7 ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS. ELIMINATION REACTIONS OF ALKYL HALIDES

SOLUTIONS TO PROBLEMS

7.1 (a) (*E*)-1-Bromo-1-chloro-1-pentene or (*E*)-1-Bromo-1-chloropent-1-ene

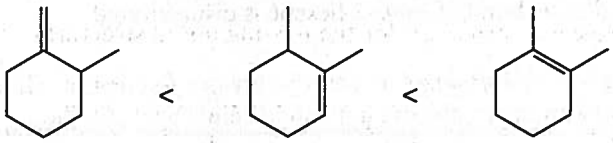
(b) (*E*)-2-Bromo-1-chloro-1-iodo-1-butene or (*E*)-2-Bromo-1-chloro-1-iodobut-1-ene

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

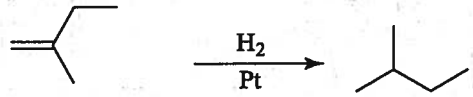
(d) (*Z*)-1-Chloro-1-iodo-2-methyl-1-butene or (*Z*)-1-Chloro-1-iodo-2-methylbut-1-ene

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

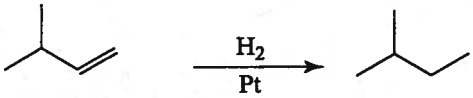
(f) (*Z*,3*S*)-1-Bromo-2-chloro-3-methyl-1-hexene or (*Z*,3*S*)-1-Bromo-2-chloro-3-methylhex-1-ene

7.2  Order of increasing stability

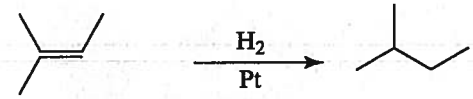
7.3 (a), (b)



2-Methyl-1-butene (disubstituted) $\xrightarrow[\text{pressure}]{H_2, Pt}$ $\Delta H° = -119$ kJ mol^{-1}

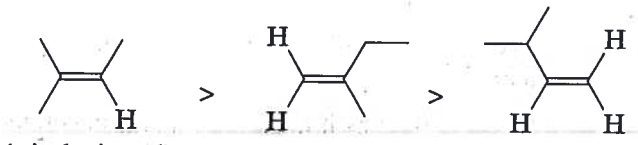


3-Methyl-1-butene (monosubstituted) $\xrightarrow[\text{pressure}]{H_2, Pt}$ $\Delta H° = -127$ kJ mol^{-1}



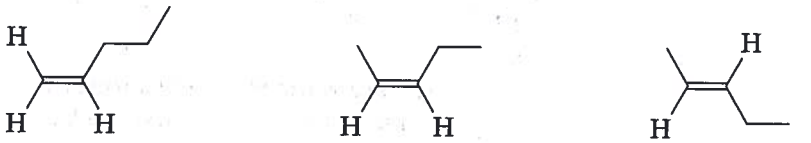
2-Methyl-2-butene (trisubstituted) $\xrightarrow[\text{pressure}]{H_2, Pt}$ $\Delta H° = -113$ kJ mol^{-1}

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

(d) 

(trisubstituted) (disubstituted) (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.

(e) 

1-Pentene *cis*-2-Pentene *trans*-2-Pentene

(f) Order of stability: *trans*-2-pentene > *cis*-2-pentene >1-pentene

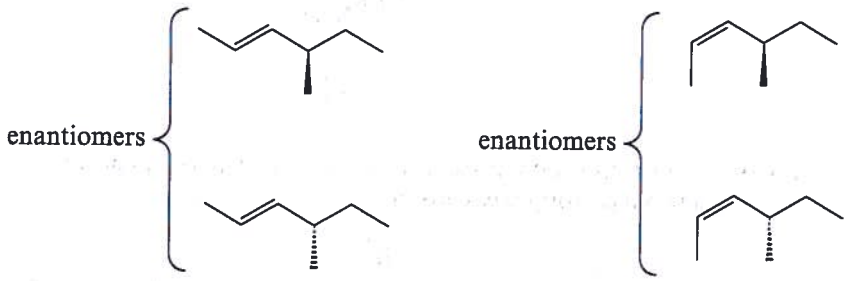
7.4 (a) 2,3-Dimethyl-2-butene would be the more stable because the double bond is tetrasubstituted. 2-Methyl-2-pentene has a trisubstituted double bond.

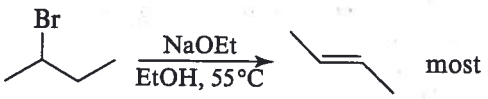
(b) *trans*-3-Hexene would be the more stable because alkenes with trans double bonds are more stable than those with cis double bonds.

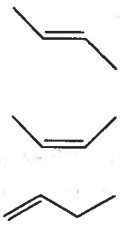
(c) *cis*-3-Hexene would be more stable because its double bond is disubstituted. The double bond of 1-hexene is monosubstituted.

(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.

7.5 *Four stereoisomers*. However only *two fractions* are found as enantiomer pairs are indistinguishible by distillation.



7.6 

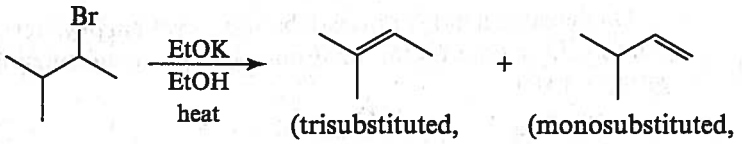


most

less

least

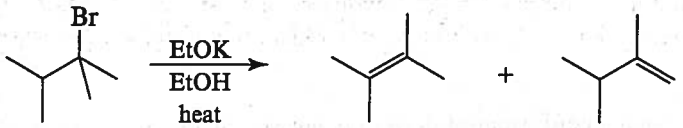
7.7 (a)



(trisubstituted, more stable) Major product

(monosubstituted, less stable) Minor product

(b)

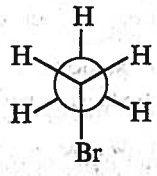


(tetrasubstituted, more stable) Major product

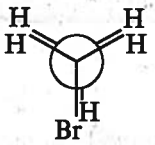
(disubstituted, less stable) Minor product

7.8 *t*-BuOK in *t*-BuOH

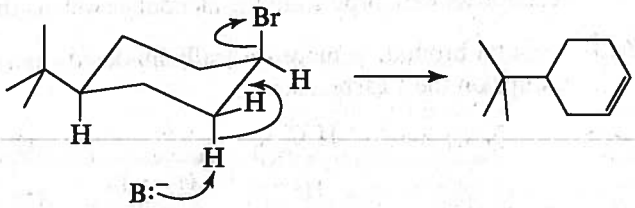
7.9 An anti coplanar transition state allows the molecule to assume the more stable staggered conformation,



whereas a syn coplanar transition state requires the molecule to assume the less stable eclipsed conformation.

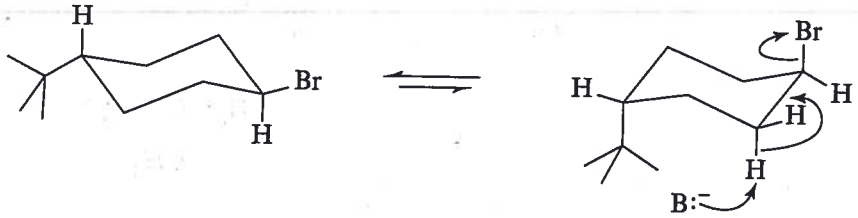


7.10 *cis*-1-Bromo-4-*tert*-butylcyclohexane can assume an anti coplanar transition state in which the bulky *tert*-butyl group is equatorial.



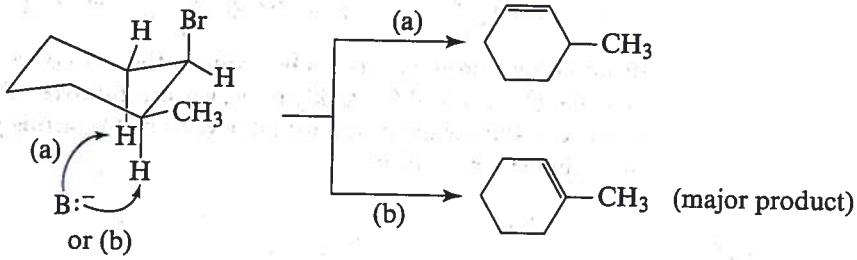
The conformation (above), because it is relatively stable, is assumed by most of the molecules present, and, therefore, the reaction is rapid.

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



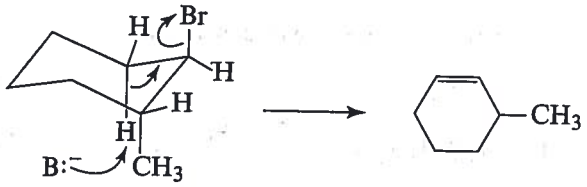
Such a conformation is of high energy; therefore, very few molecules assume this conformation. The reaction, consequently, is very slow.

7.11 (a) Anti coplanar elimination can occur in two ways with the cis isomer.



cis-1-Bromo-2-methylcyclohexane

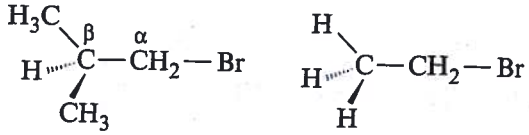
(b) Anti coplanar elimination can occur in only one way with the trans isomer.



trans-1-Bromo-2-methylcyclohexane

7.12 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 as well as the desired alkene.

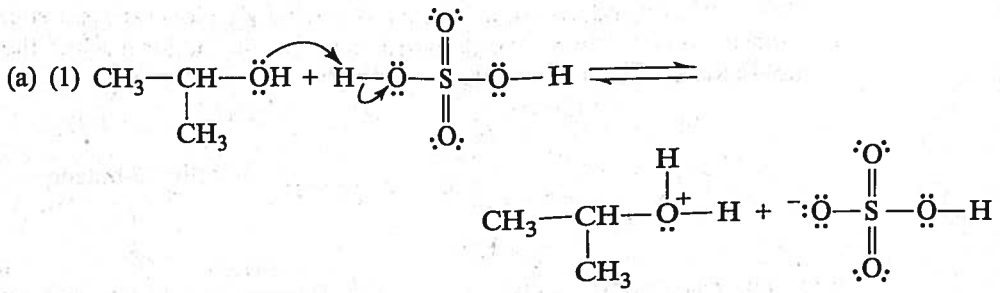
7.13 Isobutyl bromide is more sterically hindered than ethyl bromide because of the methyl groups on the β carbon atom.



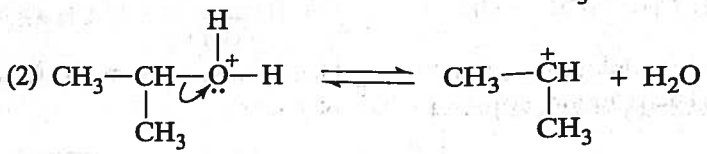
Isobutyl bromide Ethyl bromide

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.

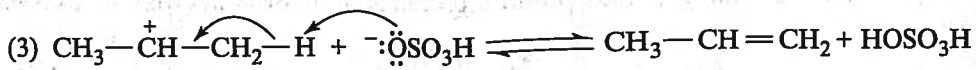
7.14 (a) (1)



(2)

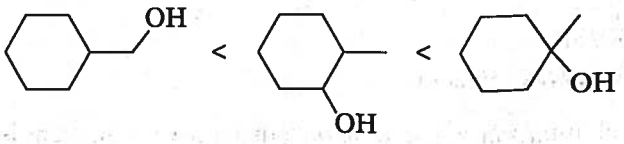


(3)



(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 HO^- ion, and such steps almost never occur.

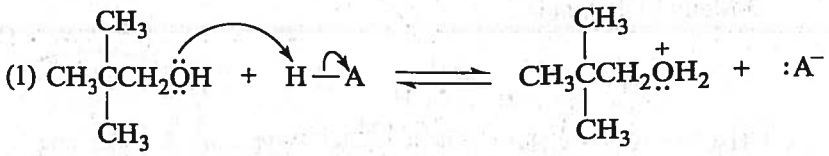
7.15



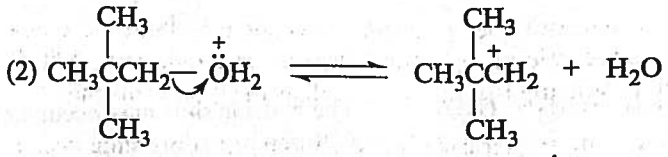
1° 2° 3°

Order of increasing case of dehydration

7.16 (1)

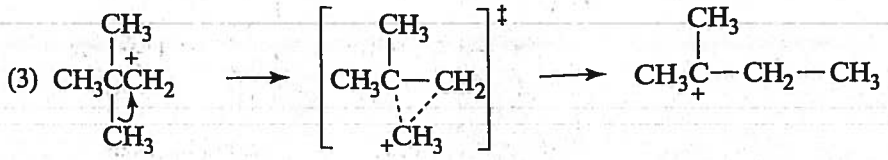


(2)



1° Carbocation

(3)



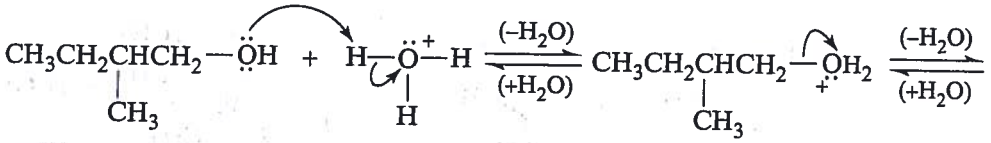
1° Carbocation Transition state 3° Carbocation

[Steps (2) and (3), ionization and rearrangement, may occur simultaneously.]

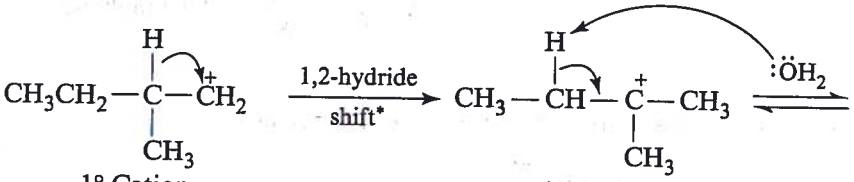


2-Methyl-2-butene

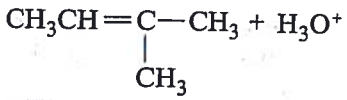
7.17



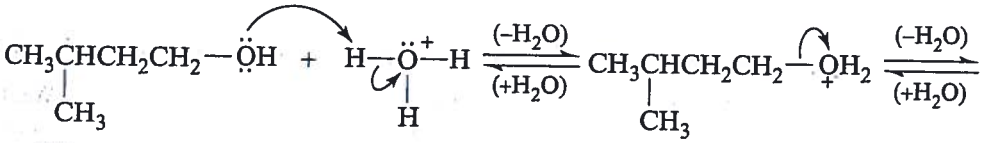
2-Methyl-1-butanol



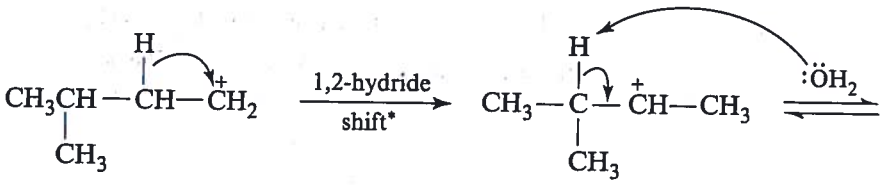
1° Cation 3° Cation

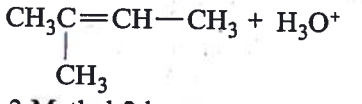


2-Methyl-2-butene



3-Methyl-1-butanol

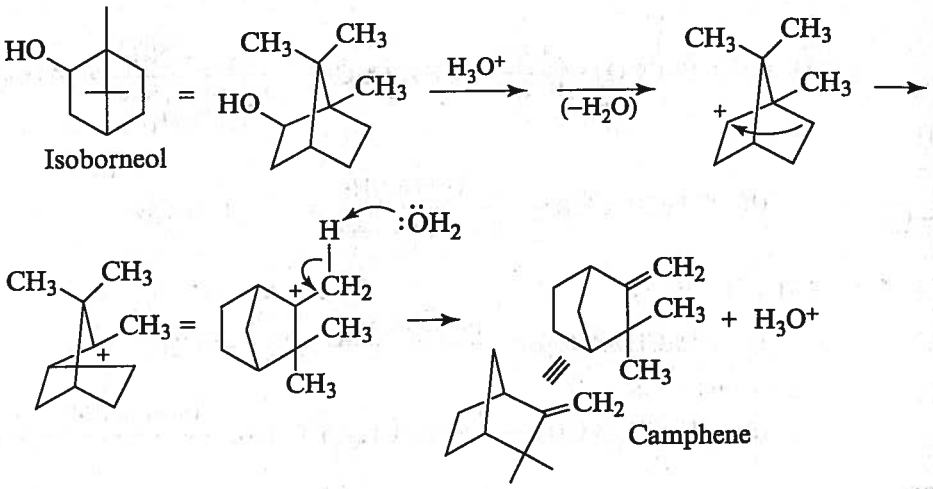




2-Methyl-2-butene

* The hydride shift may occur simultaneously with the preceding step.

7.18



7.19 (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

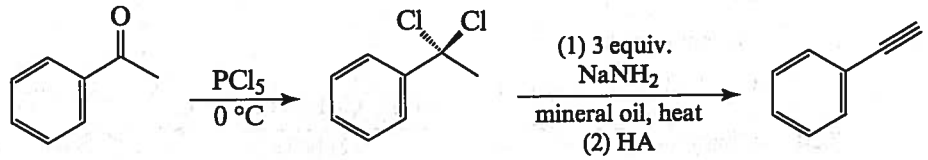
(d) $CH_3C{\equiv}C{:}^- + H{-}\ddot{O}CH_2CH_3 \longrightarrow CH_3C{\equiv}CH + {}^-{:}\ddot{O}CH_2CH_3$

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

7.20



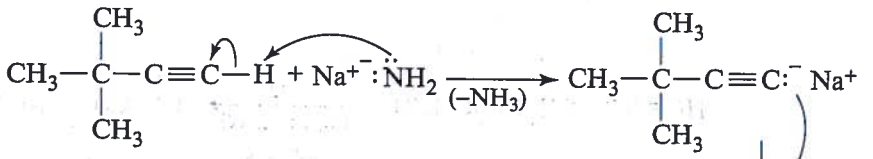
7.21 (a) $CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[0\ ^\circ C]{PCl_5} CH_3CCl_2CH_3 \xrightarrow[\text{mineral oil, heat}]{\text{(1) 3 } NaNH_2,\ \text{(2) } {}^+NH_4} CH_3C{\equiv}CH$

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

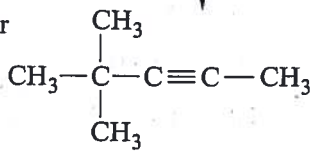
(c) $CH_3CHBrCH_2Br \xrightarrow{\text{[same as (b)]}} CH_3C{\equiv}CH$

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

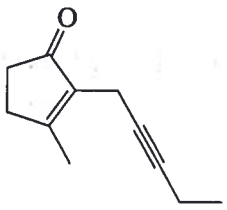
7.22



(Starting the synthesis with 1-propyne and attempting to alkylate with a *tert*-butyl substrate would not work because elimination would occur instead of substitution.)

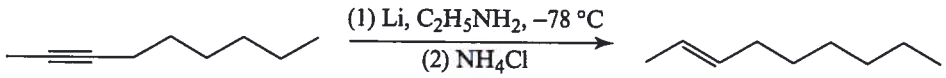


7.23



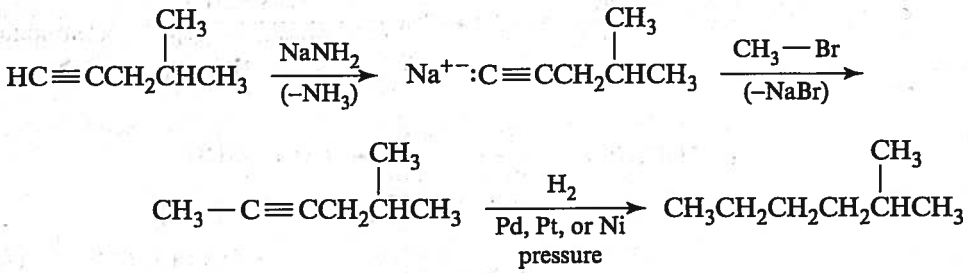
Compound A

7.24

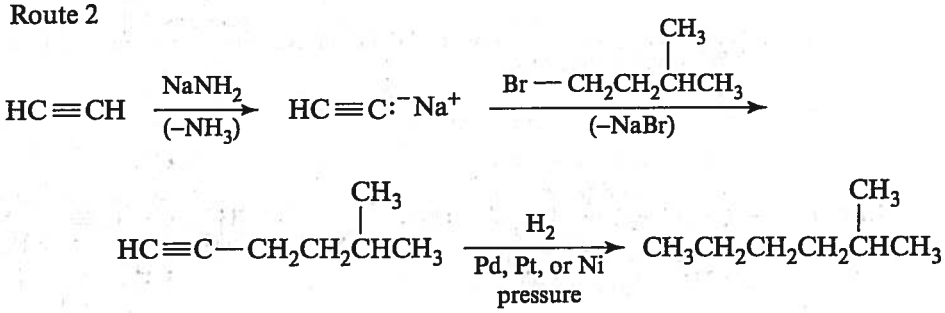


(*E*)-2-Nonene

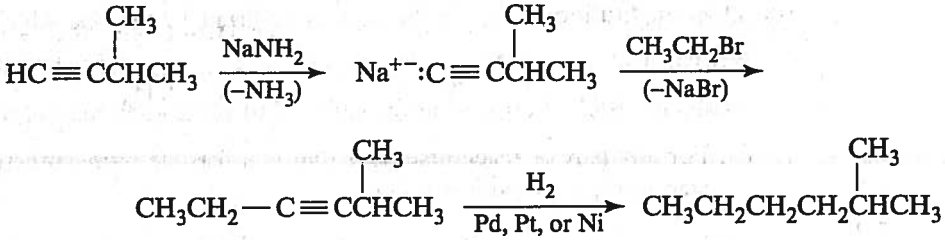
7.25 Route 1



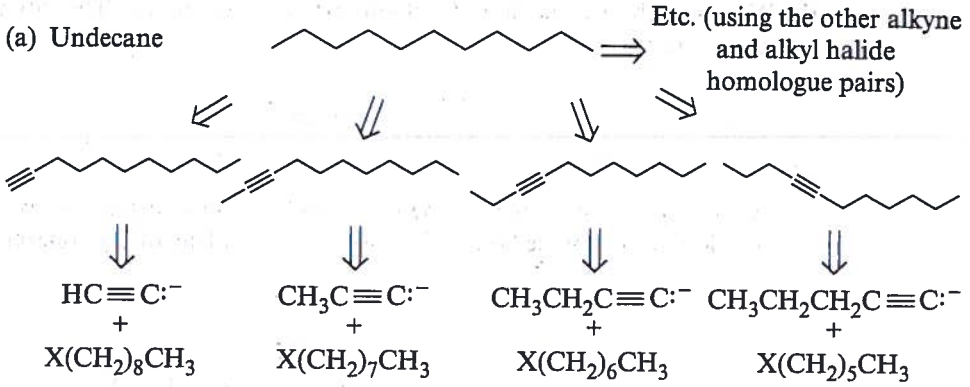
Route 2



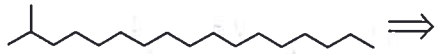
Route 3



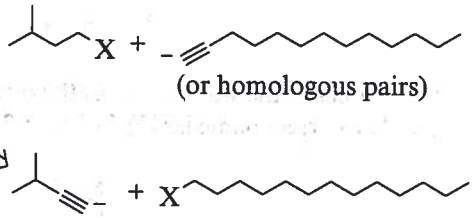
7.26 (a) Undecane

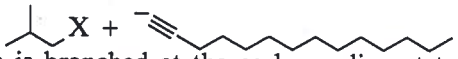
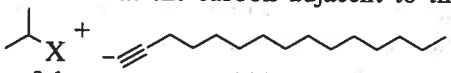


2-Methylheptadecane

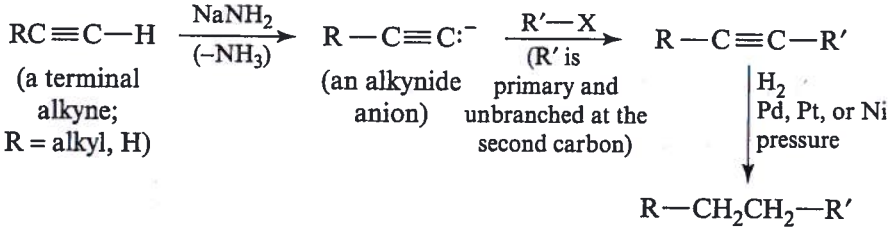


(after hydrogenation of the alkyne from one of the possible retrosynthetic disconnections)



(Note that  is not a good choice because the alkyl halide is branched at the carbon adjacent to the one which bears the halogen. Neither would  work because the alkyl halide is secondary. Both of these routes would lead to elimination instead of substitution.)

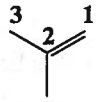
(b) For any pair of reactants above that is a feasible retrosynthetic disconnection, the steps for the synthesis would be



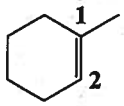
7.27 (a) We designate the position of the double bond by using the *lower* number of the two numbers of the doubly bonded carbon atoms, and the chain is numbered from the end nearer the double bond. The correct name is *trans*-2-pentene.



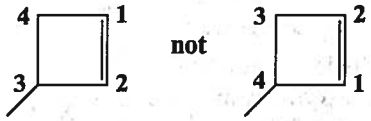
(b) We must choose the longest chain for the base name. The correct name is 2-methylpropene.



(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.



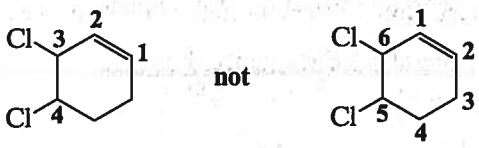
(d) We must number the ring starting with the double bond in the direction that gives the substituent the lower number. The correct name is 3-methylcyclobutene.



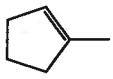
(e) We number in the way that gives the double bond *and the substituent* the lower number. The correct name is (*Z*)-2-chloro-2-butene or (*Z*)-2-chlorobut-2-ene.

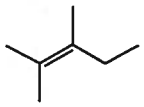


(f) We number the ring starting with the double bond so as to give the substituents the lower numbers. The correct name is 3,4-dichlorocyclohexene.



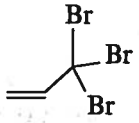
7.28 (a) 

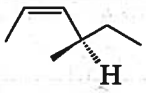
(b) 

(c) 

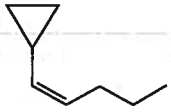
(d) 

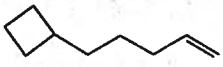
(e) 

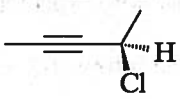
(f) 

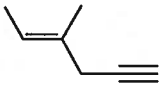
(g) 

(h) 

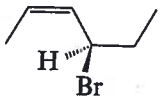
(i) 

(j) 

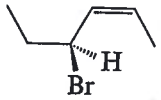
(k) 

(l) 

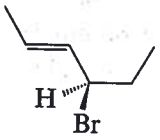
7.29 (a)



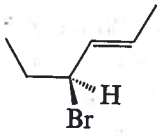
(2*Z*,4*R*)-4-Bromo-2-hexene
or
(2*Z*,4*R*)-4-Bromohex-2-ene



(2*Z*,4*S*)-4-Bromo-2-hexene
or
(2*Z*,4*S*)-4-Bromohex-2-ene

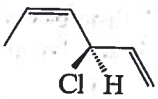


(2*E*,4*R*)-4-Bromo-2-hexene
or
(2*E*,4*R*)-4-Bromohex-2-ene

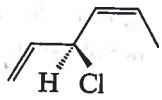


(2*E*,4*S*)-4-Bromo-2-hexene
or
(2*E*,4*S*)-4-Bromohex-2-ene

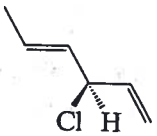
(b)



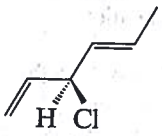
(3*R*,4*Z*)-3-Chloro-1,4-hexadiene
or
(3*R*,4*Z*)-3-Chlorohexa-1,4-diene



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

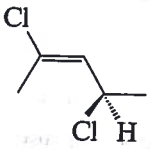


(3*R*,4*E*)-3-Chloro-1,4-hexadiene
or
(3*R*,4*E*)-3-Chlorohexa-1,4-diene

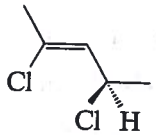


(3*S*,4*E*)-3-Chloro-1,4-hexadiene
or
(3*S*,4*E*)-3-Chlorohexa-1,4-diene

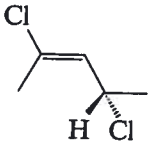
(c)



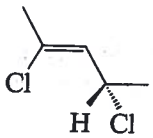
(2*E*,4*R*)-2,4-Dichloro-2-pentene
or
(2*E*,4*R*)-2,4-Dichloropent-2-ene



(2*Z*,4*R*)-2,4-Dichloro-2-pentene
or
(2*Z*,4*R*)-2,4-Dichloropent-2-ene

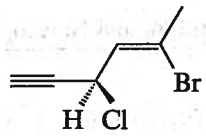


(2*E*,4*S*)-2,4-Dichloro-2-pentene
or
(2*E*,4*S*)-2,4-Dichloropent-2-ene

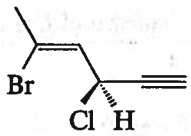


(2*Z*,4*S*)-2,4-Dichloro-2-pentene
or
(2*Z*,4*S*)-2,4-Dichloropent-2-ene

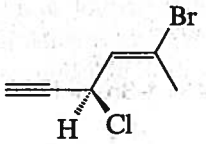
(d)



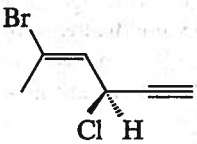
(3*R*,4*Z*)-5-Bromo-3-chloro-4-hexen-1-yne
or
(3*R*,4*Z*)-5-Bromo-3-chlorohex-4-en-1-yne



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



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



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

An IUPAC* rule covers those cases in which a double bond and a triple bond occur in the same molecule:

> Numbers as low as possible are given to double and triple bonds as a set, even though this may at times give "-yne" a lower number than "-ene." If a choice remains, preference for low locants is given to the double bonds.

*International Union of Pure and Applied Chemistry, www.iupac.org.

7.30 (a) (*E*)-3,5-Dimethyl-2-hexene or (*E*)-3,5-dimethylhex-2-ene

(b) 4-Chloro-3-methylcyclopentene

(c) 6-Methyl-3-heptyne or 6-methylhept-3-yne

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

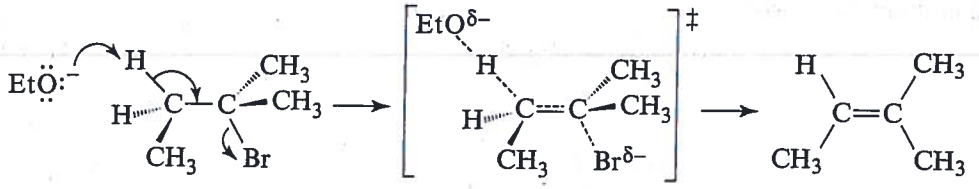
(e) (4*Z*,3*R*)-3-Chloro-4-hepten-1-yne or (4*Z*,3*R*)-3-chlorohept-4-en-1-yne

(f) 2-Pentyl-1-heptene or 2-pentylhept-1-ene

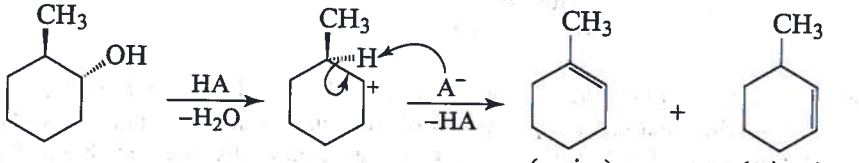
7.31 1-Pentanol > 1-pentyne > 1-pentene > pentane
(See Section 3.8 for the explanation.)

Mechanisms of Dehydrohalogenation, Dehydration, and Nucleophilic Substitution

7.32



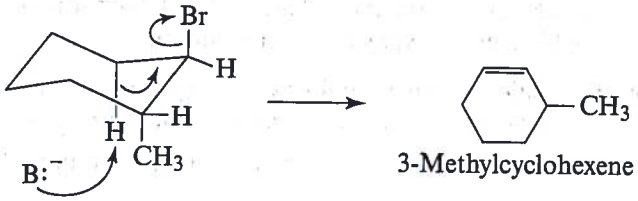
7.33 Dehydration of *trans*-2-methylcyclohexanol proceeds through the formation of a carbocation (through an E1 reaction of the protonated alcohol) and leads preferentially to the more stable alkene. 1-Methylcyclohexene (below) is more stable than 3-methylcyclohexene (the minor product of the dehydration) 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 coplanar transition state. Such a transition state is possible only for the elimination leading to 3-methylcyclohexene (cf. Review Problem 7.11).



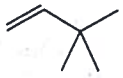
3-Methylcyclohexene

7.34 (a)



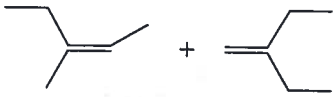
major minor

(b)



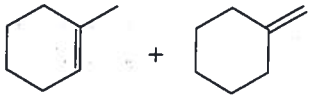
only product

(c)



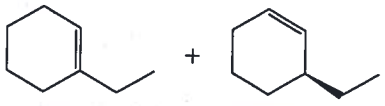
major (+ stereoisomer) minor

(d)



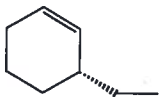
major minor

(e)

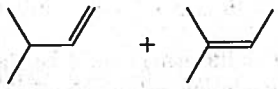


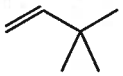
major minor

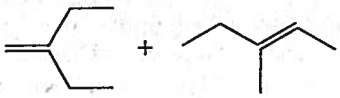
(f)

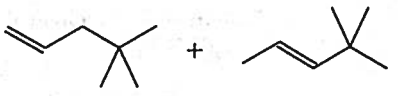


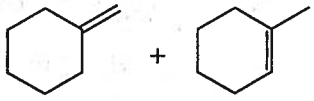
only product

7.35 (a)  major + minor

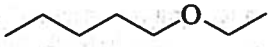
(b)  only product

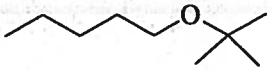
(c)  major + minor (+ stereoisomer)

(d)  major + minor (+ stereoisomer)

(e)  major + minor

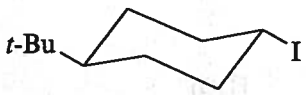
7.36 *tert*-Butyl alcohol and *tert*-butyl methyl ether are formed via an S_N1 mechanism. The rate of the reaction is independent of the concentration of methoxide ion (from sodium methoxide). This, however, is only one reaction that causes *tert*-butyl bromide to disappear. A competing reaction that 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.

7.37 (a) The major product would be  (by an S_N2 mechanism) because the substrate is primary and the nucleophile-base is not hindered. Some  would be produced by an E2 mechanism.

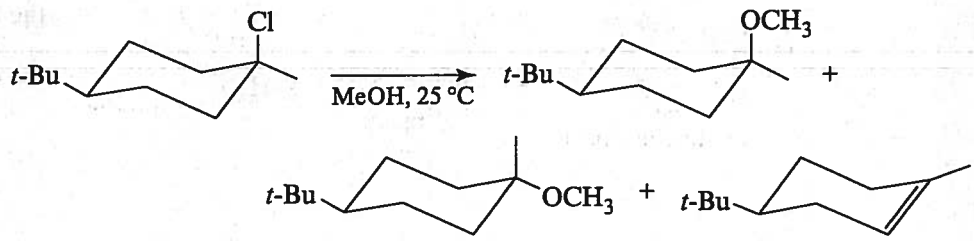
(b) The major product would be  (by an E2 mechanism), even though the substrate is primary, because the base is a hindered strong base. Some  would be produced by an S_N2 mechanism.

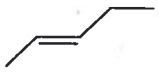
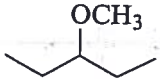
(c) For all practical purposes,  (by an E2 mechanism) would be the only product because the substrate is tertiary and the base is strong.

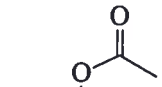
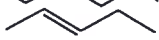
(d) Same answer as (c) above.

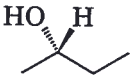
(e)  (formed by an S_N2 mechanism) would, for all practical purposes, be the only product. Iodide ion is a very weak base and a good nucleophile.

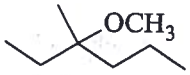
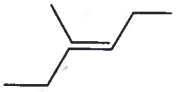
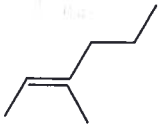
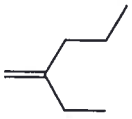
(f) Because the substrate is tertiary and the base weak, an S_N1 reaction (solvolysis) will occur, accompanied by elimination (E1). At 25°C, the S_N1 reaction would predominate.

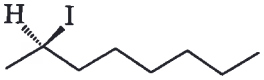


(g)  [also (*Z*)] (by an E2 mechanism) would be the major product because the substrate is secondary and the base/nucleophile is a strong base. Some of the ether  would be formed by an S_N2 pathway.

(h) The major product would be  (by an S_N2 mechanism) because the acetate ion is a weak base. Some  and  might be formed by an E2 pathway.

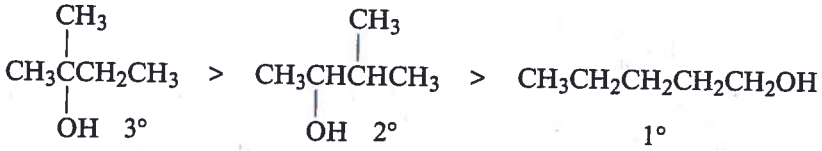
(i)  [also (*Z*)] and  (by E2) would be major products, and  [(*S*) isomer] (by S_N2) would be the minor product.

(j)  (by S_N1) would be the major product.  [also (*Z*)],  [also (*Z*)], and  (by E1) would be minor products.

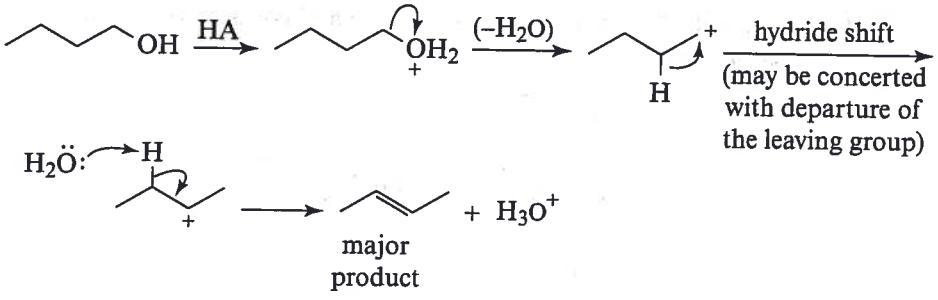
(k)  (by S_N2) would be the only product.

(l) 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.)

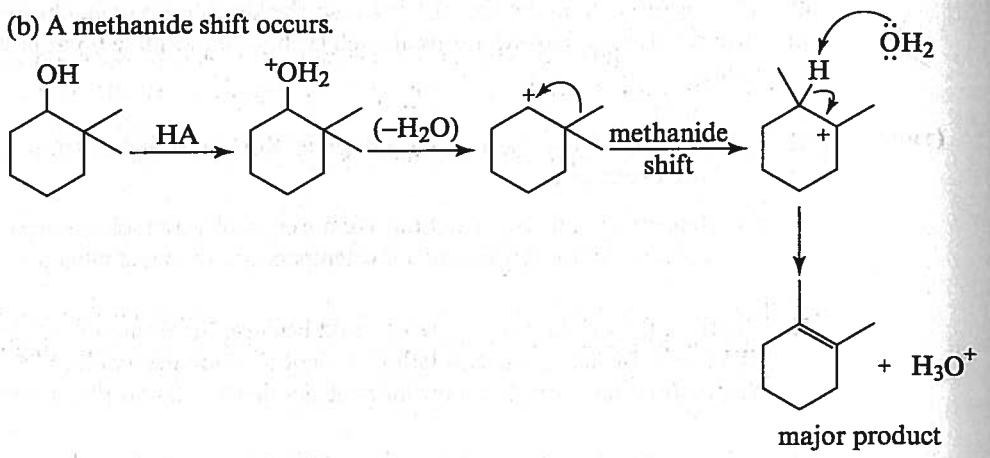
7.38



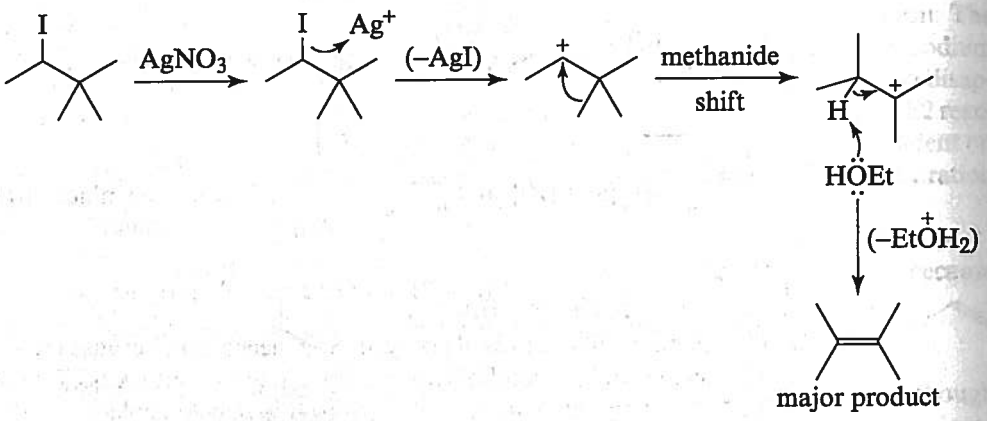
7.39 (a) A hydride shift occurs.



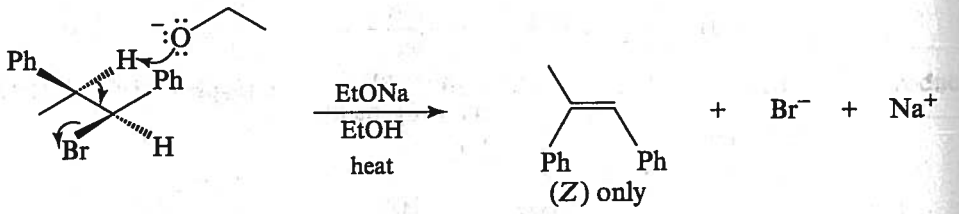
(b) A methanide shift occurs.



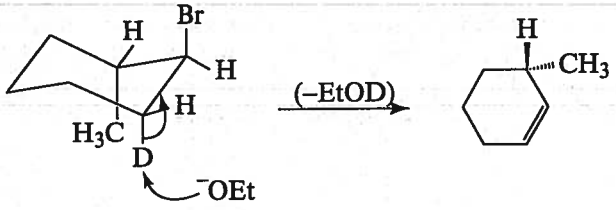
(c) A methanide shift occurs.



(d) The required anti coplanar transition state leads only to (*Z*) alkene:



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



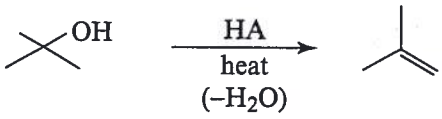
7.41 The alkene cannot be formed because the double bond in the product is too highly strained. Recall that the atoms at each carbon of a double bond prefer to be in the same plane.

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

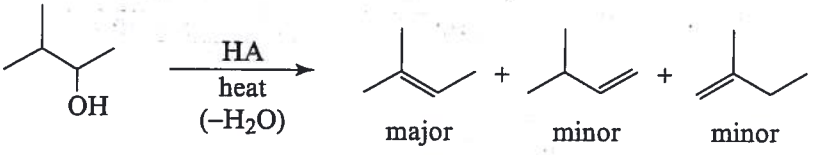
(b) Here we want an S_N1 reaction. We use ethanol as the solvent *and as the nucleophile*, and we carry out the reaction at a low temperature so that elimination will be minimized.

7.43 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.

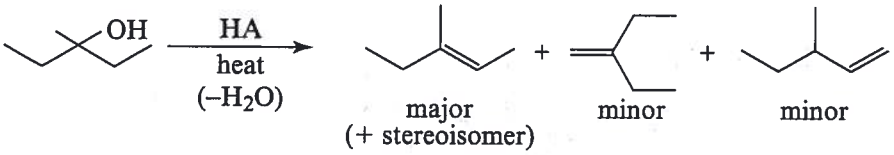
7.44 (a)



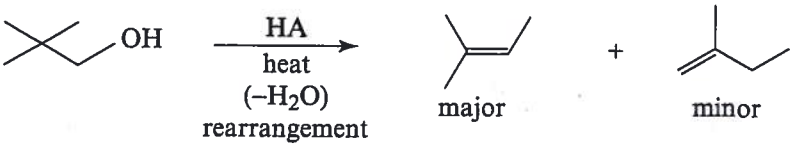
(b)



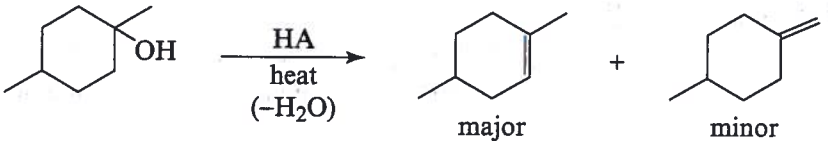
(c)



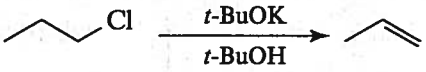
(d)

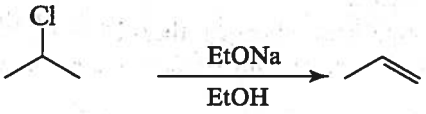


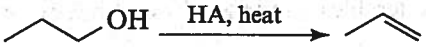
(e)

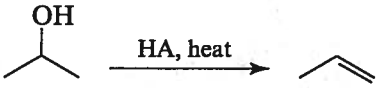


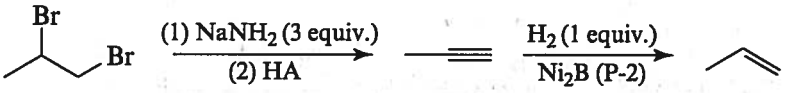
Synthesis of Alkenes and Alkynes

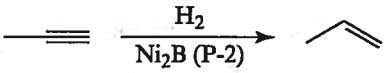
7.45 (a) 

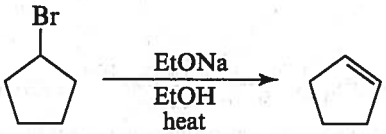
(b) 

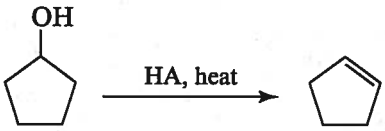
(c) 

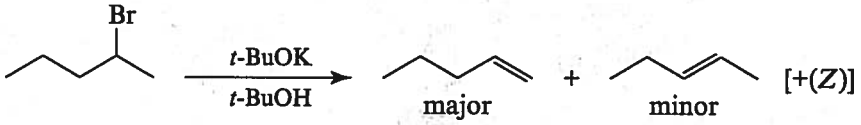
(d) 

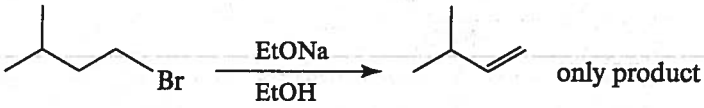
(e) 

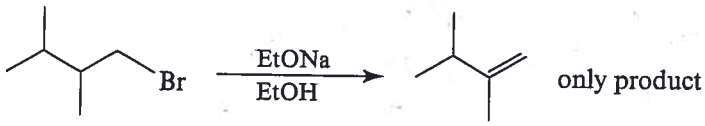
(f) 

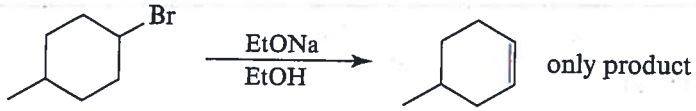
7.46 (a) 

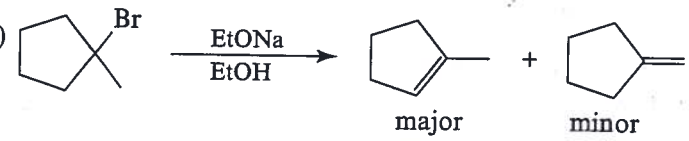
(b) 

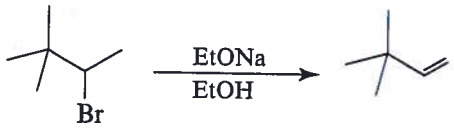
7.47 (a) 

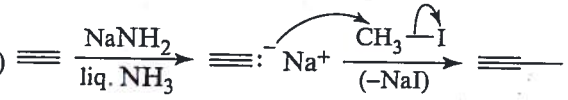
(b) 

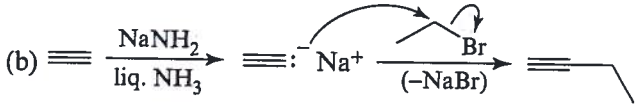
(c) 

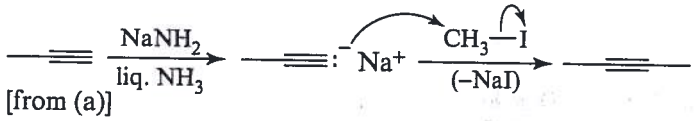
(d) 

(e) 

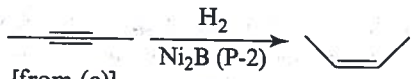
(f) 

7.48 (a) 

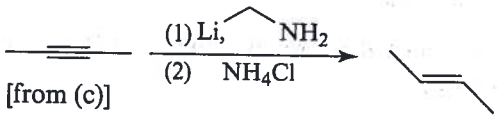
(b) 

(c) 

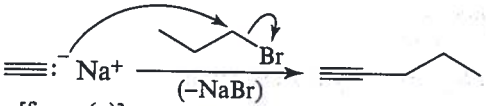
[from (a)]

(d) 

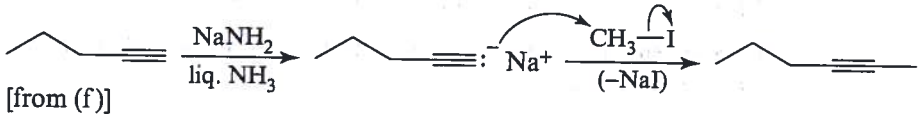
[from (c)]

(e) 

[from (c)]

(f) 

[from (a)]

(g) 

[from (f)]

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

(i) [from (g)] $\xrightarrow[(2)\ NH_4Cl]{(1)\ Li,\ NH_2}$

(j) [from (a)] $\xrightarrow[(-NaBr)]{Br}$ $\xrightarrow[liq.\ NH_3]{NaNH_2}$ $\xrightarrow{Br}$

(k) [from (j)] $\xrightarrow{D_2O}$

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

7.49 (a) Three

(b) One

Index of Hydrogen Deficiency

7.50 (a) Caryophyllene has the same molecular formula as zingiberene (Review Problem 4.21); 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 Review Problem 23.2 for the structure of caryophyllene.)

7.51 (a) $C_{30}H_{62}$ = formula of alkane
$\underline{C_{30}H_{50}}$ = 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 Review Problem 23.2 for the structural formula of squalene.)