

Chapter 6 – Alkenes: Structure and Reactivity

Chapter Outline


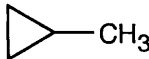
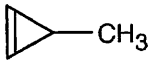

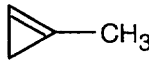

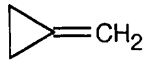

- I. Introduction to alkene chemistry (Sections 6.1 – 6.7).
 - A. Industrial preparation and use of alkenes (Section 6.1).
 1. Ethylene and propylene are the two most important organic chemicals produced industrially.
 2. Ethylene, propylene and butene are synthesized by thermal cracking.
 - a. Thermal cracking involves homolytic breaking of C–H and C–C bonds.
 - b. Thermal cracking reactions are dominated by entropy.
 - B. Calculating a molecule's degree of unsaturation (Section 6.2).
 1. The degree of unsaturation of a molecule describes the number of multiple bonds and/or rings a molecule has.
 2. To calculate degree of unsaturation of a compound, first determine the equivalent hydrocarbon formula of the compound.
 - a. Add the number of halogens to the number of hydrogens.
 - b. Subtract one hydrogen for every nitrogen.
 - c. Ignore the number of oxygens.
 3. Calculate the number of pairs of hydrogens that would be present in an alkane C_nH_{2n+2} that has the same number of carbons as the equivalent hydrocarbon of the compound of interest. The difference is the degree of unsaturation.
 - C. Naming alkenes (Section 6.3).
 1. Find the longest chain containing the double bond, and name it.
 2. Number the carbon atoms in the chain, beginning at the end nearer the double bond.
 3. Number the substituents and write the name.
 - a. Name the substituents alphabetically.
 - b. Indicate the position of the double bond.
 - c. Use the suffixes -diene, -triene, etc. if more than one double bond is present.
 4. A newer IUPAC naming system places the number locant of the double bond immediately before the -ene suffix (not used in this book).
 5. For cycloalkenes, the double bond is between C1 and C2, and substituents receive the lowest possible numbers.
 - D. Double bond geometry (Sections 6.4 – 6.5).
 1. Electronic structure of alkenes (Section 6.4).
 - a. Carbon atoms in a double bond are sp^2 -hybridized.
 - b. The two carbons in a double bond form one σ bond and one π bond.
 - c. Free rotation doesn't occur around double bonds.
 - d. 350 kJ/mol of energy is required to break a π bond.
 2. Cis–trans isomerism.
 - a. A disubstituted alkene can have substituents either on the same side of the double bond (cis) or on opposite sides (trans).
 - b. These isomers don't interconvert because free rotation about a double bond isn't possible.
 - c. Cis–trans isomerism doesn't occur if one carbon in the double bond is bonded to identical substituents.
 3. E,Z isomerism (Section 6.5).
 - a. The E,Z system is used to describe the arrangement of substituents around a double bond that can't be described by the cis–trans system.

- b. Sequence rules for *E,Z* isomers:
 - i. For each double bond carbon, rank its substituents by atomic number.
An atom with a high atomic number receives a higher priority than an atom with a lower atomic number.
 - ii. If a decision can't be reached, look at the second or third atom until a difference is found.
 - iii. Multiple-bonded atoms are equivalent to the same number of single-bonded atoms.
- E. Stability of alkenes (Section 6.6).
 - 1. Cis alkenes are less stable than trans alkenes because of steric strain between double bond substituents.
 - 2. Stabilities of alkenes can be determined experimentally by measuring:
 - a. Cis-trans equilibrium constants.
 - b. Heats of hydrogenation – the most useful method.
 - 3. The heat of hydrogenation of a cis isomer is a larger negative number than the heat of hydrogenation of a trans isomer.
This indicates that a cis isomer is of higher energy and is less stable than a trans isomer.
 - 4. Alkene double bonds become more stable with increasing substitution for two reasons:
 - a. Hyperconjugation – a stabilizing interaction between the antibonding π orbital and a filled C-H σ orbital on an adjacent substituent.
 - b. More substituted double bonds have more of the stronger sp^2 - sp^3 bonds.
- II. Electrophilic addition reactions (Sections 6.7 – 6.11).
 - A. Addition of H-X to alkenes (Sections 6.7 – 6.8).
 - 1. Mechanism of addition (Section 6.7).
 - a. The electrons of the nucleophilic π bond attack the electrophile H-X ($X = \text{Cl}, \text{Br}, \text{I}$).
 - b. Two electrons from the π bond form a new σ bond between -H and an alkene carbon.
 - c. The carbocation intermediate reacts with X^- to form a C-X bond.
 - 2. An energy diagram has two peaks separated by a valley (carbocation intermediate).
 - a. The reaction is exergonic.
 - b. The first step is slower than the second step.
 - (3. Organic reactions are often written in different ways to emphasize different points.)
 - 4. Orientation of addition: Markovnikov's rule (Section 6.8).
 - a. In the addition of HX to a double bond, H attaches to the carbon with fewer substituents, and X attaches to the carbon with more substituents.
 - b. If the carbons have the same number of substituents, a mixture of products results.
 - B. Carbocation structure and stability (Section 6.9).
 - 1. Carbocations are planar; the unoccupied p orbital extends above and below the plane.
 - 2. The stability of carbocations increases with increasing substitution.
 - a. Carbocation stability can be measured by studying gas-phase dissociation enthalpies.
 - b. Carbocations can be stabilized by inductive effects of neighboring alkyl groups.
 - c. Carbocation can be stabilized by hyperconjugation: The more alkyl groups on the carbocation, the more opportunities there are for hyperconjugation.

- C. The Hammond postulate (Section 6.10).
1. The transition state for an endergonic reaction step resembles the product of that step.
 2. The transition state for an exergonic reaction step resembles the reactant for that step.
 3. In an electrophilic addition reaction, the transition state for alkene protonation resembles the carbocation intermediate.
 4. More stable carbocations form faster because their transition states are also stabilized.
- D. Carbocation rearrangements (Section 6.11).
1. In some electrophilic addition reactions, products from carbocation rearrangements are formed.
 2. The appearance of these products supports the two-step electrophilic addition mechanism, in which an intermediate carbocation is formed.
 3. Intermediate carbocations can rearrange to more stable carbocations by either a hydride shift or by an alkyl shift.
 4. In both cases a group moves to an adjacent positively charged carbon, taking its bonding electron pair with it.

Solutions to Problems

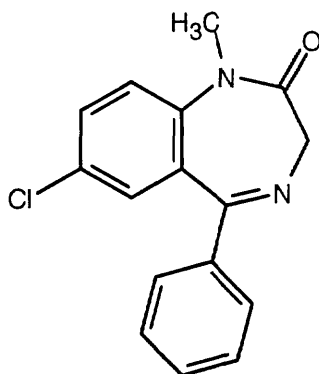
- 6.1 Strategy:** Because two hydrogens must be removed from a saturated compound to introduce an unsaturation, a compound's degree of unsaturation refers to the number of pairs of hydrogens by which its formula differs from that of the corresponding saturated compound. For example, a saturated alkane with four carbons has the formula C_4H_{10} . The compound in (a), C_4H_8 , which has two fewer (or one pair fewer) hydrogens, may have a double bond or a ring. C_8H_{14} thus has a degree of unsaturation of 1.

<i>Compound</i>	<i>Degree of Unsaturation</i>	<i>Structures</i>		
(a) C_4H_8	1	$CH_3CH=CHCH_3$ 	$CH_3CH_2CH=CH_2$ $(CH_3)_2C=CH_2$ 	
(b) C_4H_6	2	$CH_2=CHCH=CH_2$ $CH_3CH_2C\equiv CH$ 	$CH_3CH=C=CH_2$  	$CH_3C\equiv CCH_3$  
(c) C_3H_4	2	$H_2C=C=CH_2$	$CH_3C\equiv CH$	

- 6.2 Strategy:** Unlike the hydrocarbons in the previous problems, the compounds in this problem contain additional elements. Review the rules for these elements.

Solution:

- (a) Subtract one hydrogen for each nitrogen present to find the formula of the equivalent hydrocarbon – C_6H_4 . Compared to the alkane C_6H_{14} , the compound of formula C_6H_4 has 10 fewer hydrogens, or 5 fewer hydrogen pairs, and has a degree of unsaturation of 5.
- (b) $C_6H_5NO_2$ also has 5 degrees of unsaturation because oxygen doesn't affect the equivalent hydrocarbon formula of a compound.
- (c) A halogen atom is equivalent to a hydrogen atom in calculating the equivalent hydrocarbon formula. For $C_8H_9Cl_3$, the equivalent hydrocarbon formula is C_8H_{12} , and the degree of unsaturation is 3.
- (d) $C_9H_{16}Br_2$ – one degree of unsaturation.
- (e) $C_{10}H_{12}N_2O_3$ – 6 degrees of unsaturation.
- (f) $C_{20}H_{32}ClN$ – 5 degrees of unsaturation.
- 6.3** A C_{16} hydrocarbon with 11 degrees of unsaturation (three rings and eight double bonds) has a formula $C_{16}H_{34} - H_{22} = C_{16}H_{12}$. Adding two hydrogens (because of the two nitrogens) and subtracting one hydrogen (because of the chlorine), gives the formula $C_{16}H_{13}ClN_2O$ for Diazepam.

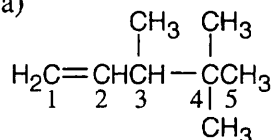


Diazepam

- 6.4 Strategy:** (1) Find the longest chain containing the double bond and name it. In (a), the longest chain is a pentene.
- (2) Identify the substituents. There are three methyl groups in (a).
- (3) Number the substituents, remembering that the double bond receives the lowest possible number. The methyl groups are attached to C3 and C4 (two methyl groups).
- (4) Name the compound, remembering to use the prefix "tri-" before "methyl" and remembering to use a number to signify the location of the double bond. The name of the compound in (a) is 3,4,4-trimethyl-1-pentene.

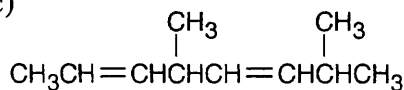
Solution:

(a)



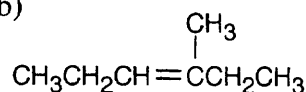
3,4,4-Trimethyl-1-pentene

(c)



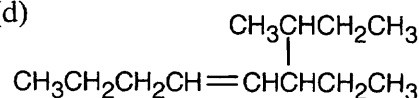
4,7-Dimethyl-2,5-octadiene

(b)



3-Methyl-3-hexene

(d)

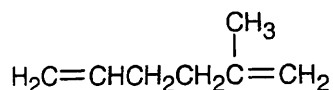


6-Ethyl-7-methyl-4-nonene

6.5 Strategy: It's much easier to draw a structure from a given name than it is to name a structure. First, draw the carbon chain, placing the double bond or bonds in the designated locations. Then attach the cited groups in the proper positions.

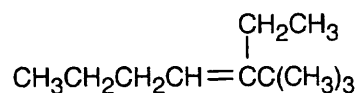
Solution:

(a)



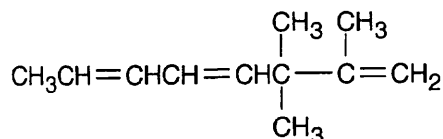
2-Methyl-1,5-hexadiene

(b)



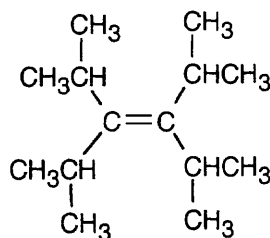
3-Ethyl-2,2-dimethyl-3-heptene

(c)



2,3,3-Trimethyl-1,4,6-octatriene

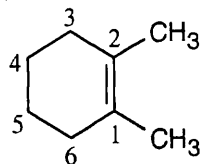
(d)



3,4-Diisopropyl-2,5-dimethyl-3-hexene

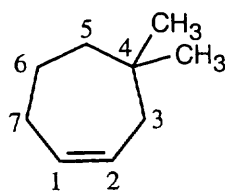
6.6

(a)



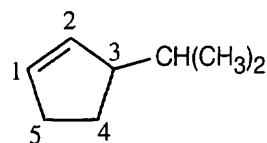
1,2-Dimethyl-cyclohexene

(b)



4,4-Dimethyl-cycloheptene

(c)



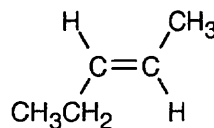
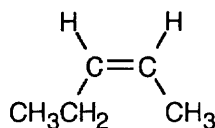
3-Isopropyl-cyclopentene

6.7 Compounds (c), (e), and (f) can exist as cis-trans isomers.

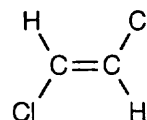
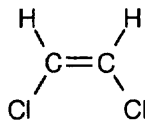
cis

trans

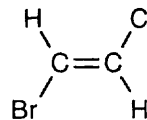
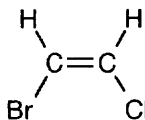
(c) $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$



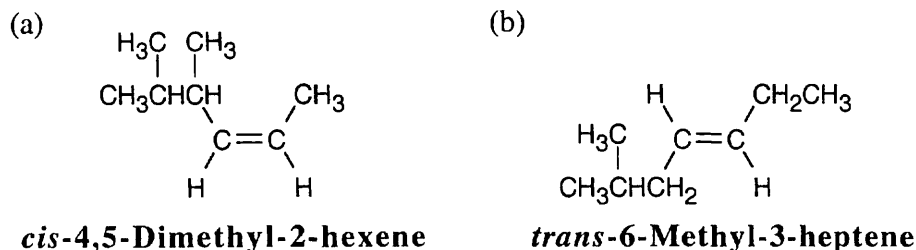
(e) $\text{ClCH}=\text{ClCH}$



(f) $\text{BrCH}=\text{CHCl}$



6.8



6.9 Strategy: Review the sequence rules presented in Section 6.5. A summary:

Rule 1: An atom with a higher atomic number has priority over an atom with a lower atomic number.

Rule 2: If a decision can't be reached by using Rule 1, look at the second, third, or fourth atom away from the double-bond carbon until a decision can be made.

Rule 3: Multiple-bonded atoms are equivalent to the same number of single-bonded atoms.

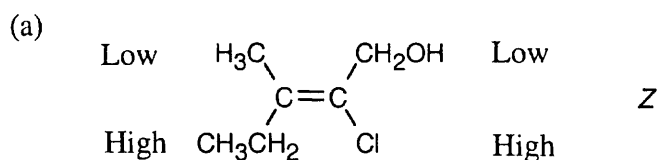
Solution:

High	Low	Rule	High	Low	Rule
(a) -Br	-H	1	(b) -Br	-Cl	1
(c) -CH ₂ CH ₃	-CH ₃	2	(d) -OH	-NH ₂	1
(e) -CH ₂ OH	-CH ₃	2	(f) -CH=O	-CH ₂ OH	3

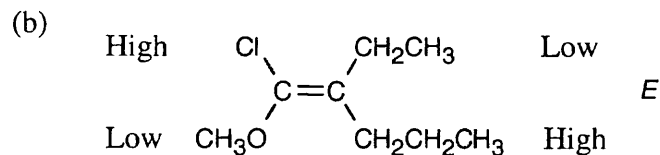
6.10 Highest priority \longrightarrow Lowest Priority

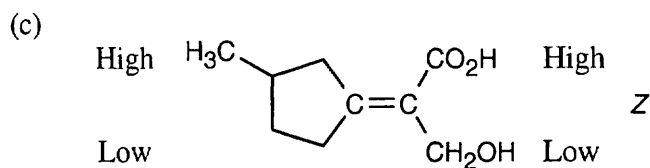
- (a) -Cl, -OH, -CH₃, -H
 (b) -CH₂OH, -CH=CH₂, -CH₂CH₃, -CH₃
 (c) -CO₂H, -CH₂OH, -C \equiv N, -CH₂NH₂
 (d) -CH₂OCH₃, -C \equiv N, -C \equiv CH, -CH₂CH₃

6.11

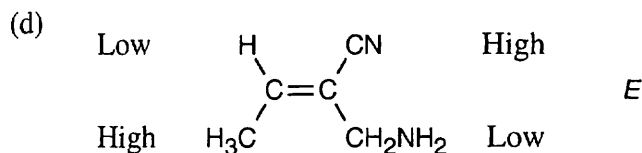


First, consider the substituents on the right side of the double bond. -Cl ranks higher than -CH₂OH by Rule 1 of the Cahn-Ingold-Prelog rules. On the left side of the double bond, -CH₂CH₃ ranks higher than -CH₃.

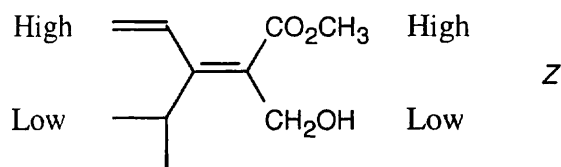




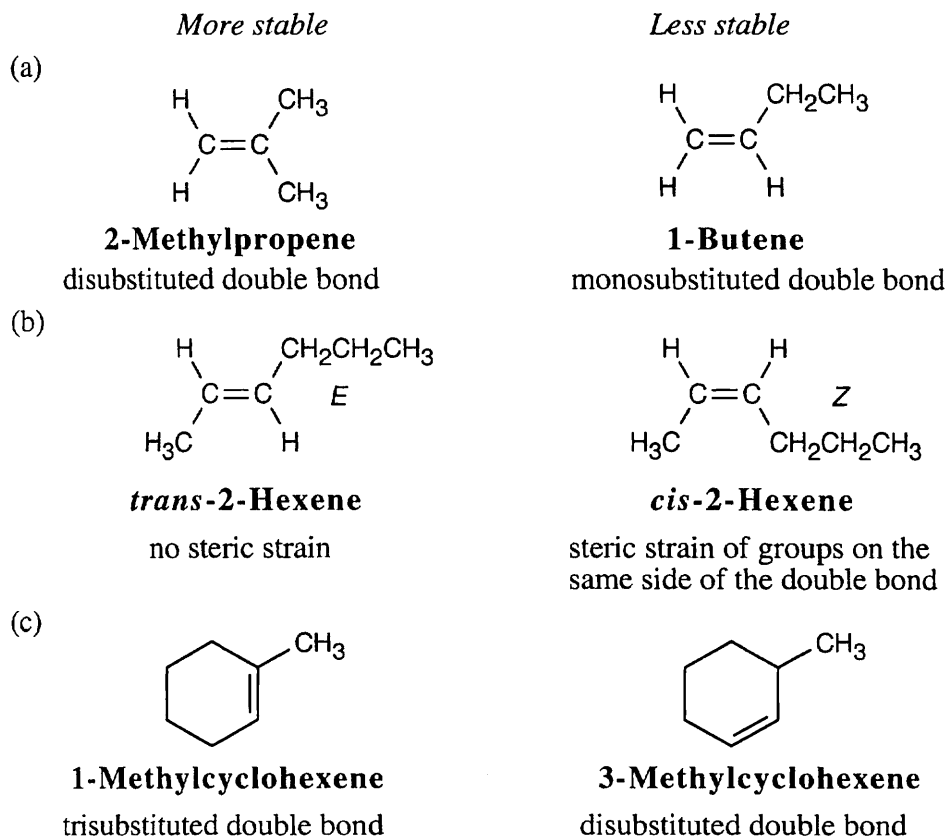
Notice that the upper substituent on the left side of the double bond is of higher priority because of the methyl group attached to the ring.



6.12

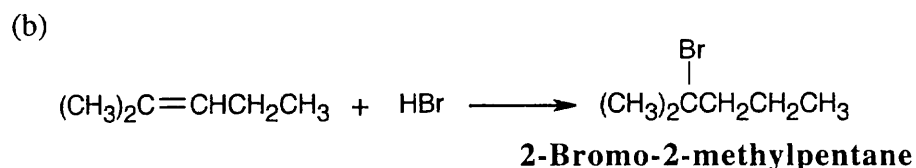
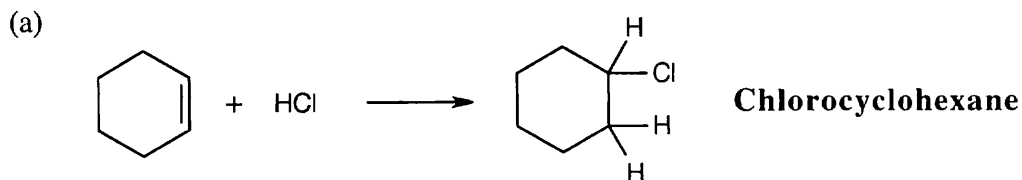


6.13

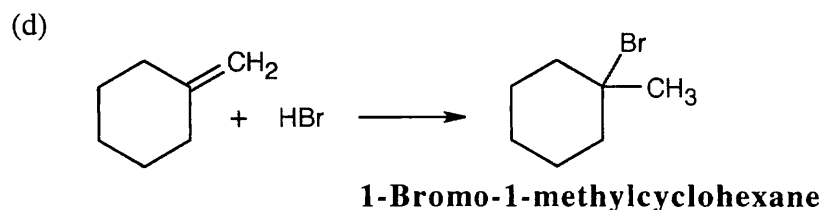
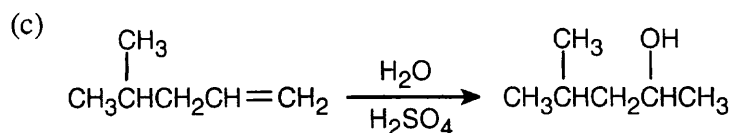


6.14 Strategy: All of these reactions are electrophilic additions of HX to an alkene. Use Markovnikov's rule to predict orientation.

Solution:

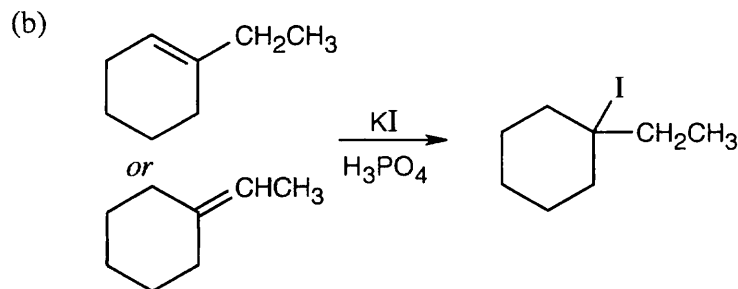
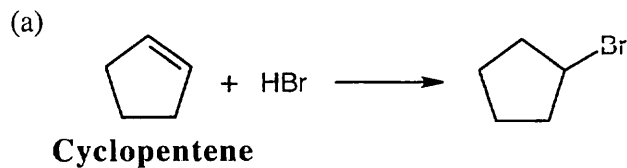


In accordance with Markovnikov's rule, H forms a bond to the carbon with fewer substituents, and Br forms a bond to the carbon with more substituents.

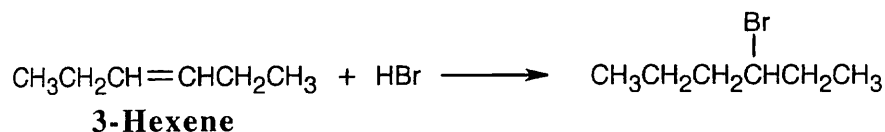


6.15 Strategy: Think backward in choosing the alkene starting material for synthesis of the desired haloalkanes. Remember that halogen is bonded to one end of the double bond and that more than one starting material can give rise to the desired product.

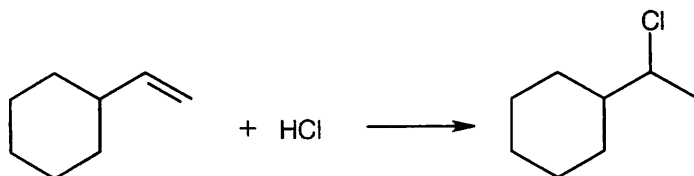
Solution:



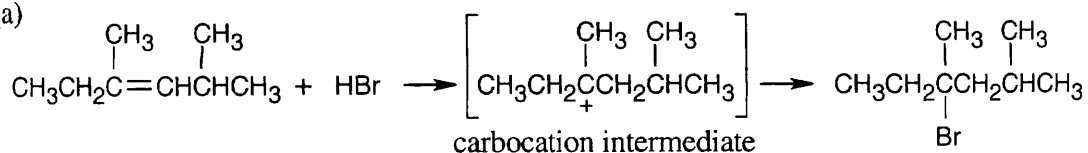
(c)



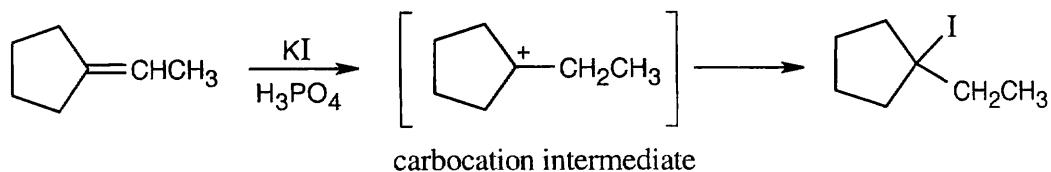
(d)

**6.16** The more stable carbocation is formed

(a)

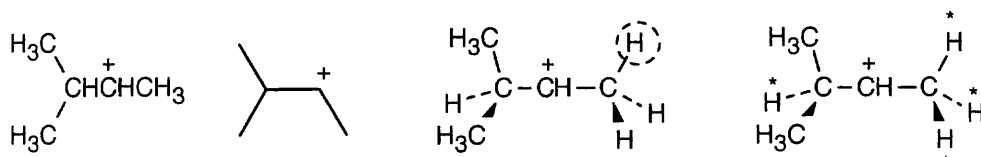


(b)

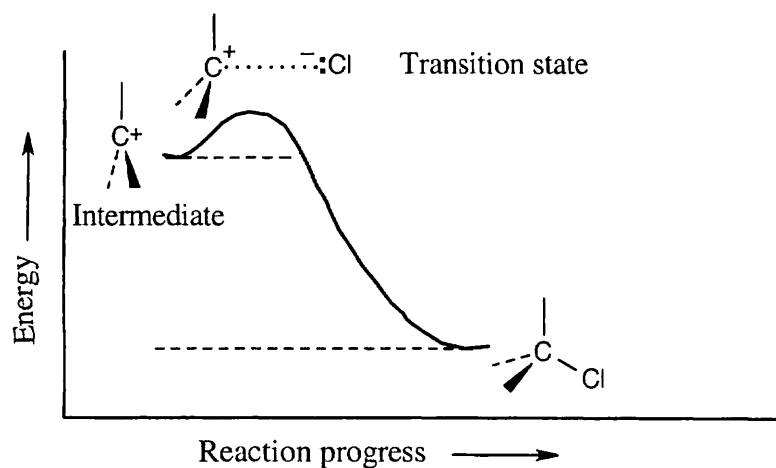


6.17 Two representations of the secondary carbocation are shown on the left below. This secondary carbocation can experience hyperconjugative overlap with two hydrogens under normal circumstances. However, in the alignment shown in the drawing, only one hydrogen (circled) is in the correct position for hyperconjugative overlap with the carbocation carbon.

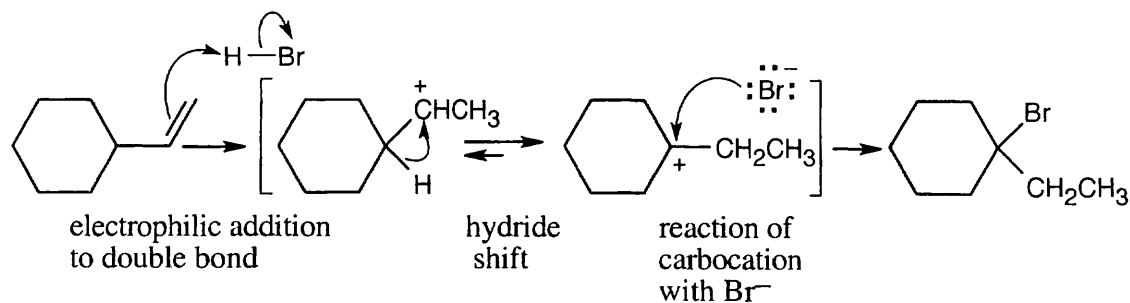
Because there is rotation about the carbon-carbon bonds, all of the hydrogens starred in the representation on the far right can be involved in hyperconjugation at some time.



6.18 The second step in the electrophilic addition of HCl to an alkene is exergonic. According to the Hammond postulate, the transition state should resemble the carbocation intermediate.



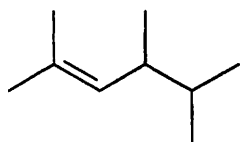
6.19



Visualizing Chemistry

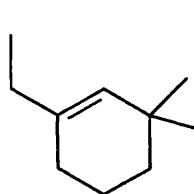
6.20

(a)



2,4,5-Trimethyl-2-hexene

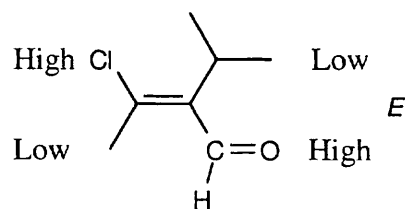
(b)



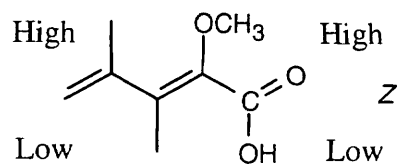
1-Ethyl-3,3-dimethylcyclohexene

6.21

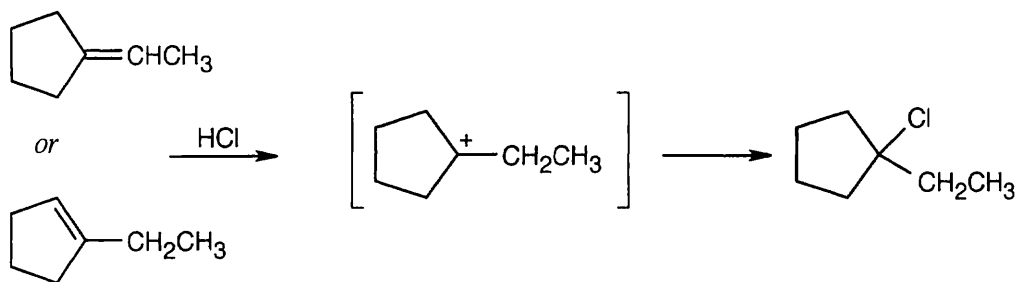
(a)



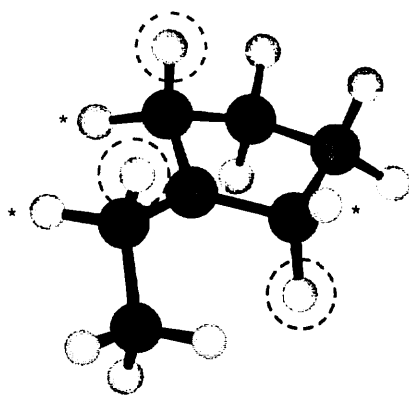
(b)



6.22



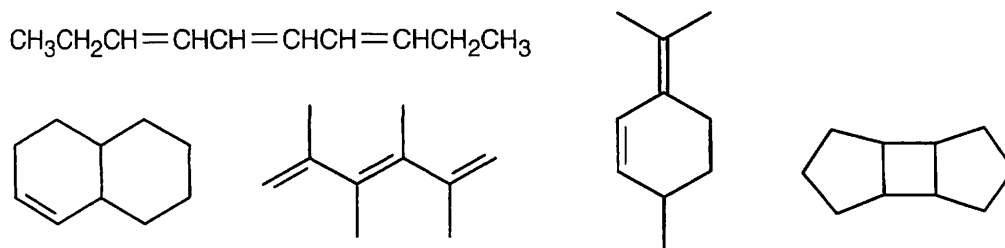
Either of the two compounds shown can form the illustrated tertiary carbocation when they react with HCl. In the conformation shown, the three circled hydrogens are aligned for maximum overlap with the vacant *p* orbital. Because of conformational mobility, the three starred hydrogens are also able to be involved in hyperconjugation.



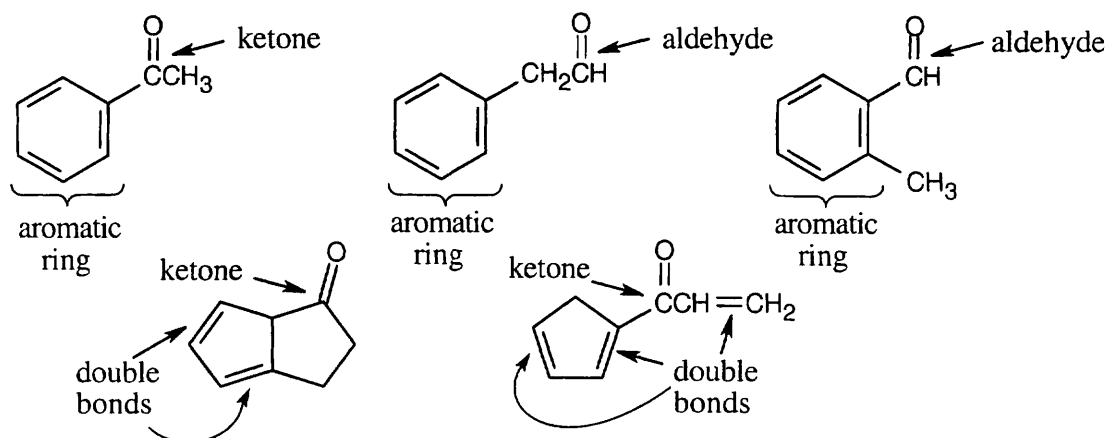
Additional Problems

- 6.23** The purpose of this problem is to give you experience in calculating the number of double bonds and/or rings in a formula. Additionally, you will learn to draw structures containing various functional groups. Remember that any formula that satisfies the rules of valency is acceptable. Try to identify functional groups in the structures that you draw.

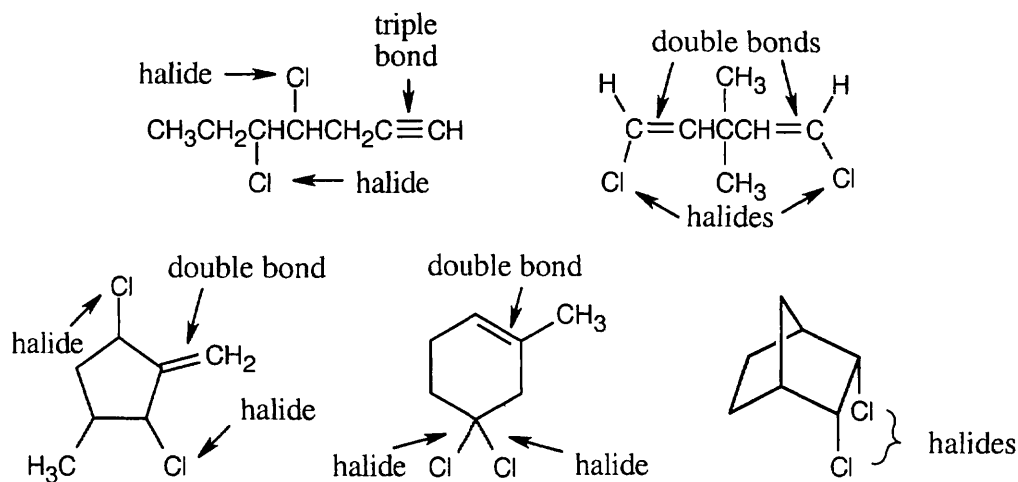
(a) C₁₀H₁₆ – 3 degrees of unsaturation. Examples:



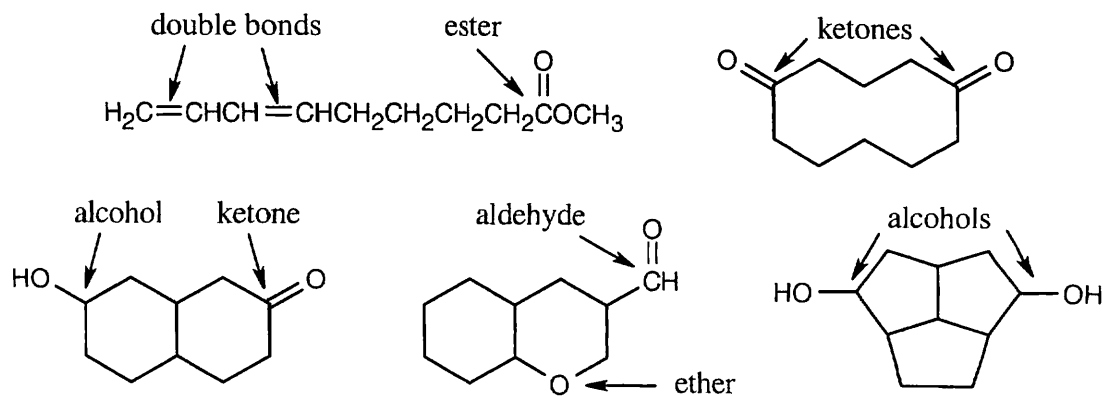
(b) C_8H_8O . The equivalent hydrocarbon is C_8H_8 , which has 5 degrees of unsaturation.

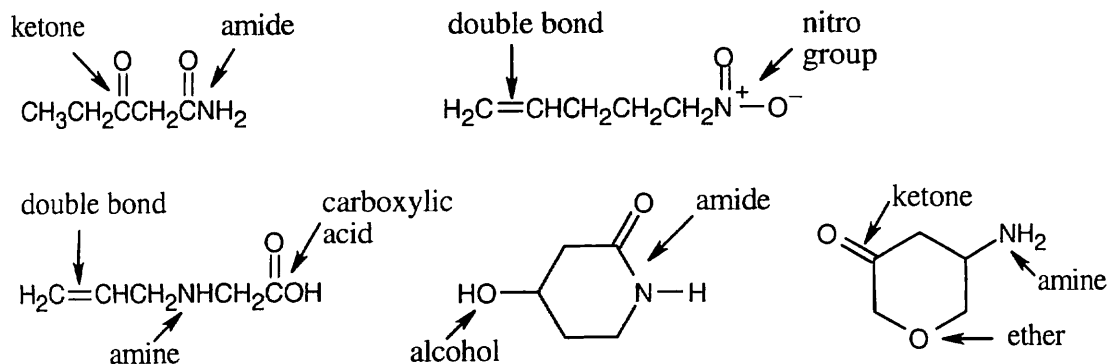
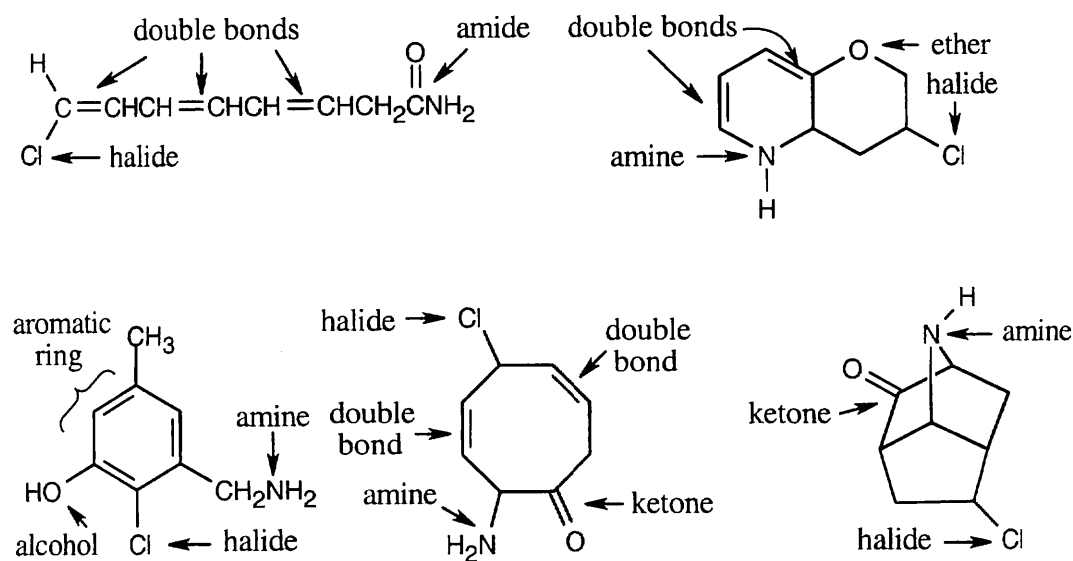


(c) $C_7H_{10}Cl_2$ has C_7H_{12} as its equivalent hydrocarbon formula. $C_7H_{10}Cl_2$ has two degrees of unsaturation.



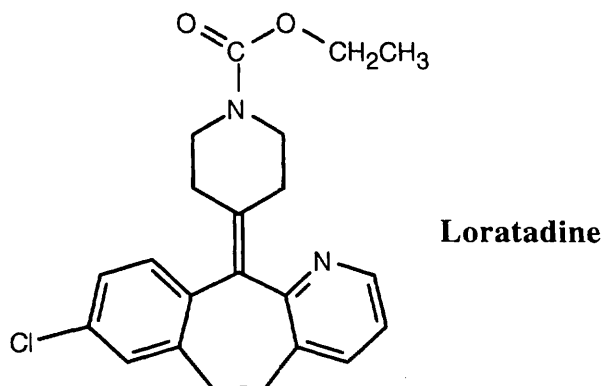
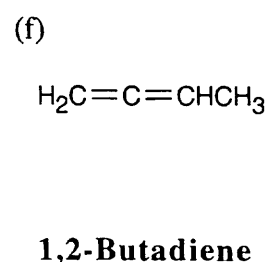
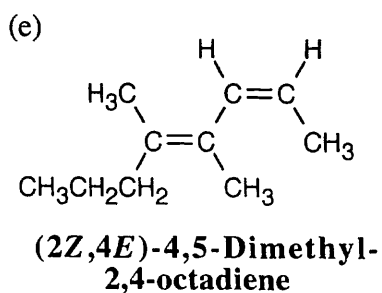
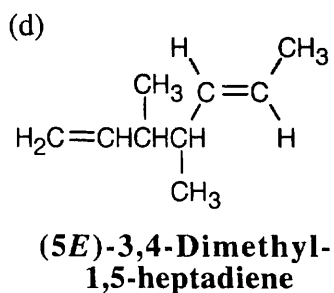
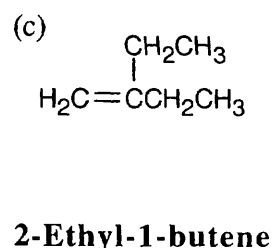
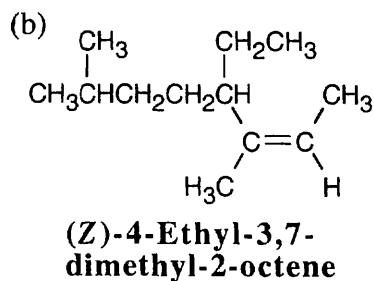
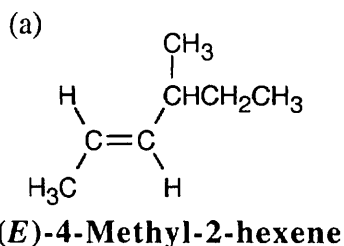
(d) $C_{10}H_{16}O_2$ – 3 degrees of unsaturation.



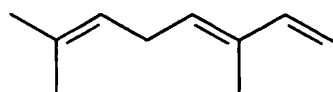
(e) $C_5H_9NO_2$ – 2 degrees of unsaturation.(f) $C_8H_{10}ClNO$ – 4 degrees of unsaturation.

6.24	Compound	Equivalent hydrocarbon formula	Degree of unsaturation	Complete formula
(a)	$C_8H_7O_2$	C_8H_{18}	3	$C_8H_{12}O_2$
(b)	C_7H_7N	C_7H_{16}	2	$C_7H_{13}N$
(c)	C_9H_7NO	C_9H_{20}	4	$C_9H_{13}NO$

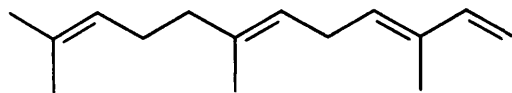
- 6.25** Solve this problem in the same way as we solved problems 6.3 and 6.24. A C_{22} hydrocarbon with 12 degrees of unsaturation (four rings and eight double bonds) has a formula $C_{22}H_{46} - H_{24} = C_{22}H_{22}$. Adding two hydrogens (because of the two nitrogens) and subtracting one hydrogen (because of the chlorine), gives the formula $C_{22}H_{23}ClN_2O_2$ for loratadine.

**6.26**

- 6.27** Because the longest carbon chain contains 8 carbons and 3 double bonds, ocimene is an *octatriene*. Start numbering at the end that will give the lower number to the first double bond (1,3,6 is lower than 2,5,7). Number the methyl substituents and, finally, name the compound.

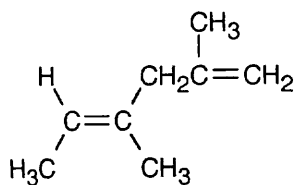
**(3E)-3,7-Dimethyl-1,3,6-octatriene**

6.28

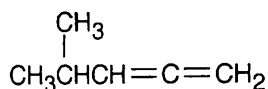
**(3E,6E)-3,7,11-Trimethyl-1,3,6,10-dodecatetraene**

6.29

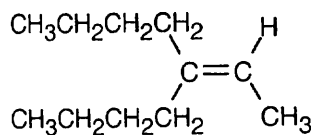
(a)

**(4E)-2,4-Dimethyl-1,4-hexadiene**

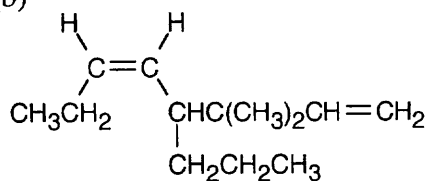
(c)

**4-Methyl-1,2-pentadiene**

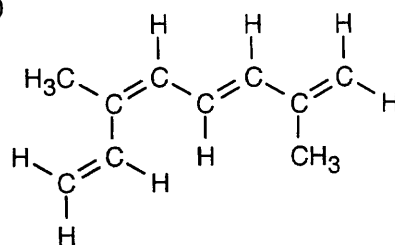
(e)

**3-Butyl-2-heptene**

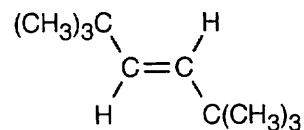
(b)

**cis-3,3-Dimethyl-4-propyl-1,5-octadiene**

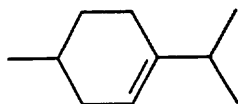
(d)

**(3E,5Z)-2,6-Dimethyl-1,3,5,7-octatetraene**

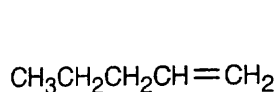
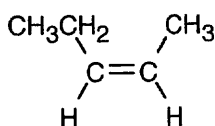
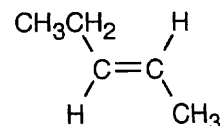
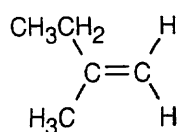
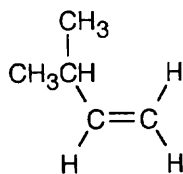
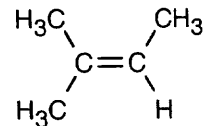
(f)

**trans-2,2,5,5-Tetramethyl-3-hexene**

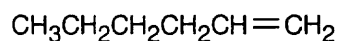
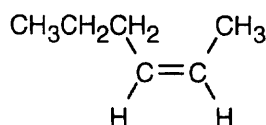
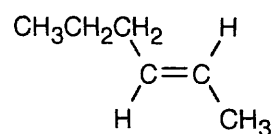
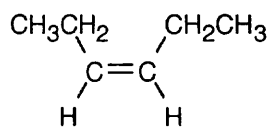
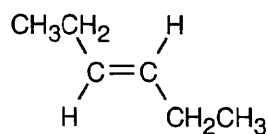
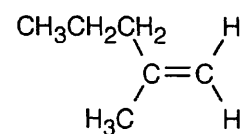
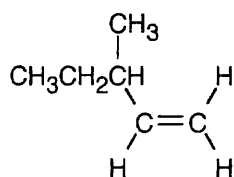
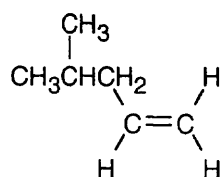
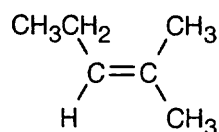
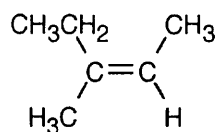
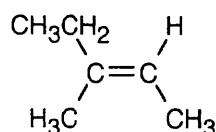
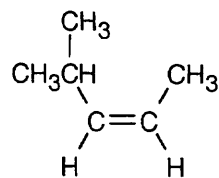
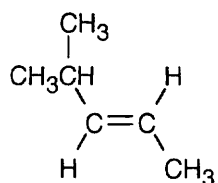
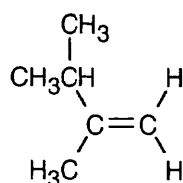
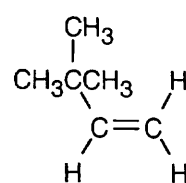
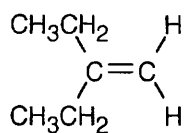
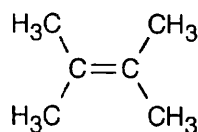
6.30

**Menthene**

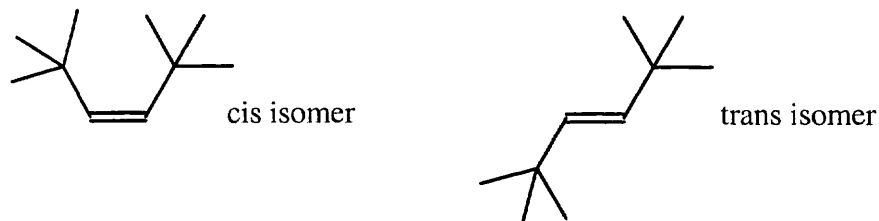
6.31

**1-Pentene****(Z)-2-Pentene****(E)-2-Pentene****2-Methyl-1-butene****3-Methyl-1-butene****2-Methyl-2-butene**

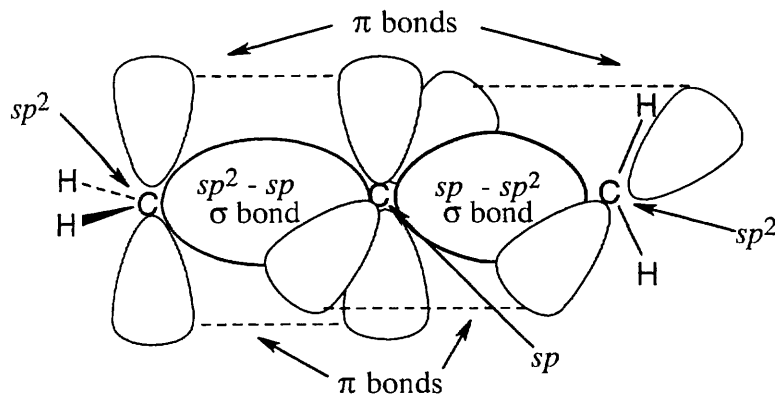
6.32

**1-Hexene****(Z)-2-Hexene****(E)-2-Hexene****(Z)-3-Hexene****(E)-3-Hexene****2-Methyl-1-pentene****3-Methyl-1-pentene****4-Methyl-1-pentene****2-Methyl-2-pentene****(Z)-3-Methyl-2-pentene****(E)-3-Methyl-2-pentene****(Z)-4-Methyl-2-pentene****(E)-4-Methyl-2-pentene****2,3-Dimethyl-1-butene****3,3-Dimethyl-1-butene****2-Ethyl-1-butene****2,3-Dimethyl-2-butene**

- 6.33** As expected, the two trans compounds are more stable than their cis counterparts. The cis–trans difference is much more pronounced for the tetramethyl compound, however. Build a model of *cis*-2,2,5,5-tetramethyl-3-hexene and notice the extreme crowding of the methyl groups. Steric strain makes the cis isomer much less stable than the trans isomer and causes *cis* $\Delta H^\circ_{\text{hydrog}}$ to have a much larger negative value than *trans* $\Delta H^\circ_{\text{hydrog}}$ for the hexene isomers.

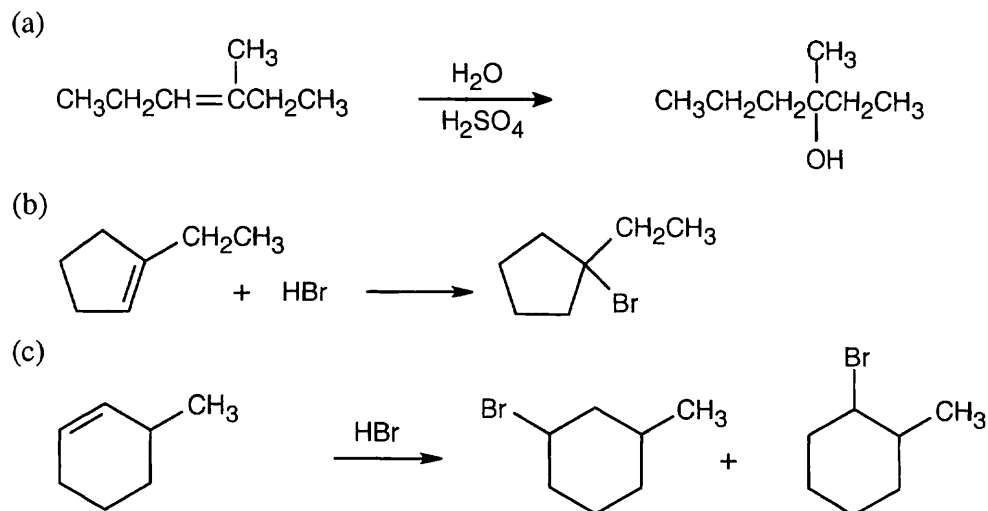


- 6.34** A model of cyclohexene shows that a six-membered ring is too small to contain a trans double bond without causing severe strain to the ring. A ten-membered ring is flexible enough to accommodate either a cis or a trans double bond, although the cis isomer has less strain than the trans isomer.
- 6.35** Build models of the two cyclooctenes and notice the large amount of torsional strain in *trans*-cyclooctene relative to *cis*-cyclooctene. This torsional strain, in addition to angle strain, causes the trans isomer to be of higher energy and to have a $\Delta H^\circ_{\text{hydrog}}$ larger than the $\Delta H^\circ_{\text{hydrog}}$ of the cis isomer.
- 6.36** Models show that the difference in strain between the two cyclononene isomers is smaller than the difference between the two cyclooctene isomers. This reduced strain is due to a combination of less angle strain and more puckering to relieve torsional strain and is reflected in the fact that the values of $\Delta H^\circ_{\text{hydrog}}$ for the two cyclononene isomers are relatively close. Nevertheless, the trans isomer is still more strained than the cis isomer.
- 6.37** The central carbon of allene forms two σ bonds and two π bonds. The central carbon is sp -hybridized, and the carbon–carbon bond angle is 180° , indicating linear geometry for the carbons of allene. The terminal $=\text{CH}_2$ units are oriented 90° with respect to each other.

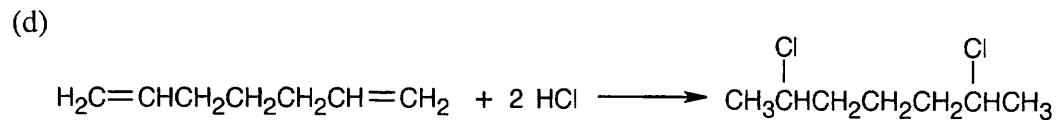


- 6.38** The heat of hydrogenation for a typical diene is $2 \times (\Delta H^\circ_{\text{hydrog}} \text{ of an alkene}) = -252 \text{ kJ/mol}$. Thus, allene, with $\Delta H^\circ_{\text{hydrog}} = -295 \text{ kJ/mol}$ is 43 kJ/mol higher in energy than a typical diene and is less stable.

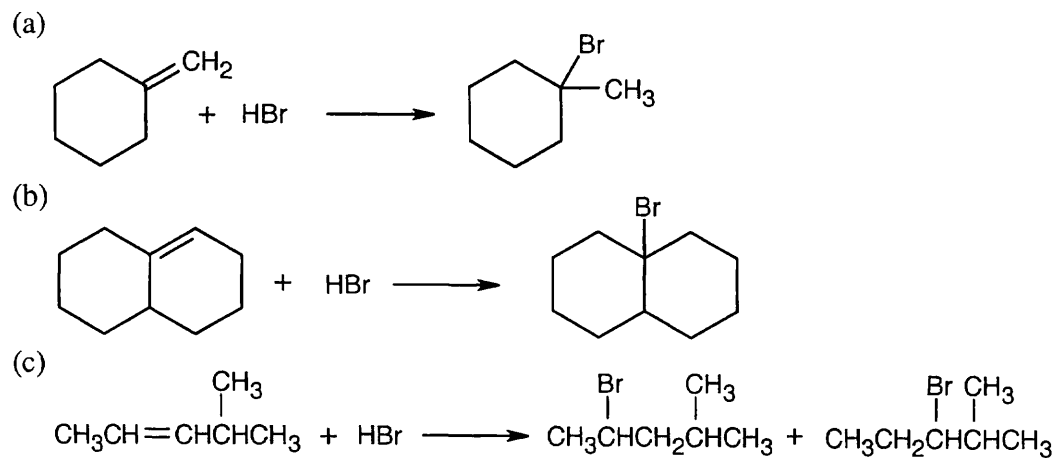
6.39



Two products are formed because the two possible carbocations are of similar stability.



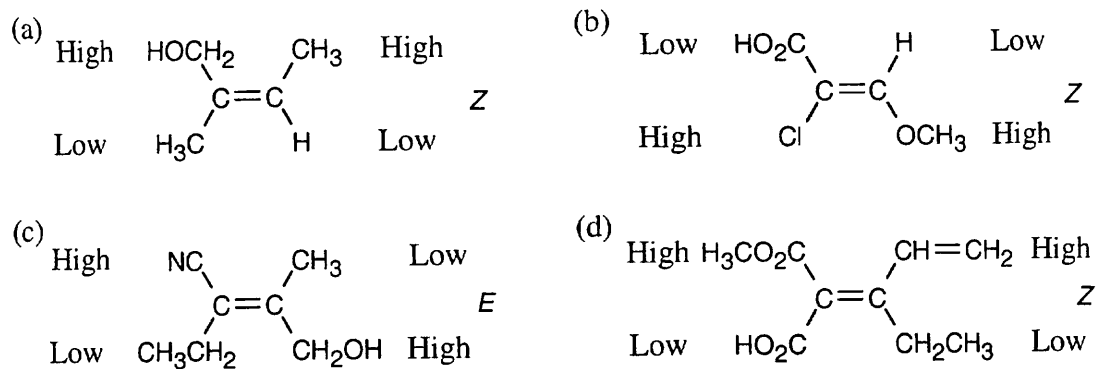
6.40



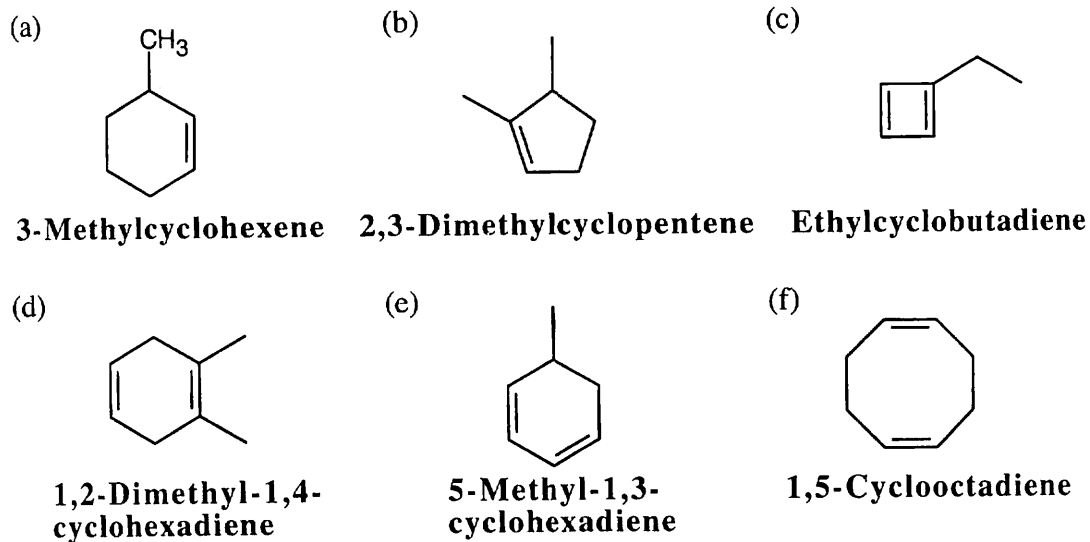
6.41 Highest priority —————> Lowest Priority

- (a) -I, -Br, -CH₃, -H
- (b) -OCH₃, -OH, -CO₂H, -H
- (c) -CO₂CH₃, -CO₂H, -CH₂OH, -CH₃
- (d) -COCH₃, -CH₂CH₂OH, -CH₂CH₃, -CH₃
- (e) -CH₂Br, -C≡N, -CH₂NH₂, -CH=CH₂
- (f) -CH₂OCH₃, -CH₂OH, -CH=CH₂, CH₂CH₃

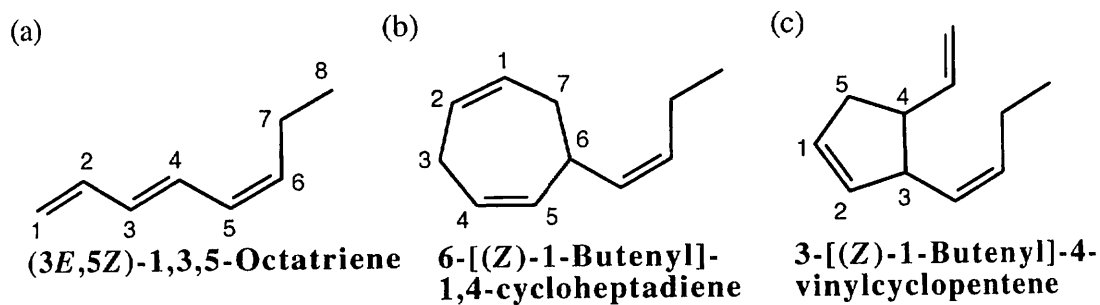
6.42



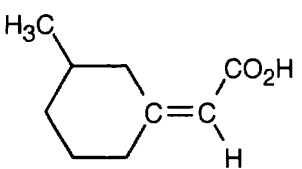
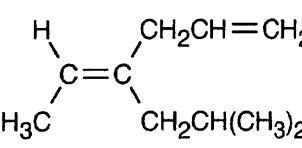
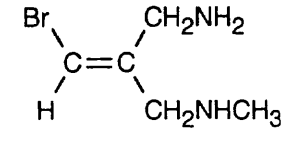
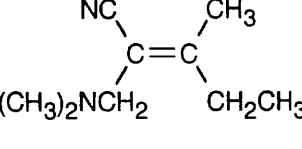
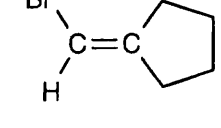
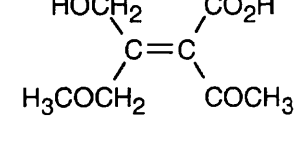
6.43



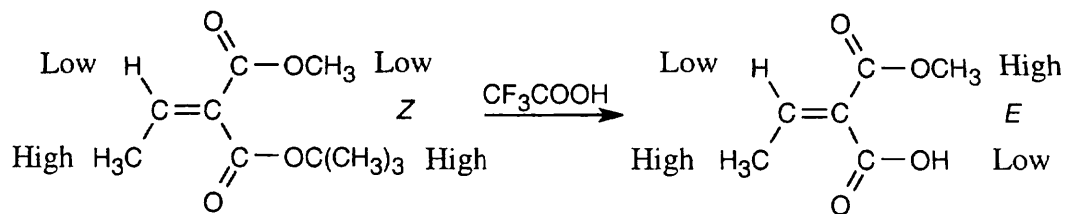
6.44



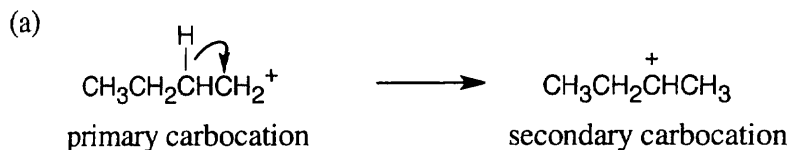
6.45

- (a)  High High Z (correct)
Low Low
- (b)  Low High E (correct)
High Low
- (c)  High Low E (incorrect)
Low High
- (d)  High Low E (correct)
Low High
- (e)  High Low This compound doesn't show E-Z isomerism.
- (f)  Low High E (correct)
High Low

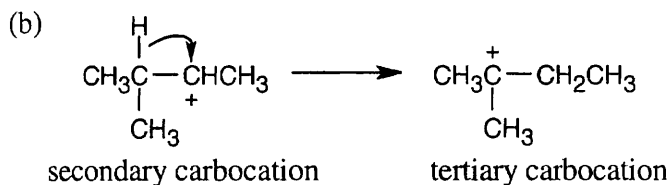
6.46 Treatment of the *tert*-butyl ester with trifluoroacetic acid cleaves the $-\text{OC}(\text{CH}_3)_3$ group and replaces it with an $-\text{OH}$ group, which has a lower priority than the $-\text{OCH}_3$ group on the upper carbon and the $-\text{OC}(\text{CH}_3)_3$ group that was removed. The result is a change in the *E,Z* designation around the double bond without breaking any of the bonds attached to the double-bond carbons.



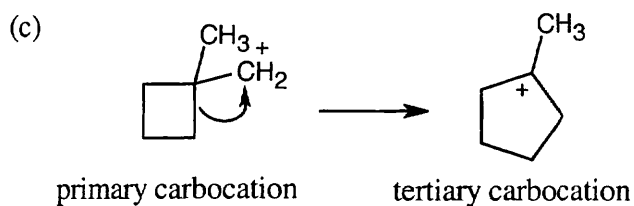
6.47



The primary carbocation rearranges to the more stable secondary carbocation by a hydride shift.

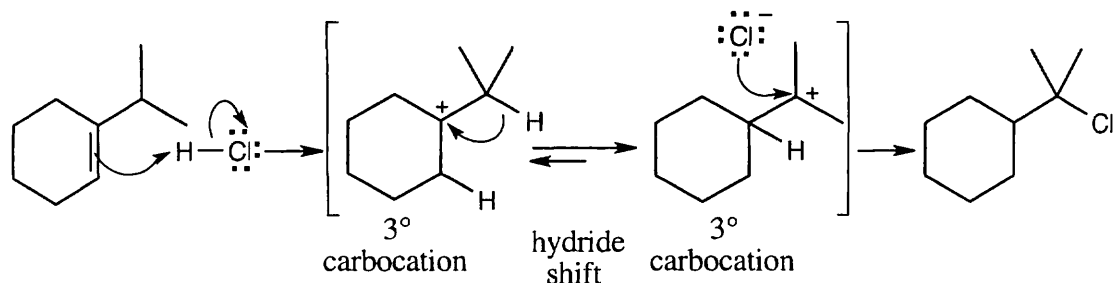


This hydride shift produces a tertiary carbocation from rearrangement of a secondary carbocation.

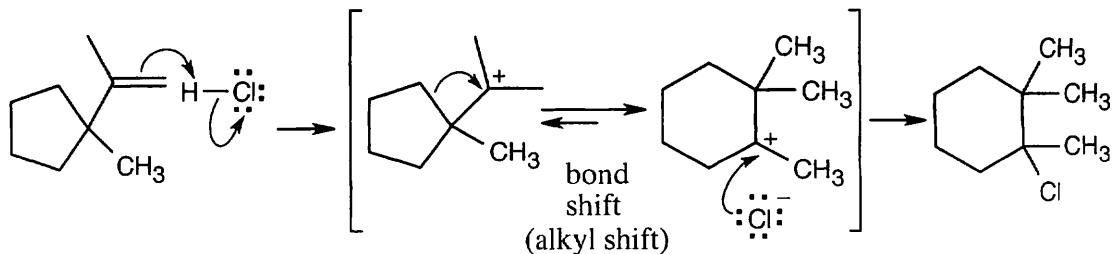


An alkyl shift forms a tertiary carbocation from a primary carbocation. In this example, rearrangement involves migration of the electrons from one of the cyclobutane ring bonds.

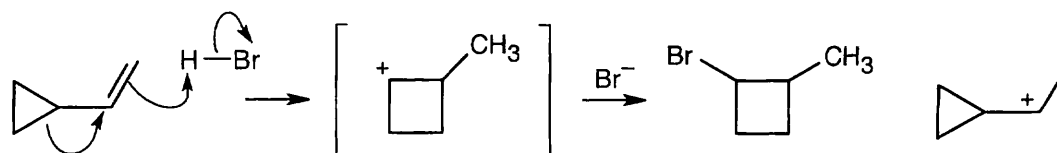
6.48



6.49



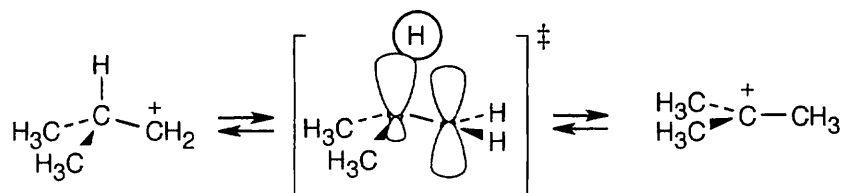
6.50



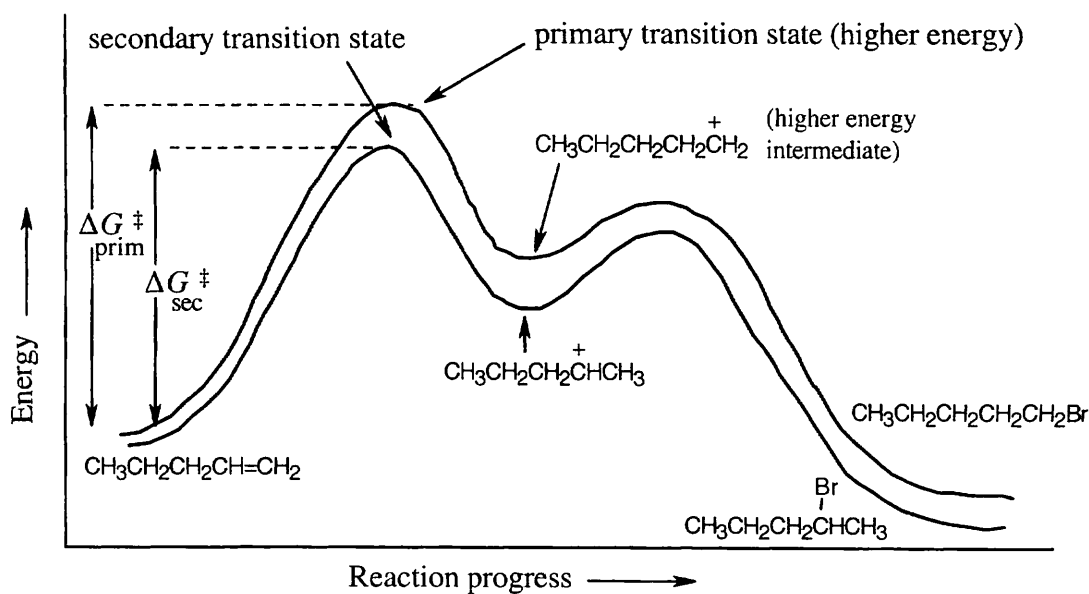
Attack of the π electrons of the double bond on H^+ yields the carbocation pictured on the far right. A bond shift (alkyl shift) produces the bracketed intermediate, which reacts with Br^- to yield 1-bromo-2-methylcyclobutane.

- 6.51 (a) $\text{C}_{27}\text{H}_{46}\text{O}$ 5 degrees of unsaturation
 (b) $\text{C}_{14}\text{H}_9\text{Cl}_5$ 8 degrees of unsaturation
 (c) $\text{C}_{20}\text{H}_{34}\text{O}_5$ 4 degrees of unsaturation
 (d) $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ 6 degrees of unsaturation
 (e) $\text{C}_{21}\text{H}_{28}\text{O}_5$ 8 degrees of unsaturation
 (f) $\text{C}_{17}\text{H}_{23}\text{NO}_3$ 7 degrees of unsaturation

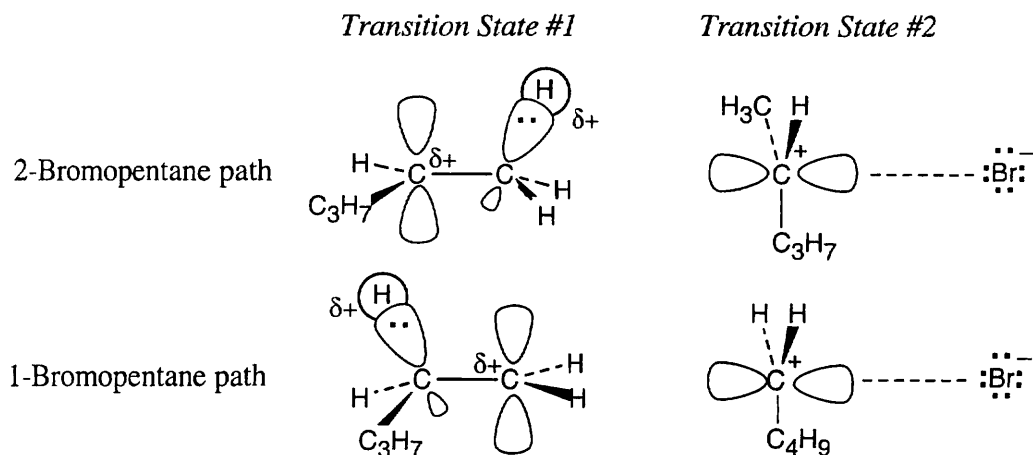
- 6.52 The reaction is exergonic because it is spontaneous. According to the Hammond postulate, the transition state should resemble the isobutyl cation.



6.53

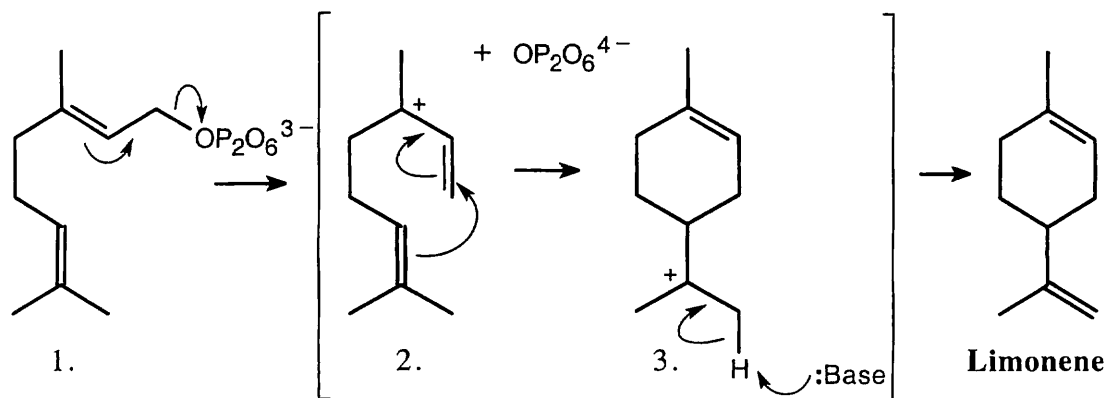


6.54



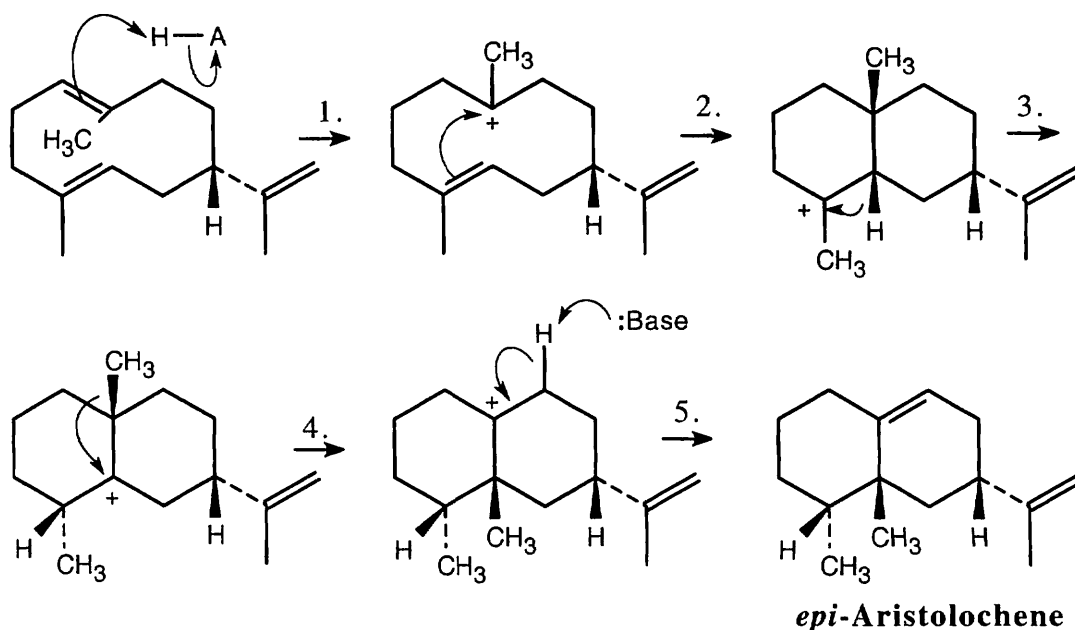
The first step (carbocation formation) is endergonic for both reaction paths, and both transition states resemble the carbocation intermediates. Transition states for the exergonic second step also resemble the carbocation intermediate. Transition state #1 for 1-bromopentane is more like the carbocation intermediate than is transition state #1 for 2-bromopentane.

6.55



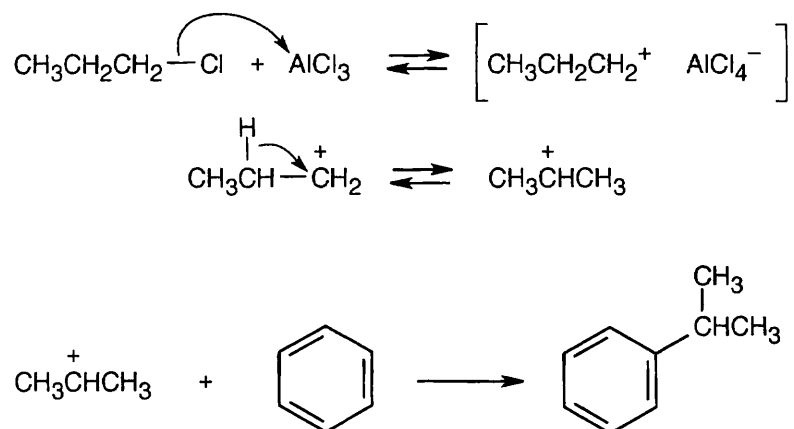
Step 2, in which the double bond electrons add to the carbocation, is an alkene electrophilic addition.

6.56

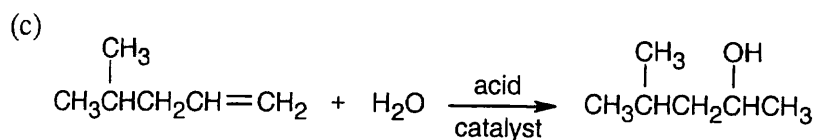
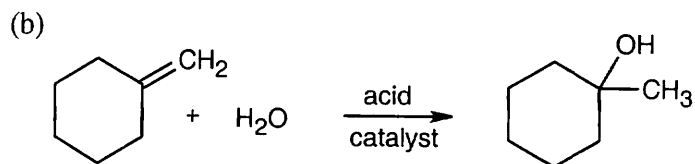
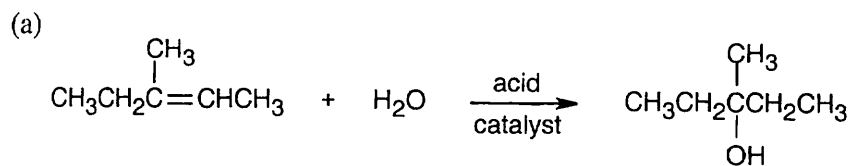


Steps 1 and 2 are alkene electrophilic additions, and steps 3 and 4 involve carbocation rearrangements.

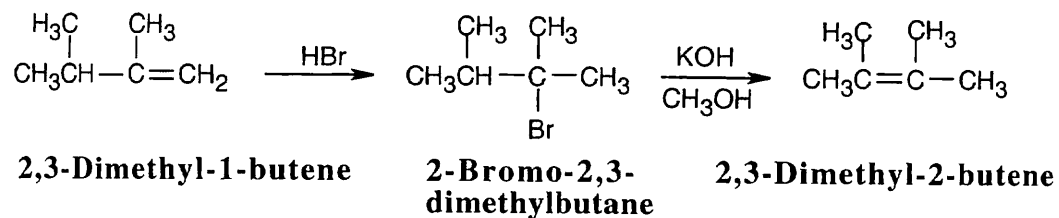
- 6.57** Reaction of 1-chloropropane with the Lewis acid AlCl_3 forms a carbocation. The less stable propyl carbocation undergoes a hydride shift to produce the more stable isopropyl carbocation, which reacts with benzene to give isopropylbenzene.



6.58



6.59



The product, 2,3-dimethyl-2-butene, is formed by elimination of HBr from 2-bromo-2,3-dimethylbutane. The product has the more substituted double bond.