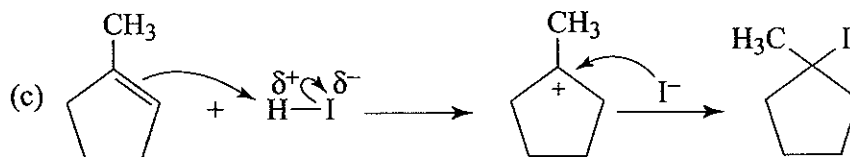
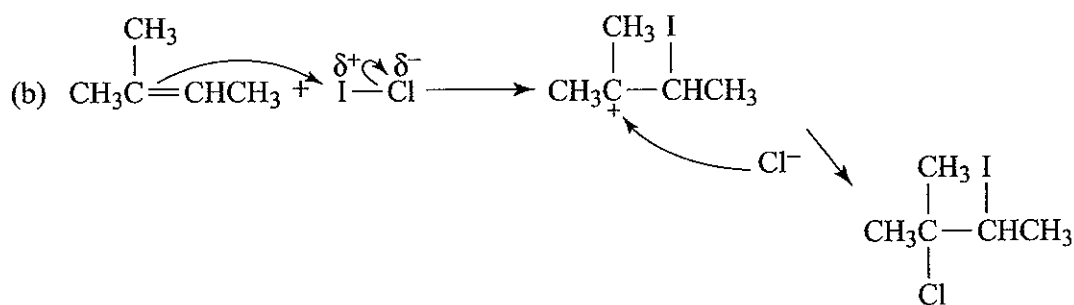
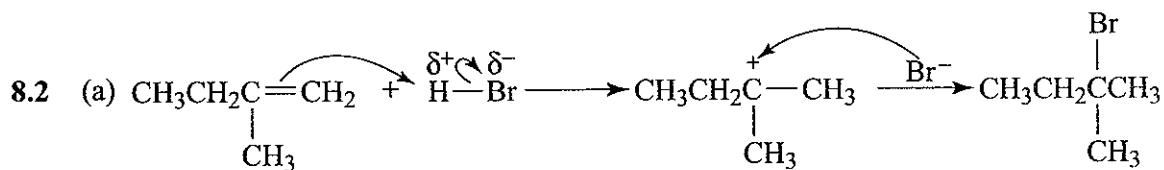
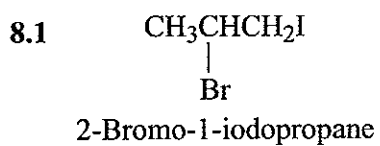
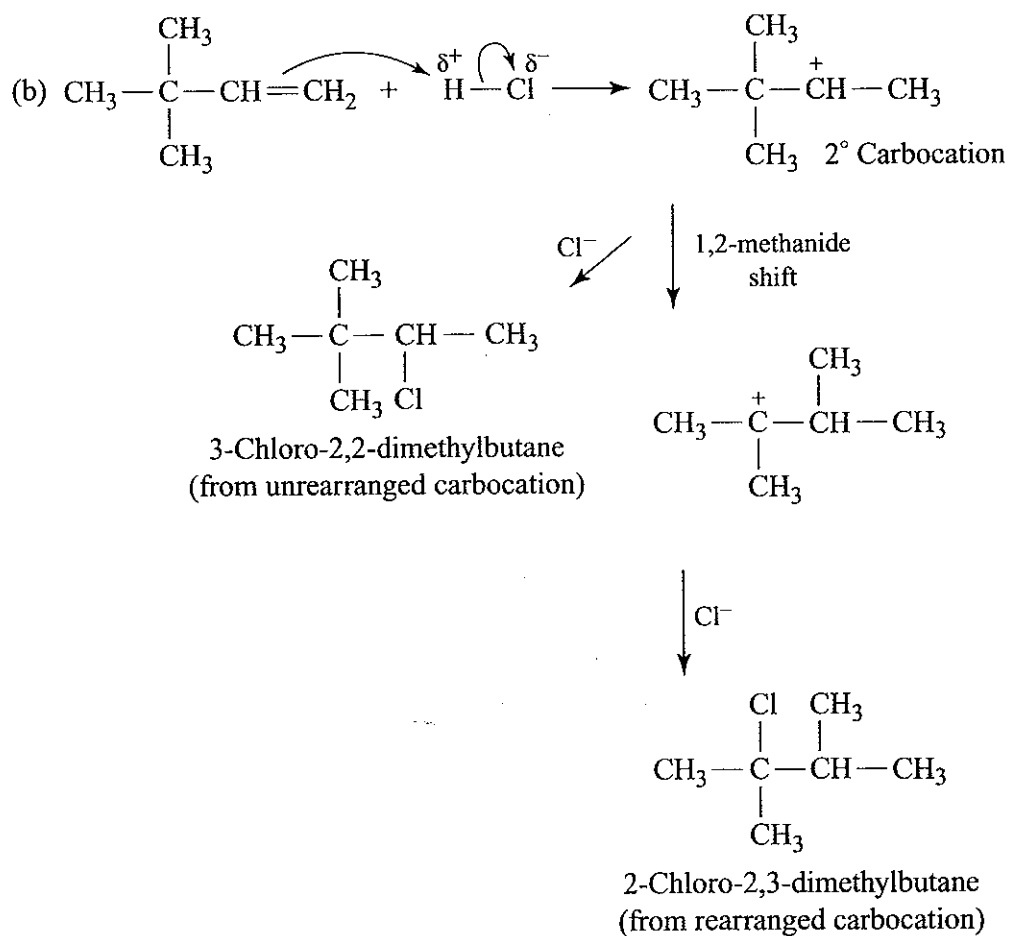
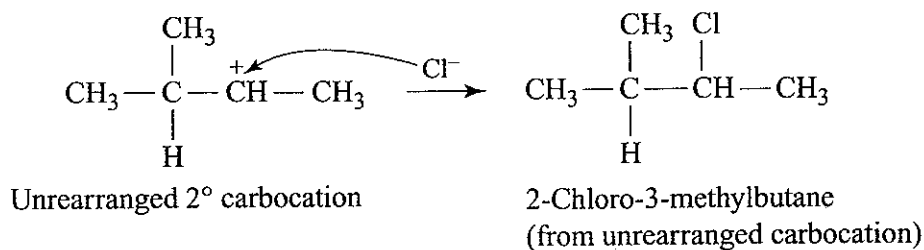
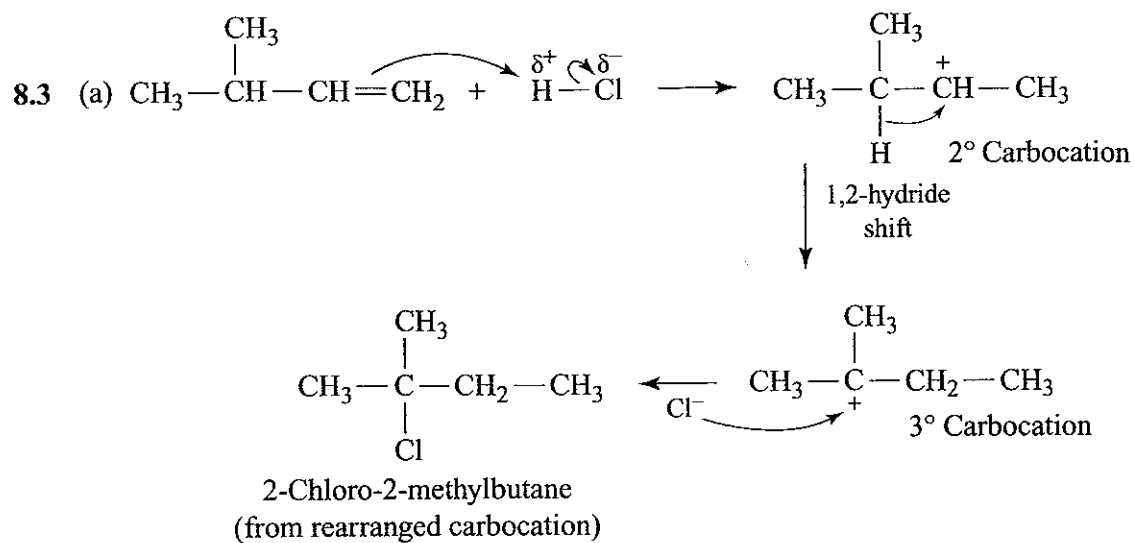


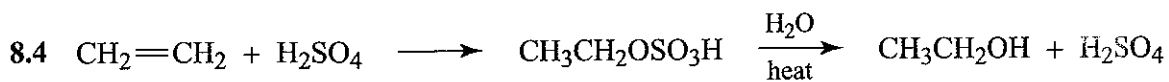
8

ALKENES AND ALKYNES II: ADDITION REACTIONS

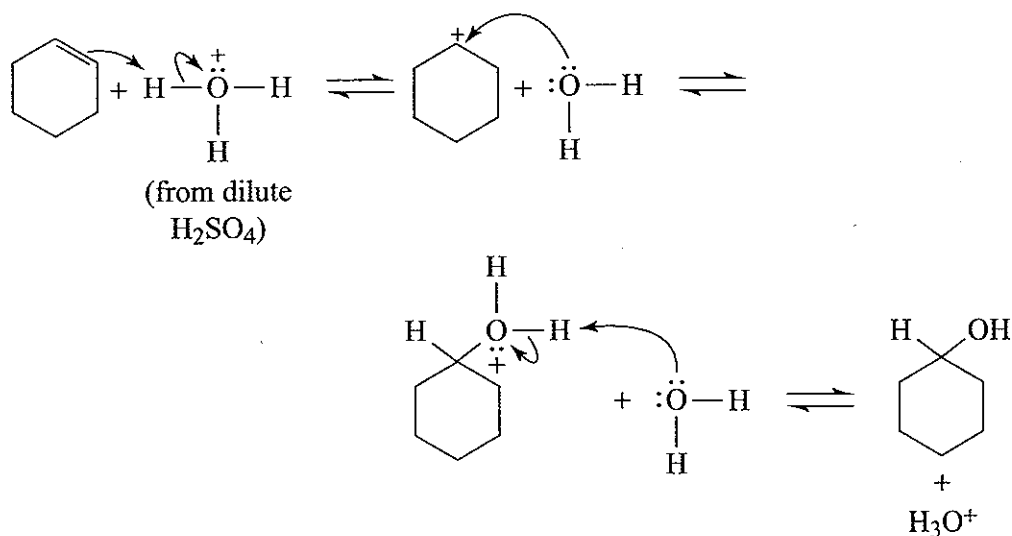
SOLUTIONS TO PROBLEMS



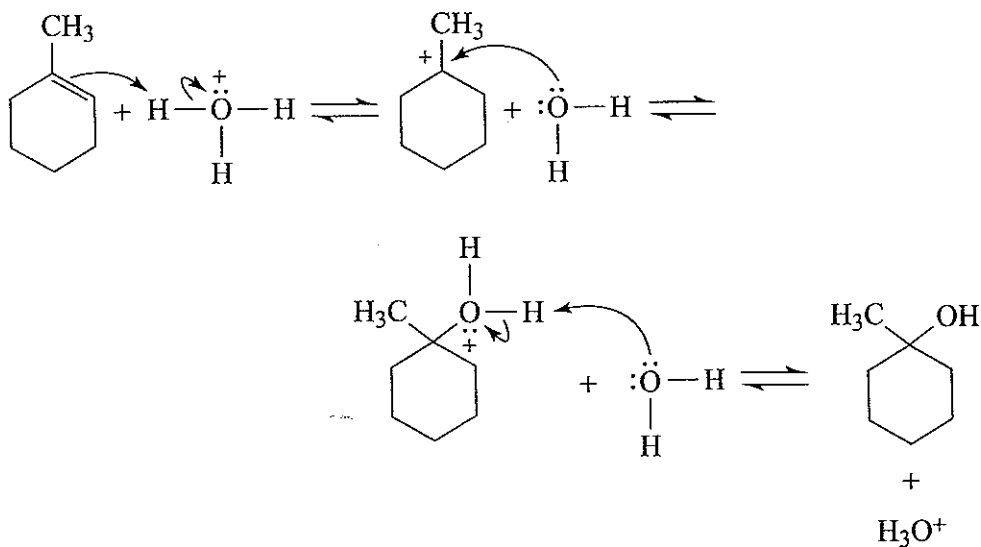


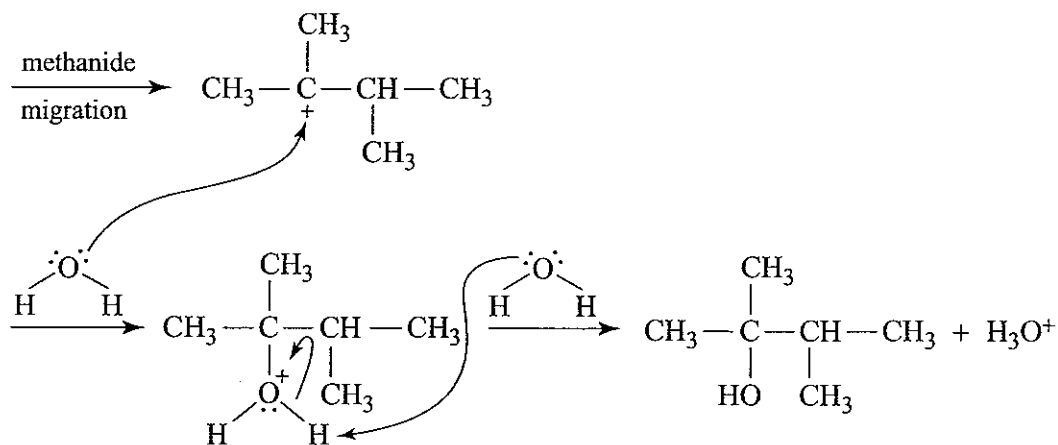
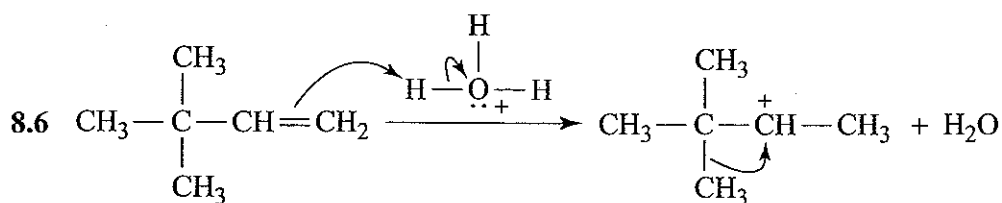


- 8.5 (a) Use a high concentration of water because we want the carbocation produced to react with water. And use a strong acid whose conjugate base is a very weak nucleophile. (For this reason we would not use HI, HBr, or HCl.) An excellent method, therefore, is to use dilute sulfuric acid.

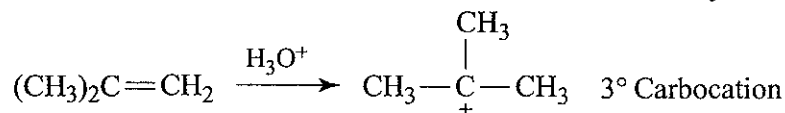


- (b) Use a low concentration of water (i.e., use concentrated H_2SO_4) and use a higher temperature to encourage elimination. Distill cyclohexene from reaction mixture as it is formed, so as to draw the equilibrium toward product.
- (c) 1-Methylcyclohexanol would be the product because a 3° carbocation would be formed as the intermediate.

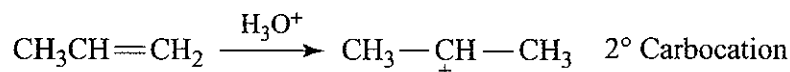




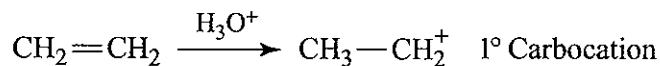
8.7 The order reflects the relative ease with which these alkenes accept a proton and form a carbocation. $(\text{CH}_3)_2\text{C}=\text{CH}_2$ reacts faster because it leads to a tertiary cation,



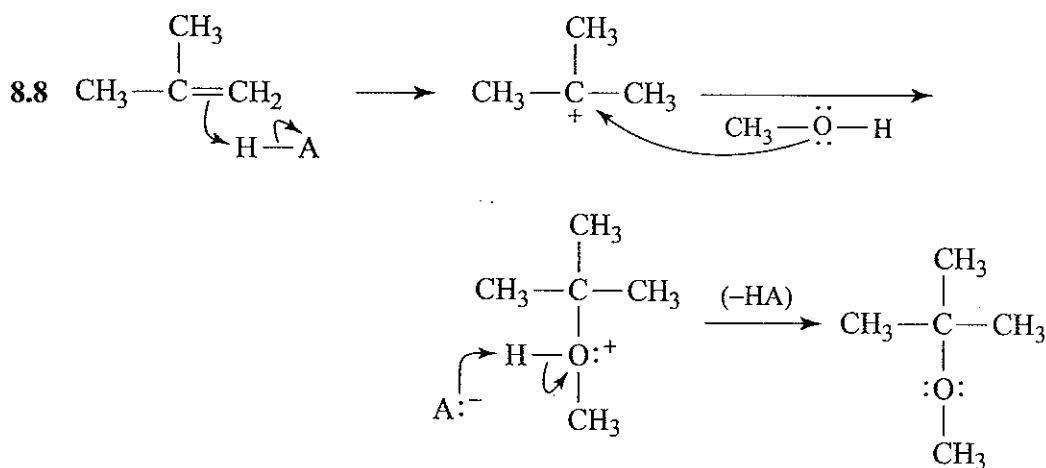
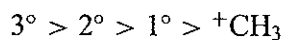
$\text{CH}_3\text{CH}=\text{CH}_2$ leads to a secondary cation,

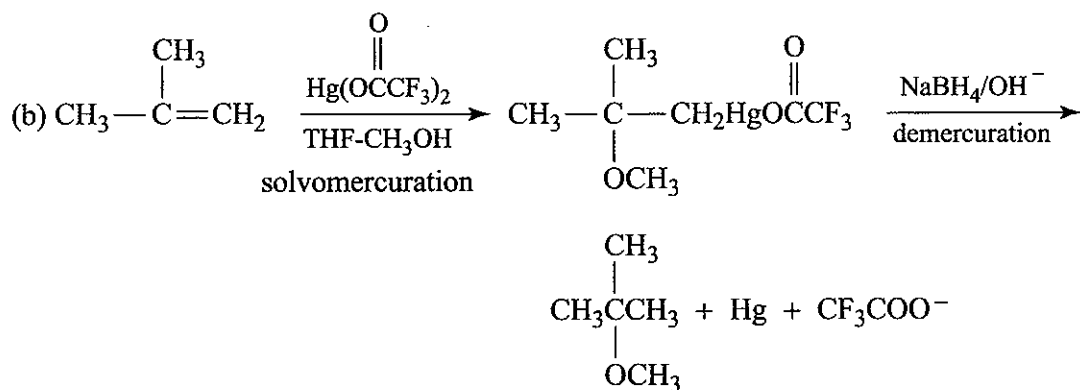
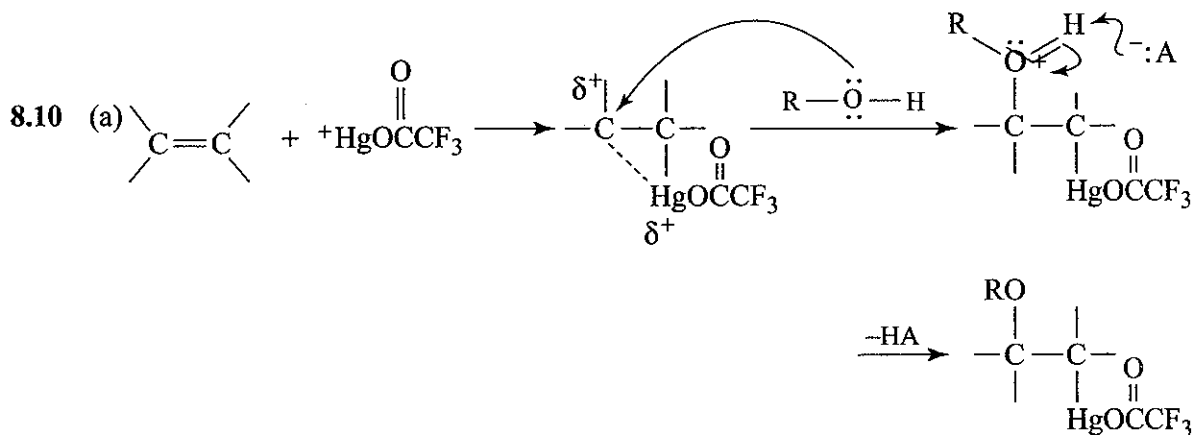
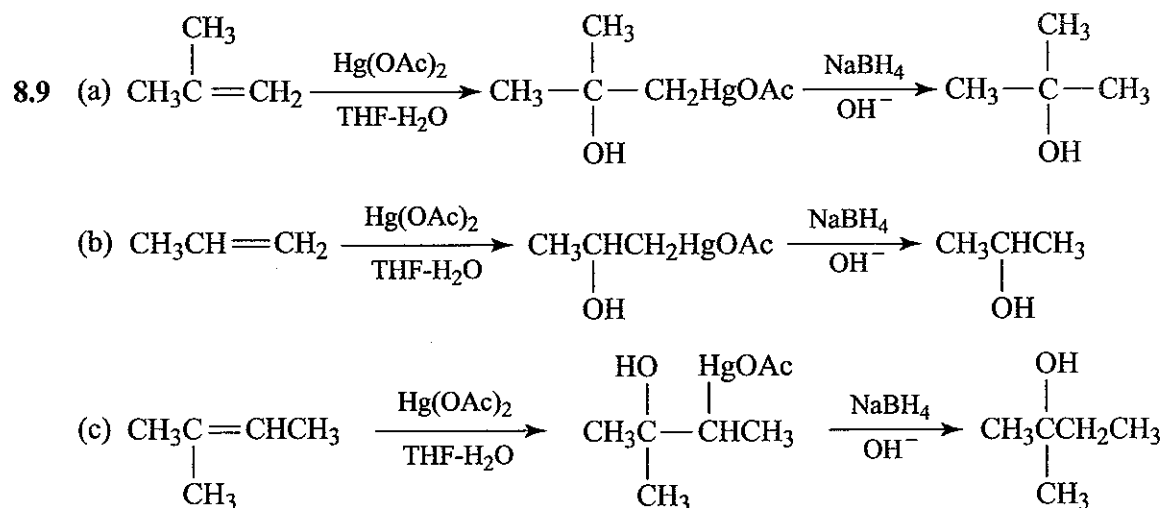


and $\text{CH}_2=\text{CH}_2$ reacts most slowly because it leads to a primary carbocation.

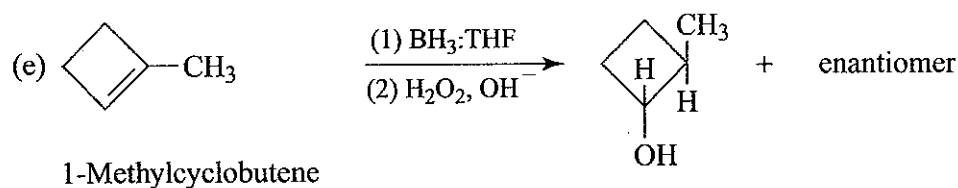
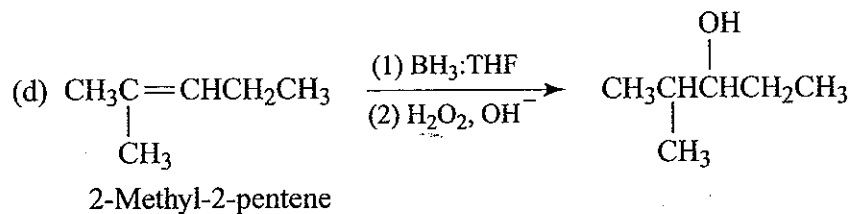
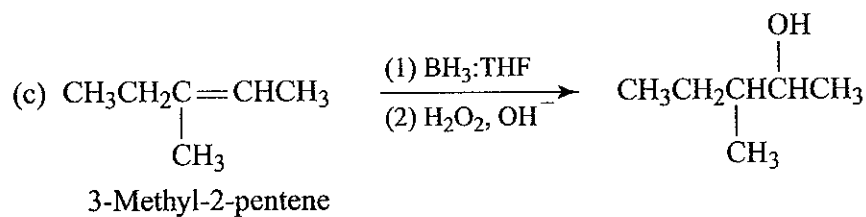
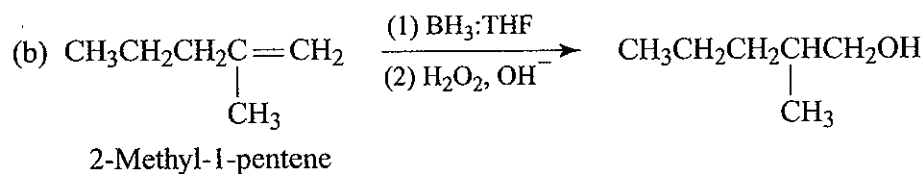
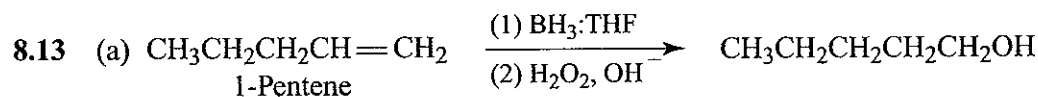
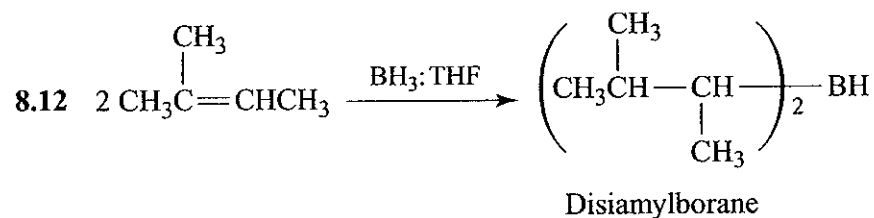
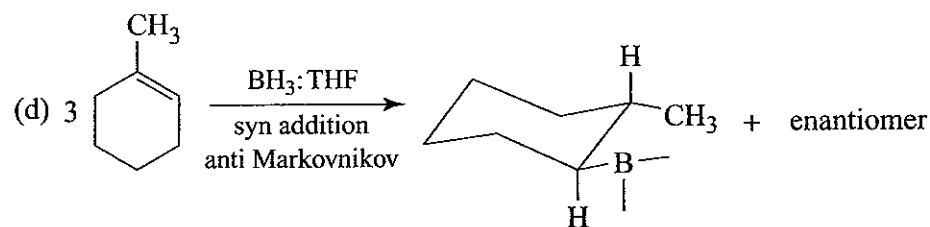
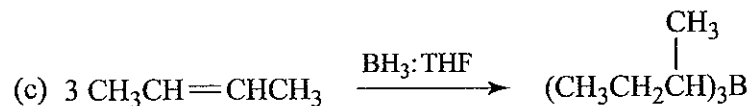
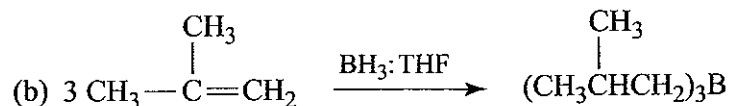


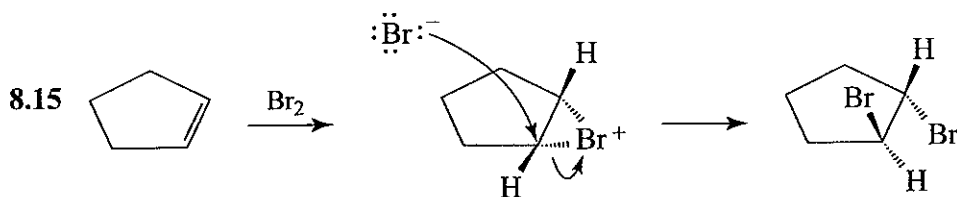
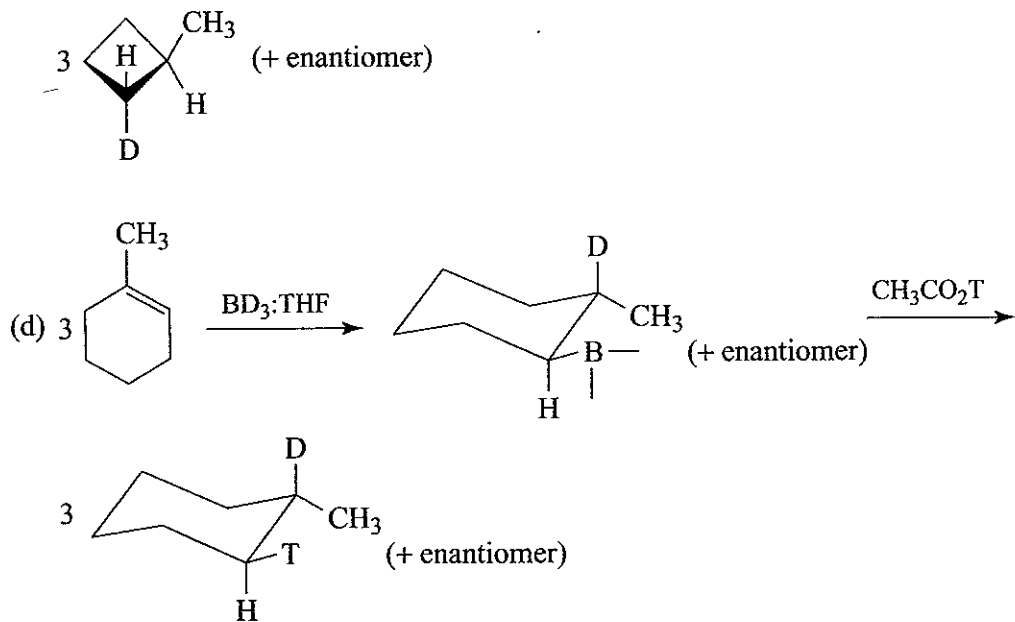
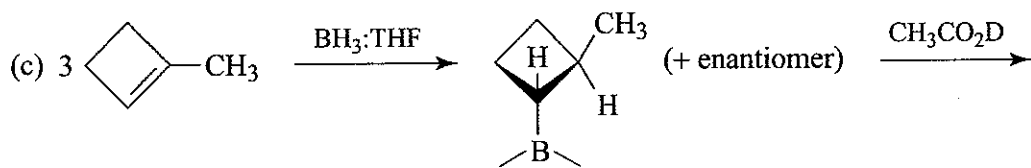
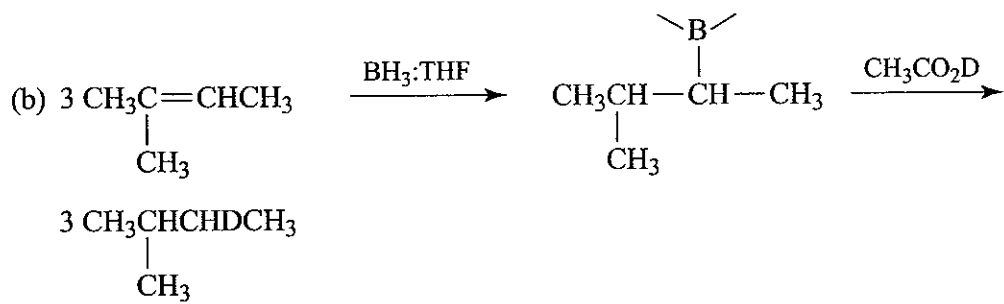
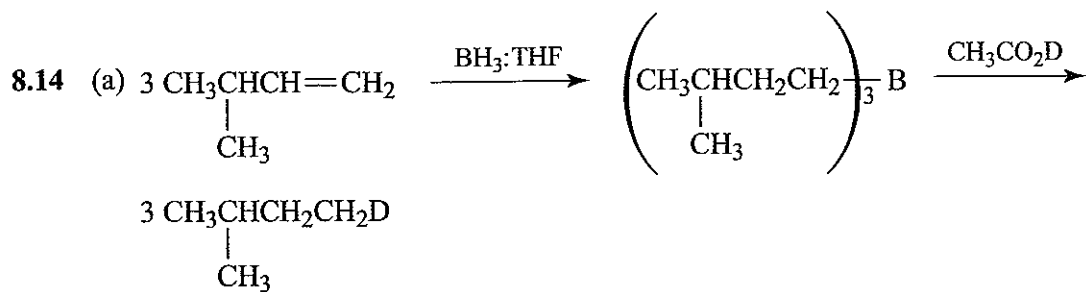
Recall that formation of the carbocation is the rate-determining step in acid-catalyzed hydration and that the order of stabilities of carbocations is the following:

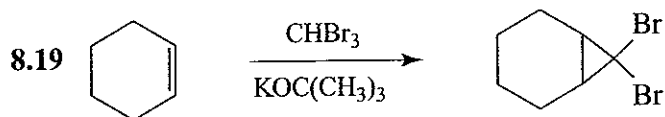
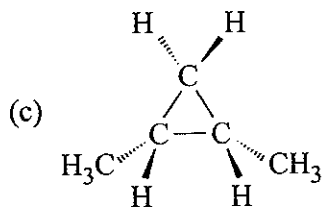
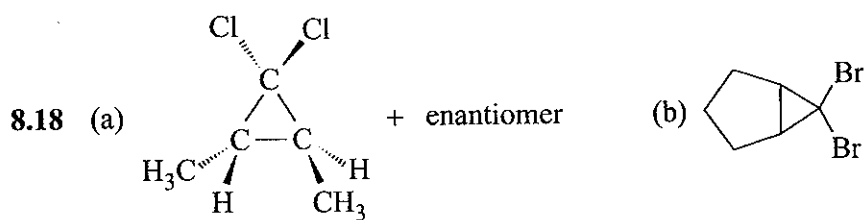
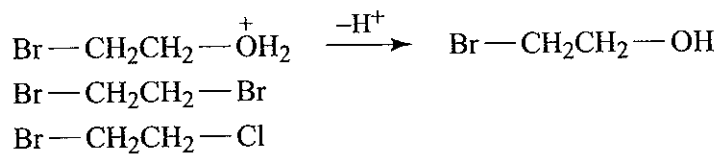
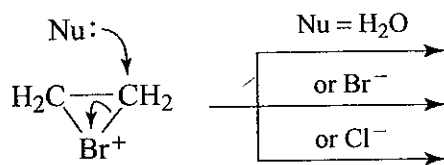
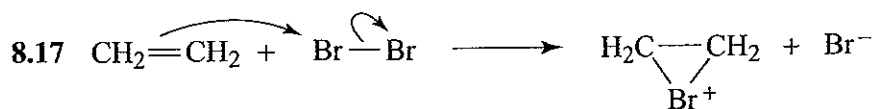
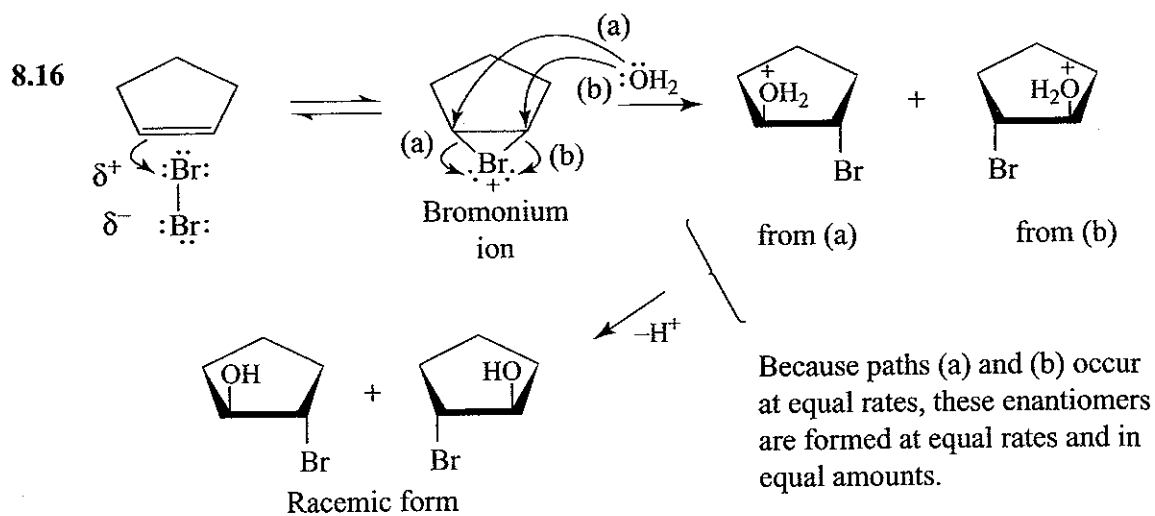


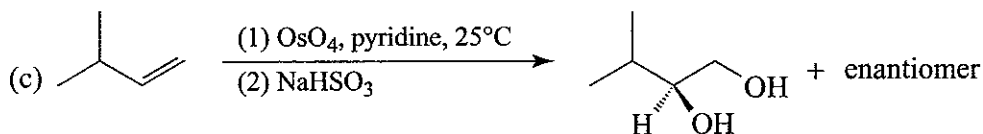
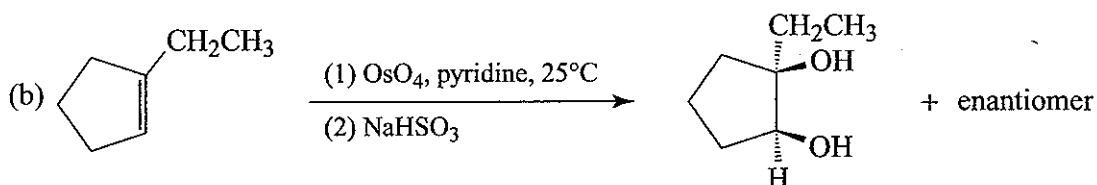
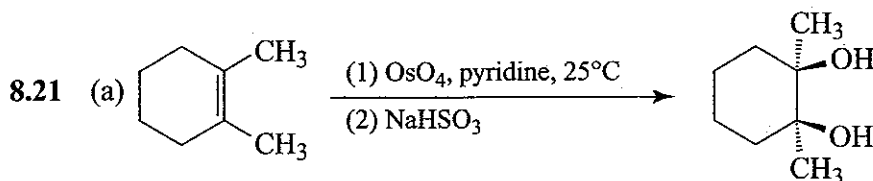
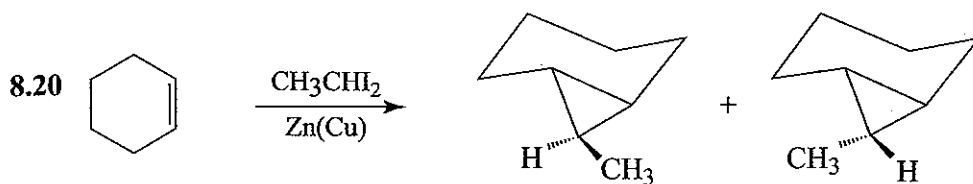


- (c) The electron-withdrawing fluorine atoms in mercuric trifluoroacetate enhance the electrophilicity of the cation. Experiments have demonstrated that for the preparation of tertiary alcohols in satisfactory yields, the trifluoroacetate must be used rather than the acetate.

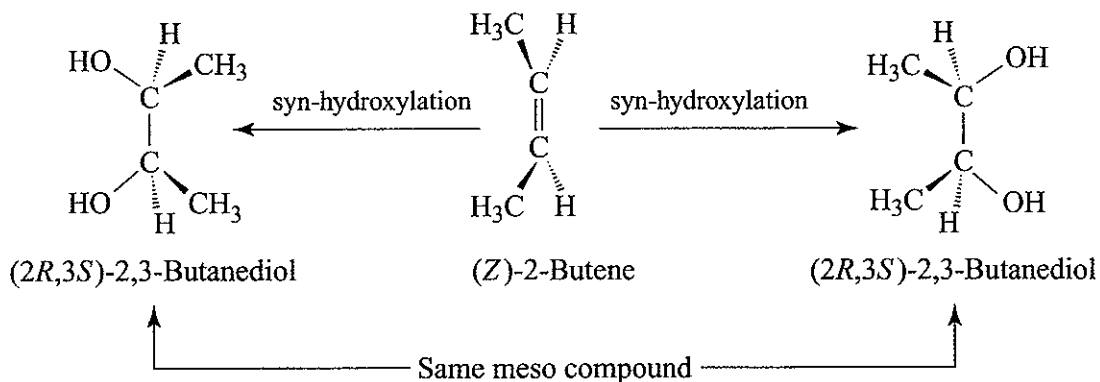




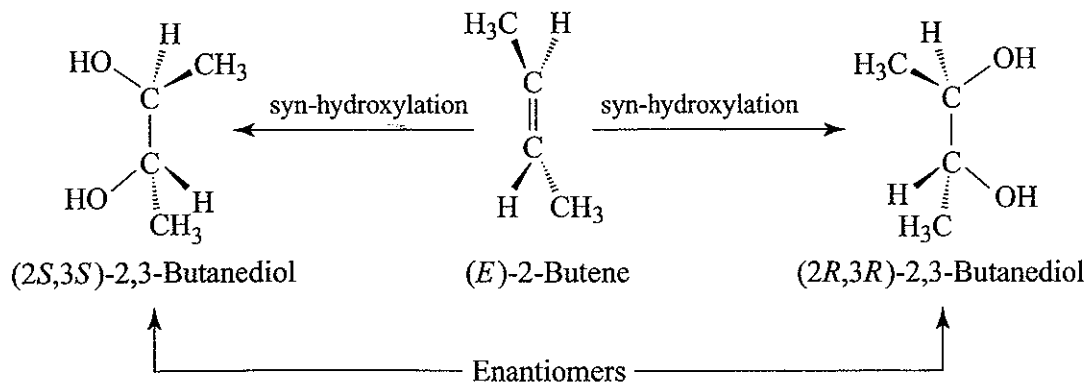


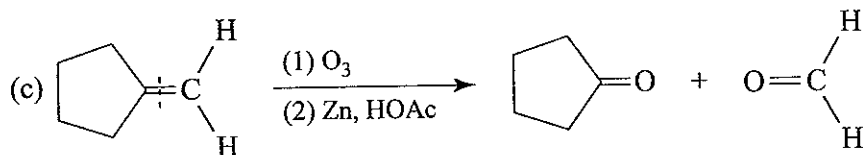
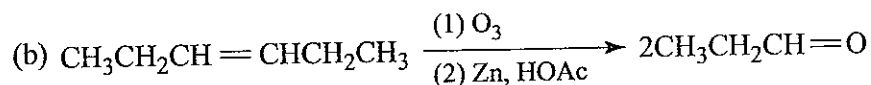
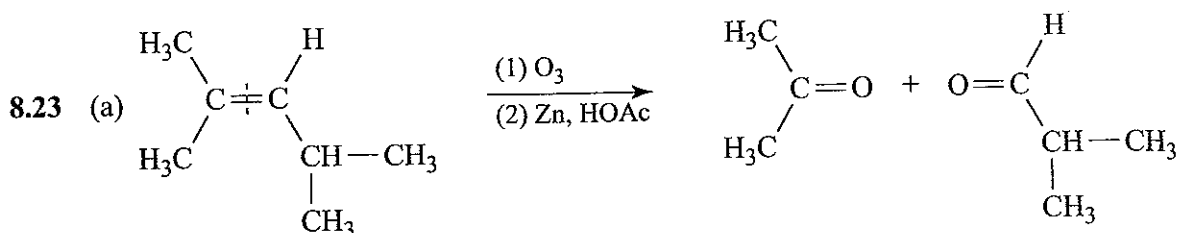


8.22 (a) Syn-hydroxylation at either face of this (*Z*)-alkene leads to the meso compound (*2R,3S*)-2,3-butanediol.

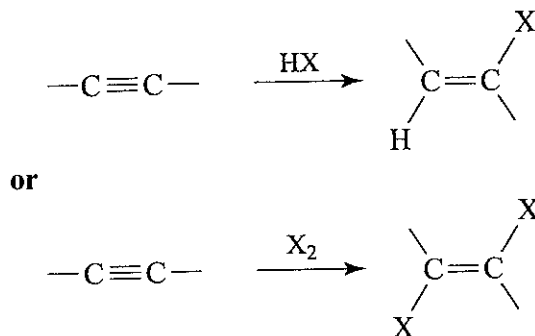


(b) Syn-hydroxylation at one face of this (*E*)-alkene leads to the (*2R,3R*)-enantiomer; at the other face, which is equally likely, it leads to the (*2S,3S*)-enantiomer.





8.24 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.”

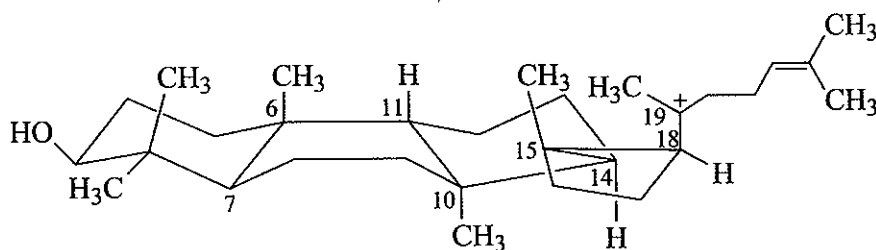
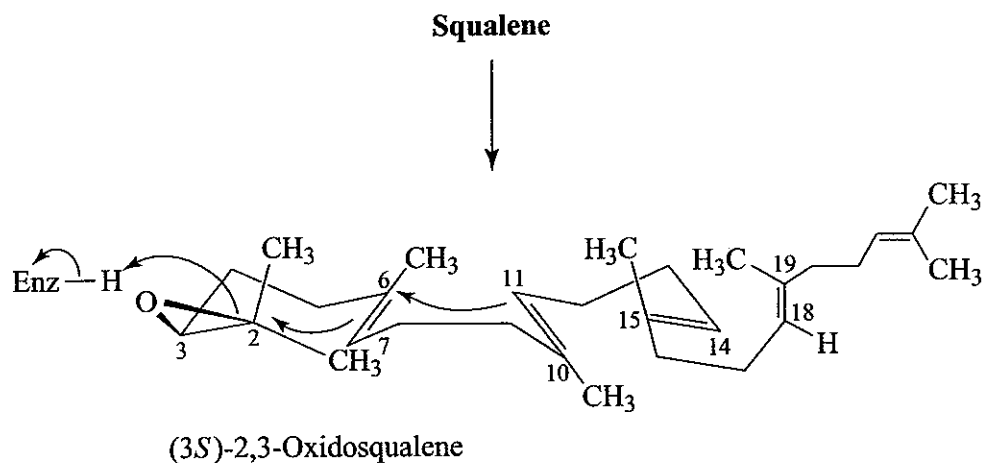
8.25 The molecular formula and the formation of octane from **A** and **B** indicate that both compounds are unbranched octynes. Since **A** yields only $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ on ozonolysis, **A** must be the symmetrical octyne $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$. The IR absorption for **B** shows the presence of a terminal triple bond. Hence **B** is $\text{CH}_3(\text{CH}_2)_5\text{C}\equiv\text{CH}$.

Since **C** (C_8H_{12}) gives $\text{HO}_2\text{C}(\text{CH}_2)_6\text{CO}_2\text{H}$ 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.

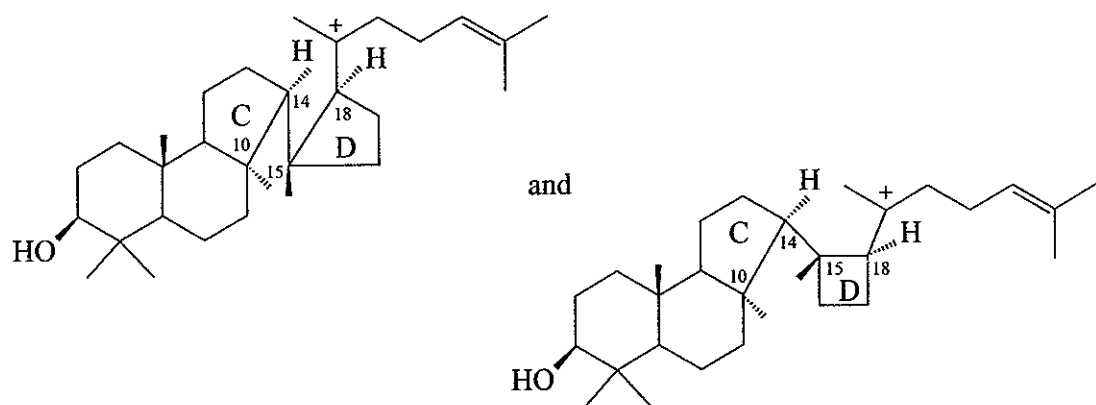
Answer to the Study Problem related to cholesterol biosynthesis, page 352.

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 351). 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

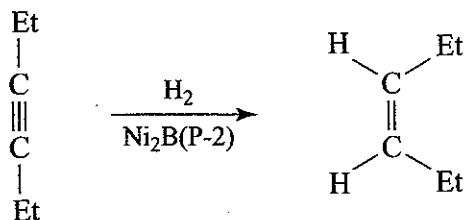
instead of anti-Markovnikov addition between C10 and C15, as shown in the following scheme, a developing *tertiary* carbocation would result at C15, along with formation of a five-membered "C" ring. Then, Markovnikov addition of C15 (as it becomes like a tertiary carbocation) to C18 would lead to a four-membered "D" ring and a tertiary carbocation at C19.



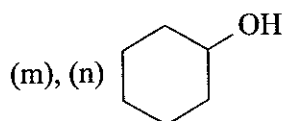
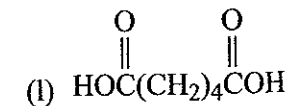
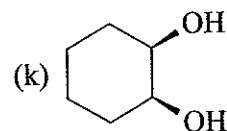
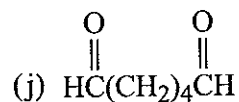
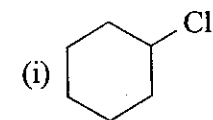
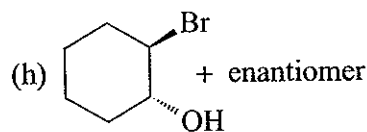
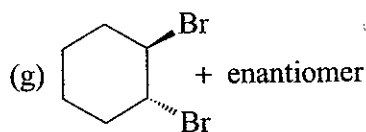
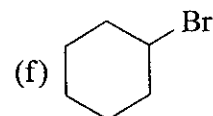
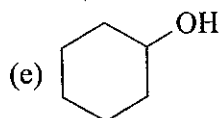
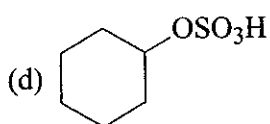
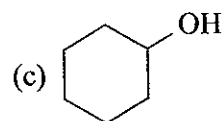
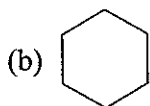
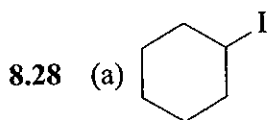
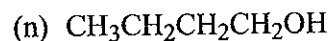
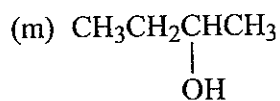
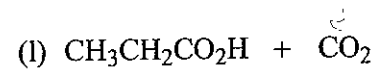
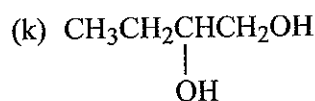
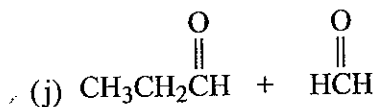
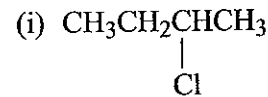
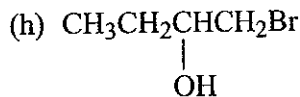
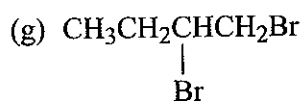
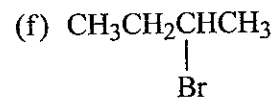
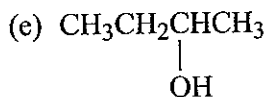
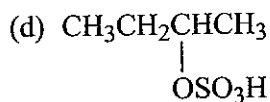
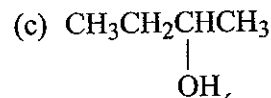
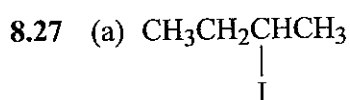
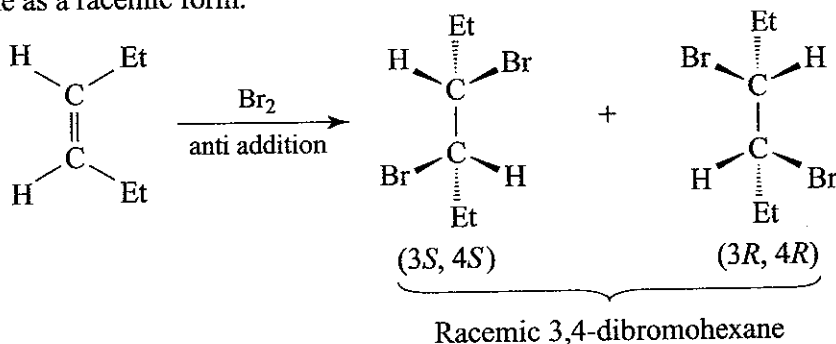
which is the same as:

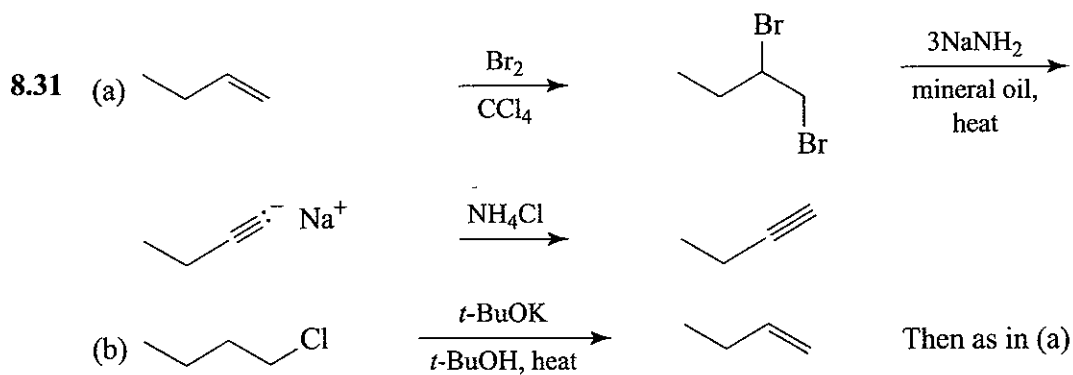
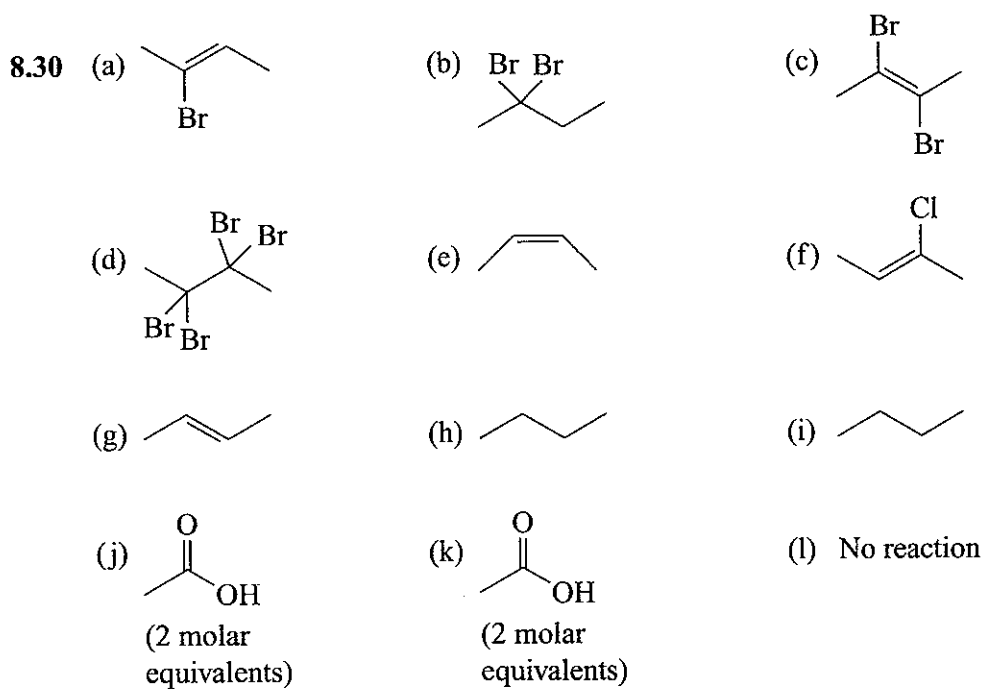
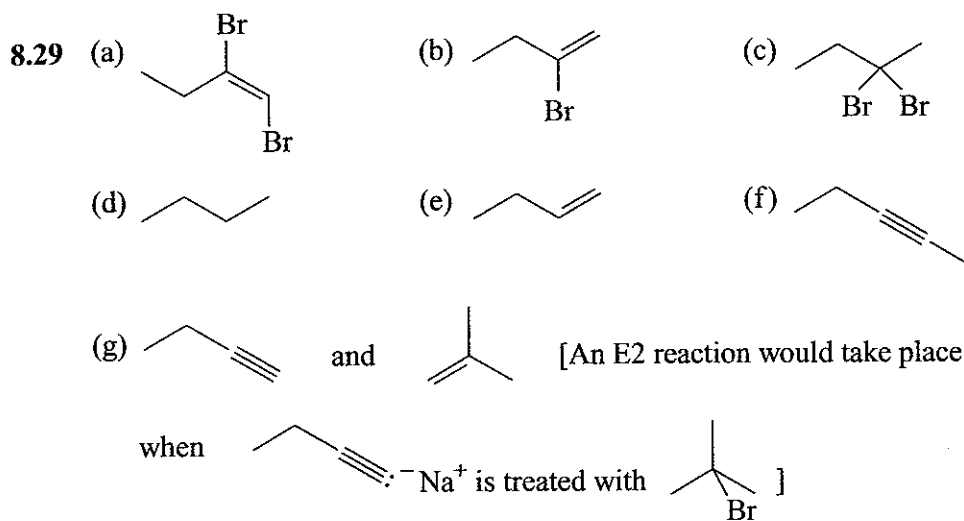


8.26 By converting the 3-hexyne to *cis*-3-hexene using $H_2/Ni_2B(P-2)$.



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.

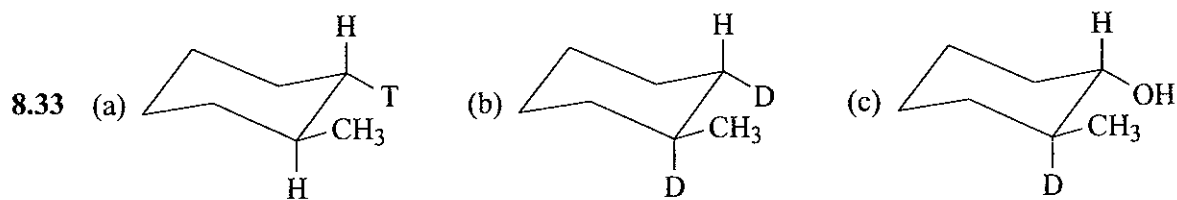
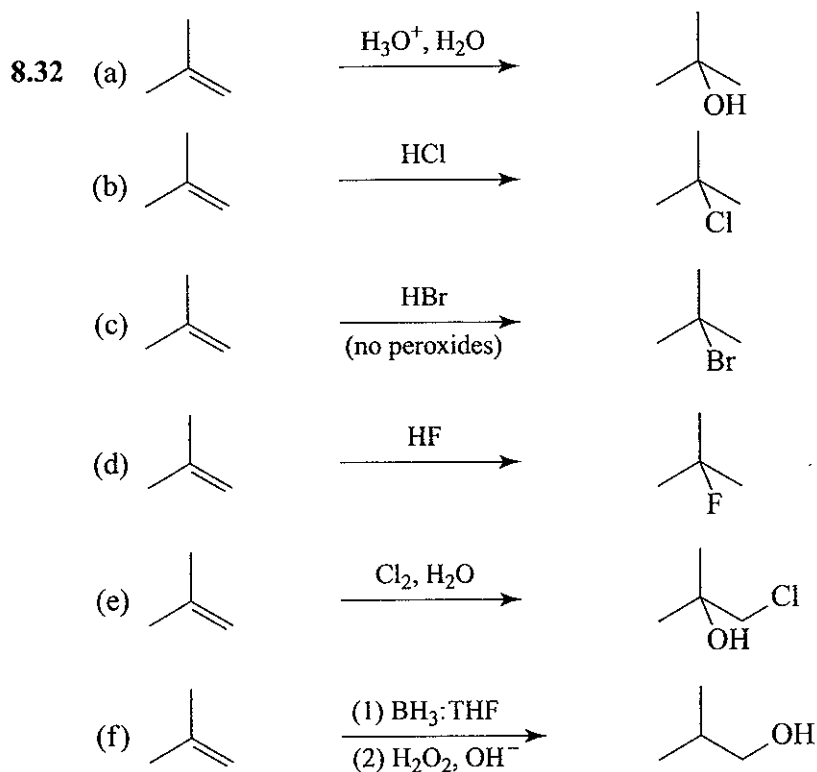
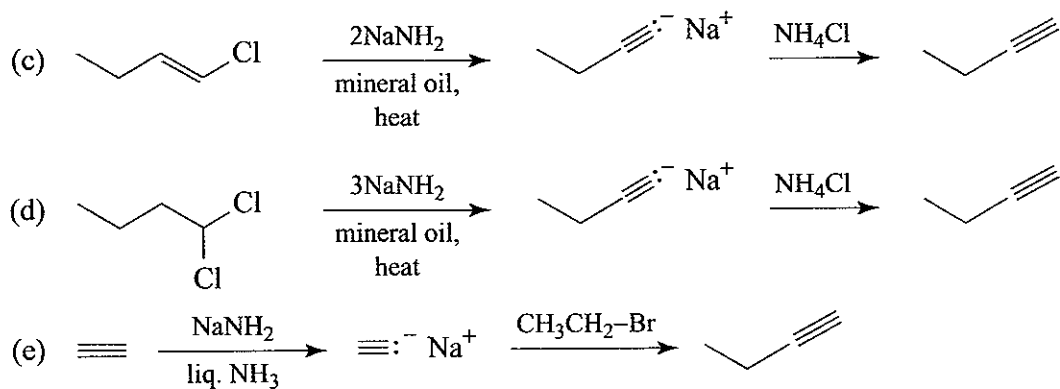




1-3,4-

O₂

OH

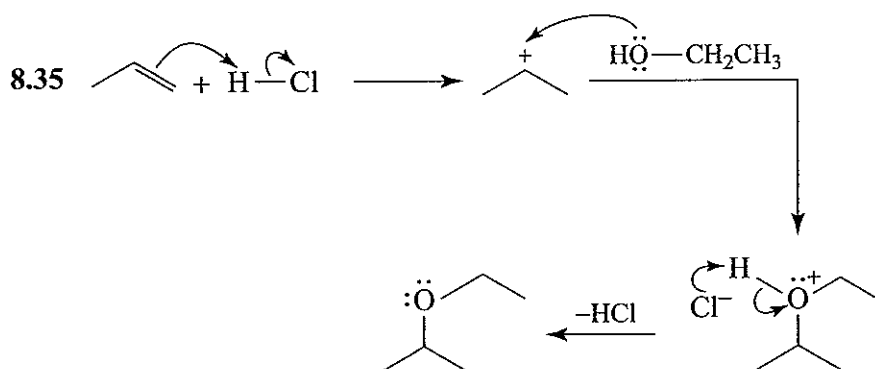
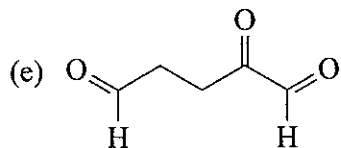
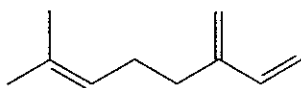


Problems

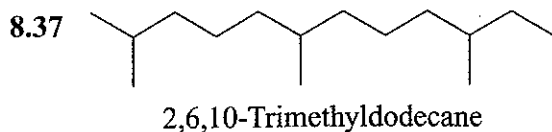
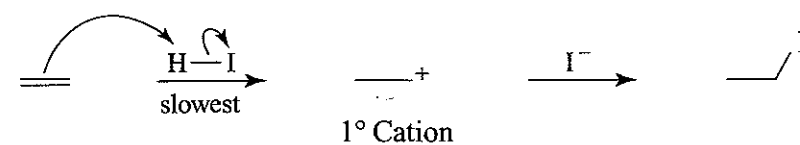
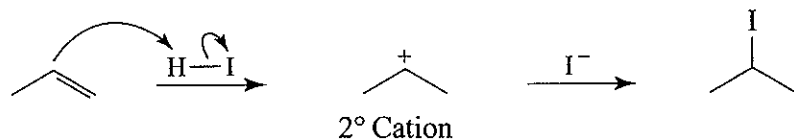
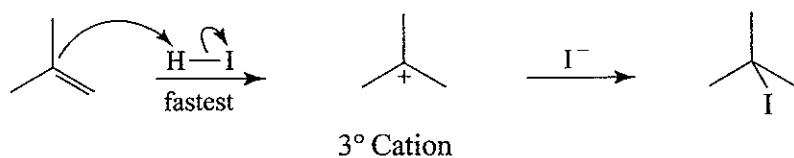
- 8.34 (a) $C_{10}H_{22}$ (saturated alkane)
 $C_{10}H_{16}$ (formula of myrcene)
 $H_6 = 3$ pairs of hydrogen atoms
 Index of hydrogen deficiency (IHD) = 3

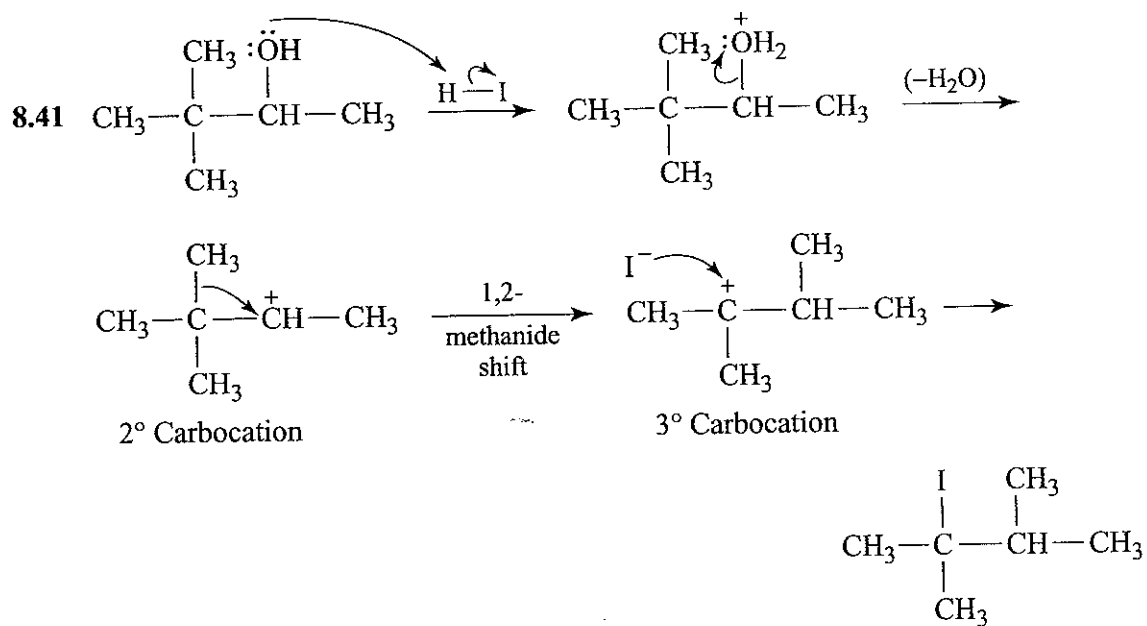
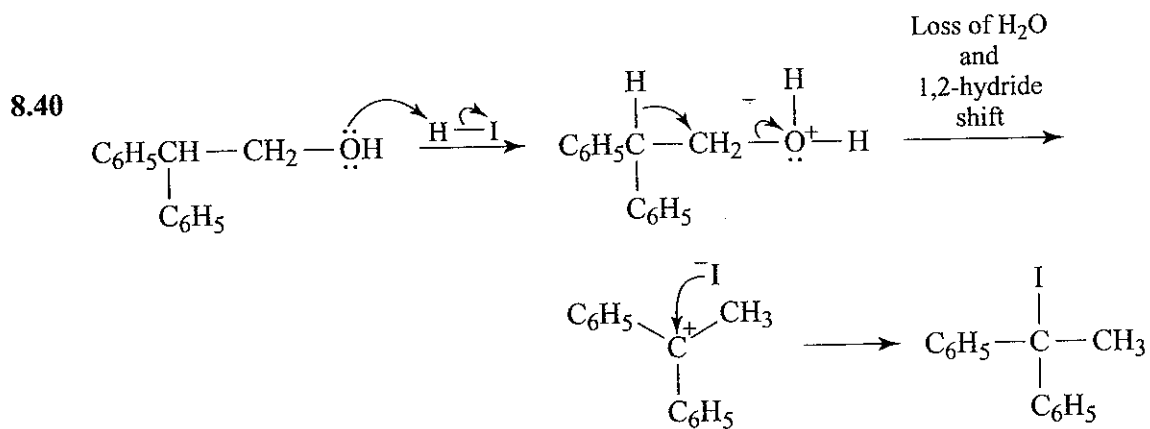
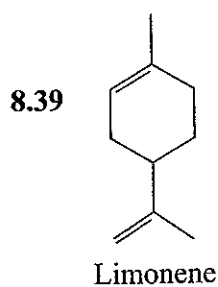
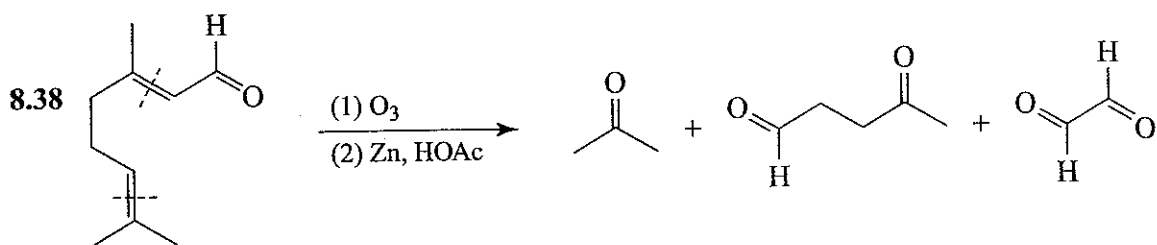
(b) Myrcene contains no rings because complete hydrogenation gives $C_{10}H_{22}$, which corresponds to an alkane.

- (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

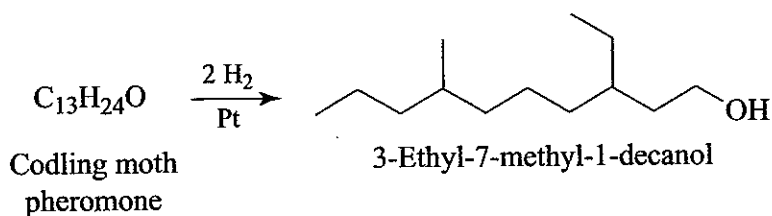


- 8.36 The rate-determining step in each reaction is the formation of a carbocation when the alkene accepts a proton from HI. When 2-methylpropene reacts, it forms a 3° carbocation (the most stable); therefore, it reacts fastest. When ethene reacts, it forms a 1° carbocation (the least stable); therefore,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

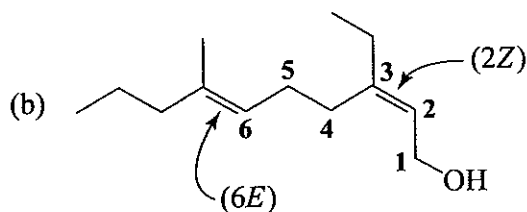
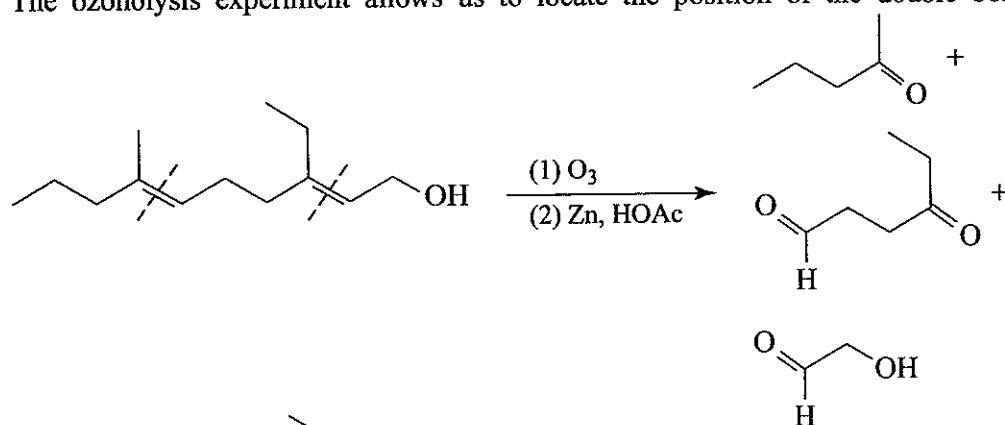




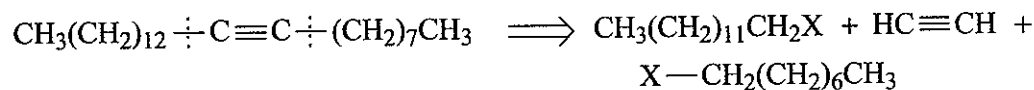
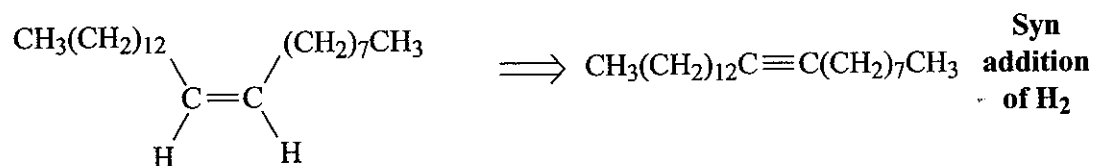
8.42 (a) The hydrogenation experiment discloses the carbon skeleton of the pheromone.



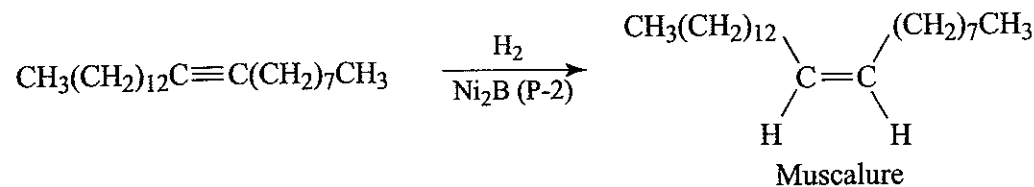
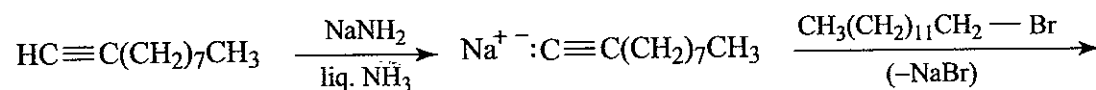
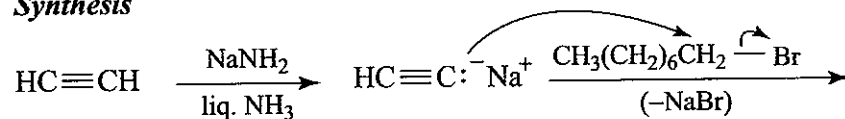
The ozonolysis experiment allows us to locate the position of the double bonds.

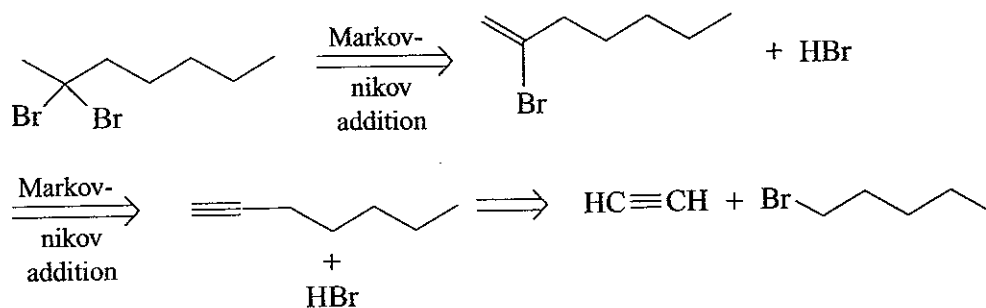
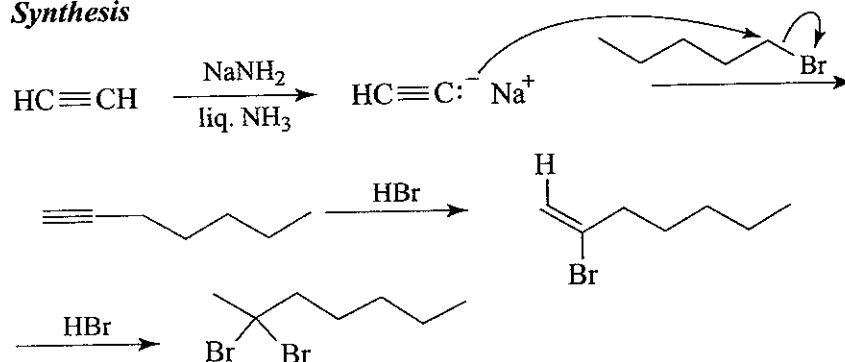


8.43 *Retrosynthetic analysis*

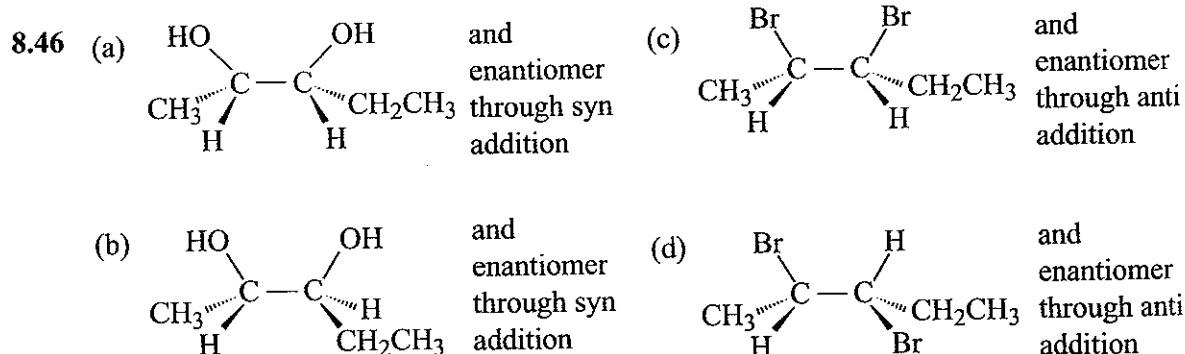


Synthesis

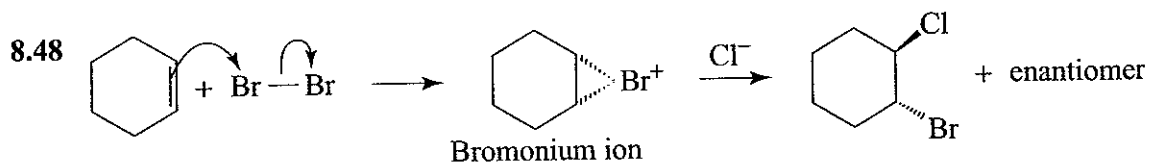


8.44 *Retrosynthetic analysis**Synthesis*

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



- 8.47 (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*)-]



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

- 8.49 (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 $1620\text{--}1680\text{ cm}^{-1}$ 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 $515\text{--}690\text{ cm}^{-1}$ region while pentane does not.
- (e) For 1-pentyne, see (a). The interior triple bond of 2-pentyne gives relatively weak absorption in the $2100\text{--}2260\text{ cm}^{-1}$ region.
- (f) For 1-pentene, see (b). 1-Pentanol has a broad absorption band in the $3200\text{--}3550\text{ cm}^{-1}$ region.
- (g) See (a) and (f).
- (h) 1-Bromo-2-pentene has double bond absorption in the $1620\text{--}1680\text{ cm}^{-1}$ region which 1-bromopentane lacks.
- (i) 2-Penten-1-ol has double bond absorption in the $1620\text{--}1680\text{ cm}^{-1}$ region not found in 1-pentanol.

8.50 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.

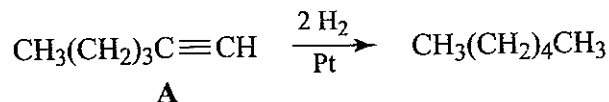
8.51 The index of hydrogen deficiency of **A**, **B**, and **C** is two.

$$\frac{\text{C}_6\text{H}_{14} - \text{C}_6\text{H}_{10}}{\text{H}_4} = 2 \text{ pairs of hydrogen atoms}$$

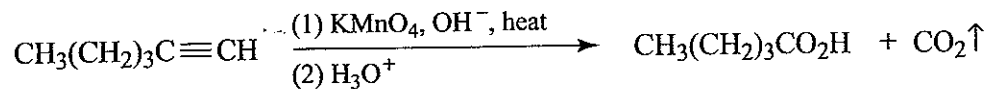
This result suggests the presence of a triple bond, two double bonds, a double bond and a ring, or two rings. The fact that **A**, **B**, and **C** all decolorize Br_2/CCl_4 and dissolve in concd H_2SO_4 suggests they all have a carbon-carbon multiple bond.

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

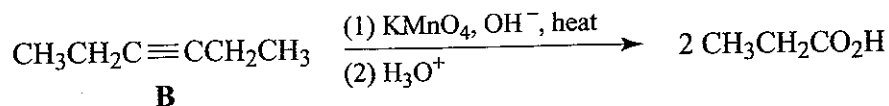
Since **A** gives hexane on catalytic hydrogenation, **A** must be 1-hexyne.



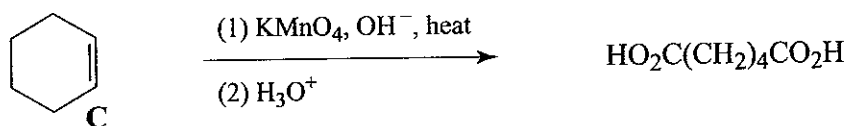
This is confirmed by the oxidation experiment



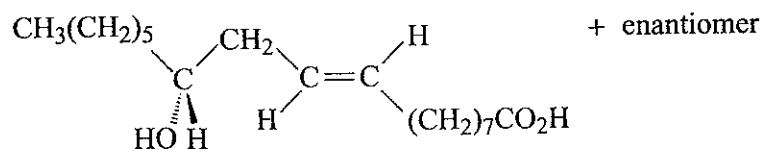
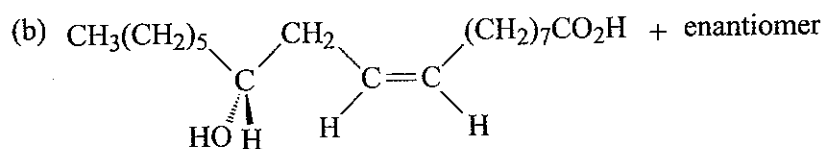
Hydrogenation of **B** to hexane shows that its chain is unbranched, and the oxidation experiment shows that **B** is 3-hexyne.



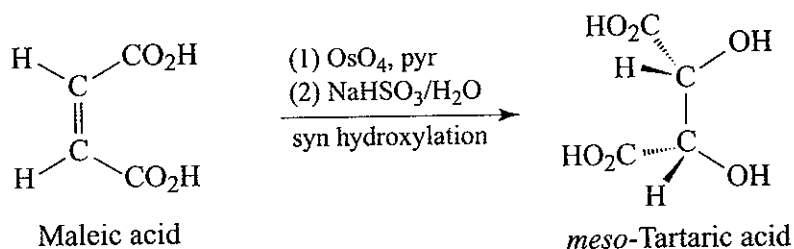
Oxidation of **C** shows that it is cyclohexene.



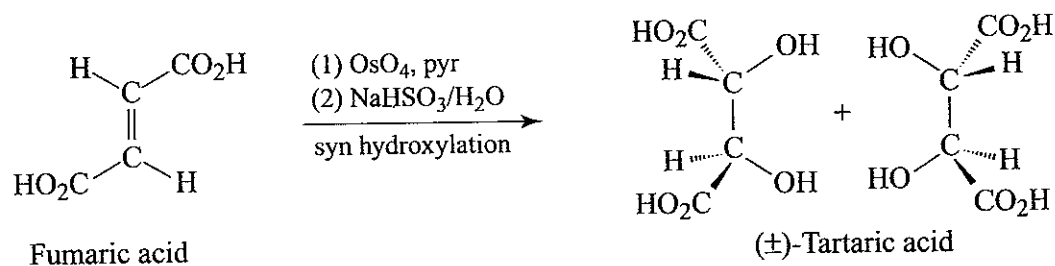
8.52 (a) Four



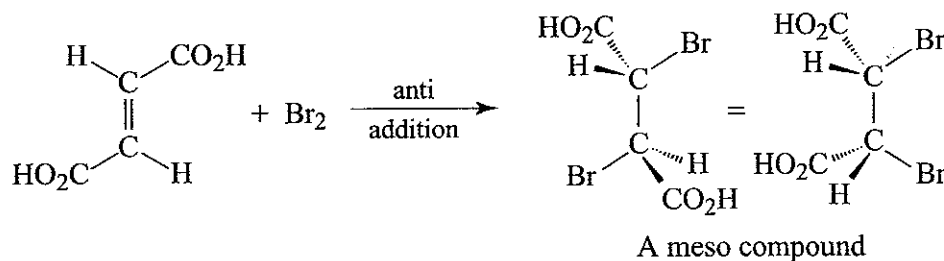
8.53 Hydroxylations by OsO_4 are syn hydroxylations (cf. Section 8.16). Thus, maleic acid must be the cis-dicarboxylic acid:



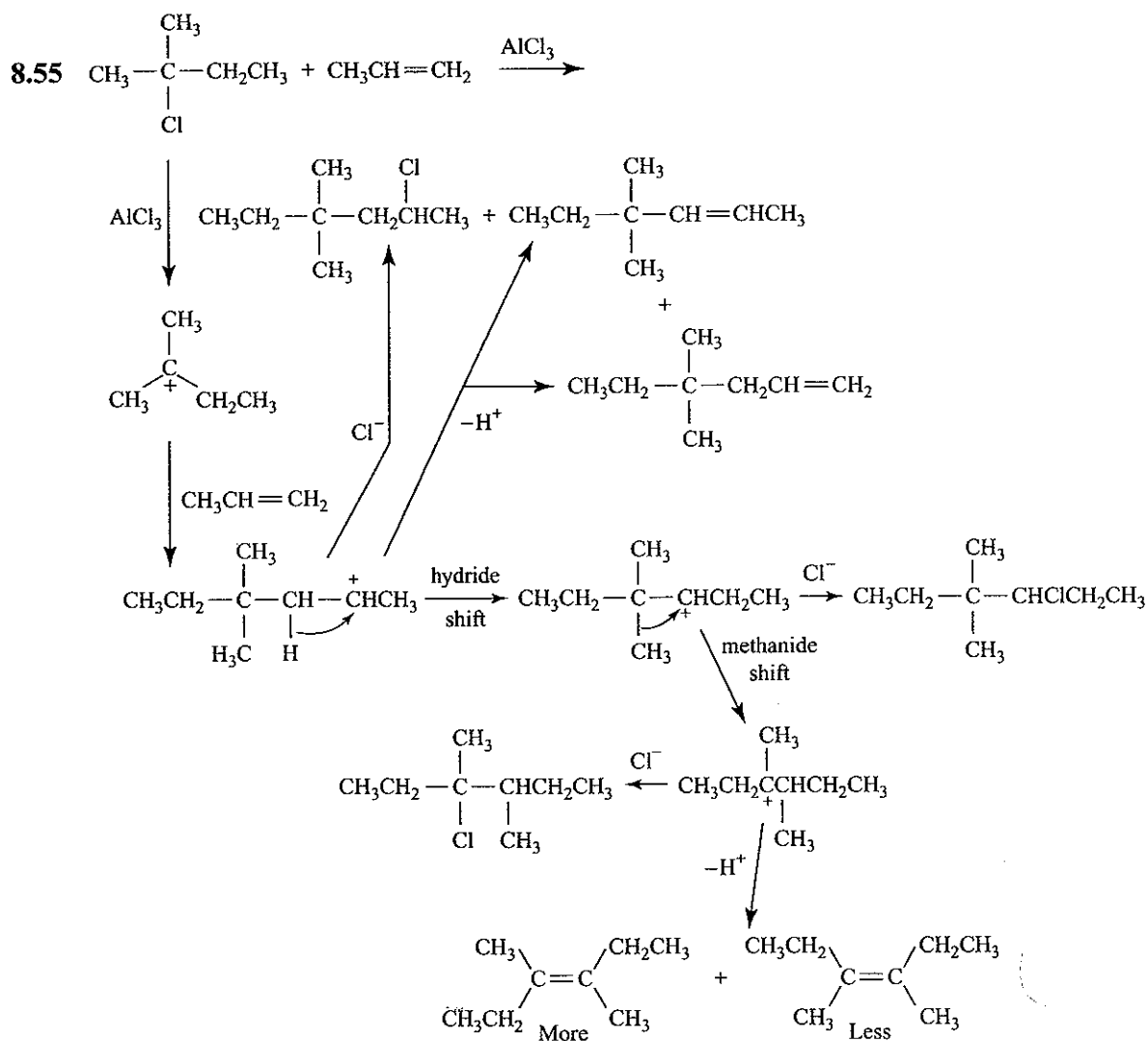
Fumaric acid must be the trans-dicarboxylic acid:



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

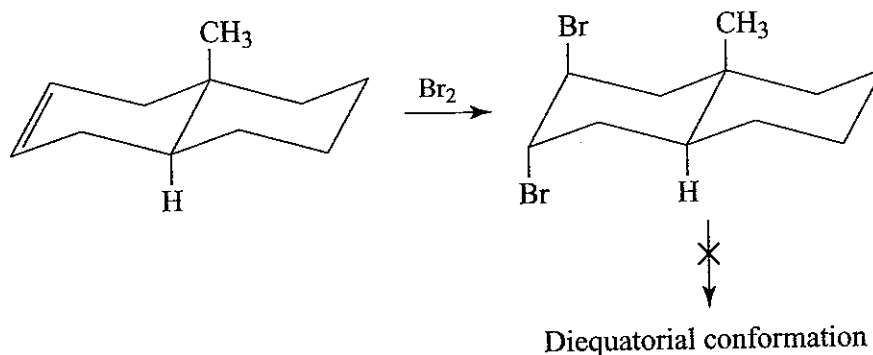


- (b) Maleic acid adds bromine to yield a racemic form.

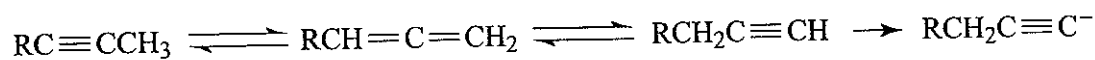


- 8.56 The catalytic hydrogenation involves syn addition of hydrogen to the predominantly less hindered face of the cyclic system (the face lacking 1,3-diaxial interactions when the molecule is adsorbed on the catalyst surface). This leads to I, even though II is the more stable of the two isomers since both methyl groups are equatorial in II.

- 8.57 The bicyclic compound is a *trans*-decalin derivative. The fused nonhalogenated ring prevents the ring flip of the bromine-substituted ring necessary to give equatorial bromines.

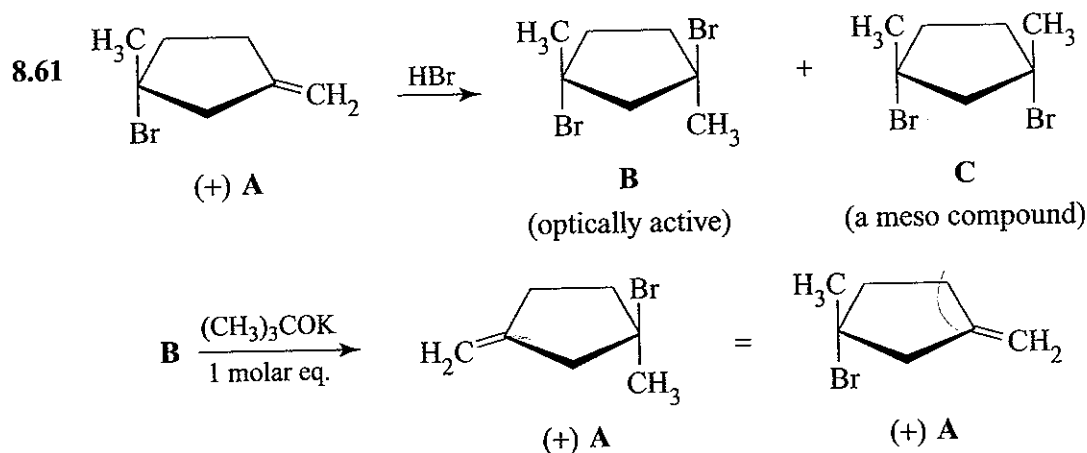


- 8.58 Though II is the product predicted by application of the Zaitsev rule, it actually is less stable than I due to crowding about the double bond. Hence I is the major product (by about a 4:1 ratio).
- 8.59 The terminal alkyne component of the equilibrium established in base is converted to a salt by NaNH_2 , effectively shifting the equilibrium completely to the right.

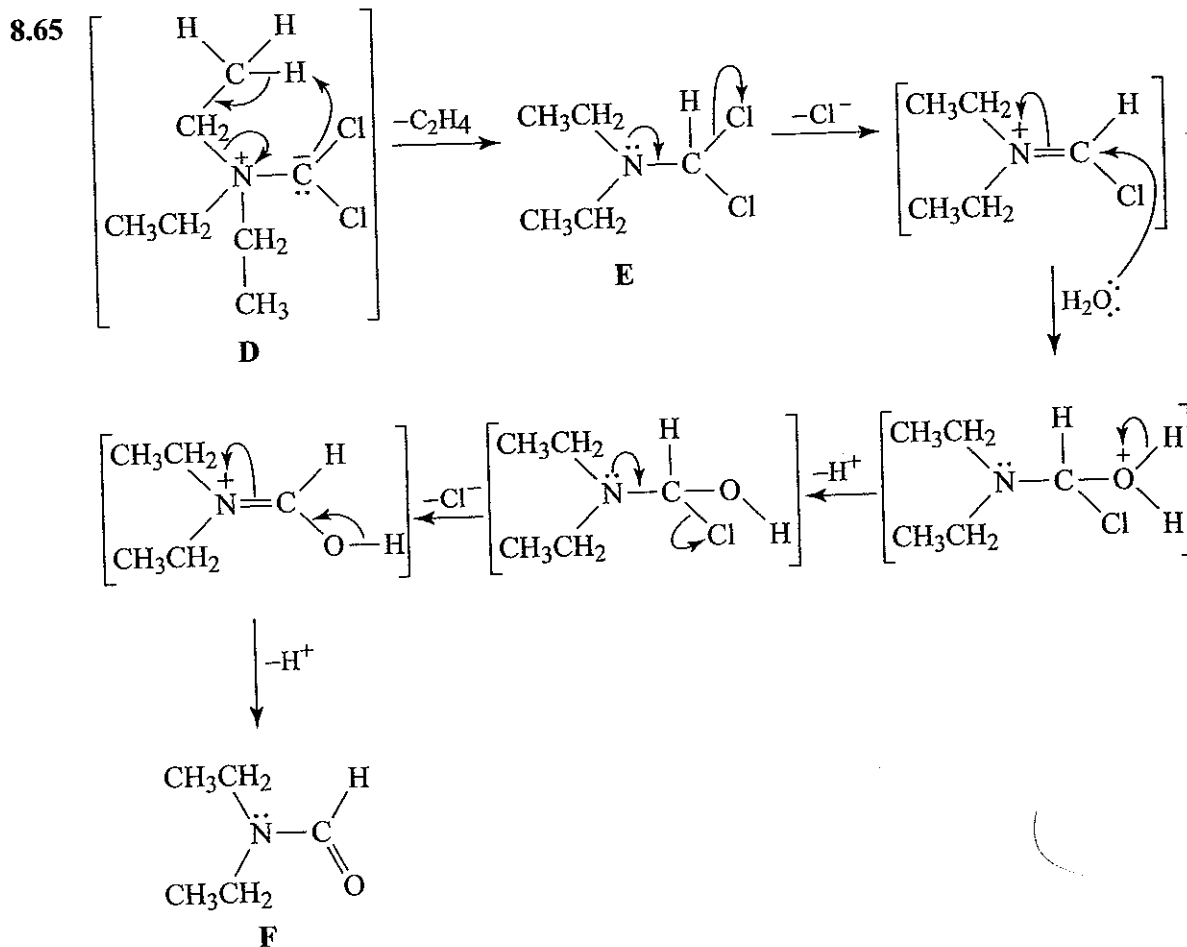


NaOH is too weak a base to form a salt with the terminal alkyne. Of the equilibrium components with NaOH , the internal alkyne is favored since it is the most stable of these structures. Very small amounts of the allene and the terminal alkyne are formed.

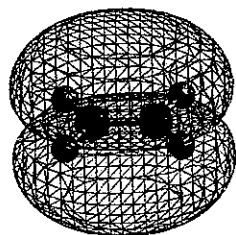
- 8.60 $\text{RC}\equiv\text{CH}$ is initially converted to $\text{RC}\equiv\text{C}^-$ by the sodium amide. The negative charge on this species discourages the donation of an electron by Na , the first step in a dissolving metal reduction (p. 297).
When $(\text{NH}_4)_2\text{SO}_4$ is present, the alkynide ion is protonated and the now-neutral species will undergo a dissolving metal reduction to an alkene.



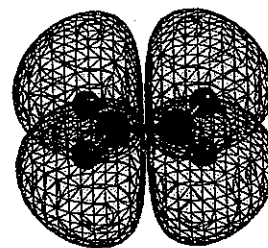
Challenge Problems



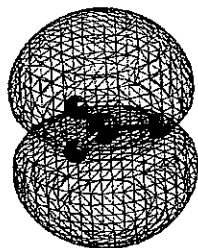
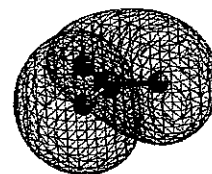
- 8.66 The HOMO and LUMO orbitals of ethene and BH_3 are shown here. In our discussion of the mechanism of hydroboration we mentioned the importance of the "vacant p orbital" of the boron. This is the LUMO of BH_3 in actuality, and it is this orbital that interacts with the π bond of ethene as the HOMO.



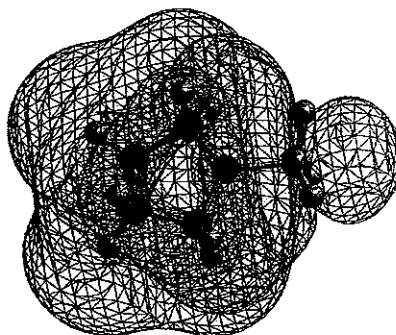
HOMO of ethene



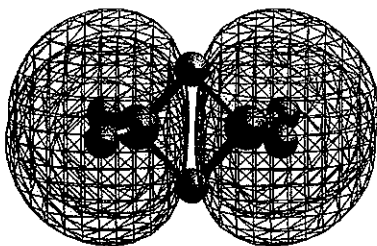
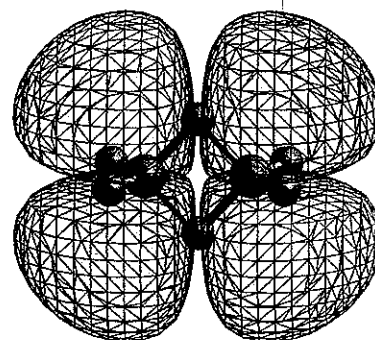
LUMO of ethene

LUMO of BH_3 HOMO of BH_3

- 8.67 The LUMO of the $\text{BH}_3:\text{THF}$ complex has a lobe (in red in the Chem3D version) which extends outward from the boron, much like the p orbital that is the LUMO of a hypothetical BH_3 monomer. This orbital is in position to accept the donation of electrons from a Lewis base such as an alkene π bond.

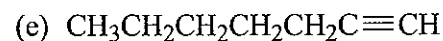
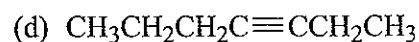
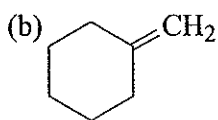
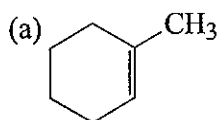


- 8.68 It is the LUMO of diborane that interacts with the HOMO of an alkene (the bonding π molecular orbital) or other Lewis base. Inspection of the LUMO for diborane shows that its lobes include part of the region between the partially bonded bridging hydrogen atoms and each boron atom, but that the major portion of each lobe is oriented away from these hydrogens and the boron such that electron density from a Lewis base could interact with the LUMO without hindrance. In a sense, the LUMO appears almost as if it is a "squashed" p orbital similar to what would be available with BH_3 as a monomer. The HOMO of diborane, on the other hand, has lobes localized about four of the boron—hydrogen bonds. As occupied orbitals, they are not available for bonding with the occupied orbital of a Lewis base.

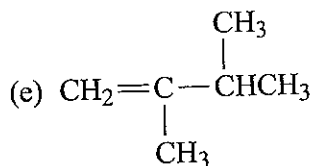
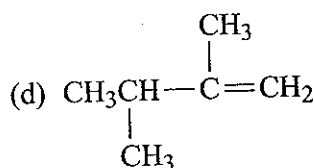
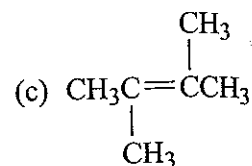
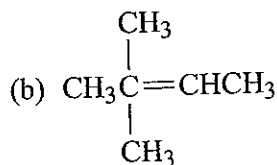
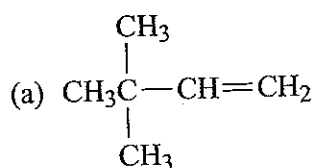

 HOMO of B_2H_6

 LUMO of B_2H_6

QUIZ

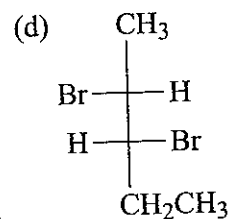
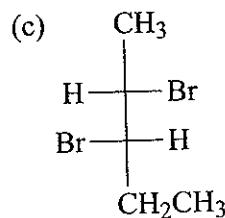
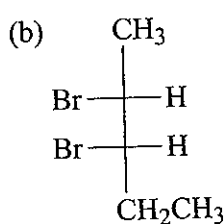
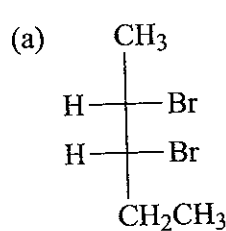
- 8.1 A hydrocarbon whose molecular formula is C_7H_{12} , on catalytic hydrogenation (excess H_2/Pt), yields C_7H_{16} . The original hydrocarbon adds bromine and also exhibits an IR absorption band at 3300 cm^{-1} . Which of the following is a plausible choice of structure for the original hydrocarbon?



8.2 Select the major product of the dehydration of the alcohol, $\text{CH}_3\text{C}(\text{CH}_3)(\text{OH})\text{CH}_2\text{CH}_3$

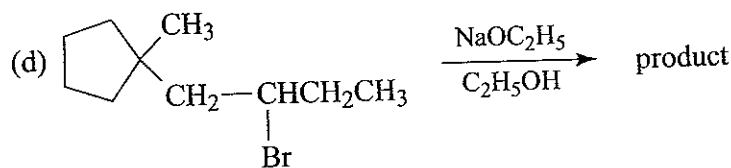
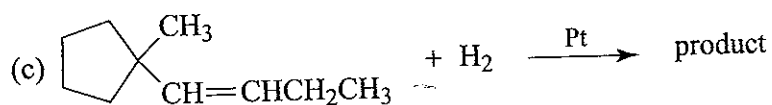
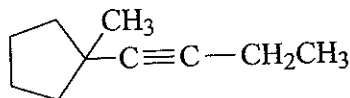


8.3 Give the major product of the reaction of *cis*-2-pentene with bromine.

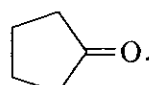


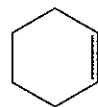
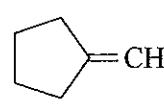
(e) A racemic mixture of (c) and (d)

8.4 The compound shown here is best prepared by which sequence of reactions?





- 8.5 A compound whose formula is C_6H_{10} (Compound A) reacts with H_2/Pt in excess to give a product C_6H_{12} , which does not decolorize Br_2/CCl_4 . Compound A does not show IR absorption in the $3200-3400\text{ cm}^{-1}$ region.

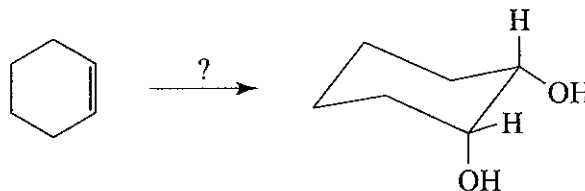
Ozonolysis of A gives 1 mol of $HCHO$ and 1 mol of . Give the structure of A.

- (a)  (b) $CH_3CH_2CH_2C\equiv CCH_3$ (c) $CH_3CH_2CH_2CH_2C\equiv CH$
- (d)  (e) $CH_2=CHCH_2CH_2CH=CH_2$

- 8.6 Compound B (C_5H_{10}) does not dissolve in cold, concentrated H_2SO_4 . What is B?

- (a) $CH_2=CHCH_2CH_2CH_3$ (b) $CH_3CH=CHCH_2CH_3$
- (c)  (d) 

- 8.7 Which reaction sequence converts cyclohexene to *cis*-1,2-cyclohexanediol? That is,



- (a) H_2O_2 (b) (1) O_3 (2) $Zn/HOAc$
- (c) (1) OsO_4 (2) $NaHSO_3/H_2O$ (d) (1) $RC(=O)OOH$ (2) H_3O^+/H_2O
- (e) More than one of these

- 8.8 Which of the following sequences leads to the best synthesis of the compound $CH_3CH_2C\equiv CH$? (Assume that the quantities of reagents are sufficient to carry out the desired reaction.)

- (a) $CH_3CH_2CH=CH_2 \xrightarrow{Br_2} \xrightarrow[H_2O]{NaOH}$
- (b) $CH_3CH_2CH=CH_2 \xrightarrow{Br_2} \xrightarrow{NaNH_2}$
- (c) $CH_3CH_2CH_2CHBr_2 \xrightarrow{H_2SO_4}$
- (d) $CH_3CH_2CH_2CH_3 \xrightarrow[light]{Br_2} \xrightarrow{NaNH_2}$
- (e) $CH_3CH_2CH=CH_2 \xrightarrow{O_3} \xrightarrow{Zn, HOAc}$