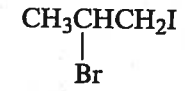
8 ALKENES AND ALKYNES II: ADDITION REACTIONS

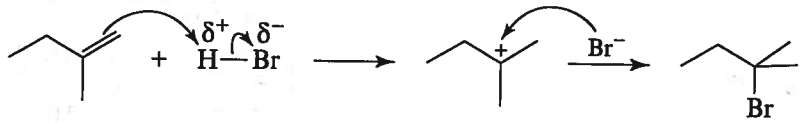
SOLUTIONS TO PROBLEMS

8.1

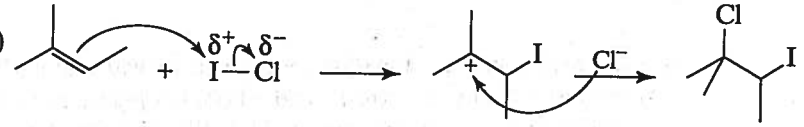


2-Bromo-1-iodopropane

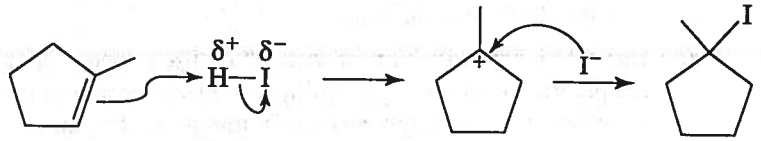
8.2 (a)



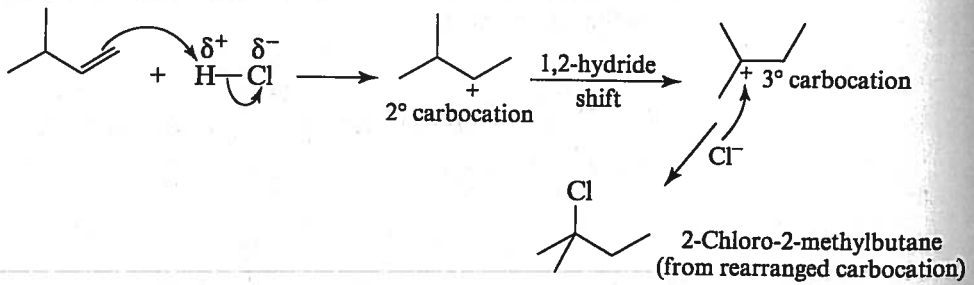
(b)

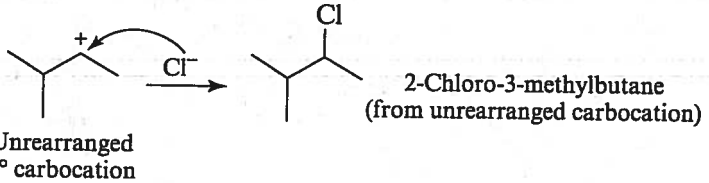


(c)



8.3 (a)

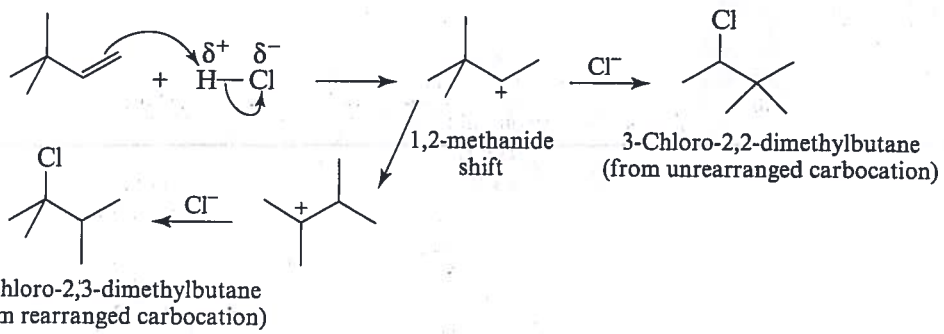




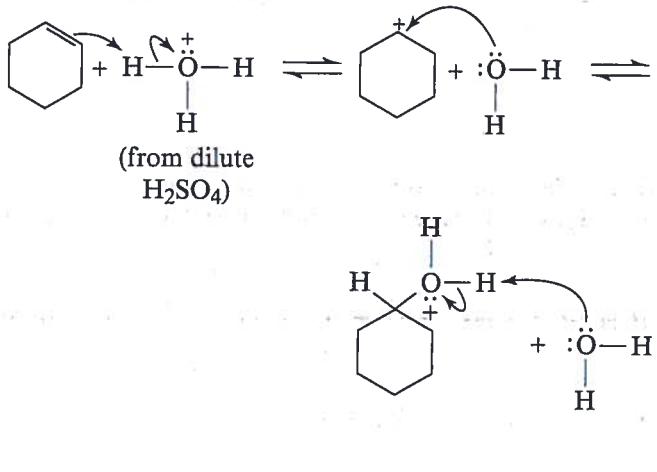
Unrearranged 2° carbocation

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

(b)



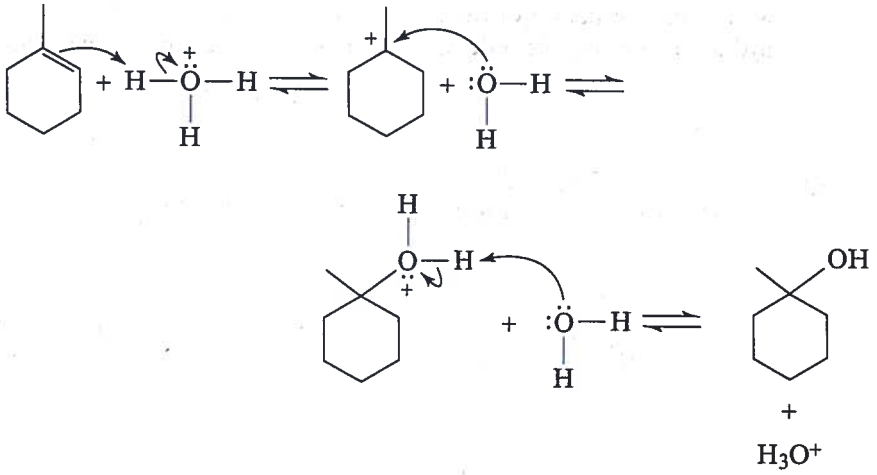
8.4 (a)



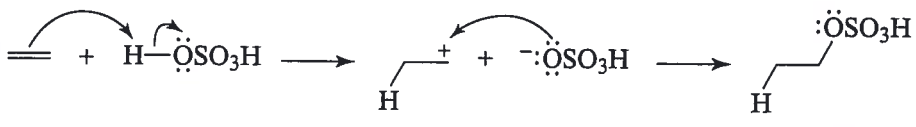
(b) Use a high concentration of water because we want the carbocation produced to react with water. And use a strong acid whose conjugate base is a very weak nucleophile. (For this reason we would not use HI, HBr, or HCl.) An excellent method, therefore, is to use dilute sulfuric acid.

(c) Use a low concentration of water (i.e., use concentrated H_2SO_4) and use a higher temperature to encourage elimination. Distill cyclohexene from reaction mixture as it is formed, so as to draw the equilibrium toward product.

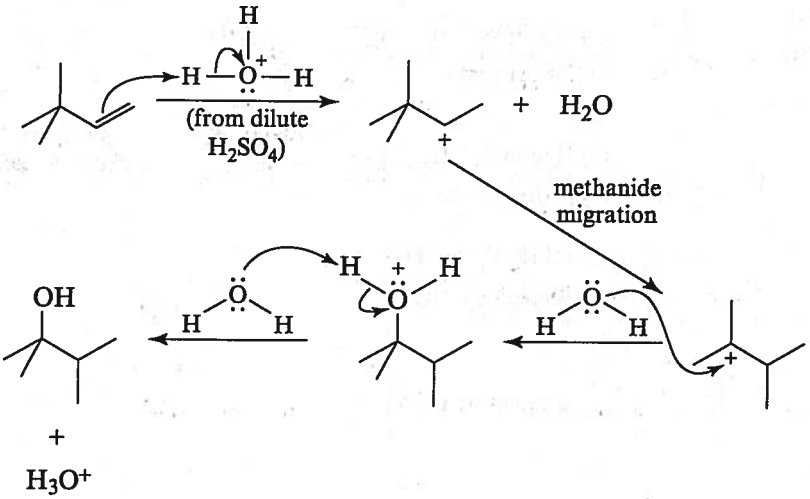
(d) 1-Methylcyclohexanol would be the product because a 3° carbocation would be formed as the intermediate.



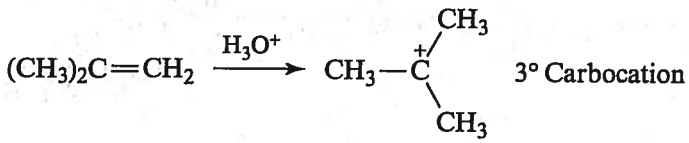
8.5



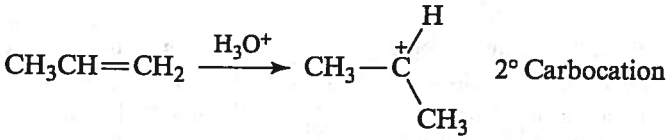
8.6



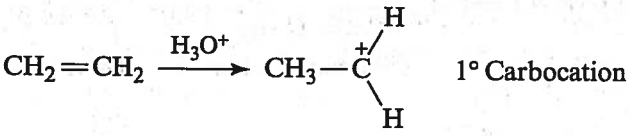
8.7 The order reflects the relative ease with which these alkenes accept a proton and form a carbocation. $(CH_3)_2C{=}CH_2$ reacts faster because it leads to a tertiary cation,



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



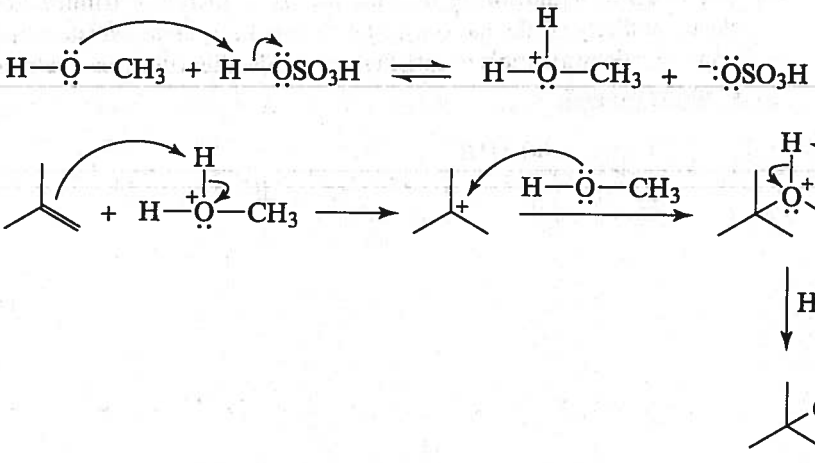
and $CH_2{=}CH_2$ reacts the slowest because it leads to a primary carbocation.

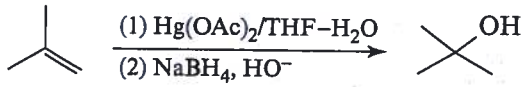


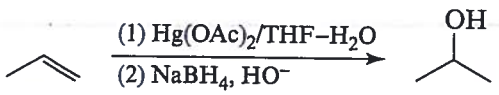
Recall that formation of the carbocation is the rate-determining step in acid-catalyzed hydration and that the order of stabilities of carbocations is the following:

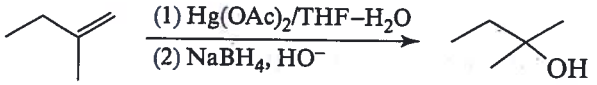
$$3° > 2° > 1° > {}^+CH_3$$

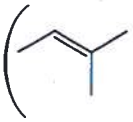
8.8

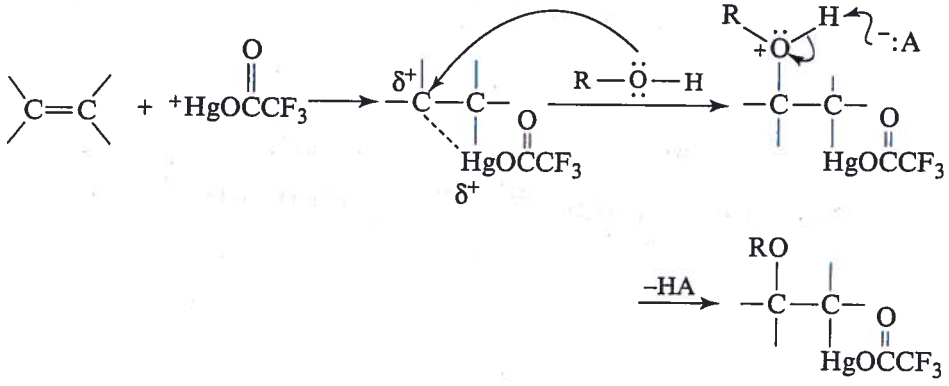


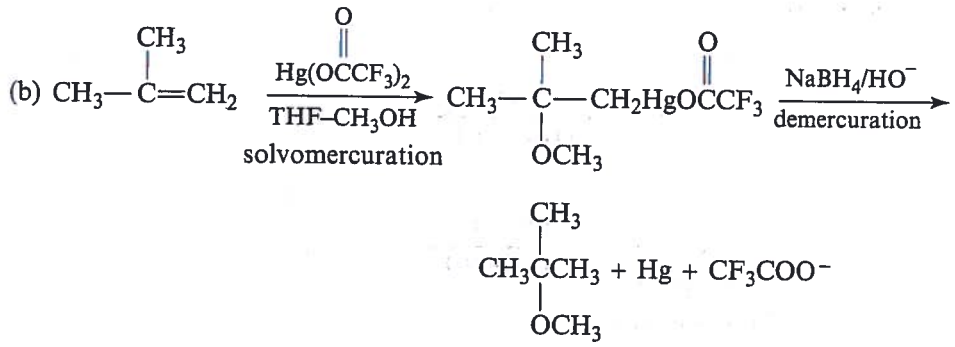
8.9 (a) 

(b) 

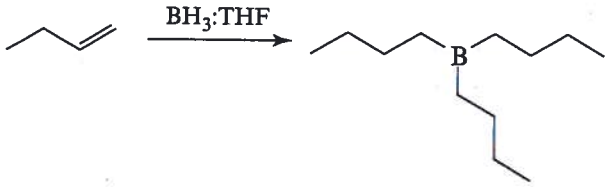
(c) 

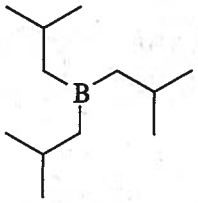
( can also be used.)

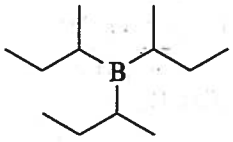
8.10 (a) 

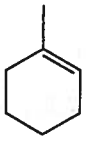
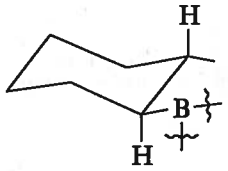
(b) 

(c) The electron-withdrawing fluorine atoms in mercuric trifluoroacetate enhance the electrophilicity of the cation. Experiments have demonstrated that for the preparation of tertiary alcohols in satisfactory yields, the trifluoroacetate must be used rather than the acetate.

8.11 (a) 3 

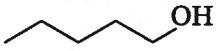
(b) 3  BH_3:THF → 

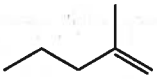
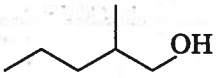
(c) 3  (or cis isomer) BH_3:THF → 

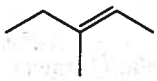
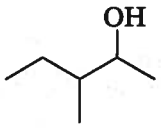
(d) 3  BH_3:THF, syn addition, anti Markovnikov →  + enantiomer

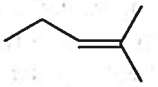
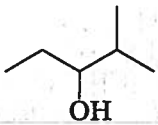
8.12 $2\,CH_3C(CH_3)=CHCH_3 \xrightarrow{BH_3:THF} [CH_3CH(CH_3)CH(CH_3)]_2BH$

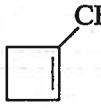
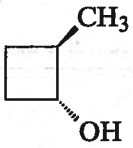
Disiamylborane

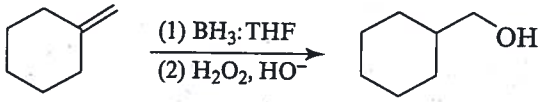
8.13 (a)  (1) BH_3:THF, (2) H_2O_2, HO^- → 

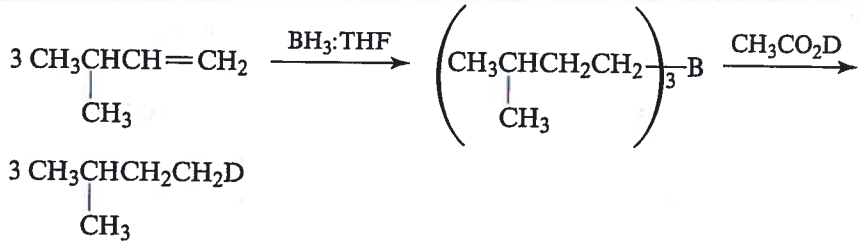
(b)  (1) BH_3:THF, (2) H_2O_2, HO^- → 

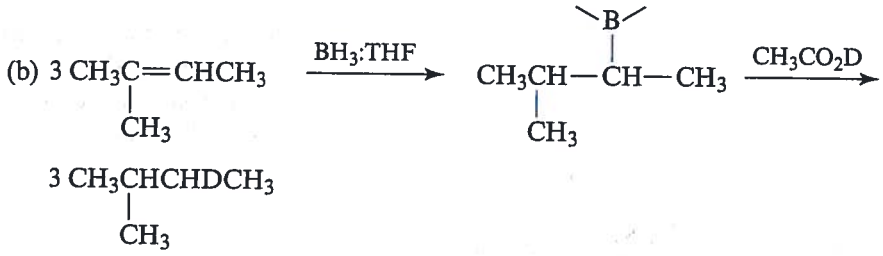
(c)  [or (*Z*) isomer] (1) BH_3:THF, (2) H_2O_2, HO^- → 

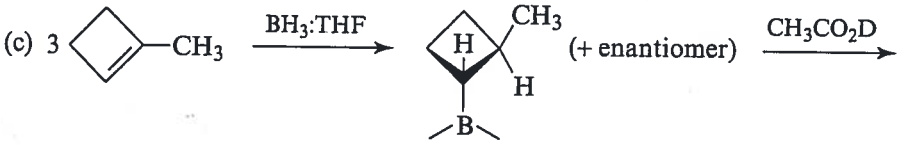
(d)  (1) BH_3:THF, (2) H_2O_2, HO^- → 

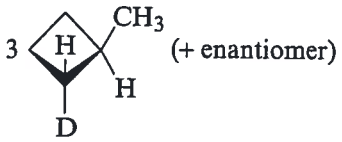
(e)  (1) BH_3:THF, (2) H_2O_2, HO^- →  + enantiomer

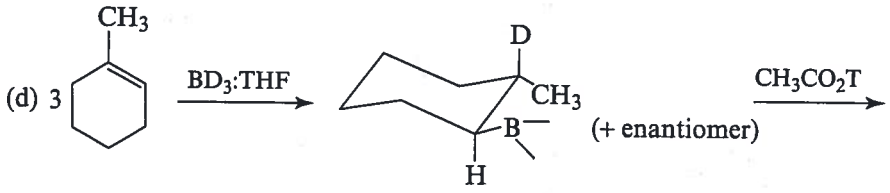
(f) 
(1) BH3:THF
(2) H2O2, HO−
OH

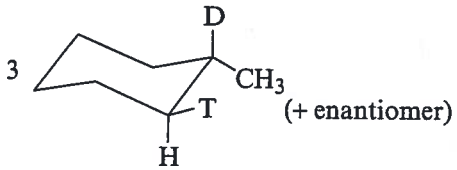
8.14 (a) 
3 CH3CHCH=CH2
CH3
BH3:THF
CH3CHCH2CH2
3
B
CH3CO2D
3 CH3CHCH2CH2D
CH3

(b) 
3 CH3C=CHCH3
CH3
BH3:THF
B
CH3CH—CH—CH3
CH3
CH3CO2D
3 CH3CHCHDCH3
CH3

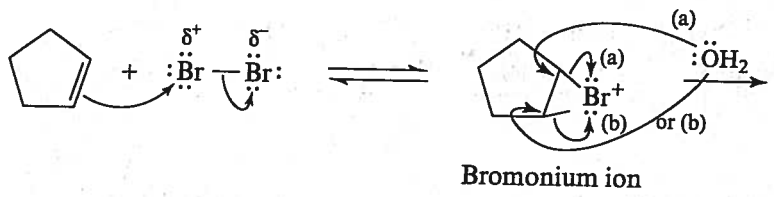
(c) 
3
CH3
BH3:THF
CH3
H
H
B
(+ enantiomer)
CH3CO2D

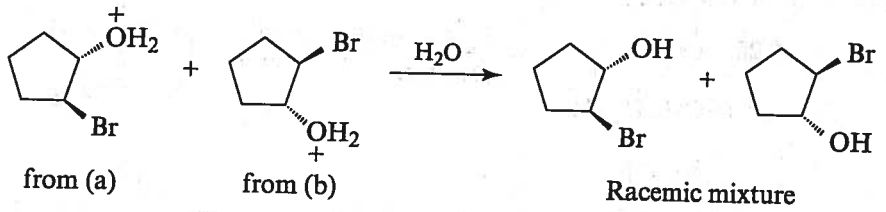

3
CH3
H
H
D
(+ enantiomer)

(d) 
CH3
3
BD3:THF
D
CH3
B
H
(+ enantiomer)
CH3CO2T


3
D
CH3
T
H
(+ enantiomer)

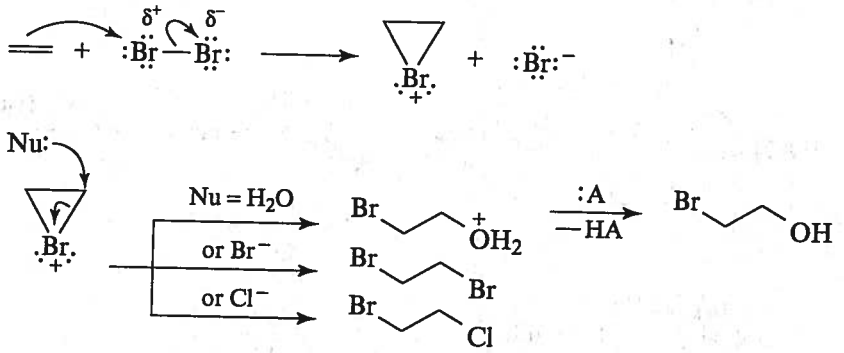
8.15



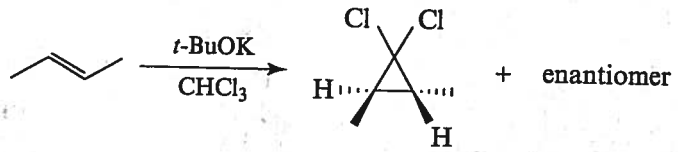


Because paths (a) and (b) occur at equal rates, these enantiomers are formed at equal rates and in equal amounts.

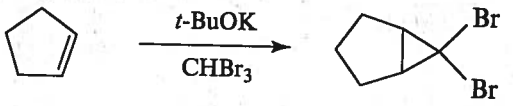
8.16



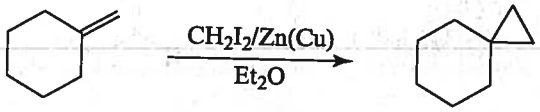
8.17 (a)



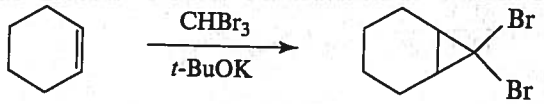
(b)



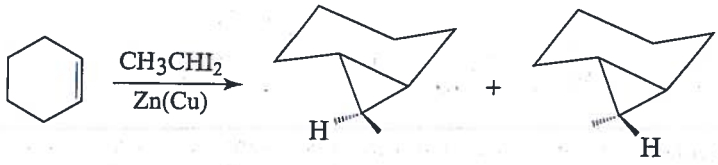
(c)



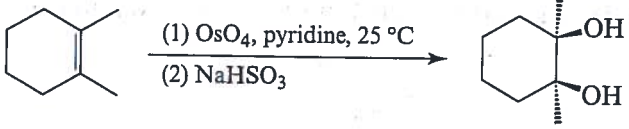
8.18



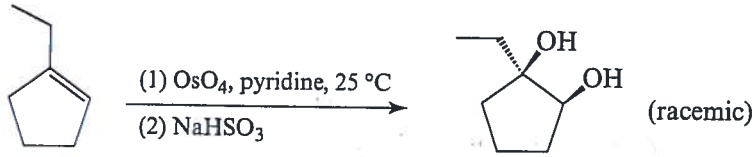
8.19



8.20 (a)

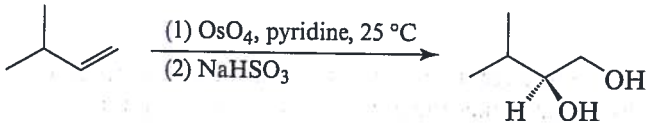


(b)



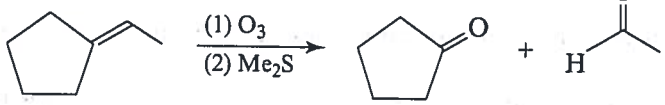
(racemic)

(c)

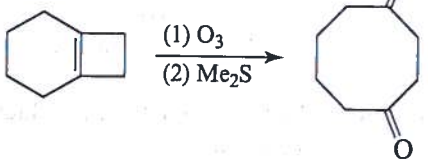


(racemic)

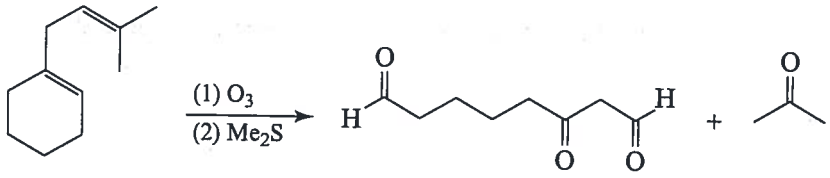
8.21 (a)



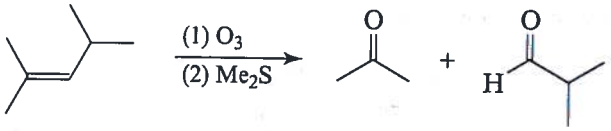
(b)



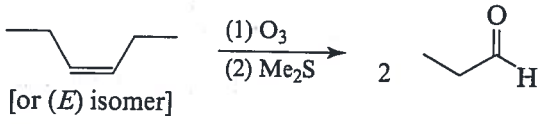
(c)



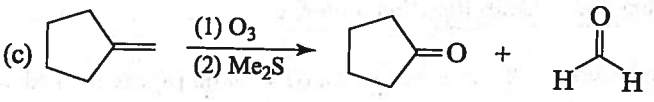
8.22 (a)



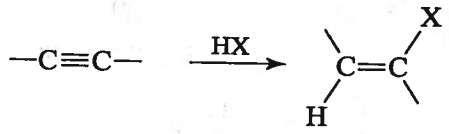
(b)



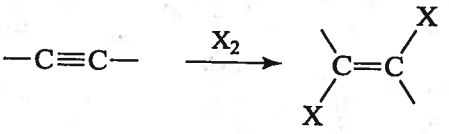
[or (*E*) isomer]

(c) 

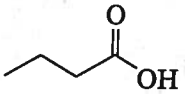
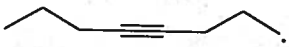
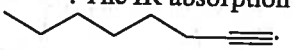
8.23 Ordinary alkenes *are* more reactive toward electrophilic reagents than alkynes. But the alkenes obtained from the addition of an electrophilic reagent to an alkyne have at least one electronegative atom (Cl, Br, etc.) attached to a carbon atom of the double bond.

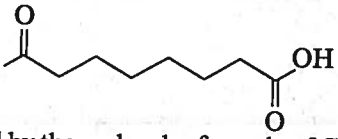


or

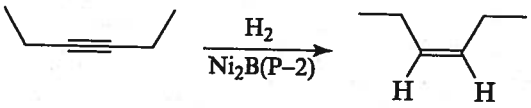


These alkenes are less reactive than alkynes toward electrophilic addition because the electronegative group makes the double bond "electron poor."

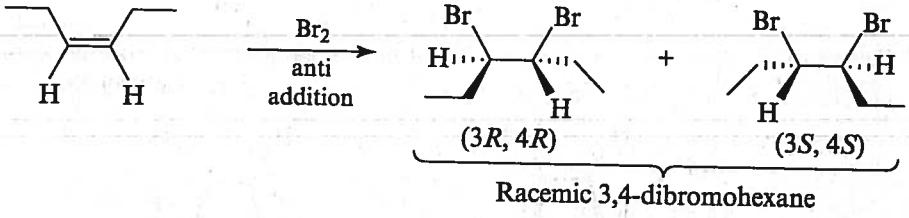
8.24 The molecular formula and the formation of octane from **A** and **B** indicate that both compounds are unbranched octynes. Since **A** yields only  on ozonolysis, **A** must be the symmetrical octyne . The IR absorption for **B** shows the presence of a terminal triple bond. Hence **B** is .

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

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

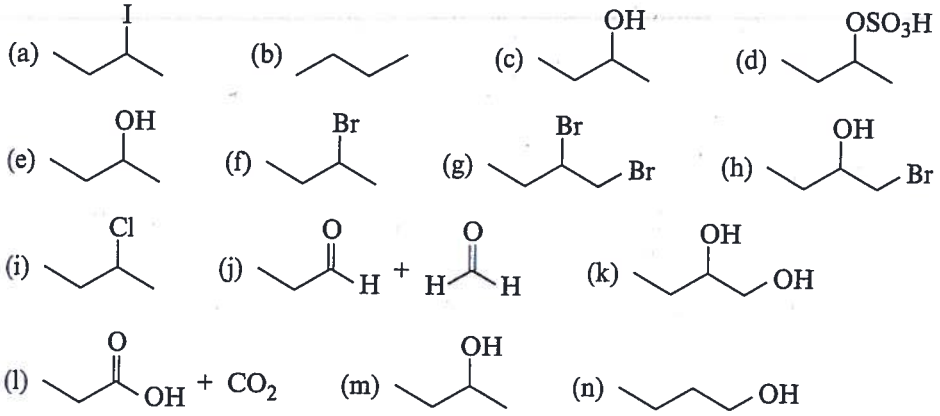


Then, addition of bromine to *cis*-3-hexene will yield (3*R*,4*R*), and (3*S*,4*S*)-3,4-dibromohexane as a racemic form.

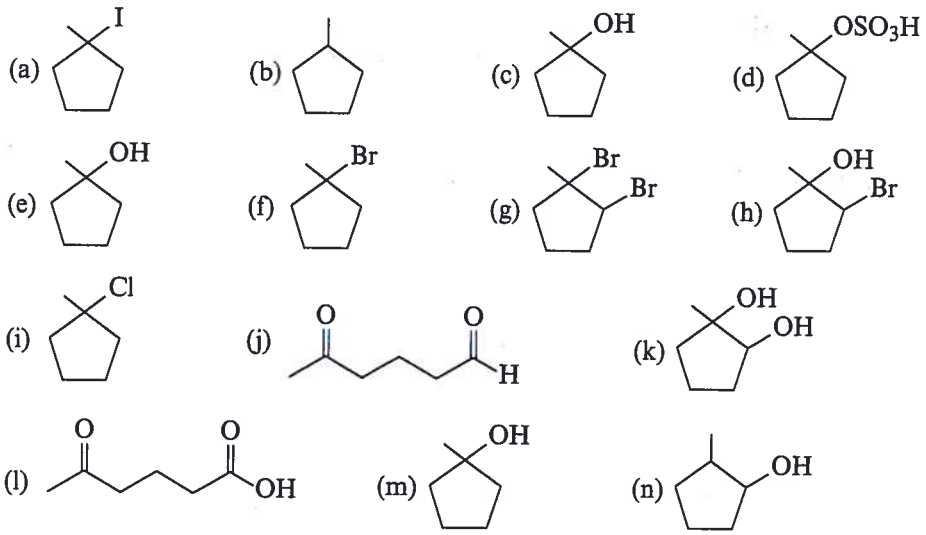


Alkenes and Alkynes Reaction Tool Kit

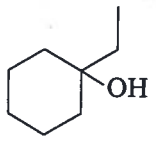
8.26 The answers to all parts except (b), (j), (l), and (n) are formed as racemic mixtures.



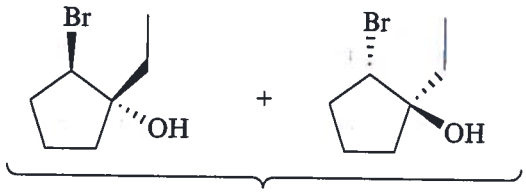
8.27 The answers to (g), (h), (k), and (n) are formed as racemic mixtures.



8.28 (a)

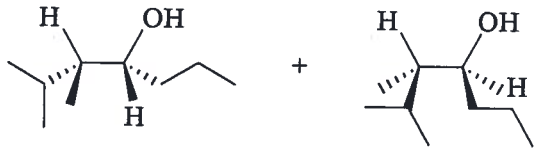


(b)

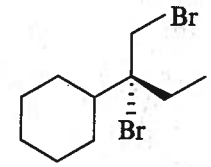
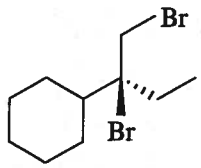


enantiomers

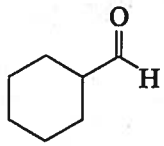
(c)

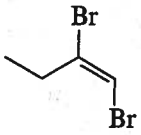
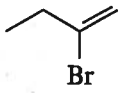
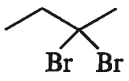


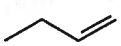
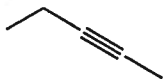
enantiomers

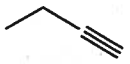
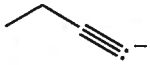
(d)  + 

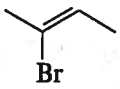
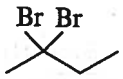
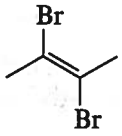
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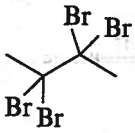
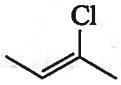
(e) 2 

8.29 (a)  (b)  (c) 

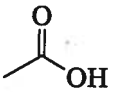
(d)  (e)  (f) 

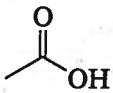
(g)  and  [An E2 reaction would take place when  is treated with ]

8.30 (a)  (b)  (c) 

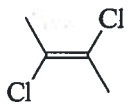
(d)  (e)  (f) 

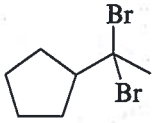
(g)  (h)  (i) 

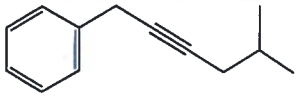
(j) 
(2 molar equivalents)

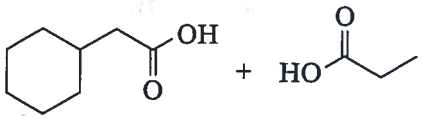
(k) 
(2 molar equivalents)

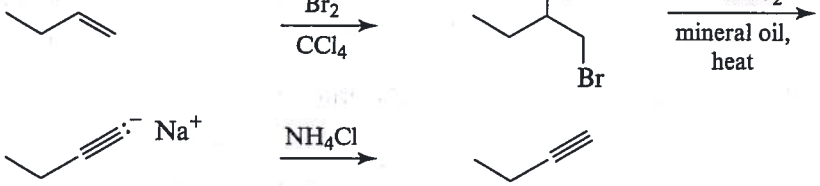
(l) No reaction

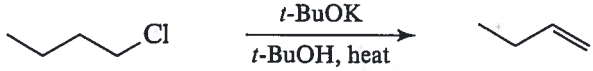
8.31 (a) 

(b) 

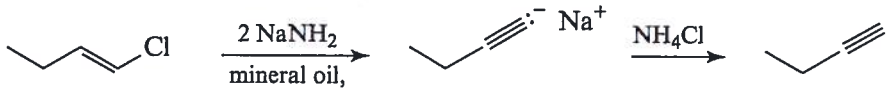
(c) 

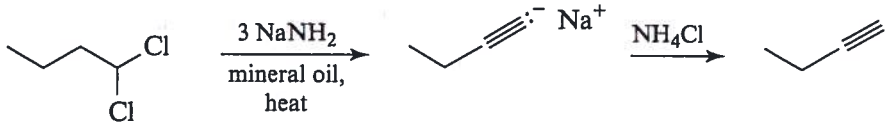
(d) 

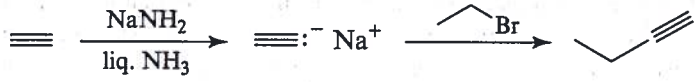
8.32 (a) 

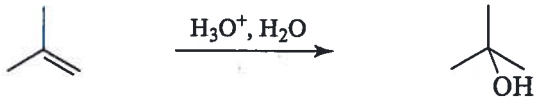
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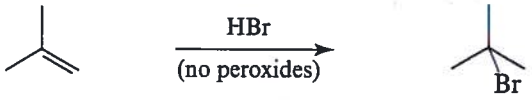
Then as in (a)

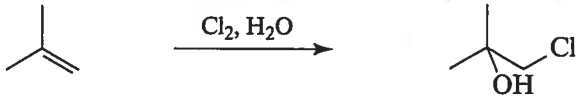
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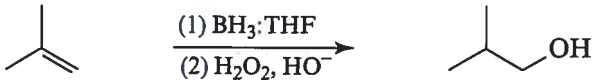
(d) 

(e) 

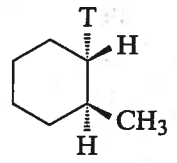
8.33 (a) 

(b) 

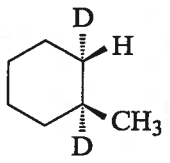
(c) 

(d) 

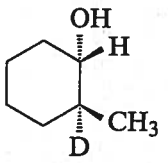
8.34 (a)

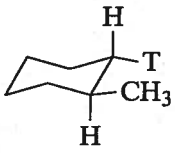


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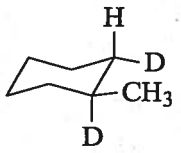


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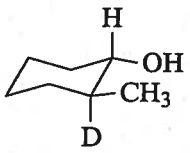




+ enantiomer

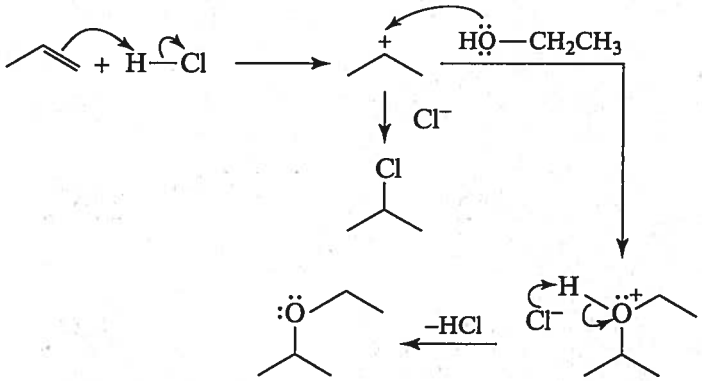


+ enantiomer



+ enantiomer

8.35



8.36 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.

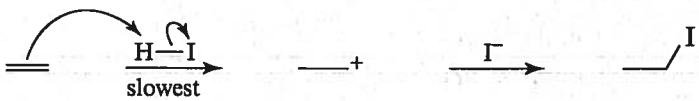


fastest

3° cation



2° cation



slowest

1° cation