

Chapter 7 – Alkenes: Reactions and Synthesis

Chapter Outline

I. Preparation of alkenes (Section 7.1).

A. Dehydrohalogenation.

Reaction of an alkyl halide with a strong base forms an alkene, with loss of HX.

B. Dehydration.

Treatment of an alcohol with a strong acid forms an alkene, with loss of H₂O.

II. Addition reactions of alkenes (Sections 7.2 – 7.6).

A. Addition of halogens (Section 7.2).

1. Br₂ and Cl₂ react with alkenes to yield 1,2-dihaloalkanes.
2. Reaction occurs with anti stereochemistry ; both bromines come from opposite sides of the molecule.
3. The reaction intermediate is a cyclic bromonium intermediate that is formed in a single step by interaction of an alkene with Br⁺.

B. Addition of hypohalous acids (Section 7.3).

1. Alkenes add HO-X (X = Br or Cl), forming halohydrins, when they react with halogens in the presence of H₂O.
2. The added nucleophile (H₂O) intercepts the bromonium ion to yield a bromohydrin.
3. Bromohydrin formation is usually achieved by NBS in aqueous DMSO.
4. Aromatic rings are inert to halohydrin reagents.

C. Addition of water to alkenes (Sections 7.4).

1. Hydration.
 - a. Water adds to alkenes to yield alcohols in the presence of a strong acid catalyst.
 - b. Although this reaction is important industrially, reaction conditions are too severe for most molecules.
2. Oxymercuration.
 - a. Addition of Hg(OAc)₂, followed by NaBH₄, converts an alkene to an alcohol.
 - b. The mechanism of addition proceeds through a mercurinium ion.
 - c. The reaction follows Markovnikov regiochemistry.

D. Addition of water to alkenes: hydroboration/oxidation (Section 7.5).

1. BH₃ adds to an alkene to produce an organoborane.

Three molecules of alkene add to BH₃ to produce a trialkylborane.
2. Treatment of the trialkylborane with H₂O₂ forms 3 molecules of an alcohol.
3. Addition occurs with syn stereochemistry.
4. Addition occurs with non-Markovnikov regiochemistry.

Hydroboration is complementary to oxymercuration/reduction.
5. The mechanism of hydroboration involves a four-center, cyclic transition state.
 - a. This transition state explains syn addition.
 - b. Stabilization of the transition state by a substituted double-bond carbon also explains non-Markovnikov regiochemistry.

E. Addition of carbenes (Section 7.6).

1. A carbene (R₂C:) adds to an alkene to give a cyclopropane.
2. The reaction occurs in a single step, without intermediates.
3. Treatment of HCCl₃ with KOH forms dichlorocarbene.

Addition of dichlorocarbene to a double bond is stereospecific, and only cis-dichlorocyclopropanes are formed.
4. The Simmons-Smith reaction (CH₂I₂, Zn-Cu) produces a nonhalogenated cyclopropane via a carbenoid reagent.

III. Reduction and oxidation of alkenes (Sections 7.7 – 7.9).

A. Reduction of alkenes (Section 7.7).

1. Catalytic hydrogenation reduces alkenes to saturated hydrocarbons.
2. The catalysts used are Pt and Pd.

Catalytic hydrogenation is a heterogeneous process that takes place on the surface of the catalyst.

3. Hydrogenation occurs with syn stereochemistry.

The reaction is sensitive to the steric environment around the double bond.

4. Alkenes are much more reactive than other functional groups.

B. Oxidation of alkenes (Sections 7.8 – 7.9).

1. Epoxidation (Section 7.8).

- a. Epoxides can be prepared by reaction of an alkene with a peroxyacid RCO_3H .

The reaction occurs in one step with syn stereochemistry.

- b. Epoxides are formed when halohydrins are treated with base.

- c. Acid-catalyzed reaction of an epoxide ring with water yields a 1,2-diol.

- i. Ring opening takes place by back-side attack of a nucleophile on the protonated epoxide ring.

- ii. A *trans*-1,2-diol is formed from an epoxycycloalkane.

2. Hydroxylation

- a. OsO_4 causes the addition of two $-\text{OH}$ groups to an alkene to form a diol.

Hydroxylation occurs through a cyclic osmate.

- b. A safer reaction uses a catalytic amount of OsO_4 and the oxidant NMO.

- c. The reaction occurs with syn stereochemistry.

2. Cleavage to carbonyl compounds (Section 7.9).

- a. O_3 causes cleavage of an alkene to produce aldehyde and/or ketone fragments.

The reaction proceeds through a cyclic molozonide, which rearranges to an ozonide that is reduced by Zn.

- b. KMnO_4 cleaves alkenes to yield ketones, carboxylic acids or CO_2 .

- c. Diols can be cleaved with HIO_4 to produce carbonyl compounds.

IV. Alkene polymers (Section 7.10).

Many types of polymers can be formed by radical polymerization of alkene monomers.

1. There are 3 steps in a polymerization reaction.

- a. *Initiation* involves homolytic cleavage of a weak bond to form a radical

The radical adds to an alkene to generate an alkyl radical.

- b. The alkyl radical adds to another alkene molecule (*propagation*) to yield a second radical.

This step is repeated many, many times.

- c. *Termination* occurs when two radical fragments combine.

2. Mechanisms of radical reactions are shown by using fishhook arrows.

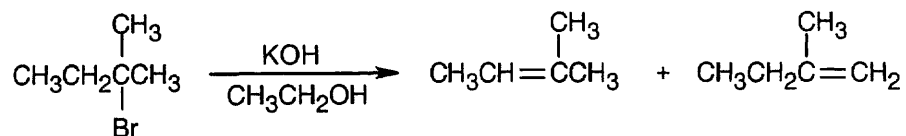
3. As in electrophilic addition reactions, the more stable radical (more substituted) is formed in preference to the less stable radical.

V. Biological additions of radicals to alkenes (Section 7.11).

Biochemical radical reactions are more controlled than laboratory radical reactions.

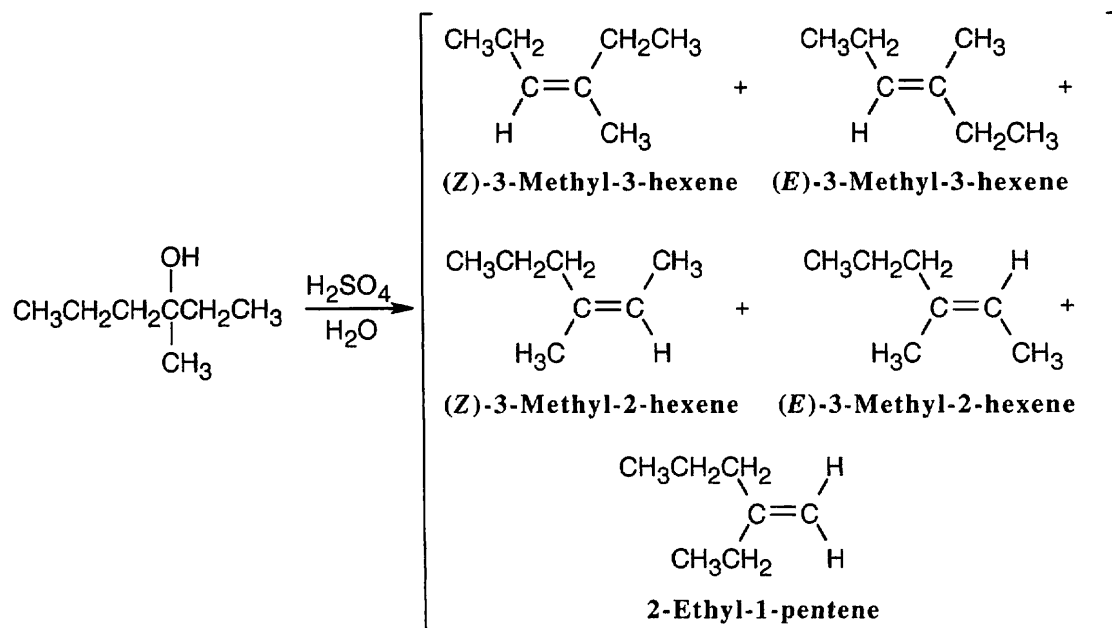
Solutions to Problems

7.1



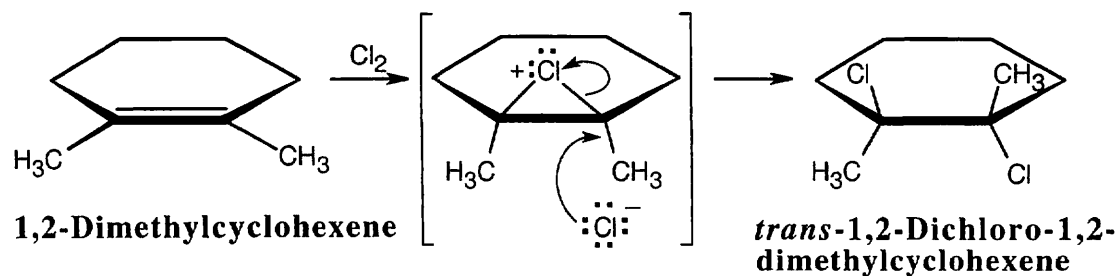
Dehydrobromination may occur in either of two directions to yield a mixture of products.

7.2



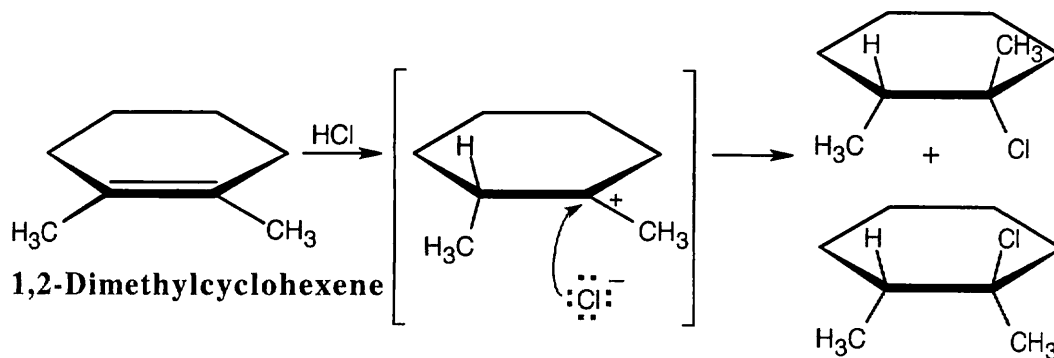
Five alkene products, including *E*, *Z* isomers, might be obtained by dehydration of 3-methyl-3-hexanol.

7.3



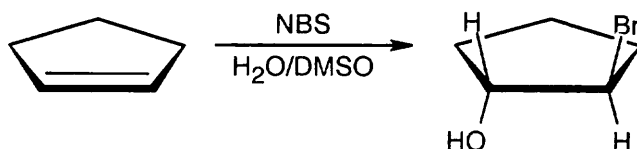
The chlorines are *trans* to one another in the product, as are the methyl groups.

7.4



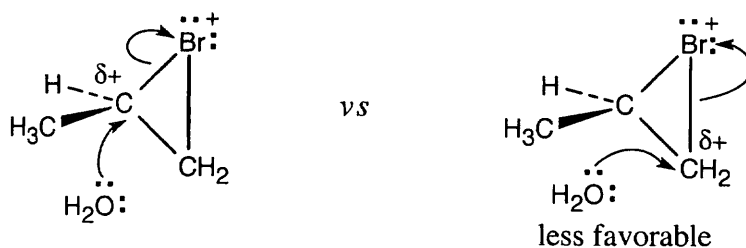
Addition of hydrogen halides involves formation of an open carbocation, not a cyclic halonium ion intermediate. The carbocation, which is sp^2 -hybridized and planar, can be attacked by chloride from either top or bottom, yielding products in which the two methyl groups can be either cis or trans to each other.

7.5



–Br and –OH are trans in the product.

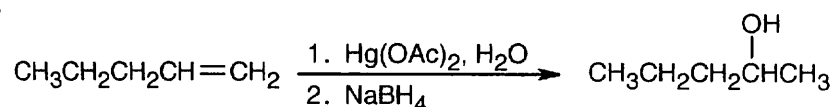
- 7.6** Reaction of the alkene with Br_2 (formed from NBS) produces a cyclic bromonium ion. When this bromonium ion is opened by water, a partial positive charge develops at the carbon whose bond to bromine is being cleaved.



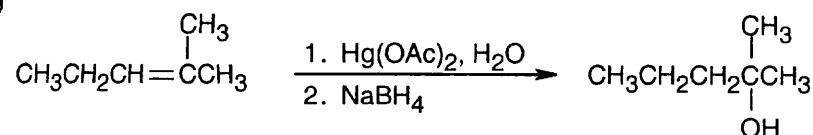
Since a secondary carbon can stabilize this charge better than a primary carbon, opening of the bromonium ion occurs at the secondary carbon to yield the Markovnikov product.

- 7.7** Keep in mind that oxymercuration is equivalent to Markovnikov addition of H_2O to an alkene.

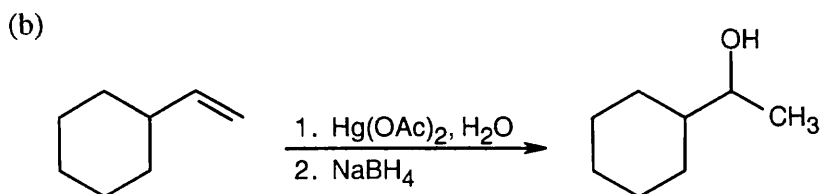
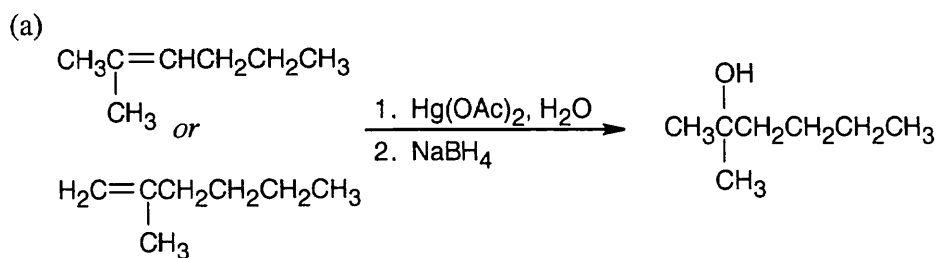
(a)



(b)



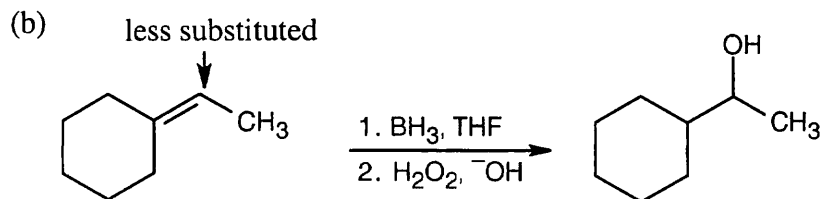
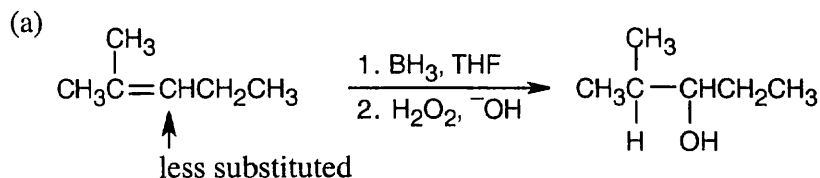
7.8 Think backwards to select the possible alkene starting materials for the alcohols pictured.



Oxymercuration occurs with Markovnikov orientation.

7.9 Strategy: Hydroboration/oxidation occurs with non-Markovnikov regiochemistry to give products in which -OH is bonded to the less highly substituted carbon.

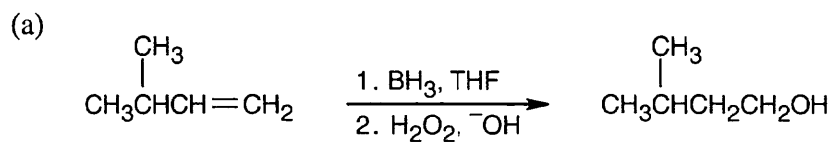
Solution:

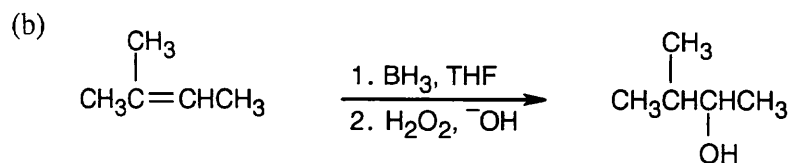


7.10 Strategy: As described in Worked Example 7.2, the strategy in this sort of problem begins with a look backward. In more complicated syntheses this approach is essential, but even in problems in which the functional group(s) in the starting material and the reagents are known, this approach is effective.

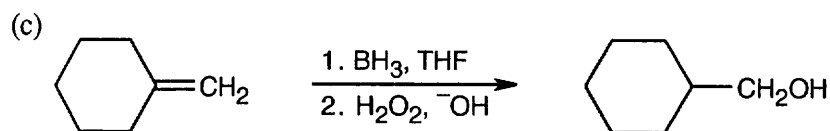
All the products in this problem result from hydroboration/oxidation of a double bond. The -OH group is bonded to the less substituted carbon of the double bond in the starting material.

Solution:

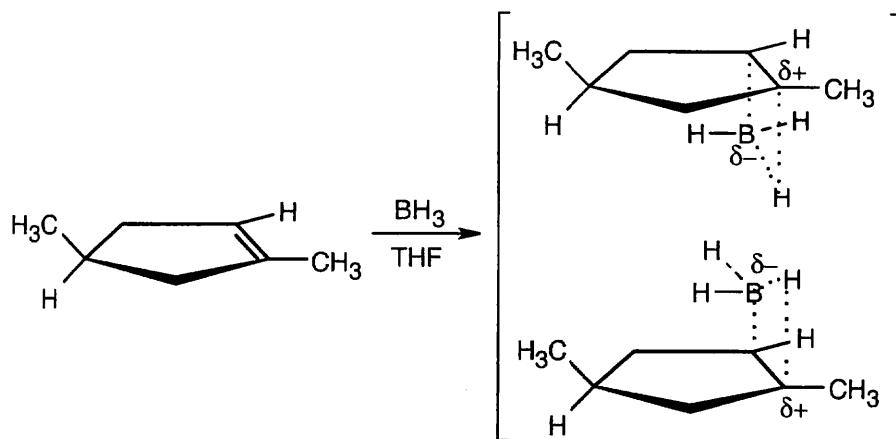




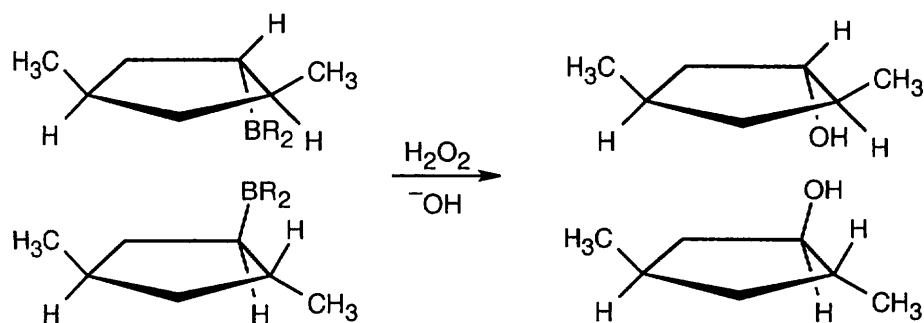
This product can also result from oxymercuration of the starting material in (a).



7.11 The drawings below show the transition states resulting from addition of BH_3 to the double bond of the cycloalkene. Addition can occur on either side of the double bond.



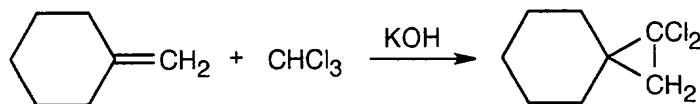
Reaction of the two neutral alkylborane adducts with hydrogen peroxide gives two alcohol isomers. In one isomer, the two methyl groups have a cis relationship, and in the other isomer they have a trans relationship.



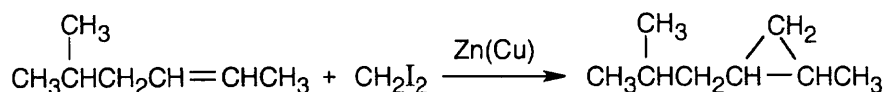
7.12 Strategy: Reaction of a double bond with chloroform under basic conditions gives a product with a cyclopropane ring in which one of the carbons has two chlorine atoms bonded to it. Reaction of a double bond with CH_2I_2 yields a product with a cyclopropane ring that has a $-\text{CH}_2-$ group.

Solution:

(a)



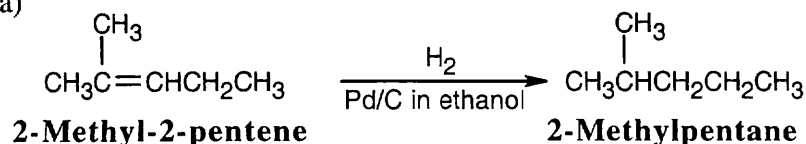
(b)



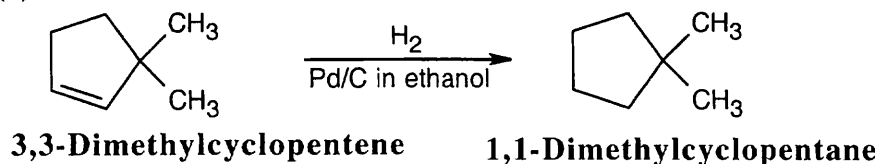
Depending on the stereochemistry of the double bond of the alkene in (b), two different isomers can be formed.

7.13 Catalytic hydrogenation produces alkanes from alkenes.

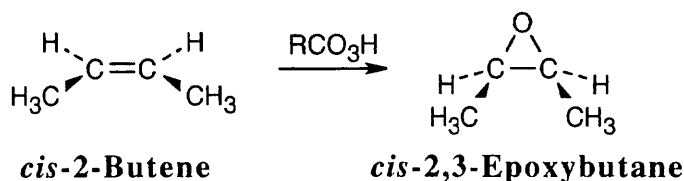
(a)



(b)



7.14 Epoxidation using *m*-chloroperoxybenzoic acid (RCO_3H) is a syn addition of oxygen to a double bond. The original bond stereochemistry is retained.

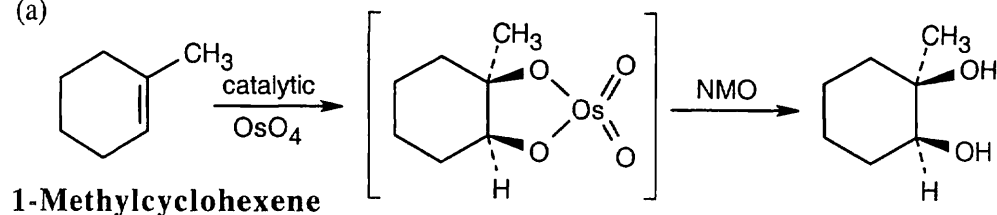


In the epoxide product, as in the alkene starting material, the methyl groups are *cis*.

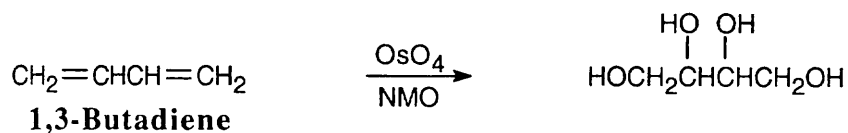
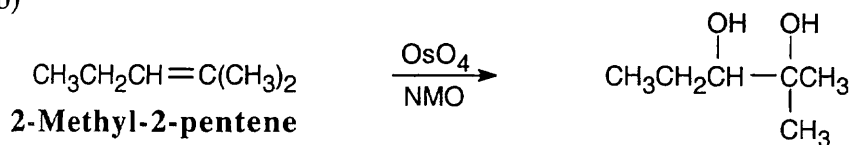
7.15 Strategy: Reaction of an alkene with a catalytic amount of OsO_4 , in the presence of *N*-morpholine *N*-oxide (NMO), yields a diol product. To pick a starting material for these products, choose an alkene that has a double bond between the diol carbons.

Solution:

(a)

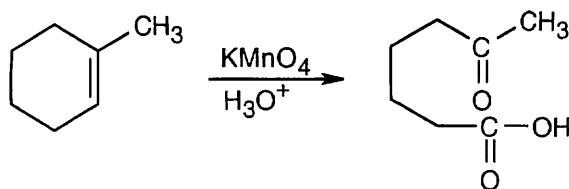


(b)

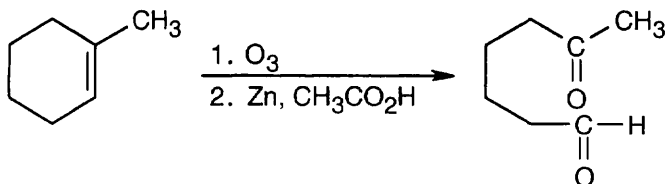


7.16 Strategy: Both sets of reactants cleave double bonds. Aqueous KMnO_4 produces a carboxylic acid from a double bond carbon that is monosubstituted and a ketone from a double bond carbon that is disubstituted. Ozone produces an aldehyde from a double bond carbon that is monosubstituted and a ketone from a double bond carbon that is disubstituted. If the double bond is part of a ring, both carbonyl groups occur in the same product molecule.

(a)

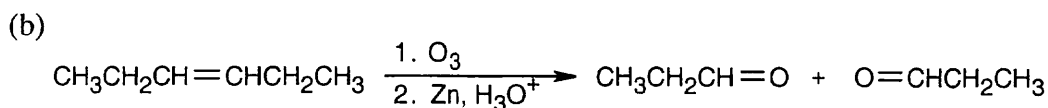
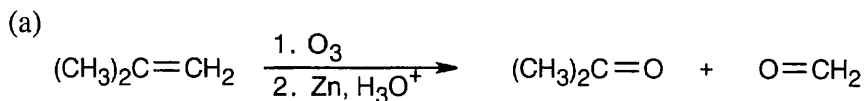


(b)

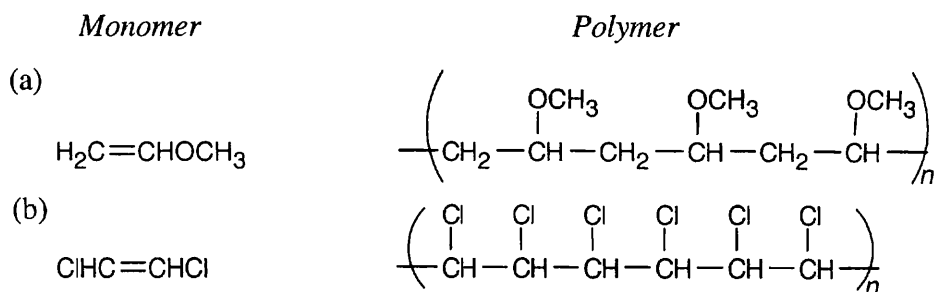


7.17 Strategy: Orient the fragments so that the oxygens point toward each other. Remove the oxygens, and draw a double bond between the remaining carbons.

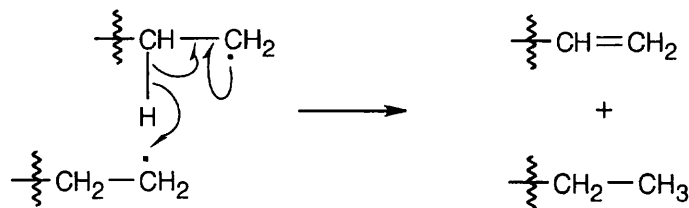
Solution:



7.18 Strategy: Find the smallest repeating unit in each polymer. This is the monomer unit.

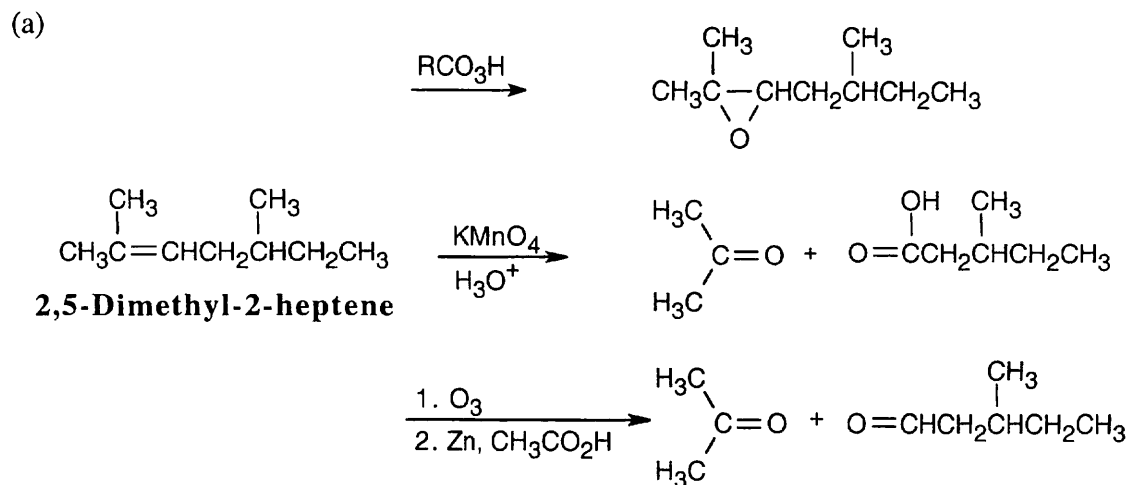


7.19 One radical abstracts a hydrogen atom from a second radical, and the remaining two electrons create a double bond.

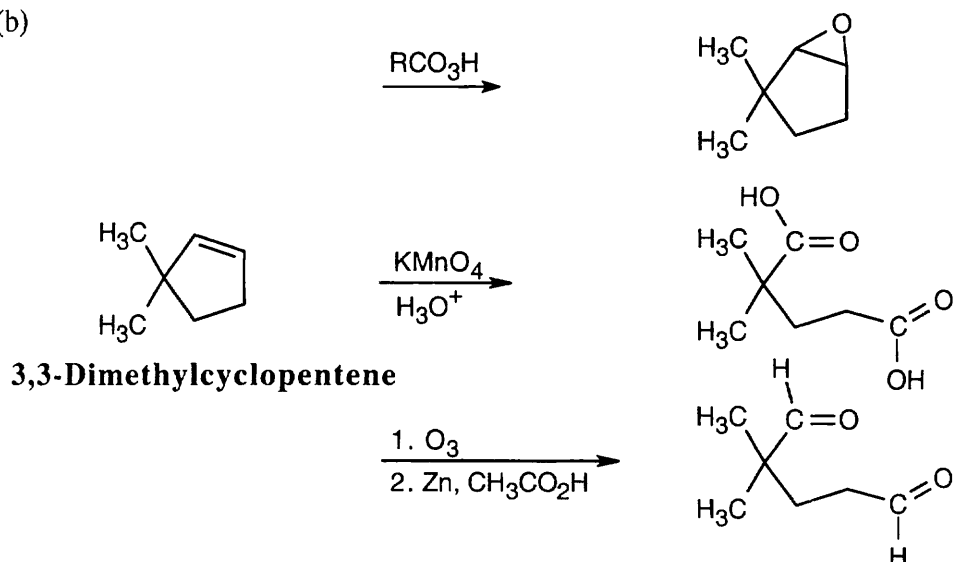


Visualizing Chemistry

7.20

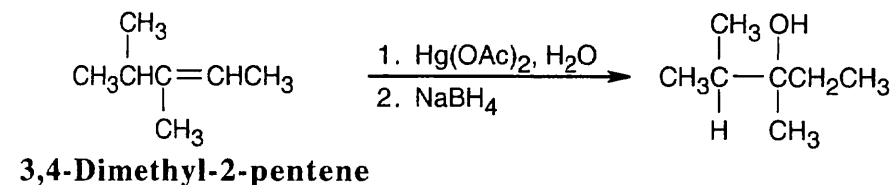
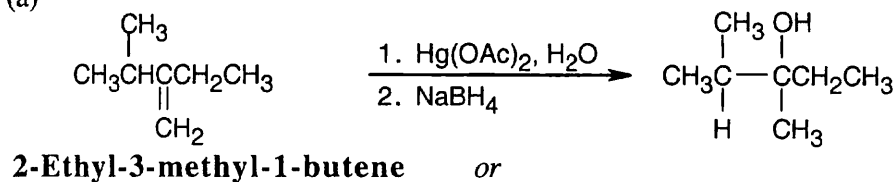


(b)



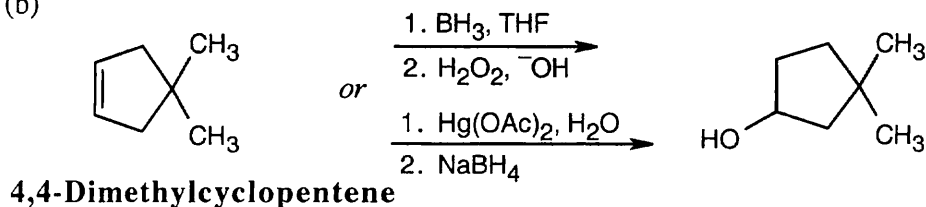
7.21

(a)



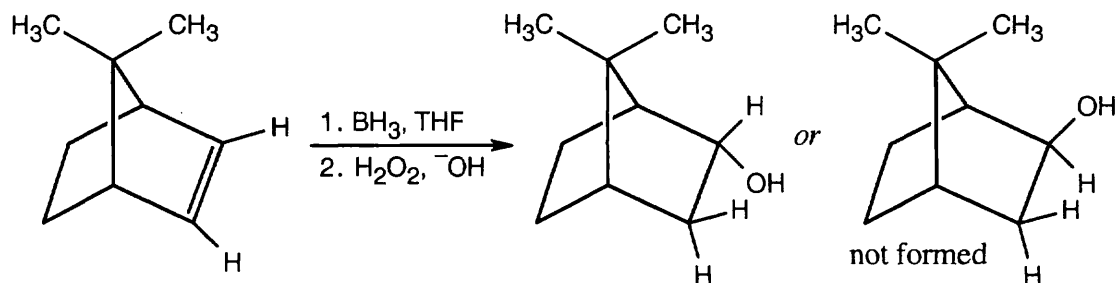
Only oxymercuration/reduction can be used to produce an alcohol that has -OH bonded to the more substituted carbon. A third alkene, 2,3-dimethyl-2-pentene, gives a mixture of tertiary alcohols when treated with either BH_3 or $\text{Hg}(\text{OAc})_2$.

(b)



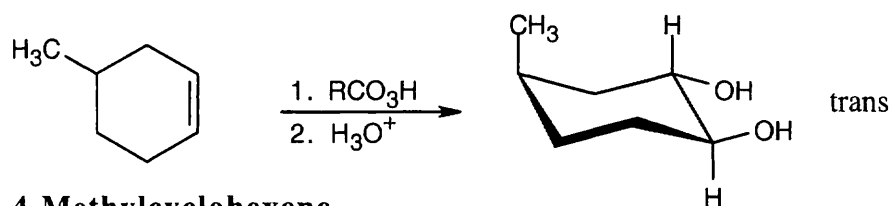
Both hydroboration/oxidation and oxymercuration yield the same alcohol product from the symmetrical alkene starting material.

7.22



Two possible alcohols might be formed by hydroboration/oxidation of the alkene shown. One product results from addition of BH_3 to the top face of the double bond (not formed), and the other product results from addition to the bottom face of the double bond (formed). Addition from the top face does not occur because a methyl group on the bridge of the bicyclic ring system blocks approach of the borane.

7.23

**4-Methylcyclohexene**

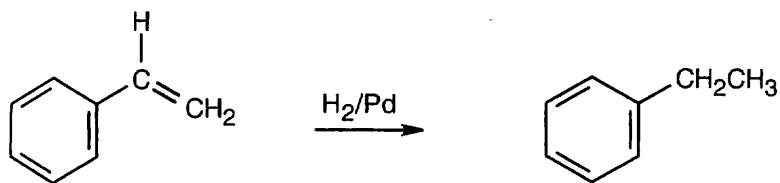
RCO_3H = *meta*-Chloroperoxybenzoic acid

Since the hydroxyl groups in the diol product have a trans relationship, the product can only be formed by epoxide hydrolysis. (Treatment of the alkene with OsO_4 yields a product in which the two $-\text{OH}$ groups have a cis relationship.)

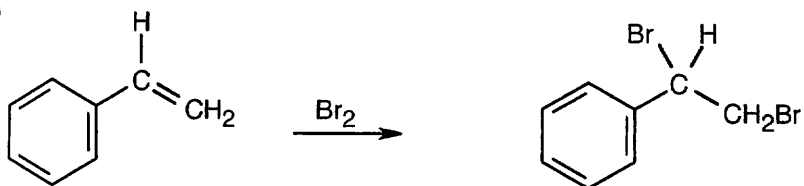
Additional Problems

7.24

(a)



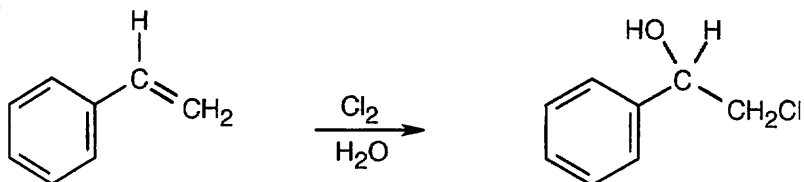
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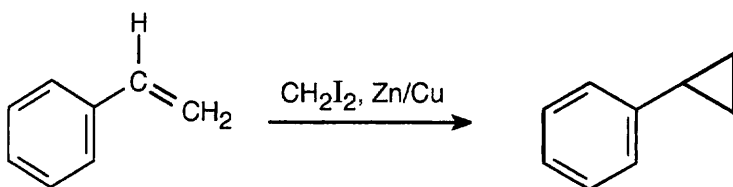
(c)



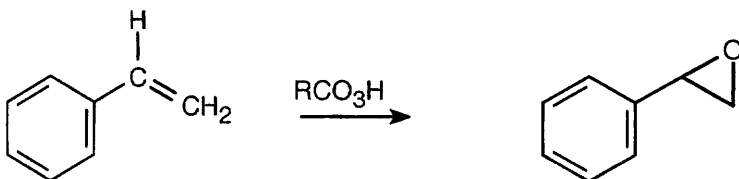
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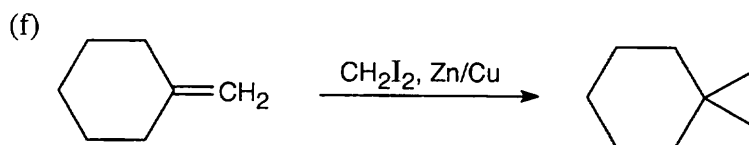
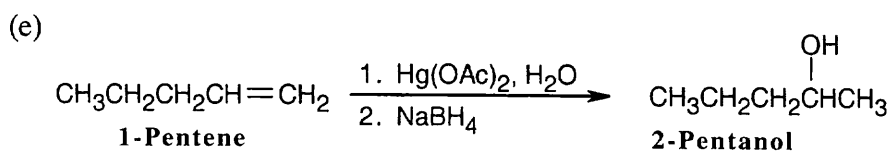
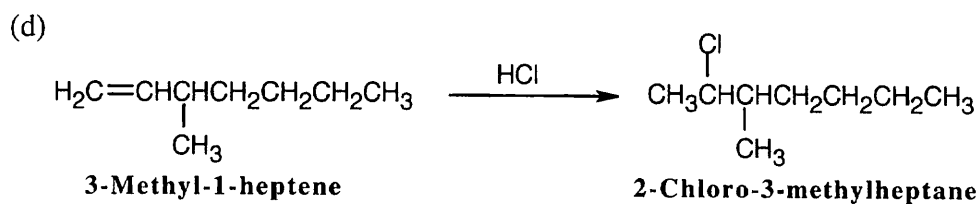
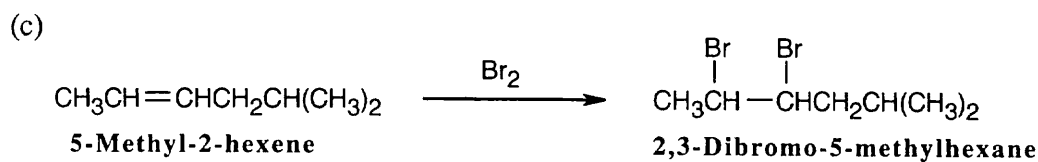
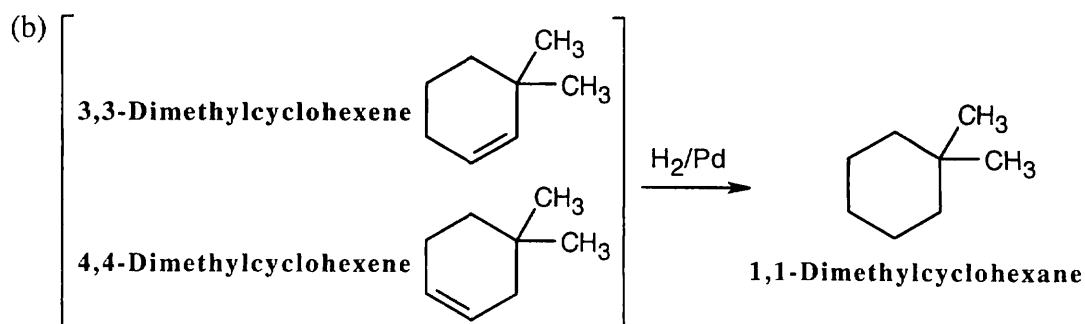
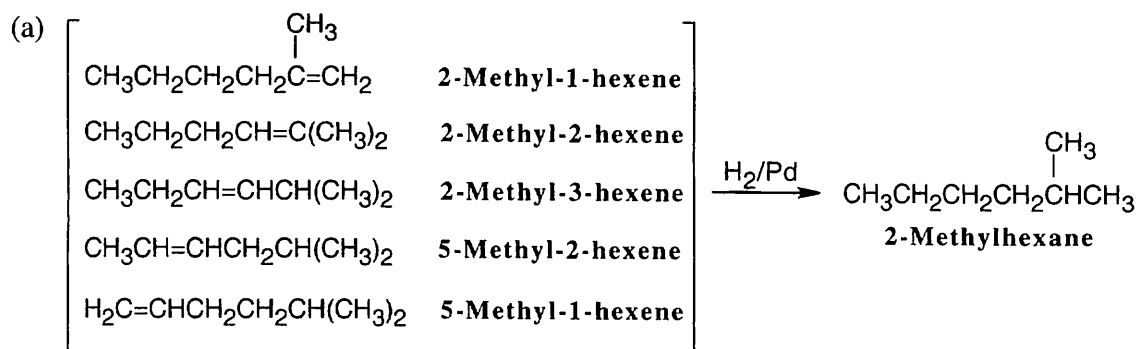
(e)



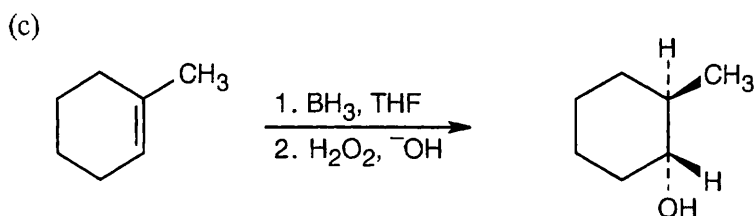
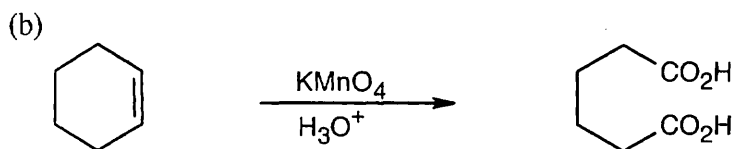
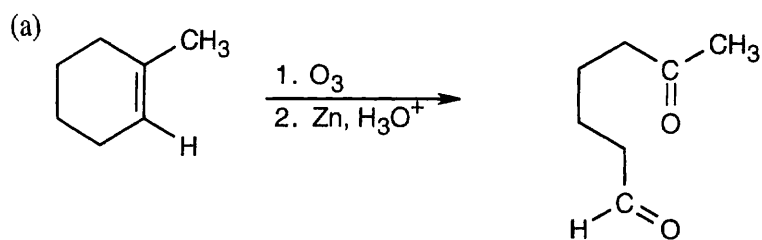
(f)

 RCO_3H = *meta*-Chloroperoxybenzoic acid

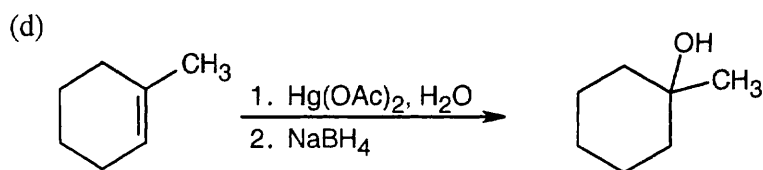
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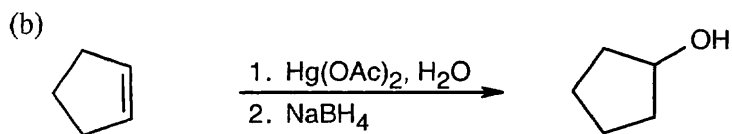
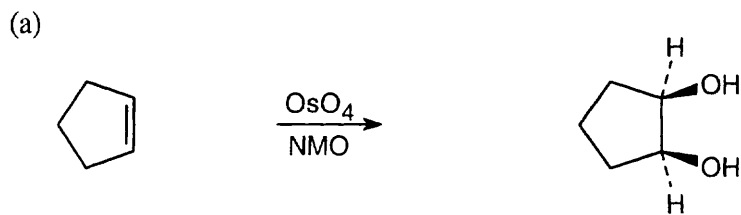
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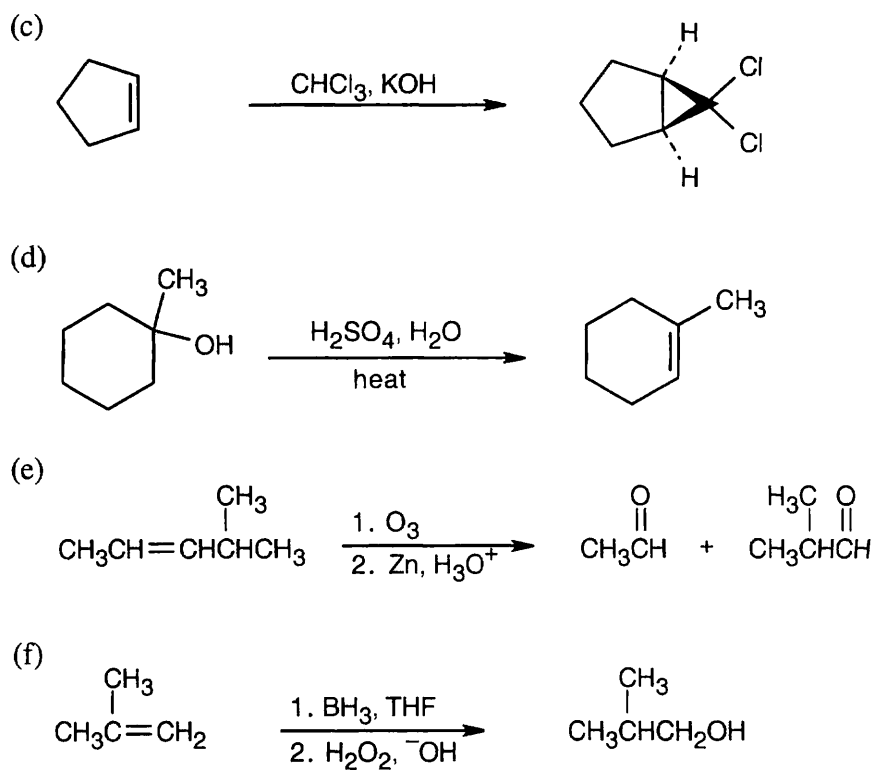
Remember that $-\text{H}$ and $-\text{OH}$ add syn across the double bond.



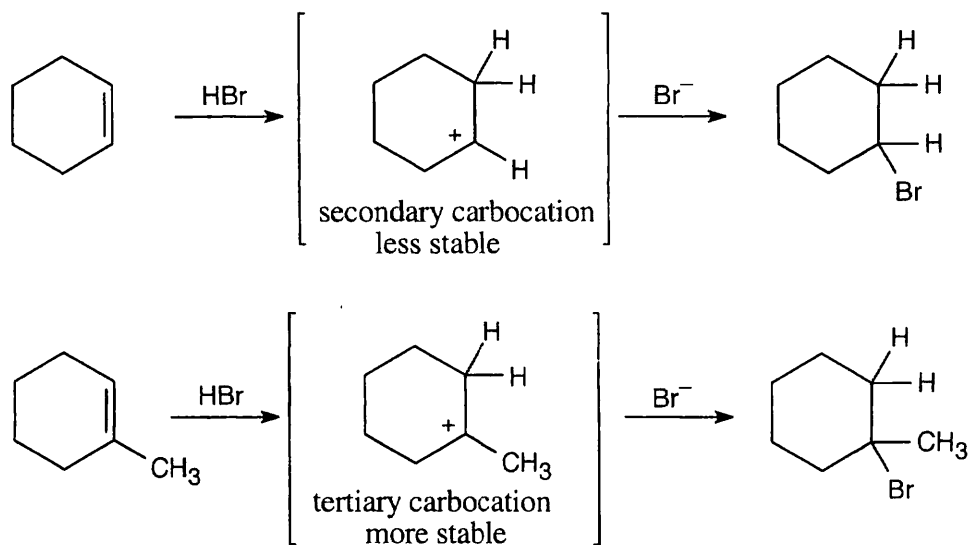
7.27



Hydroboration/oxidation is another route to this product.

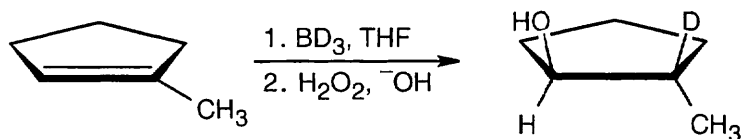


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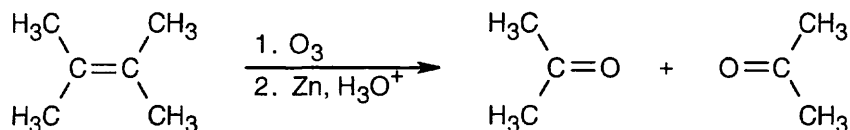


Remember from Section 6.10 that a reaction that forms a more stable carbocation intermediate is faster than a comparable reaction that forms a less stable carbocation intermediate. Thus, the reaction of 1-methylcyclohexene with HBr is faster than the reaction of cyclohexene with HBr.

- 7.29 Recall the mechanism of hydroboration and note that the hydrogen added to the double bond comes from borane. The product of hydroboration with BD_3 has deuterium bonded to the more substituted carbon; $-\text{D}$ and $-\text{OH}$ are cis to one another.

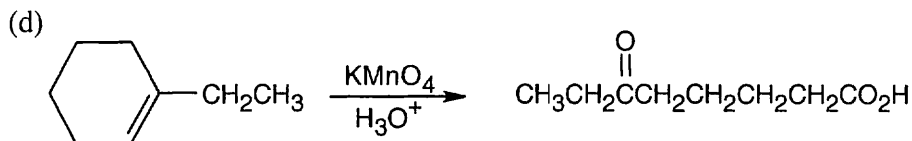
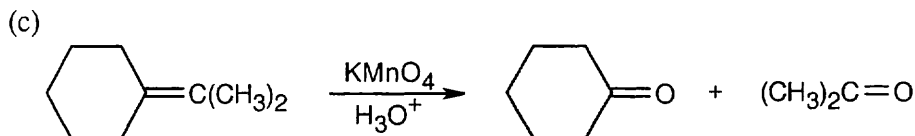
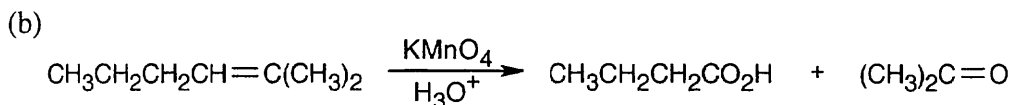
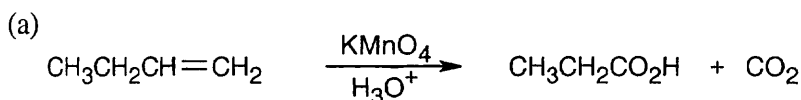


- 7.30 Because ozonolysis gives only one product, we can assume that the alkene is symmetrical.

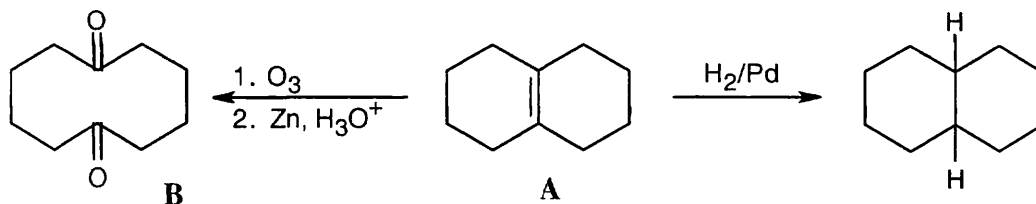


2,3-Dimethyl-2-butene

- 7.31 Remember that alkenes can give ketones, carboxylic acids, and CO_2 on oxidative cleavage with KMnO_4 in acidic solution.



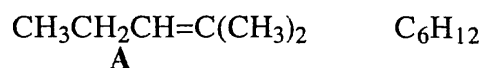
- 7.32 (a) Compound **A** has three degrees of unsaturation. Because compound **A** contains only one double bond, the other two degrees of unsaturation must be rings.
(b), (c)



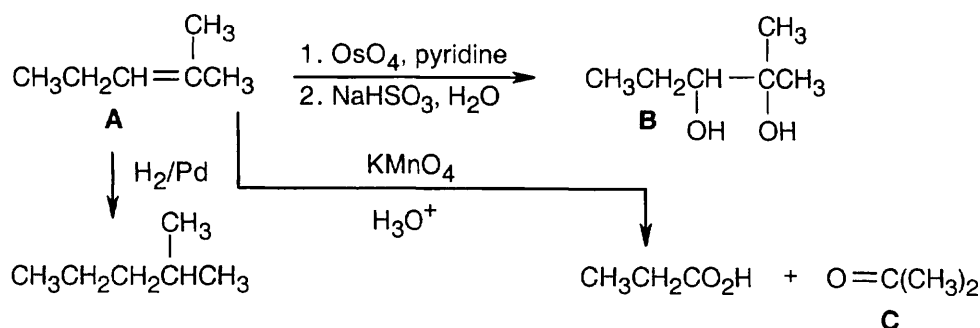
Other compounds containing two fused rings and a shared double bond also yield symmetrical diketone products.

7.33 Don't get discouraged by the amount of information in this problem. Read slowly and interpret the information phrase by phrase. We know the following:

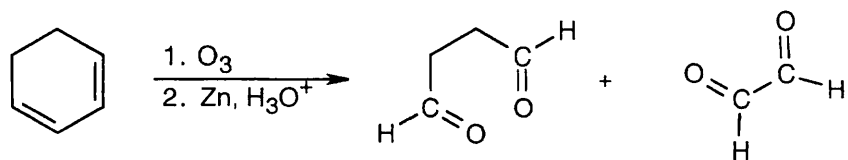
- (1) Hydrocarbon **A** (C_6H_{12}) has one double bond or ring.
- (2) Because **A** reacts with one equivalent of H_2 , it has one double bond and no ring.
- (3) Compound **A** forms a diol (**B**) when reacted with OsO_4 .
- (4) When alkenes are oxidized with $KMnO_4$ they give either carboxylic acids or ketones, depending on the substitution pattern of the double bond.
 - (a) A ketone is produced from what was originally a disubstituted carbon in the double bond.
 - (b) A carboxylic acid is produced from what was originally a monosubstituted carbon in the double bond.
- (5) One fragment from $KMnO_4$ oxidation is a carboxylic acid, $CH_3CH_2CO_2H$.
 - (a) This fragment was $CH_3CH_2CH=$ (a monosubstituted double bond) in compound **A**.
 - (b) It contains three of the six carbons of compound **A**.
- (6) (a) The other fragment contains three carbons.
 - (b) It forms ketone **C** on oxidation.
 - (c) The only three carbon ketone is acetone, $O=C(CH_3)_2$.
 - (d) This fragment was $=C(CH_3)_2$ in compound **A**.
- (7) If we join the fragment in 5(a) with the one in 6(d), we get:



The complete scheme:



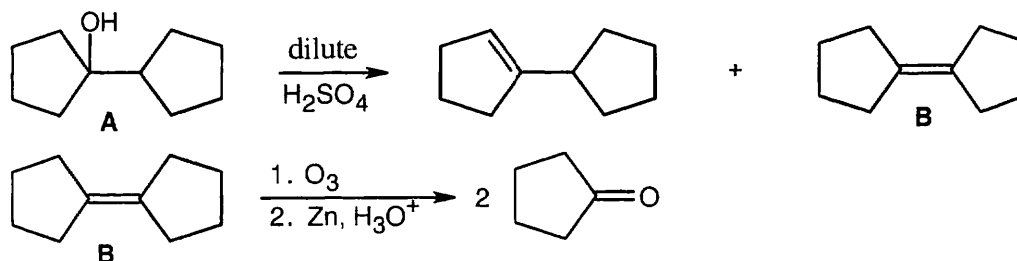
7.34 The oxidative cleavage reaction of alkenes with O_3 , followed by Zn in acid, produces aldehyde and ketone functional groups at sites where double bonds used to be. On ozonolysis, these two dienes yield only aldehydes because all double bonds are monosubstituted.



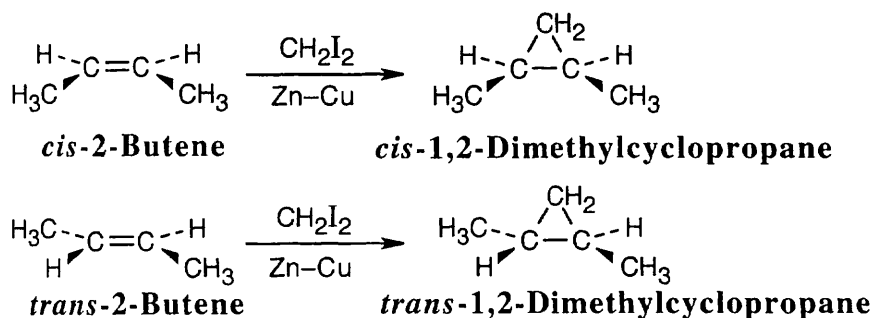
Because the other diene is symmetrical, only one dialdehyde, $OCHCH_2CHO$, is produced.

7.35 Try to solve this problem phrase by phrase.

- (1) $C_{10}H_{18}O$ has two double bonds and/or rings.
- (2) $C_{10}H_{18}O$ must be an alcohol because it undergoes reaction with H_2SO_4 to yield an alkene.
- (3) When $C_{10}H_{18}O$ is treated with dilute H_2SO_4 , a mixture of alkenes of the formula $C_{10}H_{16}$ is produced.
- (4) Since the major alkene product **B** yields only cyclopentanone, C_5H_8O , on ozonolysis, **B** and **A** contain two rings. **A** therefore has no double bonds.



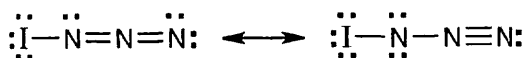
7.36



The Simmons–Smith reaction occurs with syn stereochemistry. Only *cis*-1,2-dimethylcyclopropane is produced from *cis*-2-butene, and only *trans*-1,2-dimethylcyclopropane is produced from *trans*-2-butene.

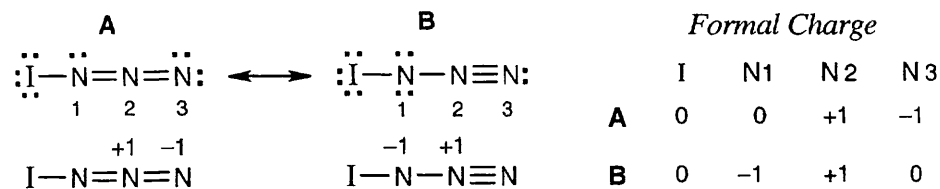
7.37

(a)



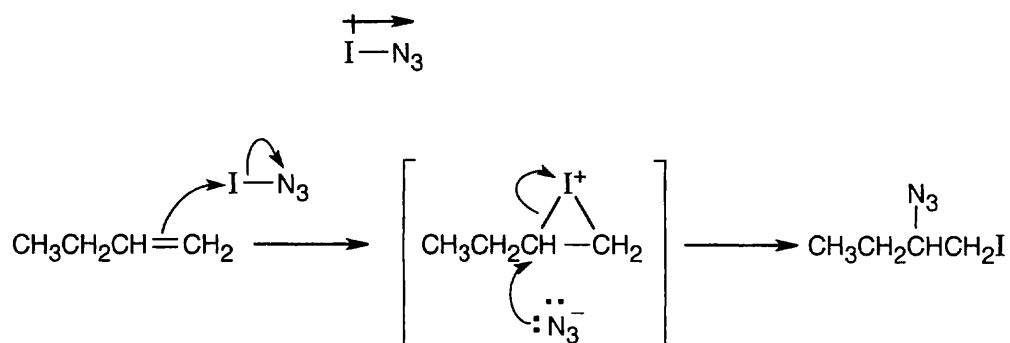
(b)

$$(\text{FC}) = \left[\begin{array}{c} \# \text{ of valence} \\ \text{electrons} \end{array} \right] - \left[\frac{\# \text{ of bonding electrons}}{2} \right] - \left[\begin{array}{c} \# \text{ nonbonding} \\ \text{electrons} \end{array} \right]$$

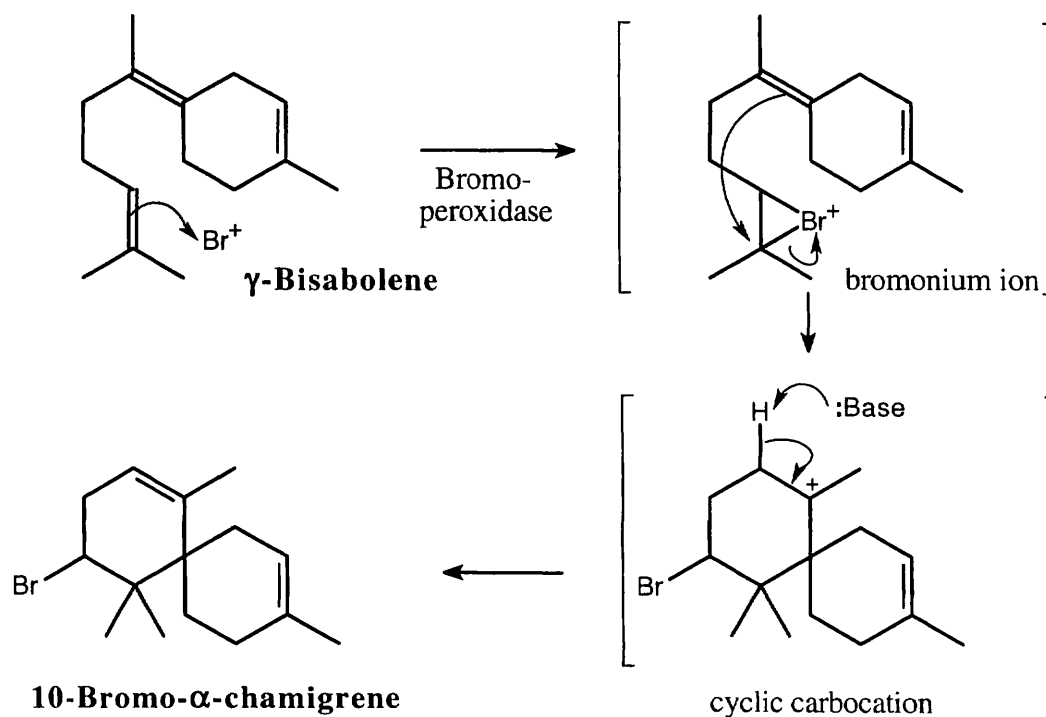


Formal charge calculations show a partial negative charge on N1.

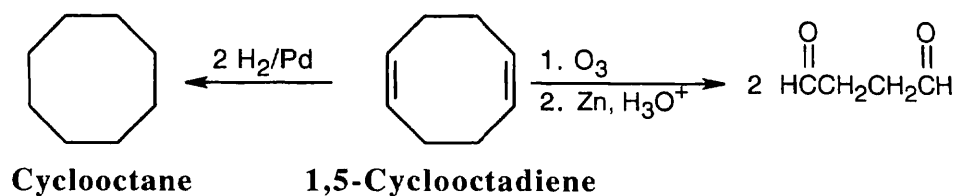
(c) Addition of IN_3 to the alkene yields a product in which $-\text{I}$ is bonded to the primary carbon and $-\text{N}_3$ is bonded to the secondary carbon. If addition occurs with Markovnikov orientation, I^+ must be the electrophile, and the reaction must proceed through an iodonium ion intermediate. Opening of the iodonium ion gives Markovnikov product for the reasons discussed in Problem 7.6. The bond polarity of iodine azide is:



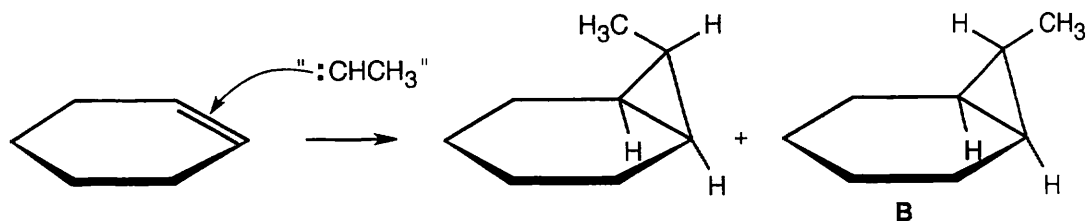
7.38



7.39



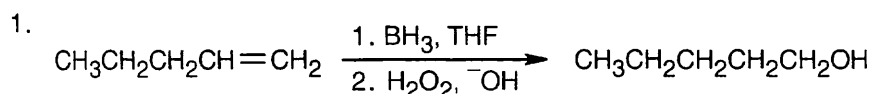
7.40



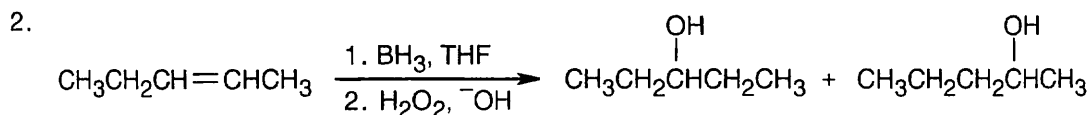
Focus on the stereochemistry of the three-membered ring. Simmons-Smith reaction of 1,1-diiodoethane with the double bond occurs with syn stereochemistry and can produce two isomers. In one of these isomers (**A**), the methyl group is on the same side of the three-membered ring as the cyclohexane ring carbons. In **B**, the methyl group is on the side of the three-membered ring opposite to the cyclohexane ring carbons.

- 7.41** (a) Addition of HI occurs with Markovnikov regiochemistry – iodine adds to the more substituted carbon.
 (b) Hydroxylation of double bonds produces cis, not trans, diols.
 (c) Ozone reacts with both double bonds of 1,4-cyclohexadiene.
 (d) Because hydroboration is a syn addition, the -H and the -OH added to the double bond must be cis to each other.

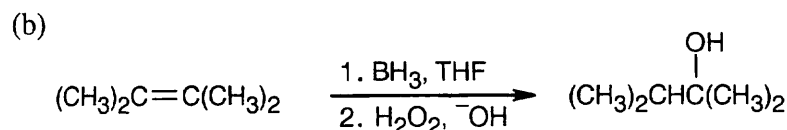
- 7.42** (a) This alcohol can't be synthesized selectively by hydroboration/oxidation. Consider the two possible starting materials.



1-Pentene yields only the primary alcohol.



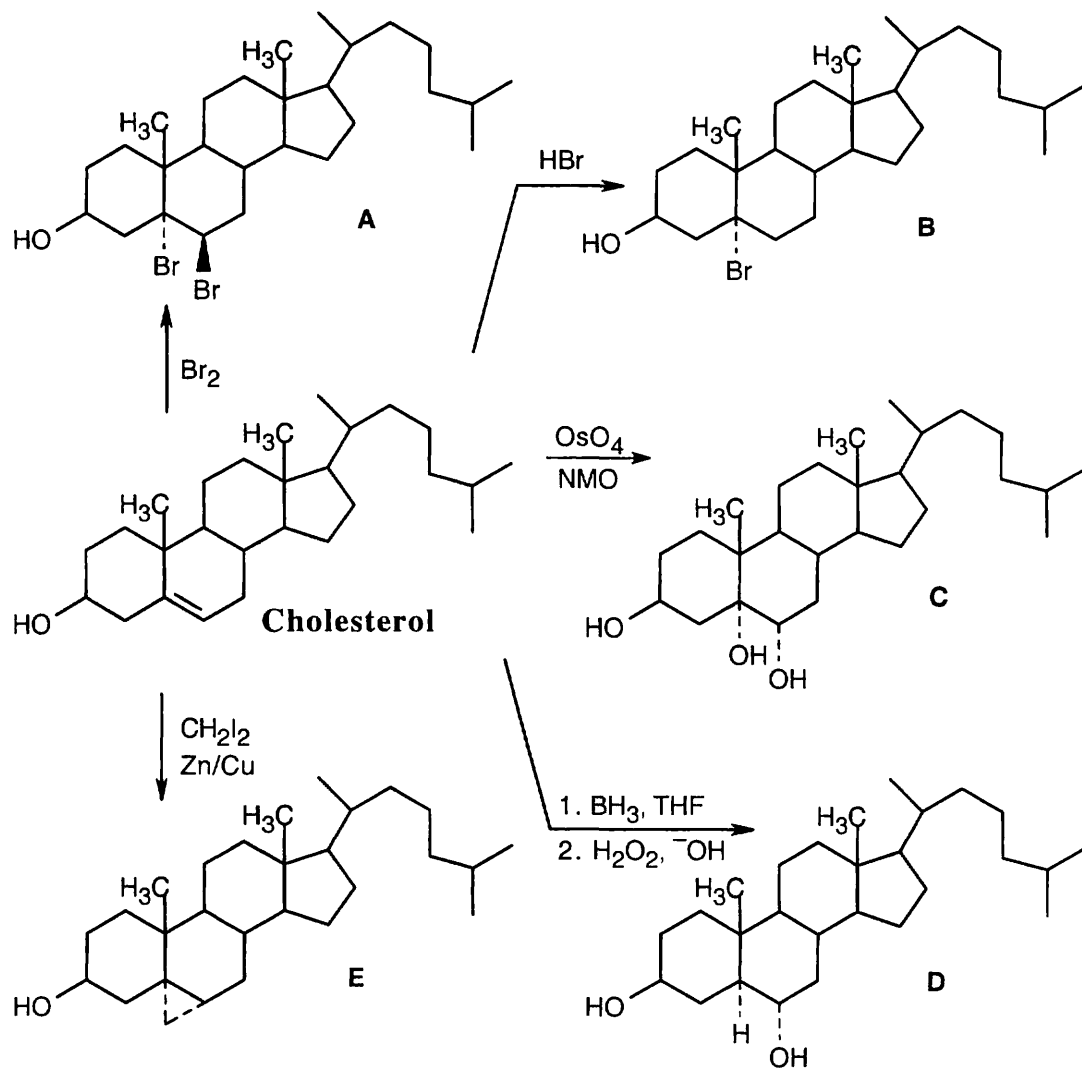
2-Pentene yields a mixture of alcohols.



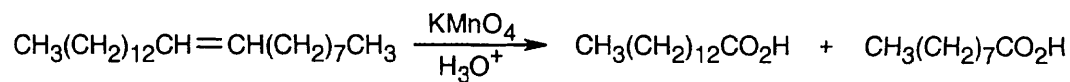
2,3-Dimethyl-2-butene yields the desired alcohol exclusively.

- (c) This alcohol can't be formed cleanly by a hydroboration reaction. The -H and -OH added to a double bond must be cis to each other.
 (d) The product shown is not a hydroboration product; hydroboration yields an alcohol in which -OH is bonded to the less substituted carbon.

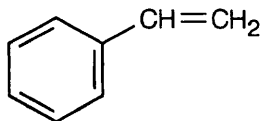
7.43



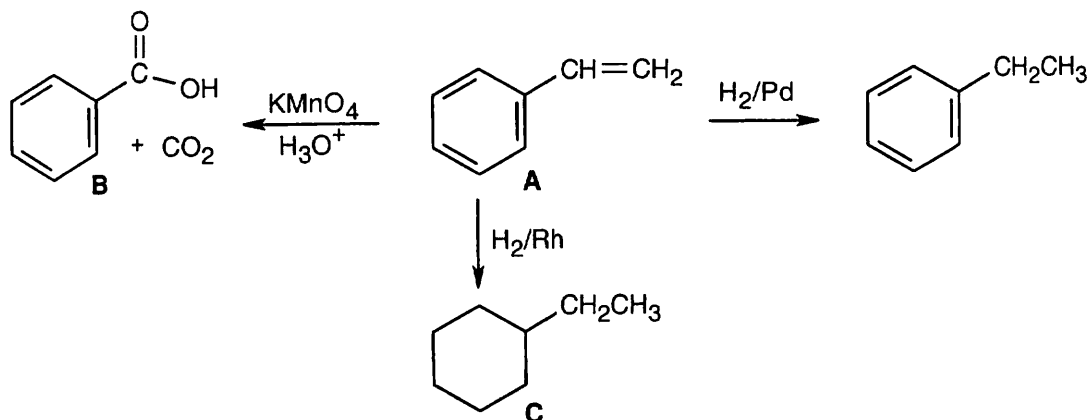
7.44



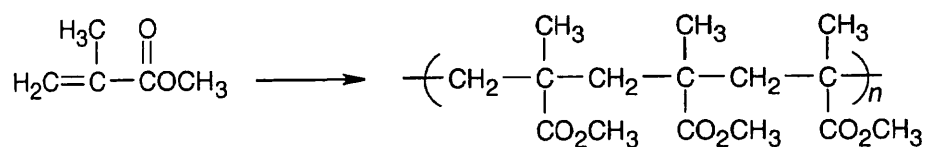
7.45 C_8H_8 has five double bonds and/or rings. One of these double bonds reacts with H_2/Pd . Stronger conditions cause the uptake of four equivalents of H_2 . C_8H_8 thus contains four double bonds, three of which are in an aromatic ring, and one $\text{C}=\text{C}$ double bond. A good guess for C_8H_8 at this point is:



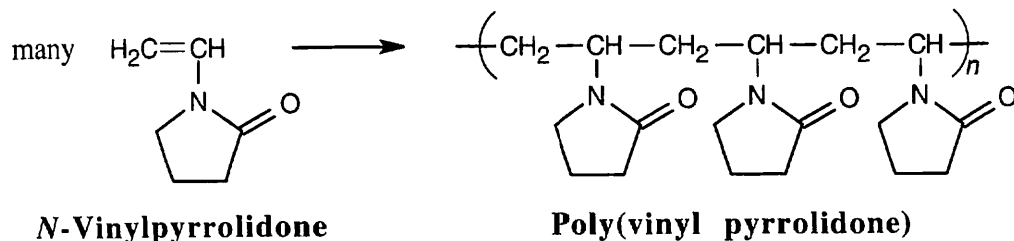
Reaction of a double bond with KMnO_4 yields cleavage products of the highest possible degree of oxidation. In this case, the products are $\text{CO}_2 + \text{C}_6\text{H}_5\text{CO}_2\text{H}$.



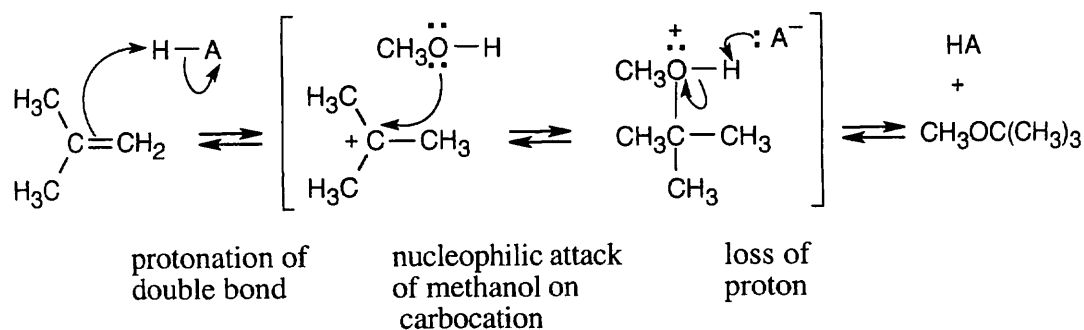
7.46



7.47

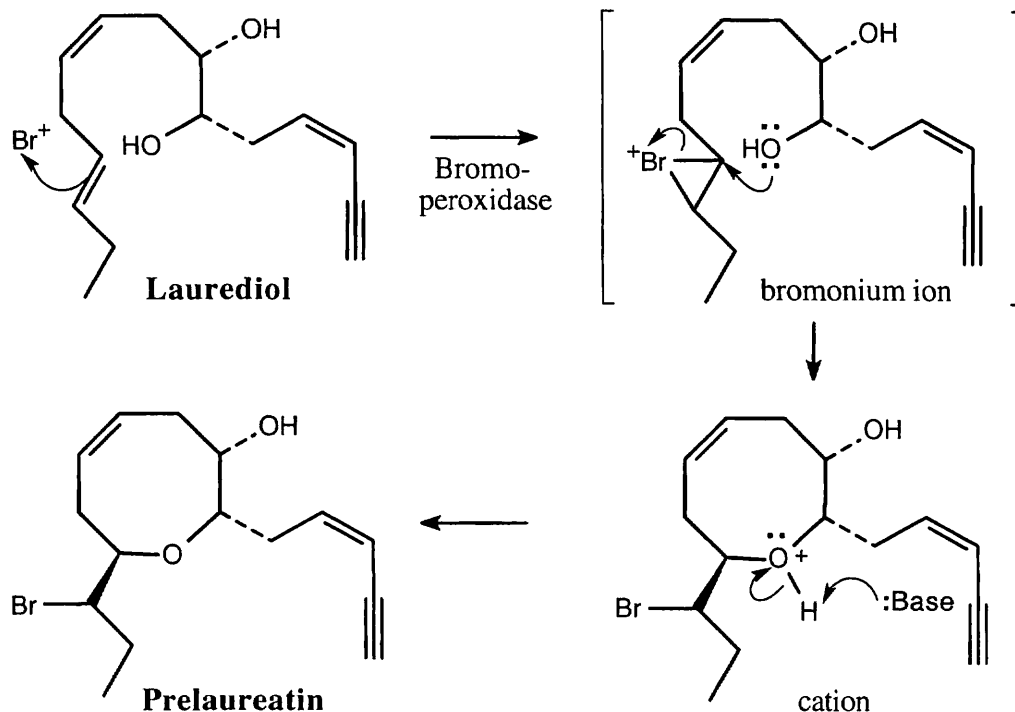


7.48



The above mechanism is the same as the mechanism shown in Section 7.4 with one exception: In this problem, methanol, rather than water, is the nucleophile, and an ether, rather than an alcohol, is the observed product.

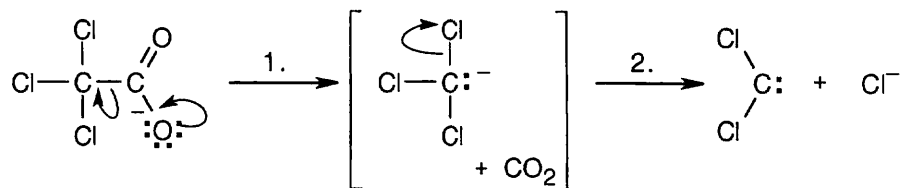
7.49



7.50 (a) Bromine dissolved in CH_2Cl_2 has a reddish-brown color. When an alkene such as cyclopentene is added to the bromine solution, the double bond reacts with bromine, and the color disappears. This test distinguishes cyclopentene from cyclopentane, which does not react with Br_2 . Alternatively, each compound can be treated with H_2/Pd . The alkene takes up H_2 , and the alkane is unreactive.

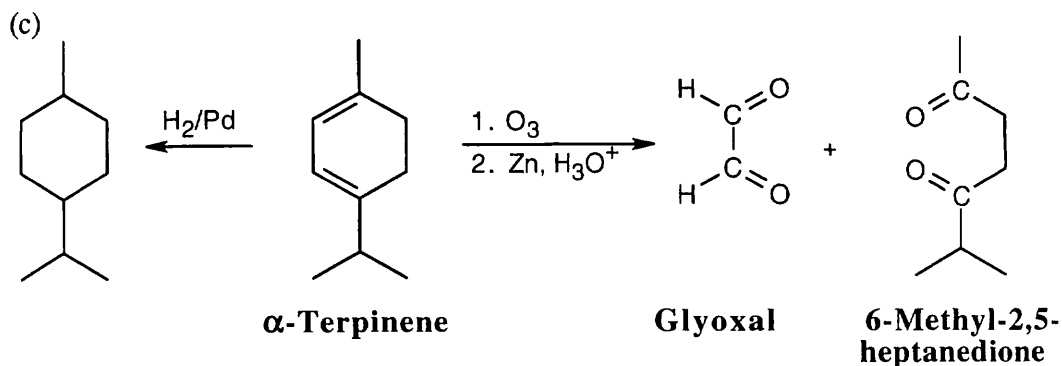
(b) An aromatic compound such as benzene is unreactive to the $\text{Br}_2/\text{CH}_2\text{Cl}_2$ reagent and can be distinguished from 2-hexene, which decolorizes $\text{Br}_2/\text{CH}_2\text{Cl}_2$. Also, an aromatic compound doesn't take up H_2 under reaction conditions used for hydrogenation of alkenes.

7.51



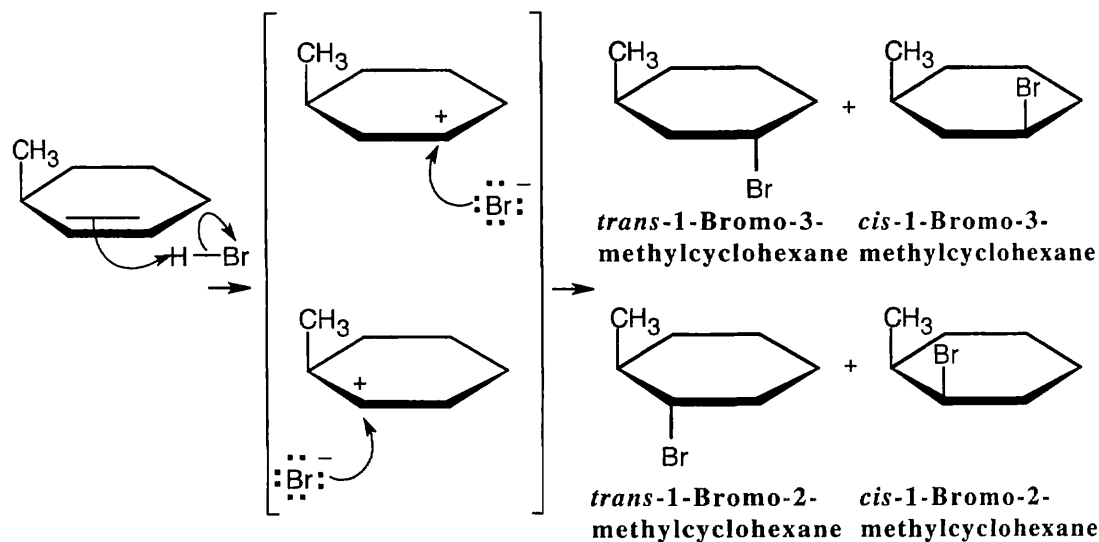
In step 1, carbon dioxide is lost from the trichloroacetate anion. In step 2, elimination of chloride anion produces dichlorocarbene. Step 2 is the same for both the above reaction and the base-induced elimination of HCl from chloroform, and both reactions proceed through the trichloromethanide anion intermediate.

- 7.52 (a) α -Terpinene, $C_{10}H_{16}$, has three degrees of unsaturation.
 (b) Hydrogenation removes only two degrees of saturation, producing a hydrocarbon $C_{10}H_{20}$, that has one ring. α -Terpinene thus has two double bonds and one ring.

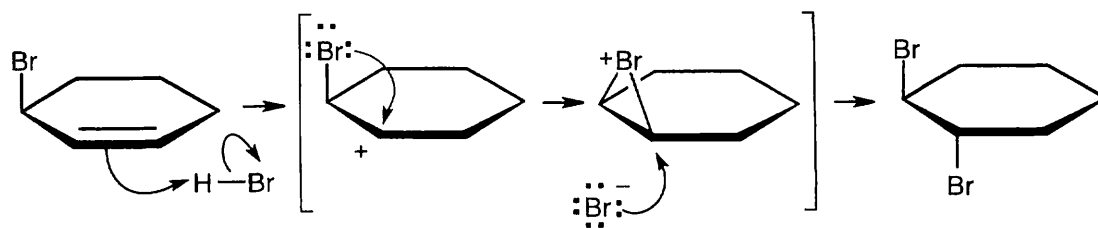


- 7.53 Make models of the cis and trans diols. Notice that it is much easier to form a five-membered cyclic periodate from the cis diol A than from the trans diol B. The cis periodate intermediate is of lower energy than the trans periodate intermediate because of the lack of strain in the cis periodate ring. Because any factor that lowers the energy of a transition state or intermediate also lowers ΔG^\ddagger and increases the rate of reaction, diol cleavage should proceed more slowly for trans diols than for cis diols.

7.54

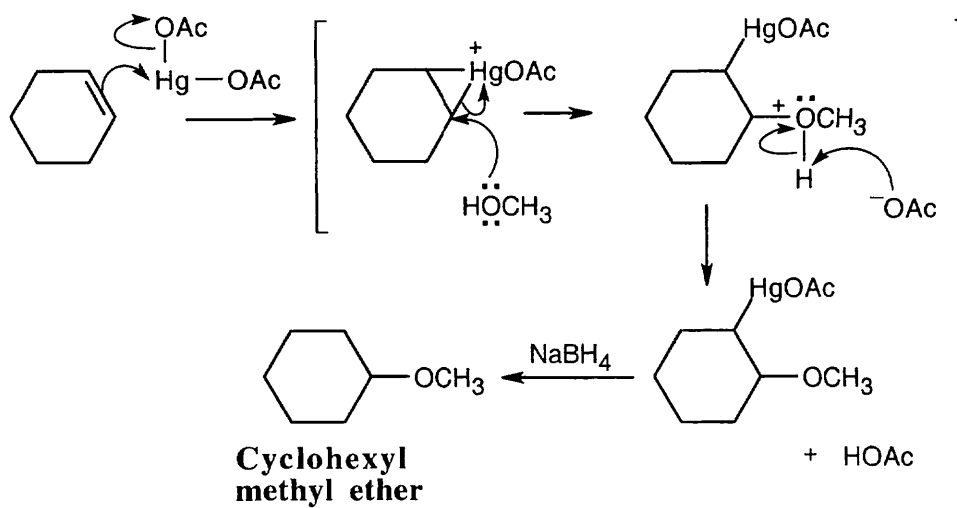


In the reaction of 3-methylcyclohexene with HBr, two intermediate carbocations of approximately equal stability are formed. Both react with bromide ion from top and bottom faces to give four different products.

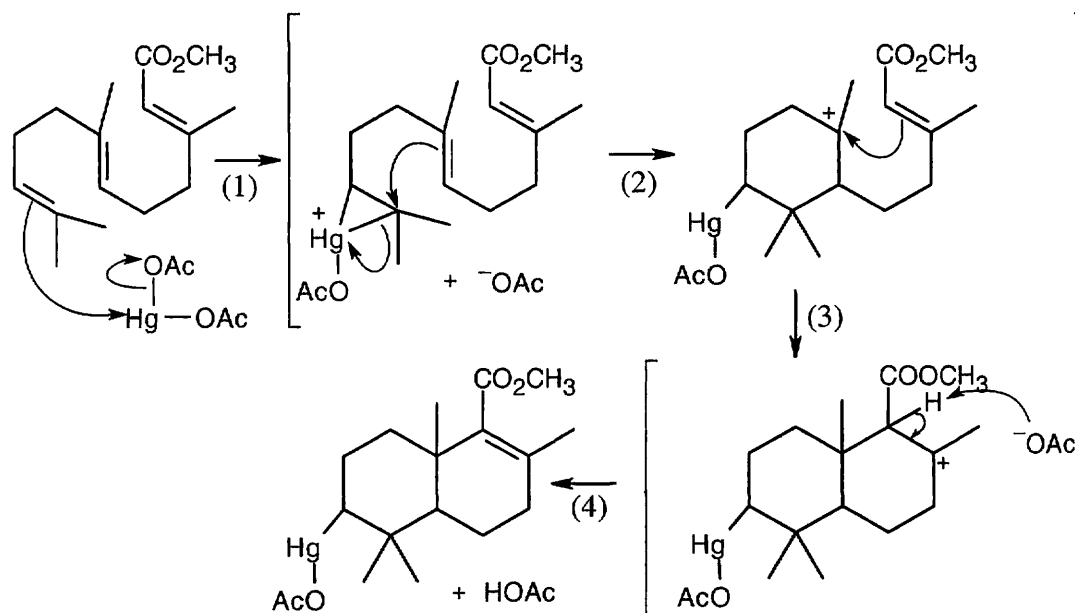


The most stable cation intermediate from protonation of 3-bromocyclohexene is a cyclic bromonium ion, which is attacked by Br^- from the opposite side to yield anti product.

7.55



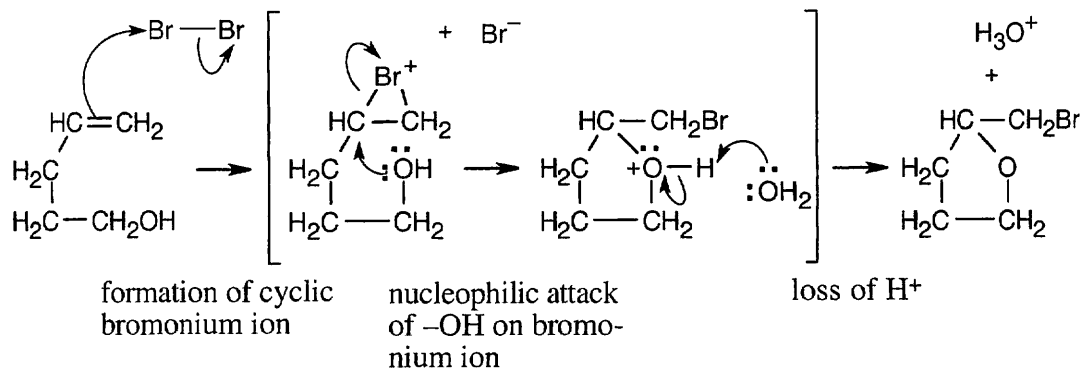
7.56



The reaction mechanism involves the following steps:

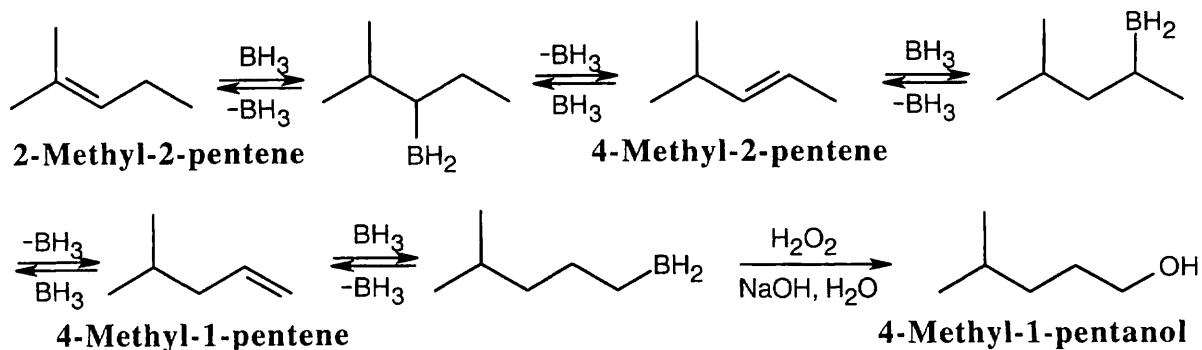
- (1) Addition of $\text{Hg}(\text{OAc})_2$ to one of the double bonds to form a cyclic mercurinium ion;
- (2) Reaction of a second double bond with the mercurinium ion to form a six-membered ring and a different carbocation;
- (3) A second cyclization forms the other ring and yields another carbocation;
- (4) Removal of $-\text{H}$ gives a double bond.

7.57

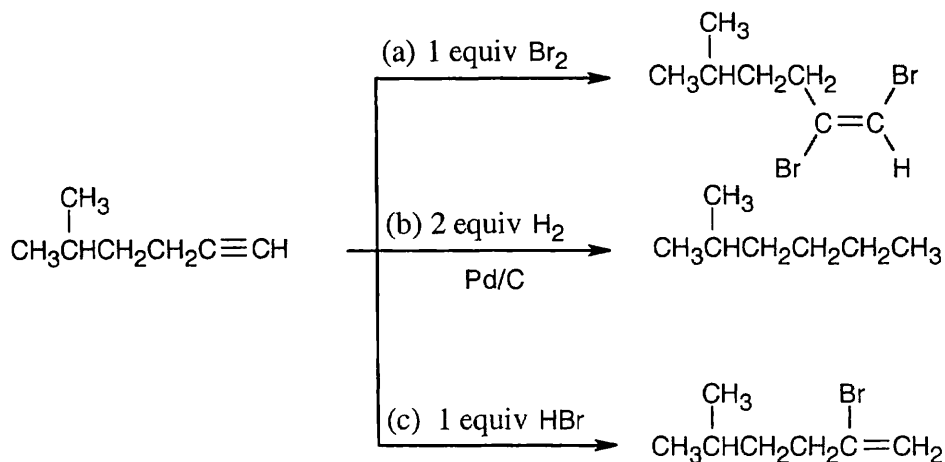


The above mechanism is the same as that for halohydrin formation, shown in Section 7.3. In this case, the nucleophile is the hydroxyl group of 4-penten-1-ol.

7.58 Hydroboration of 2-methyl-2-pentene at 160°C is reversible. The initial organoborane intermediate can eliminate BH_3 in either of two ways, yielding either 2-methyl-2-pentene or 4-methyl-2-pentene, which in turn can undergo reversible hydroboration to yield either 4-methyl-2-pentene or 4-methyl-1-pentene. The effect of these reversible reactions is to migrate the double bond along the carbon chain. A final hydroboration then yields the most stable (primary) organoborane, which is oxidized to form 4-methyl-1-pentanol.

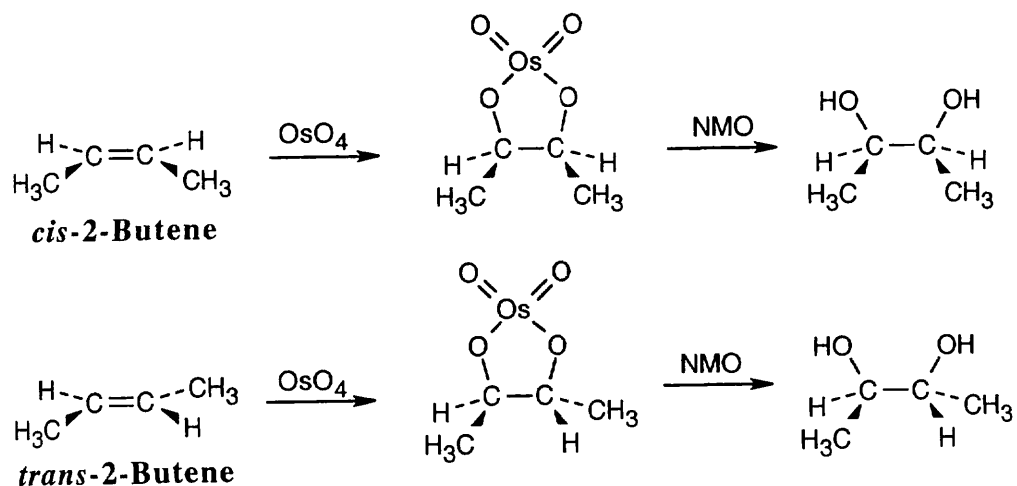


7.59



Addition of one equivalent of HX or X_2 to a triple bond occurs with Markovnikov regiochemistry to yield a product in which the two added atoms usually have a trans-relationship across the double bond.

7.60



Formation of the cyclic osmate, which occurs with syn stereochemistry, retains the *cis-trans* stereochemistry of the double bond because osmate formation is a single-step reaction. Oxidation of the osmate does not affect the stereochemistry of the carbon–oxygen bond, and the diol produced from *cis*-2-butene is a stereoisomer of the diol produced from *trans*-2-butene. We'll study this type of isomerism in Chapter 9.