overset{\overset{O}{\|}}{C}C_6H_5)CH_2\overset{\overset{O}{\|}}{C}C_6H_5$

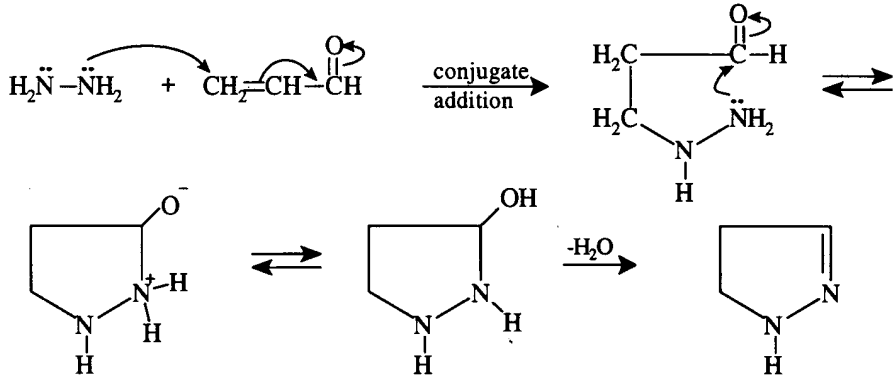
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(b)



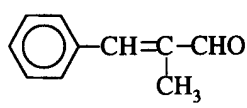


17.27



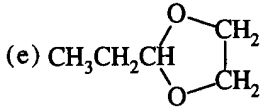
17.28

(a) $CH_3CH_2\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{C}}HCHCHO$

(b) 

(c) $CH_3CH_2\overset{\displaystyle OH}{C}HCN$

(d) $CH_3CH_2CH_2OH$

(e) 

(f) $CH_3CH_2\overset{\displaystyle O}{\overset{\|}{C}}-OH$

(g) $CH_3CH_2\overset{\displaystyle OH}{C}HCH_3$

(h) $CH_3CH_2\overset{\displaystyle O}{\overset{\|}{C}}-OH$

(i) $CH_3CH_2CH{=}NOH$

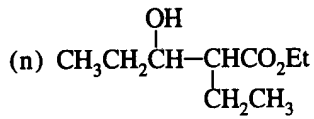
(j) $CH_3CH_2CH{=}CHC_6H_5$

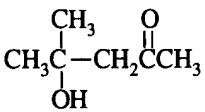
(k) $CH_3CH_2\overset{\displaystyle OH}{C}H-C_6H_5$

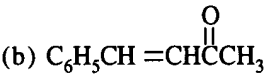
(l) $CH_3CH_2\overset{\displaystyle OH}{C}HC{\equiv}CH$

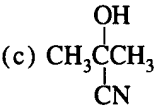
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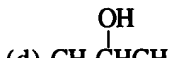
(m) $CH_3CH_2CH_3$

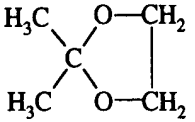
(n) 

17.29 (a) 

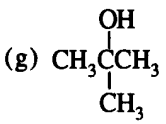
(b) 

(c) 

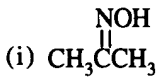
(d) 

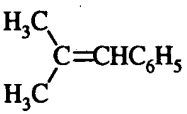
(e) 

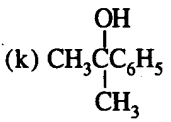
(f) No reaction

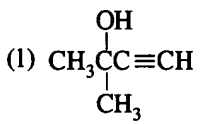
(g) 

(h) No reaction

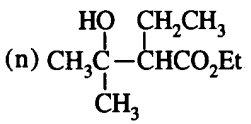
(i) 

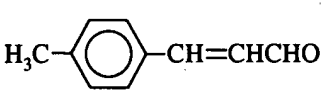
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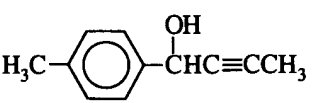
(k) 

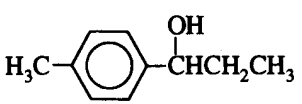
(l) 

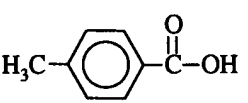
(m) $CH_3CH_2CH_3$

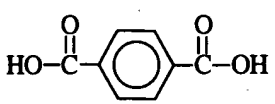
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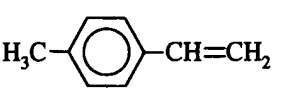
17.30 (a) 

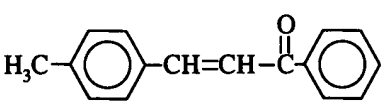
(b) 

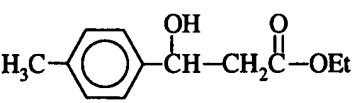
(c) 

(d) 

(e) 

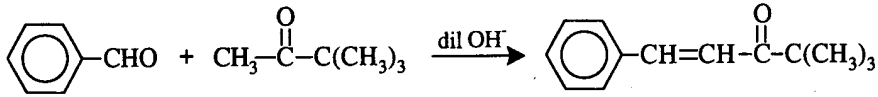
(f) 

(g) 

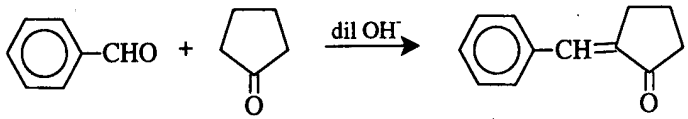
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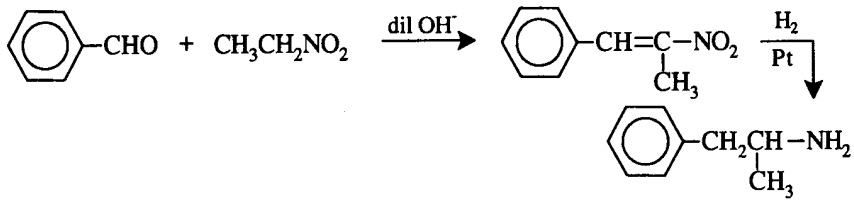
17.31 (a)



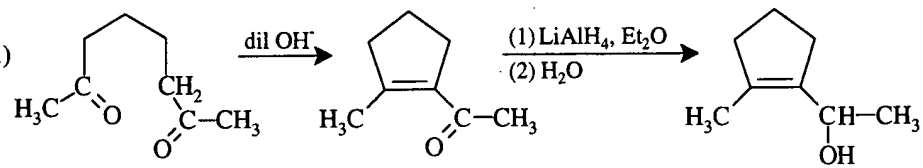
(b)



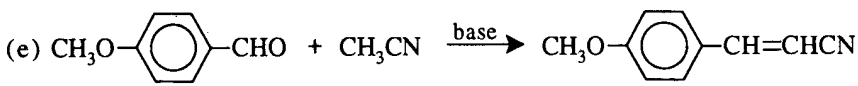
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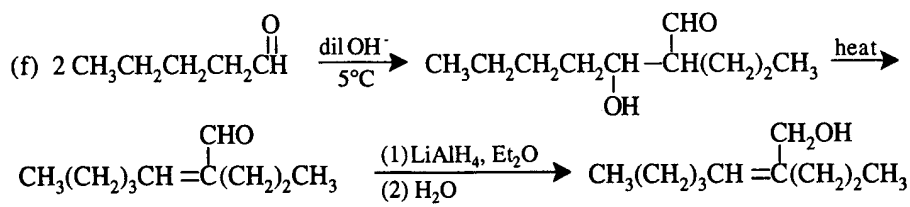
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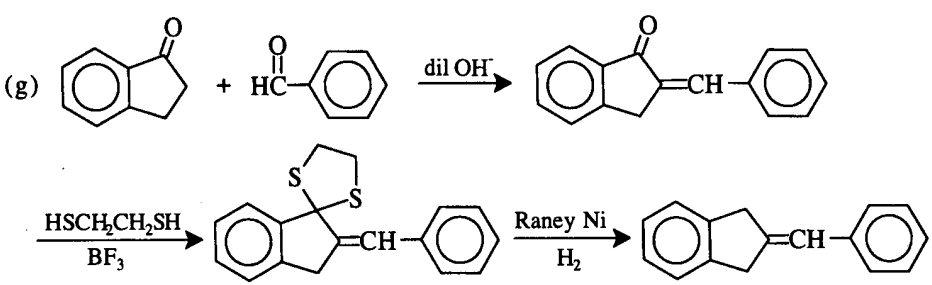
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(f)

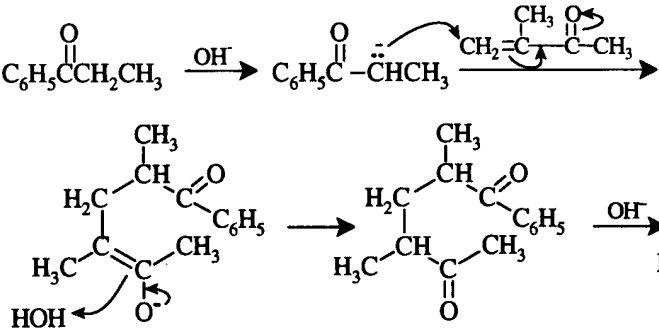


(g)

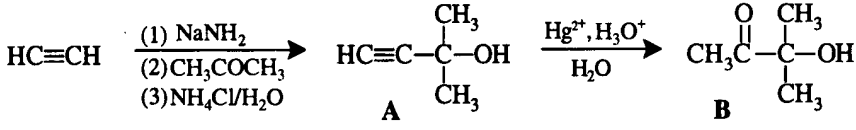


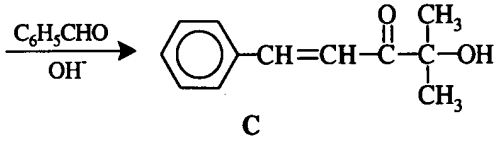
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17.32

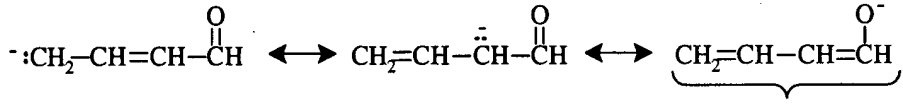


17.33



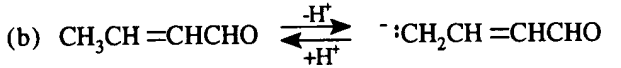


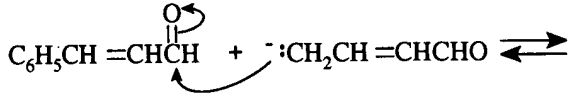
17.34 (a) The conjugate base is a hybrid of the following structures:

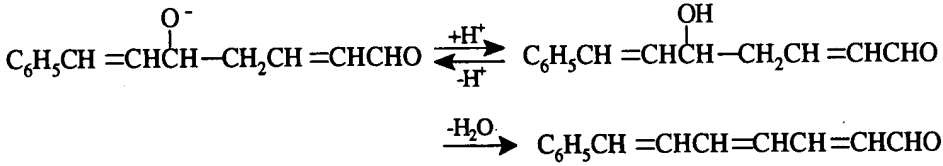


This structure is especially stable because the negative charge is on the oxygen atom.

(b)

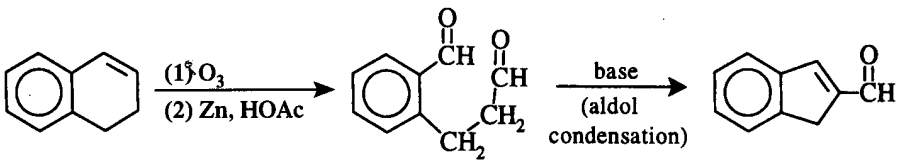




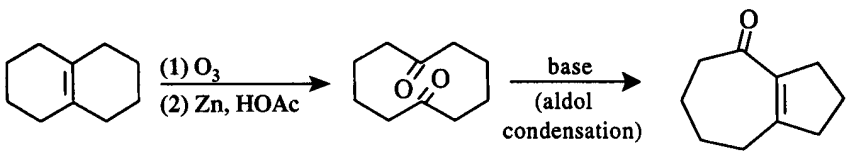


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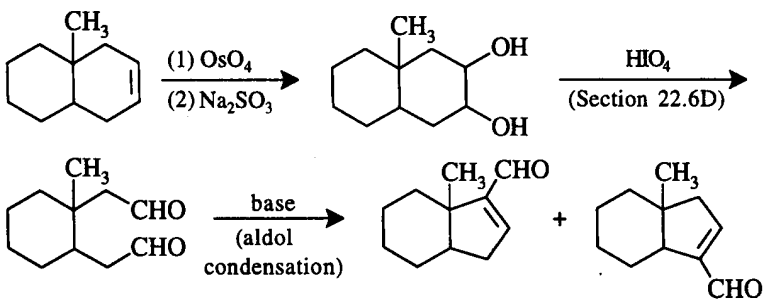
17.35 (a)



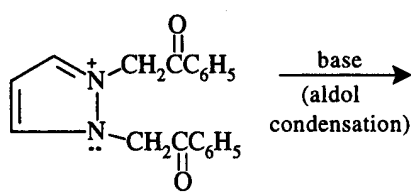
(b)



(c)



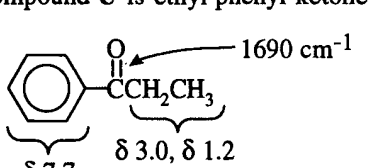
(d)



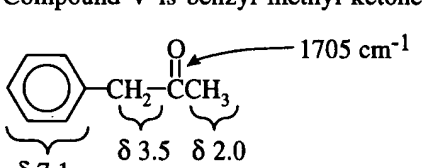
17.36 (a) In simple addition, the carbonyl peak (1665–1780-cm^{-1} region) does not appear in the product; in conjugate addition it does.

(b) As the reaction takes place, the long-wavelength absorption arising from the conjugated system should disappear. One could follow the rate of the reaction by following the rate at which this absorption peak disappears.

17.37 (a) Compound **U** is ethyl phenyl ketone:

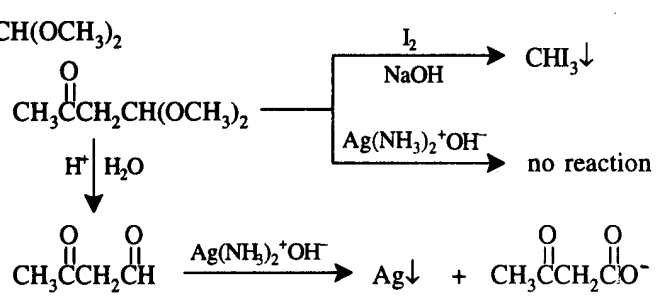


(b) Compound **V** is benzyl methyl ketone:



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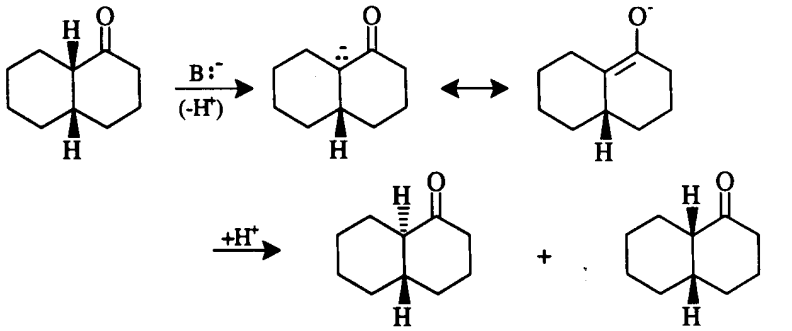
17.38 **A** is $CH_3CCH_2CH(OCH_3)_2$ (O)



(a) Singlet δ 2.1 *(c)* Triplet δ 4.7

(b) Doublet δ 2.6 *(d)* Singlet δ 3.2

17.39 Abstraction of an α hydrogen at the ring junction yields an enolate ion that can then accept a proton to form either *trans*-1-decalone or *cis*-1-decalone. Since *trans*-1-decalone is more stable, it predominates at equilibrium.

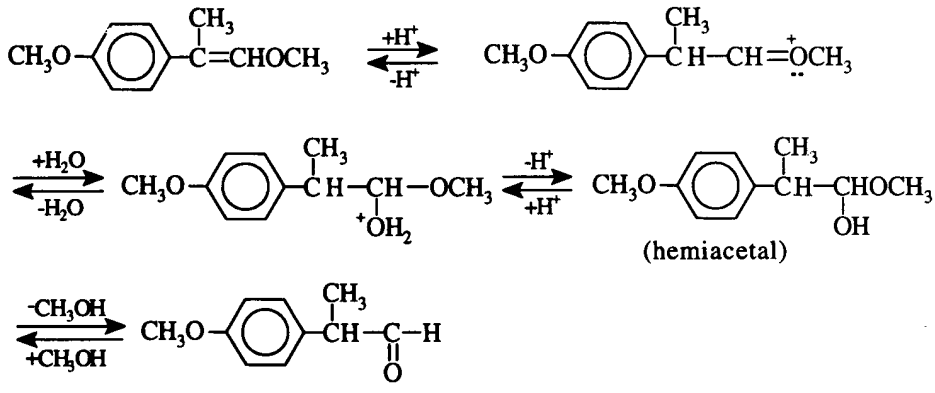


(95%)
trans-1-Decalone
(more stable)

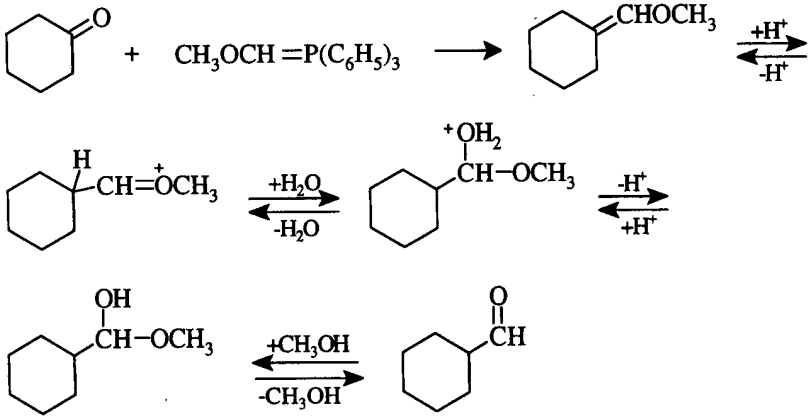
(5%)
cis-1-Decalone
(less stable)

17.40 (a) $CH_3OCH_2Br + (C_6H_5)_3P \xrightarrow{(2)\ RLi} CH_3OCH{=}P(C_6H_5)_3$

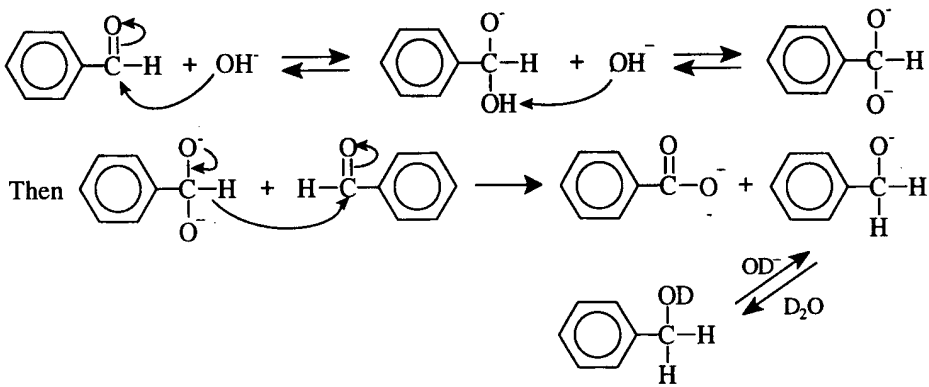
(b) Hydrolysis of the ether yields a hemiacetal that then goes on to form an aldehyde.



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(c) 

17.41 (a) The hydrogen atom that is added to the aldehyde carbon atom in the reduction must come from the other aldehyde rather than from the solvent. It must be transferred as a hydride ion and directly from molecule to molecule, since if it were ever a free species it would react immediately with the solvent. A possible mechanism is the following:

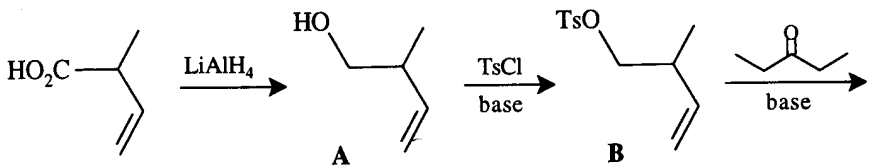


(b) Although an aldol reaction occurs initially, the aldol reaction is reversible. The Cannizzaro reaction, though slower, is irreversible. Eventually, all the product is in the form of the alcohol and the carboxylate ion.

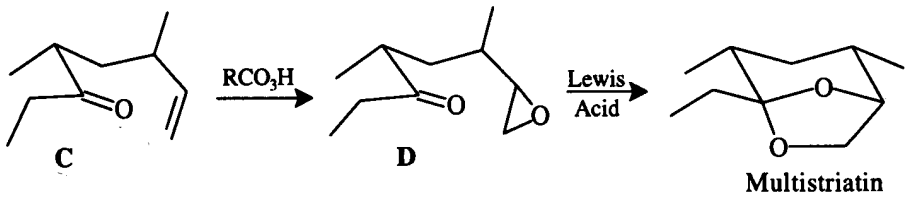
17.42 This difference in behavior indicates that, for acetaldehyde, the capture of a proton from the solvent (the reverse of the reaction by which the enolate ion is formed) occurs much more slowly than the attack by the enolate ion on another molecule.

When acetone is used, the equilibrium for the formation of the enolate ion is unfavorable, but more importantly, enolate attack on another acetone molecule is disfavored due to steric hindrance. Here proton capture (actually deuteron capture) competes very well with the aldol reaction.

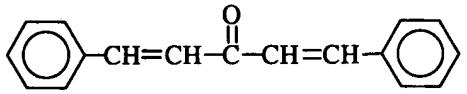
17.43



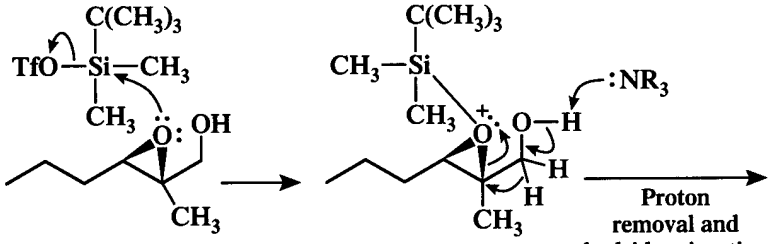
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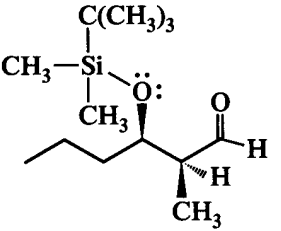


17.44 **X** is:



*17.45





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18 CARBOXYLIC ACIDS AND THEIR DERIVATIVES: NUCLEOPHILIC ADDITION-ELIMINATION AT THE ACYL CARBON

SOLUTIONS TO PROBLEMS

18.1 (a) 2-Methylbutanoic acid

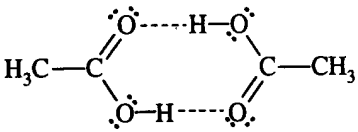
(b) 3-Pentenoic acid

(c) Sodium 4-bromobutanoate

(d) 5-Phenylpentanoic acid

(e) 3-Methyl-3-pentenoic acid

18.2 Acetic acid, in the absence of solvating molecules, exists as a dimer owing to the formation of two intermolecular hydrogen bonds:



At temperatures much above the boiling point, the dimer dissociates into the individual molecules.

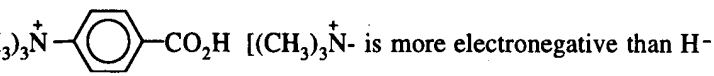
18.3 (a) CH_2FCO_2H (F– is more electronegative than H-)

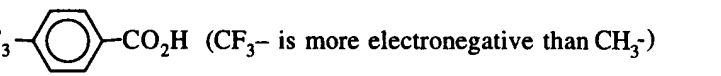
(b) CH_2FCO_2H (F– is more electronegative than Cl-)

(c) CH_2ClCO_2H (Cl– is more electronegative than Br-)

(d) $CH_3CHFCH_2CO_2H$ (F– is closer to $-CO_2H$)

(e) $CH_3CH_2CHFCO_2H$ (F– is closer to $-CO_2H$)

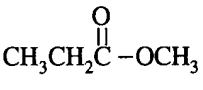
(f)  [$(CH_3)_3\overset{+}{N}$- is more electronegative than H-]

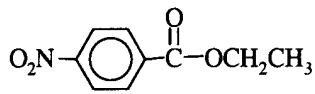
(g)  (CF_3– is more electronegative than CH_3-)

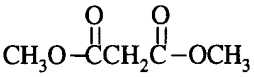
18.4 (a) The carboxyl group is an electron-withdrawing group; thus, in a dicarboxylic acid such as those in Table 18.3, one carboxyl group increases the acidity of the other.

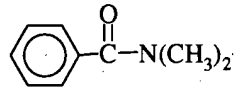
(b) As the distance between the carboxyl groups increases the acid-strengthening, inductive effect decreases.

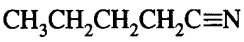
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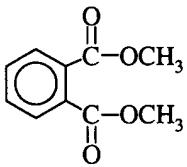
18.5 (a) 

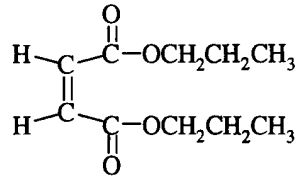
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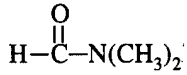
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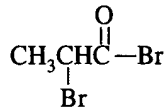
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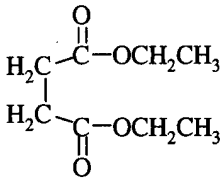
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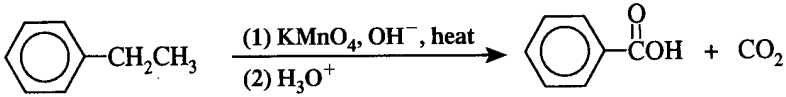
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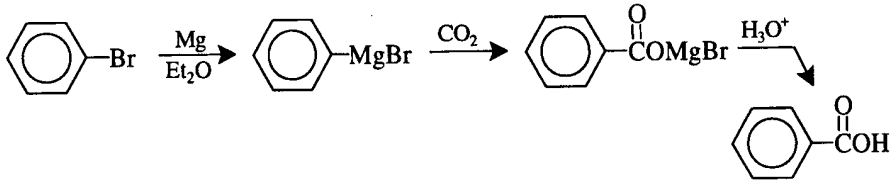
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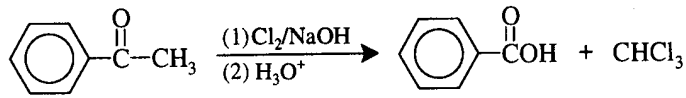
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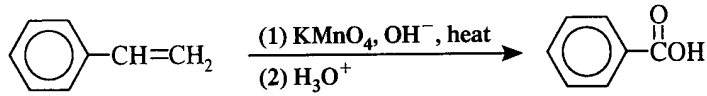
(i) 

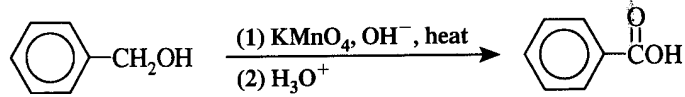
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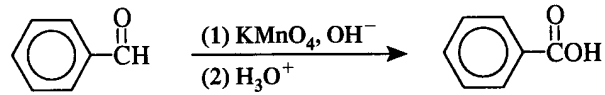
18.6 (a) 

(b) 

(c) 

(d) 

(e) 

(f) 

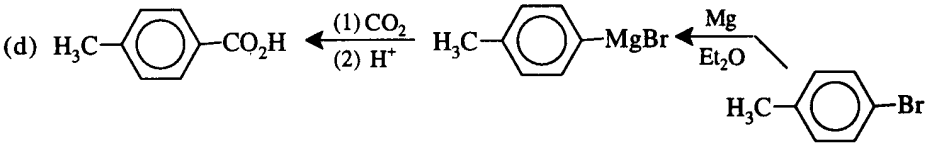
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18.7 These syntheses are easy to see if we work backward.

(a) $C_6H_5CH_2CO_2H \xleftarrow[(2)\ H^+]{(1)\ CO_2} C_6H_5CH_2MgBr \xleftarrow[Et_2O]{Mg} C_6H_5CH_2Br$

(b) $CH_3CH_2CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CO_2H \xleftarrow[(2)\ H^+]{(1)\ CO_2} CH_3CH_2CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}MgBr \xleftarrow[Et_2O]{Mg} CH_3CH_2CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}Br$

(c) $CH_2{=}CHCH_2CO_2H \xleftarrow[(2)\ H^+]{(1)\ CO_2} CH_2{=}CHCH_2MgBr \xleftarrow[Et_2O]{Mg} CH_2{=}CHCH_2Br$

(d) 

(e) $CH_3CH_2CH_2CH_2CH_2CO_2H \xleftarrow[(2)\ H^+]{(1)\ CO_2} CH_3CH_2CH_2CH_2CH_2MgBr$ (Mg, Et_2O; $CH_3CH_2CH_2CH_2CH_2Br$)

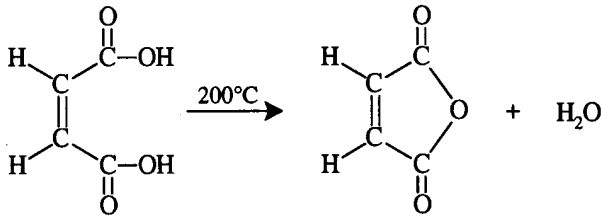
18.8 (a) $C_6H_5CH_2CO_2H \xleftarrow[(2)\ H^+,\ H_2O,\ heat]{(1)\ CN^-} C_6H_5CH_2Br$

$CH_2{=}CHCH_2CO_2H \xleftarrow[(2)\ H^+,\ H_2O,\ heat]{(1)\ CN^-} CH_2{=}CHCH_2Br$

$CH_3CH_2CH_2CH_2CH_2CO_2H \xleftarrow[(2)\ H^+,\ H_2O,\ heat]{(1)\ CN^-} CH_3CH_2CH_2CH_2CH_2Br$

(b) A nitrile synthesis. Preparation of a Grignard reagent from $HOCH_2CH_2CH_2CH_2Br$ would not be possible because of the presence of the acidic hydroxyl group.

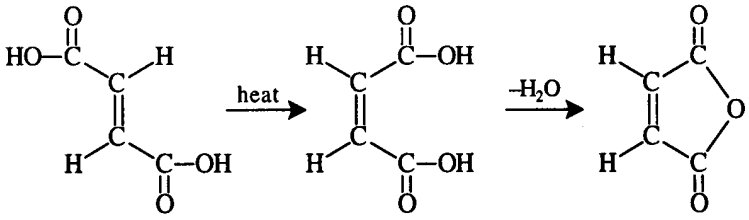
18.9 Since maleic acid is a cis dicarboxylic acid, dehydration occurs readily:



Maleic acid Maleic anhydride

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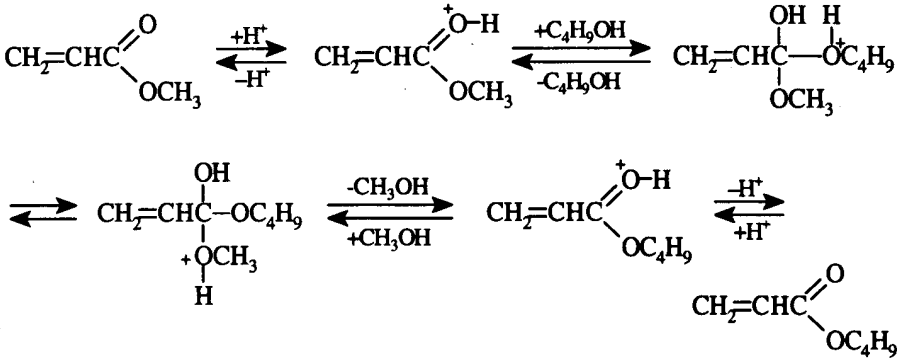
Being a trans dicarboxylic acid, fumaric acid must undergo isomerization to maleic acid first. This isomerization requires a higher temperature.



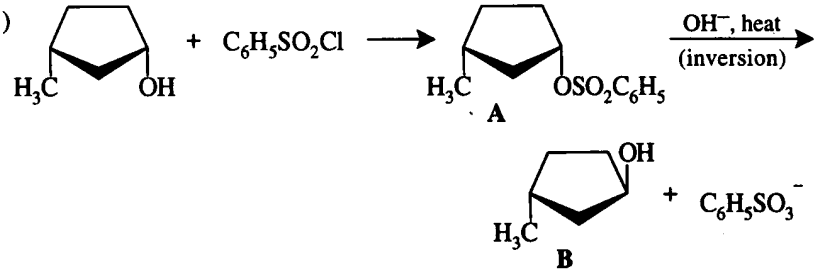
Fumaric acid

18.10 The labeled oxygen atom should appear in the carboxyl group of the acid. (Follow the reverse steps of the mechanism in Section 18.7A of the text using $H_2{}^{18}O$.)

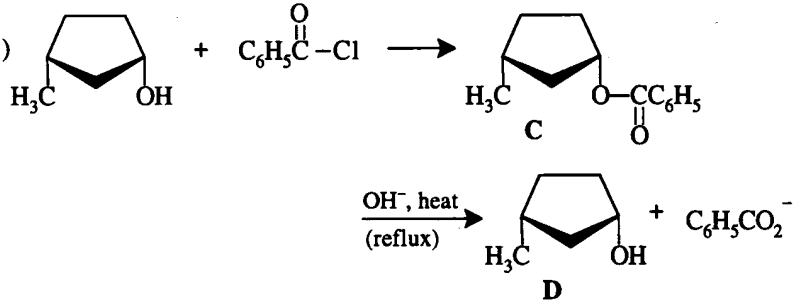
18.11



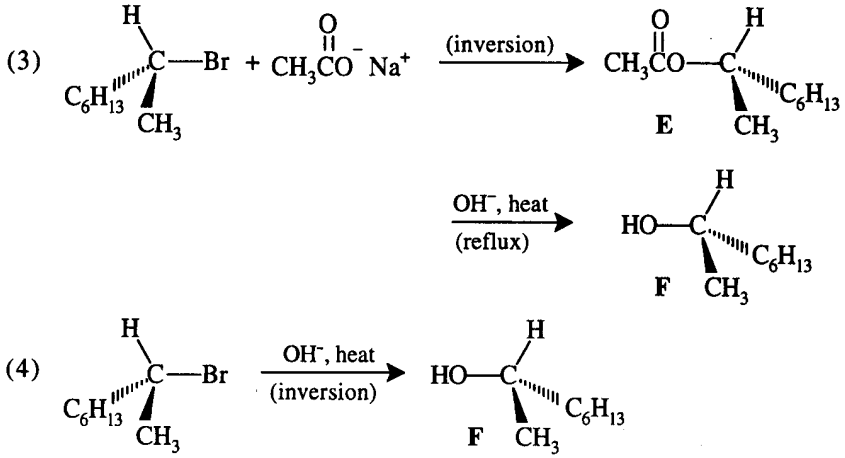
18.12 (a) (1)



(2)



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(b) Method (3) should give a higher yield of **F** than method (4). Since the hydroxide ion is a strong base and since the alkyl halide is secondary, method (4) is likely to be accompanied by considerable elimination. Method (3), on the other hand, employs a weaker base, acetate ion, in the S_N2 step and is less likely to be complicated by elimination. Hydrolysis of the ester **E** that results should also proceed in high yield.

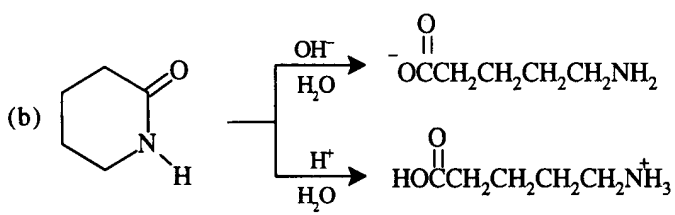
18.13 (a) Steric hindrance presented by the di-ortho methyl groups of methyl mesitoate prevents formation of the tetrahedral intermediate that must accompany attack at the acyl carbon.

(b) Carry out hydrolysis with labeled $^{18}OH^-$ in labeled $H_2{}^{18}O$. The label should appear in the methanol.

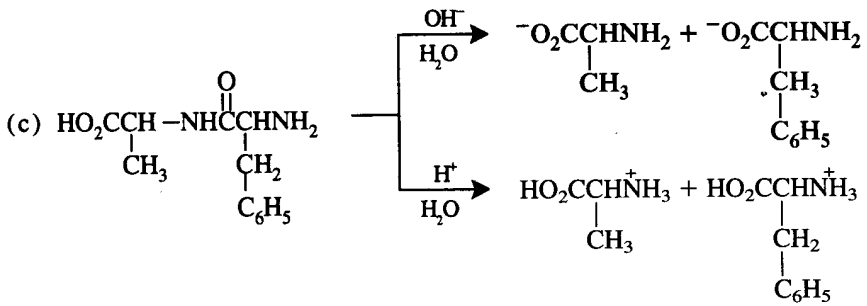
18.14 (a) $C_6H_5CN(CH_2CH_3)_2$ → (OH^-, H_2O) → $C_6H_5CO_2^- + (CH_3CH_2)_2NH$

→ (H^+, H_2O) → $C_6H_5CO_2H + (CH_3CH_2)_2NH_2^+$

(b)



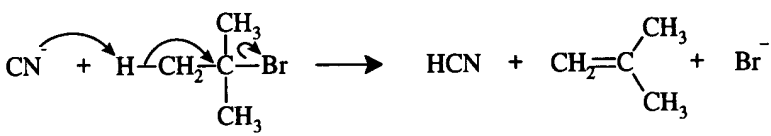
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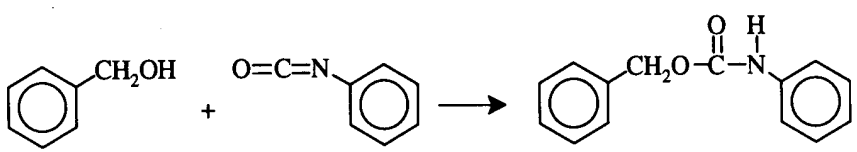
18.15 (a) $(CH_3)_3CCO_2H \xrightarrow{SOCl_2} (CH_3)_3CCOCl \xrightarrow{NH_3} (CH_3)_3CCONH_2$

$\xrightarrow[\text{heat}]{P_4O_{10}} (CH_3)_3CC{\equiv}N$

(b) An elimination reaction would take place because CN^- is a strong base.

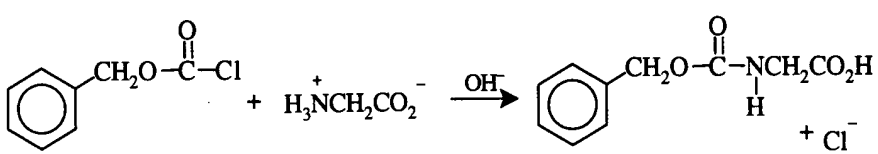


18.16 (a)

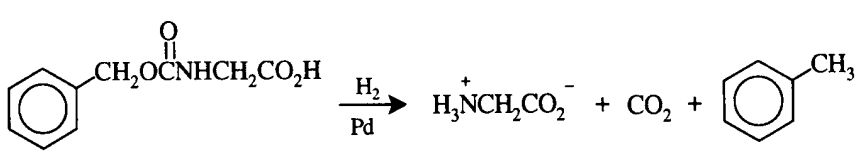


(b) $Cl{-}\overset{\overset{O}{\|}}{C}{-}Cl + 4\,CH_3NH_2 \longrightarrow CH_3\overset{H}{N}{-}\overset{\overset{O}{\|}}{C}{-}\overset{H}{N}CH_3 + 2\,CH_3\overset{+}{N}H_3 + 2\,Cl^-$

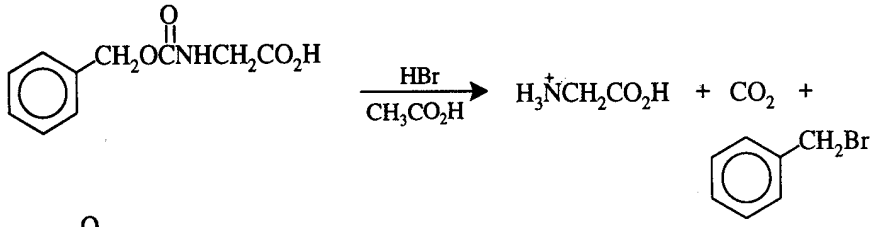
(c)

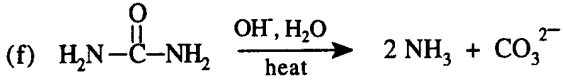


(d)

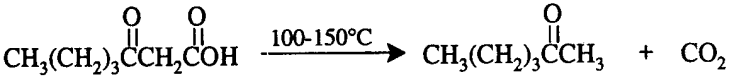


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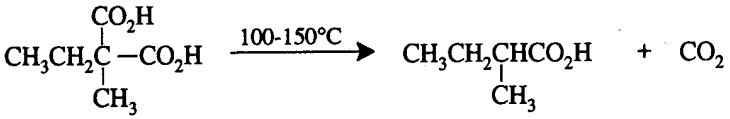
(e) 

(f) 

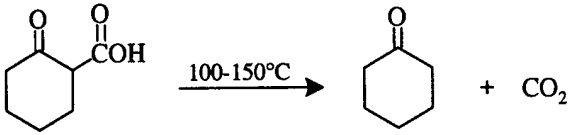
18.17 (a) By decarboxylation of a β-keto acid:



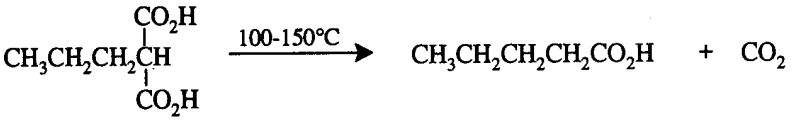
(b) By decarboxylation of a substituted malonic acid:



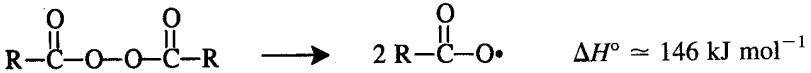
(c) By decarboxylation of a β-keto acid:



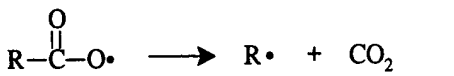
(d) By decarboxylation of a substituted malonic acid:



18.18 (a) The oxygen-oxygen bond of the diacyl peroxide has a low homolytic bond dissociation energy ($DH° \simeq 146$ kJ mol^{-1}). This allows the following reaction to occur at a moderate temperature.



(b) By decarboxylation of the carboxylate radical produced in part (a).



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(c) ***Chain Initiation***

Step 1 $R-C(=O)-O-O-C(=O)-R \xrightarrow{\text{heat}} 2\,R-C(=O)-O\bullet$

Step 2 $R-C(=O)-O\bullet \longrightarrow R\bullet + CO_2$

Chain Propagation

Step 3 $R\bullet + CH_2{=}CH_2 \longrightarrow RCH_2CH_2\bullet$

Step 4 $RCH_2CH_2\bullet + CH_2{=}CH_2 \longrightarrow RCH_2CH_2CH_2CH_2\bullet$

Step 3, 4, 3, 4, and so on.

18.19 (a) $CH_3(CH_2)_4CO_2H$

(b) $CH_3(CH_2)_4CONH_2$

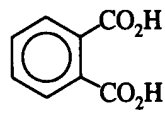
(c) $CH_3(CH_2)_4CONHC_2H_5$

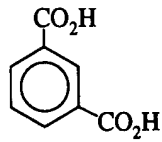
(d) $CH_3(CH_2)_4CON(C_2H_5)_2$

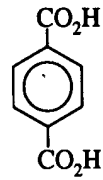
(e) $CH_3CH_2CH{=}CHCH_2CO_2H$

(f) $CH_3CH{=}CHCH_2CHCO_2H$ (CH$_3$ on the CH)

(g) $HO_2CCH_2CH_2CH_2CH_2CO_2H$

(h) 

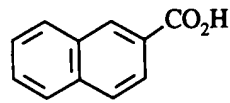
(i) 

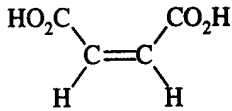
(j) 

(k) $C_2H_5O_2C-CO_2C_2H_5$

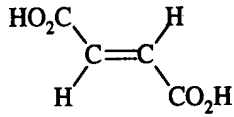
(l) $C_2H_5O_2C(CH_2)_4CO_2C_2H_5$

(m) $CH_3CH_2CO_2CH_2CH(CH_3)_2$

(n) 

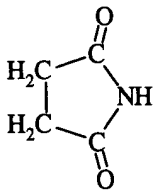
(o) 

(p) $HO_2CCHOHCH_2CO_2H$

(q) 

(r) $HO_2CCH_2CH_2CO_2H$

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(s) 

(t) $HO_2CCH_2CO_2H$

(u) $C_2H_5O_2CCH_2CO_2C_2H_5$

18.20 (a) Benzoic acid

(b) Benzoyl chloride

(c) Benzamide

(d) Benzoic anhydride

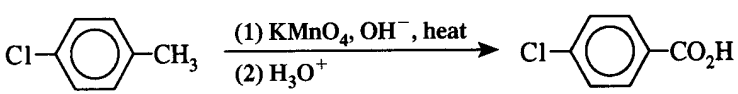
(e) Benzyl benzoate

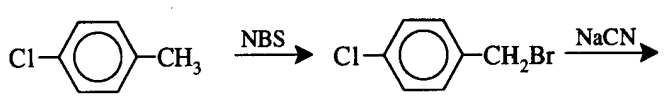
(f) Phenyl benzoate

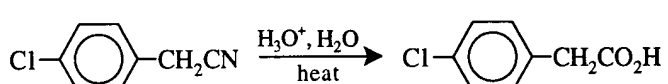
(g) Isopropyl acetate or 1-methylethyl ethanoate

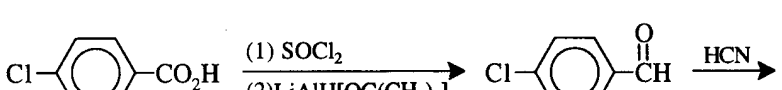
(h) *N,N*-Dimethylacetamide or *N,N*-dimethylethanamide

(i) Acetonitrile or ethanenitrile

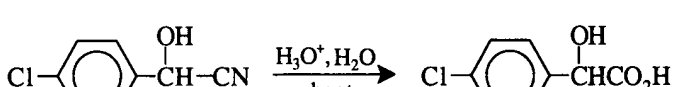
18.21 (a) 

(b) 

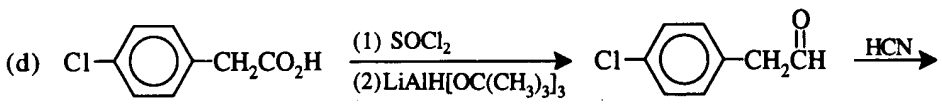


(c) 

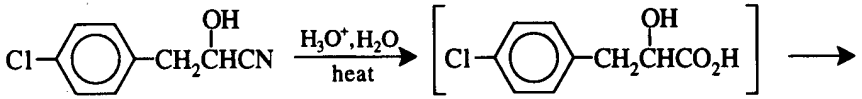
[from (a)]

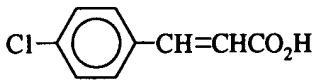


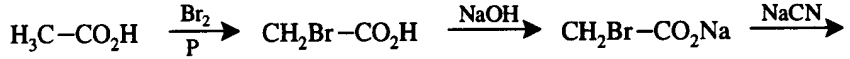
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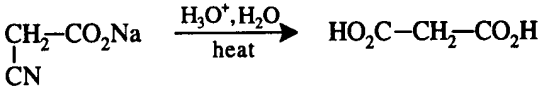
(d) 

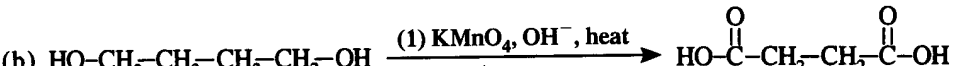
[from (b)]

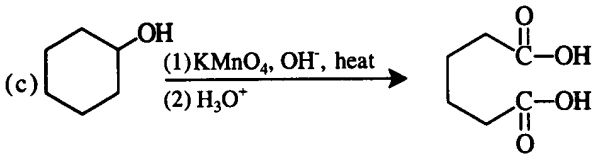


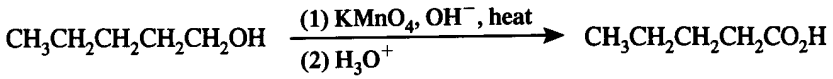


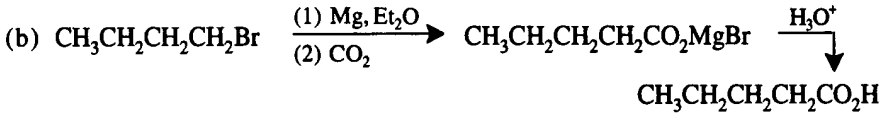
18.22 (a) 

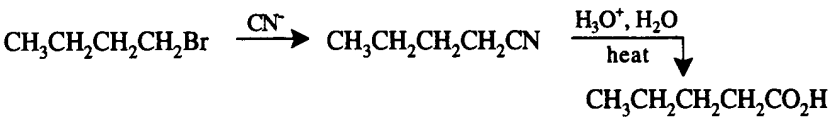


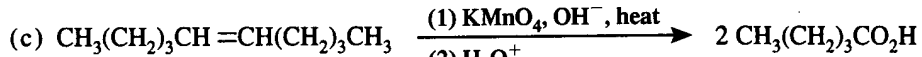
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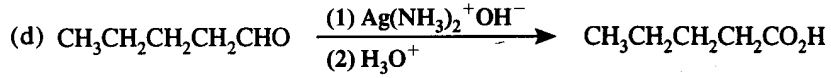
(c) 

18.23 (a) 

(b) 



(c) 

(d) 

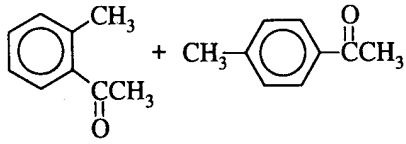
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18.24 (a) $CH_3CO_2H + HCl$

(b) $CH_3C(OH)(CH_2CH_3)_2$

(c) $CH_3CO_2CH_2(CH_2)_2CH_3$

(d) CH_3CONH_2

(e) 

(f) CH_3CHO

(g) CH_3COCH_3

(h) CH_3CO_2Na

(i) $CH_3CONHCH_3$

(j) $CH_3CONHC_6H_5$

(k) $CH_3CON(CH_3)_2$

(l) $CH_3CO_2CH_2CH_3$

(m) $(CH_3CO)_2O$

(n) $(CH_3CO)_2O$

(o) $CH_3CO_2C_6H_5$

(p) $BrCH_2COCl$

18.25 (a) $CH_3CONH_2 + CH_3CO_2^- NH_4^+$

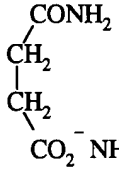
(b) $2\,CH_3CO_2H$

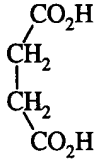
(c) $CH_3CO_2CH_2CH_2CH_3 + CH_3CO_2H$

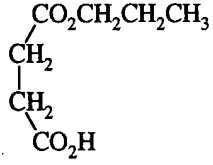
(d) $C_6H_5COCH_3 + CH_3CO_2H$

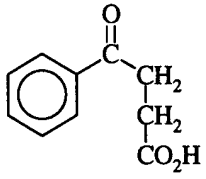
(e) $CH_3CONHCH_2CH_3 + CH_3CO_2^- CH_3CH_2NH_3^+$

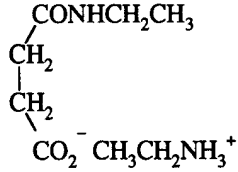
(f) $CH_3CON(CH_2CH_3)_2 + CH_3CO_2^- (CH_3CH_2)_2NH_2^+$

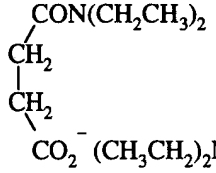
18.26 (a) 

(b) 

(c) 

(d) 

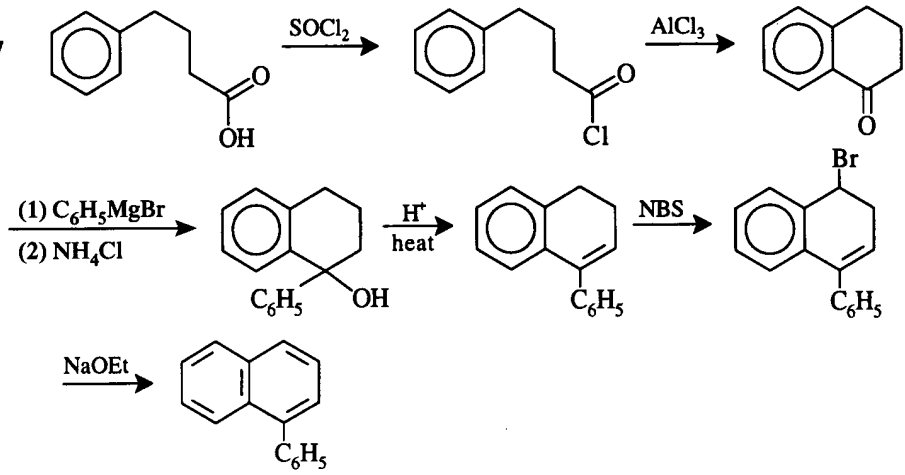
(e) 

(f) 

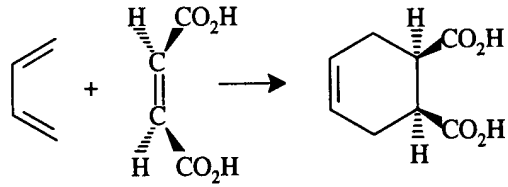
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See text, p. 677.

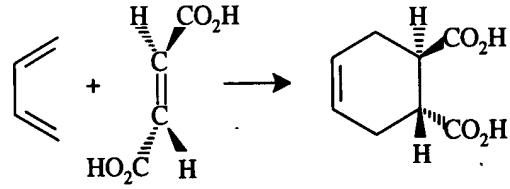
18.27



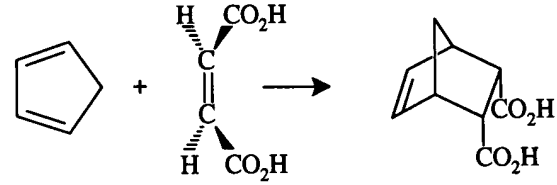
18.28 (a)



(b)



(c)



18.29 (a) $CH_3CH_2CO_2H + CH_3CH_2OH$

(b) $CH_3CH_2CO_2^- + CH_3CH_2OH$

(c) $CH_3CH_2CO_2(CH_2)_7CH_3 + CH_3CH_2OH$

(d) $CH_3CH_2CONHCH_3 + CH_3CH_2OH$

(e) $CH_3CH_2CH_2OH + CH_3CH_2OH$

(f) $CH_3CH_2\underset{\displaystyle OH}{\overset{\displaystyle C_6H_5}{\overset{|}{\underset{|}{C}}}}-C_6H_5 + CH_3CH_2OH$

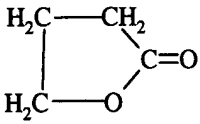
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18.30 (a) $CH_3CH_2CO_2H + NH_4^+$

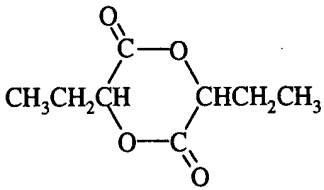
(b) $CH_3CH_2CO_2^- + NH_3$

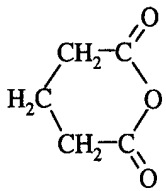
(c) CH_3CH_2CN

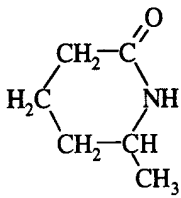
18.31 See the mechanisms in Section 18.8F, where R = CH_2CH_3 for propanamide.

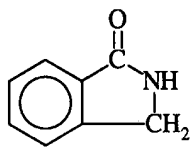
18.32 (a) 

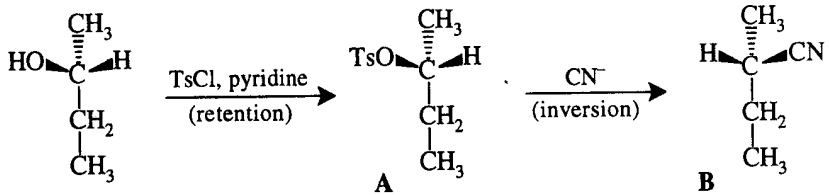
(b) $CH_3CH{=}CHCO_2H$

(c) 

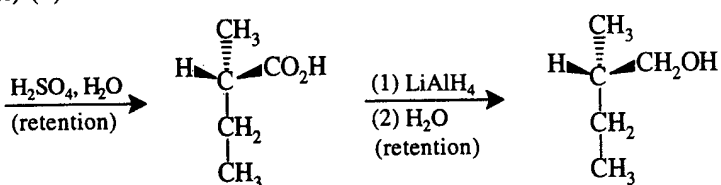
(d) 

(e) 

(f) 

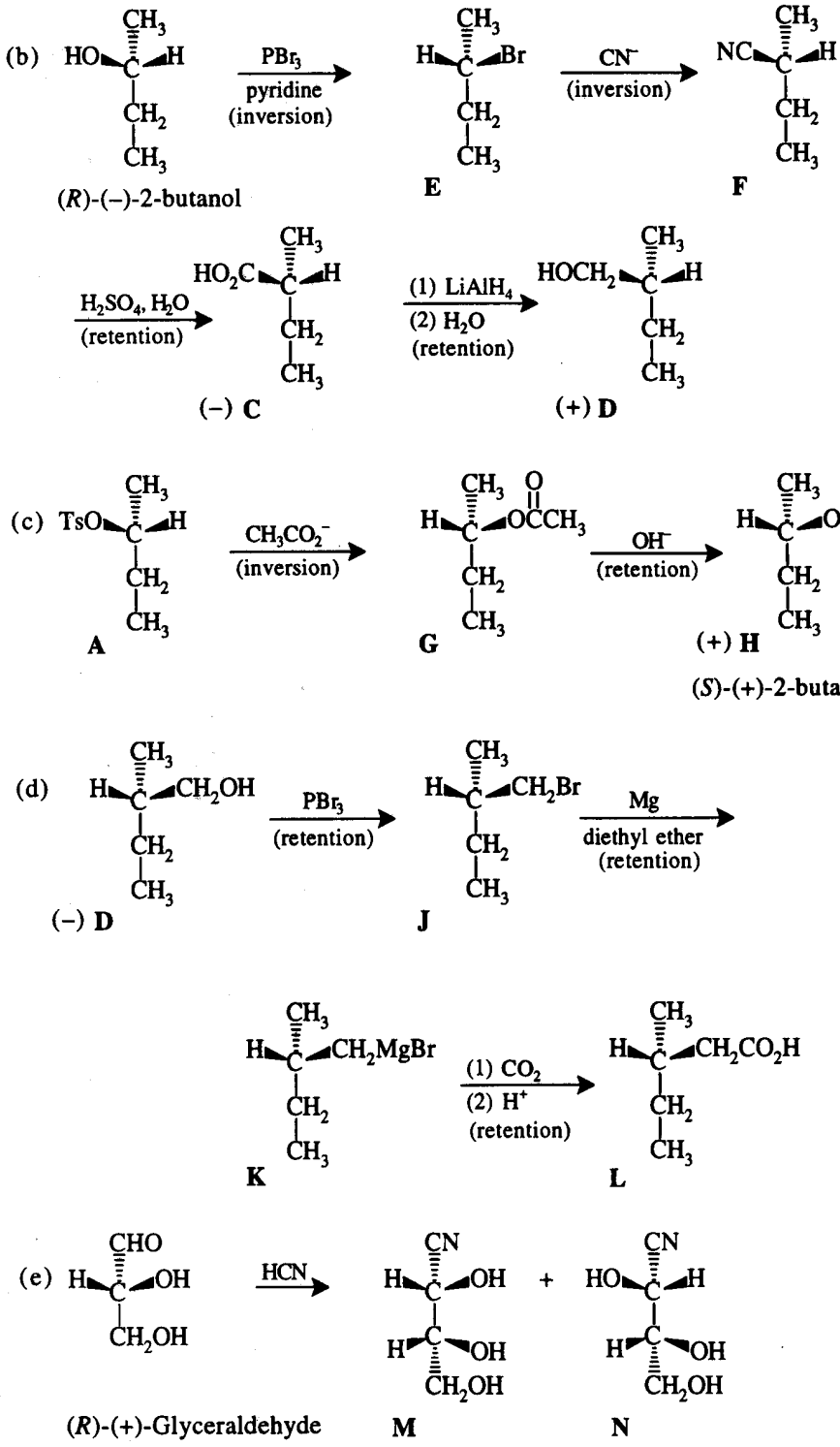
18.33 (a) 

(*R*)-(−)-2-butanol



(+) **C** (−) **D**

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(f) **M** $\xrightarrow[\text{heat}]{H_2SO_4,\ H_2O}$ **P** $\xrightarrow[HNO_3]{[O]}$ *meso*-Tartaric acid

(g) **N** $\xrightarrow[\text{heat}]{H_2SO_4,\ H_2O}$ **Q** $\xrightarrow[HNO_3]{[O]}$ (–)-Tartaric acid

18.34 (a) $CH_3CH(CH_3)CHO + HCHO \xrightarrow[H_2O]{K_2CO_3} CH_3C(CH_3)(CH_2OH)CHO$ (**A**) $\xrightarrow{HCN}$ $CH_3C(CH_3)(OH)CH(CN)CH_2OH$ (±)-**B**

(±)-**B** $\xrightarrow[\text{heat}]{H_3O^+}$ [$CH_3C(CH_3)(CH_2OH)CH(OH)CO_2H$] (±)-**C** $\xrightarrow{-H_2O}$ (±)-**D** $\xrightarrow{H_3\overset{+}{N}CH_2CH_2CO_2^-}$ (±)-pantothenic acid

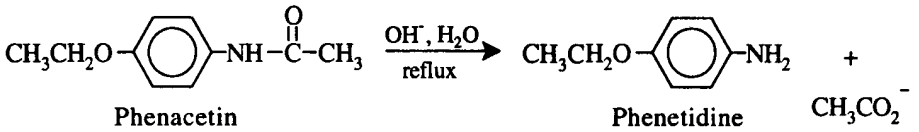
(±)-**D** $\xrightarrow{H_2NCH_2CH_2CONHCH_2CH_2SH}$ (±)-pantetheine

(b) $(HOH_2C)(CH_3)_2C(OH)CH(H)C(=O)NHCH_2CH_2C(=O)NHCH_2CH_2SH$

(c) $(HOH_2C)(CH_3)_2C(OH)CH(H)CO_2^- + H_2NCH_2CH_2CO_2^- + H_2NCH_2CH_2S^-$ (OH^-, H_2O, heat)

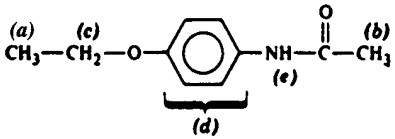
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18.35



Phenacetin Phenetidine

An interpretation of the ^1H NMR spectral data for phenacetin is as follows:



(*a*) triplet δ 1.4

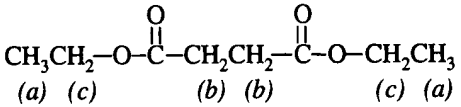
(*b*) singlet δ 2.1

(*c*) quartet δ 3.95

(*d*) multiplet δ 6.8-7.4

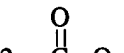
(*e*) broad singlet δ 9.0

18.36 (a)

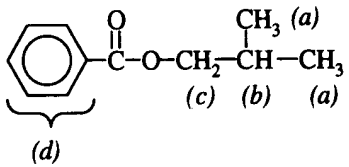


Interpretation:

(*a*) Triplet δ 1.2 (6H)
(*b*) Singlet δ 2.5 (4H)
(*c*) Quartet δ 4.1 (4H)

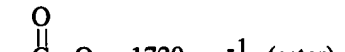


(b)

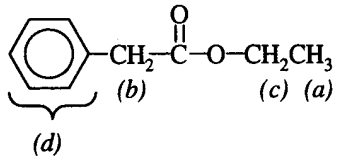


Interpretation:

(*a*) Doublet δ 1.0 (6H)
(*b*) Multiplet δ 2.1 (1H)
(*c*) Doublet δ 4.1 (2H)
(*d*) Multiplet δ 7.8 (5H)



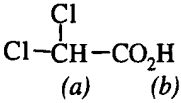
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(c) 

Interpretation:

(a) Triplet δ 1.2 (3H)
(b) Singlet δ 3.5 (2H)
(c) Quartet δ 4.1 (2H)
(d) Multiplet δ 7.3 (5H)

$-\overset{O}{\overset{\|}{C}}-O-$, 1740 cm^{-1} (ester)

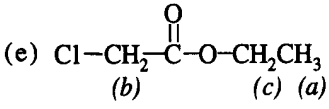
(d) 

Interpretation:

(a) Singlet δ 6.0
(b) Singlet δ 11.7

–OH , 2500-2700 cm^{-1}

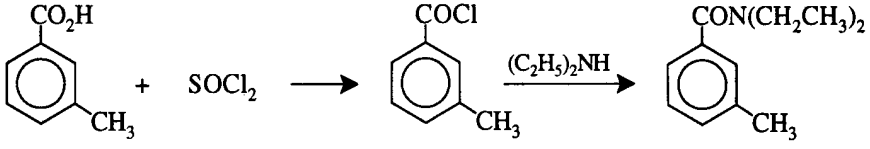
$-\overset{O}{\overset{\|}{C}}-O-$, 1705 cm^{-1} (acid)

(e) 

Interpretation:

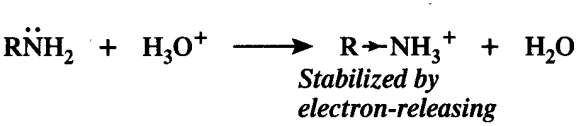
(a) Triplet δ 1.3
(b) Singlet δ 4.0
(c) Quartet δ 4.2

$-\overset{O}{\overset{\|}{C}}-O-$, 1745 cm^{-1} (ester)

18.37 

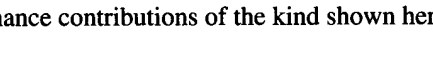
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18.38 Alkyl groups are electron releasing; they help disperse the positive charge of an alkylammonium salt and thereby help to stabilize it.

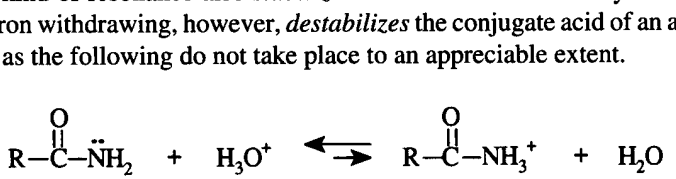


Consequently, alkylamines are somewhat stronger bases than ammonia.

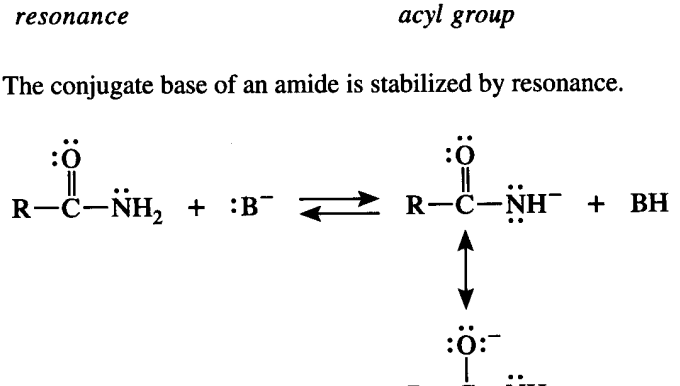
Amides, on the other hand, have acyl groups, R–C(=O)–, attached to nitrogen, and acyl groups are electron withdrawing. They are especially electron withdrawing because of resonance contributions of the kind shown here,



This kind of resonance also *stabilizes* the amide. The tendency of the acyl group to be electron withdrawing, however, *destabilizes* the conjugate acid of an amide, and reactions such as the following do not take place to an appreciable extent.

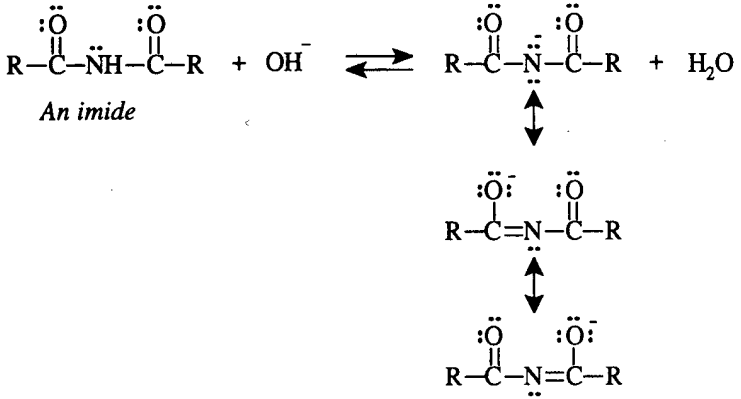


18.39 (a) The conjugate base of an amide is stabilized by resonance.



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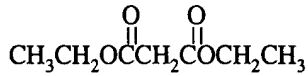
(b) The conjugate base of an imide is stabilized by an additional resonance structure,



18.40 That compound **X** does not dissolve in aqueous sodium bicarbonate indicates that **X** is not a carboxylic acid. That **X** has an IR absorption peak at 1740 cm^{-1} indicates the presence of a carbonyl group, probably that of an ester (Table 18.5). That the molecular formula of **X** ($C_7H_{12}O_4$) contains four oxygen atoms suggests that **X** is a diester.

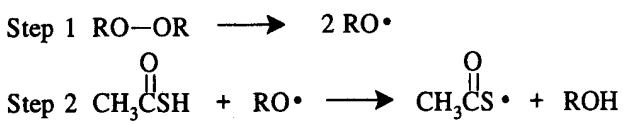
The ^{13}C spectrum shows only four signals indicating a high degree of symmetry for **X.** The single signal at δ 166.7 is that of an ester carbonyl carbon, indicating that both ester groups of **X** are equivalent.

Putting these observations together with the information gathered from DEPT ^{13}C spectra and the molecular formula leads us to the conclusion that **X** is diethyl malonate. The assignments are

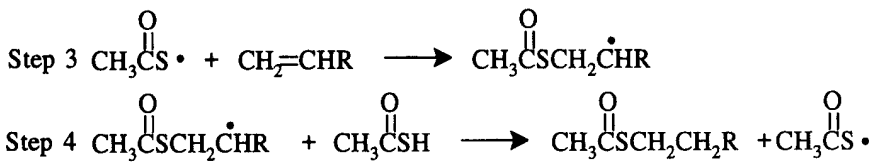


(a) δ 14.2
(b) δ 41.6
(c) δ 61.3
(d) δ 166.7

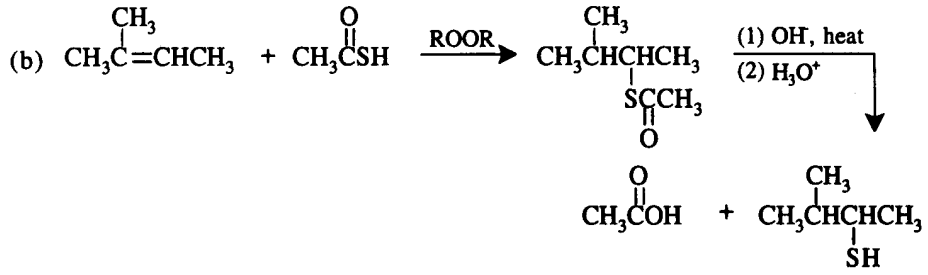
18.41 (a) ***Chain Initiation***



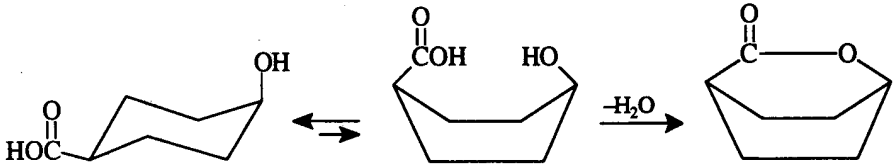
Chain Propagation



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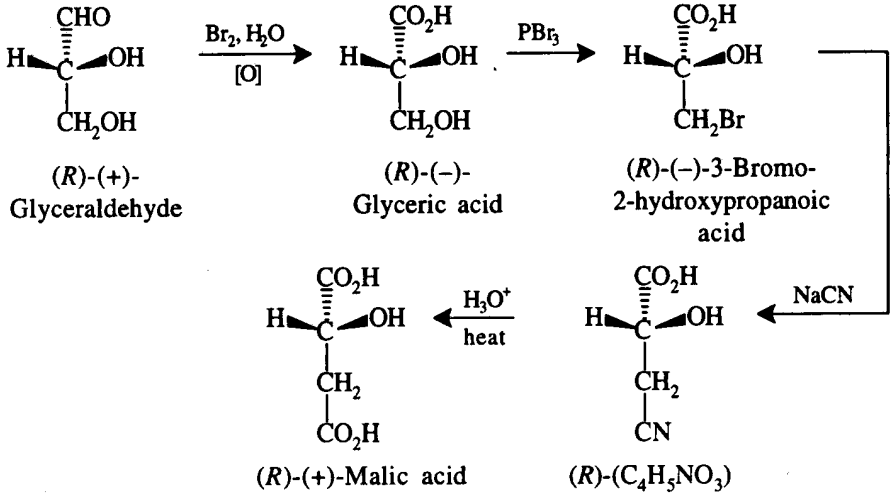


18.42 *cis*-4-Hydroxycyclohexanecarboxylic acid can assume a boat conformation that permits lactone formation.



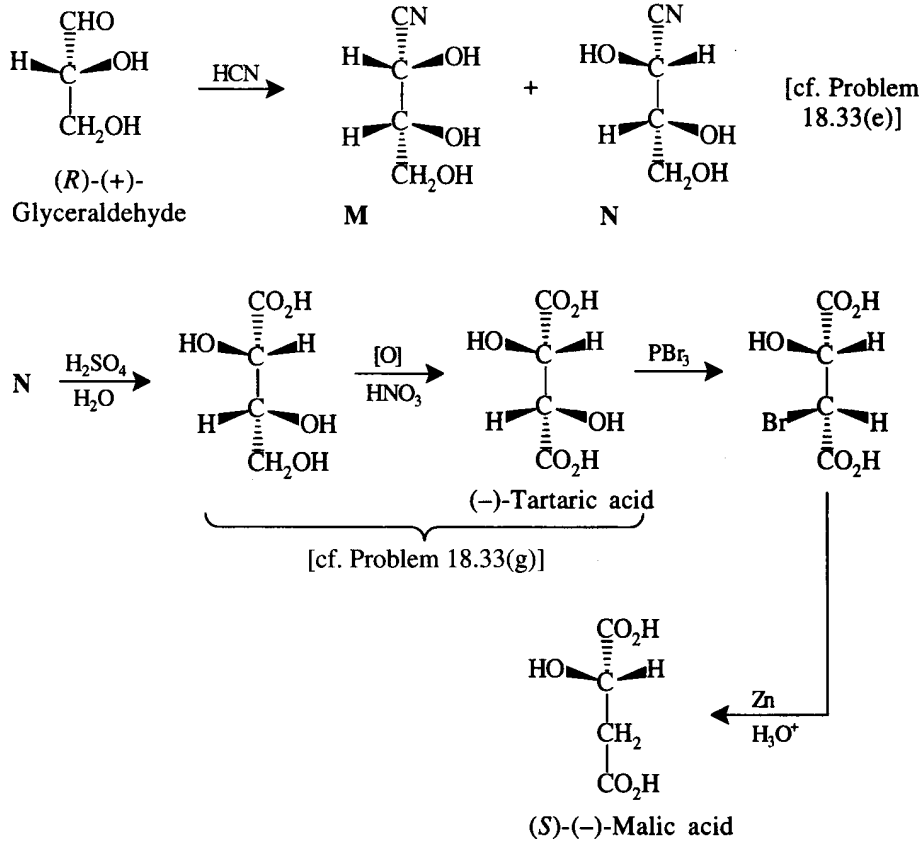
Neither of the chair conformations nor the boat form of *trans*-4-hydroxycyclohexanecarboxylic acid places the –OH group and the $-CO_2H$ group close enough together to permit lactonization.

18.43

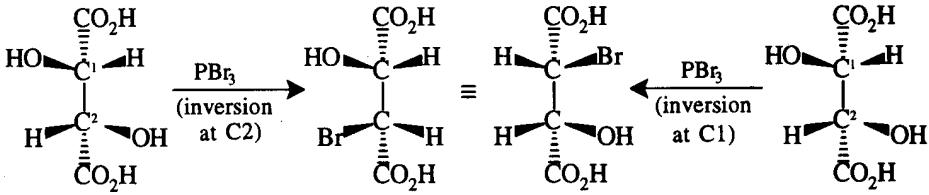


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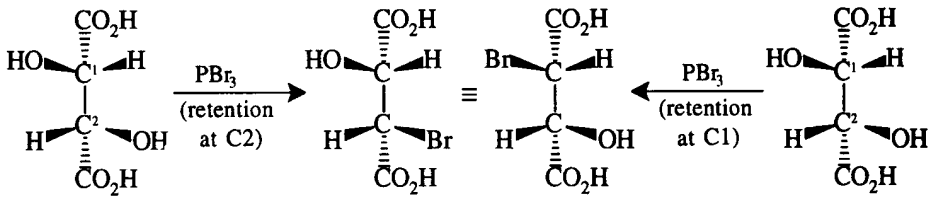
18.44 (a)



(b) Replacement of either alcoholic –OH by a reaction that proceeds with inversion produces the same stereoisomer.

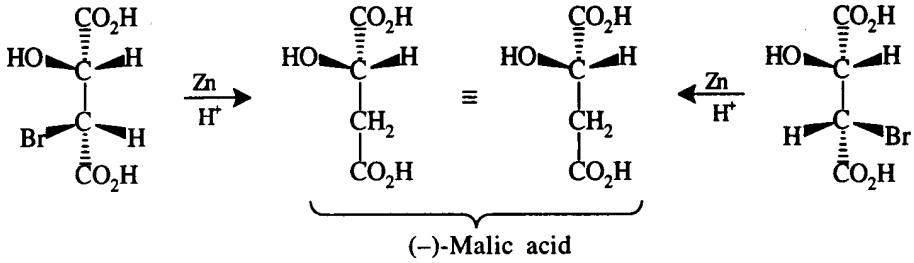


(c) Two. The stereoisomer given in (b) and the one given next, below.



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(d) It would have made no difference because treating either isomer (or both together) with zinc and acid produces (−) malic acid.



18.45 (a) $CH_3O_2C—C{\equiv}C—CO_2CH_3$. This is a Diels-Alder reaction.

(b) H_2, Pd. The disubstituted double bond is less hindered than the tetrasubstituted double bond and hence is more reactive.

(c) $CH_2{=}CH—CH{=}CH_2$. Another Diels-Alder reaction.

(d) $LiAlH_4$

(e) $CH_3—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—Cl$ and pyridine

(f) $CH_3CH_2S^-$

(g) OsO_4

(h) Raney Ni

(i) Base. This is an aldol condensation.

(j) C_6H_5Li (or C_6H_5MgBr) followed by H_3O^+

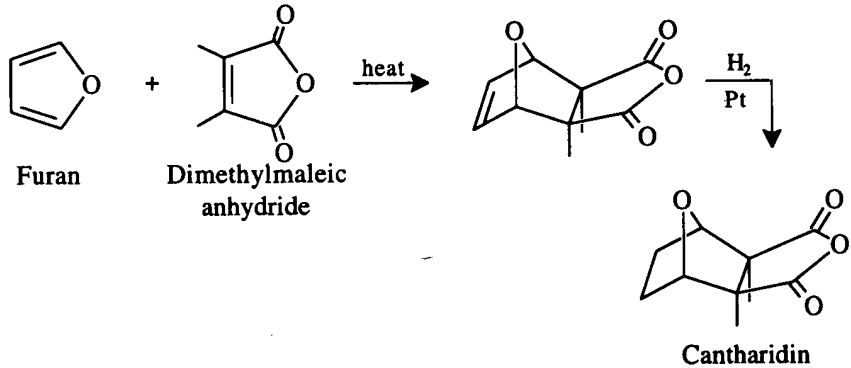
(k) H_3O^+. This is an acid-catalyzed rearrangement of an allylic alcohol.

(l) $CH_3\overset{\overset{O}{\|}}{C}Cl$, pyridine

(m) O_3, followed by oxidation

(n) Heat

18.46 (a)



Furan

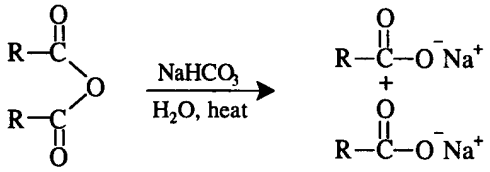
Dimethylmaleic anhydride

Cantharidin

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(b) Cantharidin apparently undergoes dehydrogenation to the Diels-Alder adduct shown here, and then the adduct spontaneously decomposes through a reverse Diels-Alder reaction to furan and dimethylmaleic anhydride. These results suggest that the attempted Diels-Alder synthesis fails because the position of equilibrium favors reactants rather than products.

18.47 The very low hydrogen content of the molecular formula of **Y** ($C_8H_4O_3$) indicates that **Y** is highly unsaturated. That **Y** dissolves slowly in warm aqueous $NaHCO_3$ suggests that **Y** is a carboxylic acid anhydride that hydrolyzes and dissolves because it forms a carboxylate salt:

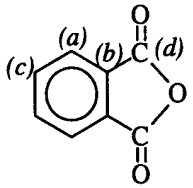


(insoluble) (soluble)

The infrared absorption peaks at 1779 and 1854 cm^{-1} are consistent with those of an aromatic carboxylic anhydride (Table 18.5).

That only four signals appear in the ^{13}C spectrum of **Y** indicates a high degree of symmetry for **Y**. Three of the signals occur in the aromatic region (δ 120–δ 140) and one signal is downfield (δ 163.1)

These signals and the information from the DEPT ^{13}C NMR spectra lead us to conclude that **Y** is phthalic anhydride. The assignments are



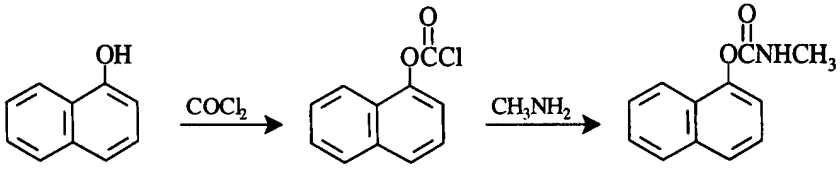
(a) δ 124.3
(b) δ 131.1
(c) δ 136.1
(d) δ 163.1

Z is phthalic acid and **AA** is ethyl hydrogen phthalate.

18.48 (a) Ethyl acetate (b) Acetic anhydride (c) *N*-Ethylacetamide.

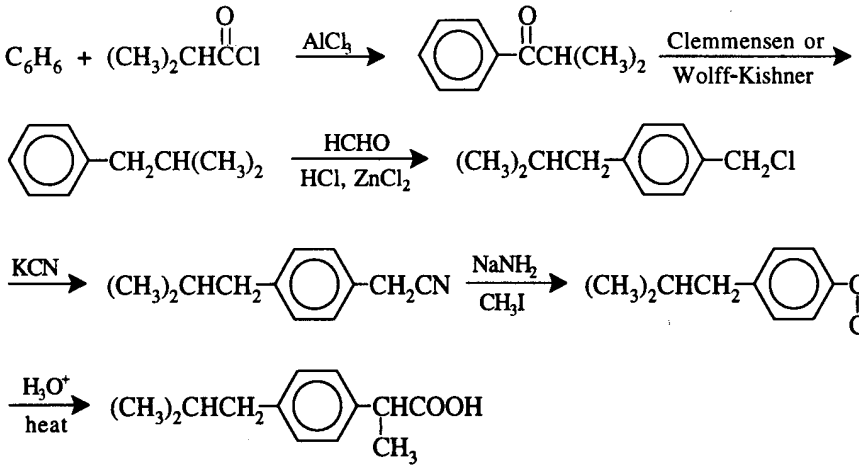
18.49 In the first instance, nucleophilic attack by the amine occurs preferentially at the less hindered carbon of the formyl group. (Recall that aldehydes are more reactive than ketones toward nucleophiles for the same reason.) In the second case, $CF_3CO_2^-$ is a better leaving group than $CH_3CO_2^-$ since the former is the conjugate base of the stronger acid.

18.50

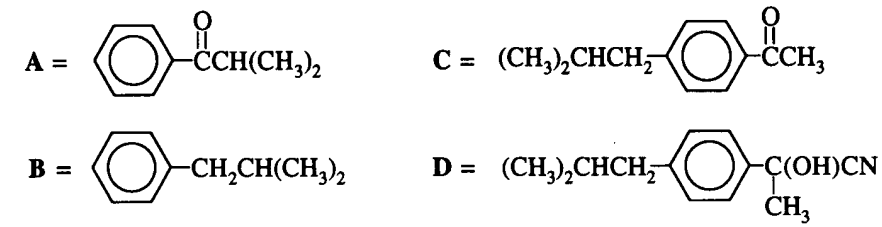


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18.51



18.52

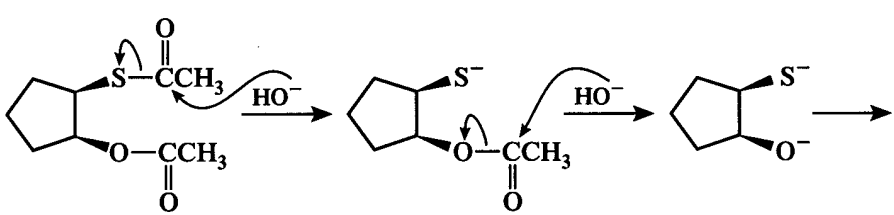


In the last step, HI/red P accomplishes both the reduction of $-OH$ to $-H$ and the hydrolysis of the nitrile function.

18.53 (a) The signal at δ 193.8 is consistent with the carbonyl carbon of an aldehyde and shows that the PCC reaction produced cinnamaldehyde.

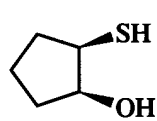
(b) The signal at δ 164.5 is consistent with the carbonyl carbon of a carboxylic acid, and suggests that the oxidation with $K_2Cr_2O_7$ in sulfuric acid produced cinnamic acid.

***18.54**



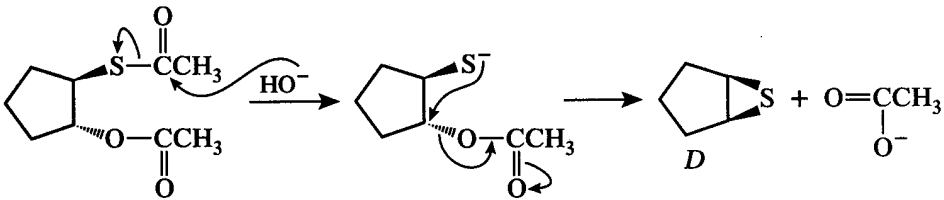
A

(IR absorption at 2550 cm^{-1} is S—H stretch)



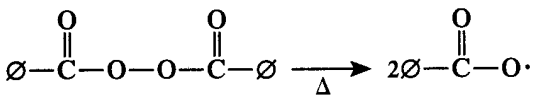
B

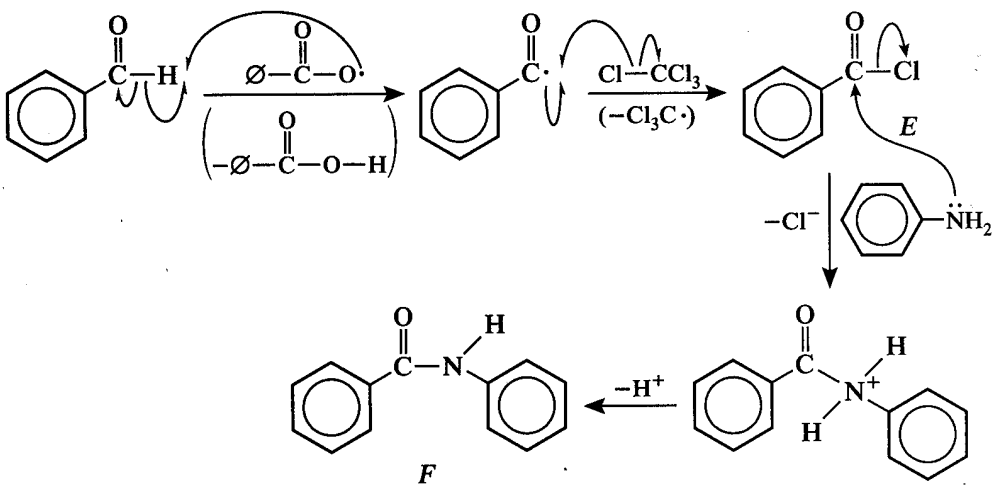
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C (IR absorption at 3020 cm^{-1} is C—H stretch for C—H of 3-membered ring)

***18.55**



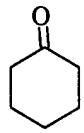


F

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B SPECIAL TOPIC
Step-Growth Polymers

SOLUTIONS TO PROBLEMS

B.1 (a)  $\xrightarrow[H_2Cr_2O_7]{[O]}$ $HO_2C(CH_2)_4CO_2H$

(b) $HO_2C(CH_2)_4CO_2H + 2\,NH_3 \longrightarrow NH_4O_2C(CH_2)_4CO_2NH_4 \xrightarrow[-2H_2O]{heat}$

$H_2NC(=O)(CH_2)_4C(=O)NH_2 \xrightarrow[catalyst]{350°C} N{\equiv}C(CH_2)_4C{\equiv}N \xrightarrow[catalyst]{4\,H_2}$

$H_2NCH_2(CH_2)_4CH_2NH_2$

(c) $CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{Cl_2} ClCH_2CH{=}CHCH_2Cl \xrightarrow{2\,NaCN}$

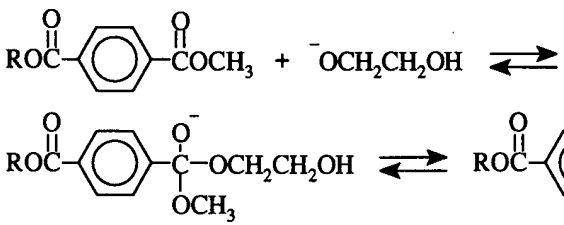
$N{\equiv}CCH_2CH{=}CHCH_2C{\equiv}N \xrightarrow[Ni]{H_2} N{\equiv}C(CH_2)_4C{\equiv}N \xrightarrow[catalyst]{4\,H_2}$

$H_2NCH_2(CH_2)_4CH_2NH_2$

(d)  $\xrightarrow{2\,HCl}$ $ClCH_2CH_2CH_2CH_2Cl \xrightarrow{2\,NaCN} N{\equiv}C(CH_2)_4C{\equiv}N$

$\xrightarrow[catalyst]{4\,H_2} H_2NCH_2(CH_2)_4CH_2NH_2$

B.2 (a) $HOCH_2CH_2OH + :B^- \rightleftharpoons HOCH_2CH_2O^- + HB$



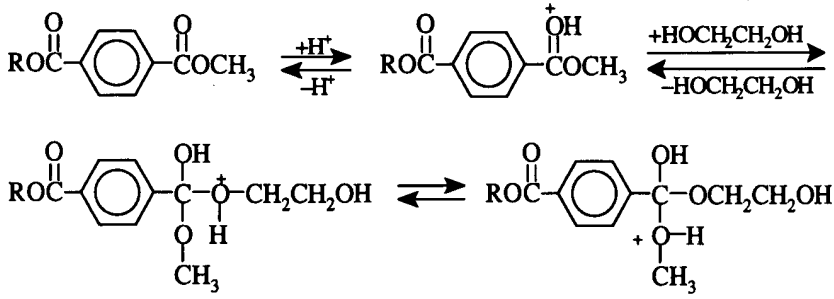
$+ CH_3O^-$

$CH_3O^- + HB \rightleftharpoons CH_3OH + :B^-$

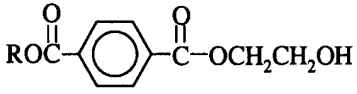
[R = CH_3- or $HOCH_2CH_2$-]

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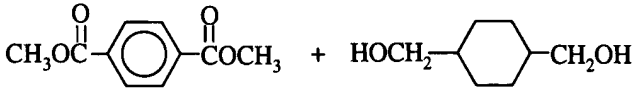
(b)



[R=CH_3- or $HOCH_2CH_2$-]

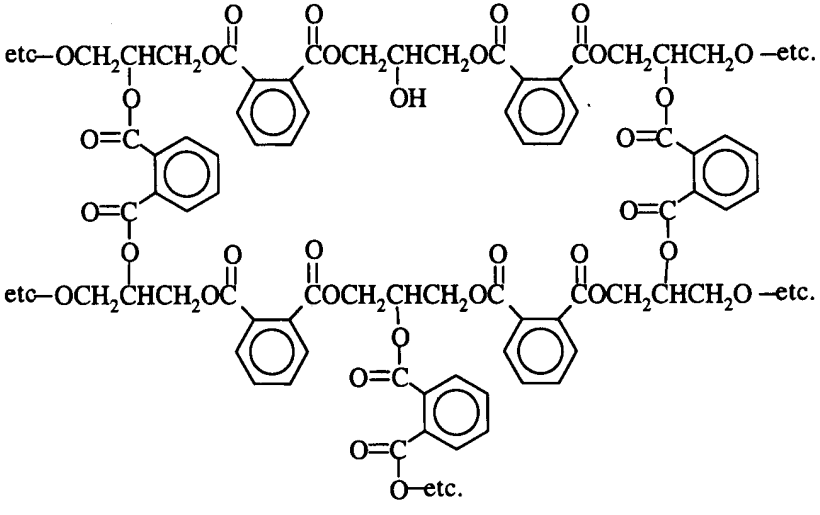


B.3 (a)

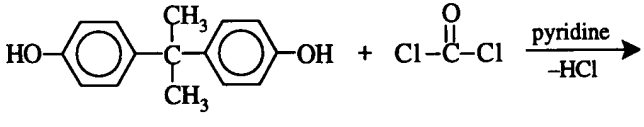


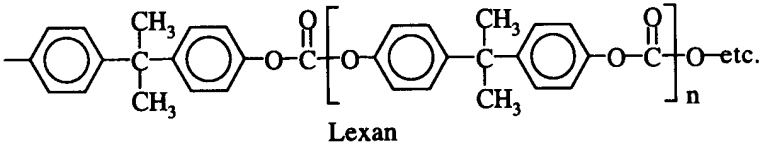
(b) By high-pressure catalytic hydrogenation

B.4



B.5

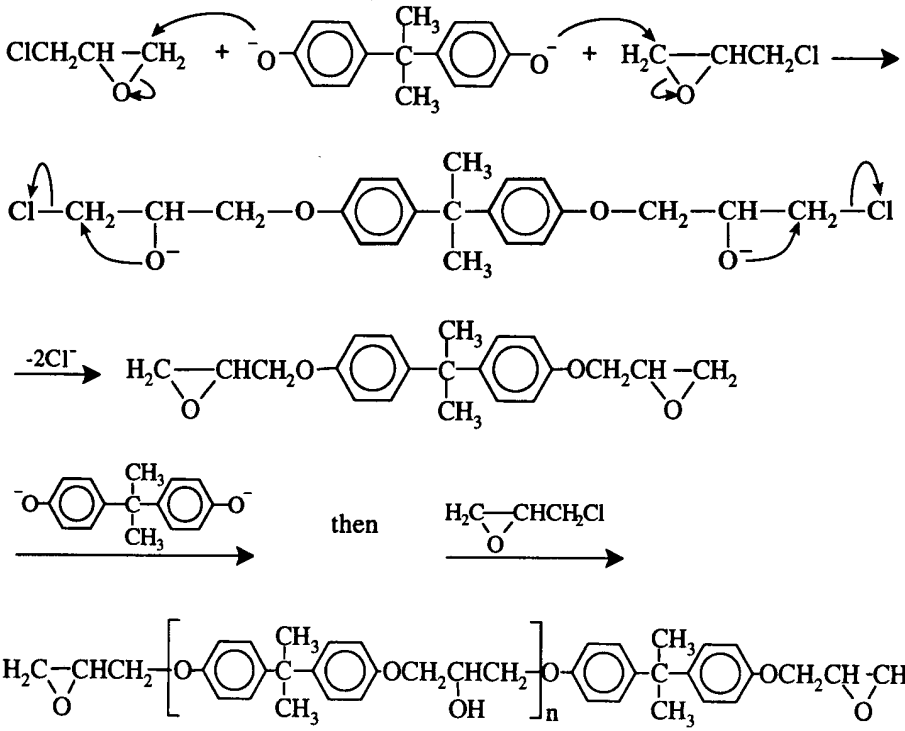




Lexan

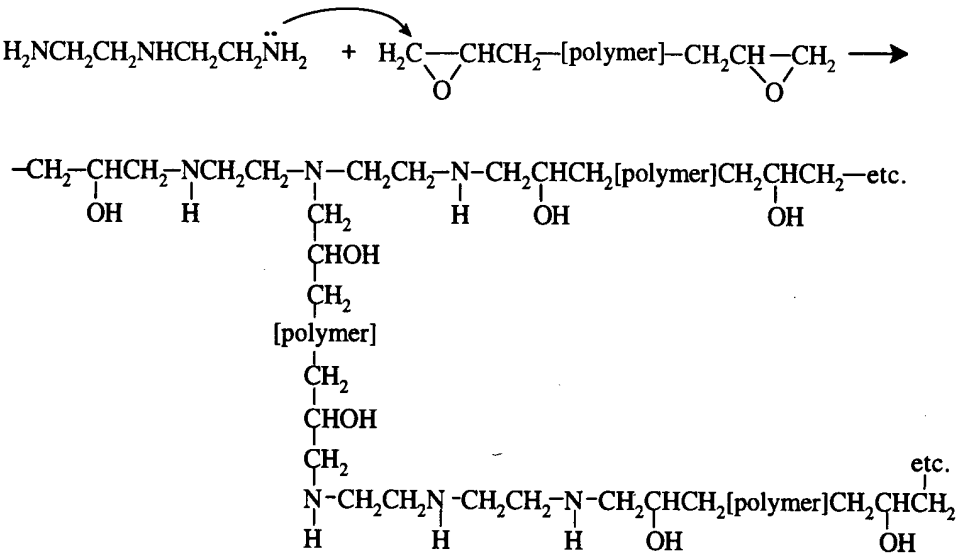
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B.6 (a) The resin is probably formed in the following way. Base converts the bisphenol A to a phenoxide ion that attacks a carbon atom of the epoxide ring of epichlorohydrin:



(b) The excess of epichlorohydrin limits the molecular weight and ensures that the resin has epoxy ends.

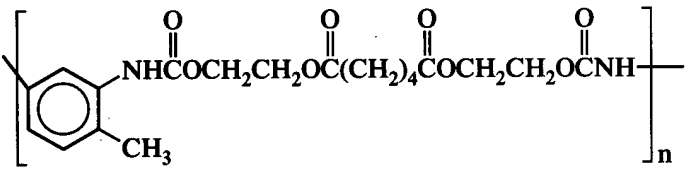
(c) Adding the hardener brings about cross linking by reacting at the terminal epoxide groups of the resin:



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B.7

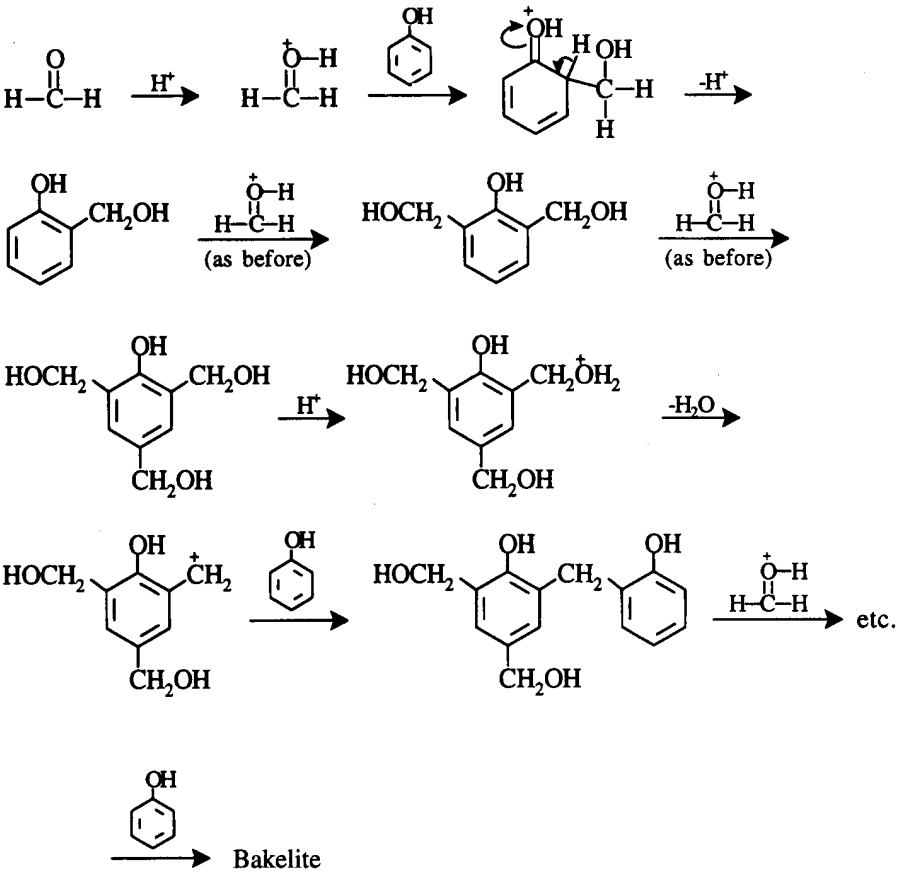
(a)



(b) To ensure that the polyester chain has $-CH_2OH$ end groups.

B.8 Because the para position is occupied by a methyl group, cross-linking does not occur and the resulting polymer remains thermoplastic (See Section B.4.)

B.9

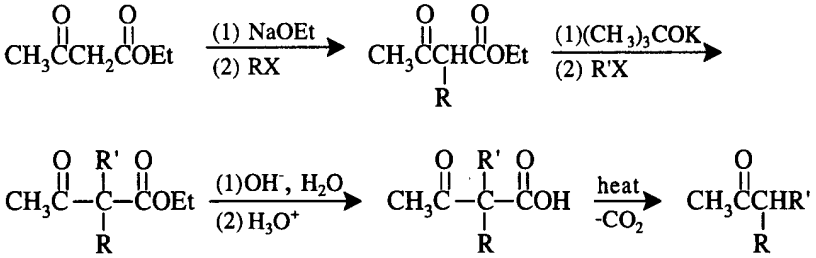


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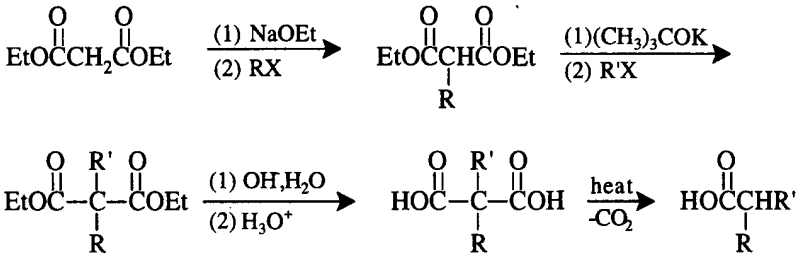
19 SYNTHESIS AND REACTIONS OF β-DICARBONYL COMPOUNDS: MORE CHEMISTRY OF ENOLATE ANIONS

SUMMARY OF ACETOACETIC ESTER AND MALONIC ESTER SYNTHESES

A. Acetoacetic Ester Synthesis

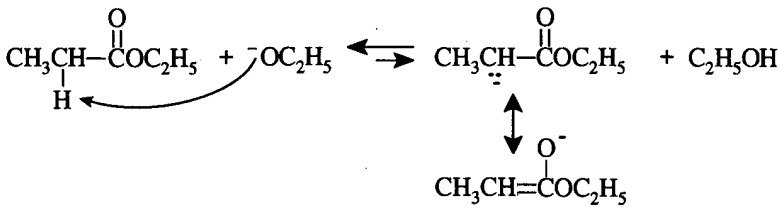


B. Malonic Ester Synthesis



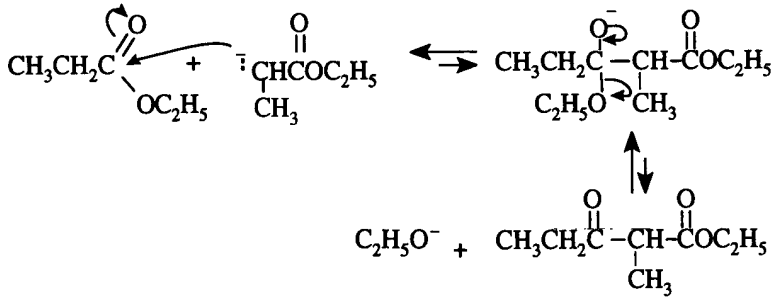
SOLUTIONS TO PROBLEMS

19.1 (a) *Step 1*

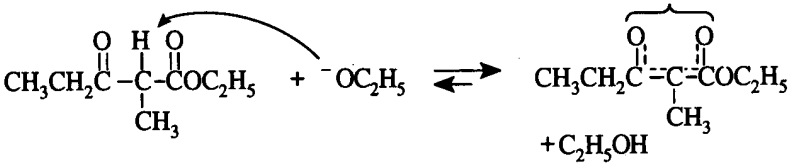


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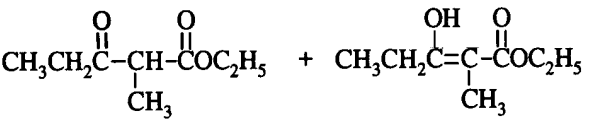
Step 2



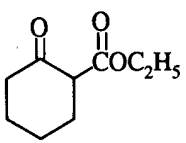
Step 3



(b)

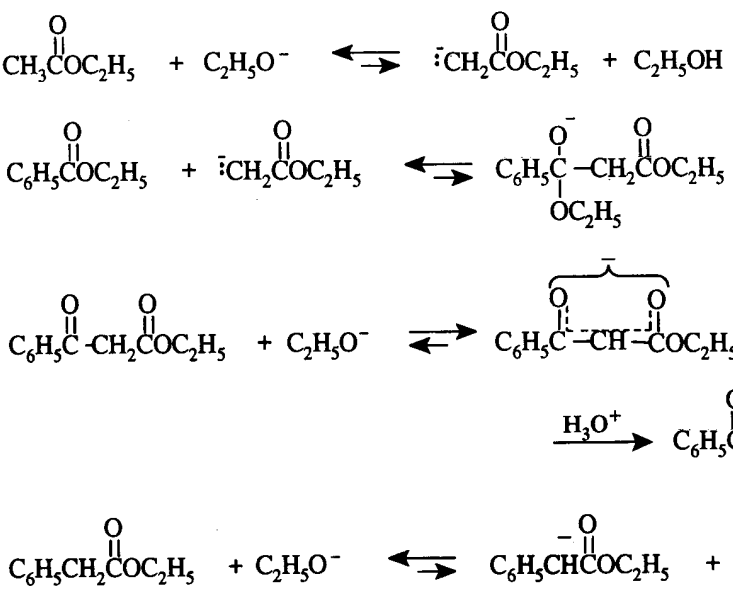


19.2 (a)

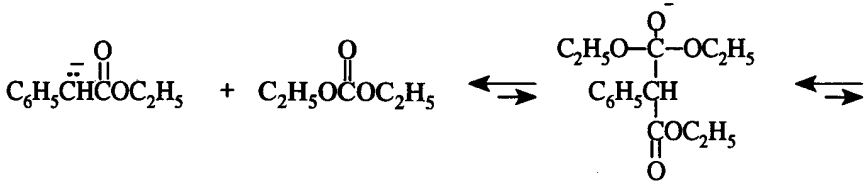


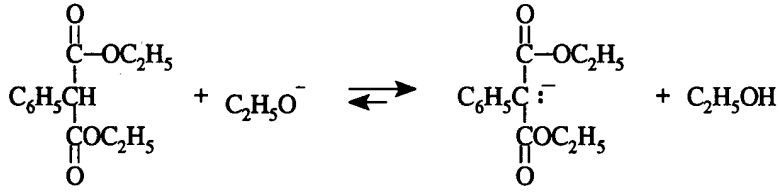
(b) To undergo a Dieckmann condensation, diethyl glutarate would have to form a highly strained four-membered ring.

19.3

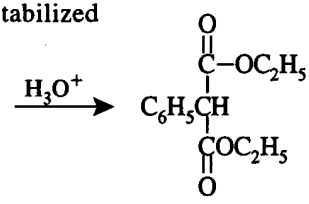


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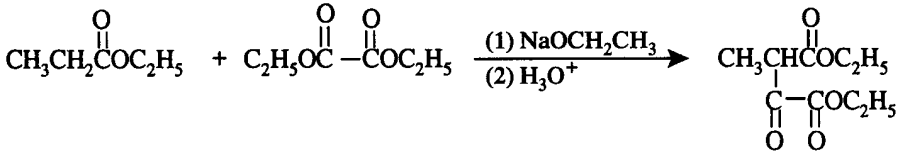




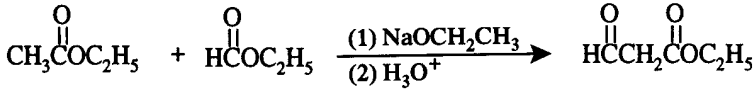
Resonance stabilized



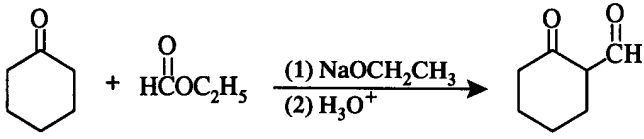
19.4 (a)



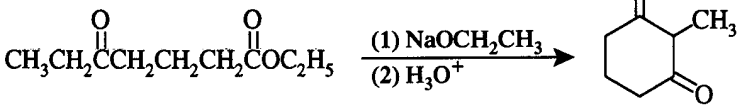
(b)



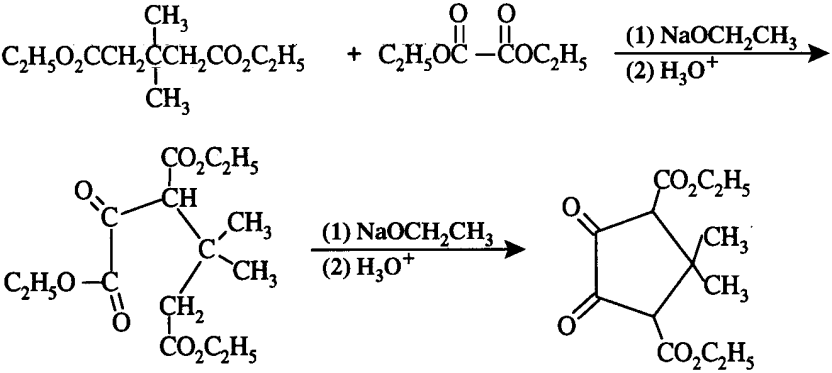
19.5 (a)



(b)

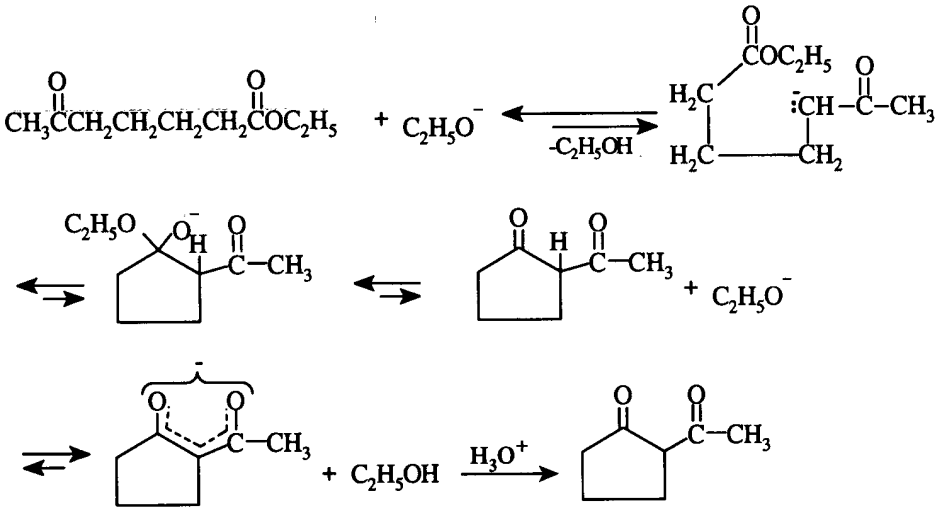


(c)



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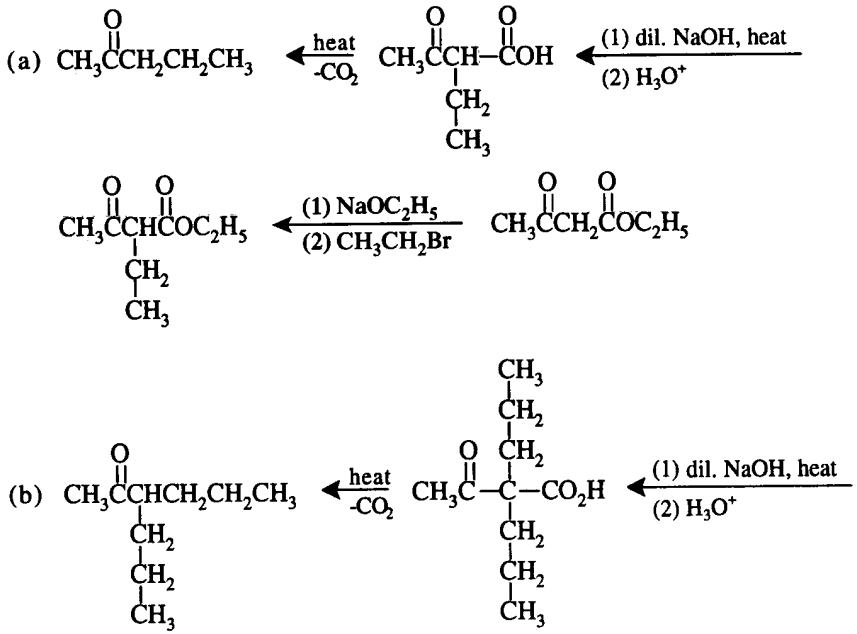
19.6



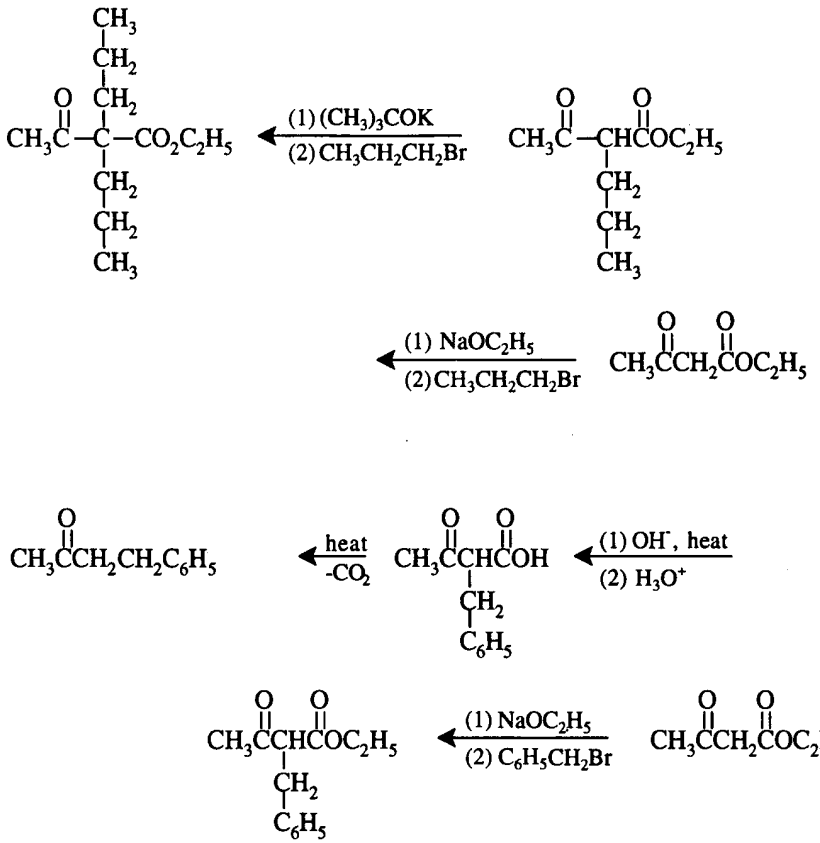
19.7 The partially negative oxygen atom of sodioacetoacetic ester acts as the nucleophile.



19.8 Again, working backward,



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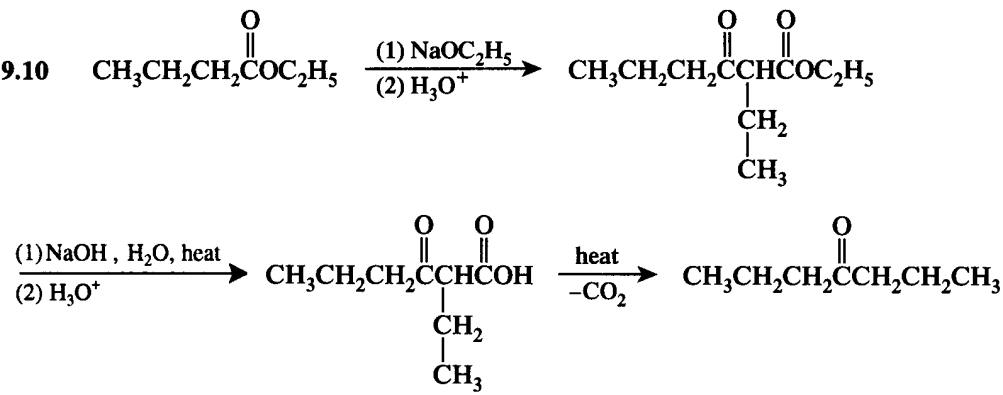


19.9 (a) Reactivity is the same as with any S_N2 reaction. With primary halides substitution is highly favored, with secondary halides elimination competes with substitution, and with tertiary halides elimination is the exclusive course of reaction.

(b) Acetoacetic ester and 2-methylpropene

(c) Bromobenzene is unreactive to nucleophilic substitution.

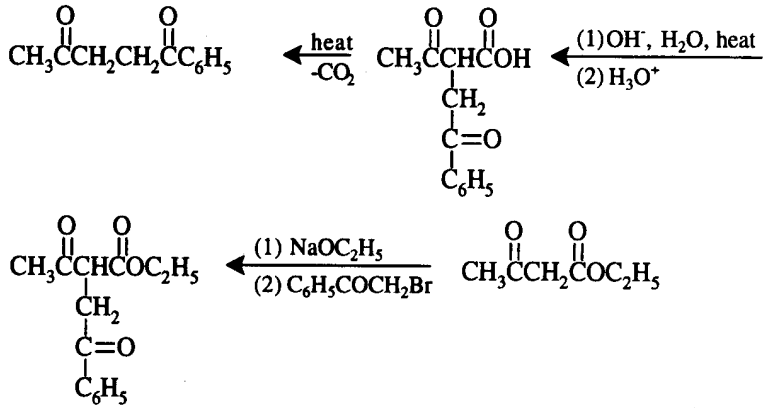
19.10



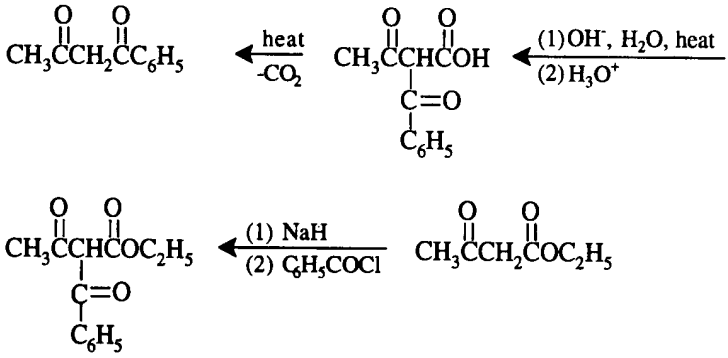
19.11 The carboxyl group that is lost more readily is the one that is β to the keto group (cf. Section 18.11 of the text).

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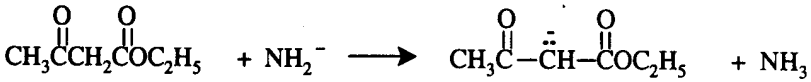
19.12



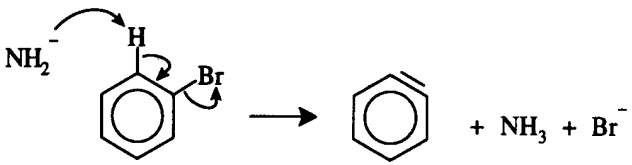
19.13



19.14 (a) One molar equivalent of $NaNH_2$ converts acetoacetic ester to its anion,

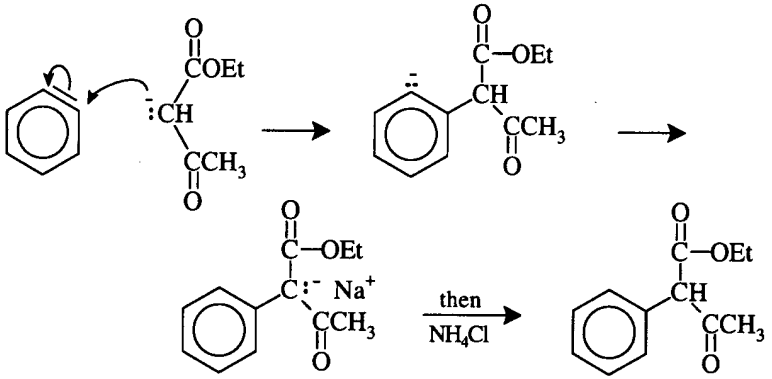


and one molar equivalent of $NaNH_2$ converts bromobenzene to benzyne (cf. Section 21.11B):



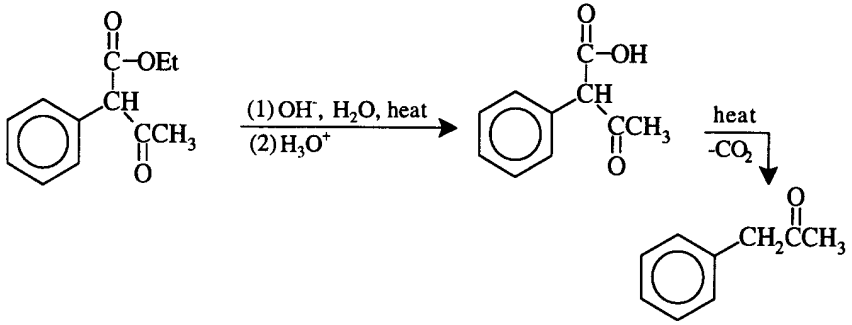
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Then the anion of acetoacetic ester adds to the benzyne as it forms in the mixture.

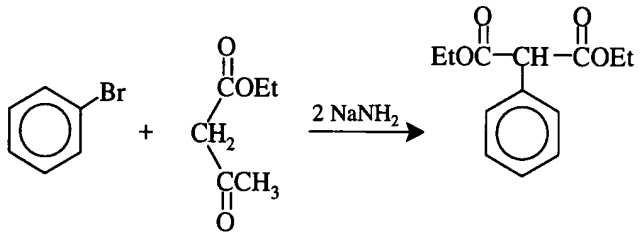


This is the end product of the addition.

(b) 1-phenyl-2-propanone, as follows:

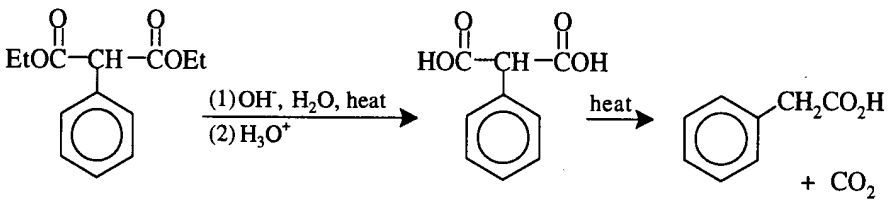


(c) By treating bromobenzene with diethyl malonate and two molar equivalents of $NaNH_2$ to form diethyl phenylmalonate.



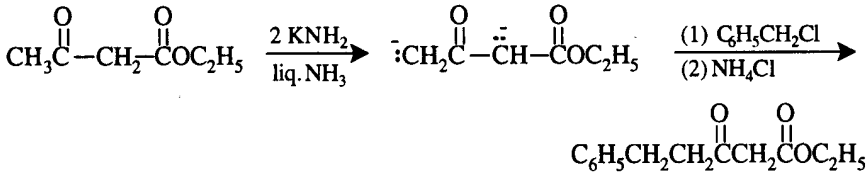
[The mechanism for this reaction is analogous to that given in part (a).]

Then hydrolysis and decarboxylation will convert diethyl phenylmalonate to phenylacetic acid.



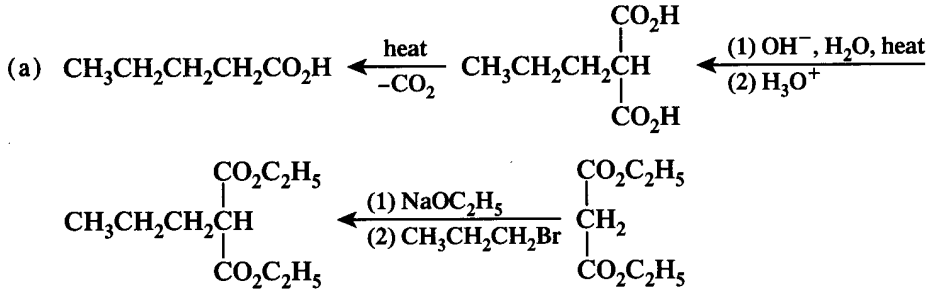
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19.15 Here we alkylate the dianion,

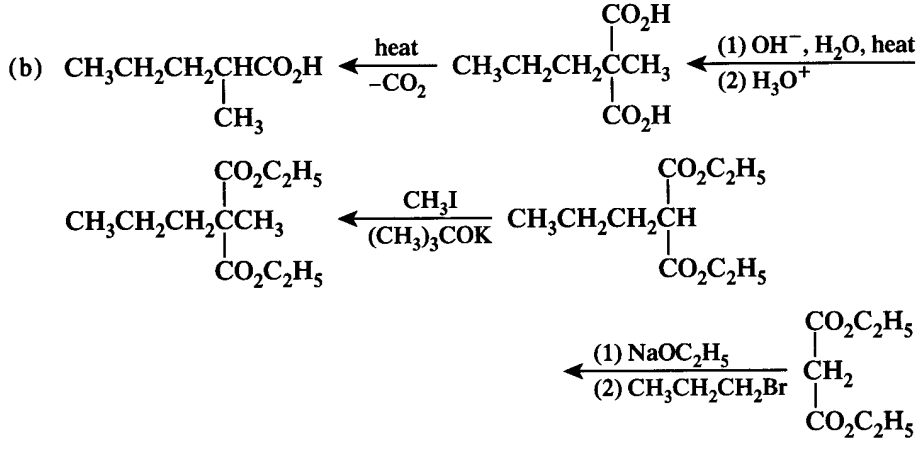


19.16 Working backward,

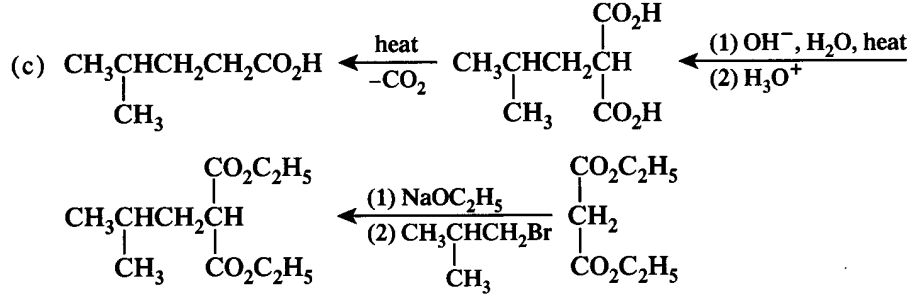
(a)



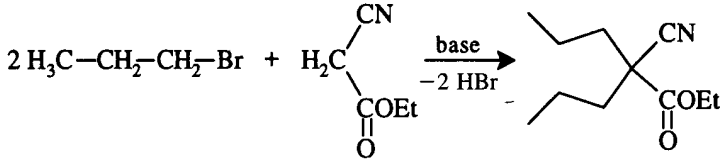
(b)



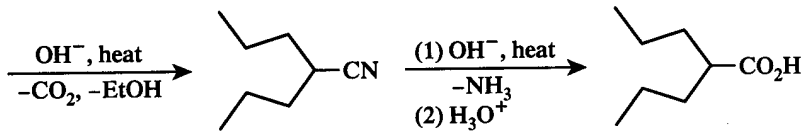
(c)



19.17

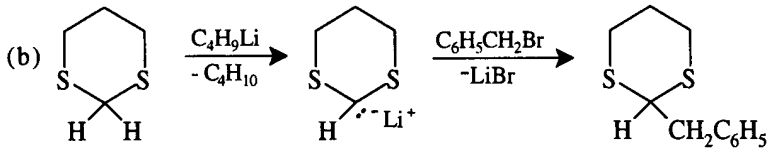


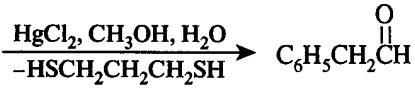
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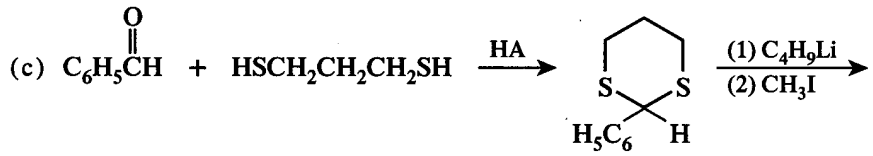


Valproic acid

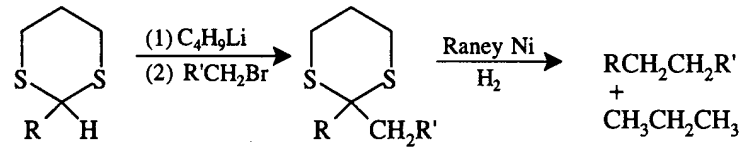
19.18 (a) Formaldehyde, 

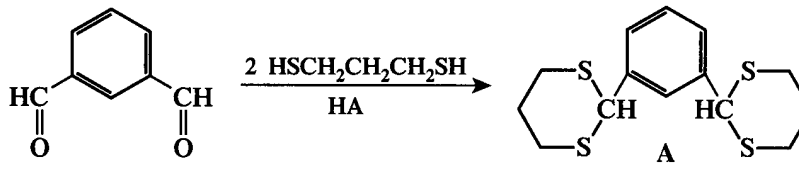
(b) 

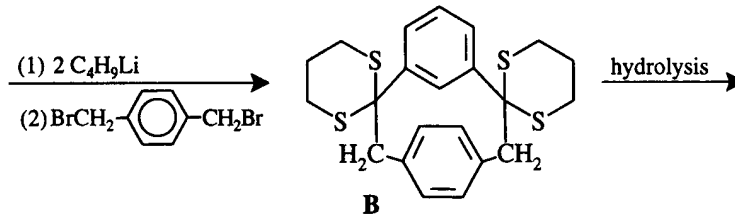


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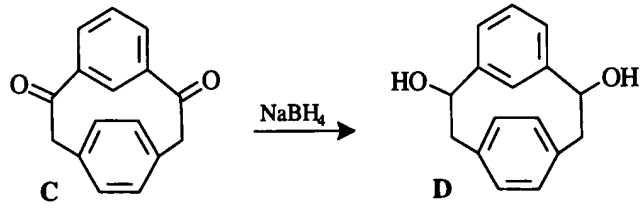
19.19 By treating the thioketal with Raney nickel.



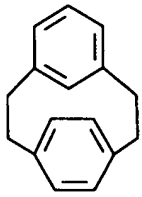
19.20 (a) 



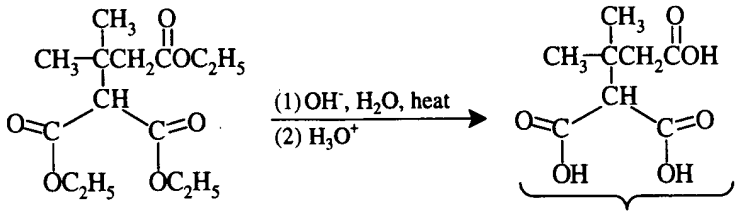
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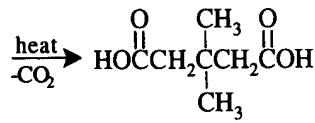


(b)

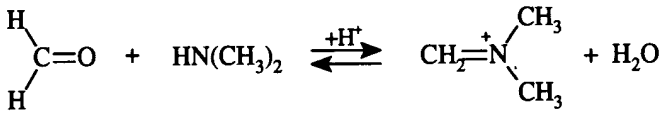


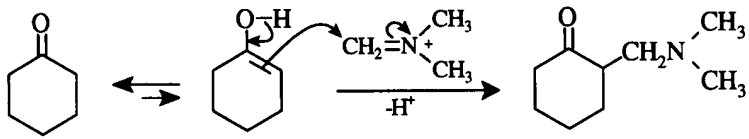
19.21



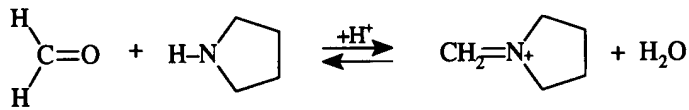


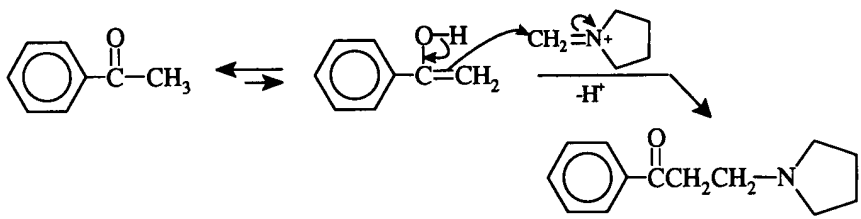
19.22 (a)



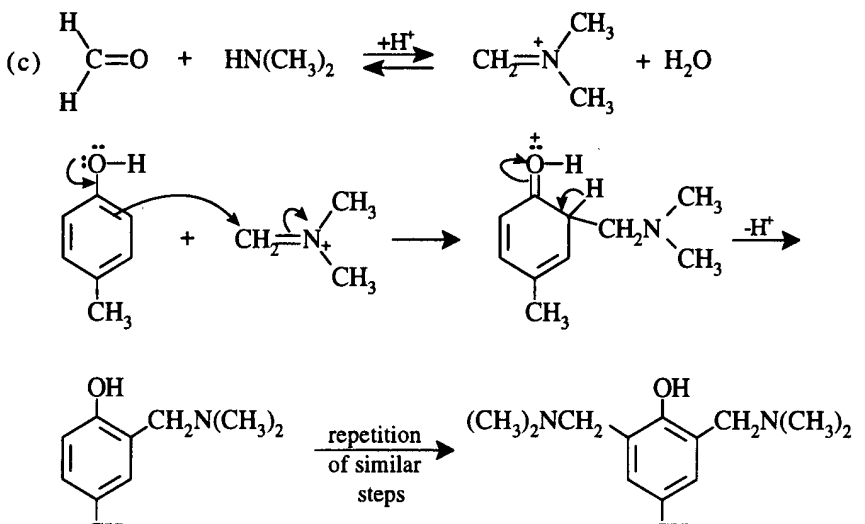


(b)

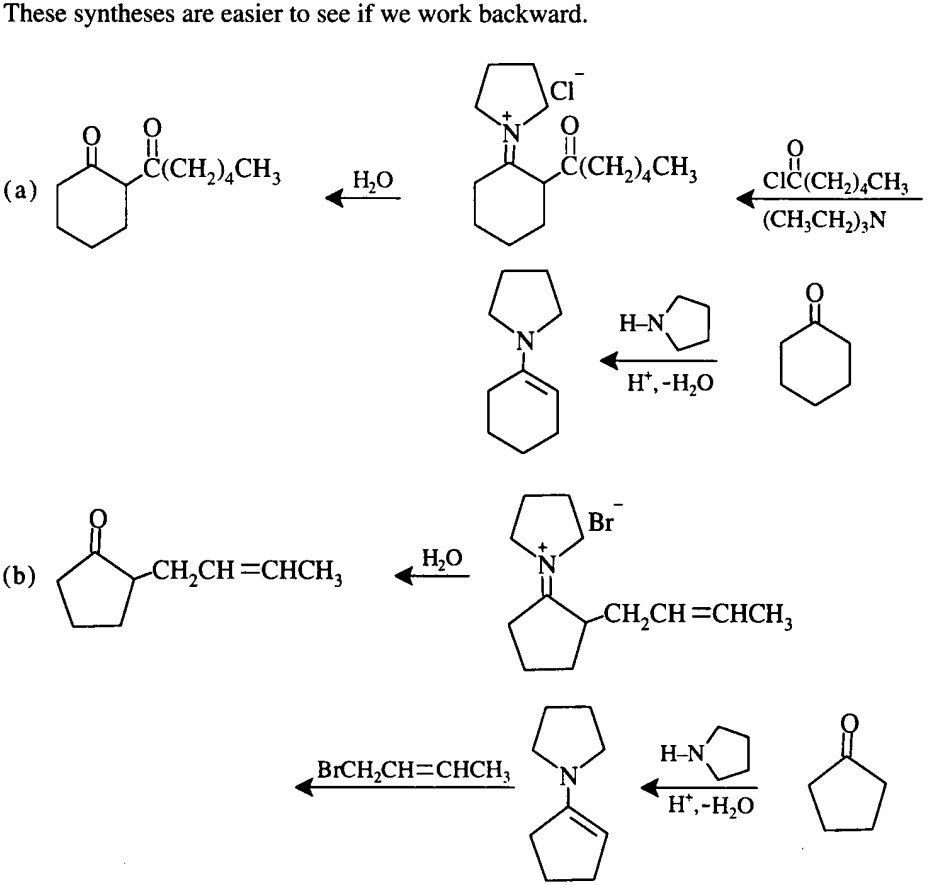




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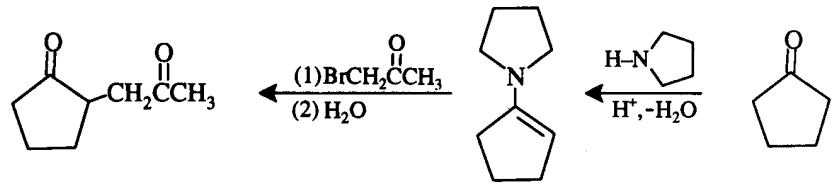


19.23 These syntheses are easier to see if we work backward.

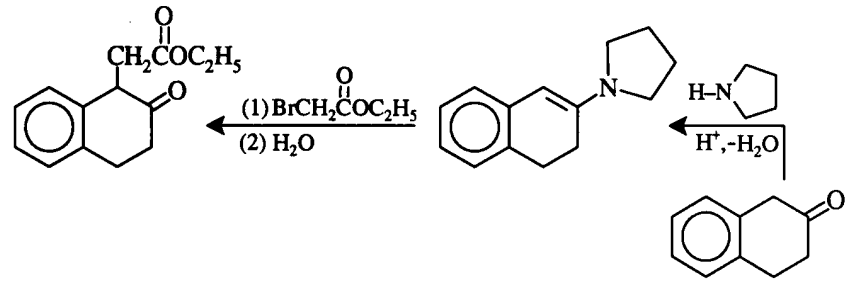


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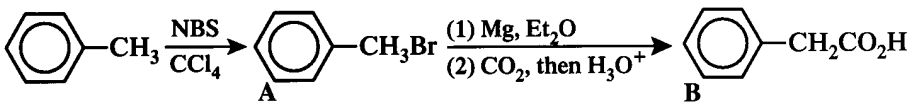
(c)



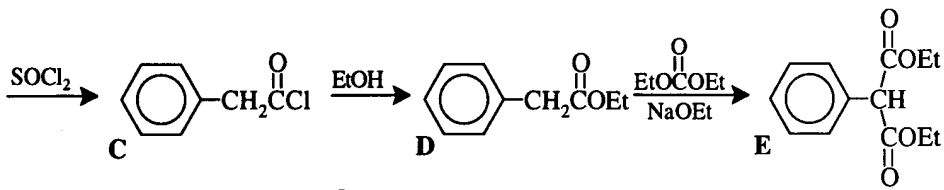
(d)



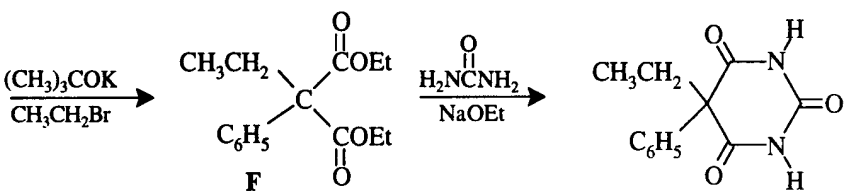
19.24 (a)



A B



C D E

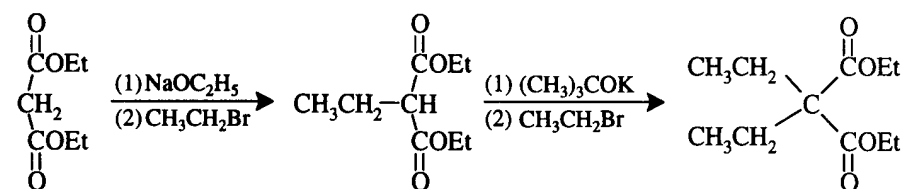


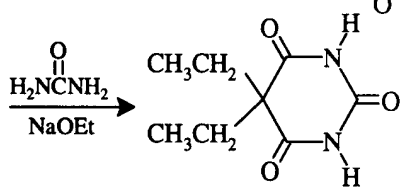
F

Phenobarbital

(b) See Section 19.3.

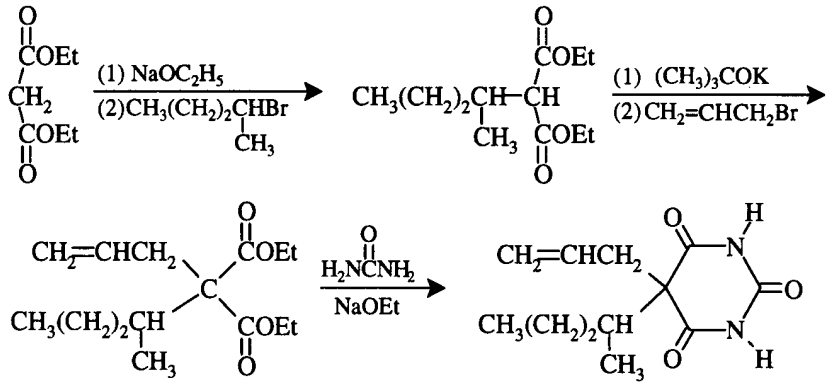
19.25



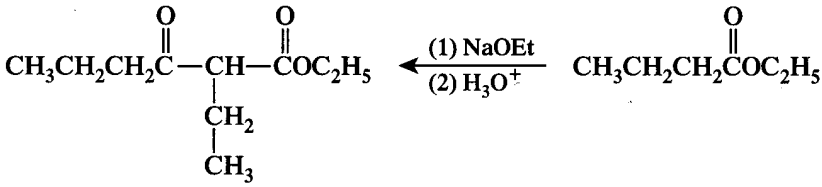


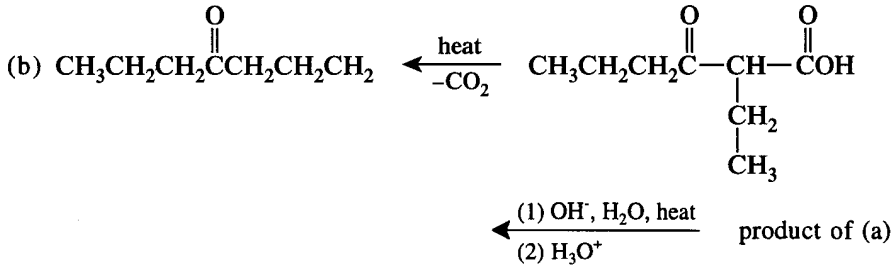
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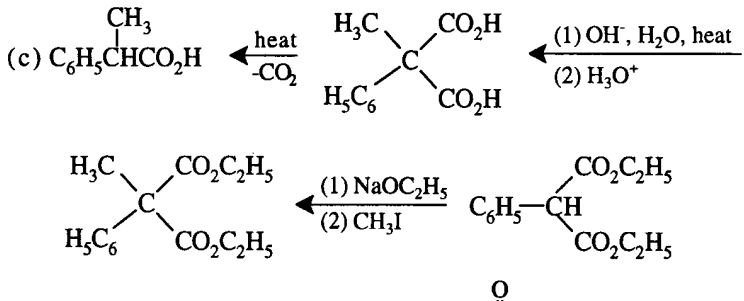
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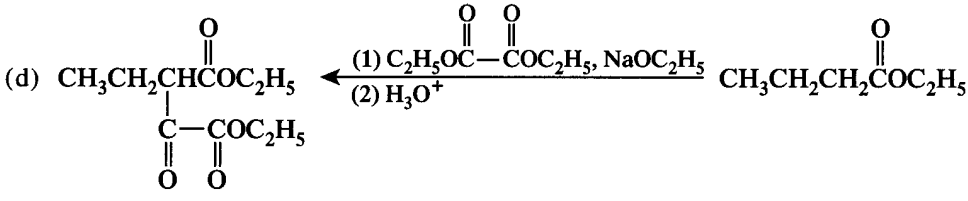


Seconal

19.26 (a) 

(b) 

(c) 

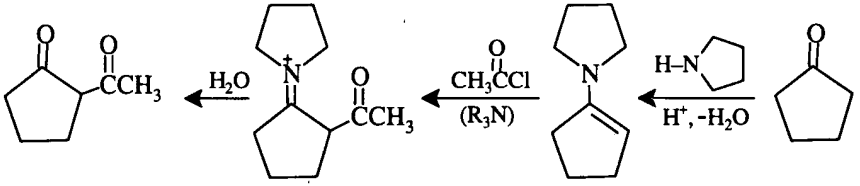
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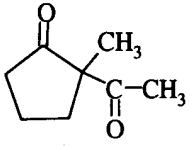
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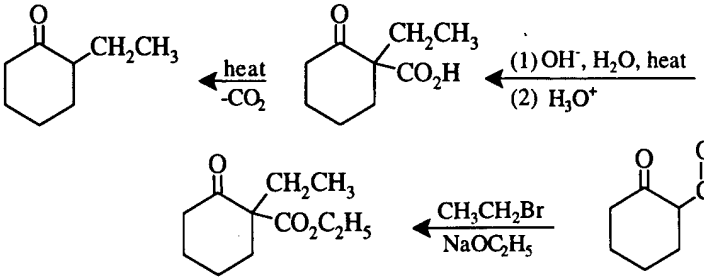
(e) $CH_3CH_2CH_2C(=O)C(=O)OC_2H_5$ ← HA, C_2H_5OH — $CH_3CH_2CH_2C(=O)C(=O)OH$

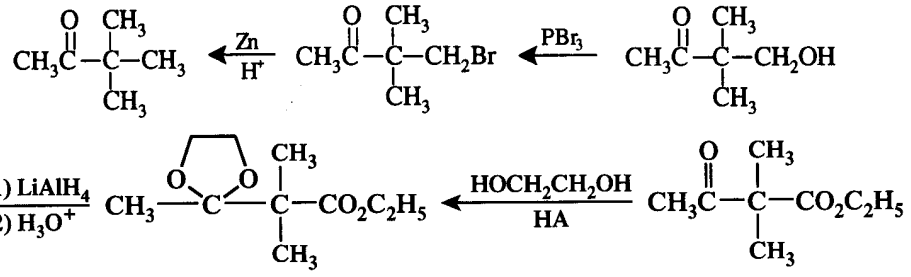
← heat, $-CO_2$ — $CH_3CH_2CH(C(=O)OH)C(=O)C(=O)OH$ ← (1) OH^-, H_2O, heat; (2) H_3O^+ — product of (d)

(f) $C_6H_5CH(C(=O)OC_2H_5)CH(=O)$ ← (1) $HCOC_2H_5$, $NaOC_2H_5$; (2) H_3O^+ — $C_6H_5CH_2C(=O)OC_2H_5$

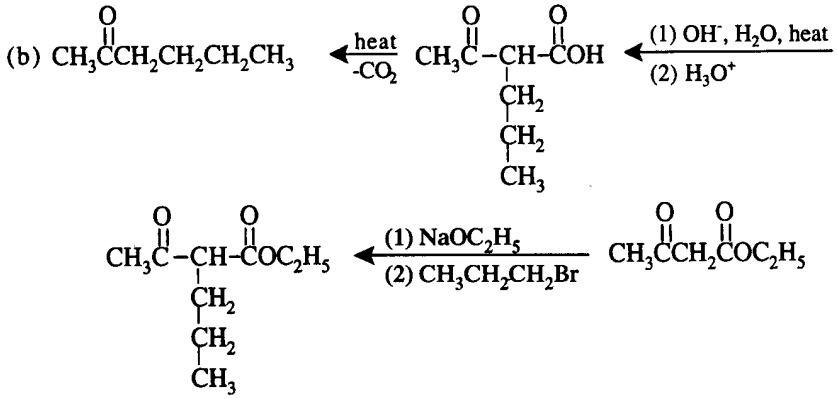
(g) 

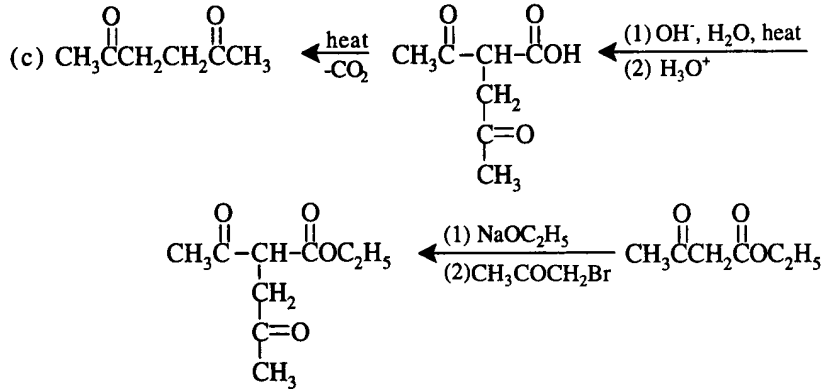
(h)  ← CH_3I, $(CH_3)_3COK$ — product of (g)

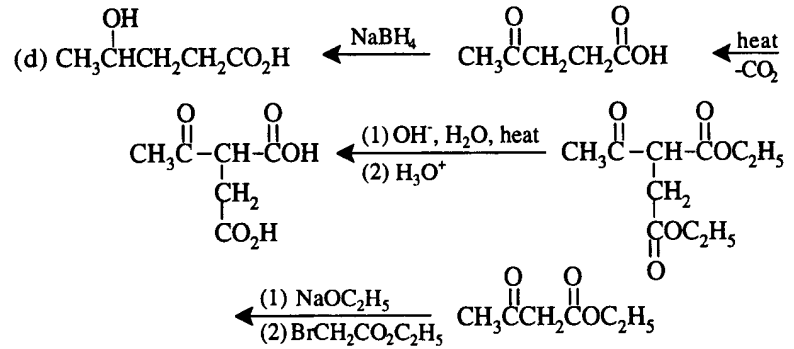
(i) 

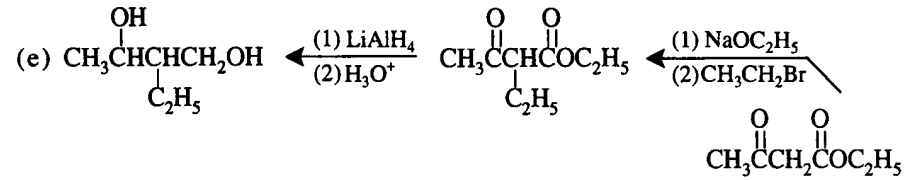
19.27 (a) 

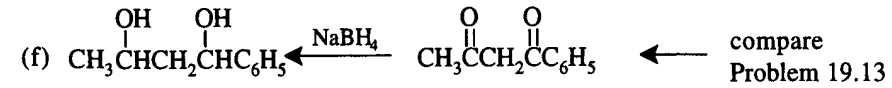
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19.28 (a) $CH_3CH_2CHCO_2H$ (CH$_3$ on the CH) $\xleftarrow[-CO_2]{\text{heat}}$ $CH_3CH_2C(CH_3)(CO_2H)_2$ $\xleftarrow[(2)\ H_3O^+]{(1)\ OH^-,\ H_2O,\ \text{heat}}$

$CH_3CH_2C(CH_3)(CO_2C_2H_5)_2$ $\xleftarrow[(2)\ CH_3I]{(1)\ KOC(CH_3)_3}$ $CH_3CH_2CH(CO_2C_2H_5)_2$

$\xleftarrow[(2)\ CH_3CH_2Br]{(1)\ NaOC_2H_5}$ $H_2C(CO_2C_2H_5)_2$

(b) $CH_3CHCH_2CH_2CH_2OH$ (CH$_3$ on the CH) $\xleftarrow[(2)\ H_3O^+]{(1)\ LiAlH_4}$ $CH_3CHCH_2CH_2CO_2H$ (CH$_3$ on the CH)

[from Problem 19.16(c)]

(c) $CH_3CH_2CHCH_2OH$ (CH_2OH on the CH) $\xleftarrow[(2)\ H_3O^+]{(1)\ LiAlH_4}$ $CH_3CH_2CH(CO_2C_2H_5)_2$

[from (a) above]

(d) $HOCH_2CH_2CH_2CH_2OH$ $\xleftarrow[(2)\ H_3O^+]{(1)\ LiAlH_4}$ $HO_2CCH_2CH_2CO_2H$ $\xleftarrow[-CO_2]{\text{heat}}$

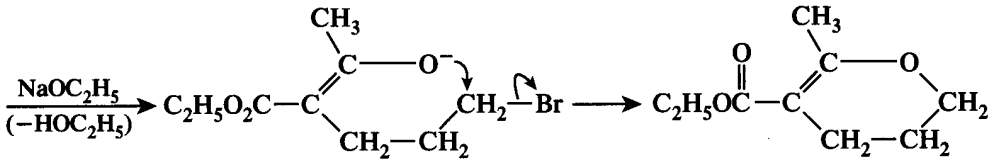
$HO_2CCH(CH_2CO_2H)CO_2H$ $\xleftarrow[\text{heat}]{HCl}$ $C_2H_5O_2CCH(CH_2CO_2C_2H_5)CO_2C_2H_5$

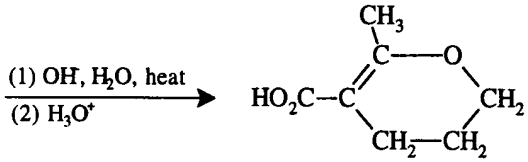
$\longleftarrow$ $C_2H_5O_2CCH_2CO_2C_2H_5$ + $NaOC_2H_5$ + $BrCH_2CO_2C_2H_5$

19.29 The following reaction took place:

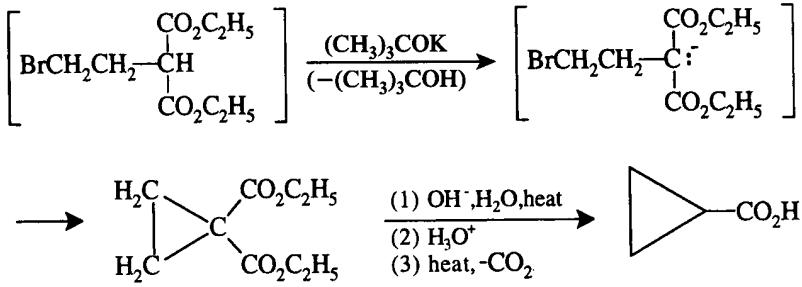
$CH_3C(=O)CH_2C(=O)OC_2H_5 + BrCH_2CH_2CH_2Br \xrightarrow{NaOC_2H_5}$ $BrCH_2CH_2CH_2CH(C(=O)CH_3)(C(=O)OC_2H_5)$

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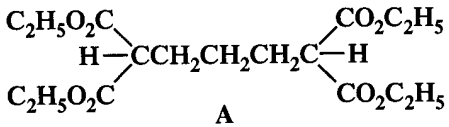




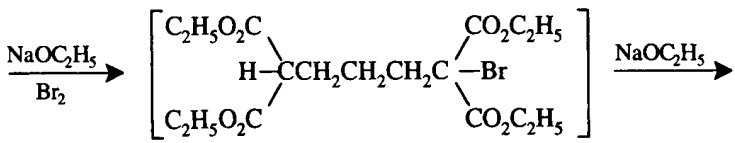
19.30 (a) $BrCH_2CH_2Br$ + $CH_2(CO_2C_2H_5)_2$ + $NaOC_2H_5$ ⟶

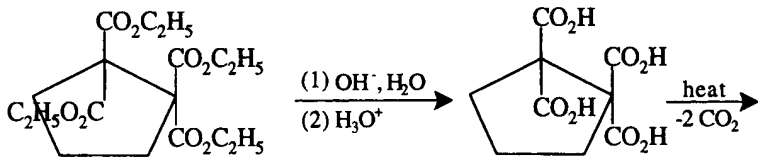


(b) 2 $NaCH(CO_2C_2H_5)_2$ + $BrCH_2CH_2CH_2Br$ ⟶



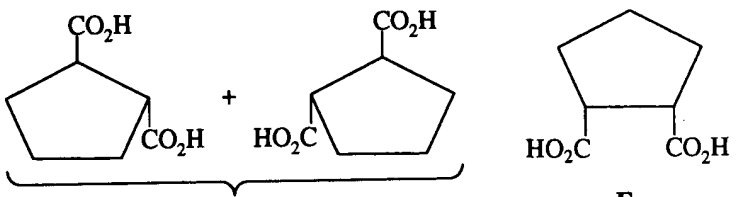
A





B C

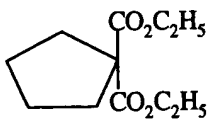
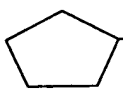
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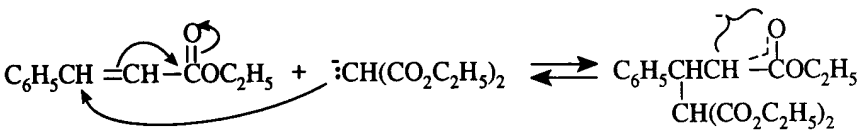
D
Racemic form

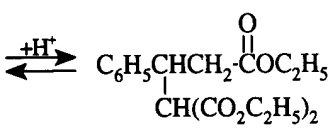
E
Meso compound

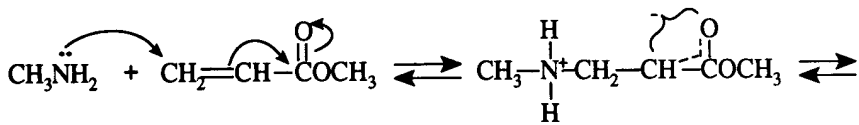
(c) $BrCH_2CH_2CH_2CH_2Br \xrightarrow{NaCH(CO_2C_2H_5)_2} BrCH_2CH_2CH_2CH_2CH(CO_2C_2H_5)_2$

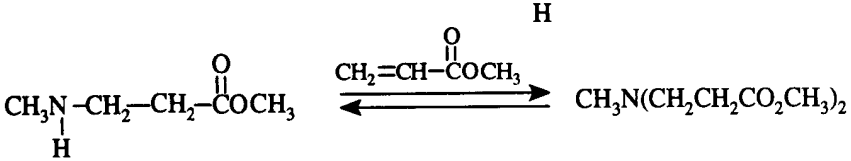
$\xrightarrow{KOC(CH_3)_3}$  $\xrightarrow[(2)\ H_3O^+]{(1)\ OH^-,\ H_2O}{(3)\ \text{heat},\ -CO_2}$ 

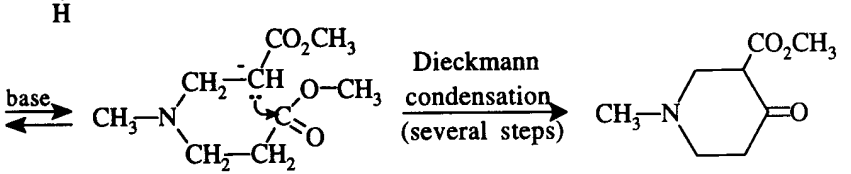
19.31 (a) $CH_2(CO_2C_2H_5)_2 + {}^-OC_2H_5 \rightleftharpoons {}^-CH(CO_2C_2H_5)_2 + C_2H_5OH$



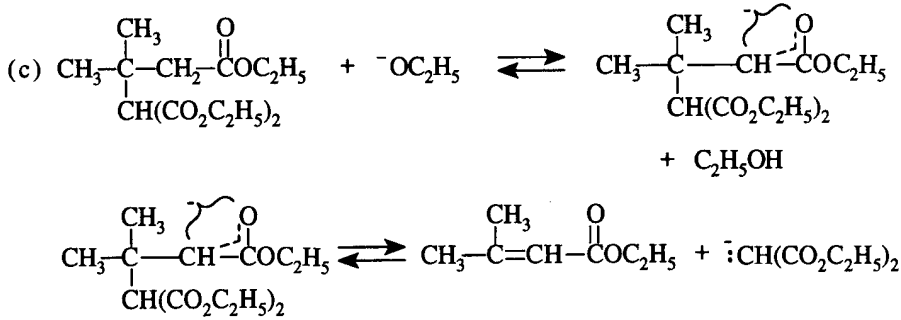


(b) 



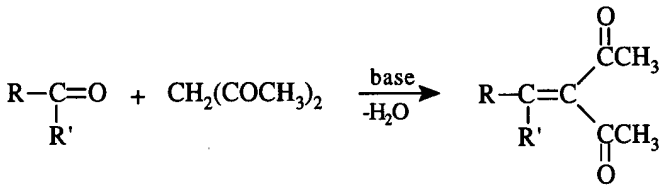


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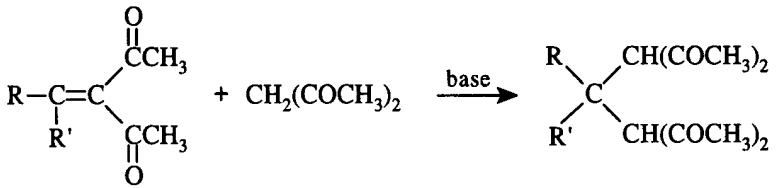
(c) 

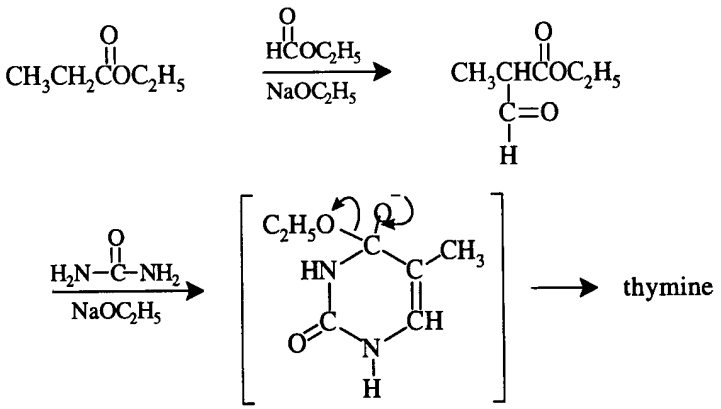
The Michael reaction is reversible, and the reaction just given is an example of a reverse Michael reaction.

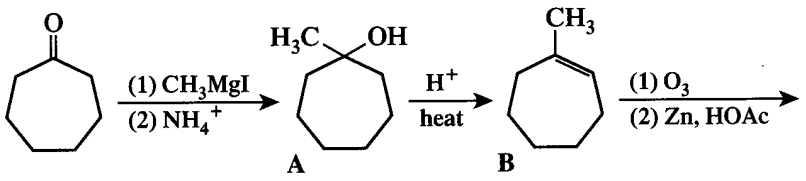
19.32 Two reactions take place. The first is a normal Knoevenagel condensation,



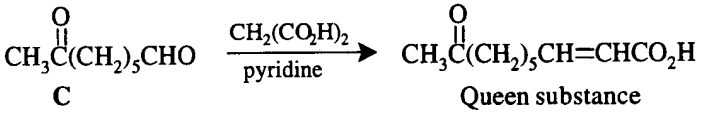
Then the α, β-unsaturated diketone reacts with a second mole of the active methylene compound in a Michael addition.



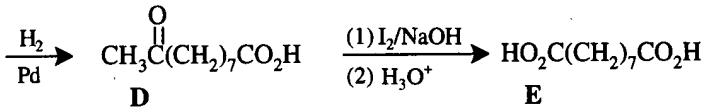
19.33 

19.34 

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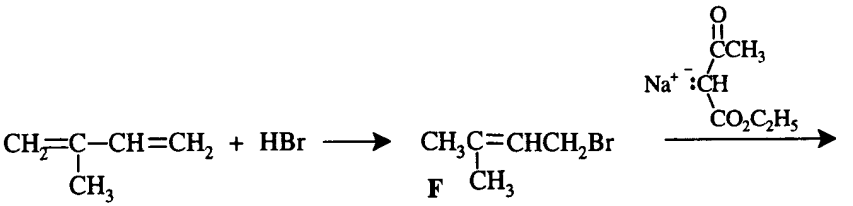


C — Queen substance

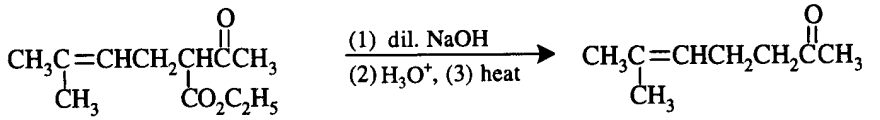


D — E

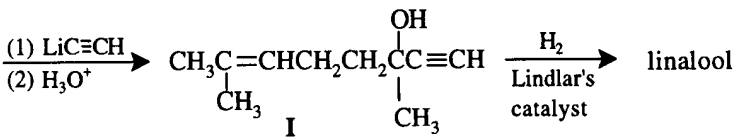
19.35



F

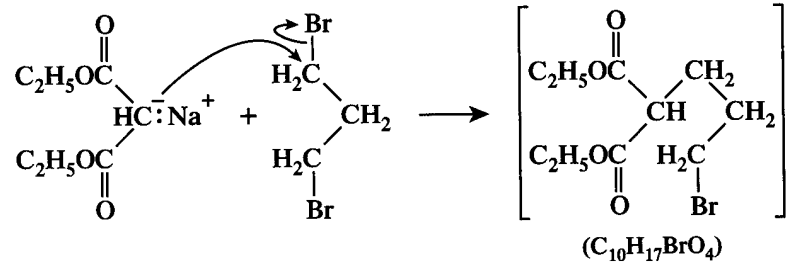


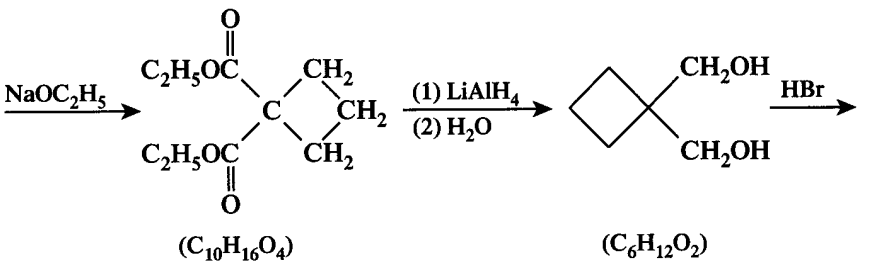
G — H

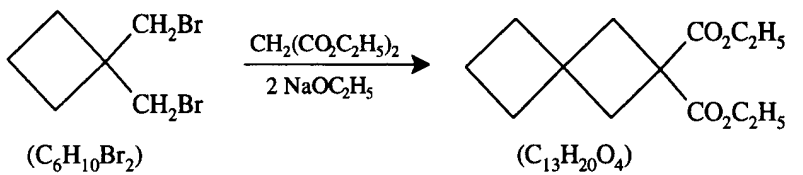


I

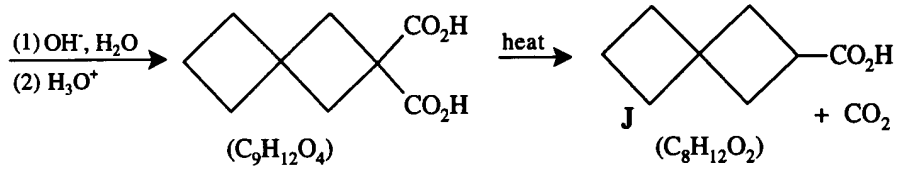
19.36



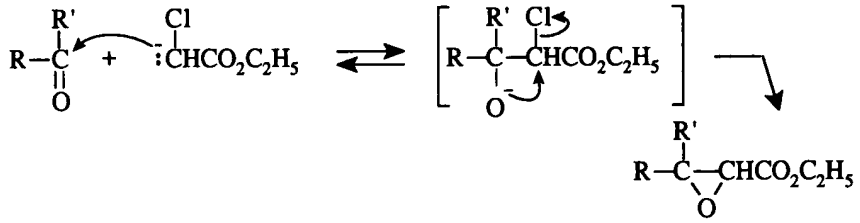




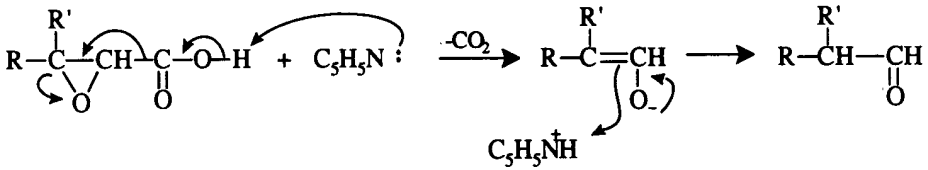
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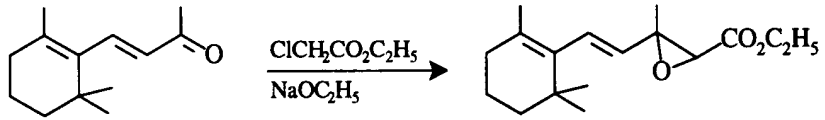
19.37 (a) $ClCH_2CO_2C_2H_5 + C_2H_5O^- \rightleftharpoons Cl-\ddot{C}HCO_2C_2H_5 + C_2H_5OH$



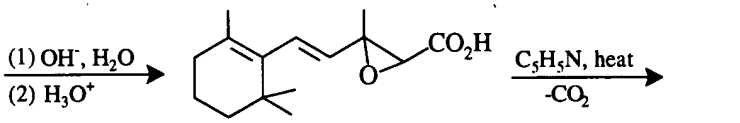
(b) Decarboxylation of the epoxy acid gives an enol anion which, on protonation, gives an aldehyde.

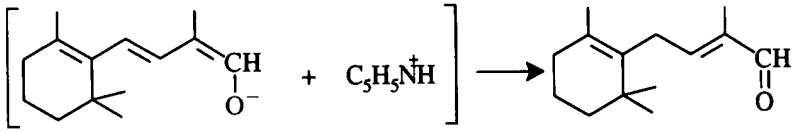


(c)

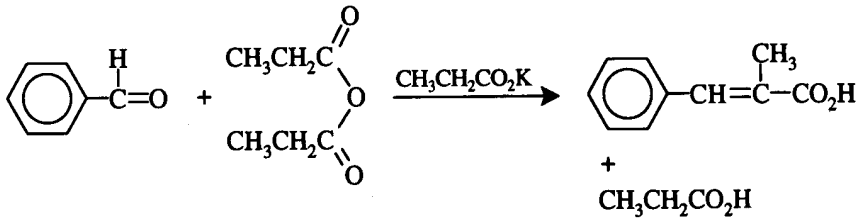


β-Ionone

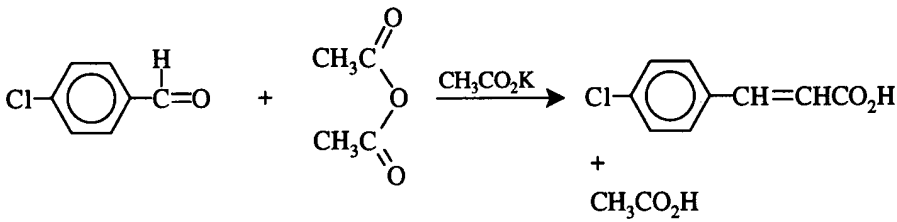


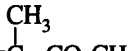


19.38 (a)



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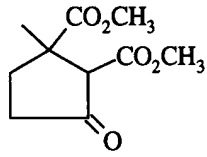
(b) 

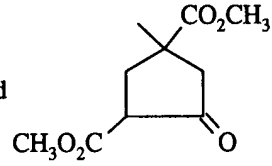
19.39 (a) 

(b) $KMnO_4$, OH^-, then H_3O^+

(c) CH_3OH, H^+

(d) CH_3ONa, then H^+

(e) and (f) 

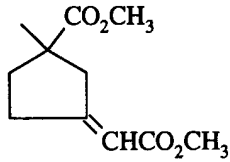
and 

(g) OH^-, H_2O, then H_3O^+

(h) heat ($-CO_2$)

(i) CH_3OH, H^+

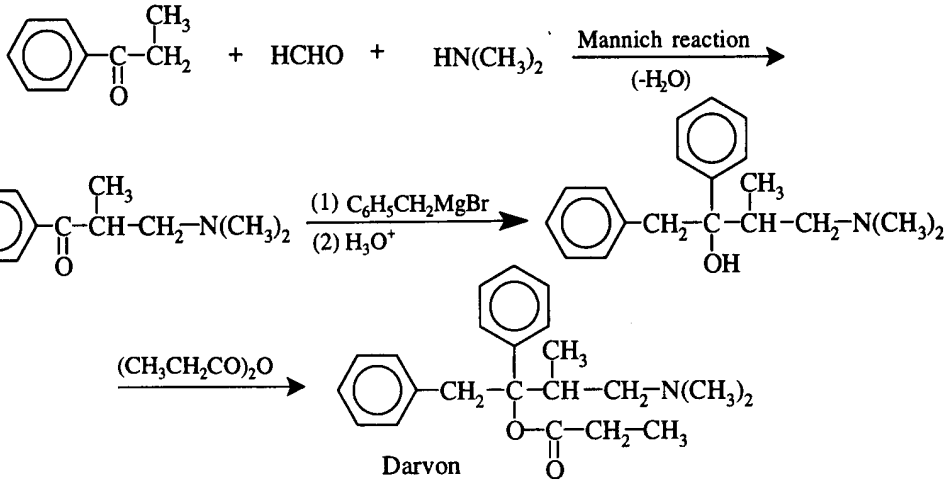
(j) $BrCH_2CO_2CH_3$, Zn, then H_3O^+

(k) 

(l) H_2, Pt

(m) CH_3ONa, then H^+

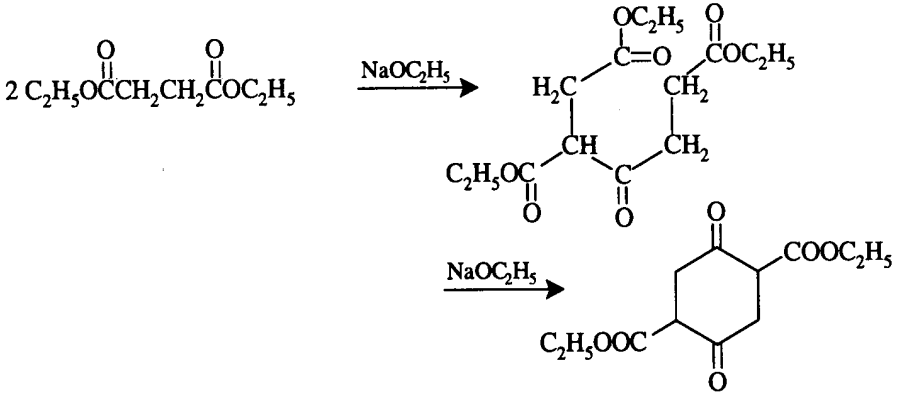
(n) $2\ NaNH_2 + 2\ CH_3I$

19.40 

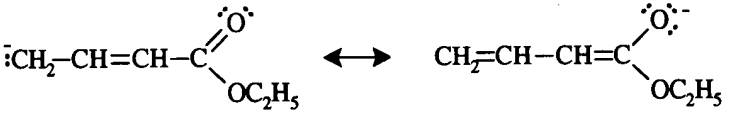
19.41 In a polar solvent, such as water, the keto form is stabilized by solvation. When the interaction with the solvent becomes minimal, the enol form achieves stability by internal hydrogen bonding.

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19.42 Intramolecular cyclization (which would give a product of formula $C_6H_8O_3$) is not favored because of ring strain. The formula of the product actually obtained suggests a 1:1 intermolecular reaction:

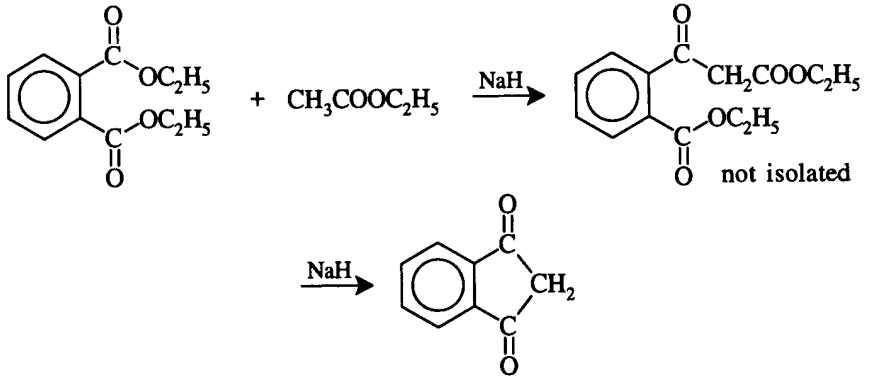


19.43 A gamma hydrogen is abstracted by base (as is an alpha hydrogen in the usual Claisen) to give a resonance-stabilized species:



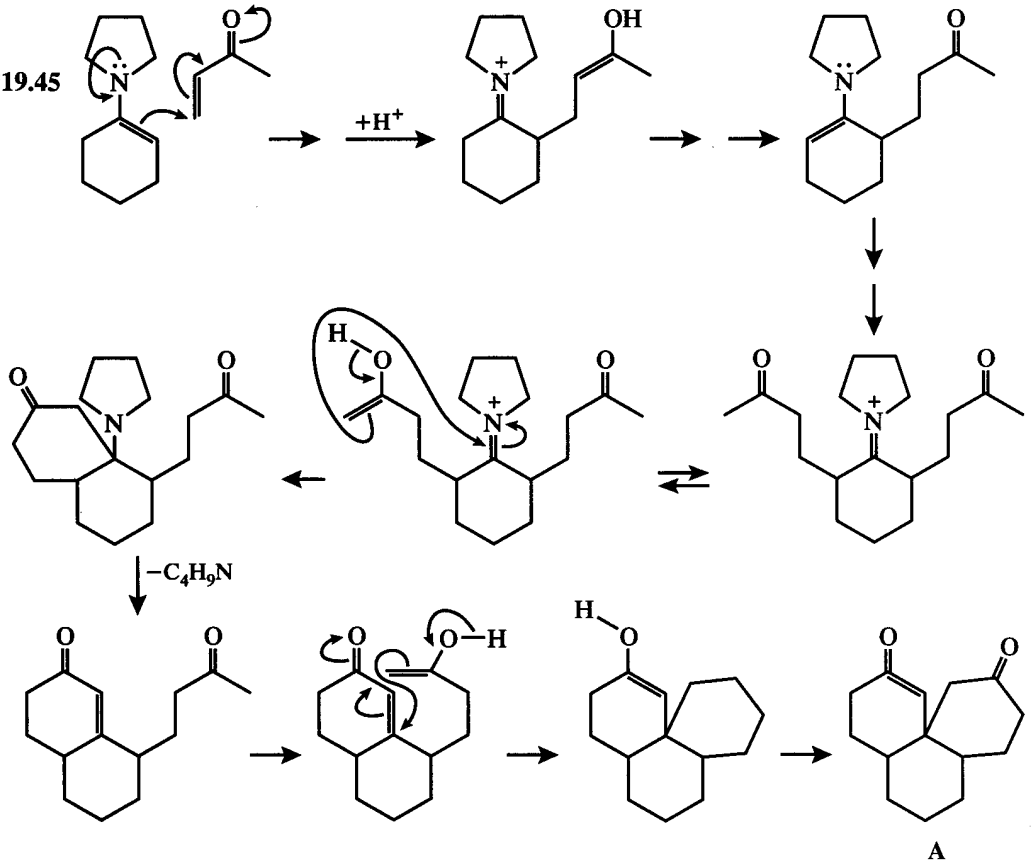
Ethyl crotonate differs from ethyl acetate by $-CH{=}CH-$, a vinyl group. The transmission of the stabilizing effect of the $-COOC_2H_5$ group is an example of the **principle of vinylogy.**

19.44 The synthesis actually involves two sequential Claisen condensations, with ethyl acetate serving as the source of the carbanionic species.

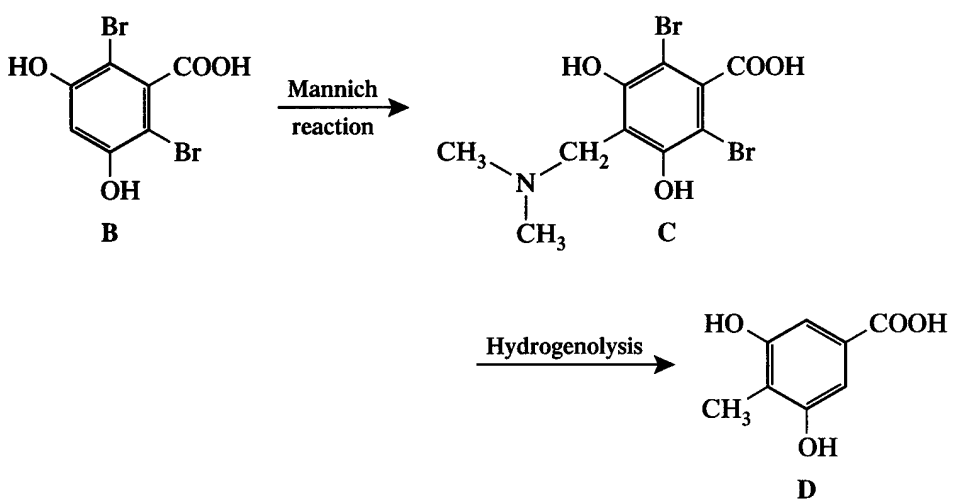


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*19.45



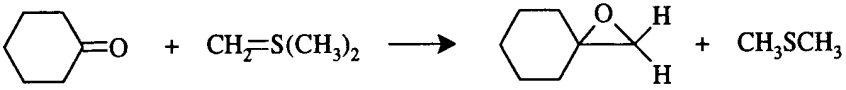
*19.46



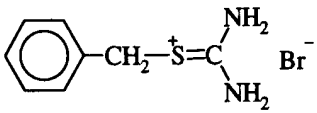
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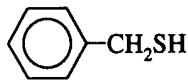
C SPECIAL TOPIC
Thiols, Sulfur Ylides, and Disulfides

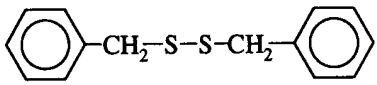
SOLUTIONS TO PROBLEMS

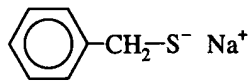
C.1 (a) 

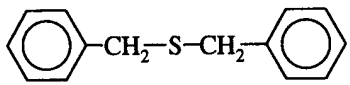
(b) 

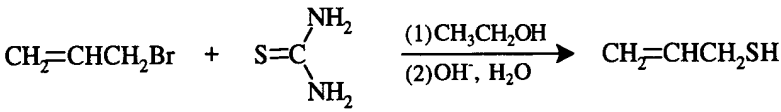
C.2 (a) 

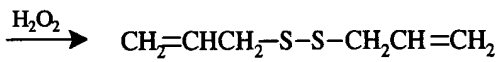
(b) 

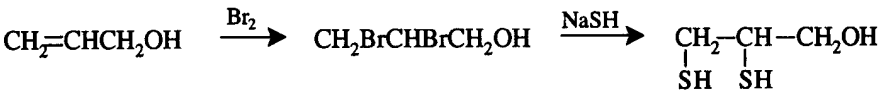
(c) 

(d) 

(e) 

C.3 



C.4 

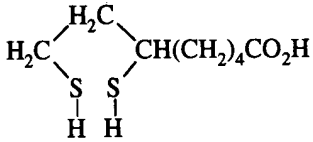
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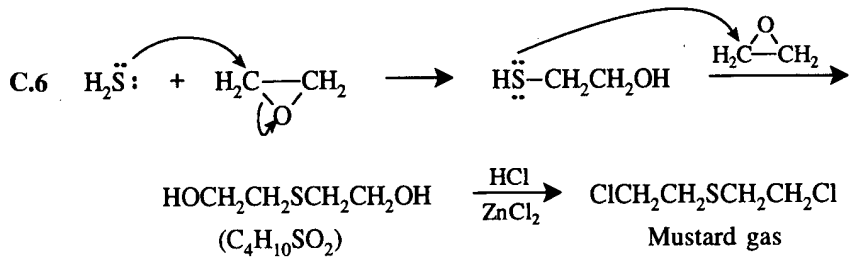
C.5 (a) $ClCH_2CH_2\overset{\overset{O}{\|}}{C}(CH_2)_4CO_2C_2H_5$ (This step is the Friedel-Crafts alkylation of an alkene)

(b) $SOCl_2$

(c) $2\ C_6H_5CH_2SH$ and KOH

(d) H_3O^+

(e) 

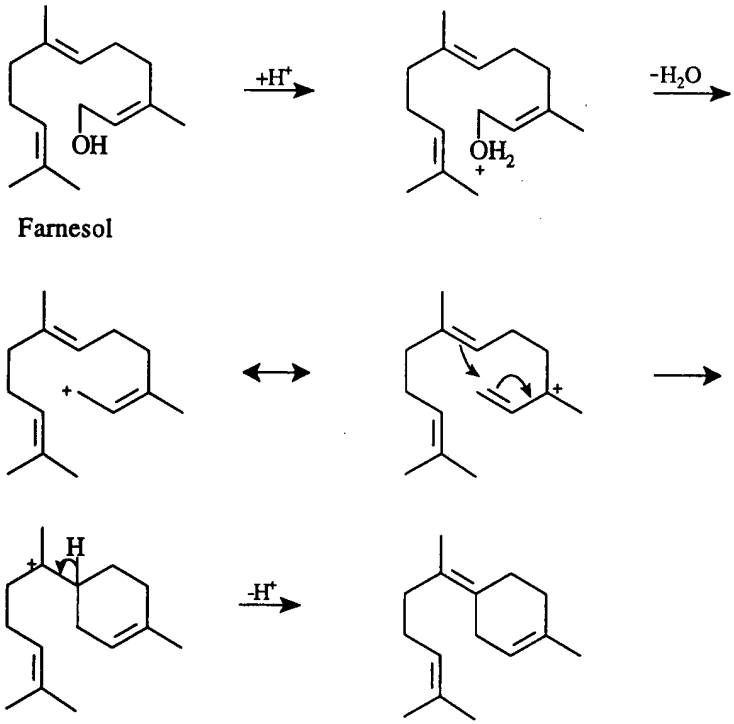
C.6 

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D SPECIAL TOPIC
Thiol Esters and Lipid Biosynthesis

SOLUTIONS TO PROBLEM

D.1



Farnesol

Bisabolene

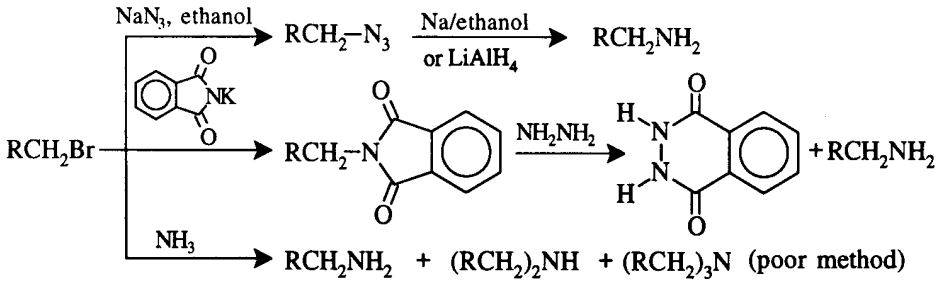
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20 AMINES

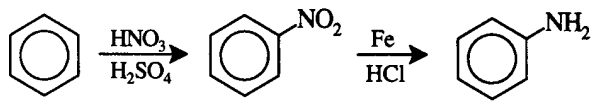
PREPARATION AND REACTIONS OF AMINES

A. Preparation

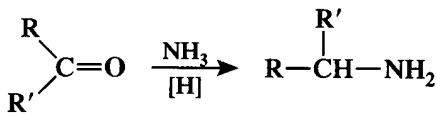
1. Preparation via nucleophilic substitution reactions.



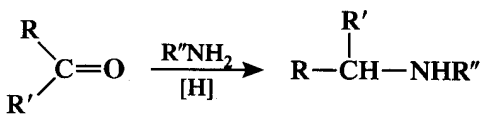
2. Preparation through reduction of nitro compounds.

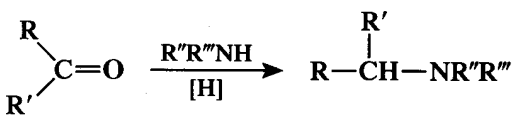


3. Preparation via reductive amination.

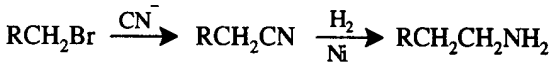


Aldehyde or ketone

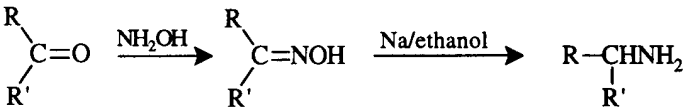


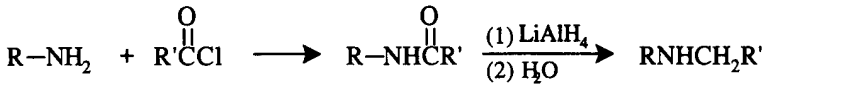


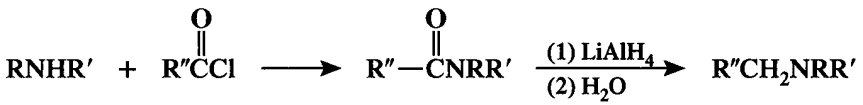
4. Preparation of amines through reduction of amides, oximes, and nitriles.



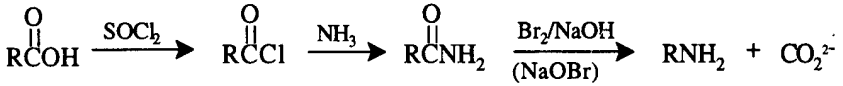
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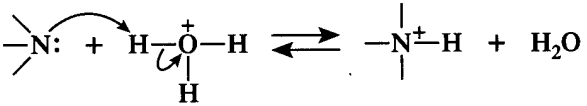
5. Preparation through the Hofmann rearangement of amides.



B. Reaction of Amines

1. As a base or a nucleophile

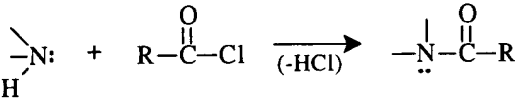
As a base



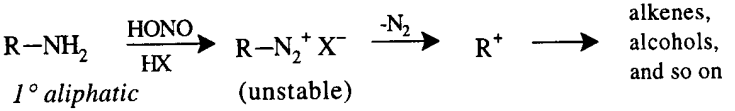
As a nucleophile in alkylation



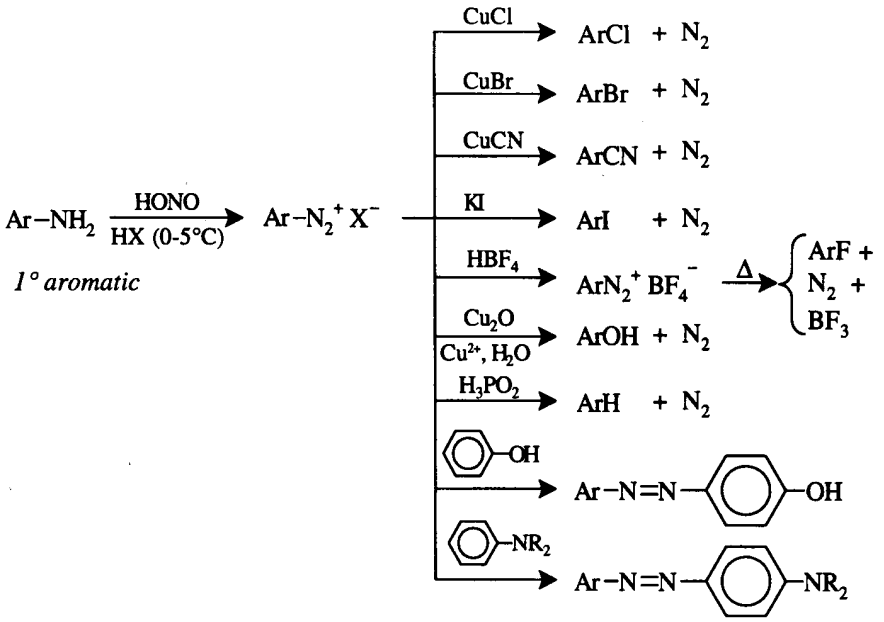
As a nucleophile in acylation



2. With nitrous acid



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$R_2NH \xrightarrow{HONO} R_2N-N=O$

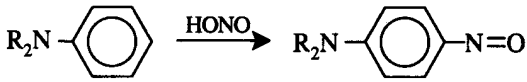
2° aliphatic

$ArNHR \xrightarrow{HONO} ArN(N=O)-R$

2° aromatic

$R_3N \xrightarrow[HX]{NaNO_2} R_3NH^+ X^- + R_3\overset{+}{N}-N=O\ X^-$

3° aliphatic



3° aromatic

3. With sulfonyl chlorides

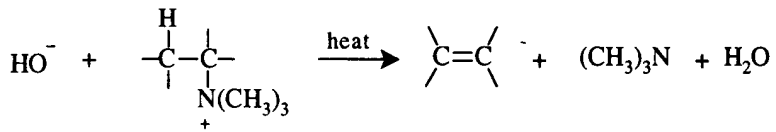
$R-NH_2 + ArSO_2Cl \xrightarrow[(-HCl)]{} RNHSO_2Ar \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [RNSO_2Ar]^- + H_2O$

1° amine

$R_2NH + ArSO_2Cl \xrightarrow[(-HCl)]{} R_2NSO_2Ar$

2° amine

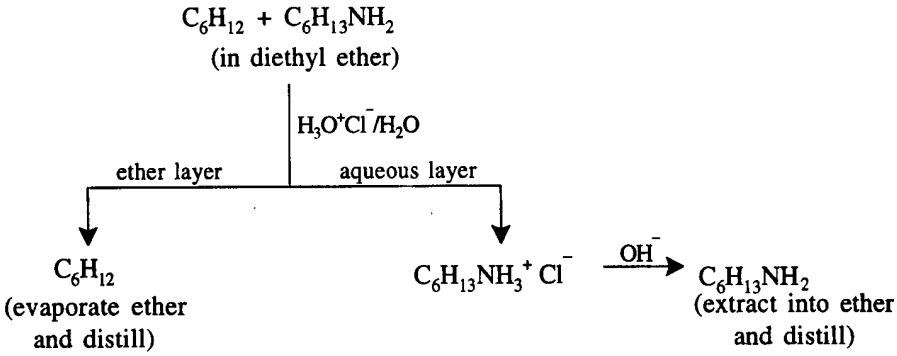
4. The Hofmann elimination



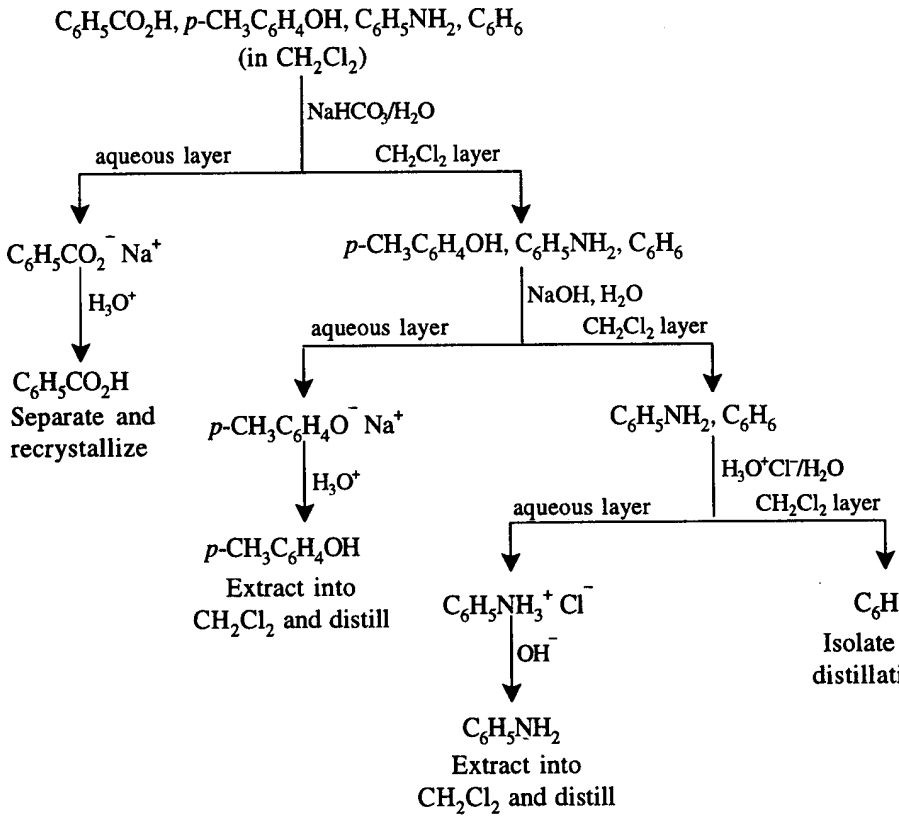
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SOLUTIONS TO PROBLEMS

20.1 Dissolve both compounds in diethyl ether and extract with aqueous HCl. This procedure gives an ether layer that contains cyclohexane and an aqueous layer that contains hexylaminium chloride. Cyclohexane may then be recovered from the ether layer by distillation. Hexylamine may be recovered from the aqueous layer by adding aqueous NaOH (to convert hexylaminium chloride to the hexylamine) and then by ether extraction and distillation.

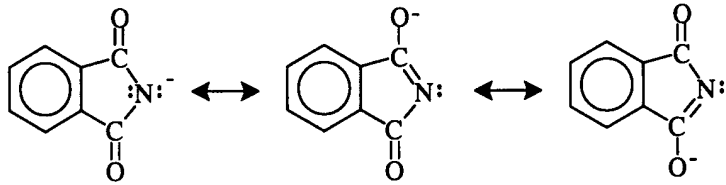


20.2 We begin by dissolving the mixture in a water-immiscible organic solvent such as CH_2Cl_2 or diethyl ether. Then, extractions with aqueous acids and bases allow us to separate the components. [We separate 4-methylphenol (*p*-cresol) from benzoic acid by taking advantage of benzoic acid's solubility in the more weakly basic aqueous $NaHCO_3$, whereas *p*-cresol requires the more strongly basic, aqueous NaOH.]



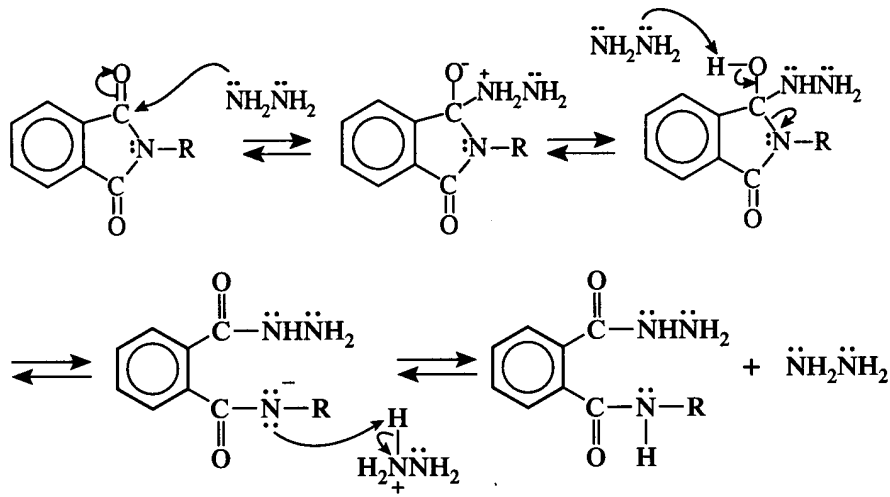
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20.3 (a) Neglecting Kekulé forms of the ring, we can write the following resonance structures for the phthalimide anion.

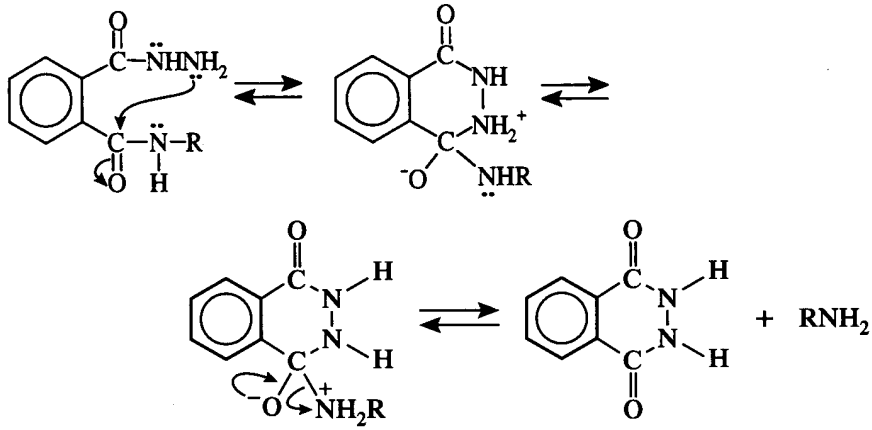


(b) Phthalimide is more acidic than benzamide because its anion is stabilized by resonance to a greater extent than the anion of benzamide. (Benzamide has only one carbonyl group attached to the nitrogen atom, and thus fewer resonance contributors are possible.)

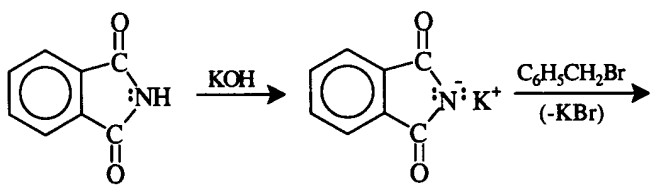
(c)



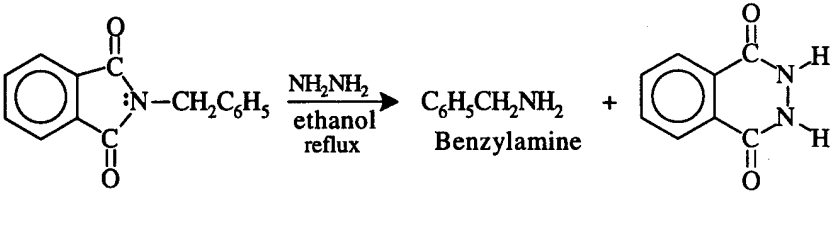
Then,



20.4



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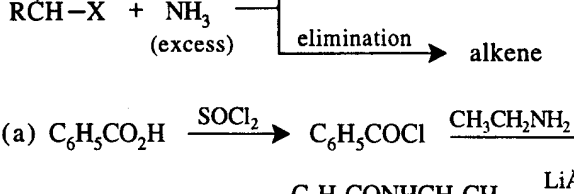
20.5 (a) $CH_3(CH_2)_3CHO + NH_3 \xrightarrow[Ni]{H_2} CH_3(CH_2)_3CH_2NH_2$

(b) $C_6H_5CH_2\overset{\overset{O}{\|}}{C}CH_3 + NH_3 \xrightarrow[Ni]{H_2} C_6H_5CH_2\underset{\underset{NH_2}{|}}{C}HCH_3$

(c) $CH_3(CH_2)_4CHO + C_6H_5NH_2 \xrightarrow[CH_3OH]{LiBH_3CN} CH_3(CH_2)_4CH_2NHC_6H_5$

(d) $C_6H_5CHO + (CH_3)_2NH \xrightarrow[CH_3OH]{LiBH_3CN} C_6H_5CH_2N(CH_3)_2$

20.6 The reaction of a secondary halide with ammonia would inevitably be accompanied by considerable elimination, thus decreasing the yield.



20.7 (a) $C_6H_5CO_2H \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow{CH_3CH_2NH_2}$

$C_6H_5CONHCH_2CH_3 \xrightarrow{LiAlH_4} C_6H_5CH_2NHCH_2CH_3$

(b) $CH_3CH_2CH_2CH_2CH_2Br \xrightarrow{NaCN} CH_3CH_2CH_2CH_2CH_2CN$

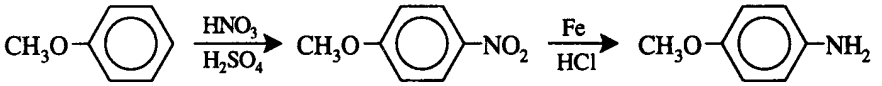
$\xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2CH_2CH_2NH_2$

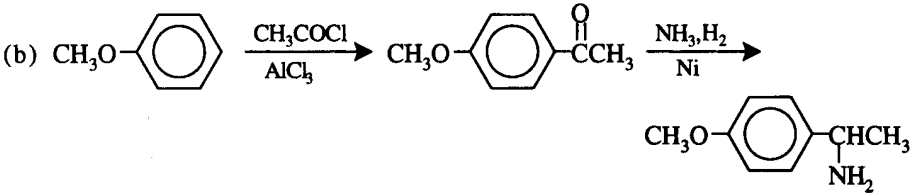
(c) $CH_3CH_2CO_2H \xrightarrow{SOCl_2} CH_3CH_2COCl \xrightarrow{(CH_3CH_2CH_2)_2NH}$

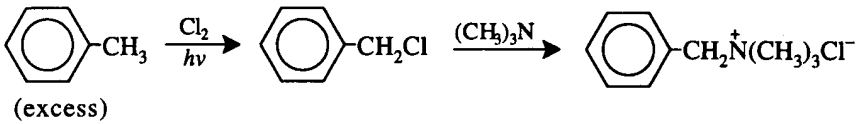
$CH_3CH_2CON(CH_2CH_2CH_3)_2 \xrightarrow{LiAlH_4} N(CH_2CH_2CH_3)_3$

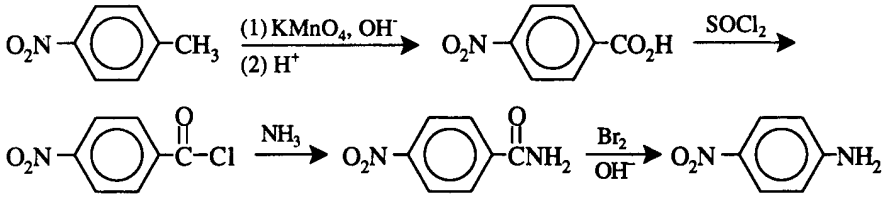
(d) $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3 \xrightarrow{NH_2OH} CH_3\overset{\overset{NOH}{\|}}{C}CH_2CH_3 \xrightarrow{Na/ethanol} CH_3\underset{\underset{NH_2}{|}}{C}HCH_2CH_3$

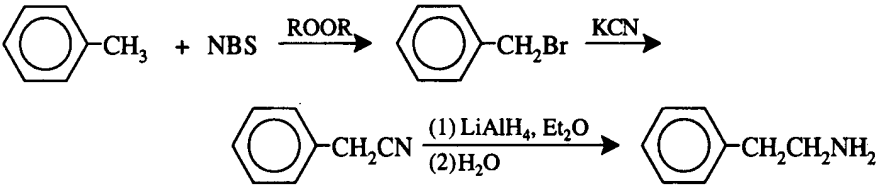
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20.8 (a) 

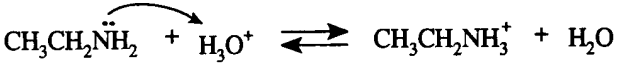
(b) 

(c) 

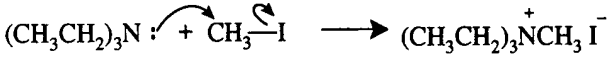
(d) 

(e) 

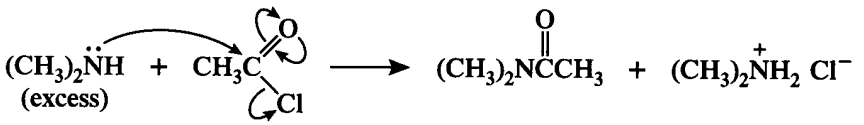
20.9 An amine acting as a base.



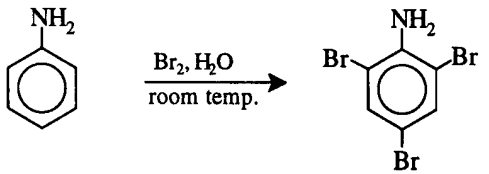
An amine acting as a nucleophile in an alkylation reaction.



An amine acting as a nucleophile in an acylation reaction.



An amino group acting as an activating group and as an ortho-para director in electrophilic aromatic substitution.



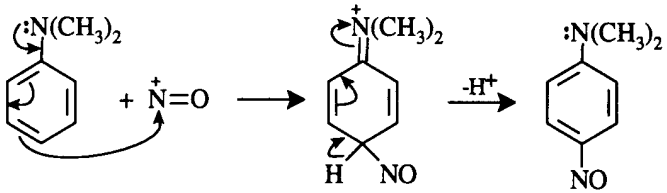
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20.10 (a, b)

$$^{-}O{-}N{=}O + H_3O^{+} \rightleftharpoons HO{-}N{=}O + H_2O$$

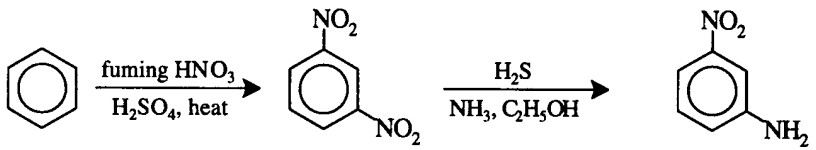
$$HO{-}N{=}O + H_3O^{+} \rightleftharpoons \underset{\displaystyle H}{\overset{\displaystyle +}{HO}}{-}N{=}O + H_2O$$

$$\underset{\displaystyle H}{\overset{\displaystyle +}{HO}}{-}N{=}O \rightleftharpoons H_2O + \overset{+}{N}{=}O$$

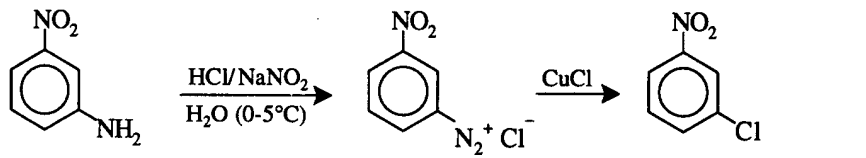


(c) The $\overset{+}{N}O$ ion is a weak electrophile. For it to react with an aromatic ring, the ring must have a powerful activating group such as –OH or $-NR_2$.

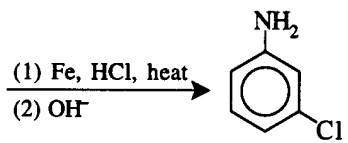
20.11 (a)



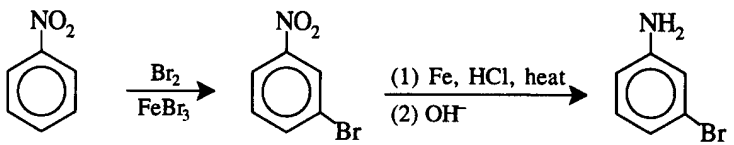
(b)



[as in (a)]

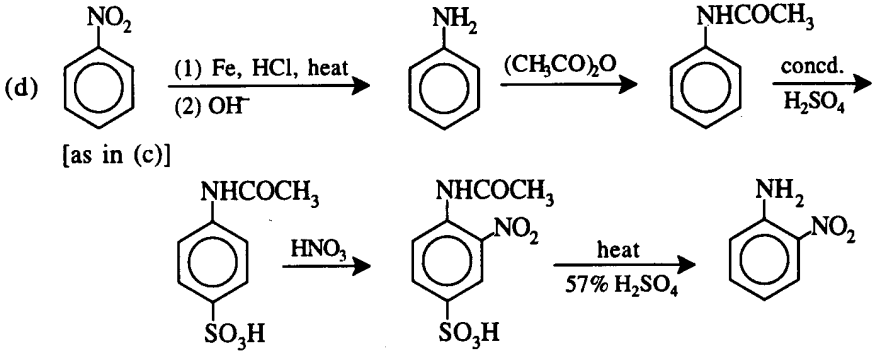


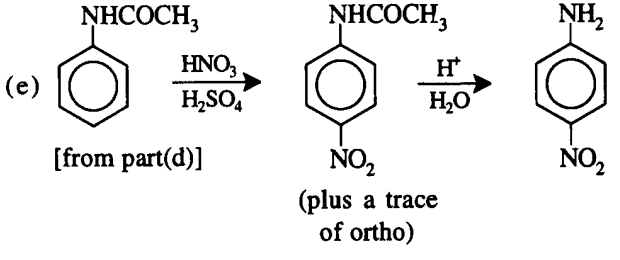
(c)



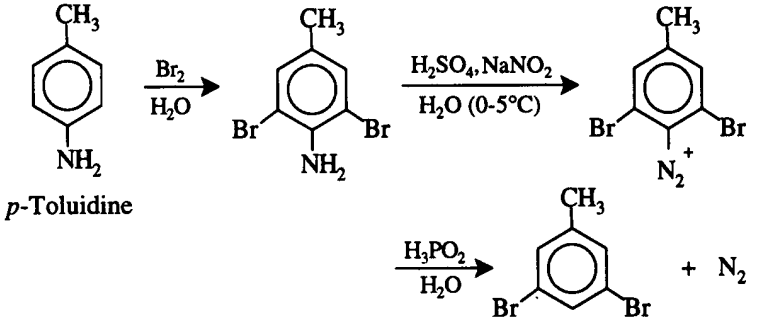
(by nitration of benzene)

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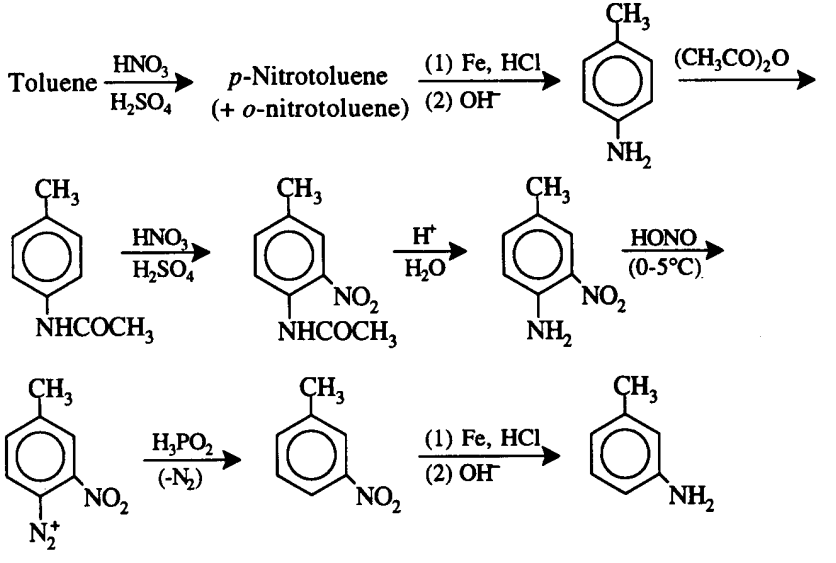




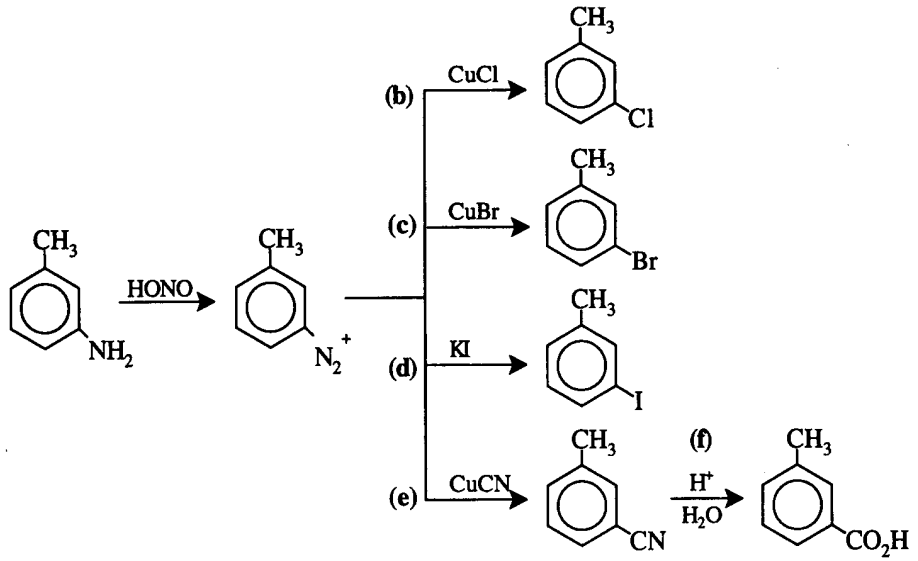
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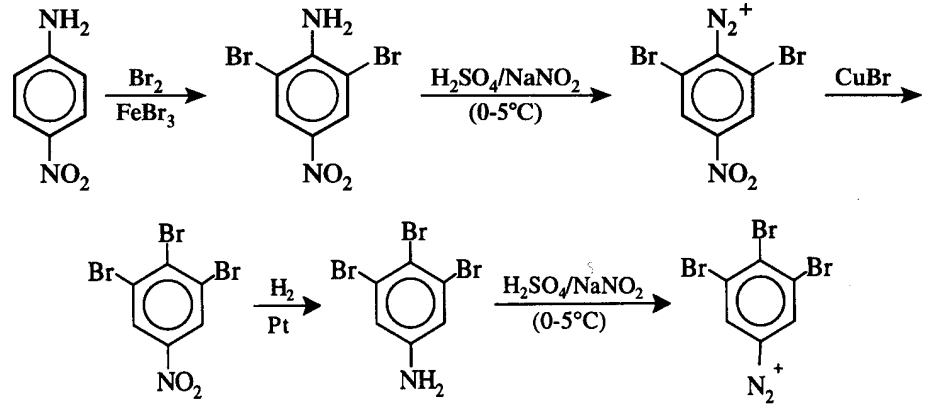
20.13 (a)



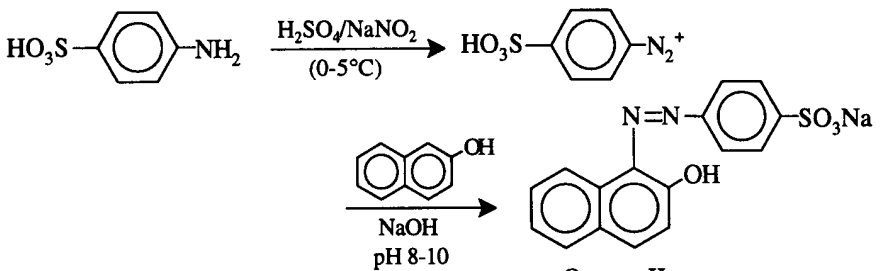
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20.14



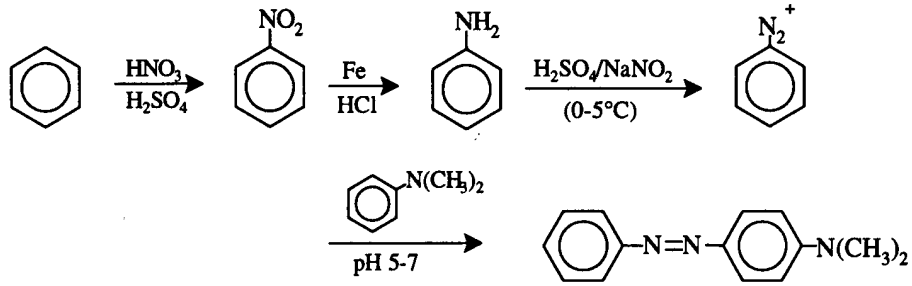
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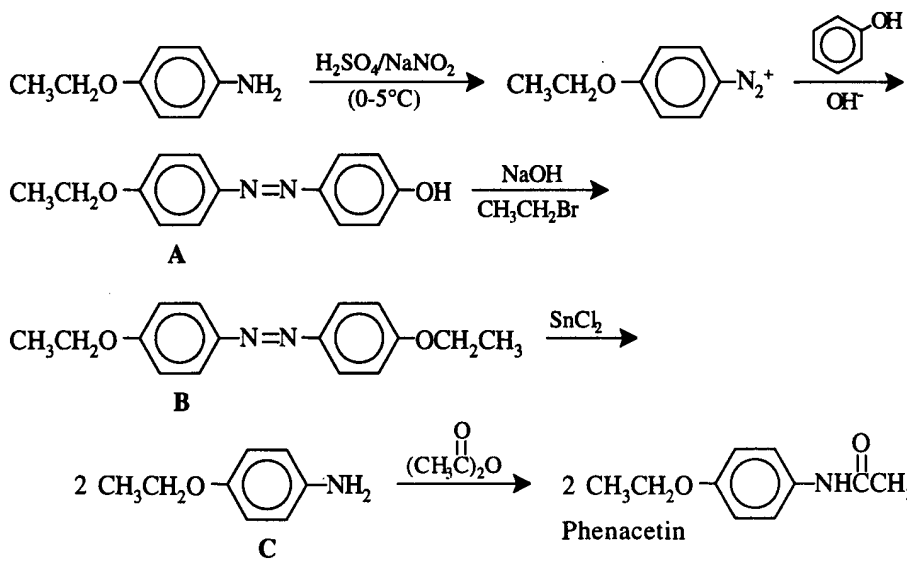
Orange II

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20.16



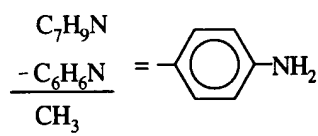
20.17



20.18 (1) That **A** reacts with benzenesulfonyl chloride in aqueous KOH to give a clear solution, which on acidification yields a precipitate, shows that **A** is a primary amine.

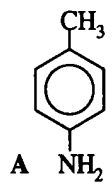
(2) That diazotization of **A** followed by treatment with 2-naphthol gives an intensely colored precipitate shows that **A** is a primary aromatic amine; that is, **A** is a substituted aniline.

(3) Consideration of the molecular formula of **A** leads us to conclude that **A** is a methylaniline (i.e., a toluidine).



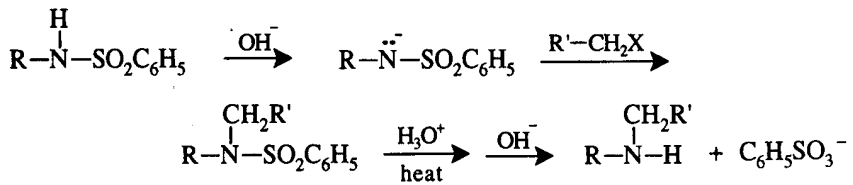
But is **A** 2-methylaniline, 3-methylaniline, or 4-methylaniline?

(4) This question is answered by the IR data. A single absorption peak in the 680–840 cm^{-1} region at 815 cm^{-1} is indicative of a para substituted benzene. Thus, **A** is 4-methylaniline (*p*-toluidine).

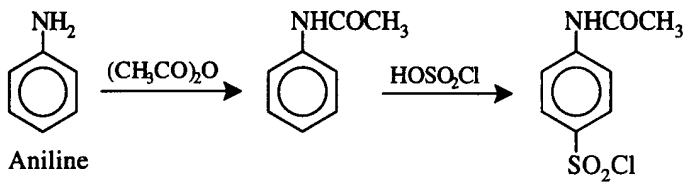


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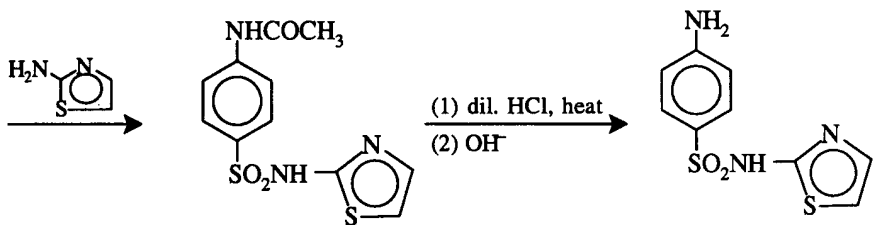
20.19 First convert the sulfonamide to its anion, then alkylate the anion with an alkyl halide, then remove the $-SO_2C_6H_5$ group by hydrolysis. For example,



20.20 (a)

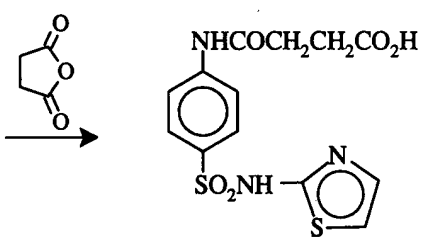


Aniline



Sulfathiazole

(b)

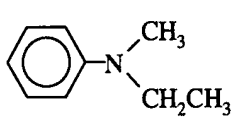


Succinylsulfathiazole

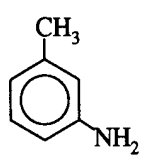
20.21 (a) $C_6H_5CH_2NHCH_3$

(b) $(CH_3CH)_3N$ (CH3 on CH)

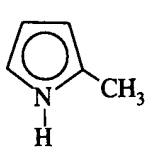
(c)



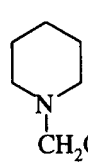
(d)



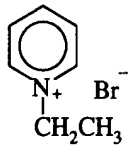
(e)

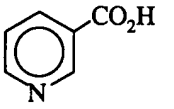


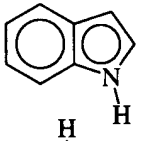
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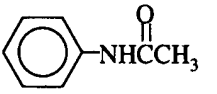


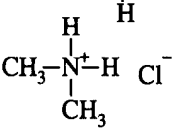
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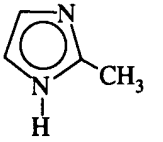
(g) 

(h) 

(i) 

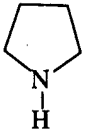
(j) 

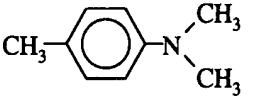
(k) 

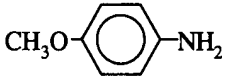
(l) 

(m) $H_2NCH_2CH_2CH_2OH$

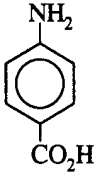
(n) $(CH_3CH_2CH_2)_4N^+\ Cl^-$

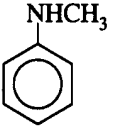
(o) 

(p) 

(q) 

(r) $(CH_3)_4N^+\ OH^-$

(s) 

(t) 

20.22 (a) Propylamine

(b) *N*-Methylaniline

(c) Isopropyltrimethylammonium iodide

(d) 2-Methylaniline (*o*-toluidine)

(e) 2-Methoxyaniline (or *o*-methoxyaniline)

(f) Pyrazole

(g) 2-Aminopyrimidine

(h) Benzylaminium chloride

(i) *N,N*-Dipropylaniline

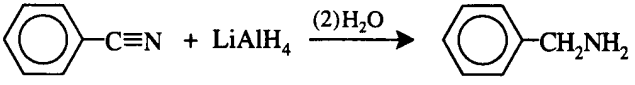
(j) Benzenesulfonamide

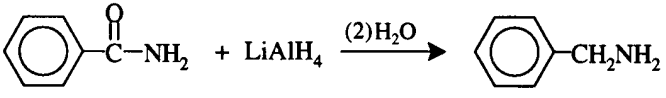
(k) Methylaminium acetate

(l) 3-Amino-1-propanol

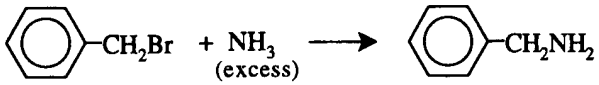
(m) Purine

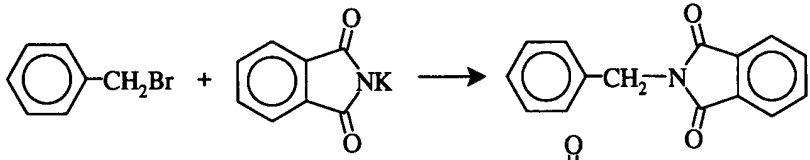
(n) *N*-Methylpyrrole

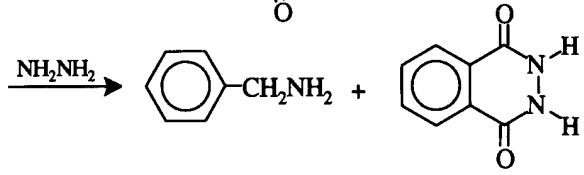
20.23 (a) 

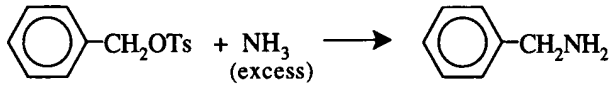
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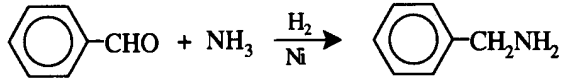
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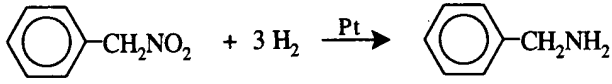
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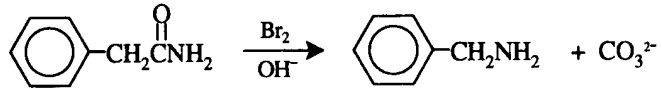


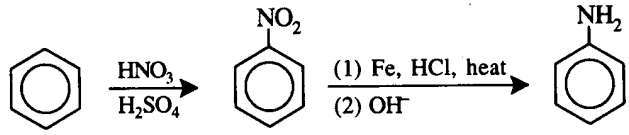


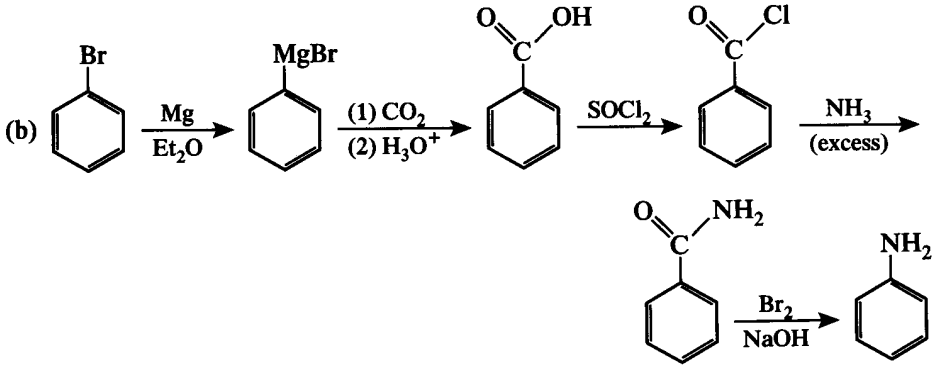
(d) 

(e) 

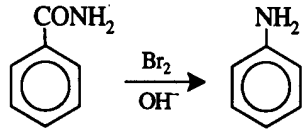
(f) 

(g) 

20.24 (a) 

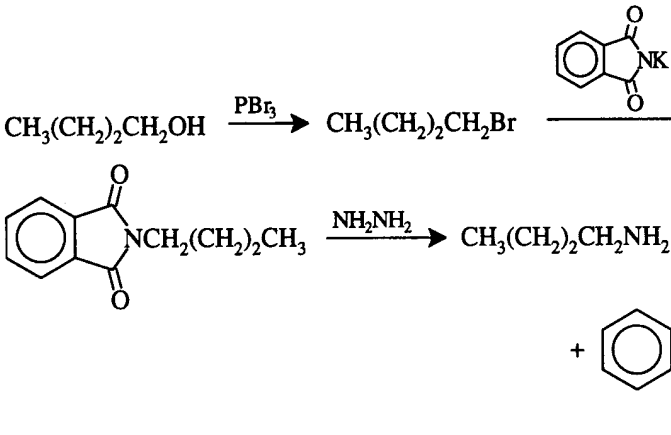
(b) 

Hofmann rearrangement

(c) 

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20.25 (a) $CH_3(CH_2)_2CH_2OH \xrightarrow{PBr_3} CH_3(CH_2)_2CH_2Br \longrightarrow$



(b) $CH_3(CH_2)_2CH_2Br \xrightarrow{NaCN} CH_3(CH_2)_3CN \xrightarrow[(2)\ H_2O]{(1)\ LiAlH_4,\ Et_2O} CH_3(CH_2)_3CH_2NH_2$

[from part(a)]

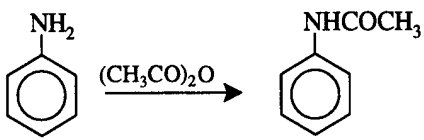
(c) $CH_3(CH_2)_2CH_2OH \xrightarrow[(2)\ H^+]{(1)\ KMnO_4,\ OH^-} CH_3CH_2CH_2CO_2H$

$\xrightarrow[(2)\ NH_3]{(1)\ SOCl_2} CH_3CH_2CH_2CONH_2 \xrightarrow[OH^-]{Br_2} CH_3CH_2CH_2NH_2$

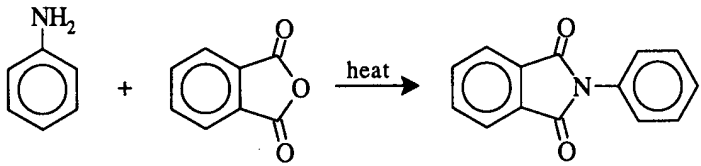
(d) $CH_3(CH_2)_2CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3CH_2CH_2CHO \xrightarrow[H_2,\ Ni]{CH_3NH_2}$

$CH_3CH_2CH_2CH_2NHCH_3$

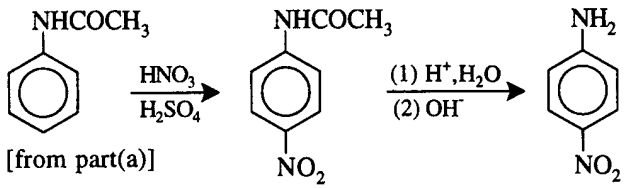
20.26 (a)



(b)

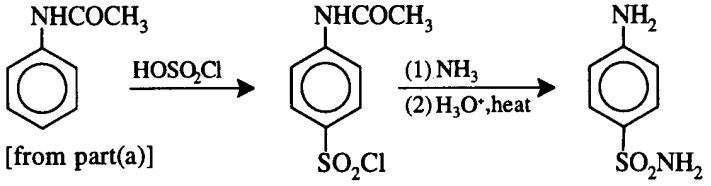


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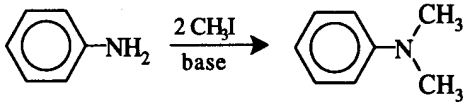


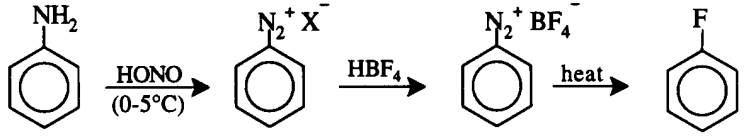
[from part(a)]

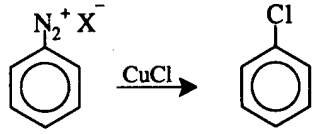
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(d) 

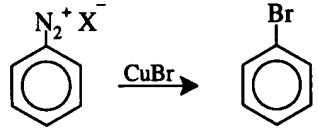
[from part(a)]

(e) 

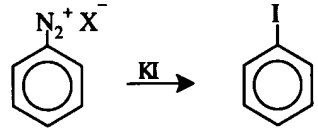
(f) 

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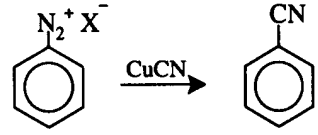
[from part(f)]

(h) 

[from part(f)]

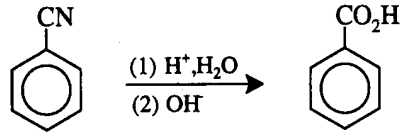
(i) 

[from part(f)]

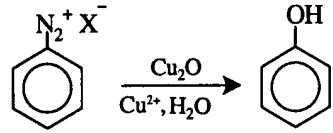
(j) 

[from part(f)]

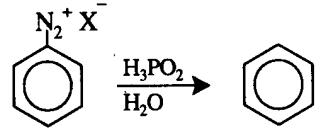
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(k) 

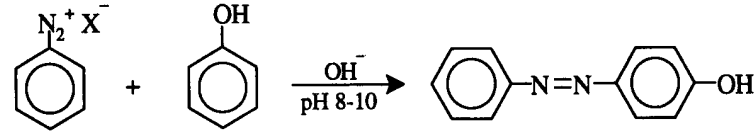
[from part(j)]

(l) 

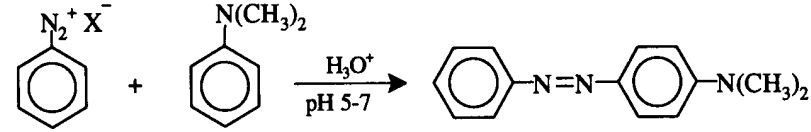
[from part(f)]

(m) 

[from part(f)]

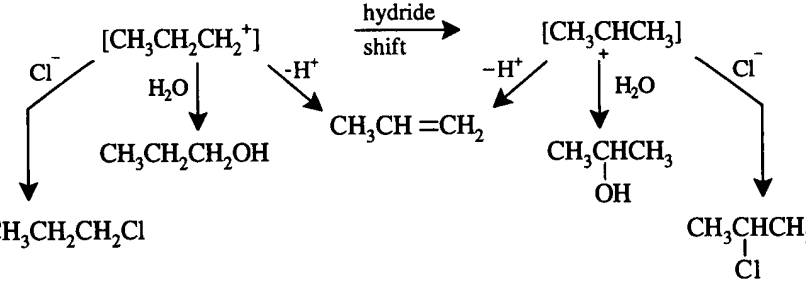
(n) 

[from part(f)] [from part(l)]

(o) 

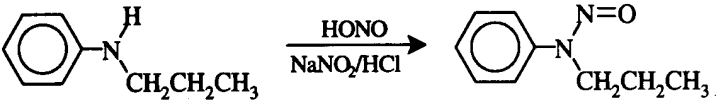
[from part(f)] [from part(e)]

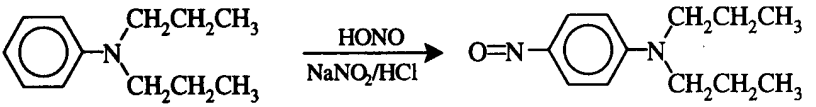
20.27 (a) $CH_3CH_2CH_2NH_2 \xrightarrow[NaNO_2/HCl]{HONO} [CH_3CH_2CH_2N_2^+] \xrightarrow{-N_2}$

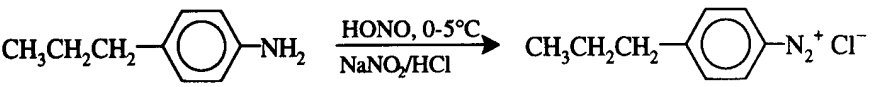


(b) $(CH_3CH_2CH_2)_2NH \xrightarrow[NaNO_2/HCl]{HONO} (CH_3CH_2CH_2)_2N-N=O$

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(c) 

(d) 

(e) 

20.28 (a) $CH_3CH_2CH_2NH_2 + C_6H_5SO_2Cl \xrightarrow[H_2O]{KOH} CH_3CH_2CH_2N^-SO_2C_6H_5\ K^+$

Clear solution

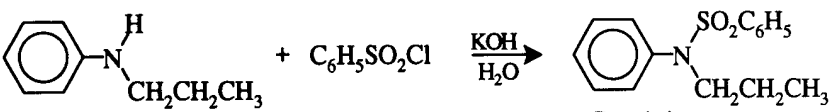
$\xrightarrow{H_3O^+} CH_3CH_2CH_2NHSO_2C_6H_5$

Precipitate

(b) $(CH_3CH_2CH_2)_2NH + C_6H_5SO_2Cl \xrightarrow[H_2O]{KOH} (CH_3CH_2CH_2)_2NSO_2C_6H_5$

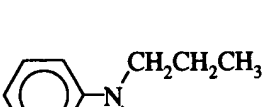
Precipitate

$\xrightarrow{H_3O^+}$ No reaction (precipitate remains)

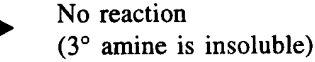
(c) 

Precipitate

$\xrightarrow{H_3O^+}$ No reaction (precipitate remains)

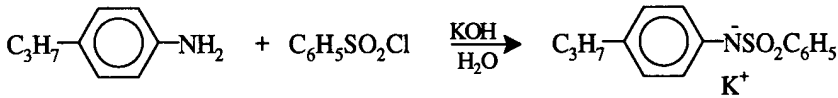
(d) 

$+ C_6H_5SO_2Cl \xrightarrow[H_2O]{KOH}$ No reaction (3° amine is insoluble)

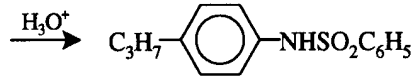
$\xrightarrow{H_3O^+}$ 

3° Amine dissolves

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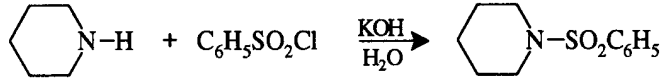
(e) 

Clear solution



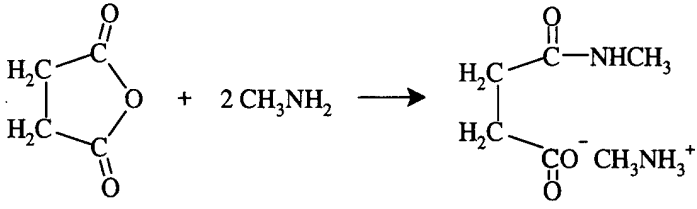
Precipitate

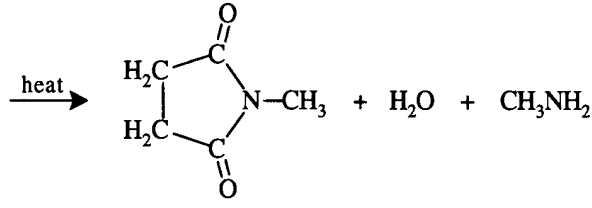
20.29 (a) 

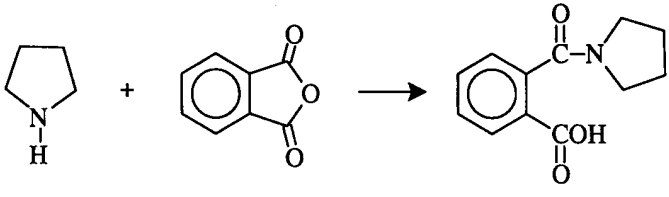
(b) 

20.30 (a) $2\,CH_3CH_2NH_2 + C_6H_5COCl \longrightarrow CH_3CH_2NHCOC_6H_5 + CH_3CH_2NH_3^+\,Cl^-$

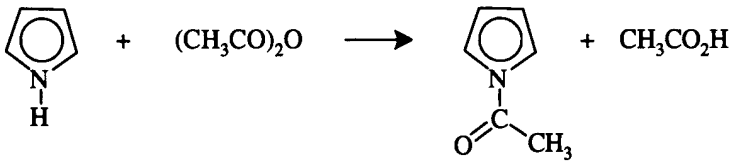
(b) $2\,CH_3NH_2 + (CH_3C)_2O \longrightarrow CH_3NHCCH_3 + CH_3\overset{+}{N}H_3\ CH_3CO^-$

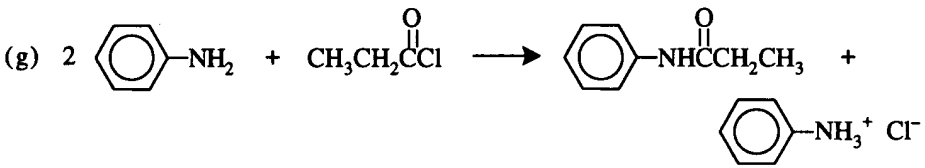
(c) 

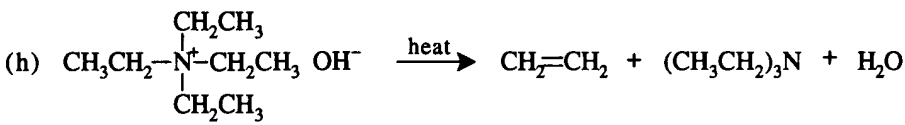
(d) [product of (c)] 

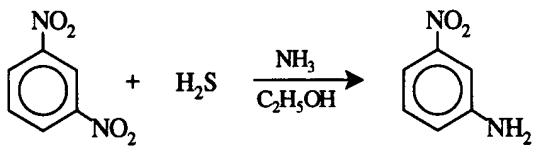
(e) 

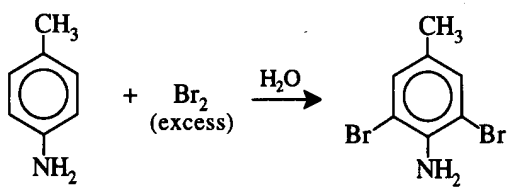
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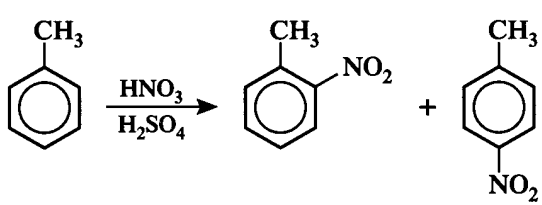
(f) 

(g) 

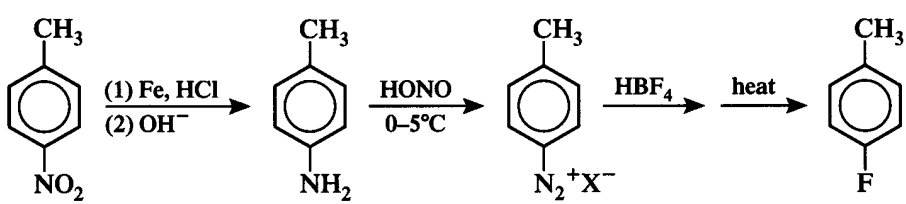
(h) 

(i) 

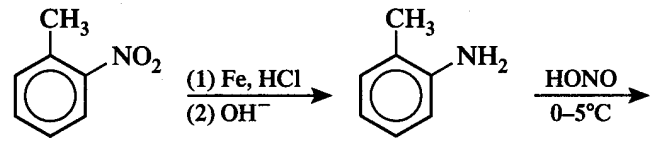
(j) 

20.31 (a) 

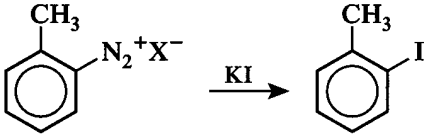
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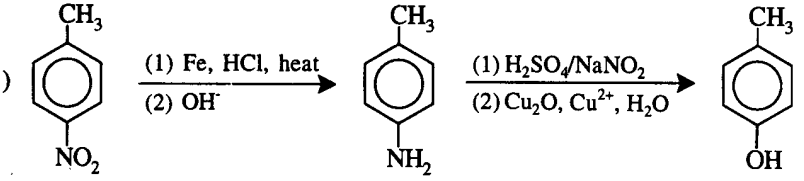


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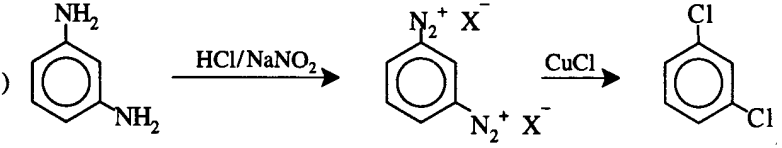
(b) 

[from part (a)]

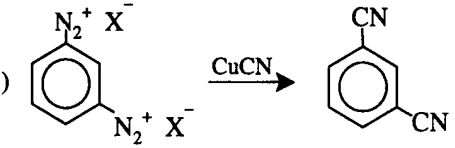


(c) 

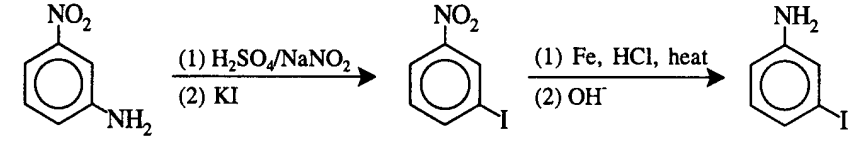
[from part (a)]

(d) 

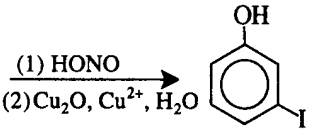
[by reduction of *m*-dinitrobenzene, cf. Problem 20.11(a)]

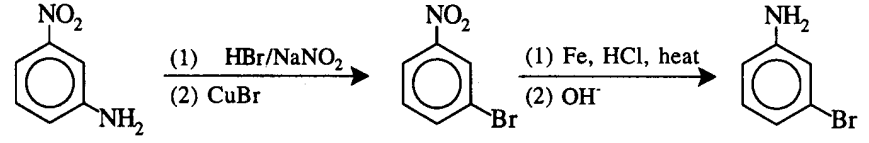
(e) 

[from part (d)]

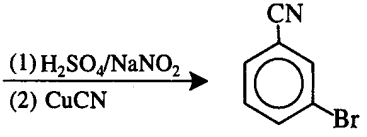
(f) 

[from Problem 20.11(a)]



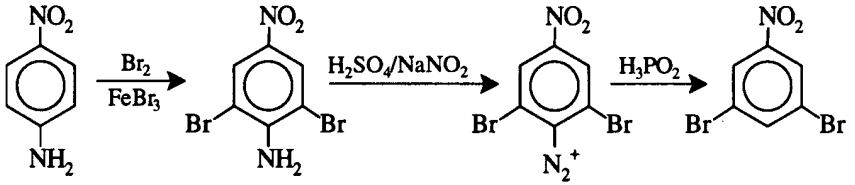
(g) 

[from Problem 20.11(a)]



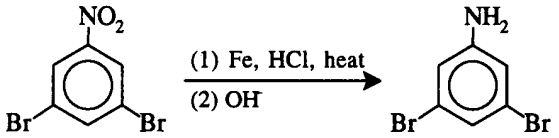
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(h)



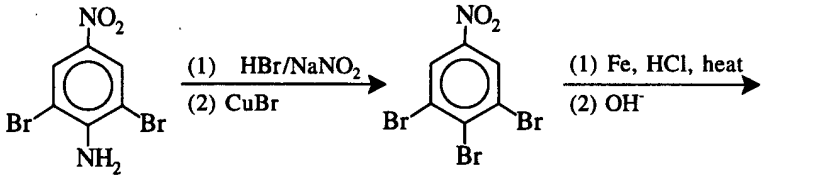
[from Problem 20.11(e)]

(i)

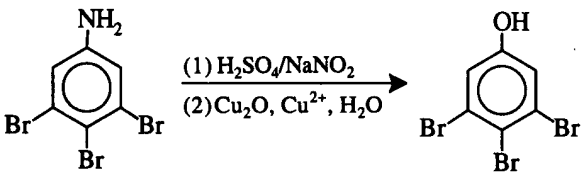


[from part (h)]

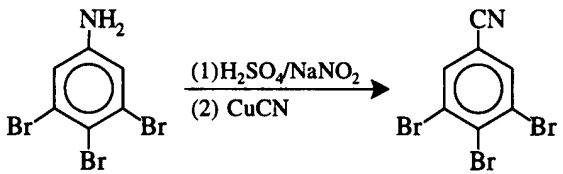
(j)



[from part (h)]

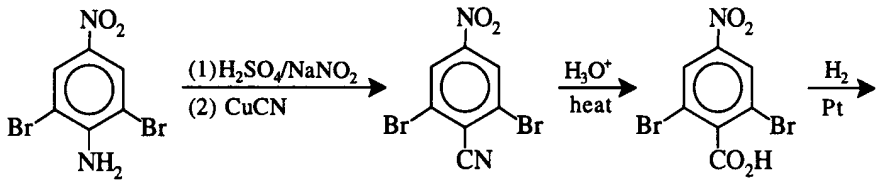


(k)

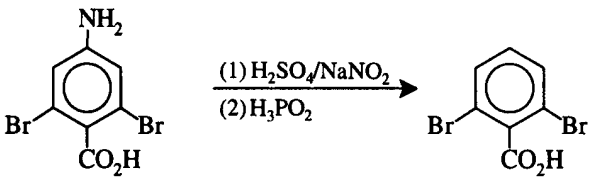


[from part (j)]

(l)

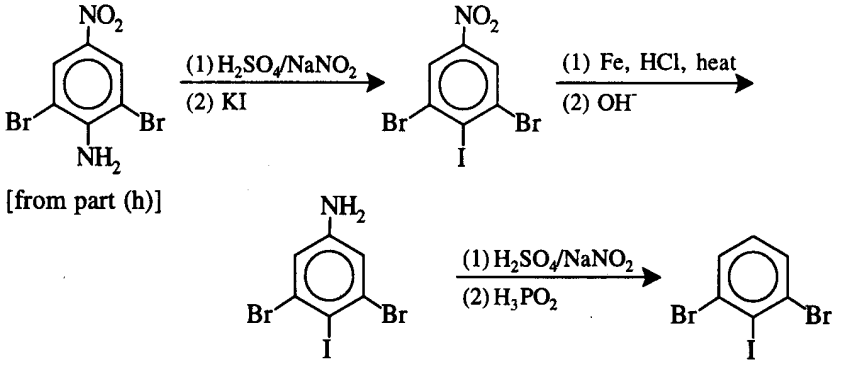


[from part (h)]



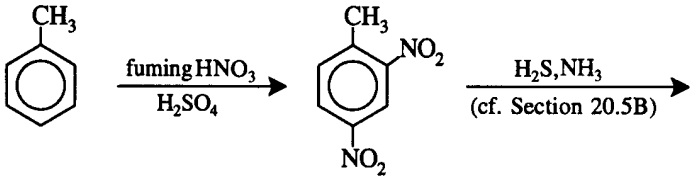
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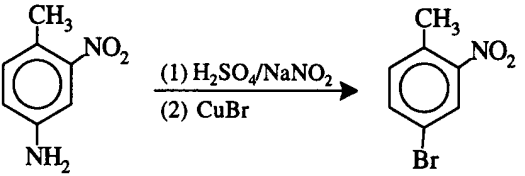
(m)



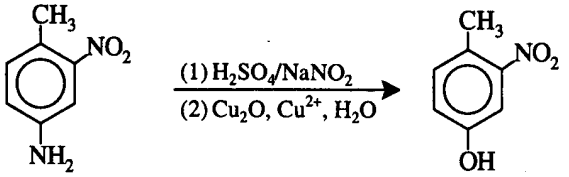
[from part (h)]

(n)



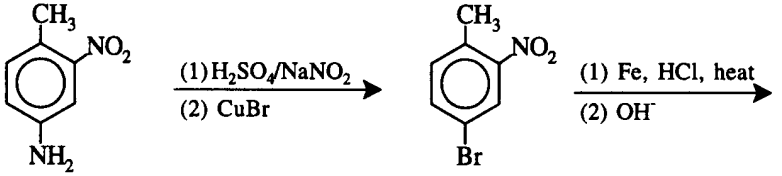


(o)

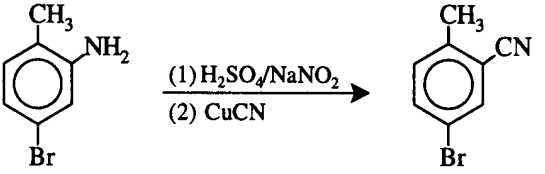


[from part (n)]

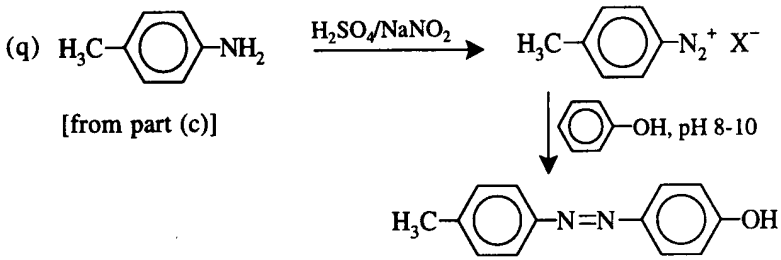
(p)

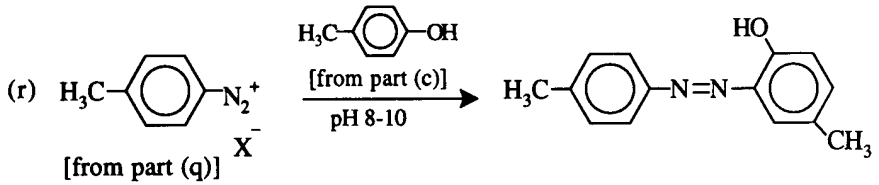


[from part (n)]



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(q) 

(r) 

20.32 (a) Benzylamine dissolves in dilute HCl at room temperature,

$$C_6H_5CH_2NH_2 + H_3O^+ + Cl^- \xrightarrow{25°C} C_6H_5CH_2\overset{+}{N}H_3\ Cl^-$$

benzamide does not dissolve:

$$C_6H_5CONH_2 + H_3O^+ + Cl^- \xrightarrow{25°C} \text{No reaction}$$

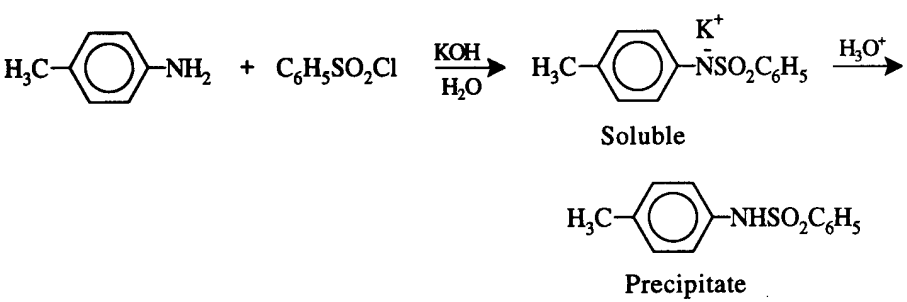
(b) Allylamine reacts with (and decolorizes) bromine in carbon tetrachloride instantly,

$$CH_2{=}CHCH_2NH_2 + Br_2 \xrightarrow{CCl_4} \underset{\text{Br Br}}{CH_2CHCH_2NH_2}$$

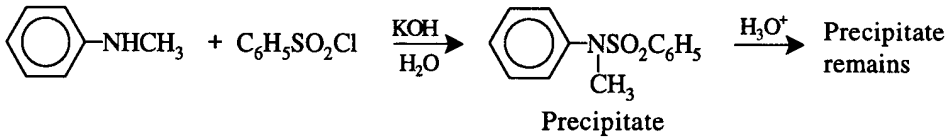
propylamine does not:

$$CH_3CH_2CH_2NH_2 + Br_2 \xrightarrow{CCl_4} \text{No reaction if the mixture is not heated or irradiated}$$

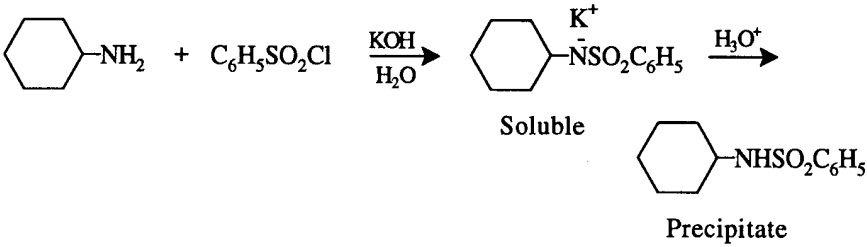
(c) The Hinsberg test:

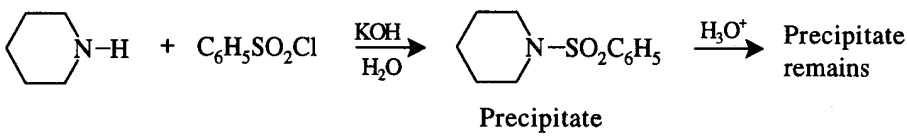


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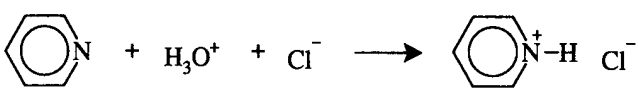


(d) The Hinsberg test:

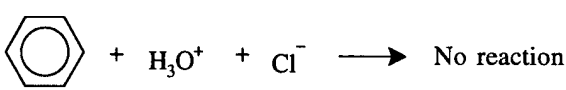




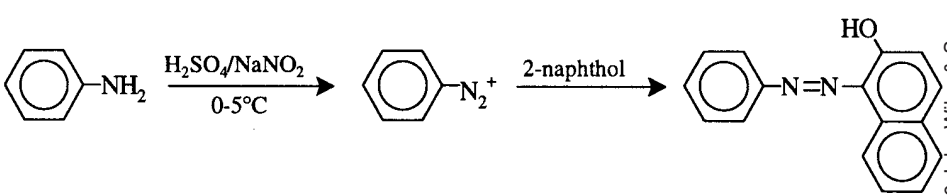
(e) Pyridine dissolves in dilute HCl,



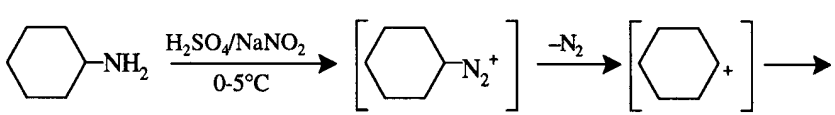
benzene does not:



(f) Aniline reacts with nitrous acid at 0-5°C to give a stable diazonium salt that couples with 2-naphthol, yielding an intensely colored azo compound.



Cyclohexylamine reacts with nitrous acid at 0-5°C to yield a highly unstable diazonium salt—one that decomposes so rapidly that the addition of 2-naphthol gives no azo compound.



alkenes, alcohols, and so on $\xrightarrow{\text{2-naphthol}}$ No reaction

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(g) The Hinsberg test:

$$(C_2H_5)_3N + C_6H_5SO_2Cl \xrightarrow[H_2O]{KOH} \text{No reaction} \xrightarrow{H_3O^+} \underset{\text{Soluble}}{(C_2H_5)_3\overset{+}{N}H}$$

$$(C_2H_5)_2NH + C_6H_5SO_2Cl \xrightarrow[H_2O]{KOH} \underset{\text{Precipitate}}{(C_2H_5)_2NSO_2C_6H_5} \xrightarrow{H_3O^+} \text{Precipitate remains}$$

(h) Tripropylaminium chloride reacts with aqueous NaOH to give a water insoluble tertiary amine.

$$\underset{\text{Water soluble}}{(CH_3CH_2CH_2)_3NH^+\ Cl^-} \xrightarrow[H_2O]{NaOH} \underset{\text{Water insoluble}}{(CH_3CH_2CH_2)_3N}$$

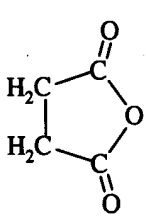
Tetrapropylammonium chloride does not react with aqueous NaOH (at room temperature), and the tetrapropylammonium ion remains in solution.

$$\underset{\text{Water soluble}}{(CH_3CH_2CH_2)_4N^+\ Cl^-} \xrightarrow[H_2O]{NaOH} \underset{\text{Water soluble}}{(CH_3CH_2CH_2)_4N^+}\ [Cl^- \text{ or } OH^-]$$

(i) Tetrapropylammonium chloride dissolves in water to give a neutral solution. Tetrapropylammonium hydroxide dissolves in water to give a strongly basic solution.

20.33 Follow the procedure outlined in the answer to Problem 20.2. Toluene will show the same solubility behavior as benzene.

20.34



$$+ NH_3 \xrightarrow{(2)\ H^+} H_2NCCH_2CH_2COH$$

$$\xrightarrow[-CO_3^{2-}]{Br_2,\ OH^-} H_2NCH_2CH_2CO_2^- \xrightarrow{H^+} H_3\overset{+}{N}CH_2CH_2CO_2^-$$

20.35 (a) $HOCH_2(CH_2)_8CH_2OH \xrightarrow{2\ PBr_3} BrCH_2(CH_2)_8CH_2Br \xrightarrow{2(CH_3)_3N}$

$$(CH_3)_3\overset{+}{N}CH_2(CH_2)_8CH_2\overset{+}{N}(CH_3)_3\ 2\ Br^-$$

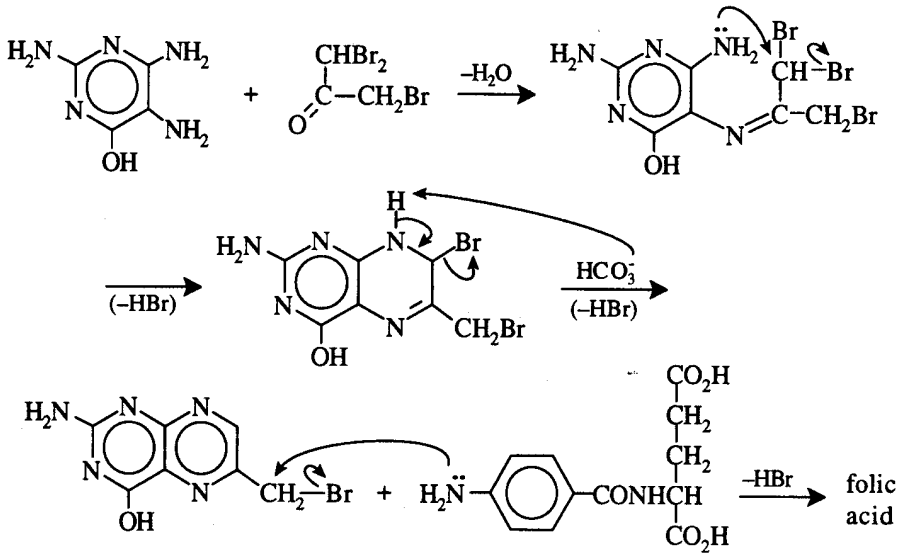
(b) $HO_2CCH_2CH_2CO_2H + 2\ BrCH_2CH_2OH \xrightarrow[(-2\ H_2O)]{H^+}$

$$BrCH_2CH_2O_2CCH_2CH_2CO_2CH_2CH_2Br \xrightarrow{2(CH_3)_3N}$$

$$(CH_3)_3\overset{+}{N}CH_2CH_2O_2CCH_2CH_2CO_2CH_2CH_2\overset{+}{N}(CH_3)_3\ 2\ Br^-$$

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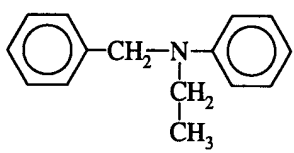
20.36



20.37 The results of the Hinsberg test indicate that compound **W** is a tertiary amine. The ^{1}H NMR provides evidence for the following:

(1) Two different C_6H_5–groups (one absorbing at δ 7.2 and one at δ 6.7).
(2) A CH_3CH_2–group (the quartet at δ 3.5 and the triplet at δ 1.2).
(3) An unsplit $-CH_2-$group (the singlet at δ 4.5).

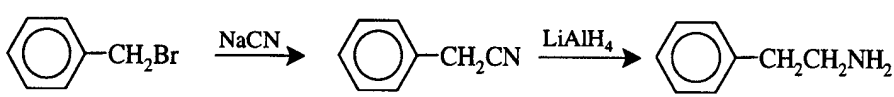
There is only one reasonable way to pull all of this together.



Thus **W** is *N*-benzyl-*N*-ethylaniline.

20.38 Compound **X** is benzyl bromide, $C_6H_5CH_2Br$. This is the only structure consistent with the ^{1}H NMR and IR data. (The monosubstituted benzene ring is strongly indicated by the (5H), δ 7.3 ^{1}H NMR absorption and is confirmed by the peaks at 690 and 770 cm^{-1} in the IR spectrum.)

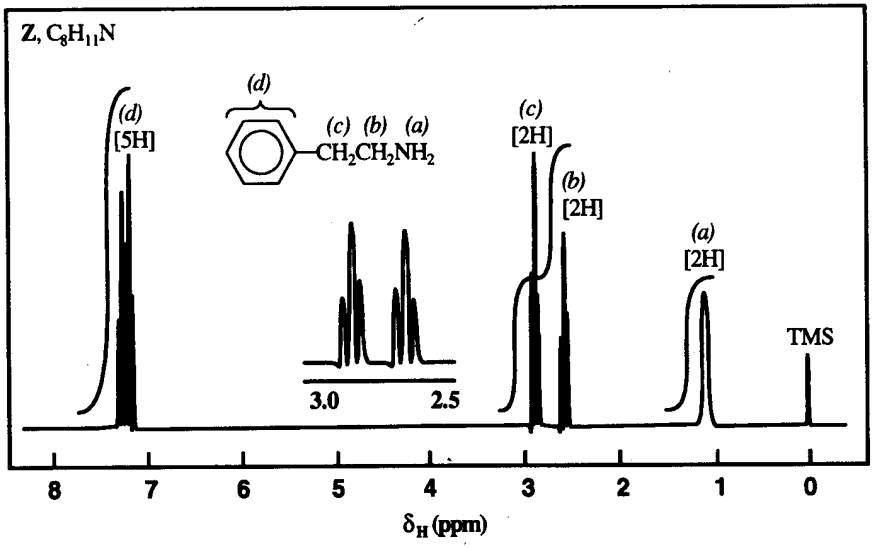
Compound **Y**, therefore, must be phenylacetonitrile, ($C_6H_5CH_2CN$) and **Z** must be 2-phenylethylamine, $C_6H_5CH_2CH_2NH_2$.

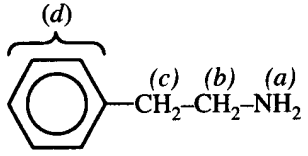


X C_7H_7Br **Y** C_8H_7N **Z** $C_8H_{11}N$

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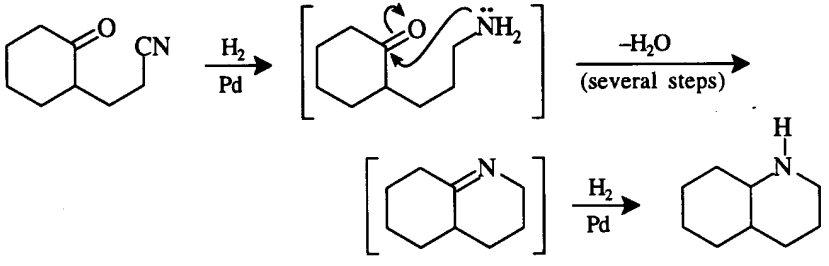
Interpretations of the IR and ^{1}H NMR spectra of **Z** are as follows.





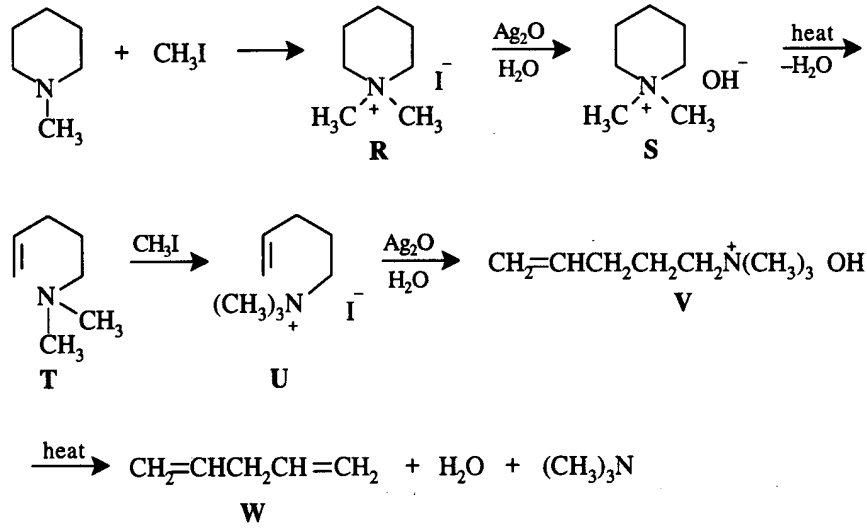
(*a*) singlet δ 1.0
(*b*) triplet δ 2.7
(*c*) triplet δ 2.9
(*d*) multiplet δ 7.25

20.39

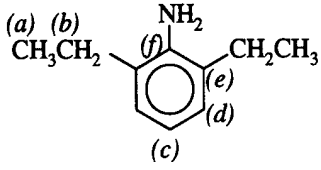


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20.40



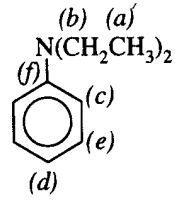
20.41 That **A** contains nitrogen and is soluble in dilute HCl suggests that **A** is an amine. The two IR absorption bands in the 3300–3500-cm^{-1} region suggest that **A** is a primary amine. The ^{13}C spectrum shows only two signals in the upfield aliphatic region. There are four signals downfield in the aromatic region. The information from the DEPT spectra suggests an ethyl group *or two equivalent ethyl groups.* Assuming the latter, and assuming that **A** is a primary amine, we can conclude from the molecular formula that **A** is 2,6-diethylaniline. The assignments are



(a) δ 12.9
(b) δ 24.2
(c) δ 118.1
(d) δ 125.9
(e) δ 127.4
(f) δ 141.5

(An equally plausible answer would be that **A** is 3,5-diethylaniline.)

20.42 That **B** dissolves in dilute HCl suggests that **B** is an amine. That the IR spectrum of **B** lacks bands in the 3300–3500-cm^{-1} region suggests that **B** is a tertiary amine. The upfield signals in the ^{13}C spectrum and the DEPT information suggest two equivalent ethyl groups (as was also true of **A** in the preceding problem). The DEPT information for the downfield peaks (in the aromatic region) is consistent with a monosubstituted benzene ring. Putting all of these observations together with the molecular formula leads us to conclude that **B** is *N,N*-diethylaniline. The assignments are



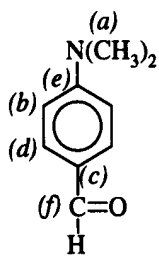
(a) δ 12.5
(b) δ 44.2
(c) δ 112.0
(d) δ 115.5
(e) δ 128.1
(f) δ 147.8

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20.43 That **C** gives a positive Tollens' test indicates the presence of an aldehyde group; the solubility of **C** in aqueous HCl suggests that **C** is also an amine. The absence of bands in the 3300–3500-cm^{-1} region of the IR spectrum of **C** suggests that **C** is a tertiary amine. The signal at δ 189.7 in the ^{13}C spectrum can be assigned to the aldehyde group. The signal at δ 39.7 is the only one in the aliphatic region and is consistent with a methyl group or with two equivalent methyl groups. The remaining signals are in the aromatic region. If we assume that **C**

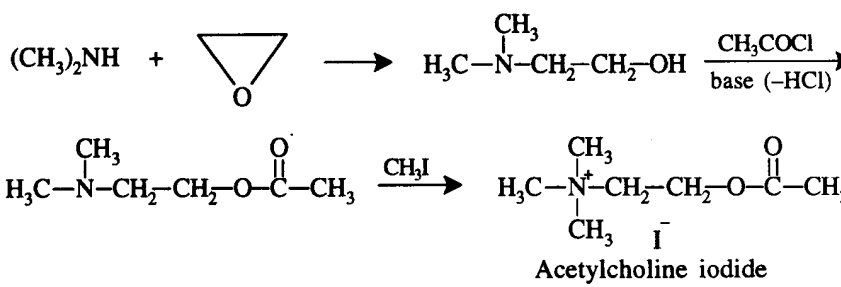


has a benzene ring containing a –CH group and a $-N(CH_3)_2$ group, then the aromatic signals and their DEPT spectra are consistent with **C** being *p*-(*N*,*N*-dimethylamino)benzaldehyde. The assignments are



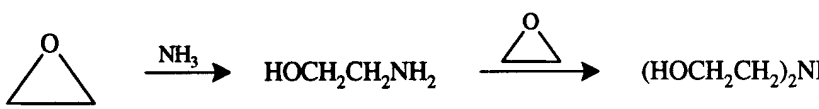
(a) δ 39.7
(b) δ 110.8
(c) δ 124.9
(d) δ 131.6
(e) δ 154.1
(f) δ 189.7

20.44

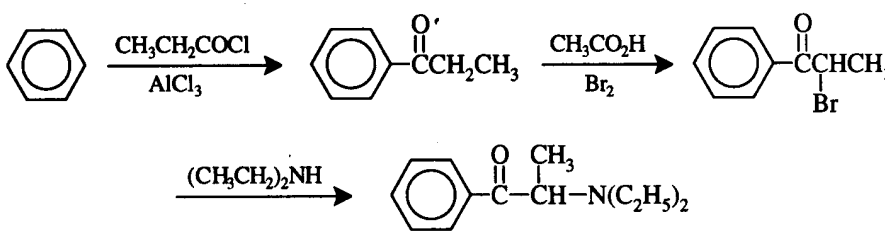


Acetylcholine iodide

20.45



20.46



Diethylpropion

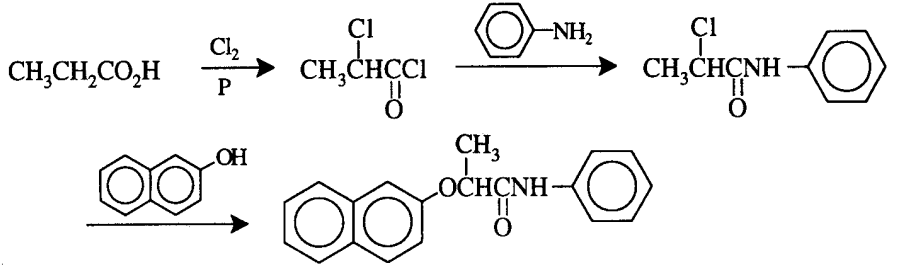
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20.47 Carry out the Hofmann reaction using a mixture of ^{15}N labeled benzamide, $C_6H_5CO{*}NH_2$, and *p*-chlorobenzamide. If the process is intramolecular, only labeled aniline, $C_6H_5{*}NH_2$, and *p*-chloroaniline, will be produced.

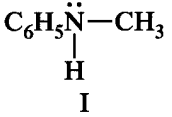
If the process is one in which the migrating moiety truly separates from the remainder of the molecule, then, in addition to the two products mentioned above, there should be produced both the unlabeled aniline and labeled *p*-chloroaniline, $p\text{-}ClC_6H_4{*}NH_2$.

Note: When this experiment is actually carried out, analysis of the reaction mixture by mass spectrometry shows that the process is intramolecular.

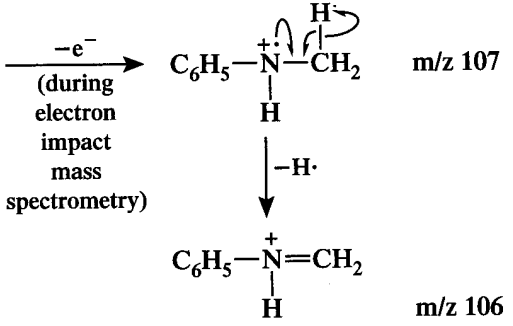
20.48



***20.49** (a)

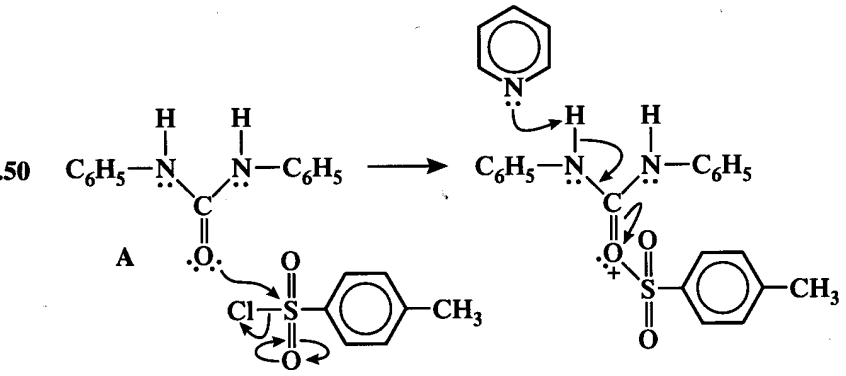


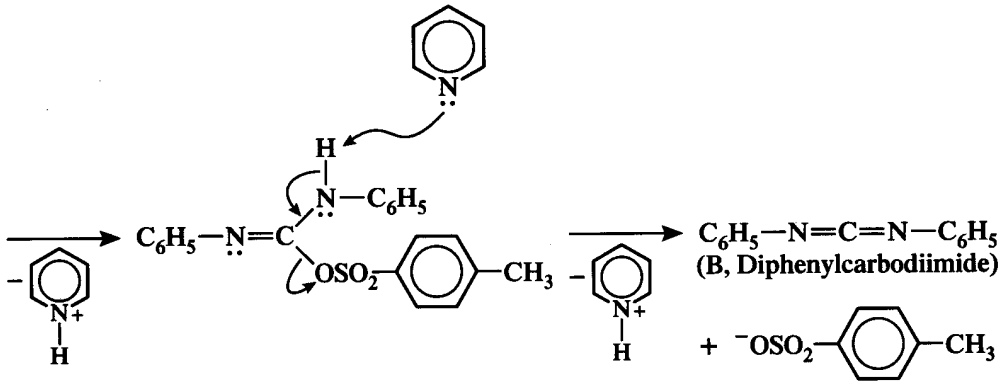
(b)



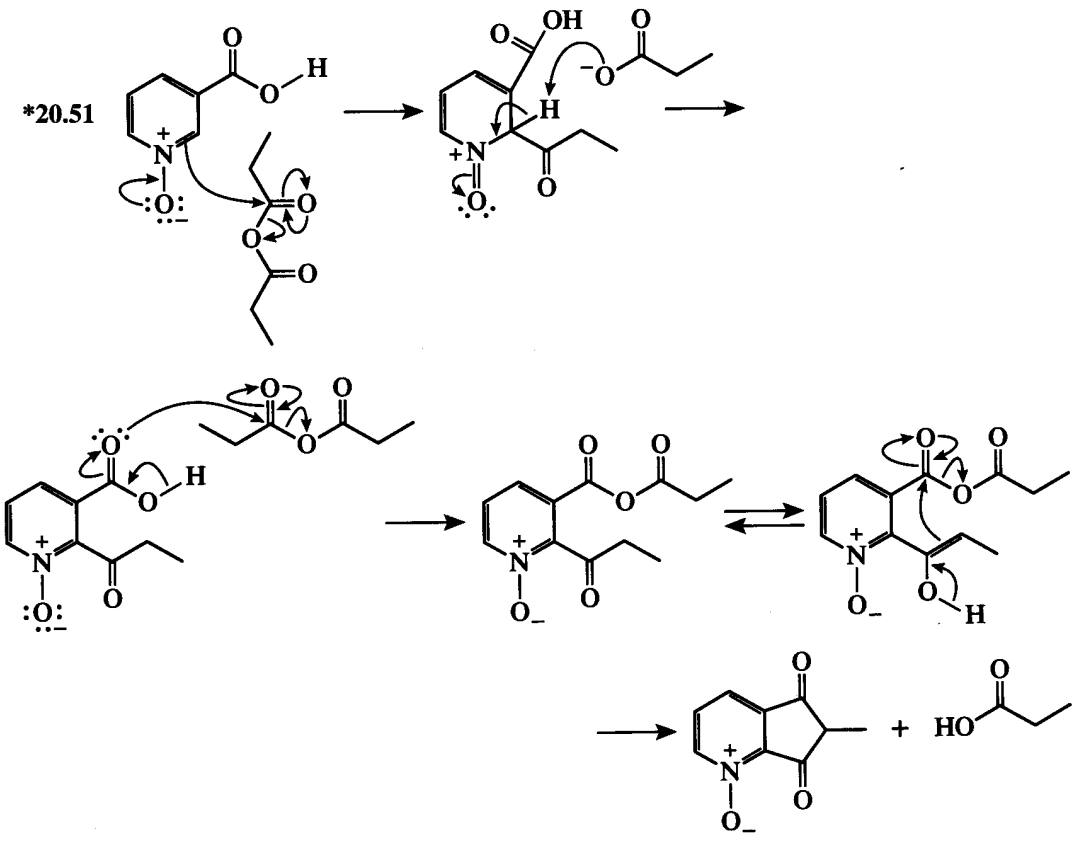
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*20.50



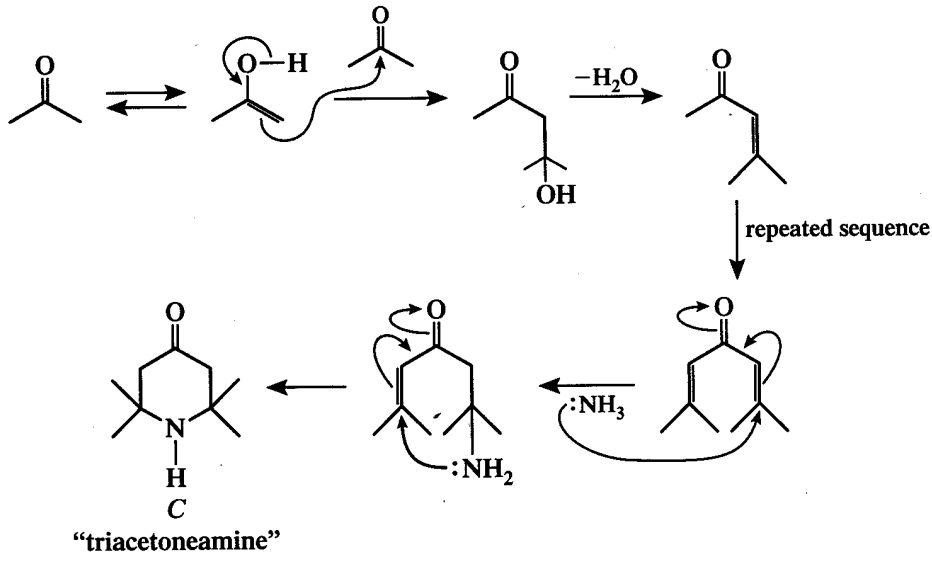


*20.51



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***20.52** An abbreviated version of one of several possible routes:



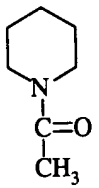
C

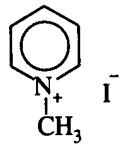
"triacetoneamine"

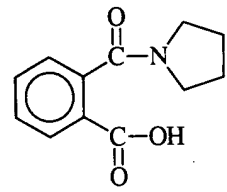
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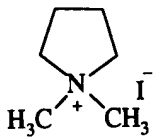
E SPECIAL TOPIC
Reactions and Synthesis of Heterocyclic Amines

SOLUTIONS TO PROBLEMS

E.1 (a) 

(b) 

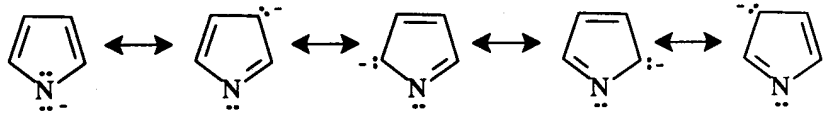
(c) 

(d) 

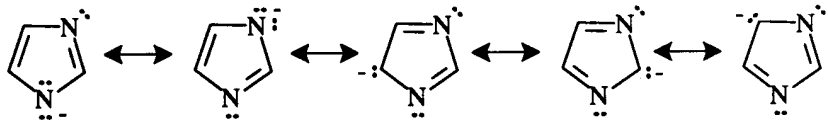
(e) $CH_2{=}CHCH_2CH_2N(CH_3)_2$

E.2 (a) The cyclopentadienyl anion.

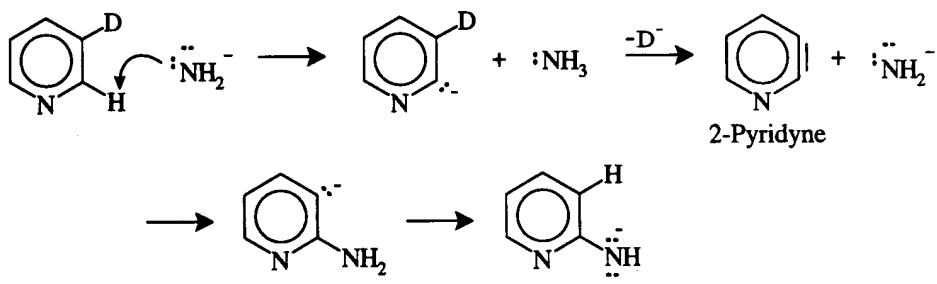
(b) The pyrrole anion is a resonance hybrid of the following structures:



The imidazole anion is a hybrid of these:



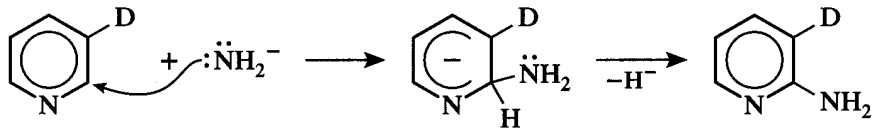
E.3 A mechanism involving a "pyridyne" intermediate would involve a net loss (of 50%) of the deuterium label.



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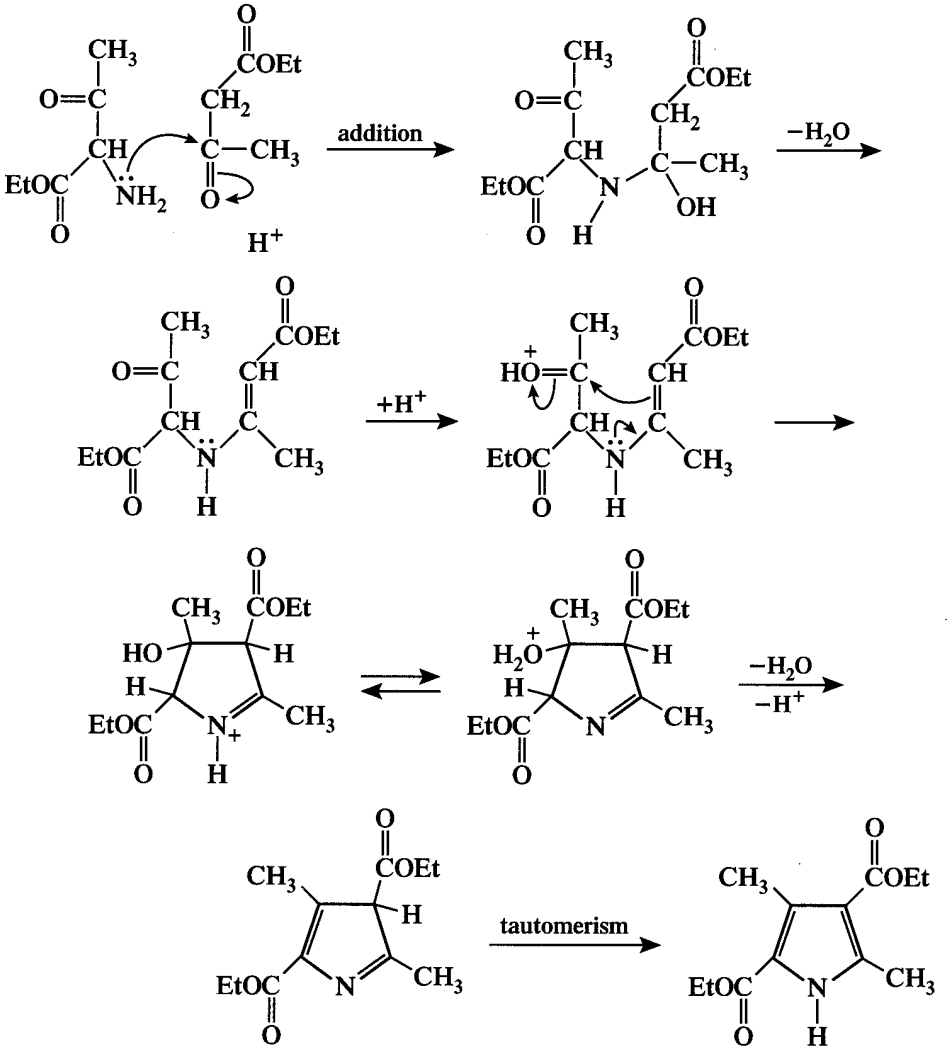
Since in the actual experiment there was no loss of deuterium, this mechanism was disallowed.

The mechanism given in Section E.4 would not be expected to result in a loss of deuterium; thus, it is consistent with the labeling experiment.

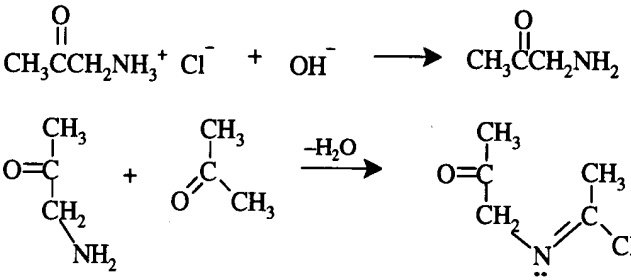


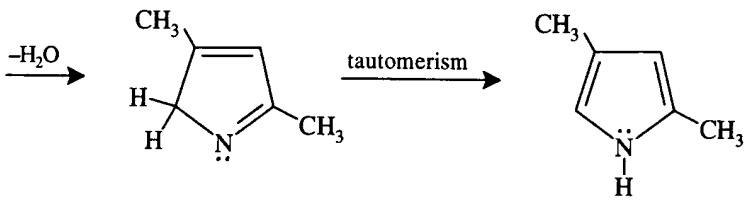
E.4 When pyridine undergoes nucleophilic substitution, the leaving group is a hydride ion—an ion that is a strong base and, consequently, a poor leaving group. With 2-halopyridines, on the other hand, the leaving groups are halide ions—ions that are weak bases and thus good leaving groups.

E.5 If we write the reactants in the following way, we can better see how the reaction occurs.

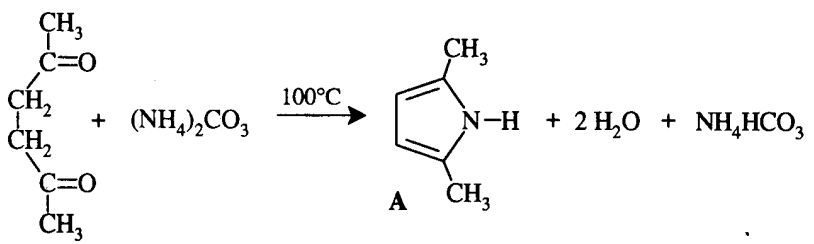


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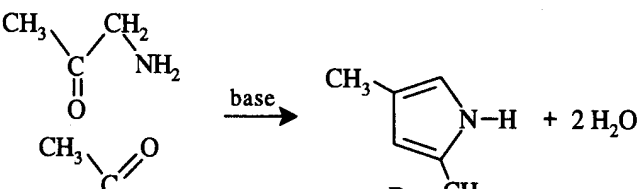


E.6 (a)



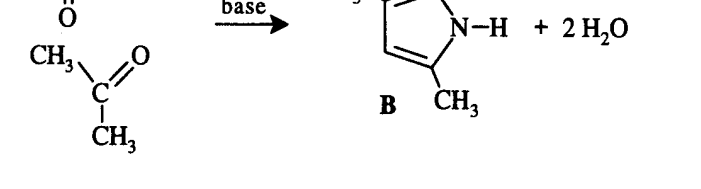
A

(b)



B

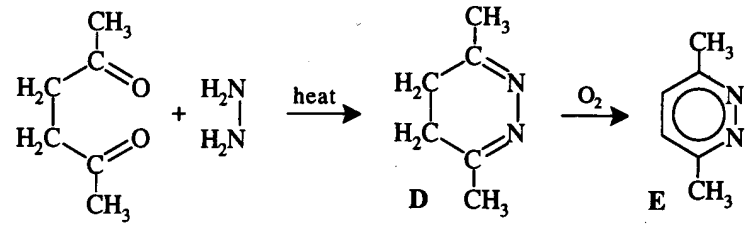
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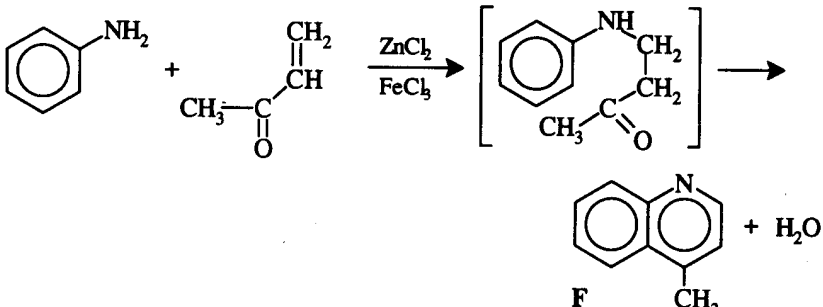
C

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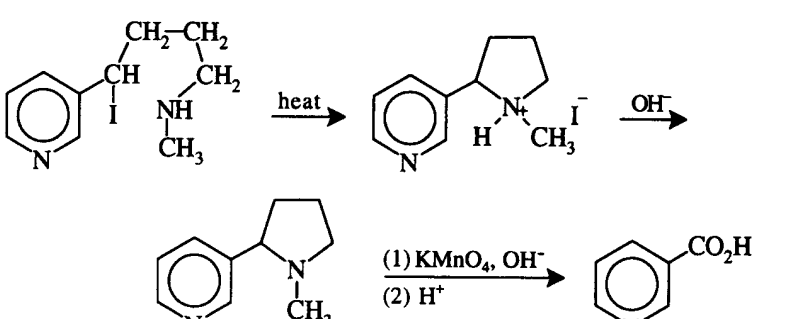
(d)



(e)



(f)



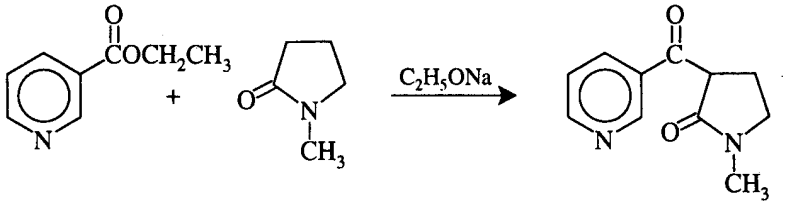
G Nicotine **H** Nicotinic acid

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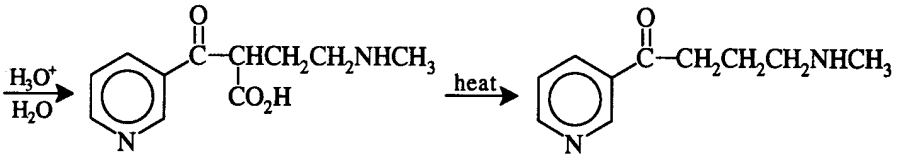
F SPECIAL TOPIC
Alkaloids

SOLUTIONS TO PROBLEMS

F.1 (a) The first step is similar to a crossed Claisen condensation (see Section 19.2A):

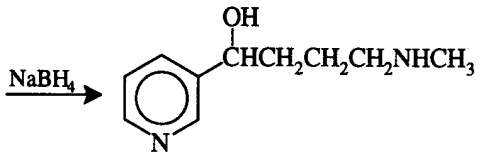


(b) This step involves hydrolysis of an amide (lactam) and can be carried out with either acid or base. Here we use acid.

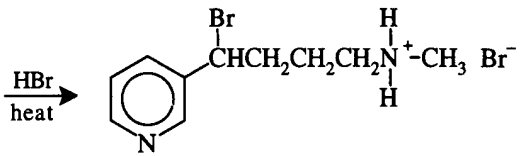


(c) This step is the decarboxylation of a substituted malonic acid; it requires only the application of heat and takes place during the acid hydrolysis of step (b).

(d) This is the reduction of a ketone to a secondary alcohol. A variety of reducing agents can be used, sodium borohydride, for example.

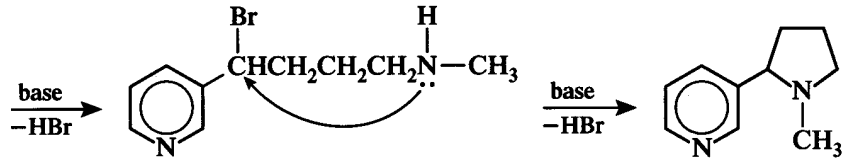


(e) Here we convert the secondary alcohol to an alkyl bromide with hydrogen bromide; this reagent also gives a hydrobromide salt of the aliphatic amine.



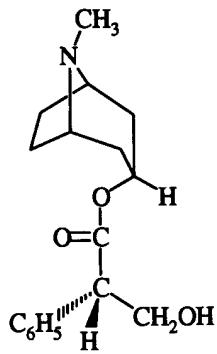
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(f) Treating the salt with base produces the secondary amine; it then acts as a nucleophile and attacks the carbon atom bearing the bromine. This reaction leads to the formation of a five-membered ring and (±) nicotine.

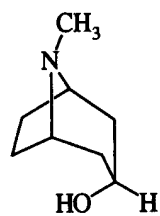


F.2 (a) The stereocenter adjacent to the ester carbonyl group is racemized by base (probably through the formation of an anion that can undergo inversion of configuration; cf. Section 17.3).

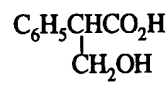
(b)



F.3 (a)

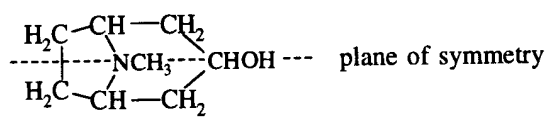


Tropine



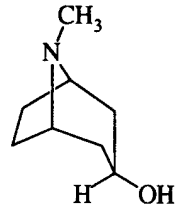
(±) Tropic acid

(b) Tropine is a meso compound; it has a plane of symmetry that passes through the CHOH group, the NCH_3 group, and between the two $-CH_2-$ groups of the five-membered ring.



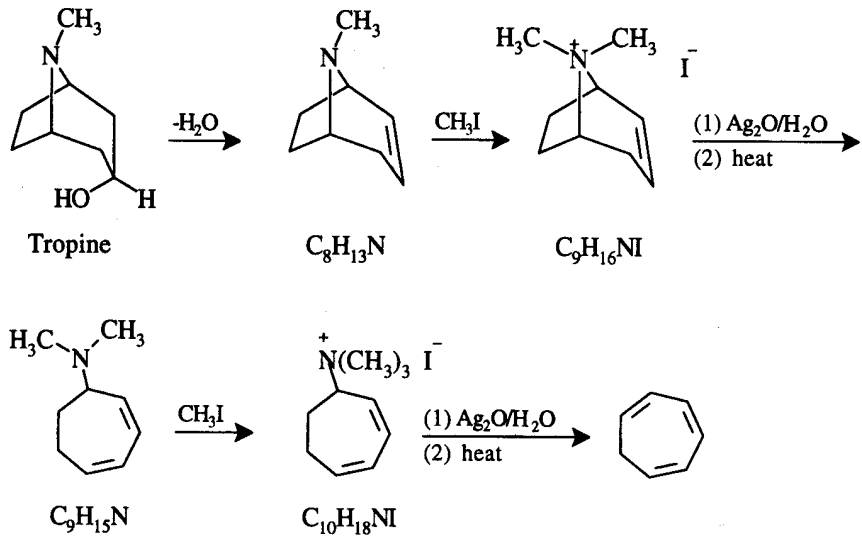
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(c)

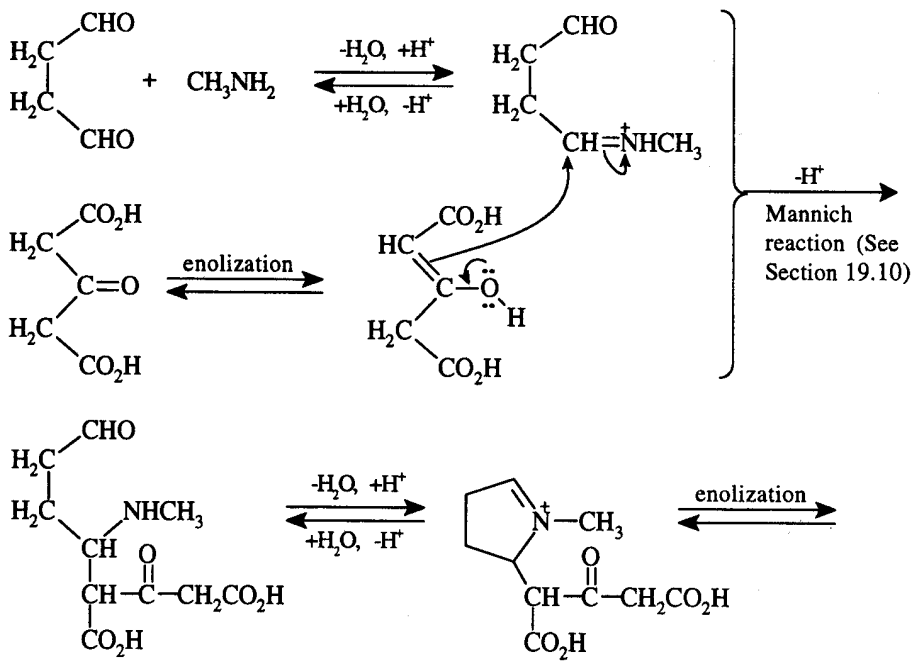


ψ-Tropine

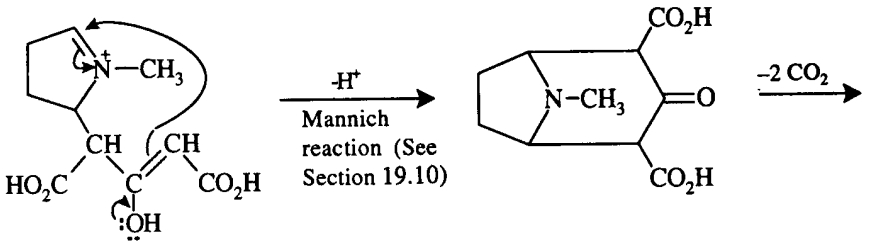
F.4

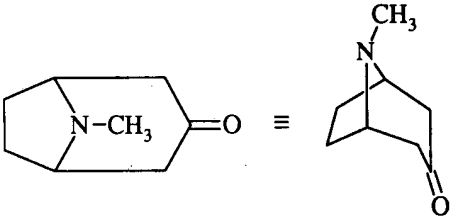


F.5 One possible sequence of steps is the following:



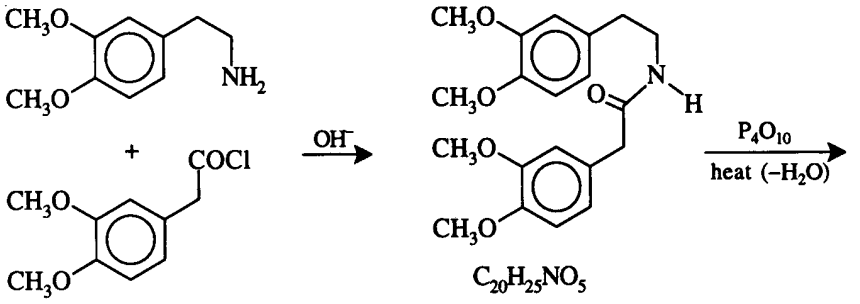
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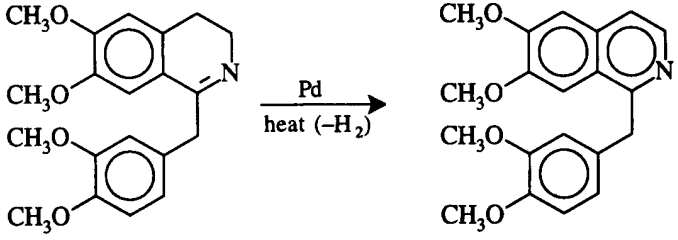




Tropinone

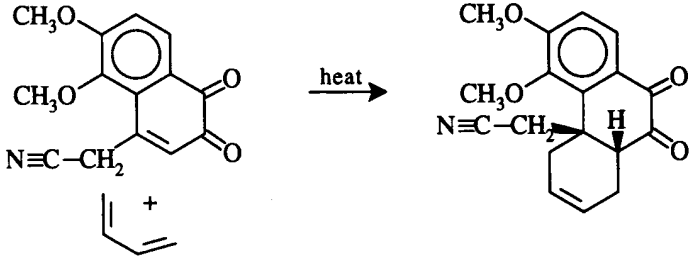
F.6





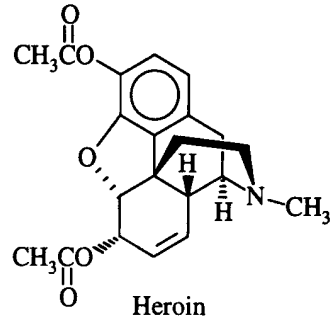
Dihydropapaverine Papaverine

F.7 A Diels-Alder reaction was carried out using 1,3-butadiene as the diene component.



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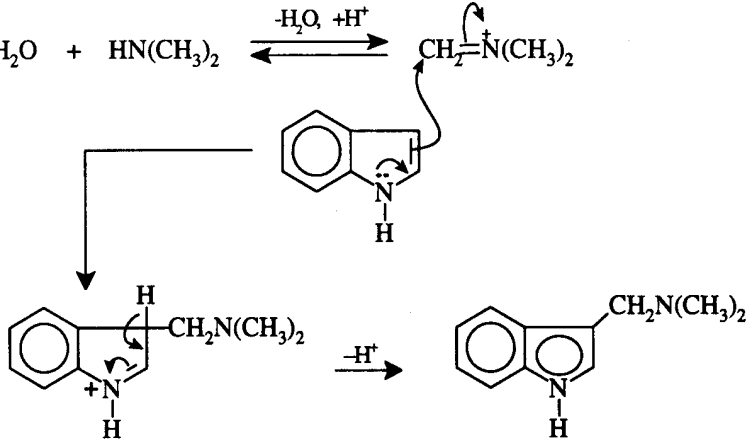
F.8 Acetic anhydride acetylates both –OH groups.



Heroin

F.9 (a) A Mannich reaction (see Section 19.10).

(b) $CH_2O + HN(CH_3)_2 \rightleftharpoons CH_2{=}\overset{+}{N}(CH_3)_2$ ($-H_2O$, $+H^+$)



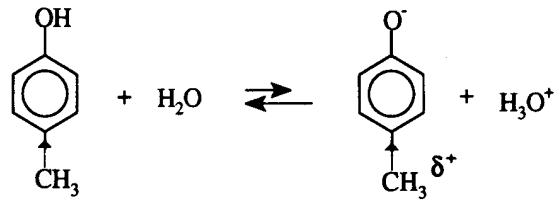
Gramine

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21 PHENOLS AND ARYL HALIDES: NUCLEOPHILIC AROMATIC SUBSTITUTION

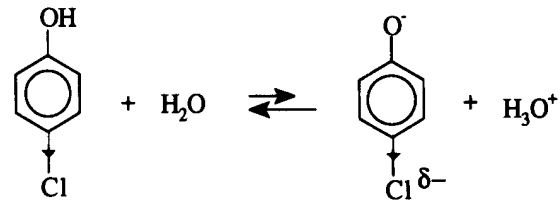
SOLUTIONS TO PROBLEMS

21.1 An electron-releasing group (i.e., $-CH_3$) changes the charge distribution in the molecule so as to make the hydroxyl oxygen less positive, causing the proton to be held more strongly; it also destabilizes the phenoxide anion by intensifying its negative charge. These effects make the substituted phenol less acidic than phenol itself.



Electron-releasing $-CH_3$ destabilizes the anion more than the acid—pK_a is larger than for phenol.

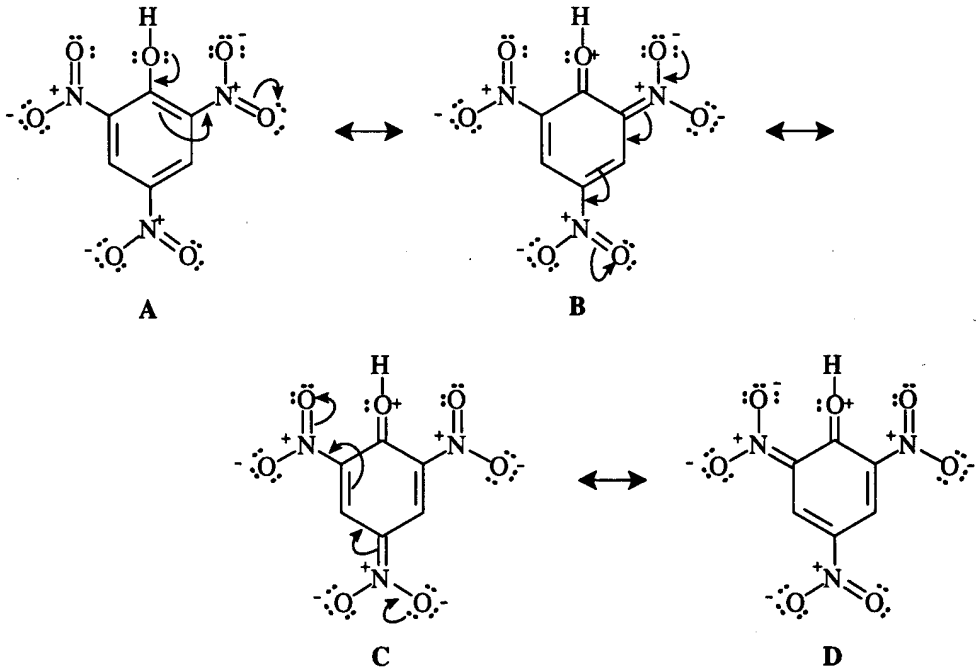
21.2 An electron-withdrawing group such as chlorine changes the charge distribution in the molecule so as to make the hydroxyl oxygen more positive, causing the proton to be held less strongly; it also can stabilize the phenoxide ion by dispersing its negative charge. These effects make the substituted phenol more acidic than phenol itself.



Electron-withdrawing chlorine stabilizes the anion by dispersing the negative charge. pK_a is smaller than for phenol.

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Nitro groups are very powerful electron-withdrawing groups by their inductive and resonance effects. Resonance structures (**B–D**) below place a positive charge on the hydroxyl oxygen. This effect makes the hydroxyl oxygen dramatically more positive, causing the proton to be held much less strongly. These contributions explain why 2,4,6-trinitrophenol (picric acid) is so exceptionally acidic.



21.3 Dissolve the mixture in a solvent such as CH_2Cl_2 (one that is immiscible with water). Using a separatory funnel, extract this solution with an aqueous solution of sodium bicarbonate. This extraction will remove the benzoic acid from the CH_2Cl_2 solution and transfer it (as a sodium benzoate) to the aqueous bicarbonate solution. Acidification of this aqueous extract will cause benzoic acid to precipitate; it can then be separated by filtration and purified by recrystallization.

The CH_2Cl_2 solution can now be extracted with an aqueous solution of sodium hydroxide. This will remove the 4-methylphenol (as its sodium salt). Acidification of the aqueous extract will cause the formation of 4-methylphenol as a water-insoluble layer. The 4-methylphenol can then be extracted into ether, the ether removed, and the 4-methylphenol purified by distillation.

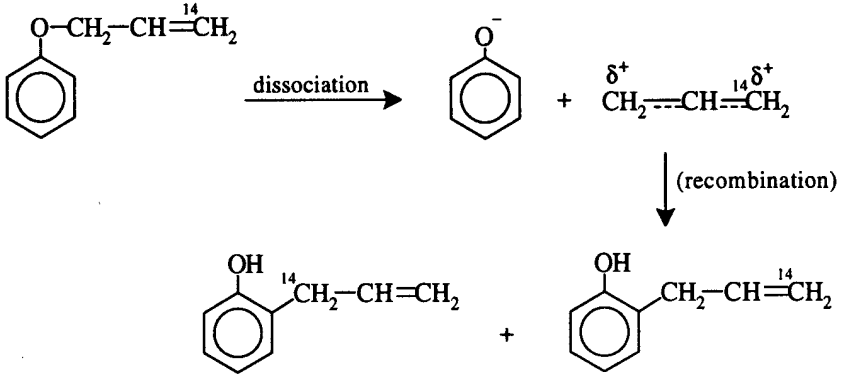
The CH_2Cl_2 solution will now contain only toluene (and CH_2Cl_2). These can be separated easily by fractional distillation.

21.4 (a) The para-sulfonated phenol, because it is the major product at the higher temperature—when the reaction is under equilibrium control.

(b) For ortho sulfonation, because it is the major reaction pathway at the lower temperature—when the reaction is under rate control.

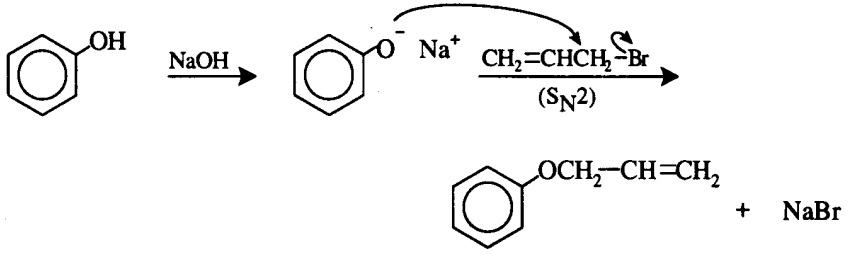
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21.5 If the mechanism involved dissociation into an allyl cation and a phenoxide ion, then recombination would lead to two products: one in which the labeled carbon atom is bonded to the ring and one in which an unlabeled carbon atom is bonded to the ring.

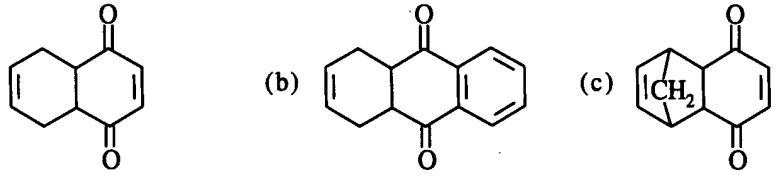


The fact that all of the product has the labeled carbon atom bonded to the ring eliminates this mechanism from consideration.

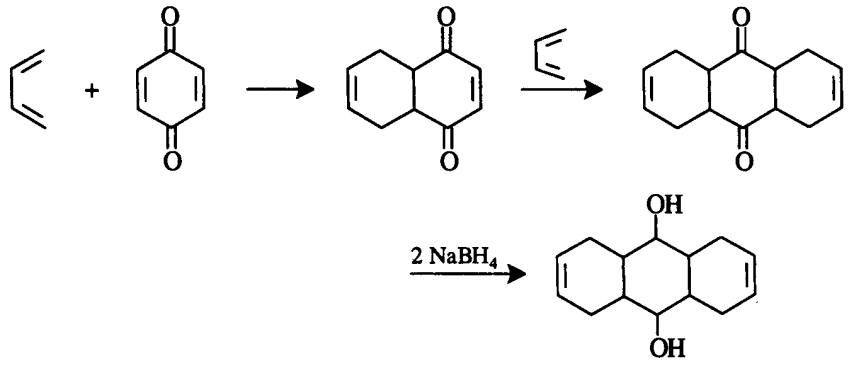
21.6



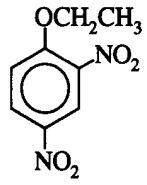
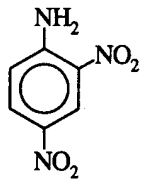
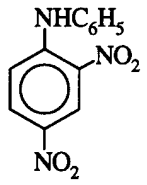
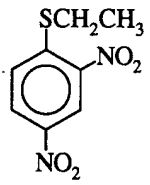
21.7 (a) (b) (c)



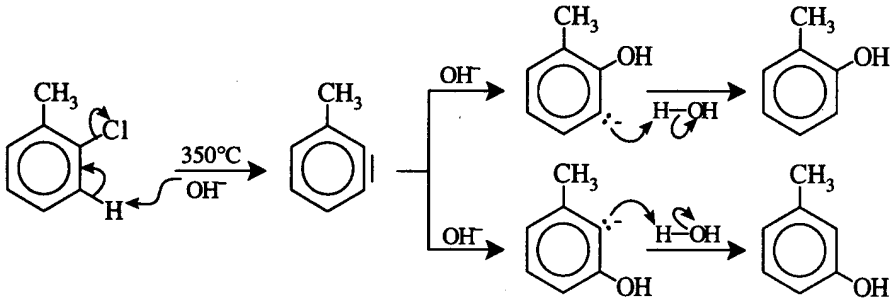
21.8



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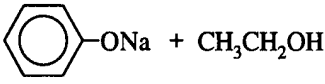
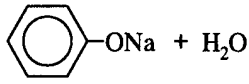
21.9 (a)  (b)  (c)  (d) 

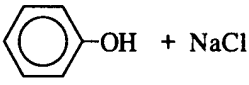
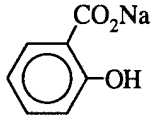
21.10 That *o*-chlorotoluene leads to the formation of two products (*o*-cresol and *m*-cresol) when submitted to the conditions used in the Dow process suggests that an elimination-addition mechanism takes place.

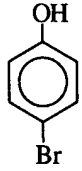


Inasmuch as chlorobenzene and *o*-chlorotoluene should have similar reactivities under these conditions, it is reasonable to assume that chlorobenzene reacts by an elimination-addition mechanism in the Dow process.

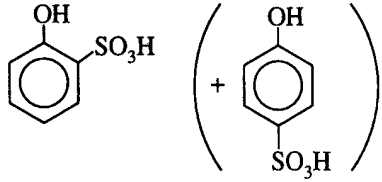
21.11 2-Bromo-1,3-dimethylbenzene, because it has no α-hydrogen, cannot undergo an elimination. Its lack of reactivity toward sodium amide in liquid ammonia suggests that those compounds (e.g., bromobenzene) that do react do so by a mechanism that begins with an elimination.

21.12 (a)  (b) 

(c)  (d) 

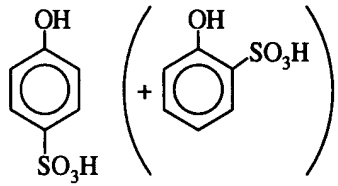
21.13 (a) 

(major)

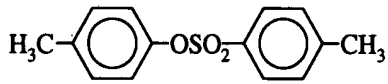
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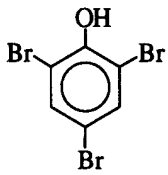
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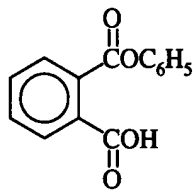
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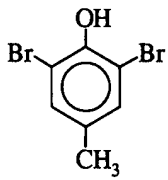
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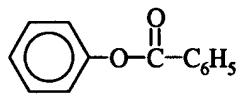
(major)

(d) 

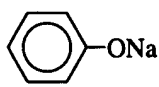
(e) 

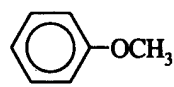
(f) 

(g) 

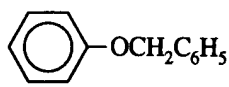
(h) 

(i) Same as (h)

(j) 

(k) 

(l) Same as (k)

(m) 

21.14 (a) 4-Chlorophenol will dissolve in aqueous NaOH; 4-chloro-1-methylbenzene will not.

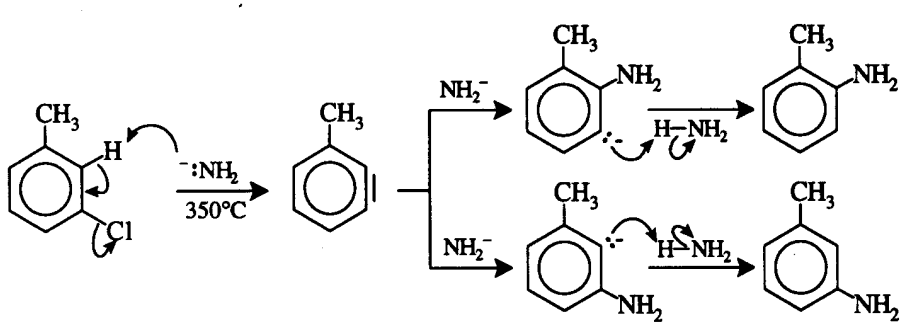
(b) 4-Methylbenzoic acid will dissolve in aqueous $NaHCO_3$; 4-methylphenol will not.

(c) Phenyl vinyl ether will react with bromine in carbon tetrachloride by addition (thus decolorizing the solution); ethyl phenyl ether will not.

(d) 2,4,6-Trinitrophenol, because it is so exceptionally acidic ($pK_a = 0.38$), will dissolve in aqueous $NaHCO_3$; 4-methylphenol ($pK_a = 10.17$) will not.

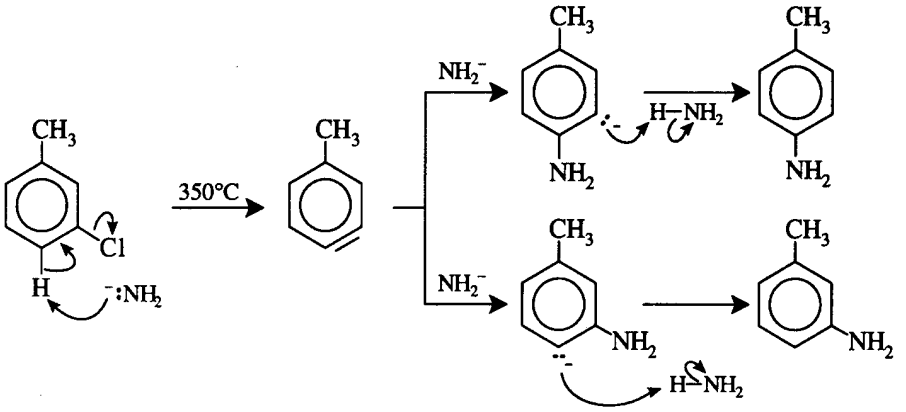
(e) 4-Ethylphenol will dissolve in aqueous NaOH; ethyl phenyl ether will not.

21.15 Both *o*- and *m*-toluidine are formed in the following way:



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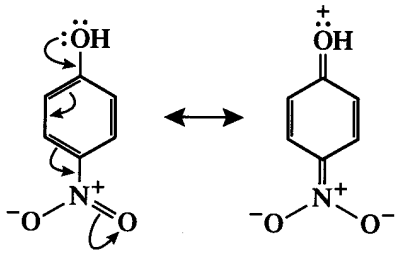
Both *m*- and *p*-toluidine are formed from another benzyne-type intermediate.



21.16 (a) 4-Fluorophenol because a fluorine substituent is more electron withdrawing than a methyl group.

(b) 4-Nitrophenol because a nitro group is more electron withdrawing than a methyl group.

(c) 4-Nitrophenol because the nitro group can exert an electron-withdrawing effect through a resonance effect.

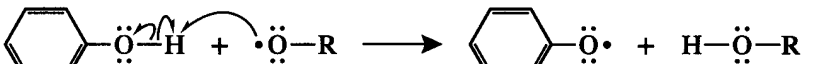


Whereas in 3-nitrophenol this resonance effect is not possible.

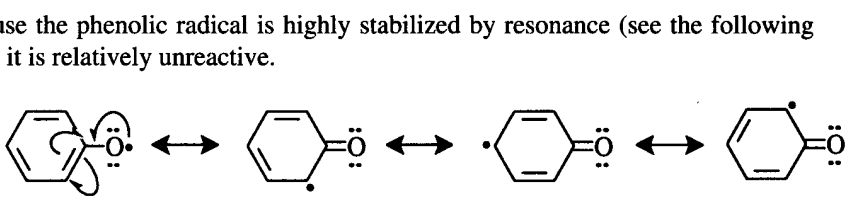
(d) 4-Methylphenol because it is a phenol, not an alcohol.

(e) 4-Fluorophenol because fluorine is more electronegative than bromine.

21.17 (a)

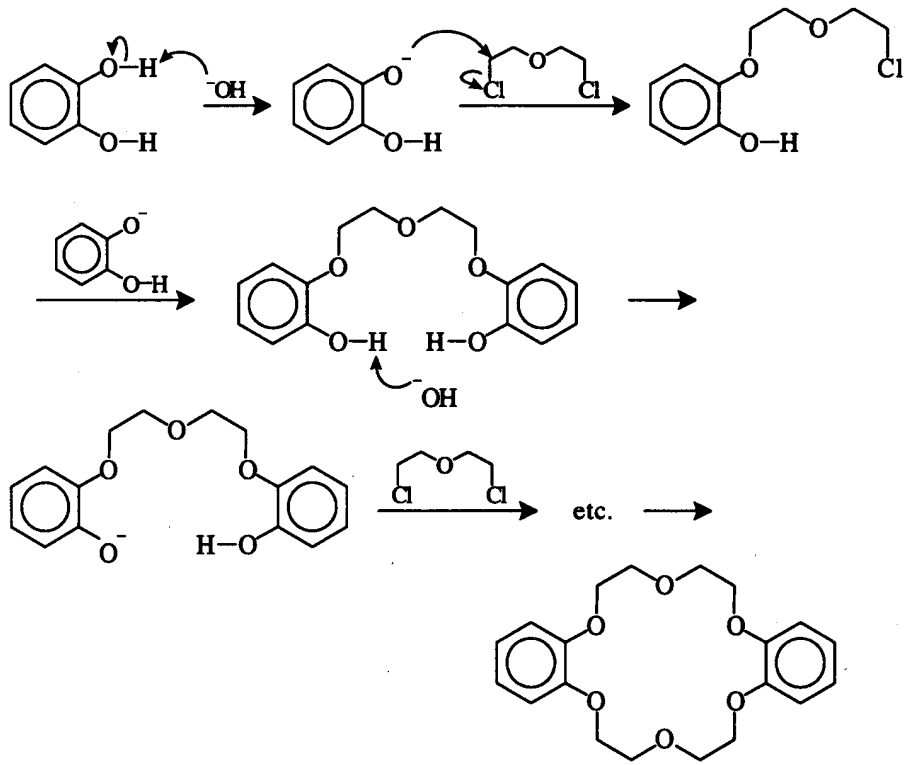


(b) Because the phenolic radical is highly stabilized by resonance (see the following structures), it is relatively unreactive.



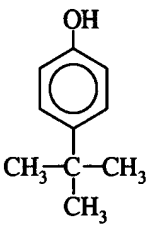
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21.18



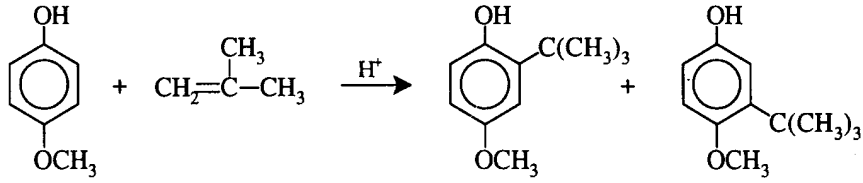
Dibenzo-18-crown-6

21.19 **X** is a phenol because it dissolves in aqueous NaOH but not in aqueous $NaHCO_3$. It gives a dibromo derivative and must therefore be substituted in the ortho or para position. The broad IR peak at 3250 cm^{-1} also suggests a phenol. The peak at 830 cm^{-1} indicates para substitution. The ^1H NMR singlet at δ 1.3 (9H) suggests nine equivalent methyl hydrogen atoms, which must be a *tert*-butyl group. The structure of **X** is



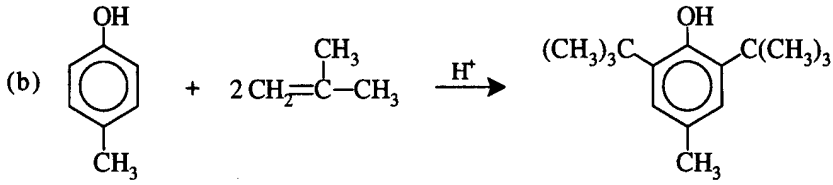
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21.20 (a)



BHA

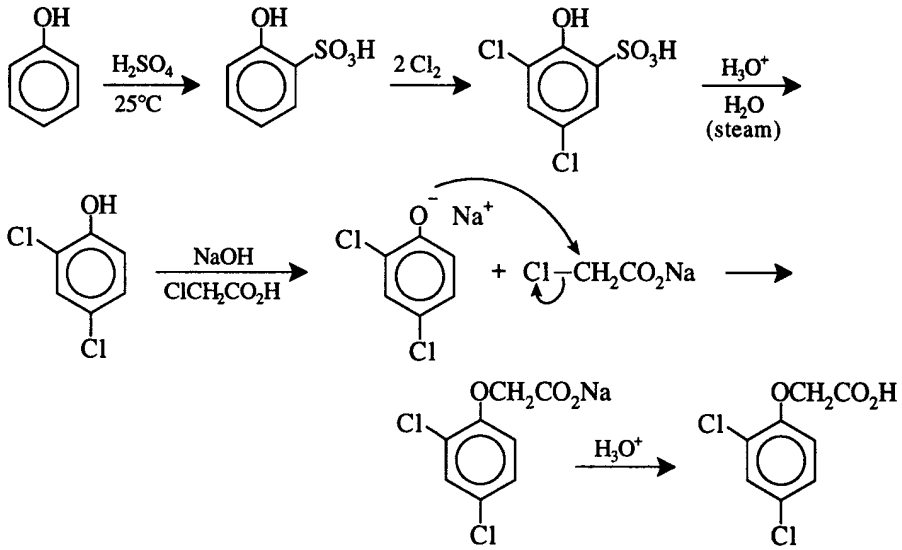
(b)



BHT

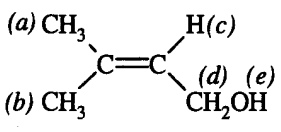
Notice that both reactions are Friedel-Crafts alkylations.

21.21



2,4-D

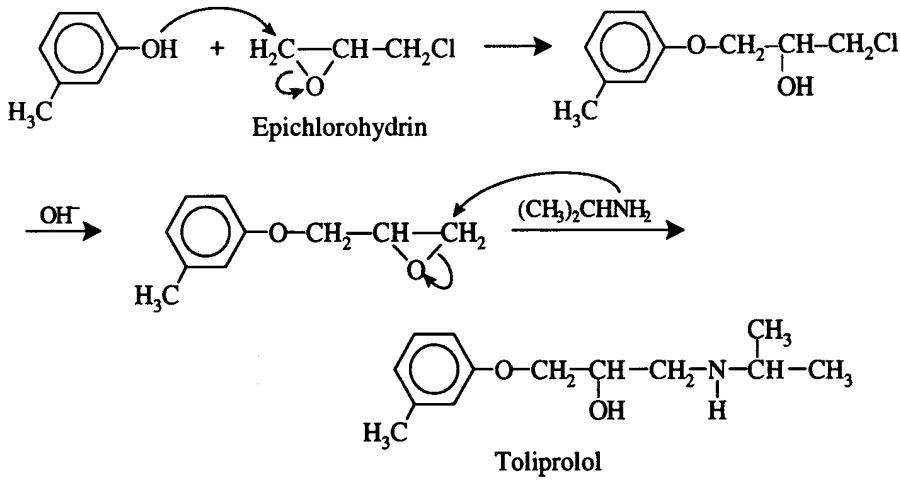
21.22 The broad IR peak at 3200–3600 cm^{-1} suggests a hydroxyl group. The two ^1H NMR peaks at δ 1.67 and δ 1.74 are not a doublet because their separation is not equal to other splittings; therefore, these peaks are singlets. Reaction with Br_2/CCl_4 suggests an alkene. If we put these bits of information together, we conclude that **Z** is 3-methyl-2-buten-1-ol.



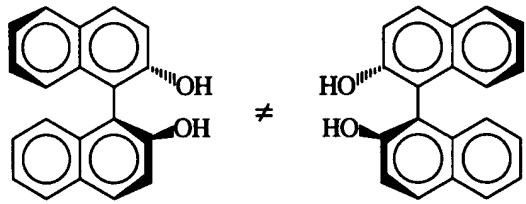
(*a*) and (*b*) singlets δ 1.67 and δ 1.74
(*c*) multiplet δ 5.40
(*d*) doublet δ 4.10
(*e*) singlet δ 2.3

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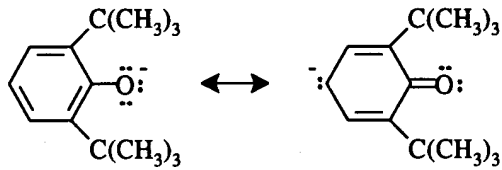
21.23



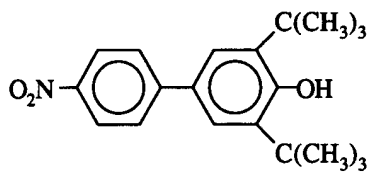
21.24 The proximity of the two -OH groups results in the two naphthalene nuclei being non-coplanar. As a result, the two enantiomeric forms are nonequivalent and can be separated by a resolution technique.



21.25 One can draw a resonance structure for the 2,6-di-*tert*-butylphenoxide ion which shows the carbon para to the oxygen as a nucleophilic center; that is, the species is an ambident nucleophile.



Given the steric hindrance about the oxygen, the nucleophilic character of the para carbon is dominant and an S_NAr reaction occurs at that position to produce this biphenyl derivative:



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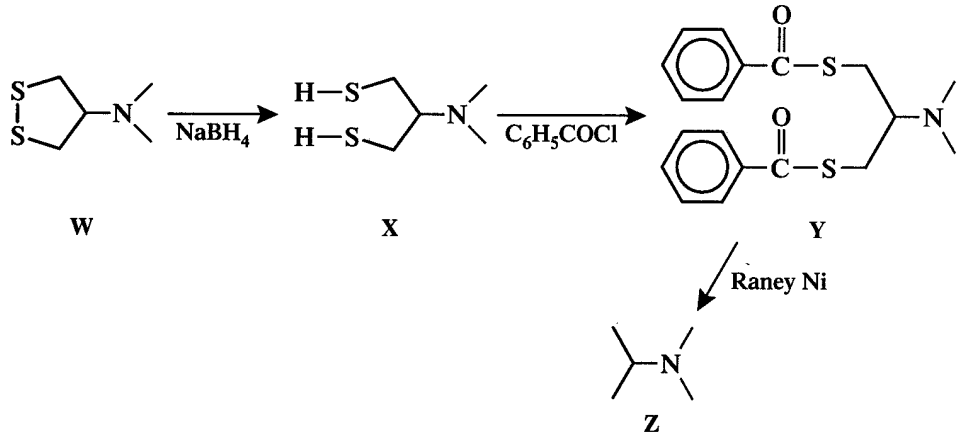
21.26 The phenoxide ion has nucleophilic character both at the oxygen and at the carbon para to it; it is ambident.



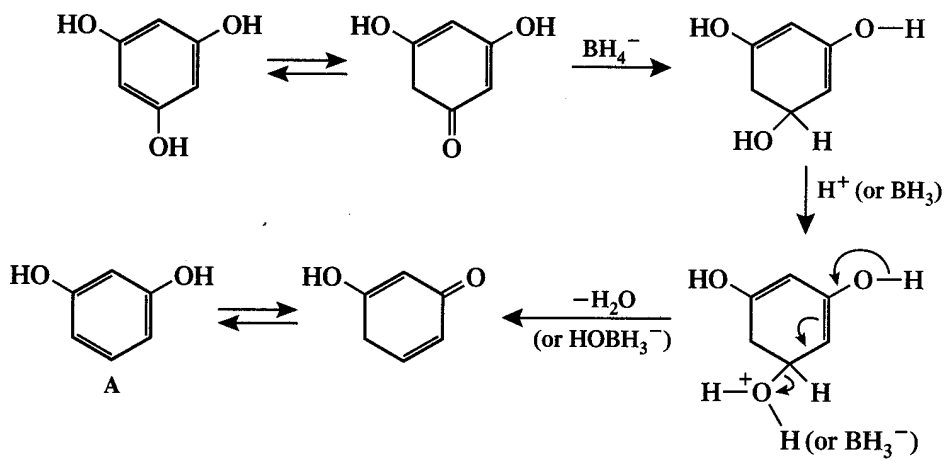
The benzyne produced by the elimination phase of the reaction can undergo addition then by attack by either nucleophilic center, reaction at oxygen producing 1 and reaction at carbon producing **2**.

21.27 H^- is expected to be a very poor leaving group because of the strong basicity of the hydride ion. In this case the reaction is favored not only by the activating nitro groups but also by the oxidant ferricyanide ion, which converts H^-, as it forms, to H_2.

*21.28



*21.29



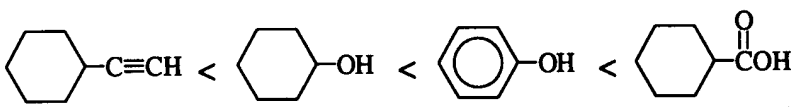
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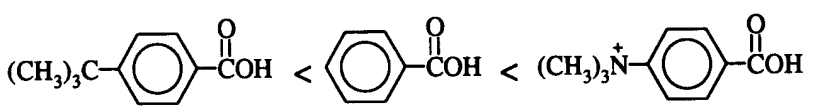
ANSWERS TO SECOND REVIEW PROBLEM SET

The problems review concepts from Chapters 13-21.

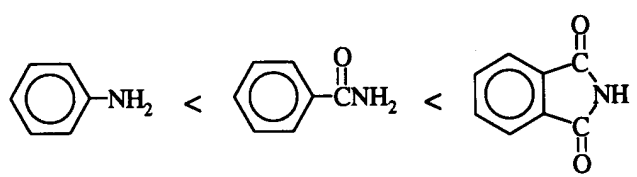
1. Increasing acidity →

(a) $CH_3\overset{O}{\overset{\|}{C}}CH_3 < CH_3CH_2OH < CH_3O\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OCH_3 < CH_3\overset{O}{\overset{\|}{C}}OH$

(b) 

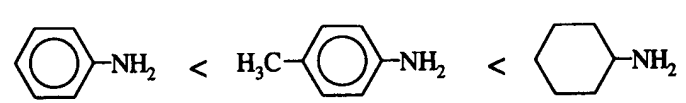
(c) 

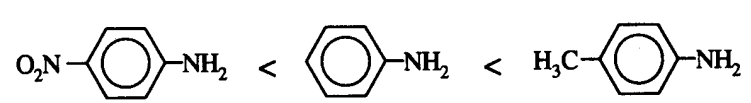
(d) $CH_3CH_2\overset{O}{\overset{\|}{C}}OH < CH_3CHCl\overset{O}{\overset{\|}{C}}OH < CH_3CCl_2\overset{O}{\overset{\|}{C}}OH$

(e) 

2. Increasing basicity →

(a) $CH_3\overset{O}{\overset{\|}{C}}NH_2 < NH_3 < CH_3CH_2NH_2$

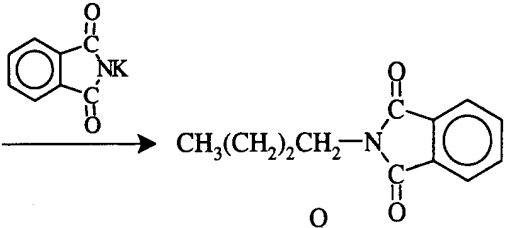
(b) 

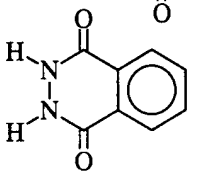
(c) 

(d) $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3NHCH_3$

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3. (a) $CH_3(CH_2)_2CH_2OH \xrightarrow[\text{(or HBr)}]{PBr_3} CH_3(CH_2)_2CH_2Br$

(b) $CH_3(CH_2)_2CH_2Br$ [from part(a)] $\longrightarrow$ 

$\xrightarrow[\text{heat}]{H_2NNH_2}$ $CH_3(CH_2)_2CH_2NH_2$ + 

(c) $CH_3(CH_2)_2CH_2Br \xrightarrow{NaCN} CH_3(CH_2)_2CH_2CN \xrightarrow{LiAlH_4} CH_3(CH_2)_3CH_2NH_2$
[from part(a)]

(d) $CH_3(CH_2)_2CH_2OH \xrightarrow[(2)\ H_3O^+]{(1)\ KMnO_4,\ OH^-,\ \text{heat}} CH_3(CH_2)_2\overset{O}{\overset{\|}{C}}OH$

(e) $CH_3(CH_2)_2CH_2CN \xrightarrow[\text{heat}]{H_3O^+, H_2O} CH_3(CH_2)_2CH_2CO_2H + NH_4^+$
[from part(c)]

(f) $CH_3(CH_2)_2\overset{O}{\overset{\|}{C}}OH \xrightarrow{SOCl_2} CH_3(CH_2)_2\overset{O}{\overset{\|}{C}}Cl$
[from part(d)]

(g) $CH_3(CH_2)_2\overset{O}{\overset{\|}{C}}Cl \xrightarrow{NH_3} CH_3(CH_2)_2\overset{O}{\overset{\|}{C}}NH_2$
[from part(f)]

(h) $CH_3(CH_2)_2\overset{O}{\overset{\|}{C}}Cl \xrightarrow[\text{base}]{CH_3(CH_2)_2CH_2OH} CH_3(CH_2)_2\overset{O}{\overset{\|}{C}}OCH_2(CH_2)_2CH_3$
[from part(f)]

(i) $CH_3(CH_2)_2\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow[(2)\ H_3O^+]{(1)\ Br_2,\ OH^-} CH_3CH_2CH_2NH_2 + CO_3^{2-}$
[from part(g)]

(j) $CH_3(CH_2)_2\overset{O}{\overset{\|}{C}}Cl$ [from part(f)] $\xrightarrow[AlCl_3]{}$  $\xrightarrow[HCl]{Zn(Hg)}$

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(k) $CH_3(CH_2)_2\overset{O}{\overset{\|}{C}}Cl$ [from part(f)] $\xrightarrow{CH_3(CH_2)_2\overset{O}{\overset{\|}{C}}ONa}$ $[CH_3(CH_2)_2\overset{O}{\overset{\|}{C}}]_2O$

(l) $CH_3(CH_2)_2CH_2Br$ [from part(a)] $\xrightarrow{Na^+ \,:\overset{CO_2Et}{\overset{|}{C}}H\overset{CO_2Et}{}}$ $CH_3(CH_2)_2CH_2\overset{CO_2Et}{\overset{|}{C}}H\overset{CO_2Et}{}$ $\xrightarrow[(2)\ H_3O^+]{(1)\ OH^-,\ H_2O,\ heat}$

$CH_3(CH_2)_2CH_2\overset{CO_2H}{\overset{|}{C}}H\overset{CO_2H}{}$ $\xrightarrow[-CO_2]{heat}$ $CH_3(CH_2)_2CH_2CH_2CO_2H$

4. (a) H_3C–C$_6$H$_4$– $\xrightarrow[FeBr_3]{Br_2}$ H_3C–C$_6$H$_4$–Br $\xrightarrow[Et_2O]{Mg}$ H_3C–C$_6$H$_4$–MgBr

(separate from ortho isomer)

$\xrightarrow[(2)\ H_3O^+]{(1)\ H_2C\overset{O}{\diagup\diagdown}CH_2}$ H_3C–C$_6$H$_4$–CH_2CH_2OH $\xrightarrow[CH_2Cl_2]{PCC}$ H_3C–C$_6$H$_4$–$CH_2\overset{O}{\overset{\|}{C}}H$

$\xrightarrow[\text{(aldol condensation)}]{OH^-}$ H_3C–C$_6$H$_4$–$CH_2CH=\overset{CH_3}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}H$

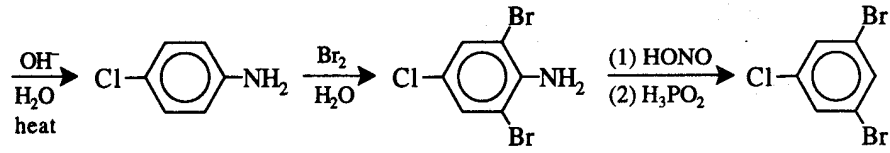
(b) C$_6$H$_5$– $\xrightarrow[HF]{CH_2=CHCH_3}$ C$_6$H$_5$–$\overset{CH_3}{\overset{|}{C}}H\overset{CH_3}{}$ $\xrightarrow[CCl_4\ (h\nu)]{NBS}$ C$_6$H$_5$–$\overset{CH_3}{\overset{|}{C}}(Br)\overset{CH_3}{}$

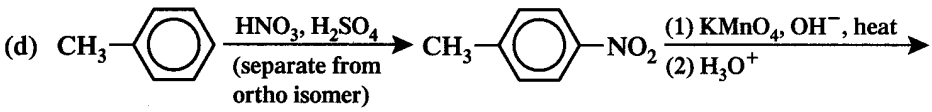
$\xrightarrow{base}$ C$_6$H$_5$–$\overset{CH_3}{\overset{|}{C}}=CH_2$ $\xrightarrow[(2)\ H_2O_2,OH^-]{(1)\ THF:\ BH_3}$ C$_6$H$_5$–$\overset{CH_3}{\overset{|}{C}}H-CH_2OH$

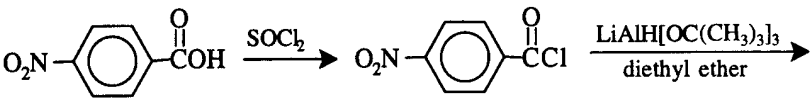
$\xrightarrow[(2)\ CH_3CH_2Br]{(1)\ NaH}$ C$_6$H$_5$–$\overset{CH_3}{\overset{|}{C}}H-CH_2OCH_2CH_3$

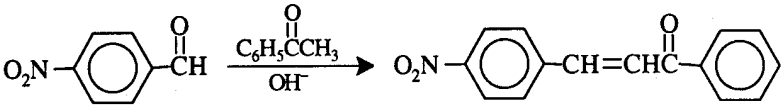
(c) H_2N–C$_6$H$_4$– $\xrightarrow{(CH_3C)_2O}$ $CH_3\overset{O}{\overset{\|}{C}}NH$–C$_6H_4$– $\xrightarrow[\text{(separate from ortho isomer)}]{Cl_2,\ FeCl_3}$ Cl–C$_6$H$_4$–$NH\overset{O}{\overset{\|}{C}}CH_3$

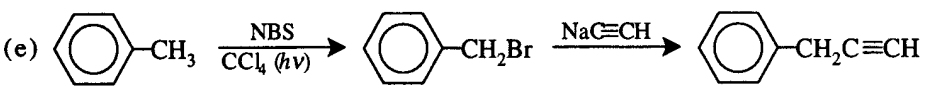
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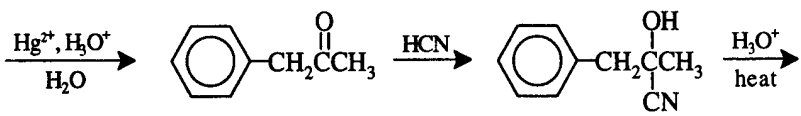


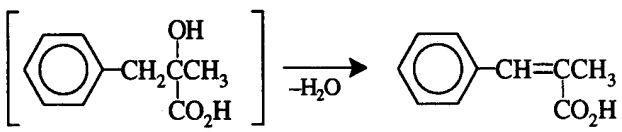




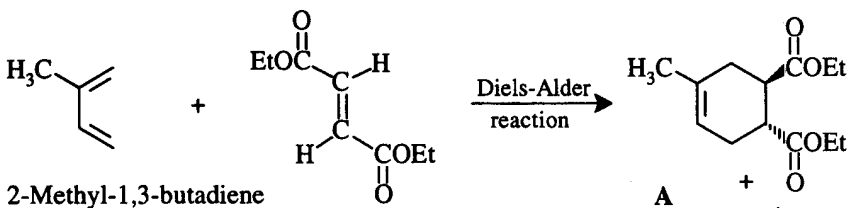


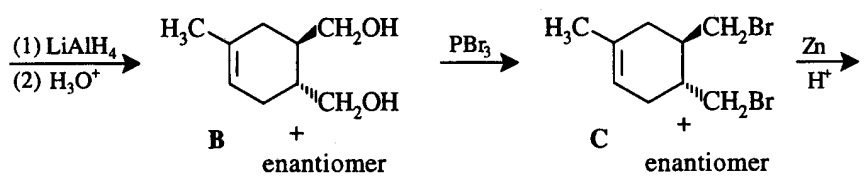


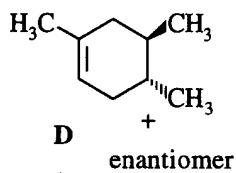




5.



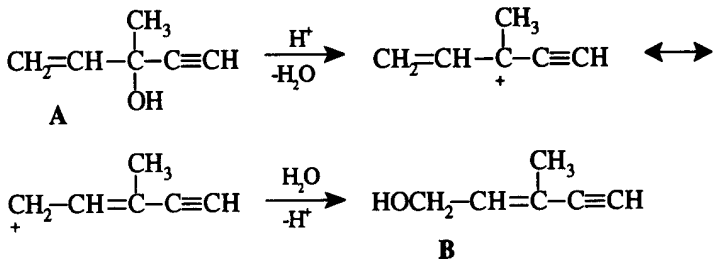




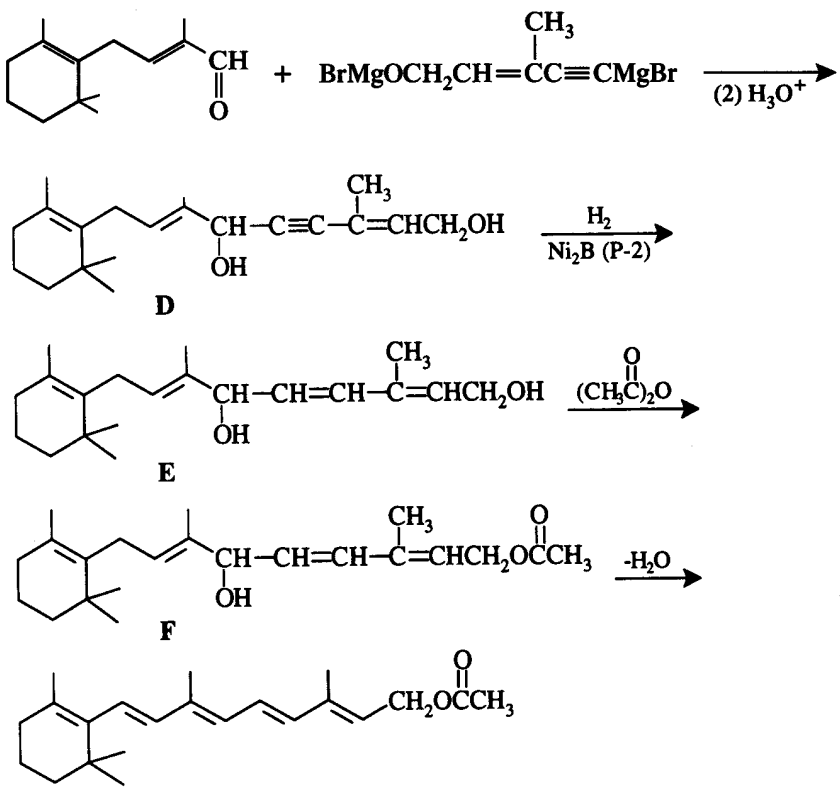
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6. (a) **A** is $CH_2{=}CHC(CH_3)(OH)C{\equiv}CH$ **C** is $BrMgOCH_2CH{=}C(CH_3)C{\equiv}CMgBr$

(b) **A** is an allylic alcohol and thus forms a carbocation readily. **B** is a conjugated enyne and is therefore more stable than **A**.



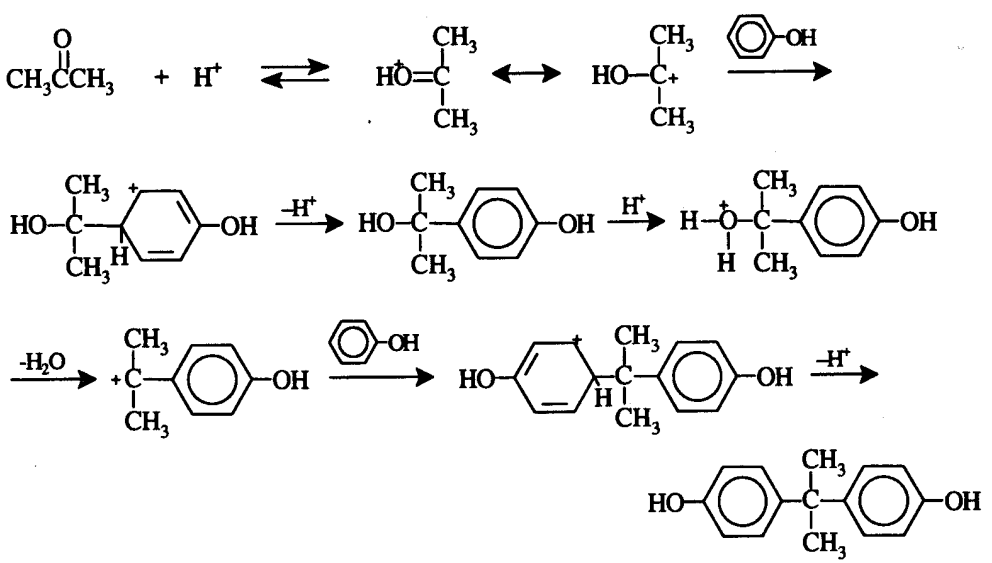
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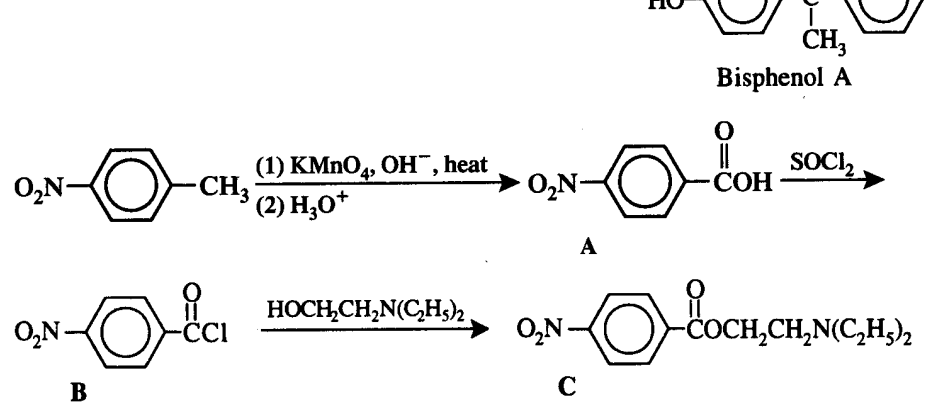
Vitamin A acetate

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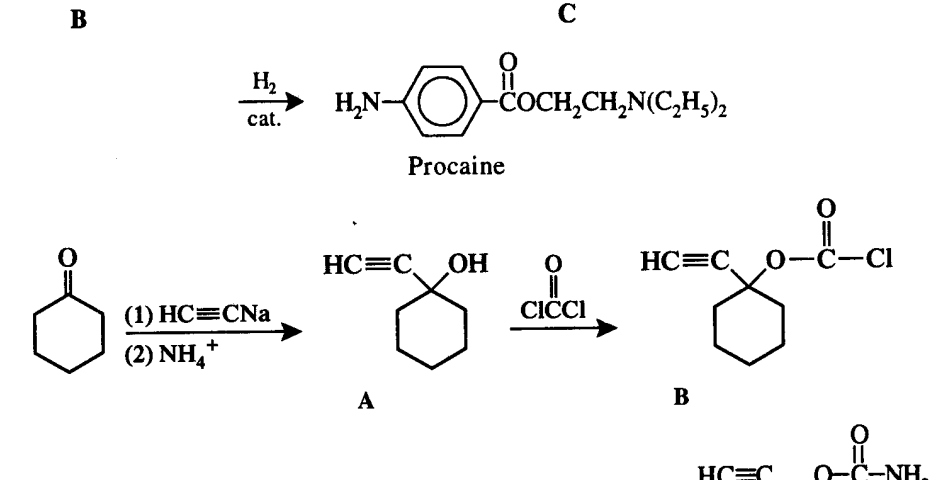
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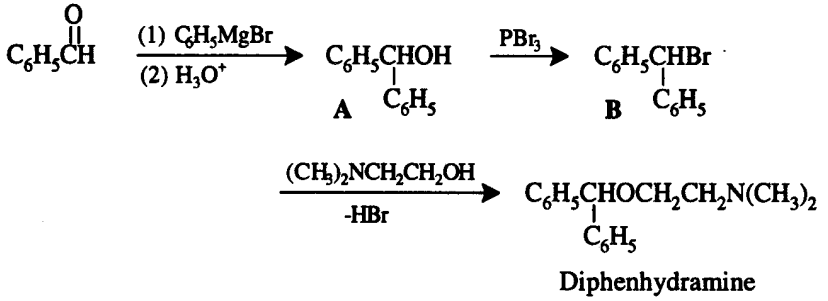
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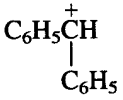
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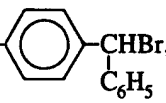


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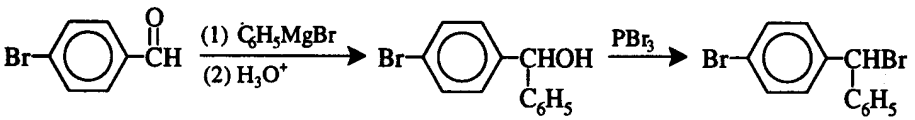
11. (a) 

(b) The last step probably takes place by an S_N1 mechanism. Diphenylmethyl bromide, **B**, ionizes readily because it forms the resonance-stabilized benzylic carbocation,

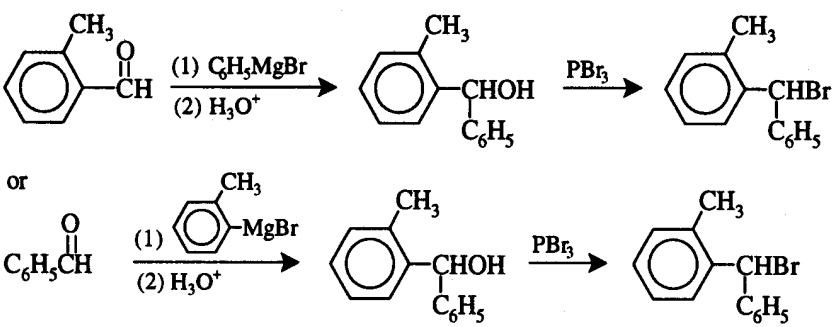


12. (a) For this synthesis we need to prepare the benzylic halide,  , and then allow it to react with $(CH_3)_2NCH_2CH_2OH$ as in Problem 11.

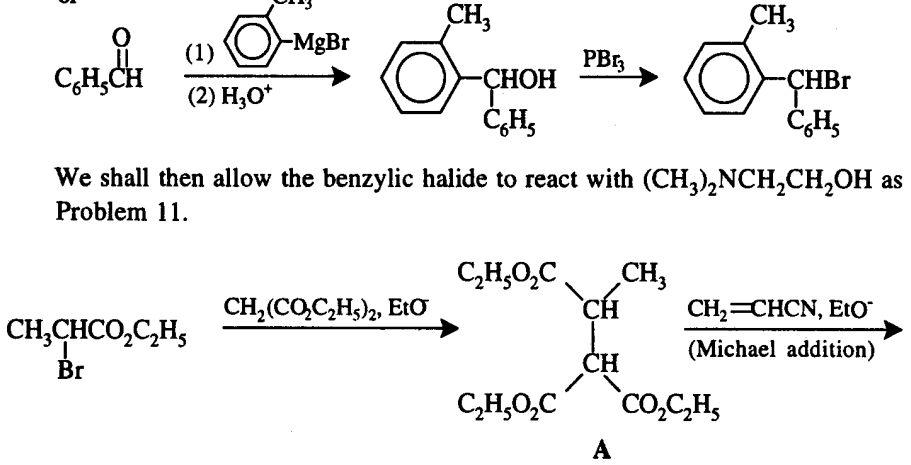
This benzylic halide can be made as follows:



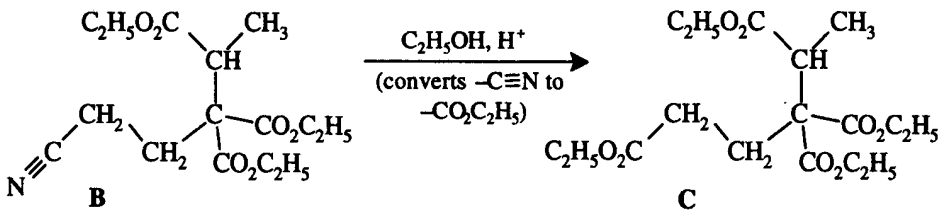
(b) For this synthesis we can prepare the requisite benzylic halide in two ways:

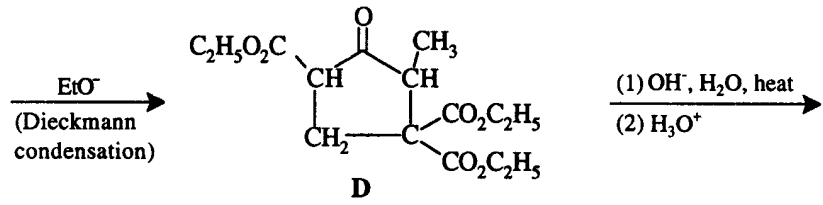


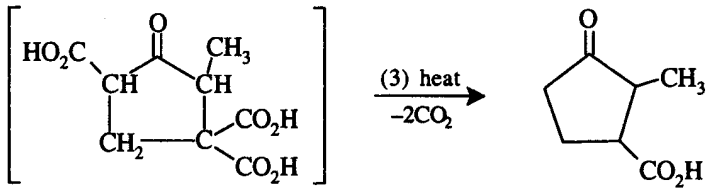
We shall then allow the benzylic halide to react with $(CH_3)_2NCH_2CH_2OH$ as in Problem 11.

13. 

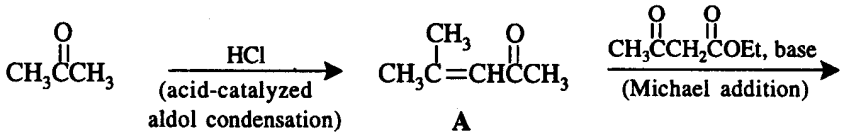
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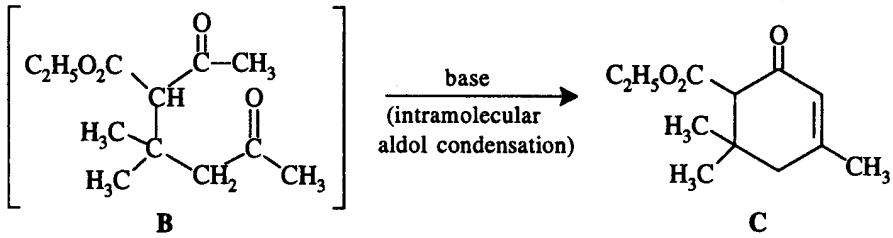


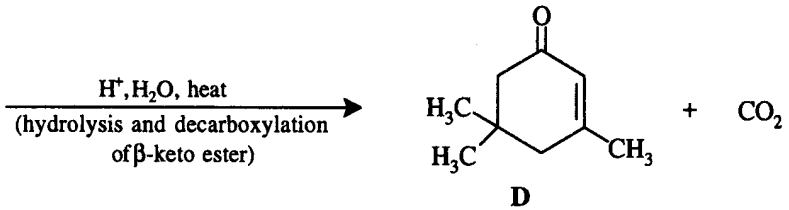




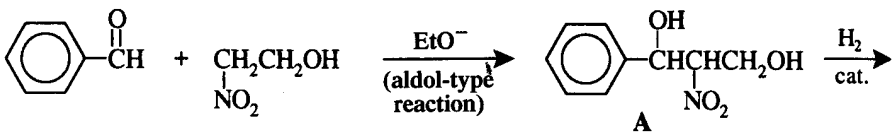
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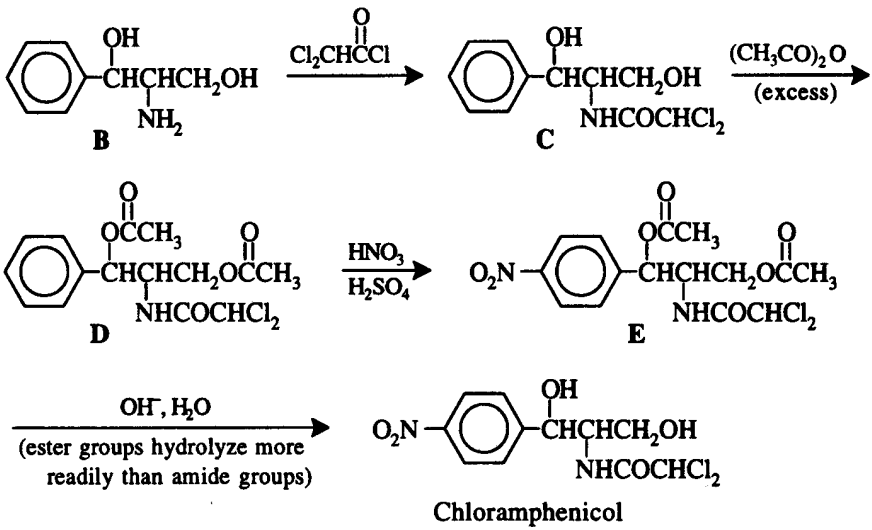




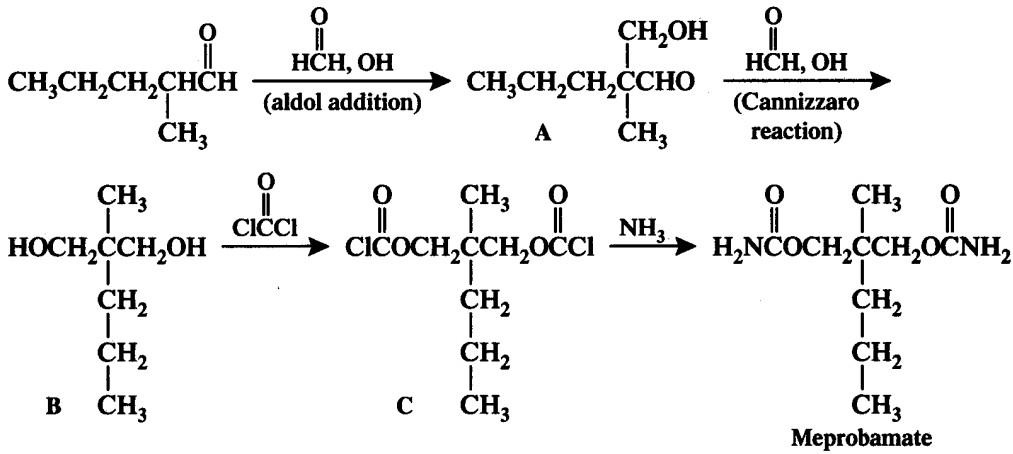
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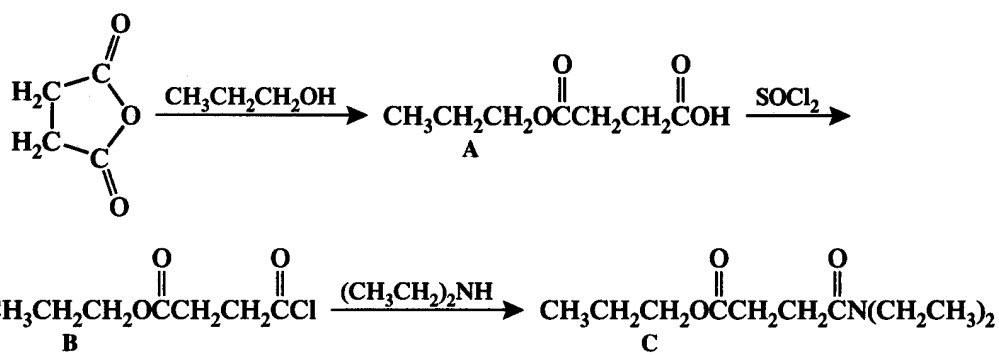
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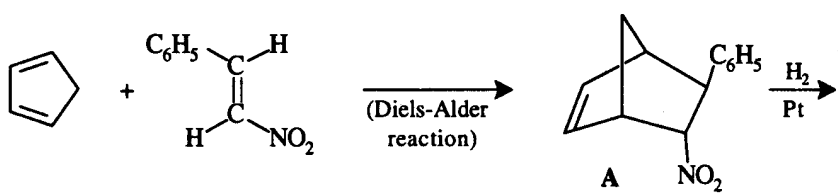
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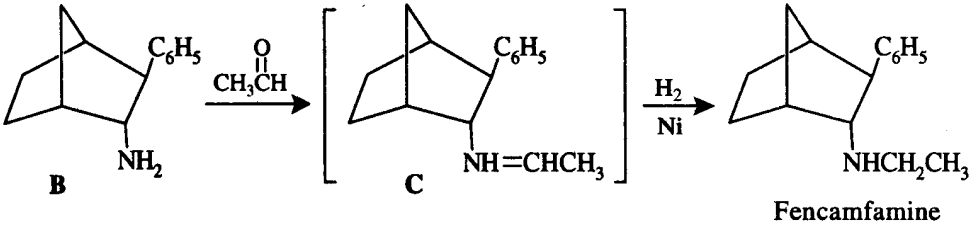
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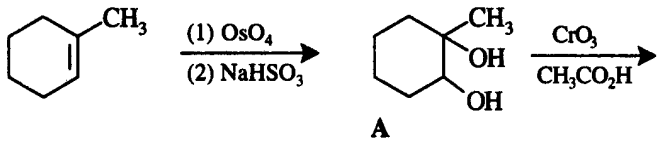
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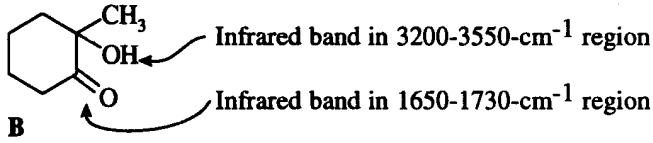


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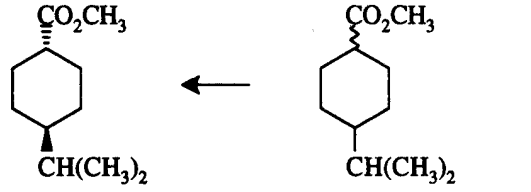
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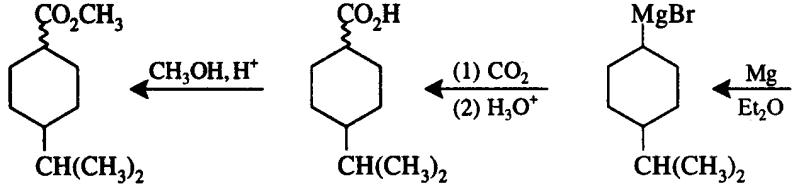


Notice that the second step involves the oxidation of a secondary alcohol in the presence of a tertiary alcohol. This selectivity is possible because tertiary alcohols do not undergo oxidation readily (Section 11.8)

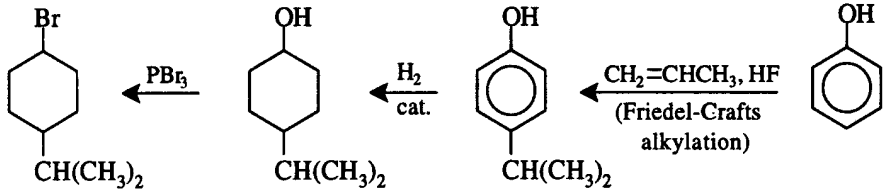
20. Working backward, we notice that methyl *trans*-4-isopropylcyclohexanecarboxylate has both large groups equatorial and is, therefore, more stable than the corresponding cis isomer. This stability of the trans isomer means that, if we were to synthesize the cis isomer or a mixture of both the cis and trans isomers, we could obtain the desired trans isomer by a base-catalyzed isomerization (epimerization):



We could synthesize a mixture of the desired isomers from phenol in the following way:



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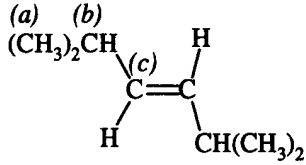
21. That **Y** gives a green opaque solution when treated with CrO_3 in aqueous H_2SO_4 indicates that **Y** is a primary or secondary alcohol. That **Y** gives a negative iodoform test indicates that **Y** does not contain the grouping $-\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$. The ^{13}C spectrum of **Y** contains only four signals indicating that some of the carbons in **Y** are equivalent. The information from DEPT spectra helps us conclude that **Y** is 2-ethyl-1-butanol.

(a) (b) (c) (d)
$(CH_3CH_2)_2CHCH_2OH$

(a) δ 11.1
(b) δ 23.0
(c) δ 43.6
(d) δ 64.6

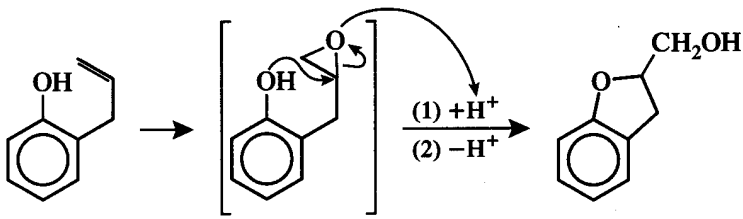
Notice that the most downfield signal is a CH_2 group. This indicates that this carbon atom bears the –OH group and that **Y** is a primary alcohol. The most upfield signals indicate the presence of the ethyl groups.

22. That **Z** decolorizes bromine in CCl_4 indicates that **Z** is an alkene. We are told that **Z** is the more stable isomer of a pair of stereoisomers. This fact suggests that **Z** is a *trans* alkene. That the ^{13}C spectrum contains only three signals, even though **Z** contains eight carbon atoms, indicates that **Z** is highly symmetric. The information from DEPT spectra indicates that the upfield signals of the alkyl groups arise from equivalent isopropyl groups. We conclude, therefore, that **Z** is *trans*-2,5-dimethyl-3-hexene.



(a) δ 22.8
(b) δ 31.0
(c) δ 134.5

23.



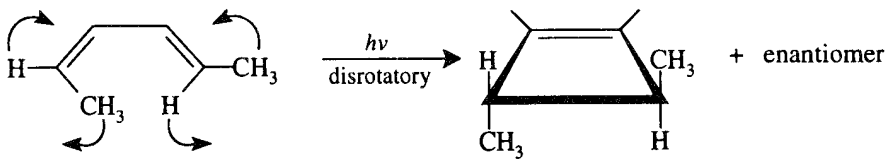
B

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G SPECIAL TOPIC
Electrocyclic and Cycloaddition Reactions

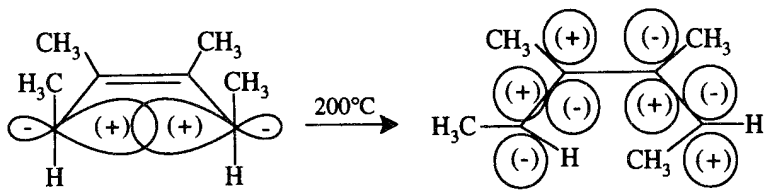
SOLUTIONS TO PROBLEMS

G.1 According to the Woodward-Hoffmann rule for electrocyclic reactions of $4n$ π-electron systems (Section G.2A), the photochemical cyclization of *cis, trans*-2,4-hexadiene should proceed with *disrotatory motion.* Thus, it should yield *trans*-3,4-dimethylcyclobutene:



cis, trans-2,4-Hexadiene — *trans*-3,4-Dimethylcyclobutene

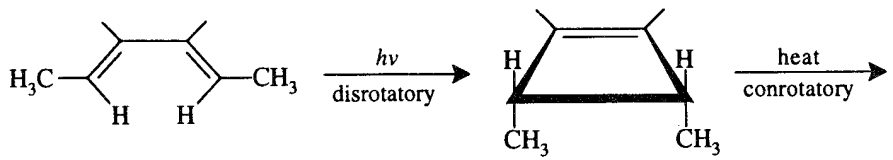
G.2 (a)



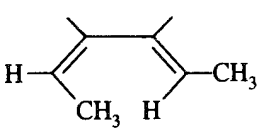
ψ_2 of a hexadiene
(Section G.2A)

(b) This is a thermal electrocyclic reaction of a $4n$ π-electron system; it should, *and does,* proceed with conrotatory motion.

G.3



trans, trans-2,4-Hexadiene — *cis*-3,4-Dimethylcyclobutene

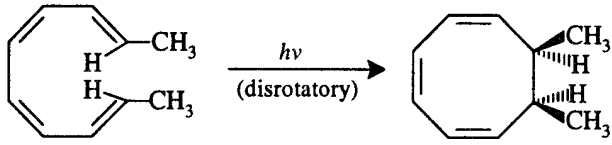


cis, trans-2,4-Hexadiene

Here we find that two consecutive electrocyclic reactions (the first photochemical, the second thermal), provide a stereospecific synthesis of *cis,trans*-2,4-hexadiene from *trans, trans*-2,4-hexadiene.

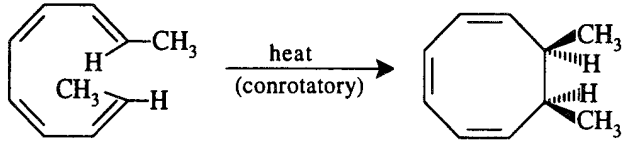
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G.4 (a) This is a photochemical electrocyclic reaction of an eight π-electron system—a $4n$ π-electron system where $n = 2$. It should, therefore, proceed with disrotatory motion.



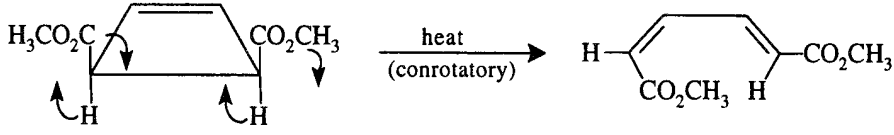
cis-7, 8-Dimethyl-1, 3, 5-cyclooctatriene

(b) This is a thermal electrocyclic reaction of the eight π-electron system. It should proceed with conrotatory motion.

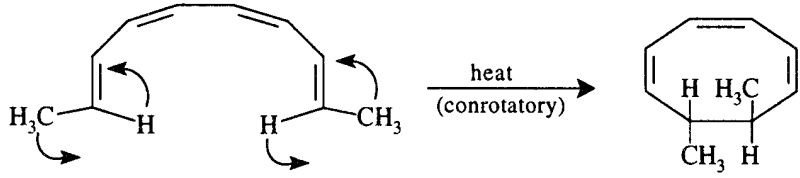


cis-7, 8-Dimethyl-1, 3, 5-cyclooctatriene

G.5 (a) This is conrotatory motion, and since this is a $4n$ π-electron system (where $n = 1$) it should occur under the influence of heat.

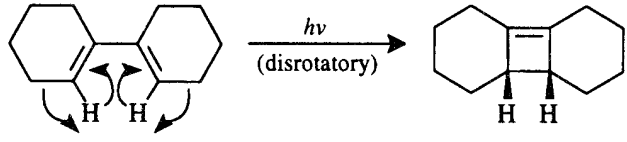


(b) This is conrotatory motion, and since this is also a $4n$ π-electron system (where $n = 2$) it should occur under the influence of heat.



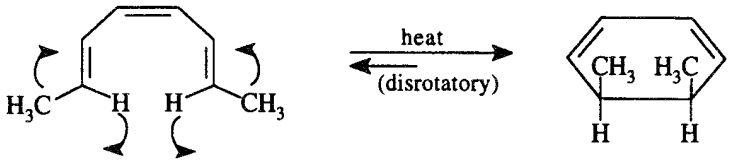
+ enantiomer

(c) This is disrotatory motion. This, too, is a $4n$ π-electron system (where $n = 1$); thus it should occur under the influence of light.

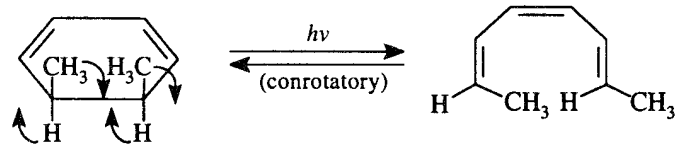


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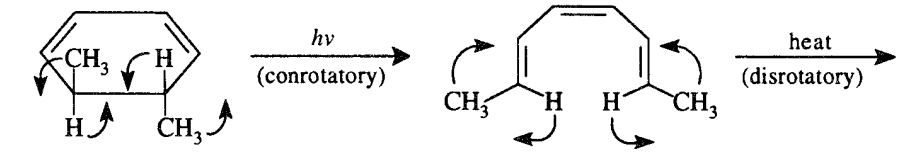
G.6 (a) This is a $(4n + 2)$ π-electron system (where $n = 1$); a thermal reaction should take place with disrotatory motion:



(b) This is also a $(4n + 2)$ π-electron system; a photochemical reaction should take place with conrotatory motion.

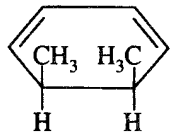


G.7 Here we need a conrotatory ring opening of *trans*-5,6-dimethyl-1,3-cyclohexadiene (to produce *trans,cis,trans*-2,4,6-octatriene); then we need a disrotatory cyclization to produce *cis*-5,6-dimethyl-1,3-cyclohexadiene.



trans-5,6-Dimethyl-1,3-cyclohexadiene

trans, cis, trans-2,4,6-Octatriene

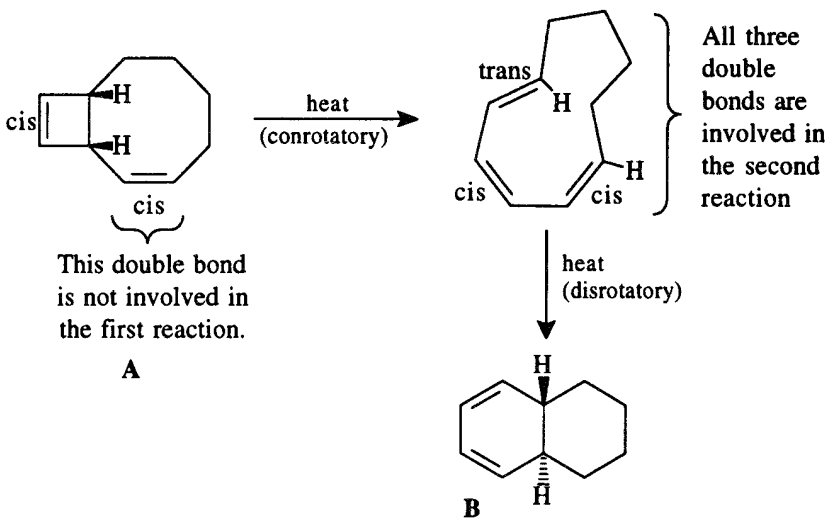


cis-5,6-Dimethyl-1,3-cyclohexadiene

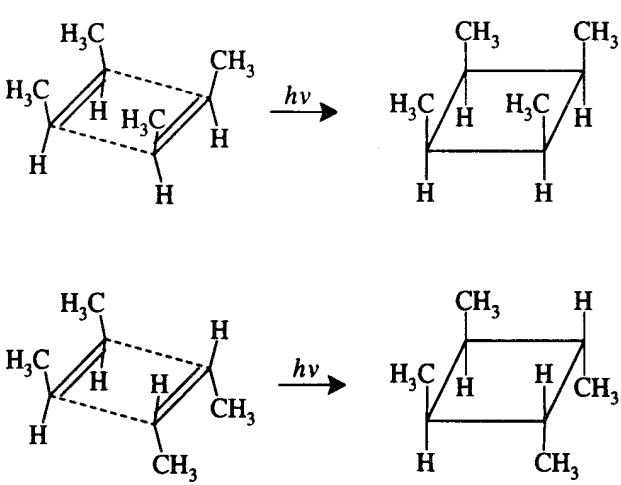
Since both reactions involve $(4n + 2)$ π-electron systems, we apply light to accomplish the first step and heat to accomplish the second. It would also be possible to use heat to produce *trans,cis,cis*-2,4,6-octatriene and then use light to produce the desired product.

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G.8 The first electrocyclic reaction is a thermal, conrotatory ring opening of a $4n$ π-electron system. The second electrocyclic reaction is a thermal, disrotatory ring closure of a $(4n + 2)$ π-electron system.

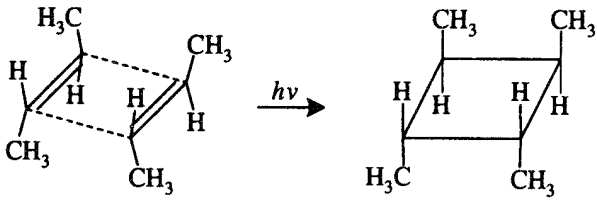


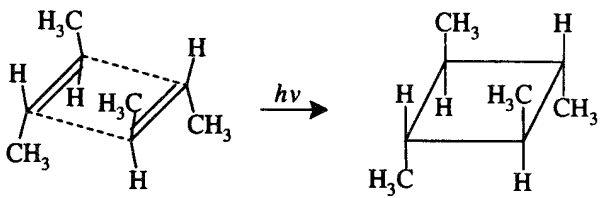
G.9 (a) There are two possible products that can result from a concerted cycloaddition. They are formed when *cis*-2-butene molecules come together in the following ways:



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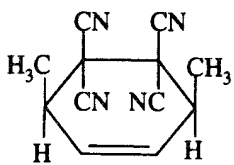
(b) There are two possible products that can be obtained from *trans*-2-butene as well.



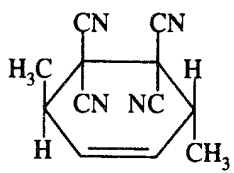


G.10 This is an intramolecular [2 + 2] cycloaddition.

G.11 (a)



(b)



+

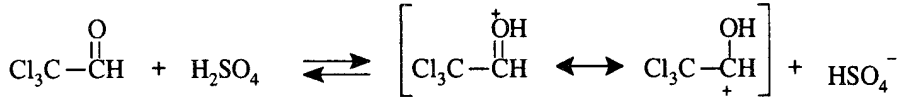
Enantiomer

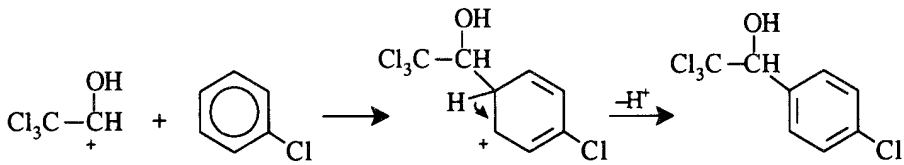
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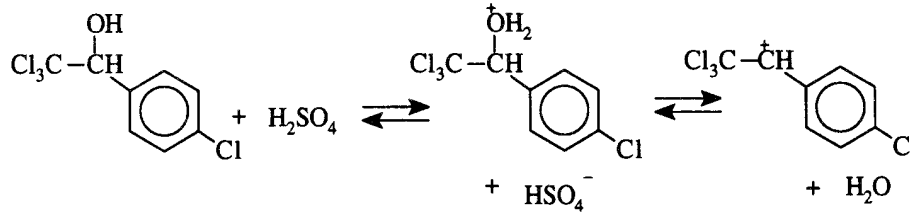
H SPECIAL TOPIC
Organic Halides and Organometallic Compounds in the Environment

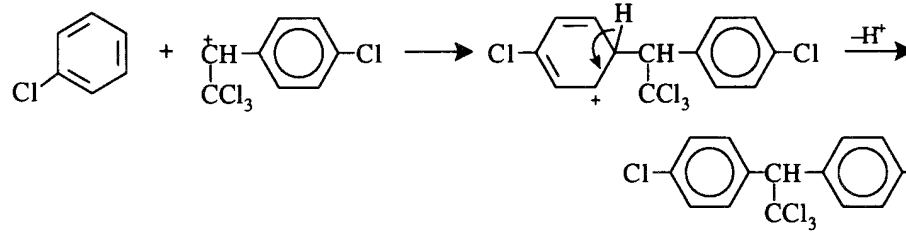
SOLUTIONS TO PROBLEMS

H.1



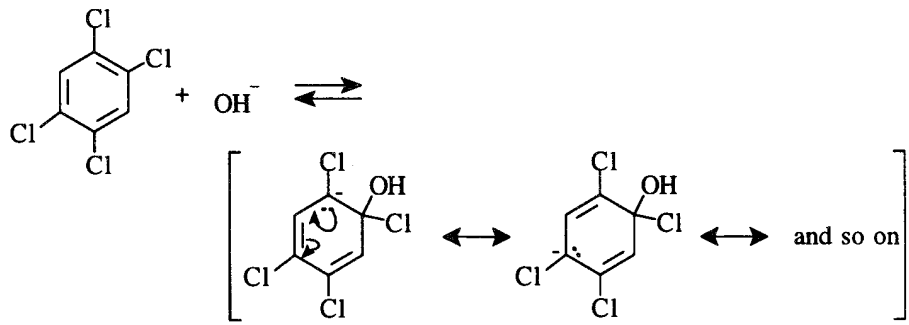




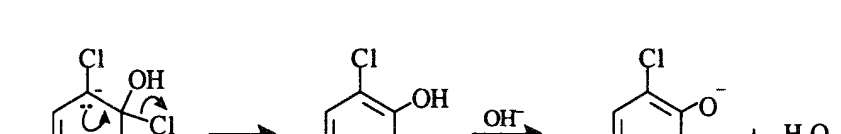


H.2 An elimination reaction.

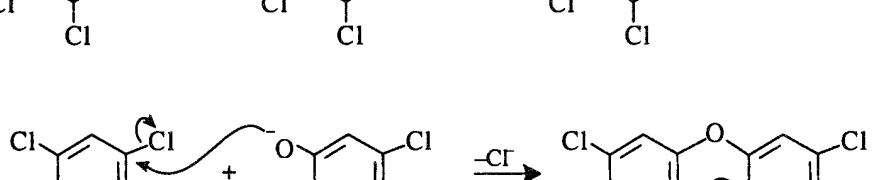
H.3 (a)



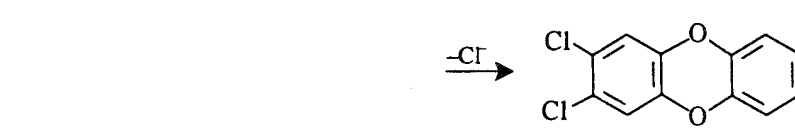
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(b)



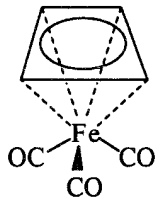
H.4 An S_N2 reaction:



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SOLUTIONS TO PROBLEMS

I.1



Cyclobutadiene iron tricarbonyl

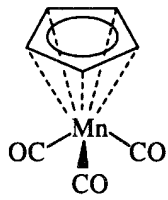
d^n = (Total number of valence electrons (both *s* and *d* electrons) of elemental iron) − (oxidation state of the metal in the complex)

$d^n = 8 - 0 = 8$

(Total number of valence electrons of iron in the complex) = (d^n + electrons donated by ligands)

= 8 + 3(CO) + cyclobutadiene

= 8 + 3(2) + 4 = 18



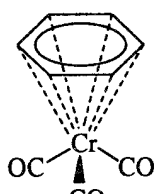
Cyclopentadienylmanganese tricarbonyl

$d^n = 7 - 1 = 6$

(Total number of valence electrons of Mn in complex) = 6 + 3(CO) + Cp

= 6 + 3(2) + 6 = 18

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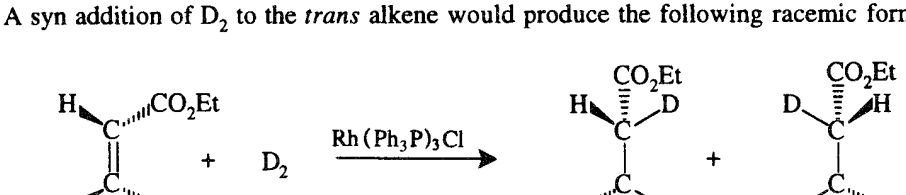
Benzene chromium tricarbonyl

$d^n = 6 - 0 = 6$

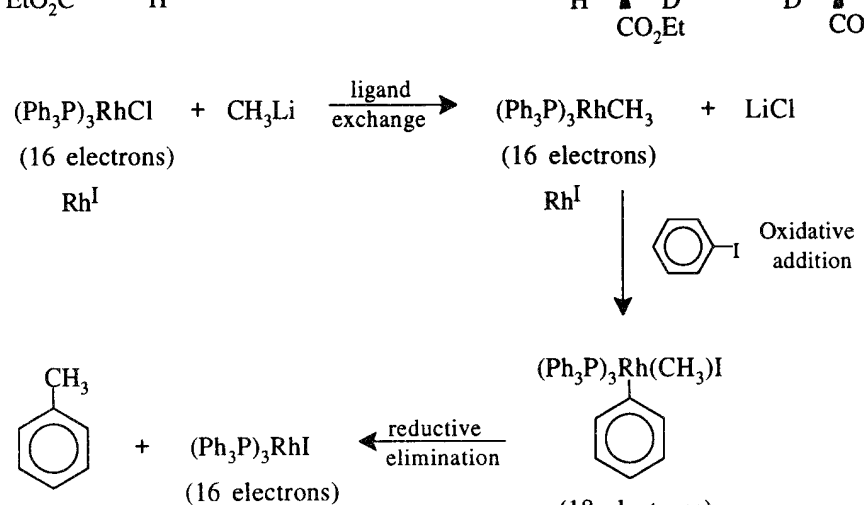
Total number of valence electrons of Cr in complex = 6 + 3(CO) + benzene

= 6 + 3(2) + 6 = 18

I.2 A syn addition of D_2 to the *trans* alkene would produce the following racemic form.

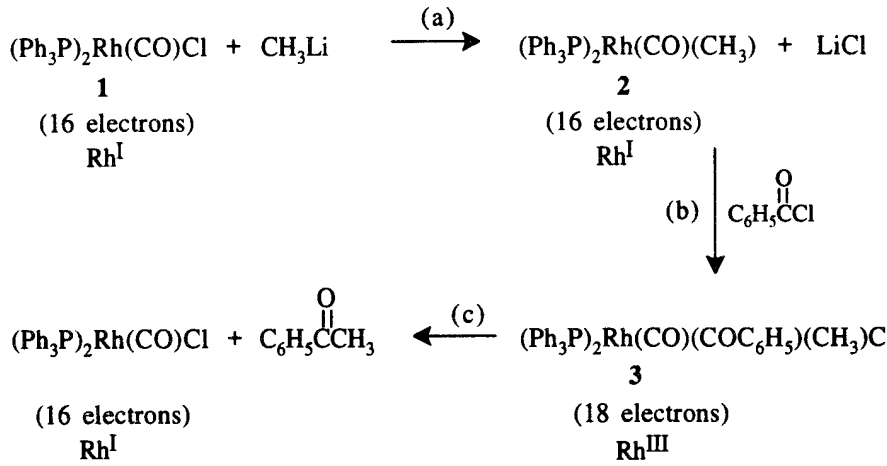


I.3



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I.4



(a) Is a ligand exchange

(b) Is an oxidative addition

(c) Is a reductive elimination

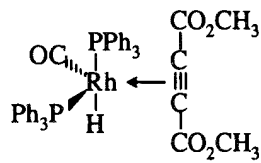
I.5

1. $(Ph_3P)_3Rh(CO)H \xrightarrow{-Ph_3P} (Ph_3P)_2Rh(CO)H$ **Ligand dissociation**

   (18 electrons, Rh^I) (16 electrons, Rh^I)

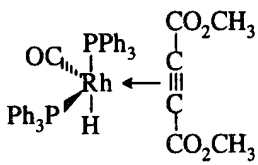
2. $(Ph_3P)_2Rh(CO)H \xrightarrow{CH_3OCC{\equiv}CCOCH_3}$ **Ligand association**

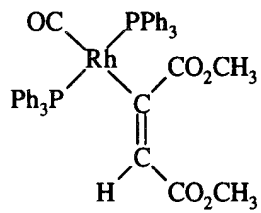
   (16 electrons, Rh^I)



(18 electrons, Rh^I)

3. **Insertion**

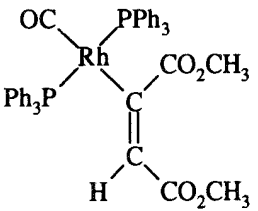




(18 electrons, Rh^I)

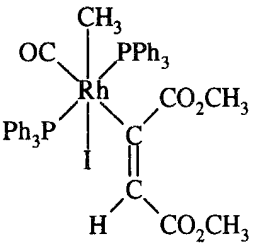
(16 electrons, Rh^I)

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4. 

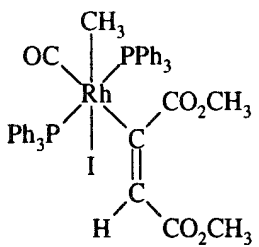
(16 electrons, Rh^{I})

CH3–I

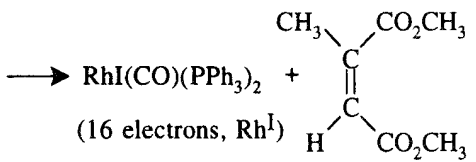


(18 electrons, Rh^{III})

Oxidative addition

5. 

(18 electrons, Rh^{III})



(16 electrons, Rh^{I})

Reductive elimination

I.6 

Oxidative addition

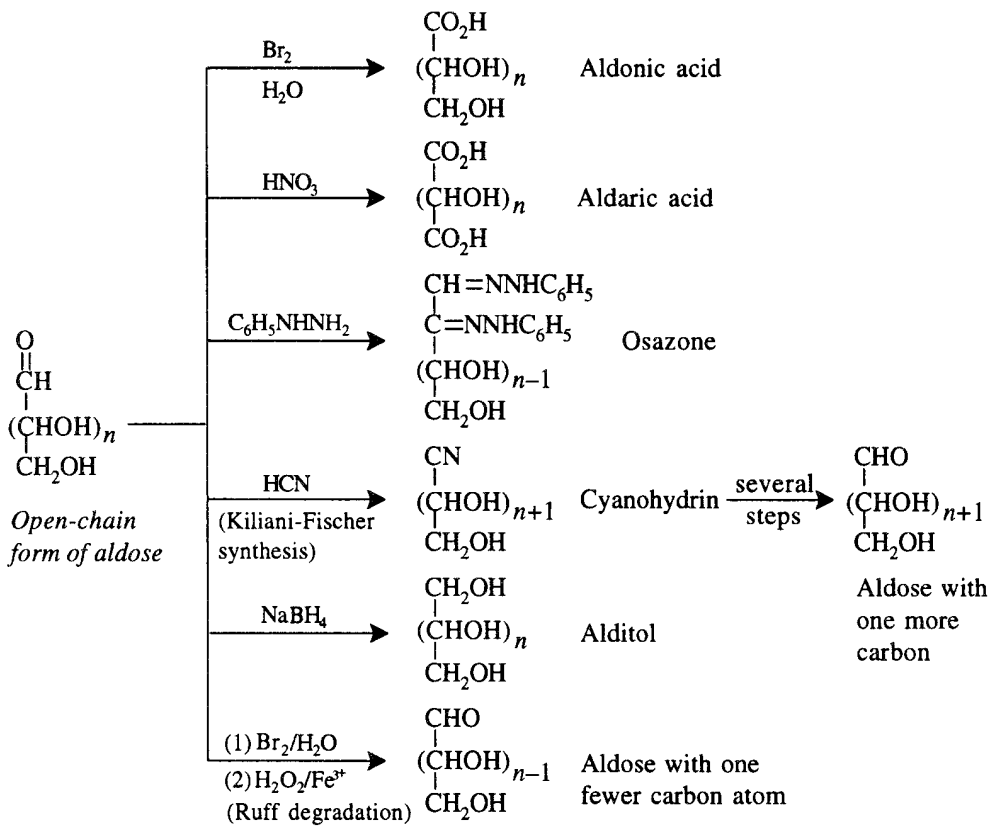


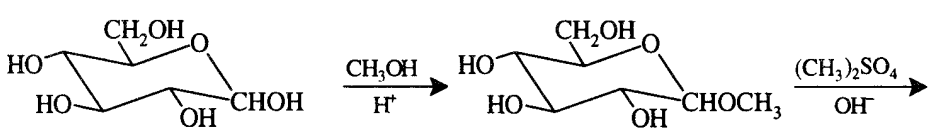
Reductive elimination

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22 CARBOHYDRATES

SUMMARY OF SOME REACTIONS OF MONOSACCHARIDES

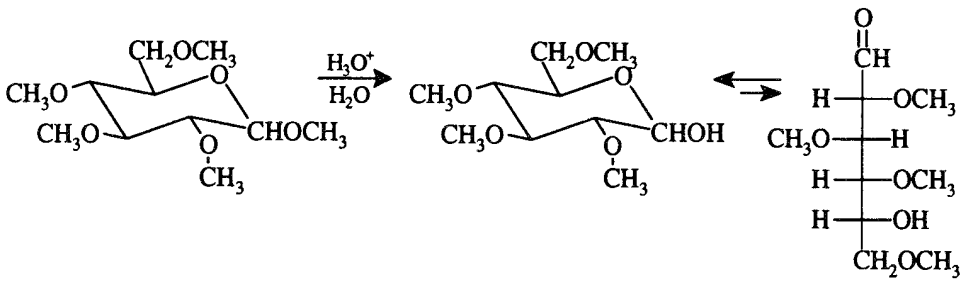




Cyclic form of D-glucose

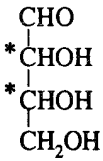
Methyl glucoside

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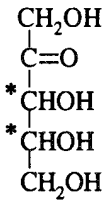


SOLUTIONS TO PROBLEMS

22.1 (a) Two,

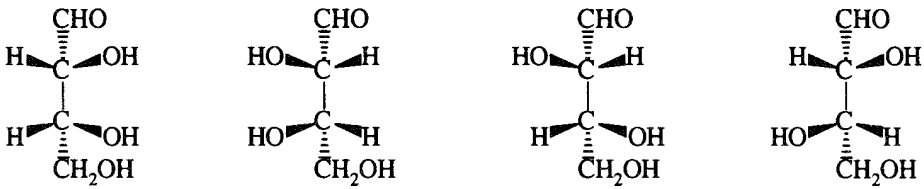


(b) Two,

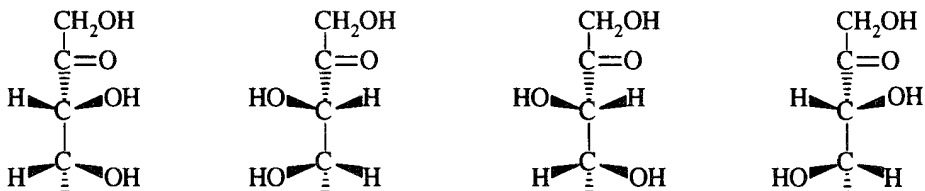


(c) There would be four stereoisomers (two sets of enantiomers) with each general structure: $2^2 = 4$.

22.2



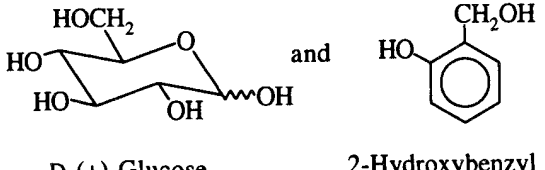
D L D L



D L D L

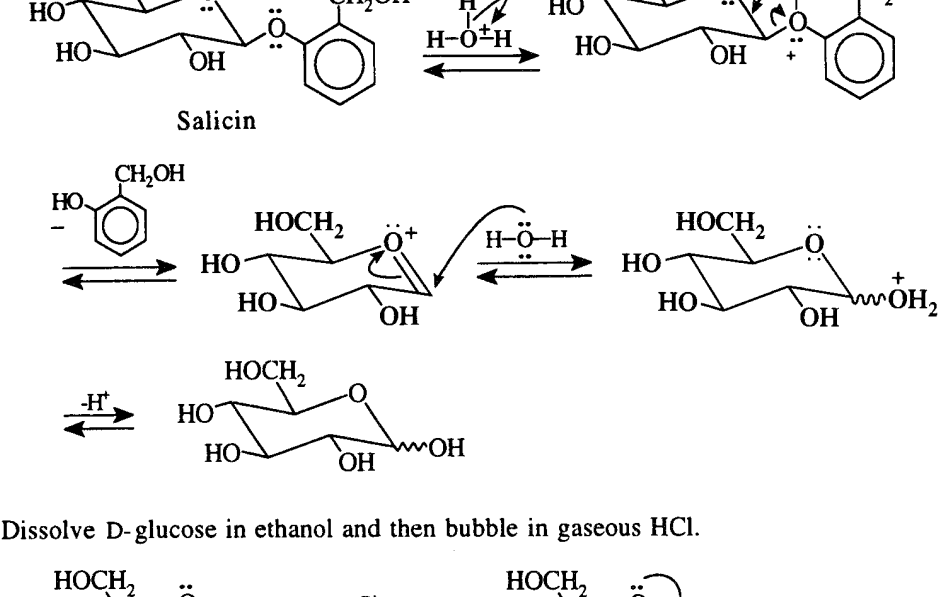
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22.3 (a)



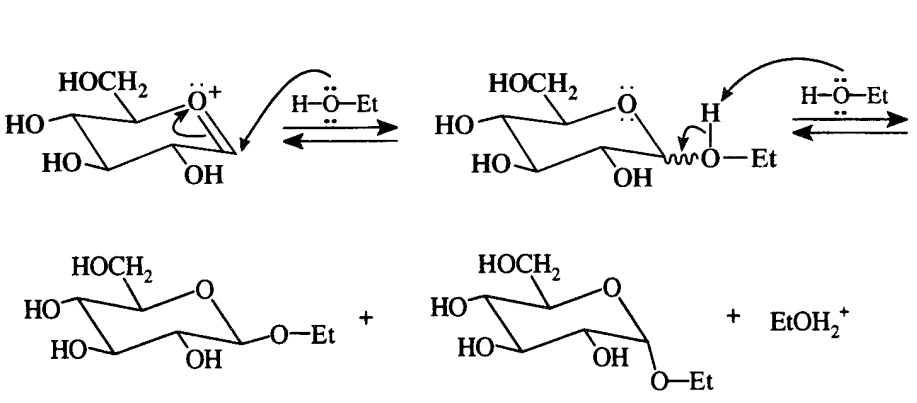
D-(+)-Glucose and 2-Hydroxybenzyl alcohol

(b)



Salicin

22.4 Dissolve D-glucose in ethanol and then bubble in gaseous HCl.



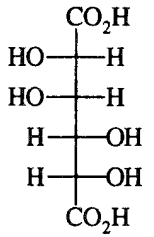
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22.5 Since glycosides are acetals, they undergo hydrolysis in aqueous acid to form cyclic hemiacetals that then undergo mutarotation.

22.6 α-D-Glucopyranose will give a positive test with Benedict's or Tollens' solution because it is a cyclic hemiacetal. Methyl α-D-glucopyranoside, because it is a cyclic acetal, will not.

22.7 (a) Yes

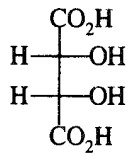
(b)



D-Mannaric acid

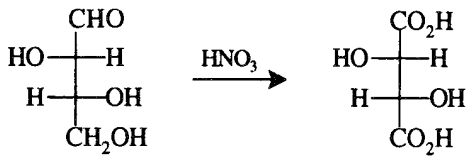
(c) Yes

(d)



(e) No

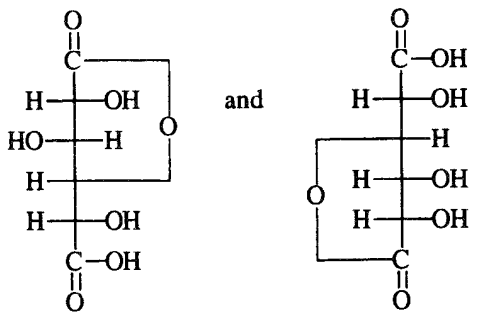
(f)



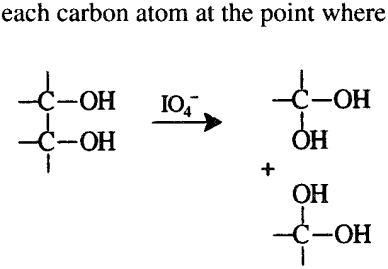
D-Threose D-Tartaric acid

(g) The aldaric acid obtained from D-erythrose is *meso*-tartaric acid; the aldaric acid obtained from D-threose is D-tartaric acid.

22.8

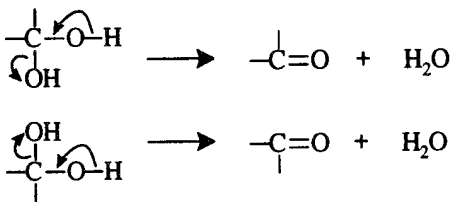


22.9 One way of predicting the products from a periodate oxidation is to place an –OH group on each carbon atom at the point where C–C bond cleavage has occurred:

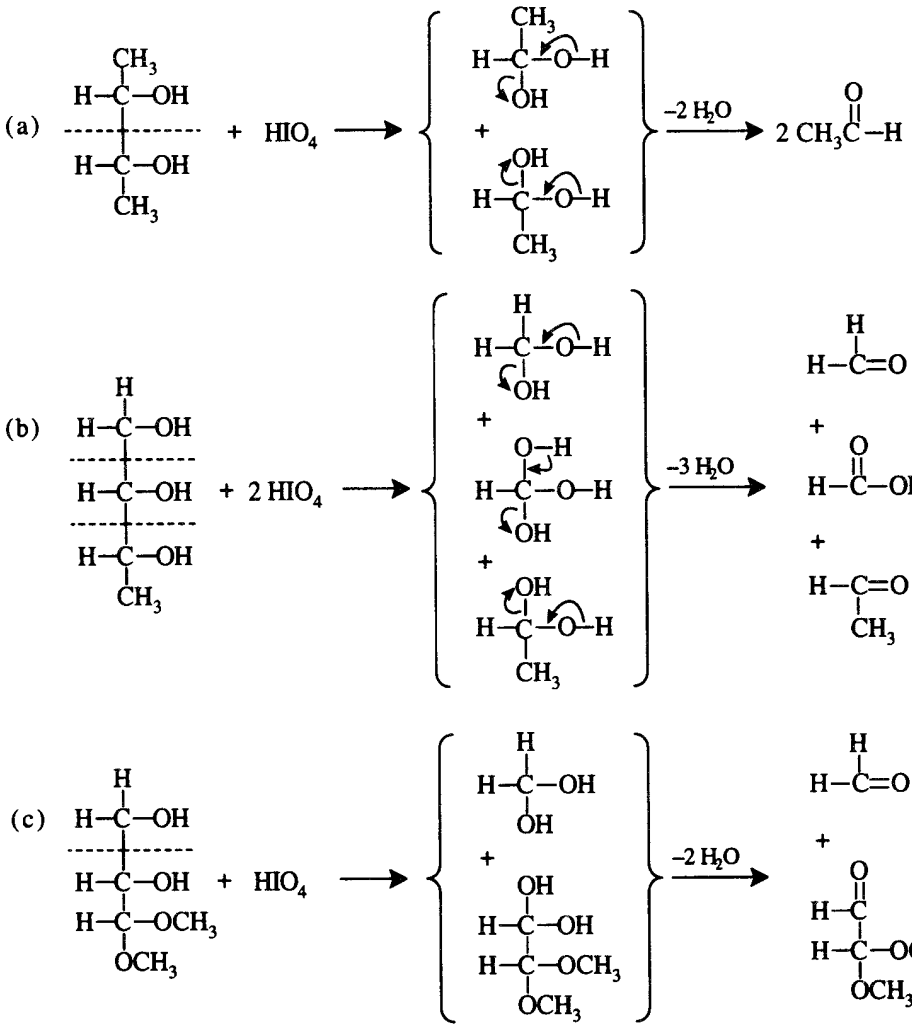


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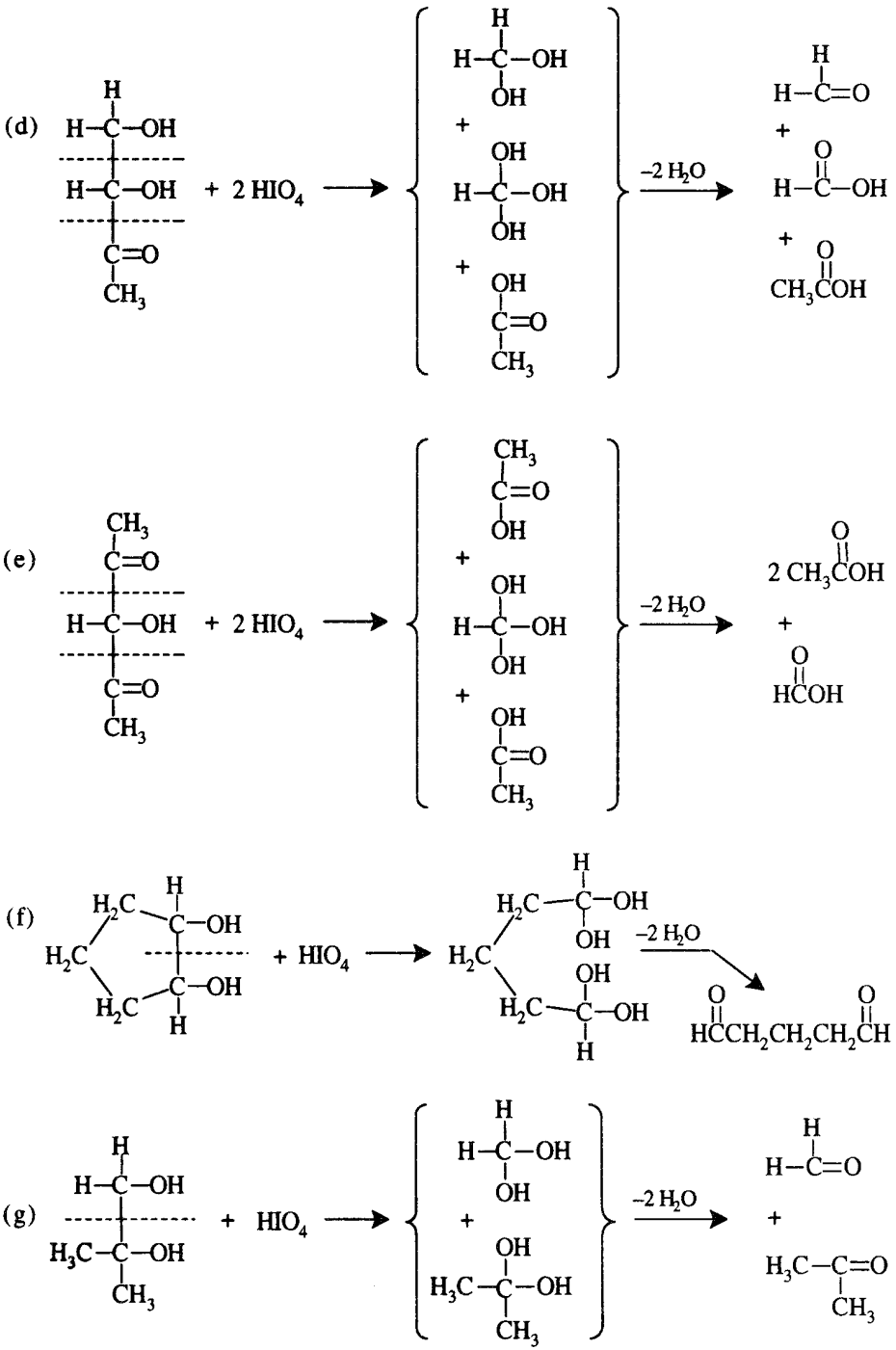
Then if we recall (Section 16.7A) that *gem*-diols are usually unstable and lose water to produce carbonyl compounds, we get the following results:



Let us apply this procedure to several examples here while we remember that for every C–C bond that is broken 1 mol of HIO_4 is consumed.

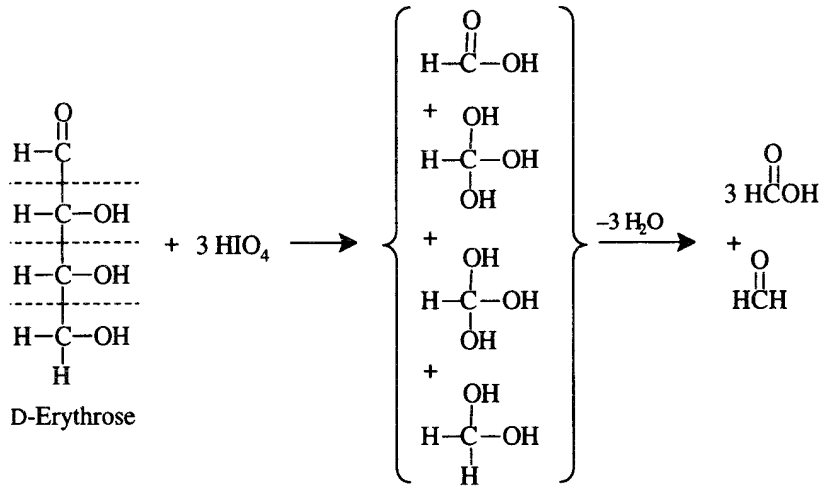


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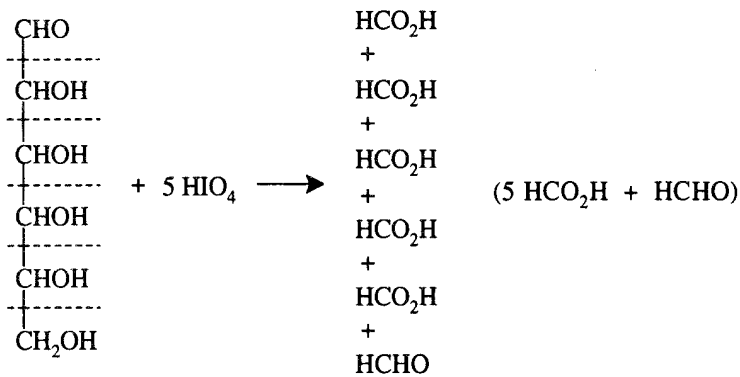


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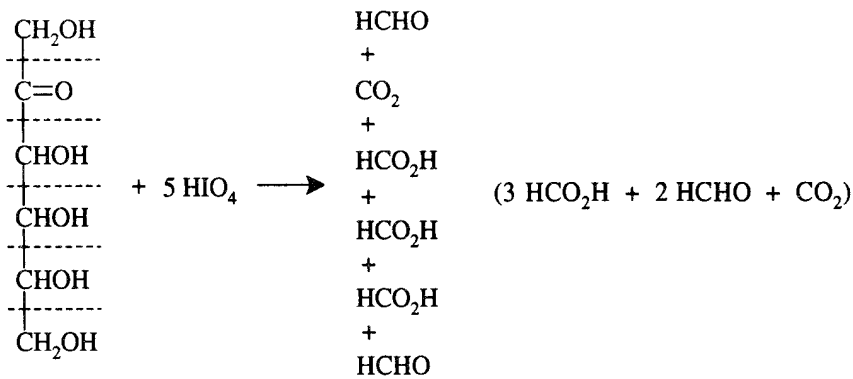
(h)



22.10 Oxidation of an aldohexose and a ketohexose would each require 5 mol of HIO_4 but would give different results.



Aldohexose

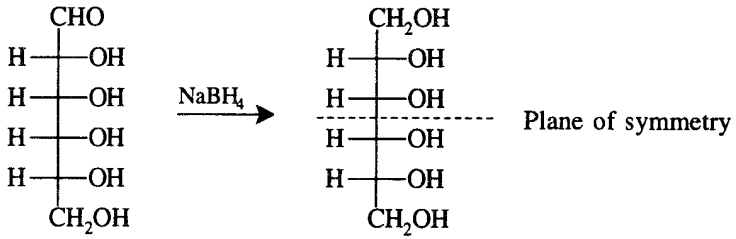


Ketohexose

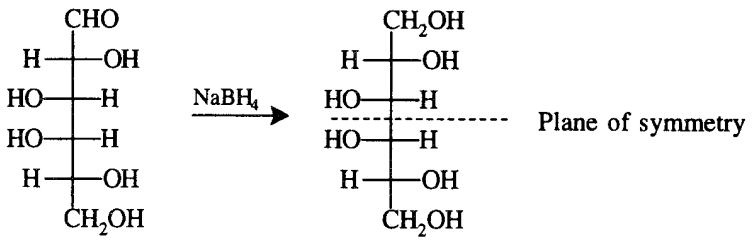
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22.11 (a) Yes, D-glucitol would be optically active; only those alditols whose molecules possess a plane of symmetry would be optically inactive.

(b)

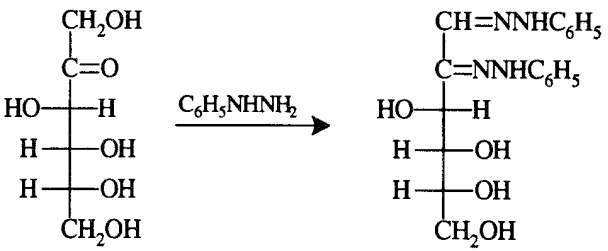


Optically inactive



Optically inactive

22.12 (a)



(b) This experiment shows that D-glucose and D-fructose have the same configurations at C3, C4, and C5.

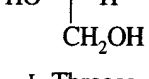
22.13 (a)



L-Erythrose

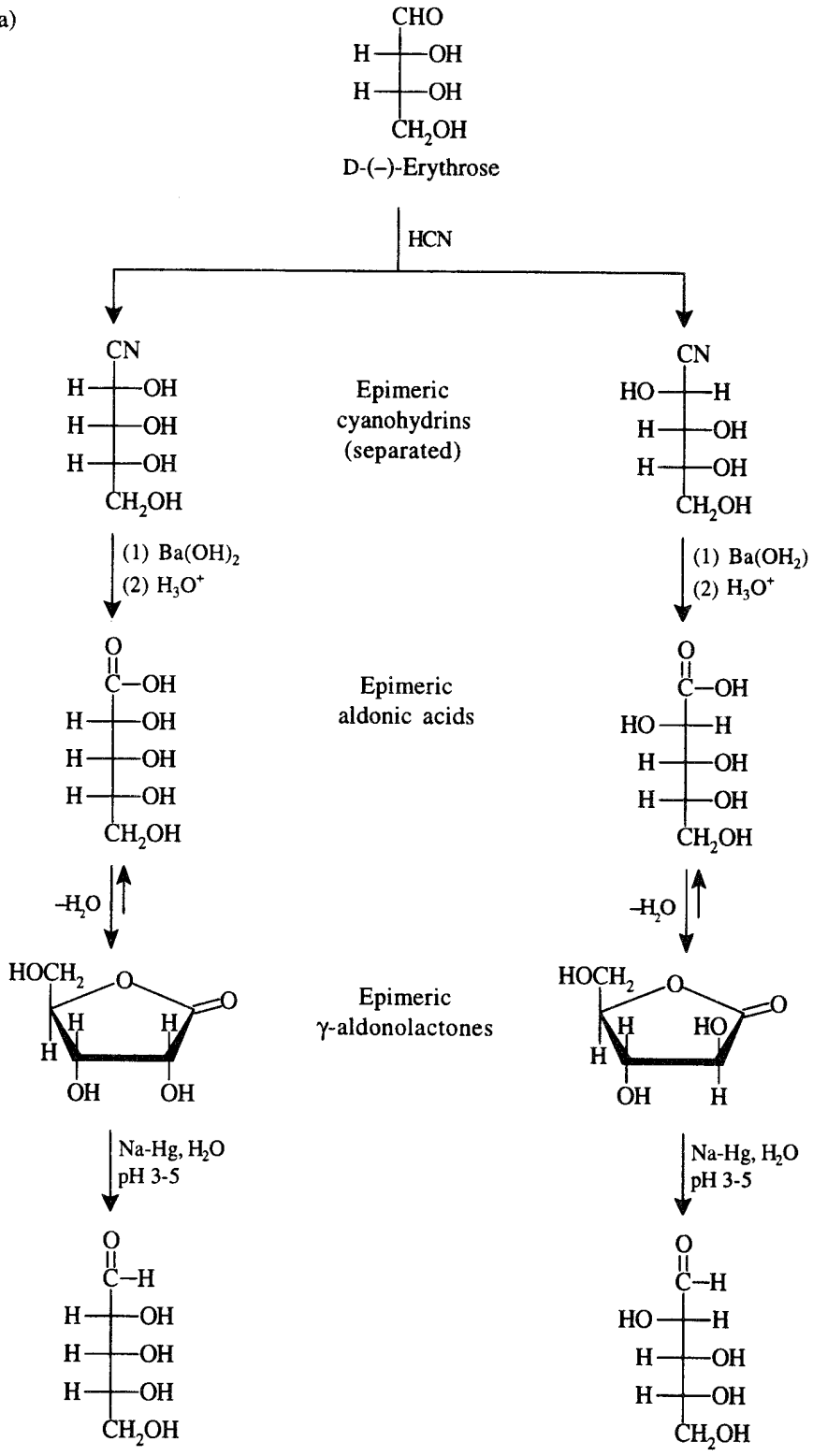
L-Threose

(b) L-Glyceraldehyde



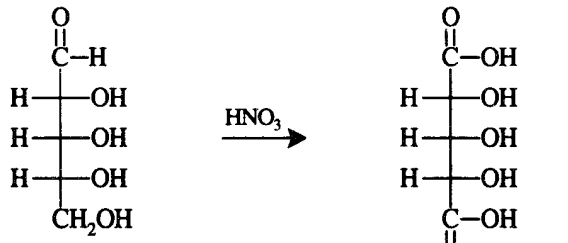
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22.14 (a)



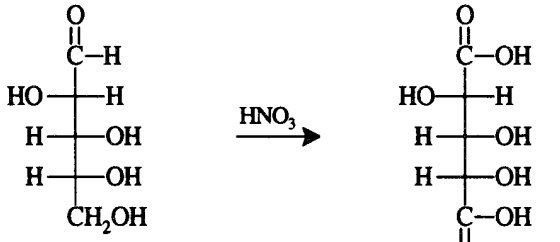
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(b)



D-(–)-Ribose

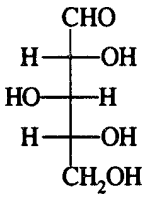
Optically inactive



D-(–)-Arabinose

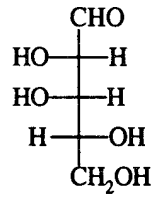
Optically active

22.15 A Kiliani-Fischer synthesis starting with D-(−)-threose would yield **I** and **II**.



I

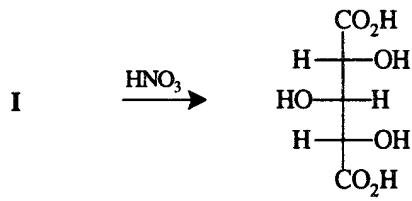
D-(+)-Xylose



II

D-(–)-Lyxose

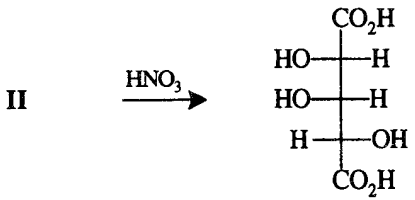
I must be D-(+)-xylose because, when oxidized by nitric acid, it yields an optically inactive aldaric acid:



Optically inactive

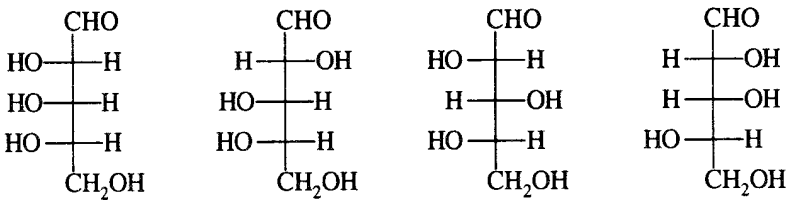
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II must be D-(−)-lyxose because, when oxidized by nitric acid, it yields an optically active aldaric acid:



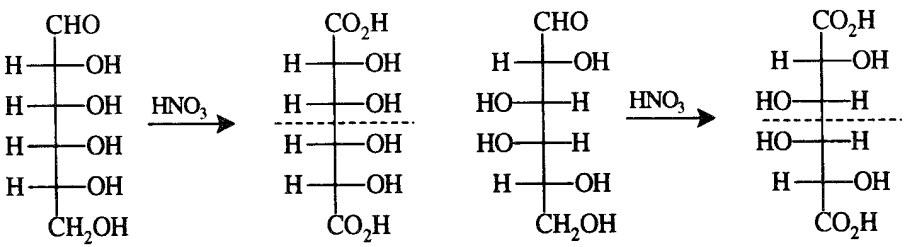
Optically active

22.16



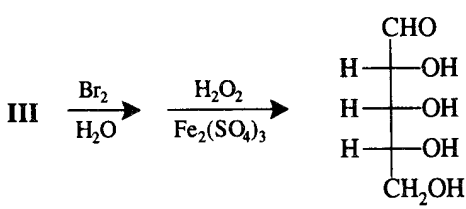
L-(+)-Ribose L-(+)-Arabinose L-(−)-Xylose L-(+)-Lyxose

22.17 Since D-(+)-galactose yields an optically inactive aldaric acid, it must have either structure **III** or structure **IV**.



III Optically inactive **IV** Optically inactive

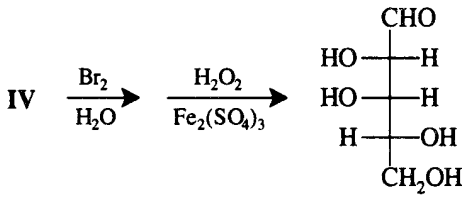
A Ruff degradation beginning with **III** would yield D-(−)-ribose



D-(−)-Ribose

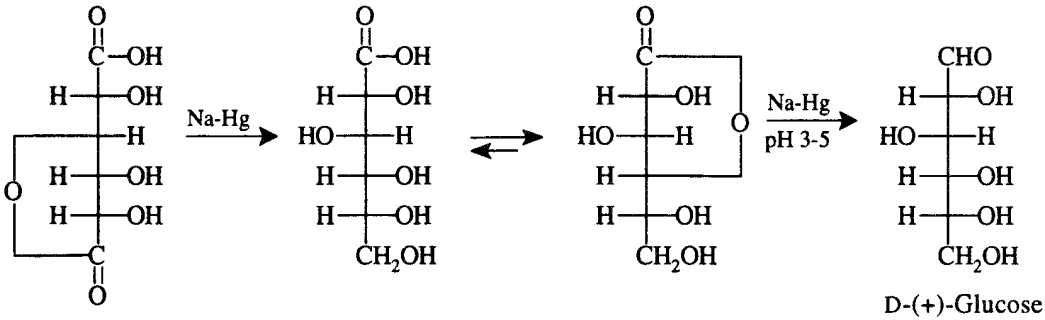
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A Ruff degradation beginning with **IV** would yield D-(−)-lyxose: thus, D-(+)-galactose must have structure **IV**.



D-(−)-Lyxose

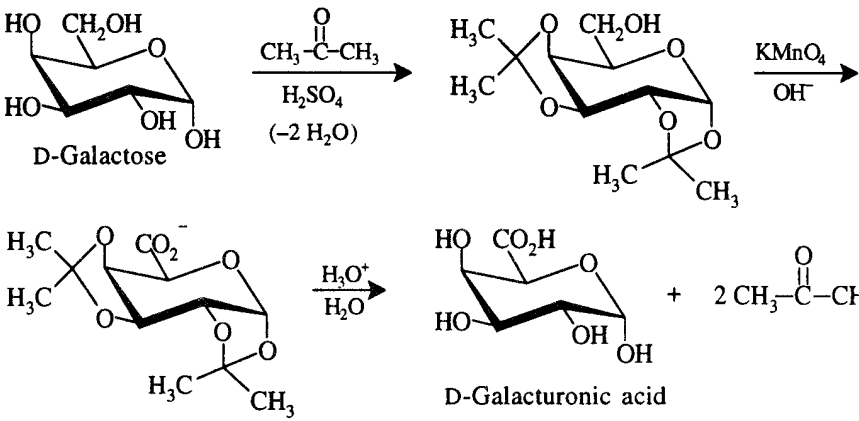
22.18 D-(+)-glucose, as shown here.



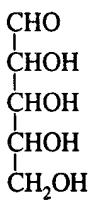
The other γ-lactone of D-glucaric acid

D-(+)-Glucose

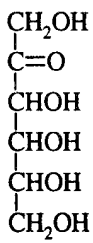
22.19



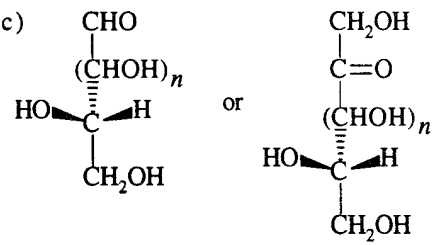
22.20 (a)



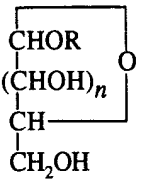
(b)

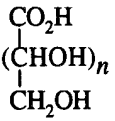


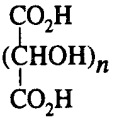
(c)

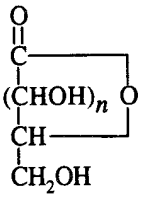


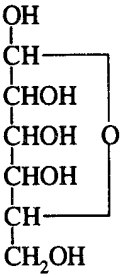
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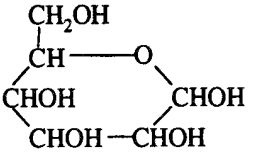
(d) 

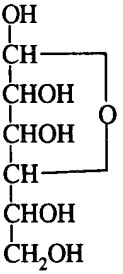
(e) 

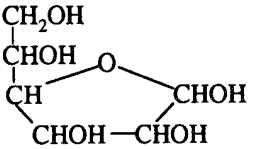
(f) 

(g) 

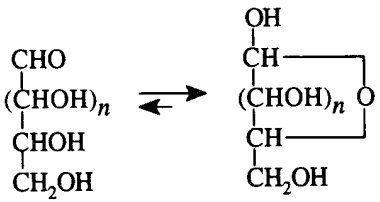
(h) 

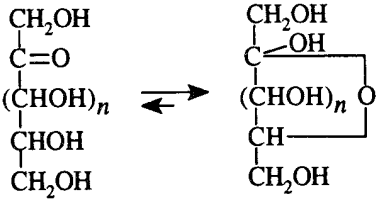
or 

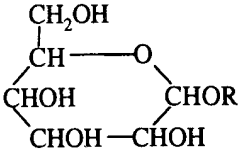
(i) 

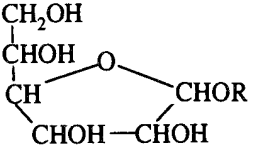
or 

(j) Any sugar that has a free aldehyde or ketone group or one that exists as a cyclic hemiacetal. The following are examples:



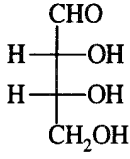
or 

(k) 

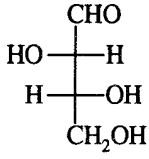
(l) 

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(m) Any two aldoses that differ only in configuration at C2. (See also Section 22.8 for a broader definition.) D-Erythrose and D-threose are examples.

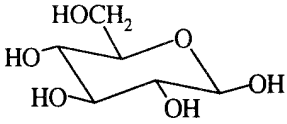


D-Erythrose

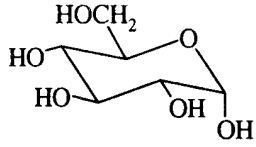


D-Threose

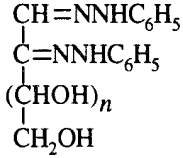
(n) Cyclic sugars that differ only in the configuration of C1. The following are examples:



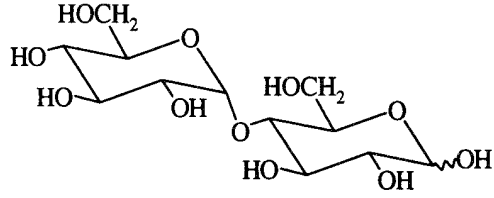
and



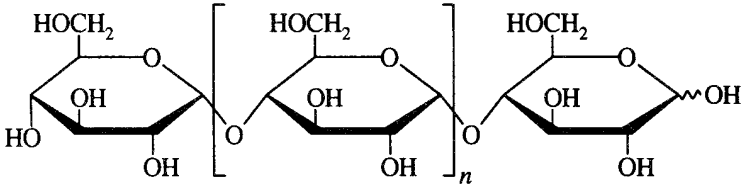
(o)



(p) Maltose is an example:

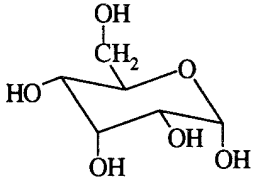


(q) Amylose is an example:

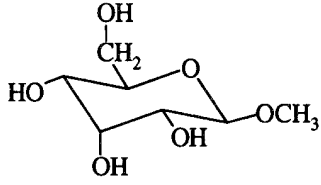


(r) Any sugar in which all potential carbonyl groups are present as acetals (i.e., as glycosides). Sucrose (Section 22.12A) is an example of a nonreducing disaccharide; the methyl D-glucopyranosides (Section 22.4) are examples of nonreducing monosaccharides.

22.21 (a)

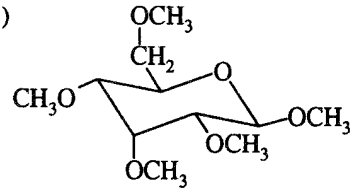


(b)

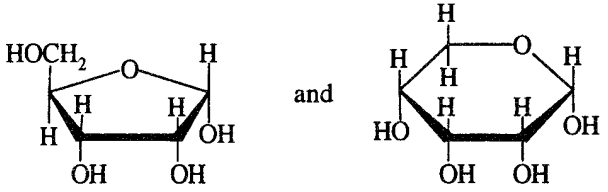


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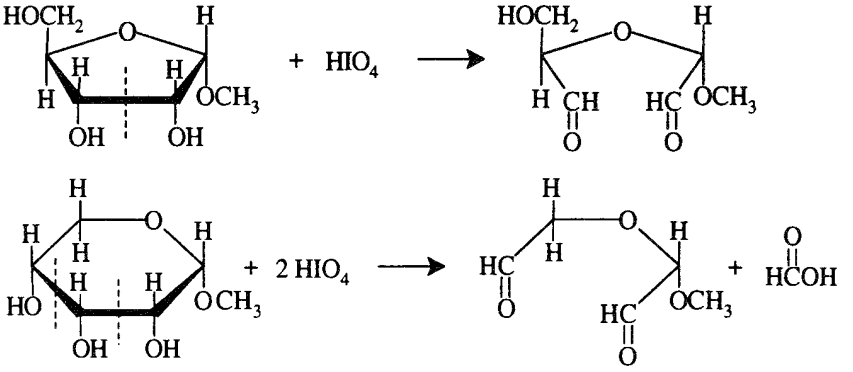
(c)



22.22 (a)



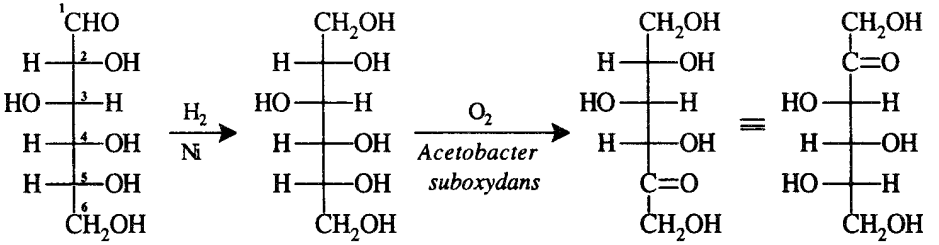
(b)



A methyl ribofuranoside would consume only 1 mol of HIO_4; a methyl ribopyranoside would consume 2 mol of HIO_4 and would also produce 1 mol of formic acid.

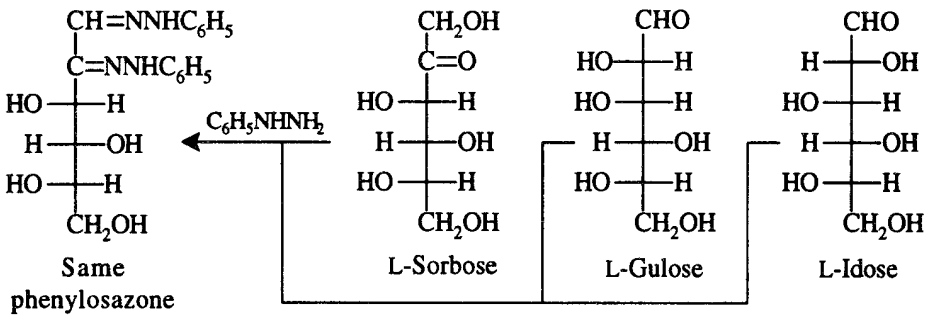
22.23 One anomer of D-mannose is dextrorotatory ($[\alpha]_D^{25} = +29.3°$); the other is levorotatory ($[\alpha]_D^{25} = -17.0°$).

22.24 The microorganism selectively oxidizes the –CHOH group of D-glucitol that corresponds to C5 of D-glucose.

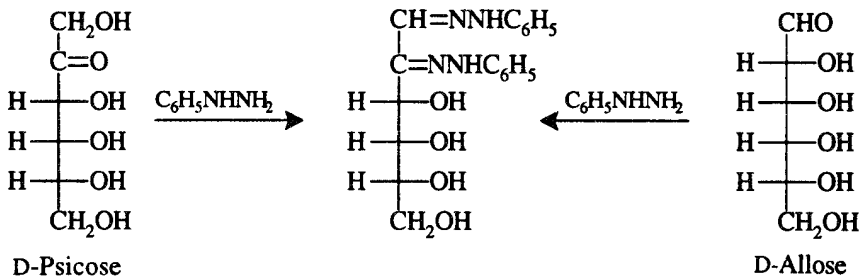


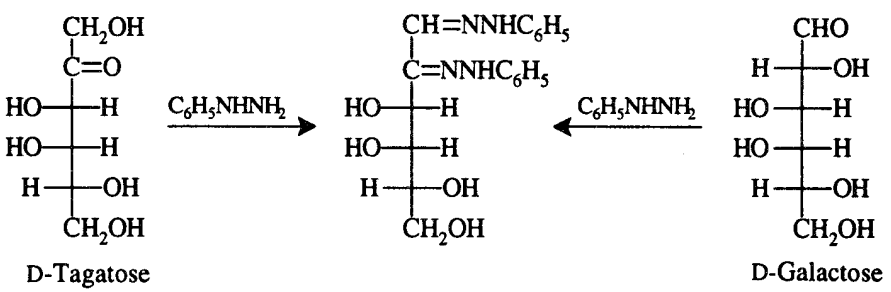
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22.25 L-Gulose and L-idose would yield the same phenylosazone as L-sorbose.

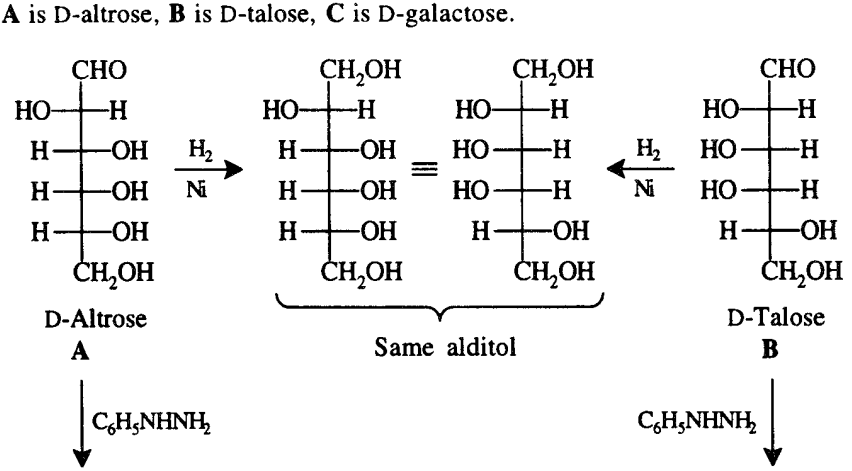


22.26

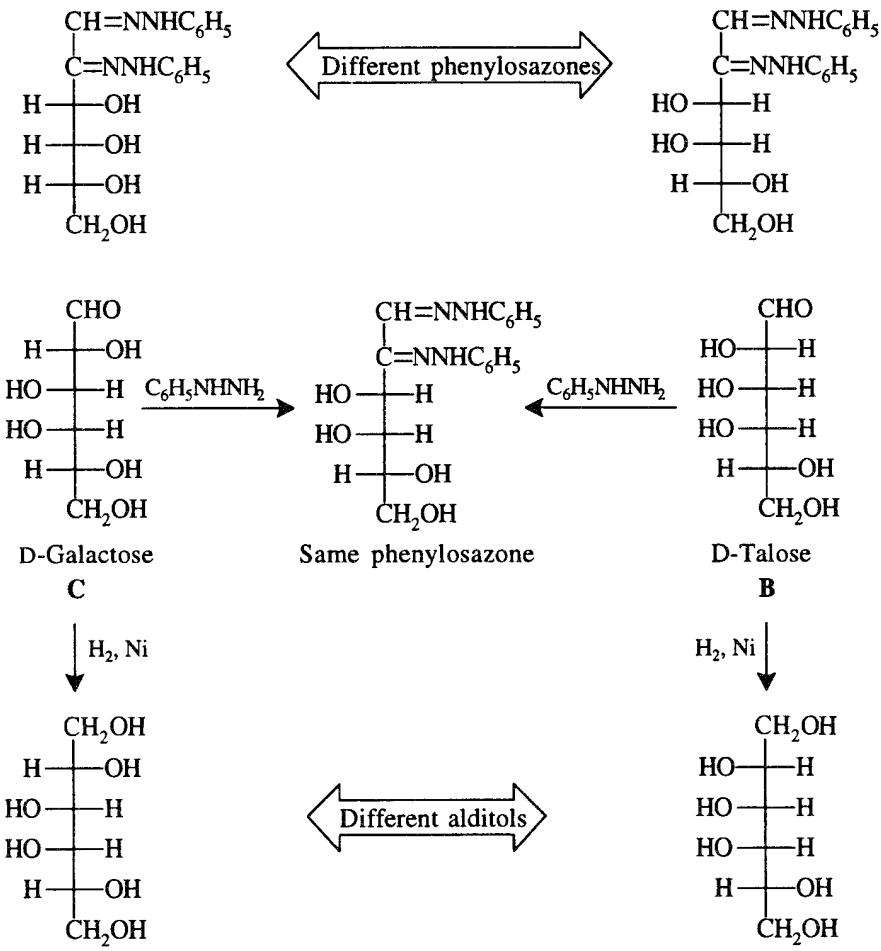




22.27 **A** is D-altrose, **B** is D-talose, **C** is D-galactose.

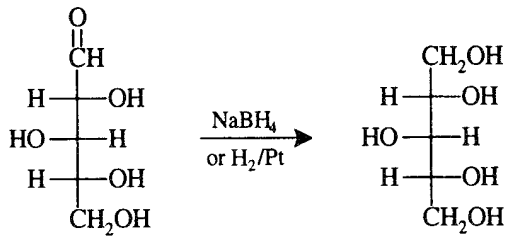


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(*Note*: If we had designated D-talose as **A**, and D-altrose as **B**, then **C** is D-allose).

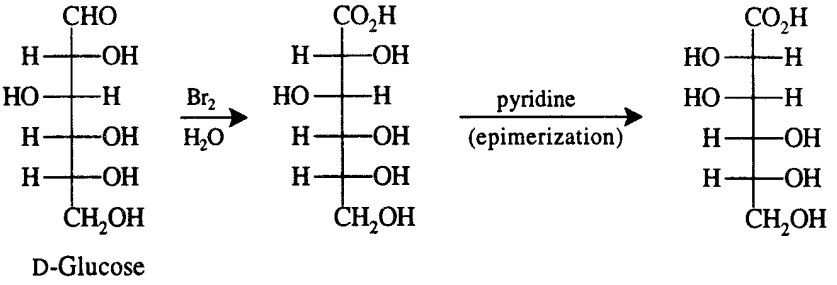
22.28



D-Xylose D-Xylitol

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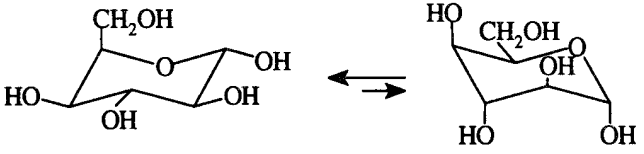
22.29



D-Glucose

D-Mannose

22.30 The conformation of D-idopyranose with four equatorial –OH groups and an axial $-CH_2OH$ group is more stable than the one with four axial –OH groups and an equatorial $-CH_2OH$ group.



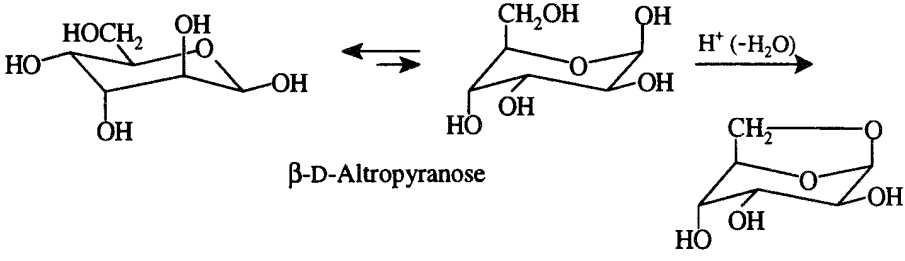
More stable

4 Equatorial –OH groups
1 Axial $-CH_2OH$ group

Less stable

4 Axial –OH groups
1 Equatorial $-CH_2OH$ group

22.31 (a) The anhydro sugar is formed when the axial $-CH_2OH$ group reacts with C1 to form a cyclic acetal.



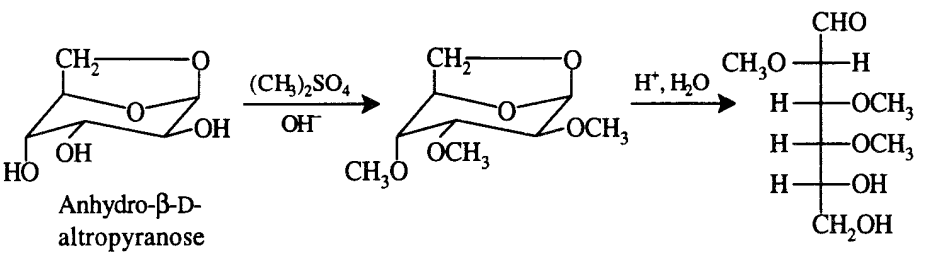
β-D-Altropyranose

Anhydro sugar

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Because the anhydro sugar is an acetal (i.e., an internal glycoside), it is a nonreducing sugar.

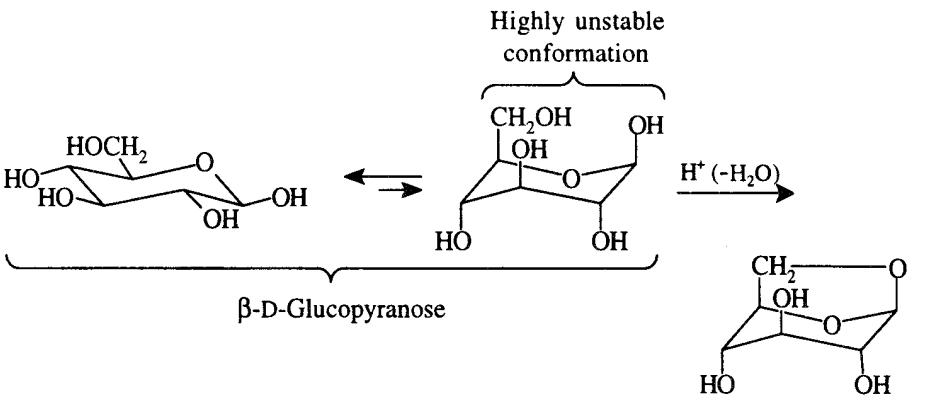
Methylation followed by acid hydrolysis converts the anhydro sugar to 2,3,4-tri-*O*-methyl-D-altrose:



Anhydro-β-D-altropyranose

2,3,4-Tri-*O*-methyl-D-altrose

(b) Formation of an anhydro sugar requires that the monosaccharide adopt a chair conformation with the $-CH_2OH$ group axial. With β-D-altropyranose this requires that two –OH groups be axial as well. With β-D-glucopyranose, however, it requires that all four –OH groups become axial and thus that the molecule adopt a very unstable conformation:



β-D-Glucopyranose

Anhydro-β-D-glucopyranose

22.32 1. The molecular formula and the results of acid hydrolysis show that lactose is a disaccharide composed of D-glucose and D-galactose. The fact that lactose is hydrolyzed by a *β-galactosidase* indicates that galactose is present as a glycoside and that the glycosidic linkage is beta to the galactose ring.

2. That lactose is a reducing sugar, forms a phenylosazone, and undergoes mutarotation indicates that one ring (presumably that of D-glucose) is present as a hemiacetal and thus is capable of existing to a limited extent as an aldehyde.

3. This experiment confirms that the D-glucose unit is present as a cyclic hemiacetal and that the D-galactose unit is present as a cyclic glycoside.

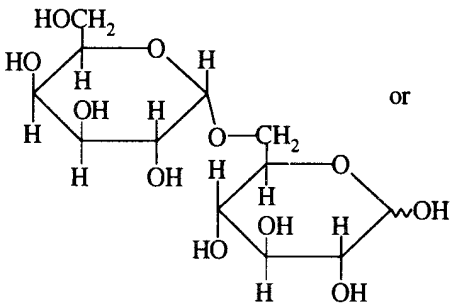
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4. That 2,3,4,6-tetra-*O*-methyl-D-galactose is obtained in this experiment indicates (by virtue of the free –OH at C5) that the galactose ring of lactose is present as a pyranoside. That the methylated gluconic acid obtained from this experiment has a free –OH group at C4 indicates that the C4 oxygen atom of the glucose unit is connected in a glycosidic linkage to the galactose unit.

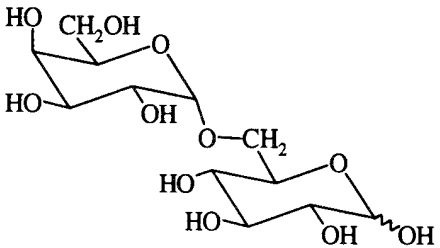
Now only the size of the glucose ring remains in question, and the answer to this is provided by experiment 5.

5. That methylation of lactose and subsequent hydrolysis gives 2,3,6-tri-*O*-methyl-D-glucose—that it gives a methylated glucose derivative with a free –OH at C4 and C5—demonstrates that the glucose ring is present as a pyranose. (We know already that the oxygen at C4 is connected in a glycosidic linkage to the galactose unit; thus, a free –OH at C5 indicates that the C5 oxygen atom is a part of the hemiacetal group of the glucose unit and that the ring is six membered.)

22.33



or



6-*O*-(α-D-Galactopyranosyl)-D-glucopyranose

We arrive at this conclusion from the data given:

1. That melibiose is a reducing sugar and that it undergoes mutarotation and forms a phenylosazone indicate that one monosaccharide is present as a cyclic hemiacetal.

2. That acid hydrolysis gives D-galatose and D-glucose indicates that melibiose is a disaccharide composed of one D-galactose unit and one D-glucose unit. That melibiose is hydrolyzed by an α-galactosidase suggests that melibiose is an α-D-galactosyl-D-glucose.

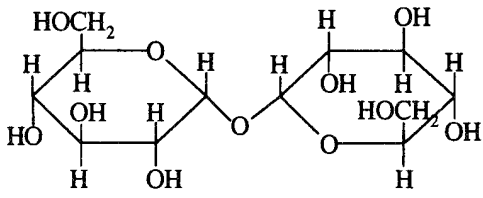
3. Oxidation of melibiose to melibionic acid and subsequent hydrolysis to give D-galactose and D-gluconic acid confirms that the glucose unit is present as a cyclic hemiacetal and that the galactose unit is present as a glycoside. (Had the reverse been true, this experiment would have yielded D-glucose and D-galactonic acid.)

Methylation and hydrolysis of melibionic acid produces 2,3,4,6-tetra-*O*-methyl-D-galactose and 2,3,4,5-tetra-*O*-methyl-D-gluconic acid. Formation of the first product—a galactose derivative with a free –OH at C5—demonstrates that the galactose ring is six membered; formation of the second product—a gluconic acid derivative with a free –OH at C6—demonstrates that the oxygen at C6 of the glucose unit is joined in a glycosidic linkage to the galactose unit.

4. That methylation and hydrolysis of melibiose gives a glucose derivative (2,3,4-tri-*O*-methyl-D-glucose) with free –OH groups at C5 and C6 shows that the glucose ring is also six membered. Melibiose is, therefore, 6-*O*-(α-D-galactopyranosyl-D-glucopyranose.

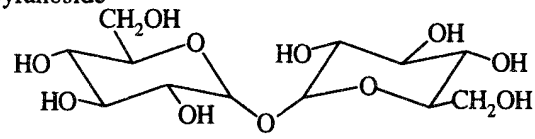
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22.34 Trehalose has the following structure:



or

α-D-Glucopyranosyl-α-D-glucopyranoside



We arrive at this structure in the following way:

1. Acid hydrolysis shows that trehalose is a disaccharide consisting only of D-glucose units.

2. Hydrolysis by α-glucosidases and not by β-glucosidases shows that the glycosidic linkages are alpha.

3. That trehalose is a nonreducing sugar, that it does not form a phenylosazone, and that it does not react with bromine water indicate that no hemiacetal groups are present. This means that C1 of one glucose unit and C1 of the other must be joined in a glycosidic linkage. Fact 2 (just cited) indicates that this linkage is alpha to each ring.

4. That methylation of trehalose followed by hydrolysis yields only 2,3,4,6-tetra-*O*-methyl-D-glucose demonstrates that both rings are six membered.

22.35 (a) Tollens' reagent or Benedict's reagent will give a positive test with D-glucose but will give no reaction with D-glucitol.

(b) D-Glucaric acid will give an acidic aqueous solution that can be detected with blue litmus paper. D-Glucitol will give a neutral aqueous solution.

(c) D-Glucose will be oxidized by bromine water and the red brown color of bromine will disappear. D-Fructose will not be oxidized by bromine water since it does not contain an aldehyde group.

(d) Nitric acid oxidation will produce an *optically active* aldaric acid from D-glucose but an *optically inactive* aldaric acid will result from D-galactose.

(e) Maltose is a reducing sugar and will give a positive test with Tollens' or Benedict's solution. Sucrose is a nonreducing sugar and will not react.

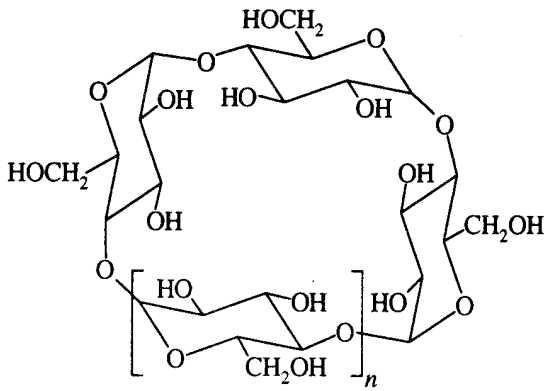
(f) Maltose will give a positive Tollens' or Benedict's test; maltonic acid will not.

(g) 2,3,4,6-Tetra-*O*-methyl-β-D-glucopyranose will give a positive test with Tollens' or Benedict's solution; methyl β-D-glucopyranoside will not.

(h) Periodic acid will react with methyl α-D-ribofuranoside because it has hydroxyl groups on adjacent carbons. Methyl 2-deoxy-α-D-ribofuranoside will not react.

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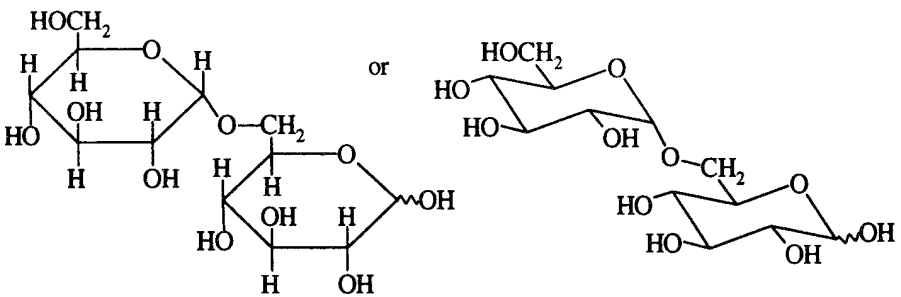
22.36 That the Schardinger dextrins are nonreducing shows that they have no free aldehyde or hemiacetal groups. This lack of reaction strongly suggests the presence of a *cyclic* structure. That methylation and subsequent hydrolysis yields only 2,3,6-tri-*O*-methyl-D-glucose indicates that the glycosidic linkages all involve C1 of one glucose unit and C4 of the next. That α-glucosidases cause hydrolysis of the glycosidic linkages indicates that they are α-glycosidic linkages. Thus, we are led to the following general structure.



n = 3, 4, or 5

Note: Schardinger dextrins are extremely interesting compounds. They are able to form complexes with a wide variety of compounds by incorporating these compounds in the cavity in the middle of the cyclic dextrin structure. Complex formation takes place, however, only when the cyclic dextrin and the guest molecule are the right size. Anthracene molecules, for example, will fit into the cavity of a cyclic dextrin with eight glucose units but will not fit into one with seven. For more information about these fascinating compounds, see Bergeron, R. J., "Cycloamyloses," *J. Chem. Educ.*, **1977,** *54,* 204–207.

22.37 Isomaltose has the following structure:



6-*O*-(α-D-Glucopyranosyl)-D-glucopyranose

(1) The acid and enzymic hydrolysis experiments tell us that isomaltose has two glucose units linked by an α linkage.

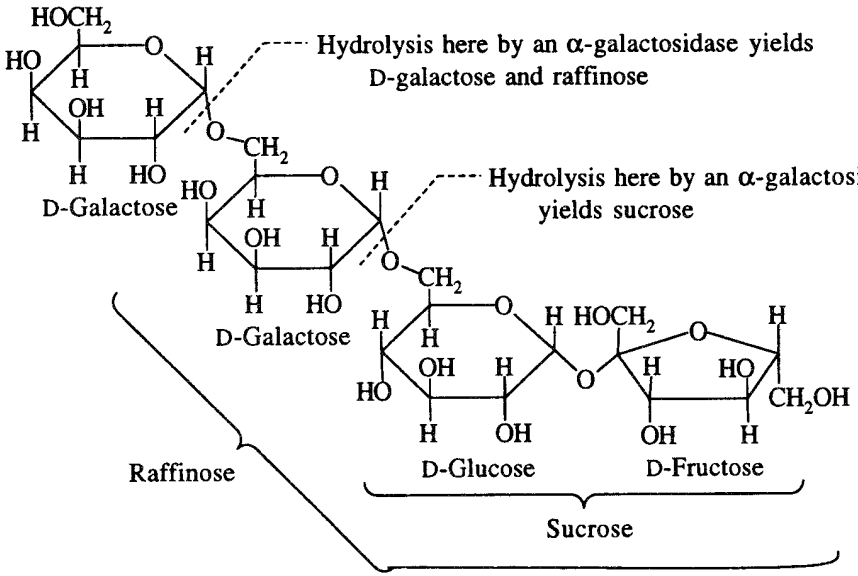
(2) That isomaltose is a reducing sugar indicates that one glucose unit is present as a cyclic hemiacetal.

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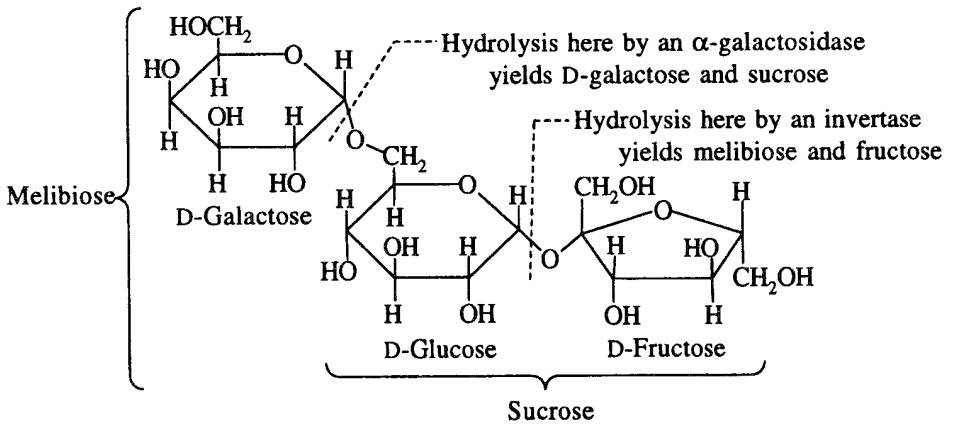
(3) Methylation of isomaltonic acid followed by hydrolysis gives us information about the size of the nonreducing pyranoside ring and about its point of attachment to the reducing ring. The formation of the first product (2,3,4,6-tetra-*O*-methyl-D-glucose)—a compound with an –OH at C5—tells us that the nonreducing ring is present as a pyranoside. The formation of 2,3,4,5-tetra-*O*-methyl-D-gluconic acid—a compound with an –OH at C6—shows that the nonreducing ring is linked to C6 of the reducing ring.

(4) Methylation of maltose itself tells the size of the reducing ring. That 2,3,4-tri-*O*-methyl-D-glucose is formed shows that the reducing ring is also six membered; we know this because of the free –OH at C5.

22.38 Stachyose has the following structure:



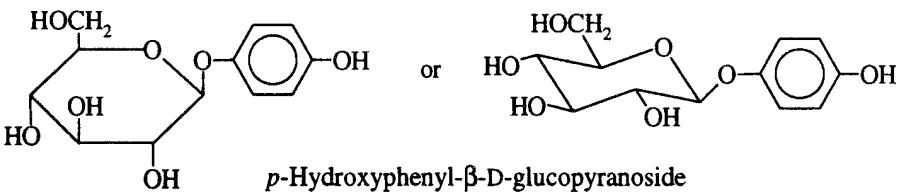
Raffinose has the following structure:



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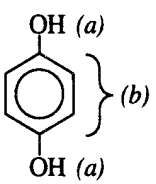
The enzymic hydrolyses (as just indicated) give the basic structure of stachyose and raffinose. The only remaining question is the ring size of the first galactose unit of stachyose. That methylation of stachyose and subsequent hydrolysis yields 2,3,4,6-tetra-*O*-methyl-D-galactose establishes that this ring is a pyranoside.

22.39 Arbutin has the following structure:



p-Hydroxyphenyl-β-D-glucopyranoside

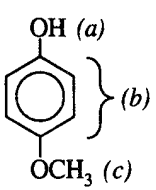
Compounds **X**, **Y**, and **Z** are hydroquinone, *p*-methoxyphenol, and *p*-dimethoxybenzene, respectively.



X

Hydroquinone

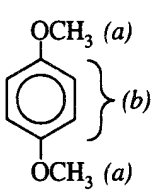
(a) Singlet δ 7.9 [2H]
(b) Singlet δ 6.8 [4H]



Y

p-Methoxyphenol

(a) Singlet δ 4.8 [1H]
(b) Multiplet δ 6.8 [4H]
(c) Singlet δ 3.9 [3H]



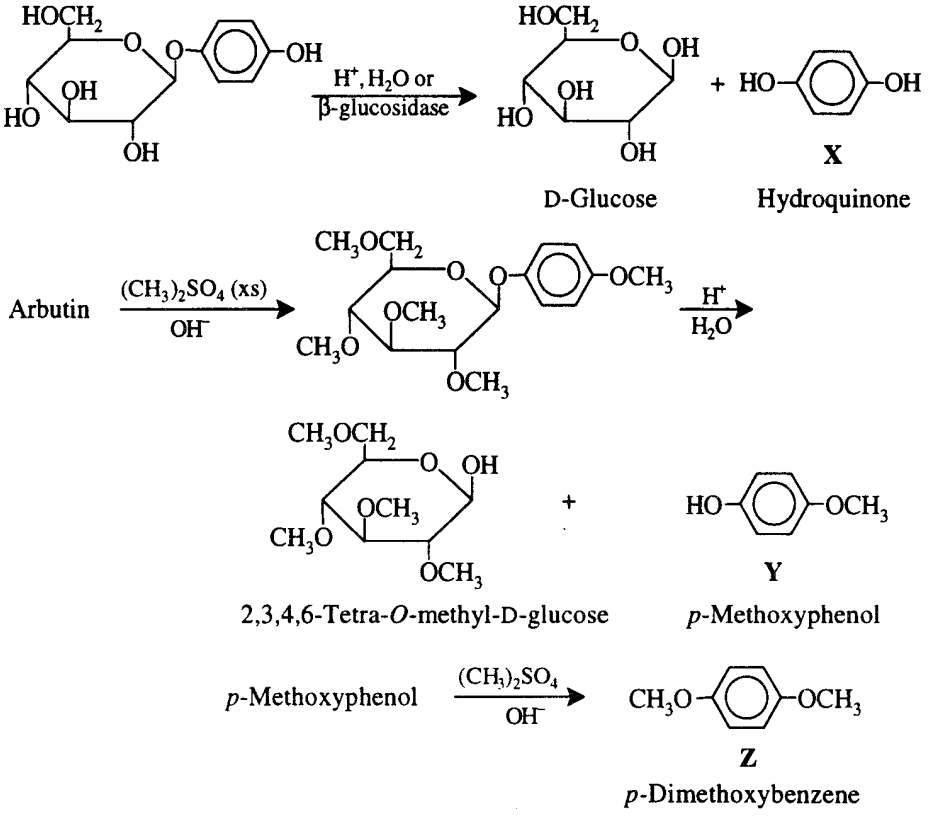
Z

p-Dimethoxybenzene

(a) Singlet δ 3.75 [6H]
(b) Singlet δ 6.8 [4H]

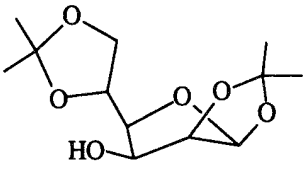
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The reactions that take place are the following:



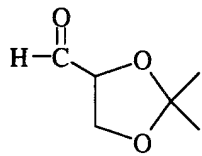
22.40 Aldotetrose **B** must be D-threose because the alditol derived from it (D-threitol) is optically active (the alditol from D-erythrose, the other possible D-aldotetrose, would be meso). Due to rotational symmetry, however, the alditol from **B** (D-threitol) would produce only two ^{13}C NMR signals. Compounds **A-F** are thus in the family of aldoses stemming from D-threose. Since reduction of aldopentose **A** produces an optically inactive alditol, **A** must be D-xylose. The two diastereomeric aldohexoses **C** and **D** produced from A by a Kiliani-Fischer synthesis must therefore be D-idose and D-gulose, respectively. **E** and **F** are the alditols derived from **C** and **D**, respectively. Alditol **E** would produce only three ^{13}C NMR signals due to rotational symmetry while **F** would produce six signals.

22.41 There are four closely spaced upfield alkyl signals in the ^{13}C NMR spectrum (δ26.5, δ25.6, δ24.9, δ24.2), corresponding to the four methyls of the two acetonide protecting groups. (The compound is, therefore, the 1,2,5,6-bis-acetonide of mannofuranose, below.)

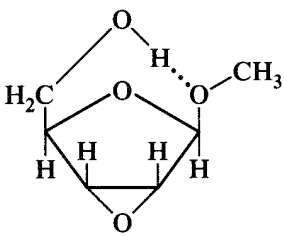


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22.42 The final product is the acetonide of glyceraldehyde (below); two molar equivalents are formed from each molar equivalent of the 1,2,5,6-bis-acetonide of mannitol.

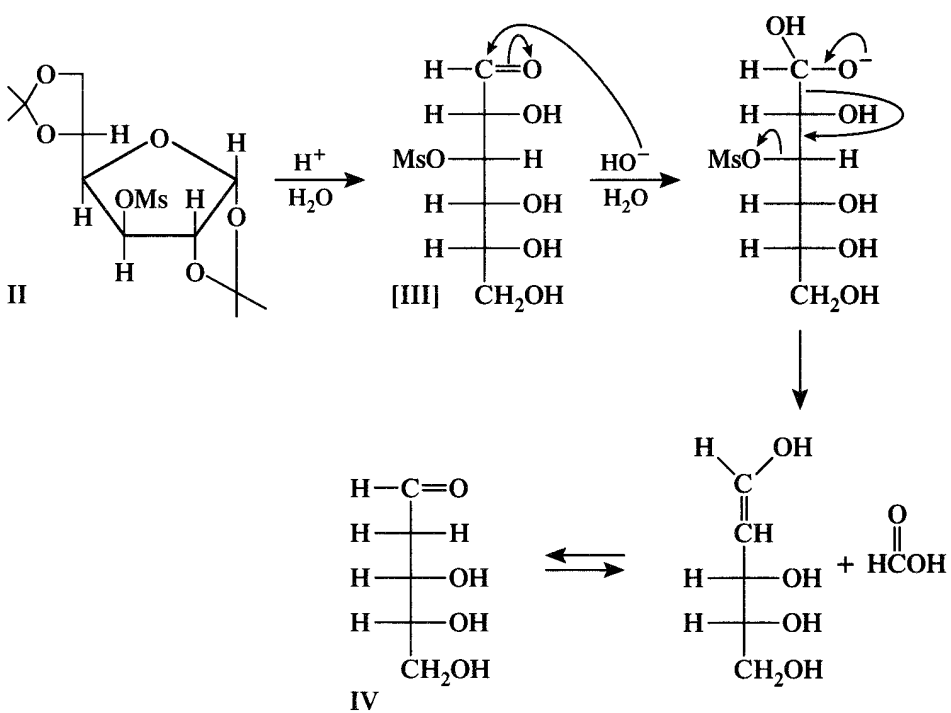


***22.43** The β-anomer can hydrogen bond intramolecularly, as in:



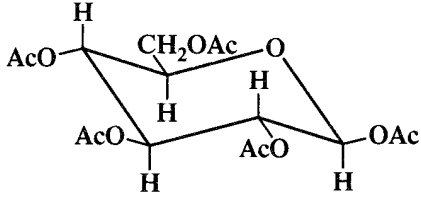
In contrast, the α-anomer can only hydrogen bond intermolecularly.

***22.44**

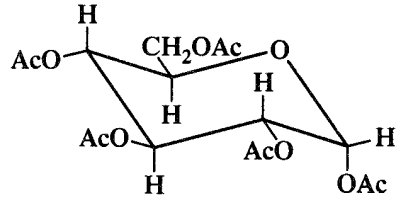


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***22.45** (a) The proton at Cl. (b) Because of the singlé neighboring hydrogen (at C2). (c and d).



V



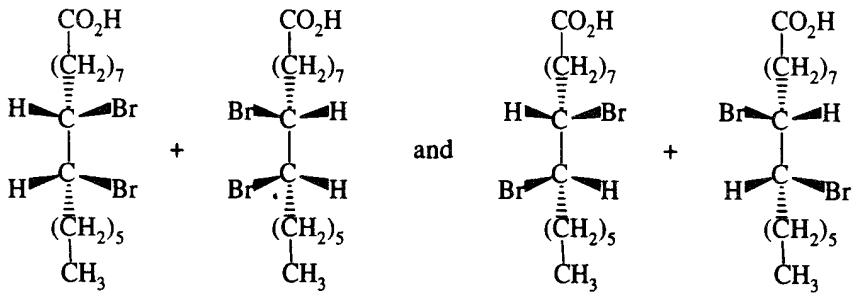
VI

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23 LIPIDS

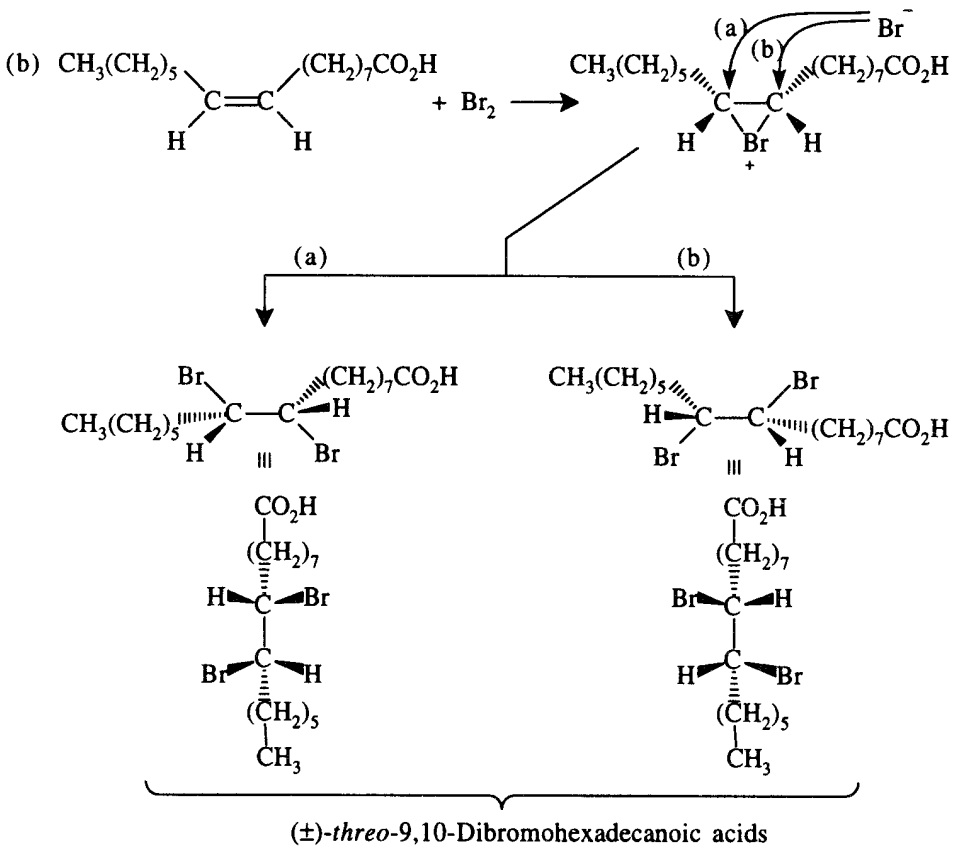
SOLUTIONS TO PROBLEMS

23.1 (a) There are two sets of enantiomers, giving a total of four stereoisomers:



erythro *threo*

(b)



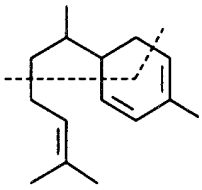
(±)-*threo*-9,10-Dibromohexadecanoic acids

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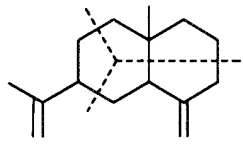
Formation of a bromonium ion at the other face of palmitoleic acid gives a result such that the *threo* enantiomers are the only products formed (obtained as a racemic modification).

The designations *erythro* and *threo* come from the names of the sugars called *erythrose* and *threose* (Section 22.9A).

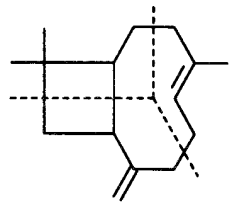
23.2



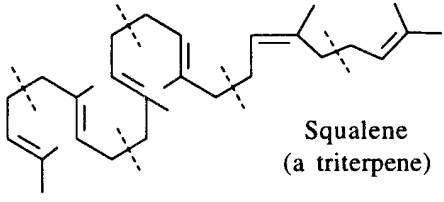
Zingiberene
(a sesquiterpene)



β-Selinene
(a sesquiterpene)

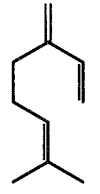


Caryophyllene
(a sesquiterpene)



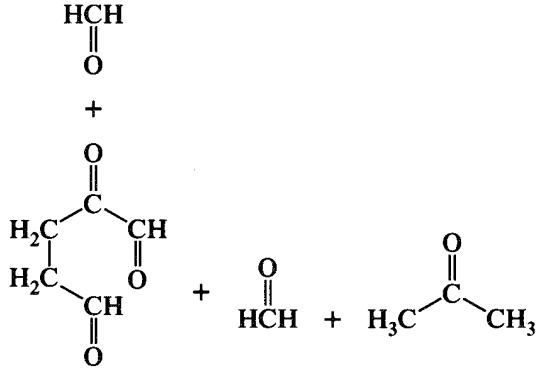
Squalene
(a triterpene)

23.3 (a)

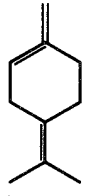


Myrcene

$\xrightarrow[(2)\ Zn,\ HOAc]{(1)\ O_3}$

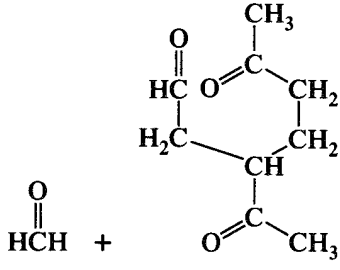


(b)



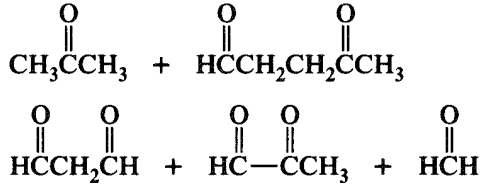
Limonene

$\xrightarrow[(2)\ Zn,\ HOAc]{(1)\ O_3}$



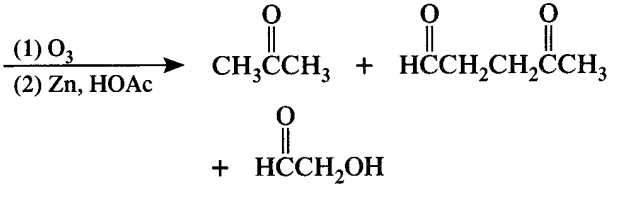
(c) α-Farnesene
(see Section 23.3)

$\xrightarrow[(2)\ Zn,\ HOAc]{(1)\ O_3}$

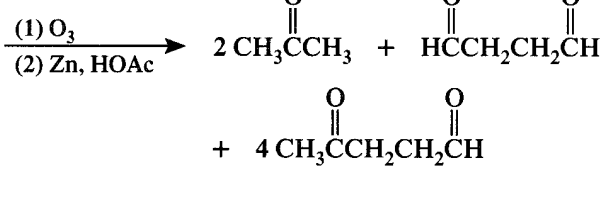


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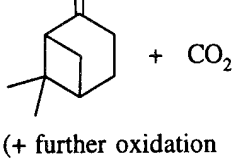
(d) **Geraniol** (see Section 23.3)



(e) **Squalene** (see Section 23.3)

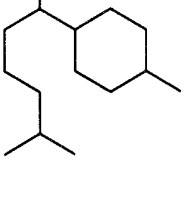


23.4 (a)

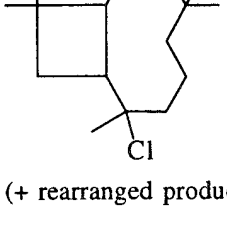


(+ further oxidation products)

(b)

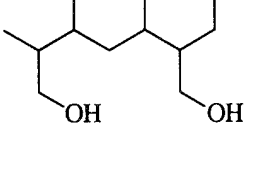


(c)



(+ rearranged products)

(d)

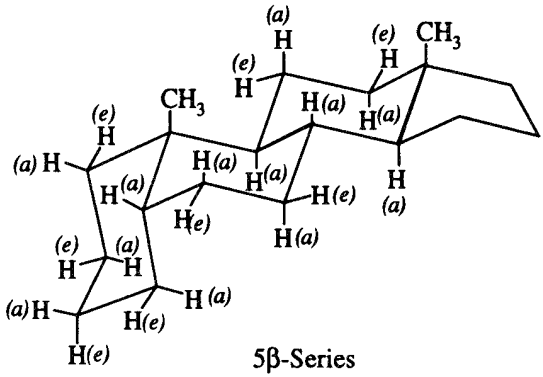


23.5 Br_2 in CCl_4 or $KMnO_4$ in H_2O at room temperature. Either reagent would give a positive result with geraniol and a negative result with menthol.

23.6

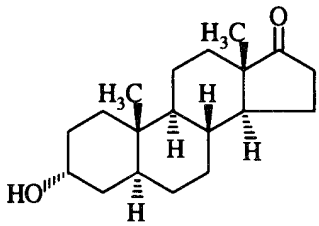
5α-Series

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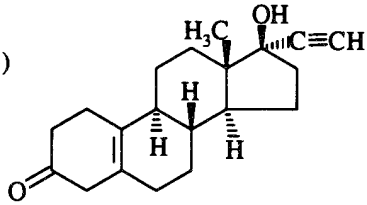
5β-Series

23.7 (a)



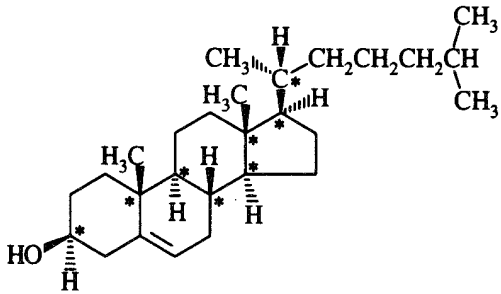
3α-Hydroxy-5α-androstan-17-one
(androsterone)

(b)



17α-Ethynyl-17β-hydroxy-5(10)-estren-3-one
(norethynodrel)

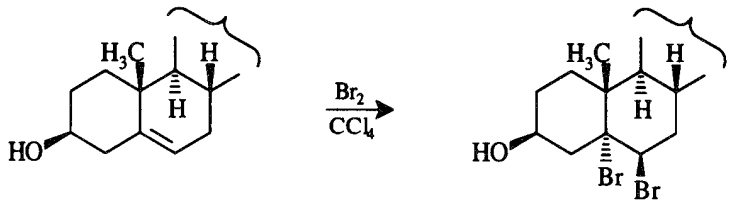
23.8



Absolute configuration of cholesterol
(5-cholesten-3β-ol)

23.9 Estrone and estradiol are *phenols* and thus are soluble in aqueous sodium hydroxide. Extraction with aqueous sodium hydroxide separates the estrogens from the androgens.

23.10 (a)

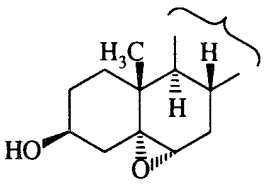


Cholesterol

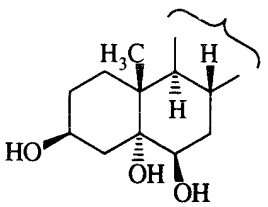
5α,6β-Dibromocholestan-3β-ol

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(b)



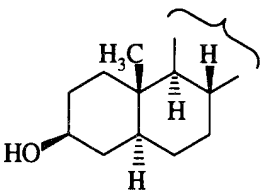
H^+, H_2O



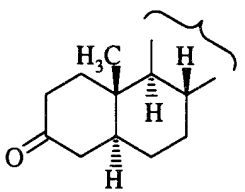
5α,6α-Epoxycholestan-3β-ol
(prepared by epoxidation
of cholesterol; cf. Section 23.4G)

Cholestan-3β,5α,6β-triol

(c)



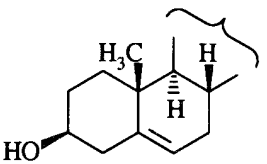
H_2CrO_4



5α–Cholestan-3β-ol
(prepared by hydrogenation
of cholesterol; cf. Section 23.4G)

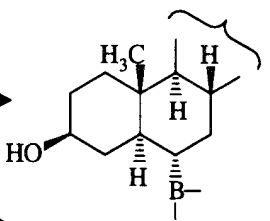
5α–Cholestan-3-one

(d)

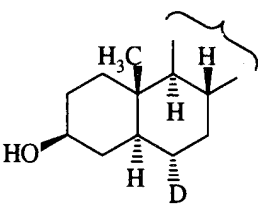


Cholesterol

THF: BH_3
(cf. Sect. 23.4G)

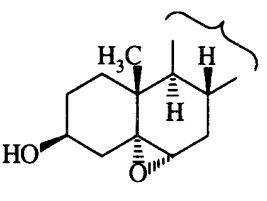


CH_3CO_2D

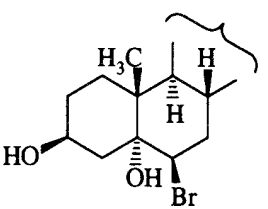


6α-Deuterio-5α-cholestan-3β-ol

(e)



HBr



5α,6α-Epoxycholestan-3β-ol

6β-Bromocholestan-3β,5α-diol

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23.11 (a) CH_2OH–$CHOH$–CH_2OH + $RCOOH$ + $R'COOH$ + H_3PO_4 + $HOCH_2CH_2\overset{+}{N}(CH_3)_3\ X^-$

(b) CH_2OH–$CHOH$–CH_2OH + $RCOOH$ + $R'COOH$ + H_3PO_4 + $HOCH_2CH_2NH_2$

(c) CH_2OH–$CHOH$–CH_2OH + $CH_3(CH_2)_nCH_2CHO$ + $R'COOH$ + H_3PO_4 + $HOCH_2CH_2\overset{+}{N}(CH_3)_3\ X^-$

23.12 (a) $CH_3(CH_2)_{16}CO_2H + C_2H_5OH \overset{H^+}{\rightleftharpoons} CH_3(CH_2)_{16}CO_2C_2H_5 + H_2O$

$CH_3(CH_2)_{16}CO_2H \xrightarrow{SOCl_2} CH_3(CH_2)_{16}COCl \xrightarrow{C_2H_5OH} CH_3(CH_2)_{16}CO_2C_2H_5$

(b) $CH_3(CH_2)_{16}COCl \xrightarrow{(CH_3)_3COH} CH_3(CH_2)_{16}CO_2C(CH_3)_3$

(c) $CH_3(CH_2)_{16}COCl \xrightarrow{NH_3} CH_3(CH_2)_{16}CONH_2$

(d) $CH_3(CH_2)_{16}COCl \xrightarrow{(CH_3)_2NH} CH_3(CH_2)_{16}CON(CH_3)_2$

(e) $CH_3(CH_2)_{16}CONH_2 \xrightarrow{LiAlH_4} CH_3(CH_2)_{16}CH_2NH_2$

(f) $CH_3(CH_2)_{16}CONH_2 \xrightarrow[OH^-]{Br_2} CH_3(CH_2)_{15}CH_2NH_2$

(g) $CH_3(CH_2)_{16}COCl \xrightarrow{LiAlH[OC(CH_3)_3]_3} CH_3(CH_2)_{16}CHO$

(h) $CH_3(CH_2)_{16}CO_2C_2H_5 \xrightarrow[Ni]{H_2} CH_3(CH_2)_{16}CH_2OH$

$CH_3(CH_2)_{16}COCl$

$\rightarrow CH_3(CH_2)_{16}CO_2CH_2(CH_2)_{16}CH_3$

(i) $CH_3(CH_2)_{16}CO_2H \xrightarrow[(2)\ H_2O]{(1)\ LiAlH_4} CH_3(CH_2)_{16}CH_2OH$

$CH_3(CH_2)_{16}CO_2C_2H_5 \xrightarrow[Ni]{H_2} CH_3(CH_2)_{16}CH_2OH$

(j) $CH_3(CH_2)_{16}COCl + (CH_3)_2CuLi \longrightarrow CH_3(CH_2)_{16}COCH_3$

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(k) $CH_3(CH_2)_{16}CH_2OH \xrightarrow{PBr_3} CH_3(CH_2)_{16}CH_2Br$

(l) $CH_3(CH_2)_{16}CH_2Br \xrightarrow[(2)H^+,\ H_2O,\ heat]{(1)\ NaCN} CH_3(CH_2)_{16}CH_2CO_2H$

23.13 (a) $CH_3(CH_2)_{11}CH_2CO_2H \xrightarrow{Br_2,\ P} CH_3(CH_2)_{11}\underset{\displaystyle Br}{\underset{|}{C}}HCO_2H$

(b) $CH_3(CH_2)_{11}\underset{\displaystyle Br}{\underset{|}{C}}HCO_2H \xrightarrow[(2)\ H_3O^+]{(1)\ OH^-,\ heat} CH_3(CH_2)_{11}\underset{\displaystyle OH}{\underset{|}{C}}HCO_2H$

(c) $CH_3(CH_2)_{11}\underset{\displaystyle Br}{\underset{|}{C}}HCO_2H \xrightarrow[(2)\ H^+]{(1)\ NaCN} CH_3(CH_2)_{11}\underset{\displaystyle CN}{\underset{|}{C}}HCO_2H$

(d) $CH_3(CH_2)_{11}\underset{\displaystyle Br}{\underset{|}{C}}HCO_2H \xrightarrow[(2)\ H^+]{(1)\ NH_3\ (excess)} CH_3(CH_2)_{11}\underset{\displaystyle NH_2}{\underset{|}{C}}HCO_2H$

or $CH_3(CH_2)_{11}\underset{\displaystyle NH_3^+}{\underset{|}{C}}HCO_2^-$

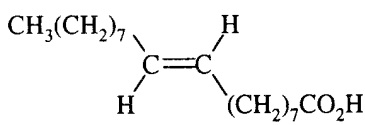
23.14 (a) $CH_3(CH_2)_5CH{=}CH(CH_2)_7CO_2H \xrightarrow{Br_2} CH_3(CH_2)_5CHBrCHBr(CH_2)_7CO_2H$

(b) $CH_3(CH_2)_5CH{=}CH(CH_2)_7CO_2H \xrightarrow[Ni]{H_2} CH_3(CH_2)_{14}CO_2H$

(c) $CH_3(CH_2)_5CH{=}CH(CH_2)_7CO_2H \xrightarrow{KMnO_4}$
$CH_3(CH_2)_5CHOHCHOH(CH_2)_7CO_2H$

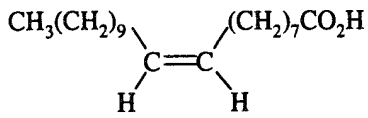
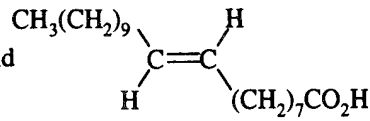
(d) $CH_3(CH_2)_5CH{=}CH(CH_2)_7CO_2H \xrightarrow{HCl}$
$CH_3(CH_2)_5CH_2CHCl(CH_2)_7CO_2H$
+
$CH_3(CH_2)_5CHClCH_2(CH_2)_7CO_2H$

23.15 Elaidic acid is *trans*-9-octadecenoic acid:



It is formed by the isomerization of oleic acid.

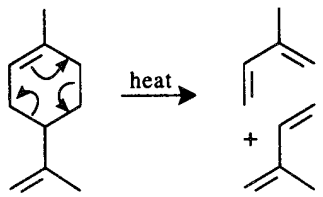
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23.16 (a)  and 

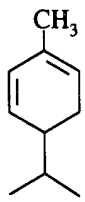
(b) Infrared spectroscopy

(c) A peak in the 675–730-cm^{-1} region would indicate that the double bond is cis; a peak in the 960–975-cm^{-1} region would indicate that it is trans.

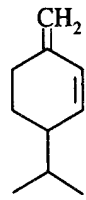
23.17 A reverse Diels-Alder reaction takes place.



23.18



α-Phellandrene



β-Phellandrene

Note: On permanganate oxidation, the $=CH_2$ group of β-phellandrene is converted to CO_2 and thus is not detected in the reaction.

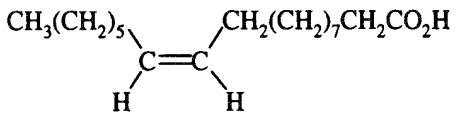
23.19

$$CH_3(CH_2)_5C{\equiv}CH + NaNH_2 \xrightarrow{\text{liq. } NH_3} \underset{\mathbf{A}}{CH_3(CH_2)_5C{\equiv}CNa}$$

$$\xrightarrow{ICH_2(CH_2)_7CH_2Cl} \underset{\mathbf{B}}{CH_3(CH_2)_5C{\equiv}CCH_2(CH_2)_7CH_2Cl} \xrightarrow{NaCN}$$

$$\underset{\mathbf{C}}{CH_3(CH_2)_5C{\equiv}CCH_2(CH_2)_7CH_2CN} \xrightarrow[H_2O]{KOH} \underset{\mathbf{D}}{CH_3(CH_2)_5C{\equiv}CCH_2(CH_2)_7CH_2CO_2K}$$

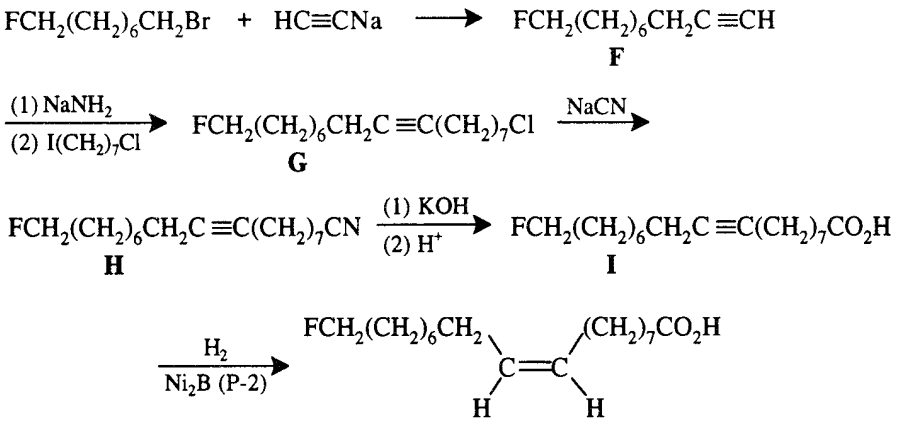
$$\xrightarrow{H_3O^+} \underset{\mathbf{E}}{CH_3(CH_2)_5C{\equiv}CCH_2(CH_2)_7CH_2CO_2H} \xrightarrow[Pd\text{-}BaSO_4]{H_2}$$



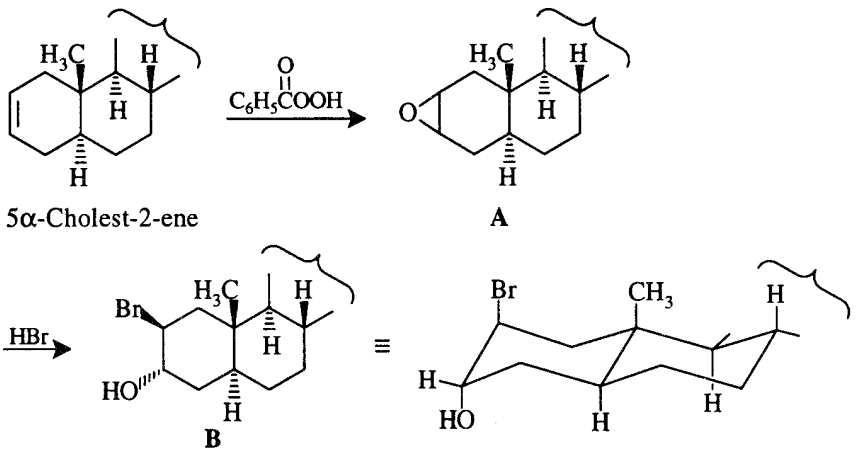
Vaccenic acid

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23.20



23.21



Here we find that epoxidation takes place at the less hindered α face (cf. Section 23.4G). Ring opening by HBr takes place in an anti fashion to give a product with diaxial substituents.

23.22 (a) $CH_2{=}CH{-}CH{=}CH_2$

(b) OH^- (Removal of the α hydrogen atom allows isomerization to the more stable compound with a trans ring junction.)

(c) $LiAlH_4$

(d) H_3O^+ and heat. (Hydrolysis of the enol ether is followed by dehydration of one alcohol group.)

(e) $HCO_2C_2H_5$, C_2H_5ONa

(f) OsO_4, then $NaHSO_3$

(g) $CH_3\overset{\overset{O}{\|}}{C}CH_3$, H^+

(h) H_2, Pd catalyst

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(i) H_3O^+, H_2O

(j) HIO_4

(k) Base and heat. (This reaction is an aldol condensation.)

(l) and (m) Na_2CrO_4, CH_3CO_2H to oxidize the aldehyde to an acid, followed by esterification.

(n) H_2 and Pt. (Hydrogen addition takes place from the less hindered α face of the molecule.)

(o), (p), and (q) $NaBH_4$ to reduce the keto group; OH^-, H_2O to hydrolyze the ester; and acetic anhydride to esterify the OH at the 3-position.

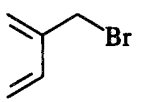
(r) and (s) $SOCl_2$ to make the acid chloride, followed by treatment with $(CH_3)_2Cd$.

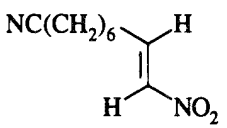
(t) $CH_3CHCH_2CH_2CH_2MgBr$, followed by H_3O^+.

(u), (v), and (w) Acetic acid and heat to dehydrate the tertiary alcohol; followed by acetic anhydride to acetylate the secondary alcohol; followed by H_2, Pt to hydrogenate the double bond.

23.23 (a) $CH_3(CH_2)_4CH$ (O)

(b) C_4H_9Li

(c) 

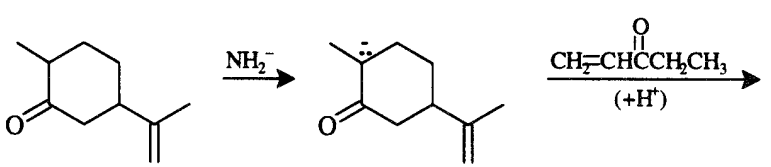
(d) 

(e) Michael addition using a basic catalyst.

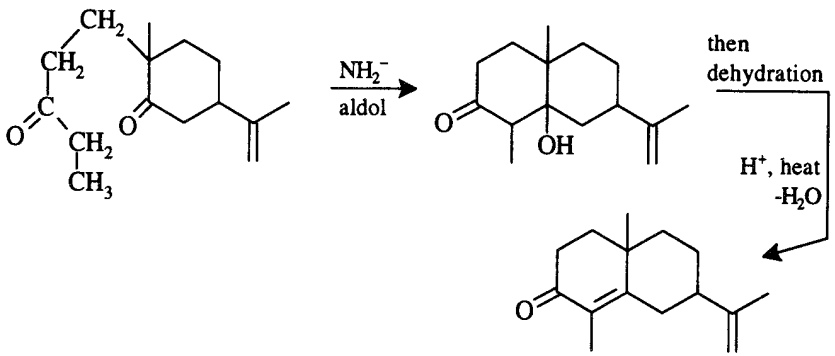
23.24 First: an elimination takes place,

$$R_3\overset{+}{N}CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3 + NH_2^- \longrightarrow CH_2{=}CH\overset{O}{\overset{\|}{C}}CH_2CH_3 + R_3N + NH_3$$

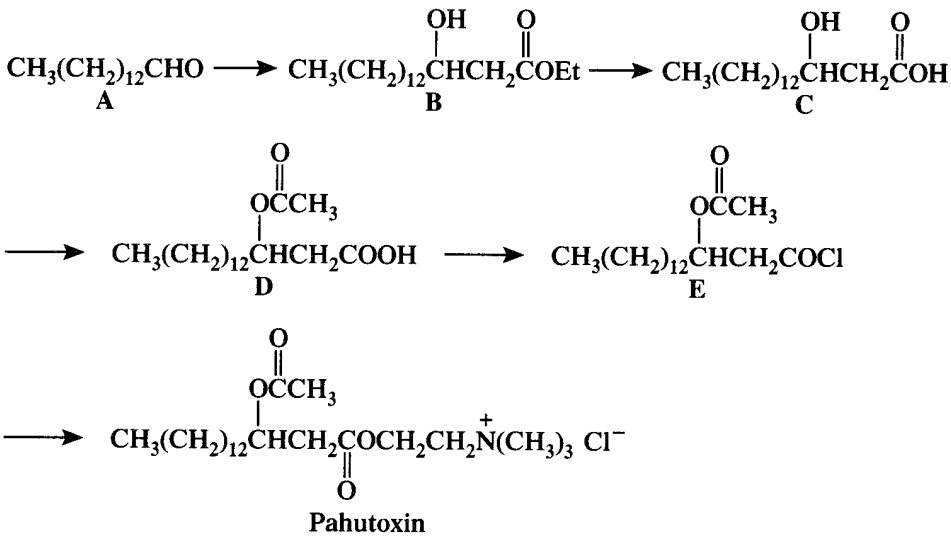
Then a conjugate addition occurs, followed by an aldol addition:



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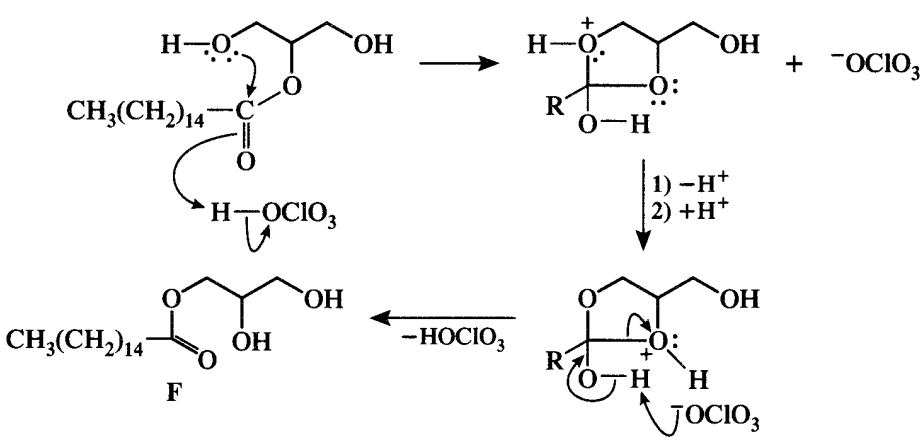


***23.25**



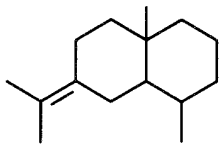
Pahutoxin

***23.26** The reaction is an intramolecular transesterification.



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23.5 The following compound is a:

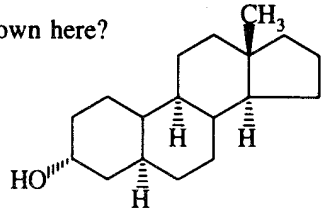


(a) Monoterpene (b) Sesquiterpene (c) Diterpene

(d) Triterpene (e) Tetraterpene

23.6 Mark off the isoprene units in the previous compound.

23.7 Which is a systematic name for the steroid shown here?



(a) 5α-Androstan-3α-ol

(b) 5β-Androstan-3β-ol

(c) 5α-Pregnan-3α-ol

(d) 5β-Pregnan-3β-ol

(e) 5α-Estran-3α-ol

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24 AMINO ACIDS AND PROTEINS

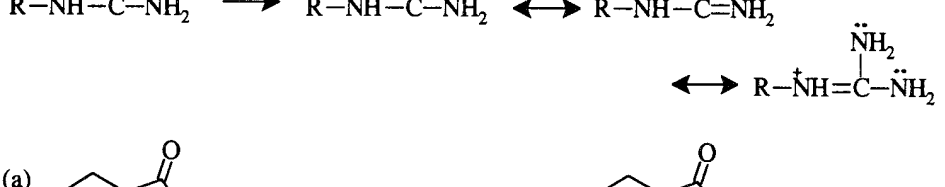
SOLUTIONS TO PROBLEMS

24.1 (a) $HO_2CCH_2CH_2\underset{\displaystyle NH_3^+}{\underset{|}{C}}HCO_2H$ (b) $^-O_2CCH_2CH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCO_2^-$

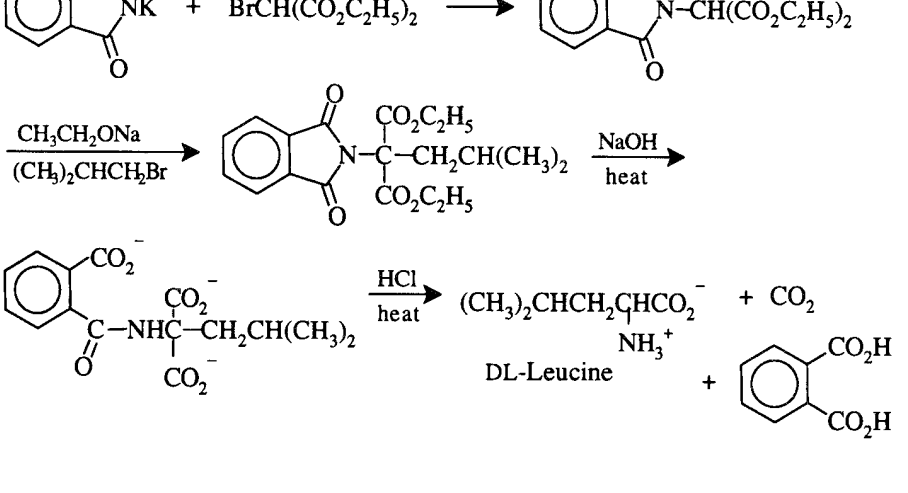
(c) $HO_2CCH_2CH_2\underset{\displaystyle NH_3^+}{\underset{|}{C}}HCO_2^-$ predominates at the isoelectric point rather than $^-O_2CCH_2CH_2\underset{\displaystyle NH_3^+}{\underset{|}{C}}HCO_2H$ because of the acid-strengthening inductive effect of the α-aminium group.

(d) Since glutamic acid is a dicarboxylic acid, acid must be added (i.e., the pH must be made lower) to suppress the ionization of the second carboxyl group and thus achieve the isoelectric point. Glutamine, with only one carboxyl group, is similar to glycine or phenylalanine and has its isoelectric point at a higher pH.

24.2 The conjugate acid is highly stabilized by resonance.

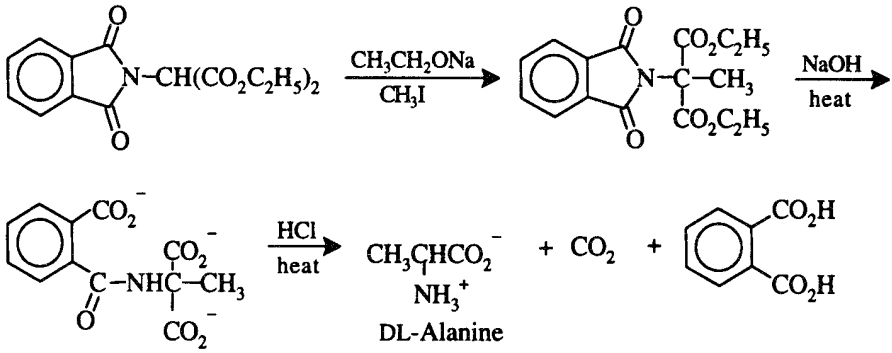


24.3 (a)

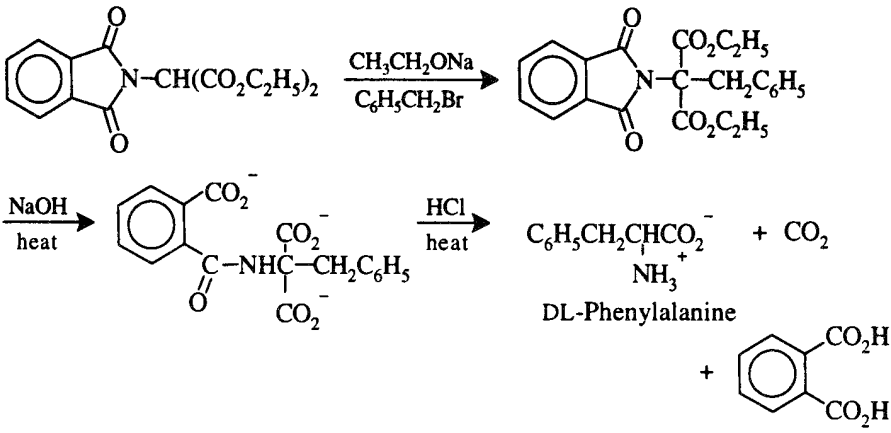


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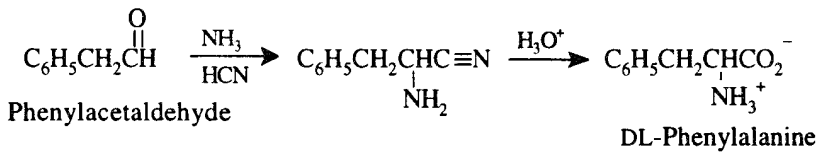
(b)



(c)



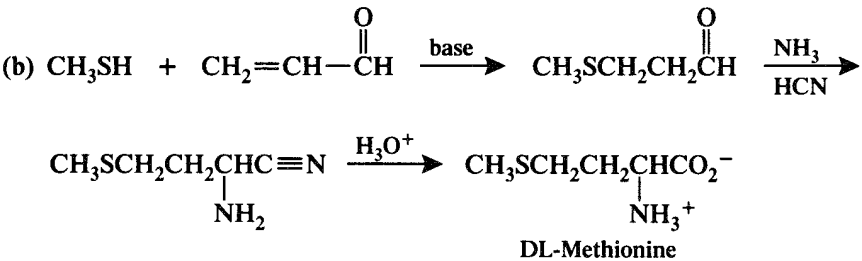
24.4 (a)



Phenylacetaldehyde

DL-Phenylalanine

(b)

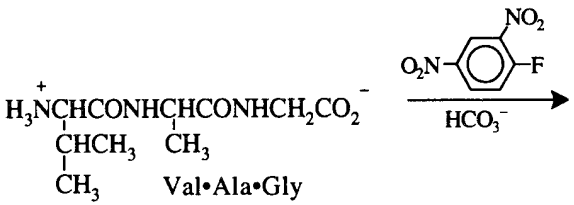


DL-Methionine

24.5 Because of the presence of an electron-withdrawing 2,4-dinitrophenyl group, the labeled amino acid is relatively nonbasic and is, therefore, insoluble in dilute aqueous acid. The other amino acids (those that are not labeled) dissolve in dilute aqueous acid.

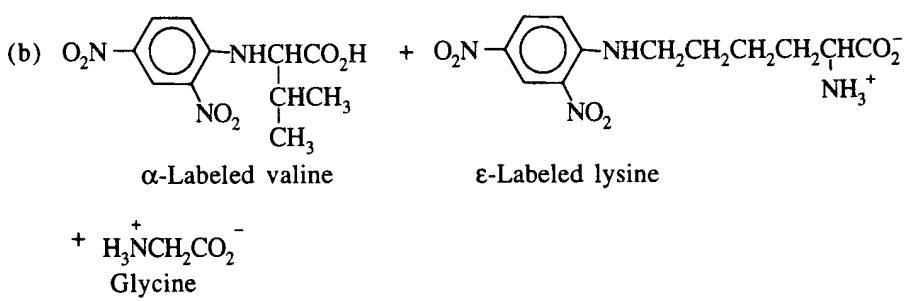
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24.6 (a)

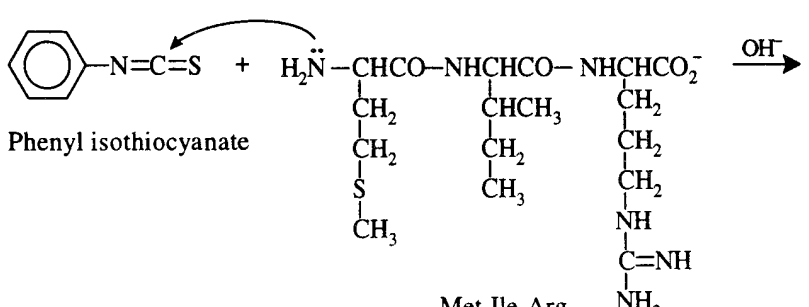


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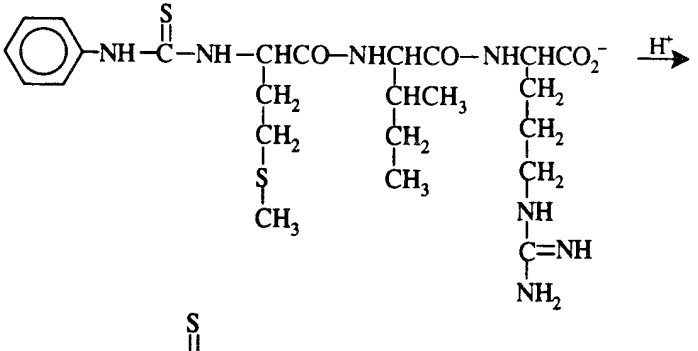
(b)

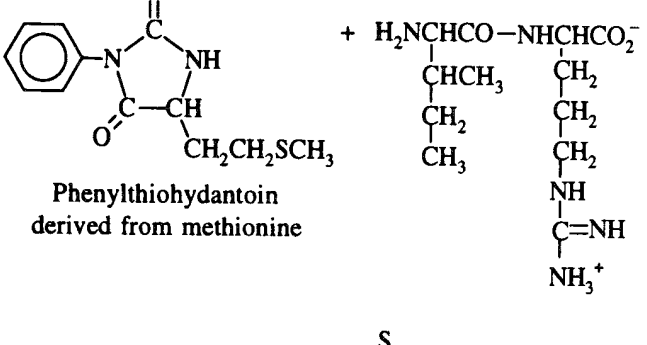


24.7

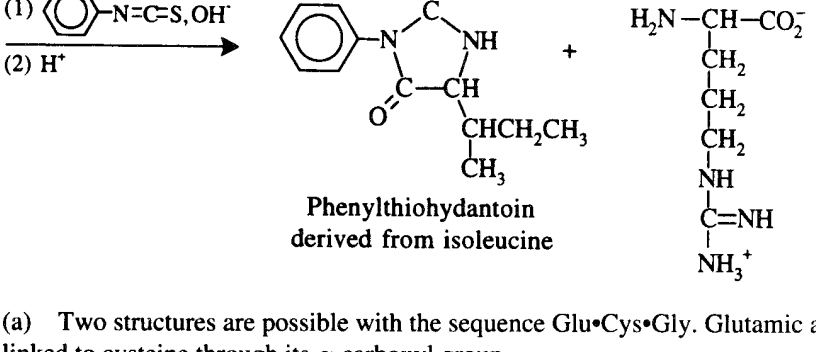


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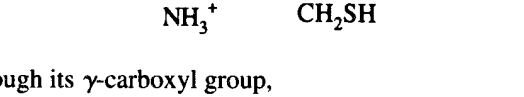


Phenylthiohydantoin
derived from methionine

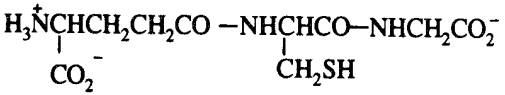


Phenylthiohydantoin
derived from isoleucine

24.8 (a) Two structures are possible with the sequence Glu•Cys•Gly. Glutamic acid may be linked to cysteine through its α-carboxyl group,



or through its γ-carboxyl group,



(b) This result shows that the second structure is correct, that in glutathione the γ-carboxyl group is linked to cysteine.

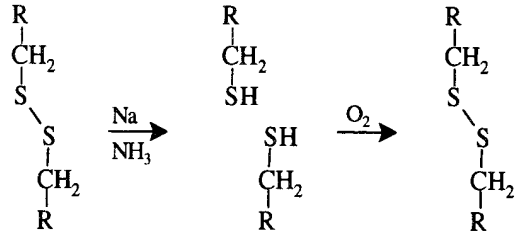
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24.9 We look for points of overlap to determine the amino acid sequence in each case.

(a) Ser • Thr
Thr • Hyp
Pro • Ser
Pro • Ser • Thr • Hyp

(b) Ala • Cys
Cys • Arg
Arg • Val
Leu • Ala
Leu • Ala • Cys • Arg • Val

24.10 Sodium in liquid ammonia brings about reductive cleavage of the disulfide linkage of oxytocin to two thiol groups; then air oxidizes the two thiol groups back to a disulfide linkage:



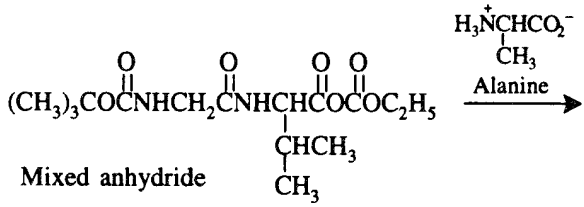
24.11 $H_3\overset{+}{N}CH_2CO_2^-$ (Glycine) + $(CH_3)_3COC(=O)OC(CH_3)_3$ (Di-*tert*-butyl carbonate) $\xrightarrow{OH^-}$

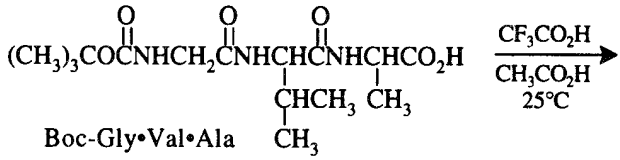
$(CH_3)_3C{-}OC(=O)NHCH_2CO_2H$ (Boc-Gly) $\xrightarrow[(2)\ ClCO_2C_2H_5]{(1)\ (C_2H_5)_3N}$

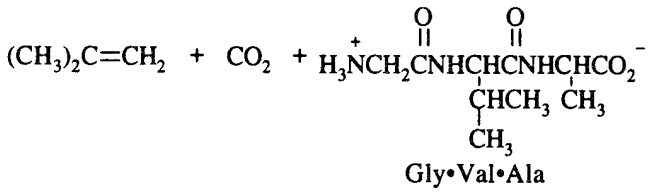
$(CH_3)_3COC(=O)NHCH_2C(=O)OC(=O)OC_2H_5$ (Mixed anhydride) $\xrightarrow[-CO_2,\ -C_2H_5OH]{H_3\overset{+}{N}CHCO_2^-\ CHCH_3\ CH_3\ \text{(Valine)}}$

$(CH_3)_3COC(=O)NHCH_2C(=O)NHCHCO_2H$ (Boc-Gly•Val; $CHCH_3$, CH_3) $\xrightarrow[(2)\ ClCO_2C_2H_5]{(1)\ (C_2H_5)_3N}$

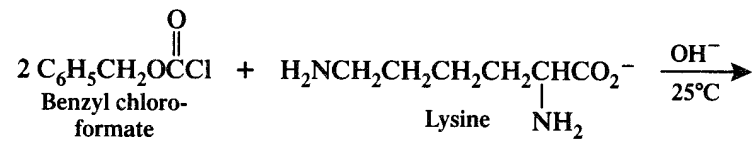
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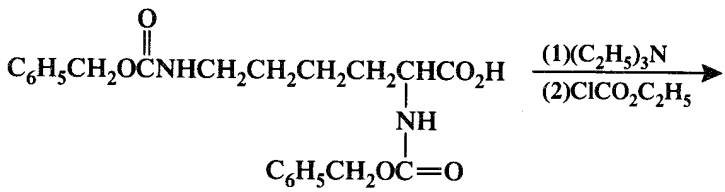


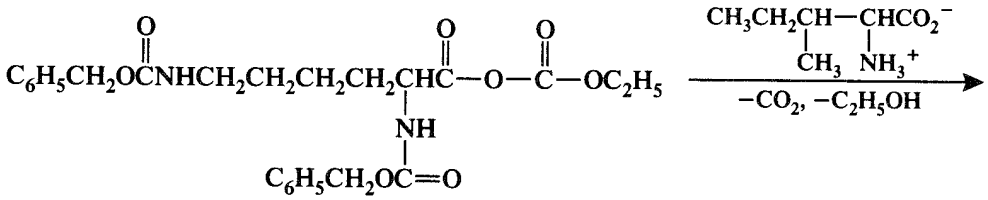


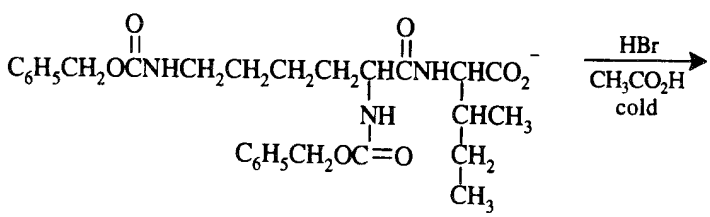


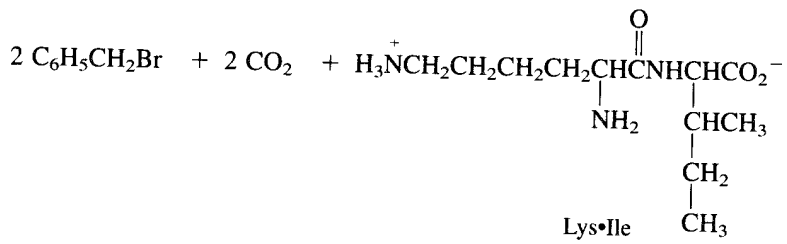
24.12 (a)



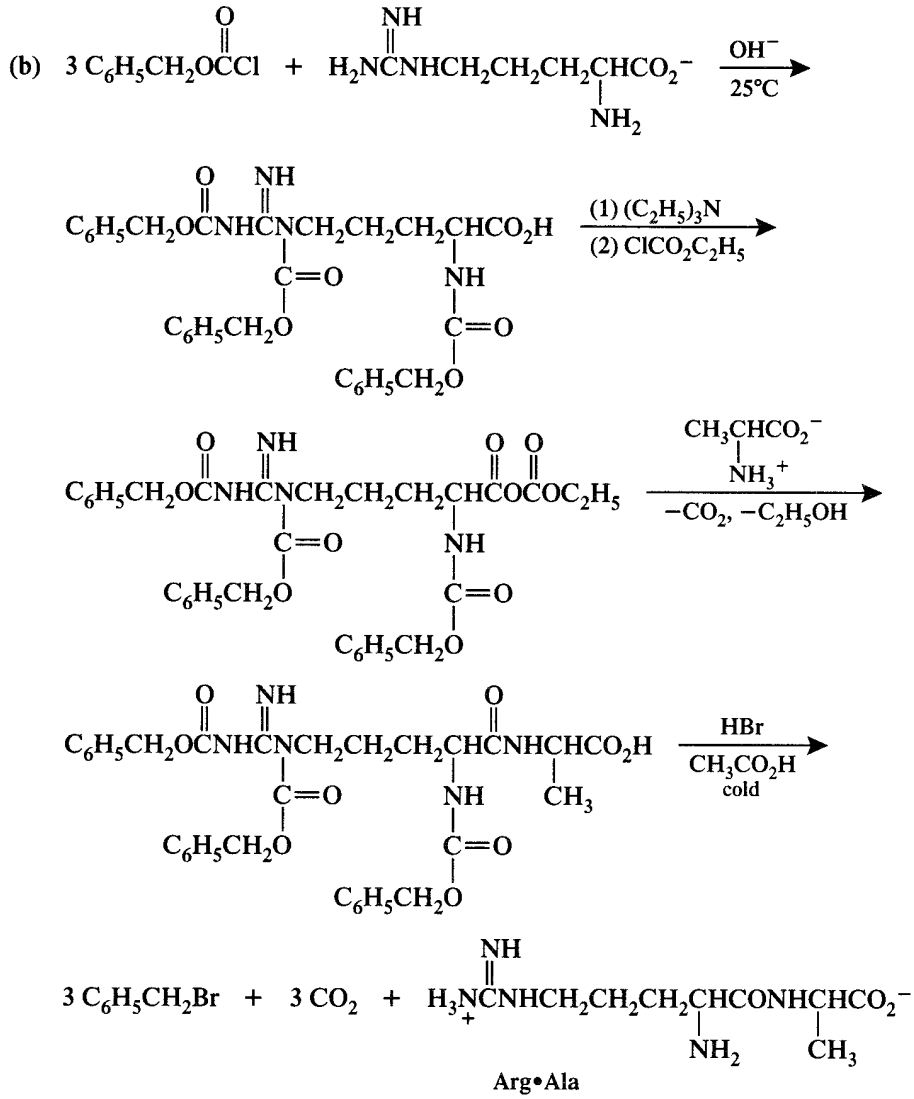






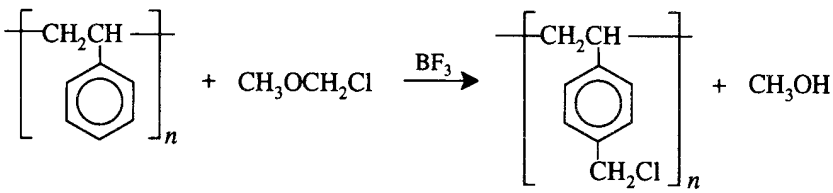


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24.13 The weakness of the benzyl-oxygen bond allows these groups to be removed by catalytic hydrogenolysis.

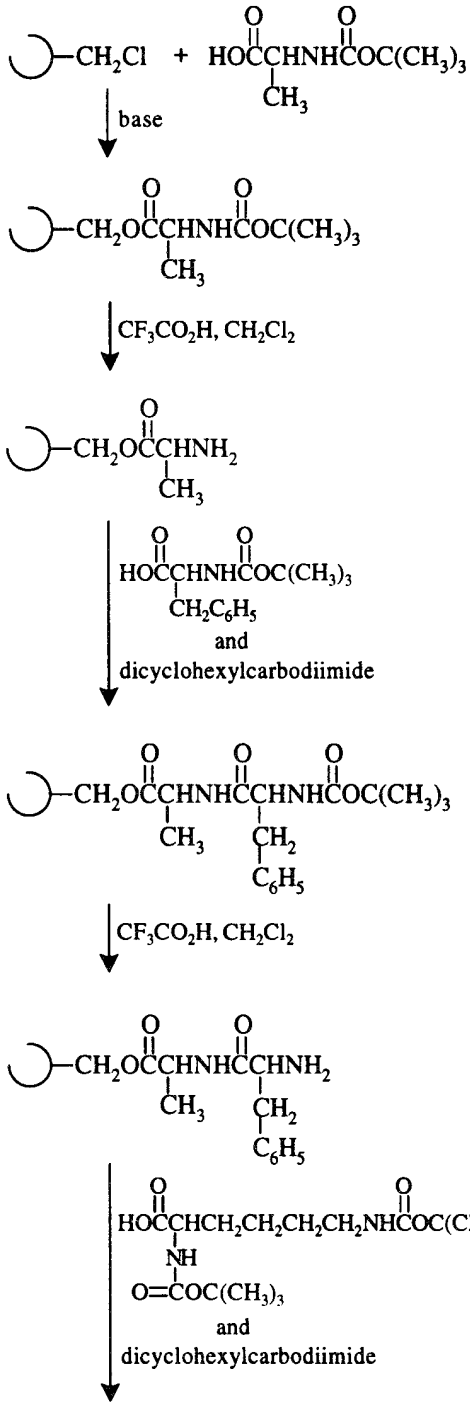
24.14 (a) An electrophilic substitution reaction:



(b) The linkage between the resin and the polypeptide is a benzylic ester. It is cleaved by HBr in CF_3CO_2H at room temperature because the carbocation that is formed initially is the relatively stable, benzylic cation.

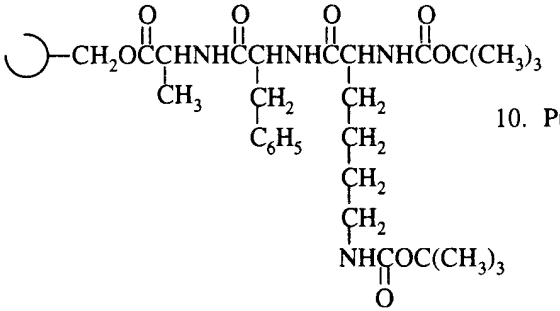
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24.15

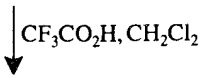


1. Add Boc-Ala.
2. Purify by washing.
3. Remove protecting group.
4. Purify by washing.
5. Add Boc-Phe.
6. Purify by washing.
7. Remove protecting group.
8. Purify by washing.
9. Add protected Lys.

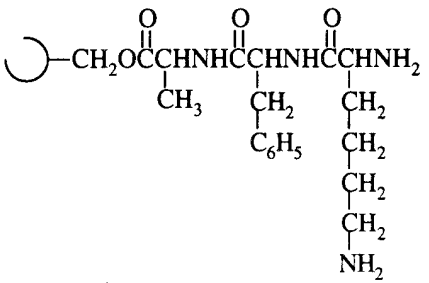
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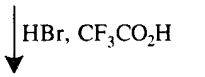
10. Purify by washing.



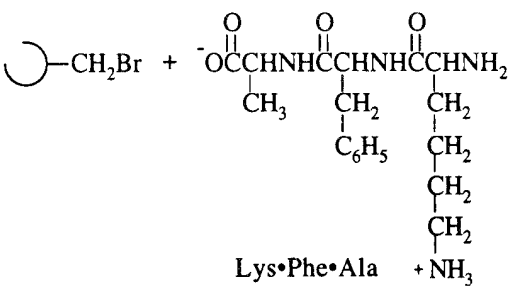
11. Remove protecting groups.



12. Purify by washing.



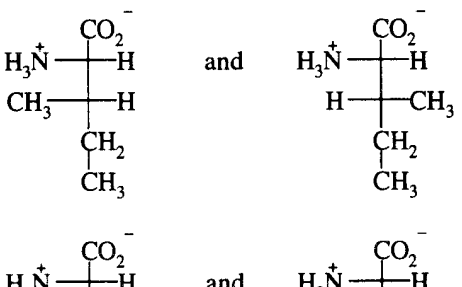
13. Detach tripeptide.



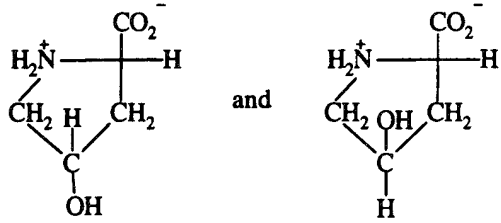
14. Isolate product.

24.16 (a) Isoleucine, threonine, hydroxyproline, and cystine.

(b)



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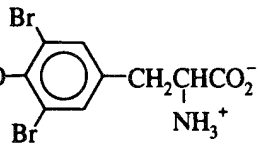
(With cystine, both stereocenters are α-carbon atoms; thus, according to the problem, both must have the L-configuration, and no isomers of this type can be written.)

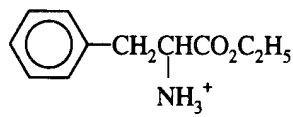
(c) Diastereomers

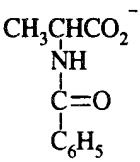
24.17 (a) Alanine



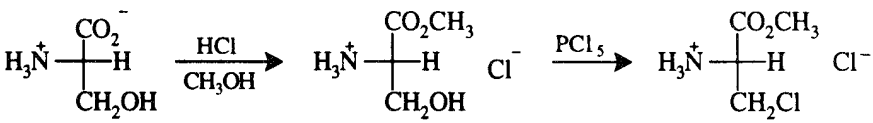
(b) Proline and hydroxyproline. All of the other amino acids have at least one primary amino group.

(c) 

(d) 

(e) 

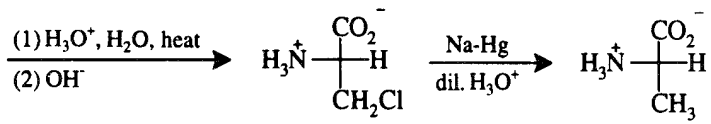
24.18 (a)



(–)-Serine

A $(C_4H_{10}ClNO_3)$

B $(C_4H_9Cl_2NO_2)$



C $(C_3H_6ClNO_2)$

L-(+)-Alanine

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(b) **B** $\xrightarrow{OH^-}$ $H_2N-CH(CO_2CH_3)-CH_2Cl$ $\xrightarrow{NaSH}$ $H_2N-CH(CO_2CH_3)-CH_2SH$

D ($C_4H_8ClNO_2$) **E** ($C_4H_9NO_2S$)

$\xrightarrow[(2)\ OH^-]{(1)\ H_3O^+,\ H_2O,\ heat}$ $H_3\overset{+}{N}-CH(CO_2^-)-CH_2SH$

L-(+)-Cysteine

(c) $H_3\overset{+}{N}-CH(CO_2^-)-CH_2CNH_2$ (O) $\xrightarrow[\text{Hofmann rearrangement}]{NaOBr,\ OH^-}$ $H_2N-CH(CO_2^-)-CH_2NH_2$ $\xleftarrow{NH_3}$ $H_3\overset{+}{N}-CH(CO_2^-)-CH_2Cl$

L-(−)-Asparagine **F** ($C_3H_7N_2O_2$) **C** [from part (a)]

24.19 (a) $CH_3CONHCH(CO_2C_2H_5)_2 + CH_2{=}CH-C{\equiv}N \xrightarrow[C_2H_5OH]{NaOC_2H_5}$ (95% yield)

$CH_3CONH-C(CO_2C_2H_5)_2-CH_2CH_2C{\equiv}N$ **G** $\xrightarrow[\text{reflux 6 h}]{\text{concd. HCl}}$ (66% yield) $HO_2CCH_2CH_2CH(NH_3^+)CO_2^-$

DL-Glutamic acid

$+ CH_3CO_2H + 2\,C_2H_5OH + NH_4^+ + CO_2$

(b) $CH_3CONH-C(CO_2C_2H_5)_2-CH_2CH_2C{\equiv}N \xrightarrow[68°C,\ 1000\ psi]{H_2,\ Ni}$ (90% yield) $\left[CH_3CONH-C(CO_2C_2H_5)_2-CH_2CH_2CH_2NH_2\right]$

$\xrightarrow{-C_2H_5OH}$ **H** $\xrightarrow[\text{reflux 4 h}]{\text{concd. HCl}}$ (97% yield) $H_3\overset{+}{N}CH_2CH_2CH_2CH(NH_3^+)CO_2^-\ Cl^-$

DL-Ornithine hydrochloride

$+ CH_3CO_2H + C_2H_5OH + CO_2$

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24.20 We look for points of overlap:

```
                                    Phe • Ser
                          Pro • Gly • Phe
                Pro •     Pro                 Ser • Pro • Phe
Arg •           Pro                                     Phe • Arg
-------------------------------------------------------------------
Arg • Pro • Pro • Gly • Phe • Ser • Pro • Phe • Arg
```

Bradykinin

24.21 1. This experiment shows that valine is the N-terminal amino acid and that valine is attached to leucine. (Lysine labeled at the ϵ-amino group is to be expected if lysine is not the N-terminal amino acid and if it is linked in the polypeptide through its α-amino group.)

2. This experiment shows that alanine is the C-terminal amino acid and that it is linked to glutamic acid.

At this point, then, we have the following information about the structure of the heptapeptide.

Val • Leu (Ala, Lys, Phe) Glu • Ala

The sequence here is unknown.

3. (a) This experiment shows that the dipeptide, **A,** is

Leu • Lys

(b) The carboxypeptidase reaction shows that the C-terminal amino acid of the tripeptide, **B,** is glutamic acid; the DNP labeling experiment shows that the N-terminal amino acid is phenylalanine. Thus, the tripeptide **B** is

Phe • Ala • Glu

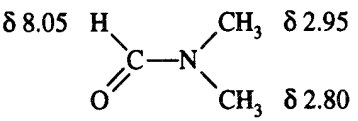
Putting these pieces together in the only way possible, we arrive at the following amino acid sequence for the heptapeptide.

```
Val • Leu
      Leu • Lys
                  Phe • Ala • Glu
                              Glu • Ala
-------------------------------------------
Val • Leu • Lys • Phe • Ala • Glu • Ala
```

24.22 At pH 2-3 the γ-carboxyl groups of polyglutamic acid are uncharged. (They are present as $-CO_2H$ groups.) At pH 5 the γ-carboxyl groups ionize and become negatively charged. (They become γ-CO_2^- groups.) The repulsive forces between these negatively charged groups cause an unwinding of the α helix and the formation of a random coil.

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24.23 The observation that the ^1H NMR spectrum taken at room temperature shows two different signals for the methyl groups suggests that they are in different environments. This would be true if rotation about the carbon-nitrogen bond was not taking place.



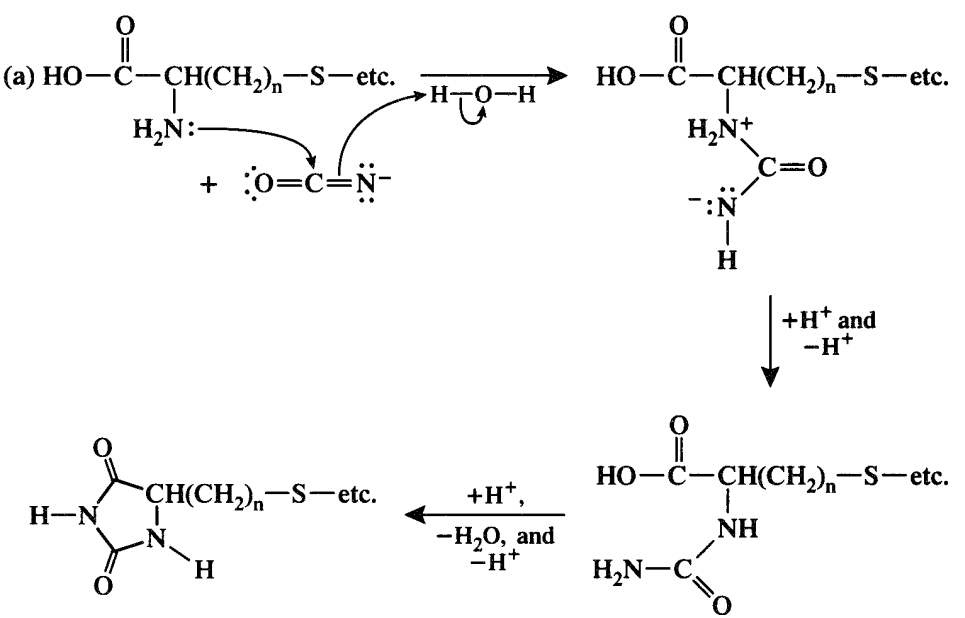
We assign the δ 2.80 signal to the methyl group that is on the same side as the electronegative oxygen atom.

The fact that the methyl signals appear as doublets (and that the formyl proton signal is a multiplet) indicates that long-range coupling is taking place between the methyl protons and the formyl proton.

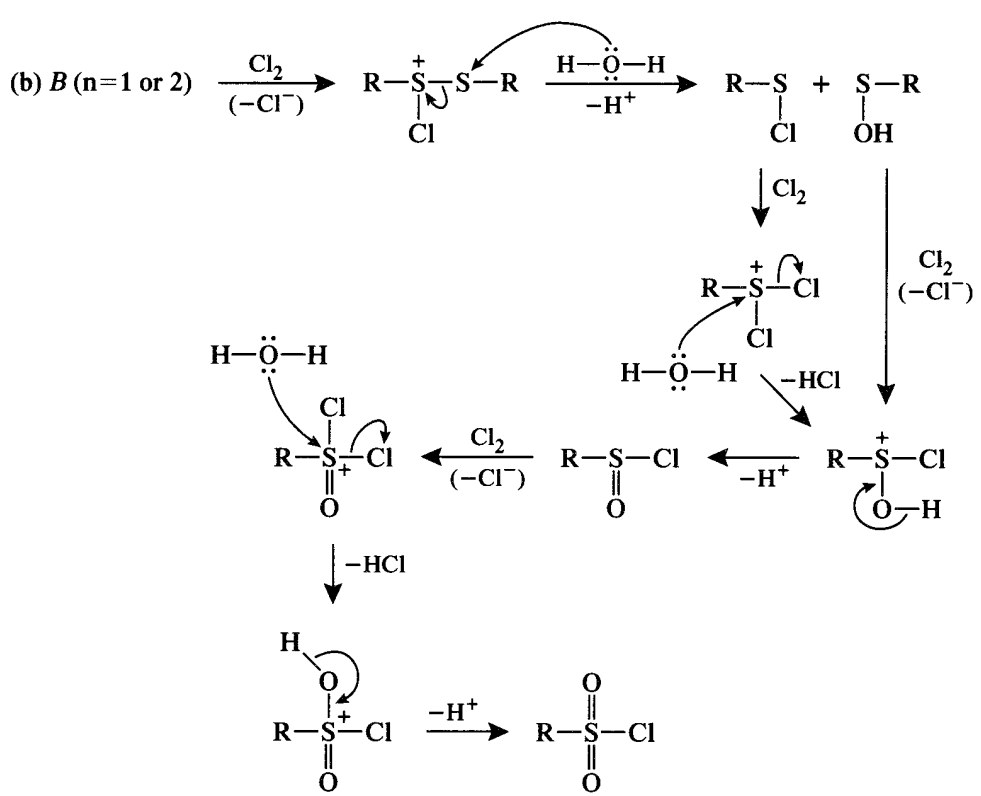
That the two doublets are not simply the result of spin-spin coupling is indicated by the observation that the distance that separates one doublet from the other changes when the applied magnetic field strength is lowered. [*Remember!* The magnitude of a chemical shift is proportional to the strength of the applied magnetic field, while the magnitude of a coupling constant is not.]

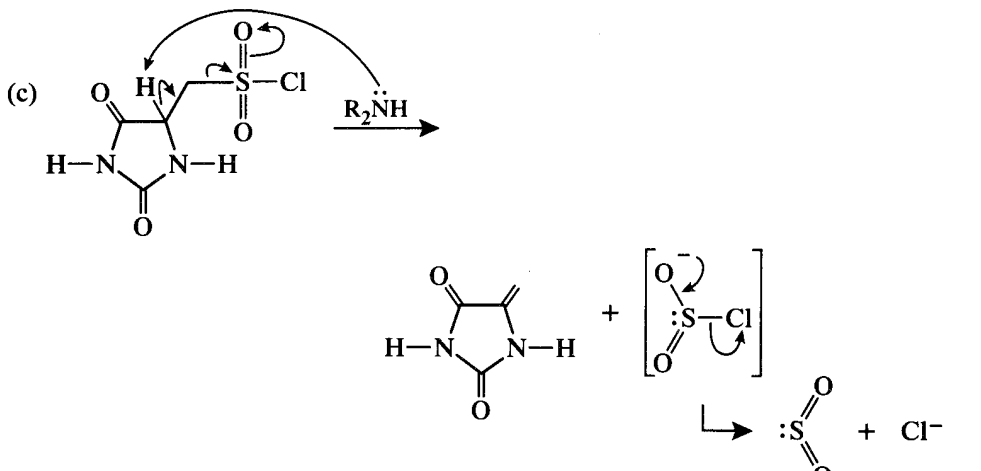
That raising the temperature (to 111°C) causes the doublets to coalesce into a single signal indicates that at higher temperatures the molecules have enough energy to surmount the energy barrier of the carbon-nitrogen bond. Above 111°C, rotation is taking place so rapidly that the spectrometer is unable to discriminate between the two methyl groups.

***24.24**



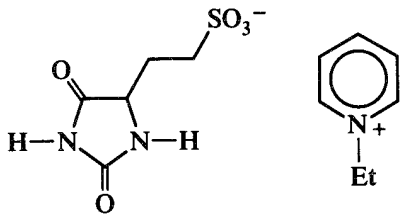
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***24.25**



(By pyridine displacement of the sulfonyloxy group of the initially formed ethyl ester.)

***24.26** (a) A large difference in the solubilities of the (*S*,*S*) and (*S*,*R*) diastereomers.

(b) Le Chatelier's Principle, which says that an equilibrium system will try to produce more of any species that is removed (here by crystallization).

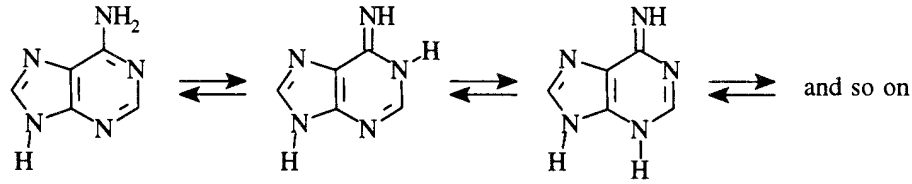
(c) Hydrogenolysis of benzyl groups, in both instances (one is preceded by simple hydrogenation of the ketone carbonyl group).

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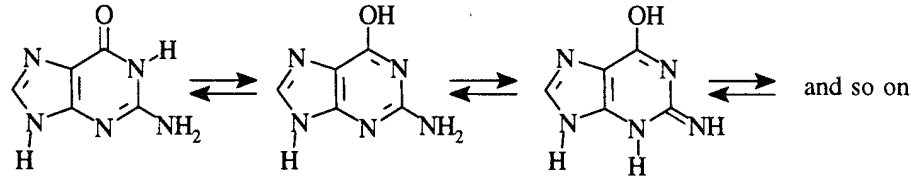
25 NUCLEIC ACIDS AND PROTEIN SYNTHESIS

SOLUTIONS TO PROBLEMS

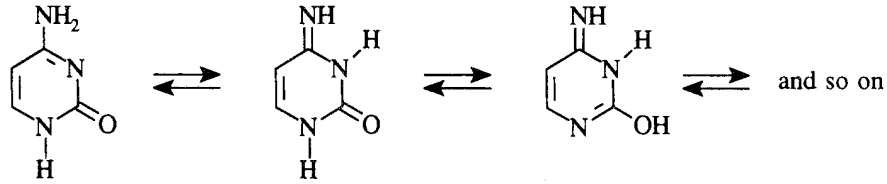
25.1 Adenine:



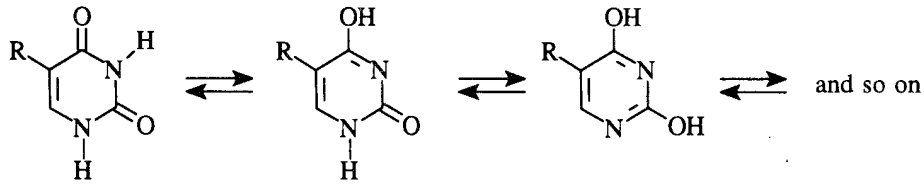
Guanine:



Cytosine:

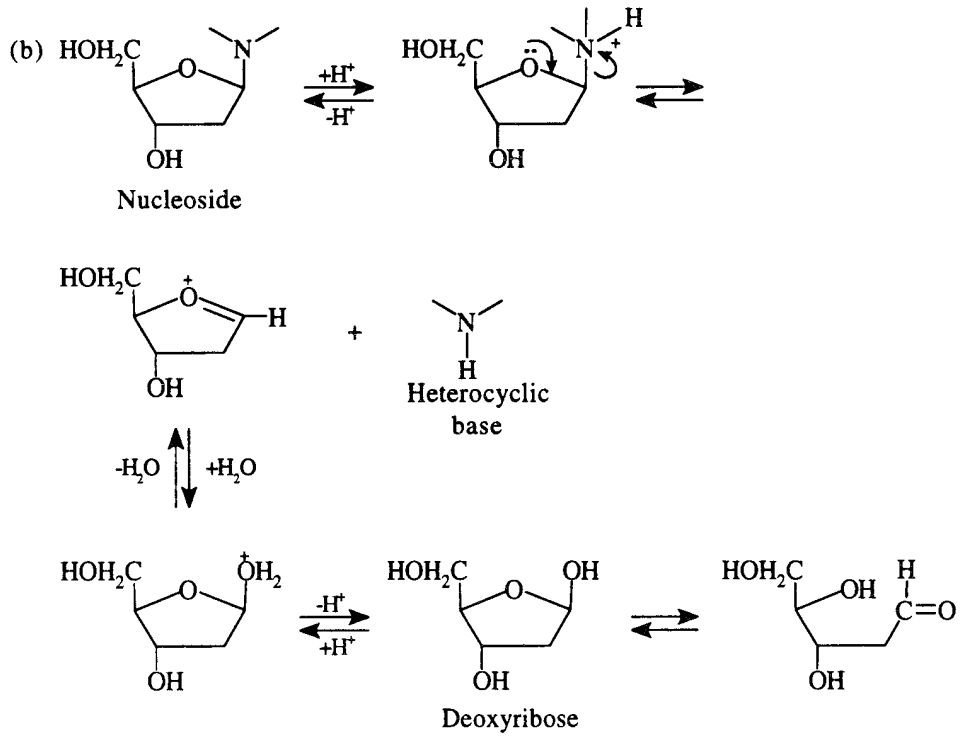


Thymine (R=CH_3) or Uracil (R=H):



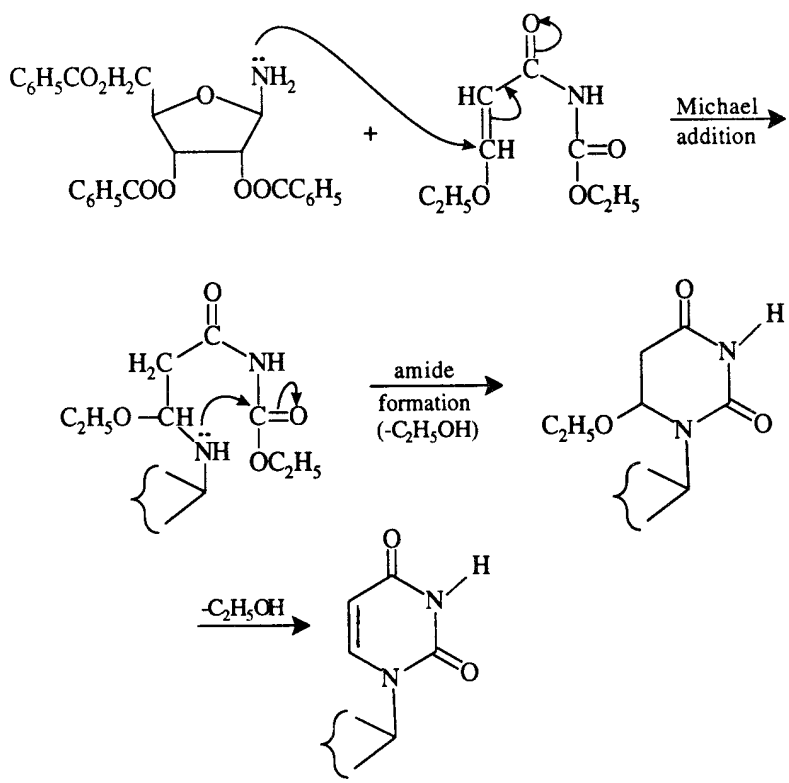
25.2 (a) The nucleosides have an *N*-glycosidic linkage that (like an *O*-glycosidic linkage) is rapidly hydrolyzed by aqueous acid but is one that is stable in aqueous base.

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25.3 The reaction appears to take place through an S_N2 mechanism. Attack occurs preferentially at the primary 5′-carbon atom rather than at the secondary 3′-carbon atom.

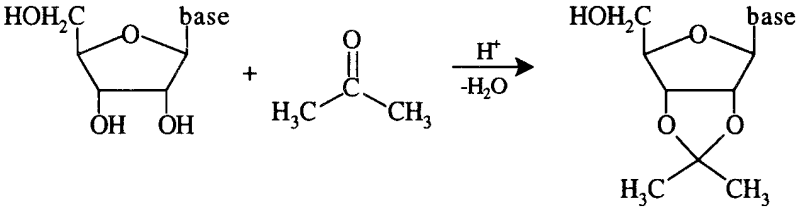
25.4



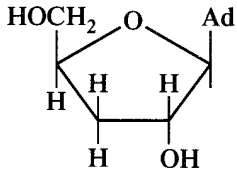
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25.5 (a) The isopropylidene group is part of a cyclic acetal and is thus susceptible to hydrolysis by mild acid.

(b) It can be installed by treating the nucleoside with acetone and a trace of acid and by simultaneously removing the water that is produced.

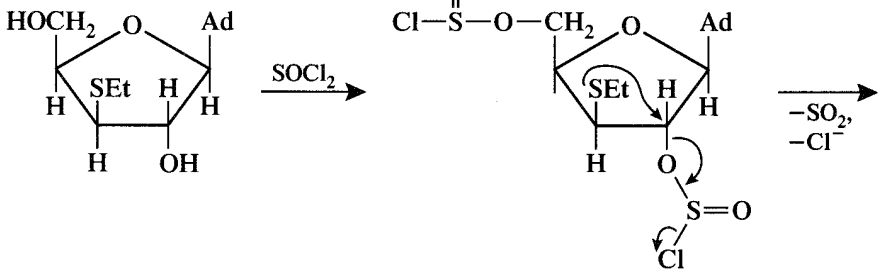


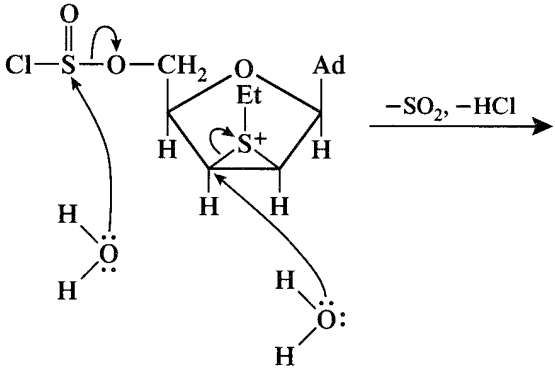
25.6 (a) Cordycepin is

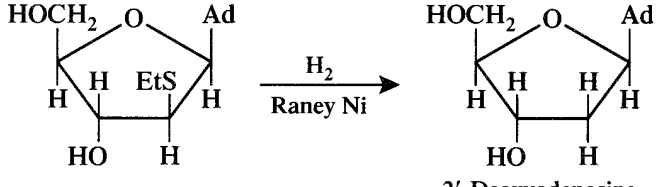


(3′-Deoxyadenosine)

(b)







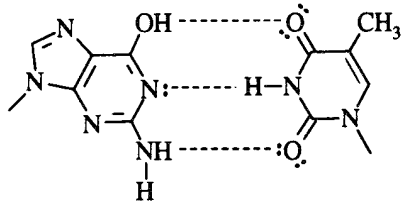
2′-Deoxyadenosine

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25.7 (a) 6×10^9 base pairs $\times \dfrac{34\ \text{Å}}{10\ \text{base pairs}} \times \dfrac{10^{-10}\ \text{m}}{\text{Å}} \cong 2\ \text{m}$

(b) $6 \times 10^{-12}\ \dfrac{\text{g}}{\text{ovum}} \times 3 \times 10^9\ \text{ova} = 1.8 \times 10^{-2}\ \text{g}$

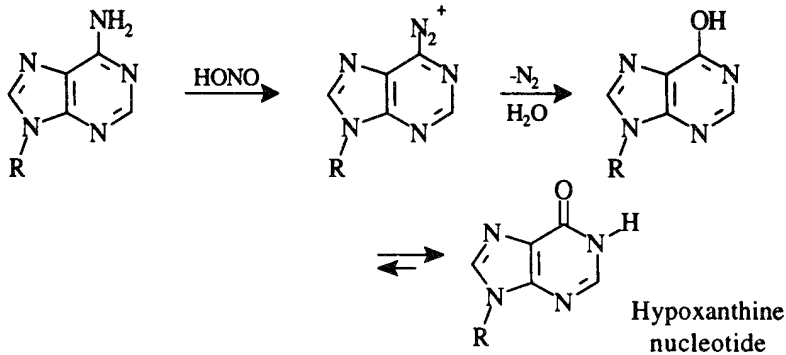
25.8 (a)



Lactim form of guanine — Thymine

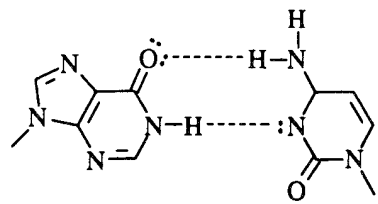
(b) Thymine would pair with adenine and thus adenine would be introduced into the complementary strand where guanine should occur.

25.9 (a) A diazonium salt and a heterocyclic analog of a phenol.



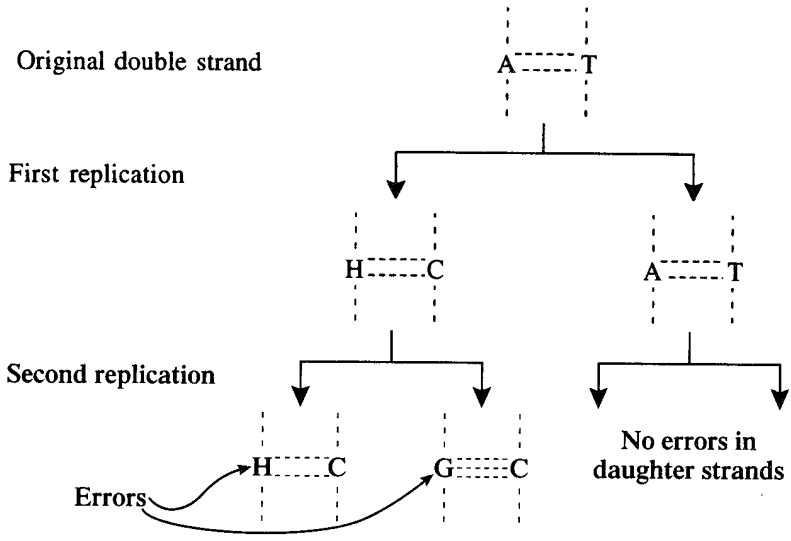
Hypoxanthine nucleotide

(b)

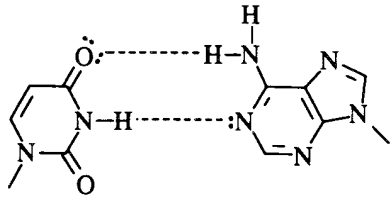


Hypoxanthine — Cytosine

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25.10



25.11

(a)	UGG	GGG	UUU	UAC	AGC	*m*RNA
(b)	Tyr	Gly	Phe	Tyr	Ser	Amino acids
(c)	ACC	CCC	AAA	AUG	UCG	Anticodons

25.12

	Arg	Ile	Cys	Tyr	Val	Amino acids
(a)	AGA	AUA	UGC	UGG	GUA	*m*RNA
(b)	TCT	TAT	ACG	ACC	CAT	DNA
(c)	UCU	UAU	ACG	ACC	CAU	Anticodons

25.13 A change from C–T–T to C–A–T or a change from C–T–C to C–A–C.

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A APPENDIX
Empirical and Molecular Formulas

In Section 1.2B, we discussed briefly the pioneering work of Berzelius, Dumas, Liebig, and Cannizzaro in devising methods for determining the formulas of organic compounds. Although the experimental procedures for these analyses have been refined, the basic methods for determining the elemental composition of an organic compound today are not substantially different from those used in the nineteenth century. A carefully weighed quantity of the compound to be analyzed is oxidized completely to carbon dioxide and water. The weights of carbon dioxide and water are carefully measured and used to find the percentages of carbon and hydrogen in the compound. The percentage of nitrogen is usually determined by measuring the volume of nitrogen (N_2) produced in a separate procedure.

Special techniques for determining the percentage composition of other elements typically found in organic compounds have also been developed, but the direct determination of the percentage of oxygen is difficult. However, if the percentage composition of all the other elements is known, then the percentage of oxygen can be determined by difference. The following examples will illustrate how these calculations can be carried out.

EXAMPLE A

A new organic compound is found to have the following elemental analysis.

Carbon	67.95%
Hydrogen	5.69
Nitrogen	26.20
Total:	99.84%

Since the total of these percentages is very close to 100% (within experimental error), we can assume that no other element is present. For the purpose of our calculation it is convenient to assume that we have a 100-g sample. If we did, it would contain the following:

67.95 g of carbon
5.69 g of hydrogen
26.20 g of nitrogen

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