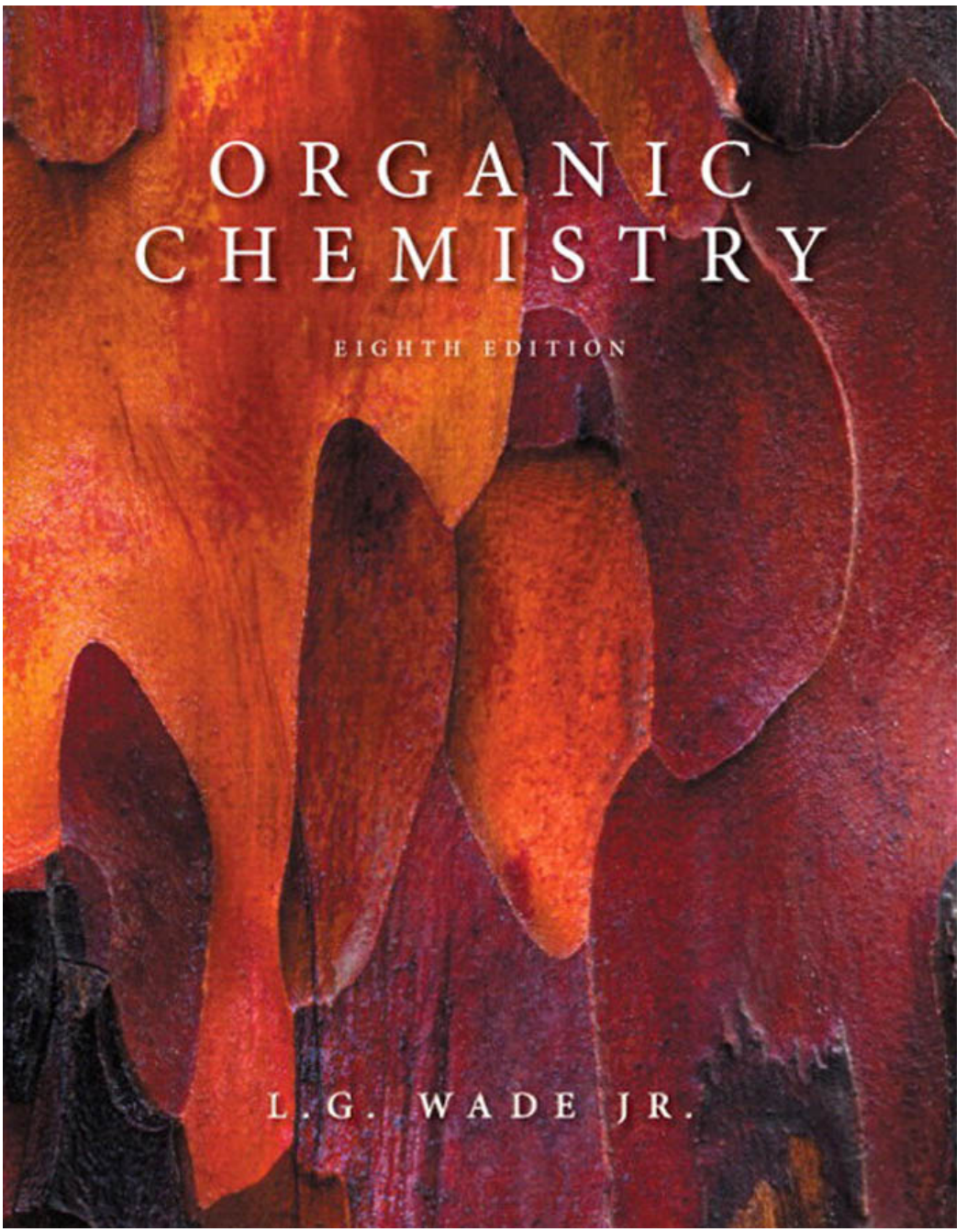

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EIGHTH EDITION

L.G. WADE, JR.

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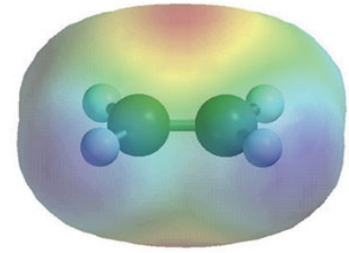
7 Structure and Synthesis of Alkenes

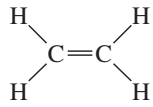


GOALS FOR CHAPTER 7

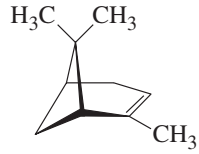
1. Draw and name alkenes and cycloalkenes.
2. Given a molecular formula, calculate the number of double bonds and rings.
3. Explain how the stability of alkenes depends on their structures.
4. Show how alkenes can be synthesized by eliminations from alkyl halides and alcohols.

7-1 Introduction

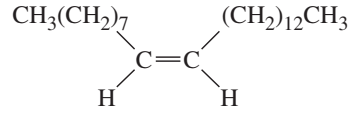
Alkenes are hydrocarbons with carbon–carbon double bonds. Alkenes are sometimes called **olefins,** a term derived from *olefiant gas*, meaning "oil-forming gas." This term originated with early experimentalists who noticed the oily appearance of alkene derivatives. Alkenes are among the most important industrial compounds (see Section 7-6), and many alkenes are also found in plants and animals. *Ethylene* is the largest-volume industrial organic compound, used to make polyethylene and a variety of other industrial and consumer chemicals. *Pinene* is a major component of *turpentine*, the paint solvent distilled from extracts of evergreen trees. *Muscalure* (*cis*-tricos-9-ene) is the sex attractant of the common housefly.



ethylene (ethene)



α-pinene



cis-tricos-9-ene, "muscalure"

The bond energy of a carbon–carbon double bond is about 611 kJ/mol (146 kcal/mol), compared with the single-bond energy of about 347 kJ/mol (83 kcal/mol). From these energies, we can calculate the approximate energy of a pi bond:

double-bond dissociation energy	611 kJ/mol	(146 kcal/mol)
subtract sigma bond dissociation energy	(−)347 kJ/mol	(−)(83 kcal/mol)
pi bond dissociation energy	264 kJ/mol	(63 kcal/mol)

This value of 264 kJ/mol is much less than the sigma bond energy of 347 kJ/mol, showing that pi bonds should be more reactive than sigma bonds.

Because a carbon–carbon double bond is relatively reactive, it is considered to be a *functional group*, and alkenes are characterized by the reactions of their double bonds. In previous chapters, we saw alkene synthesis by elimination reactions and we

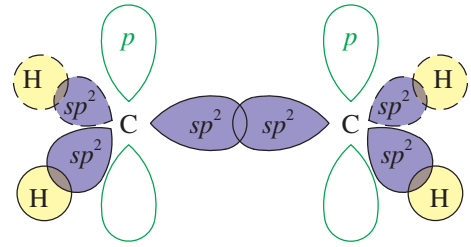
encountered a few reactions of alkenes. In this chapter, we study alkenes in more detail, concentrating on their properties and the ways they are synthesized.

7-2 The Orbital Description of the Alkene Double Bond

In a Lewis structure, the double bond of an alkene is represented by two pairs of electrons between the carbon atoms. The Pauli exclusion principle tells us that two pairs of electrons can go into the region of space between the carbon nuclei only if each pair has its own molecular orbital. Using ethylene as an example, let's consider how the electrons are distributed in the double bond.

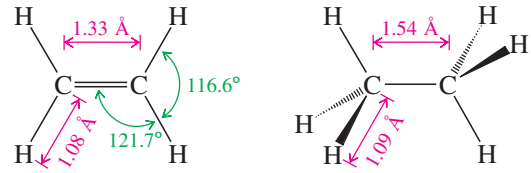
7-2A The Sigma Bond Framework

In Section 2-4, we saw how we can visualize the sigma bonds of organic molecules using hybrid atomic orbitals. In ethylene, each carbon atom is bonded to three other atoms (one carbon and two hydrogens), and there are no nonbonding electrons. Three hybrid orbitals are needed, implying sp^2 hybridization. Recall from Section 2-4 that sp^2 hybridization corresponds to bond angles of about 120°, giving optimum separation of three atoms bonded to the carbon atom.



sigma bonding orbitals of ethylene

Each of the carbon–hydrogen sigma bonds is formed by overlap of an sp^2 hybrid orbital on carbon with the 1*s* orbital of a hydrogen atom. The C—H bond length in ethylene (1.08 Å) is slightly shorter than the C—H bond in ethane (1.09 Å) because the sp^2 orbital in ethylene has more *s* character (one-third *s*) than an sp^3 orbital (one-fourth *s*). The *s* orbital is closer to the nucleus than the *p* orbital, contributing to shorter bonds.



ethylene ethane

The remaining sp^2 orbitals overlap in the region between the carbon nuclei, providing a bonding orbital. The pair of electrons in this bonding orbital forms one of the bonds between the carbon atoms. This bond is a sigma bond because its electron density is centered along the line joining the nuclei. The C=C bond in ethylene (1.33 Å) is much shorter than the C—C bond (1.54 Å) in ethane, partly because the sigma bond of ethylene is formed from sp^2 orbitals (with more *s* character) and partly because there are two bonds drawing the atoms together. The second carbon–carbon bond is a pi bond.

7-2B The Pi Bond

Two more electrons must go into the carbon–carbon bonding region to form the double bond in ethylene. Each carbon atom still has an unhybridized *p* orbital, and these overlap to form a pi-bonding molecular orbital. The two electrons in this orbital form

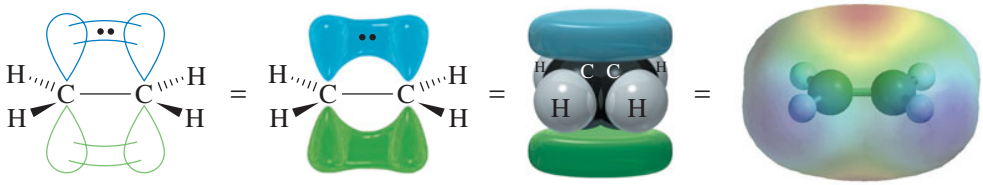


FIGURE 7-1
Parallel *p* orbitals in ethylene. The pi bond in ethylene is formed by overlap of the unhybridized *p* orbitals on the sp^2 hybrid carbon atoms. This overlap requires the two ends of the molecule to be coplanar.

the second bond between the double-bonded carbon atoms. For pi overlap to occur, these *p* orbitals must be parallel, which requires that the two carbon atoms be oriented with all their C—H bonds in a single plane (Figure 7-1). Half of the pi-bonding orbital is above the C—C sigma bond, and the other half is below the sigma bond. The pi-bonding electrons give rise to regions of high electron density (red) in the electrostatic potential map of ethylene shown in Figure 7-1.

Figure 7-2 shows that the two ends of the ethylene molecule cannot be twisted with respect to each other without disrupting the pi bond. Unlike single bonds, a carbon–carbon double bond does not permit rotation. Six atoms, including the double-bonded carbon atoms and the four atoms bonded to them, must remain in the same plane. This is the origin of cis-trans isomerism. If two groups are on the same side of a double bond (cis), they cannot rotate to opposite sides (trans) without breaking the pi bond. Figure 7-2 shows that there are two distinct isomers of but-2-ene: *cis*-but-2-ene and *trans*-but-2-ene.

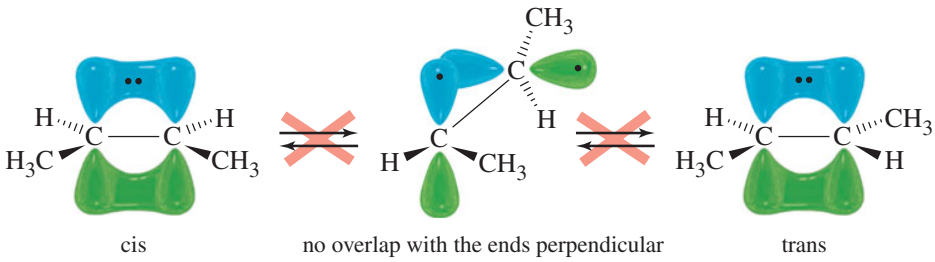
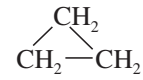


FIGURE 7-2
Distinct isomers resulting from C—C double bonds. The two isomers of but-2-ene cannot interconvert by rotation about the carbon–carbon double bond without breaking the pi bond.

7-3 Elements of Unsaturation

7-3A Elements of Unsaturation in Hydrocarbons

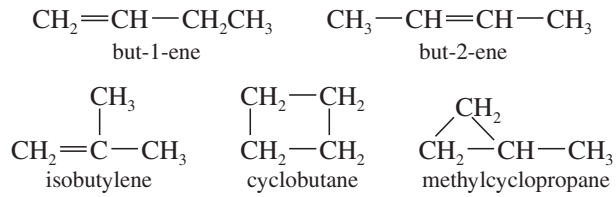
Alkenes are said to be **unsaturated** because they are capable of adding hydrogen in the presence of a catalyst. The product, an alkane, is called **saturated** because it cannot react with any more hydrogen. The presence of a pi bond of an alkene (or an alkyne) or the ring of a cyclic compound decreases the number of hydrogen atoms in a molecular formula. These structural features are called **elements of unsaturation.***
Each element of unsaturation corresponds to two fewer hydrogen atoms than in the "saturated" formula.

$CH_3—CH_2—CH_3$	$CH_3—CH{=}CH_2$		$CH_3—C{\equiv}C—H$
propane, C_3H_8	propene, C_3H_6	cyclopropane, C_3H_6	propyne, C_3H_4
saturated	one element of unsaturation	one element of unsaturation	two elements of unsaturation

Consider, for example, the formula C_4H_8. A saturated alkane would have a $C_nH_{(2n+2)}$ formula, or C_4H_{10}. The formula C_4H_8 is missing two hydrogen atoms, so it

Degree of unsaturation and *index of hydrogen deficiency* are equivalent terms.

has one element of unsaturation, either a pi bond or a ring. There are five constitutional isomers of formula C_4H_8:



When you need a structure for a particular molecular formula, it helps to find the number of elements of unsaturation. Calculate the maximum number of hydrogen atoms from the saturated formula, $C_nH_{(2n+2)}$, and see how many are missing. The number of elements of unsaturation is simply half the number of missing hydrogens. This simple calculation allows you to consider possible structures quickly, without always having to check for the correct molecular formula.

Problem-solving Hint

If you prefer to use a formula,

elements of unsaturation

$$= \frac{1}{2}(2C + 2 - H)$$

C = number of carbons

H = number of hydrogens

PROBLEM 7-1

(a) If a hydrocarbon has nine carbon atoms, three double bonds, and one ring, how many hydrogen atoms must it have?

(b) Calculate the number of elements of unsaturation implied by the molecular formula C_6H_{12}.

(c) Give five examples of structures with this formula (C_6H_{12}). At least one should contain a ring, and at least one a double bond.

PROBLEM 7-2

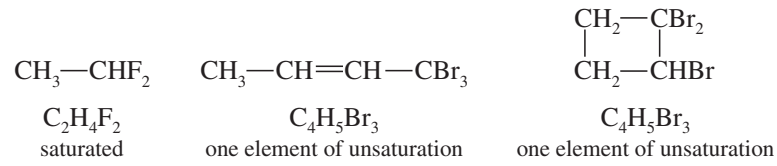
Determine the number of elements of unsaturation in the molecular formula C_4H_6. Give all nine possible structures having this formula. Remember that

a double bond = one element of unsaturation
a ring = one element of unsaturation
a triple bond = two elements of unsaturation

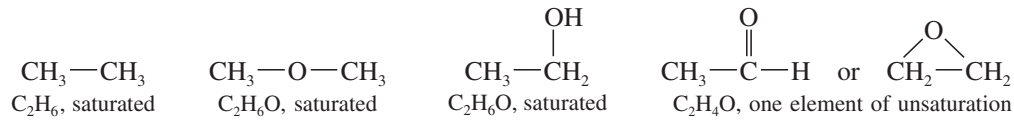
7-3B Elements of Unsaturation with Heteroatoms

Heteroatoms (*hetero*, "different") are any atoms other than carbon and hydrogen. The rule for calculating elements of unsaturation in hydrocarbons can be extended to include heteroatoms. Let's consider how the addition of a heteroatom affects the number of hydrogen atoms in the formula.

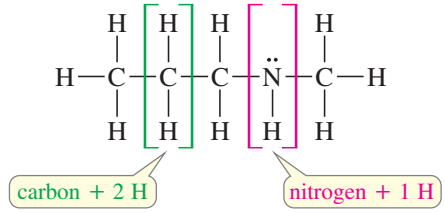
Halogens Halogens simply substitute for hydrogen atoms in the molecular formula. The formula C_2H_6 is saturated, so the formula $C_2H_4F_2$ is also saturated. C_4H_8 has one element of unsaturation, and $C_4H_5Br_3$ also has one element of unsaturation. In calculating the number of elements of unsaturation, simply *count halogens as hydrogen atoms*.



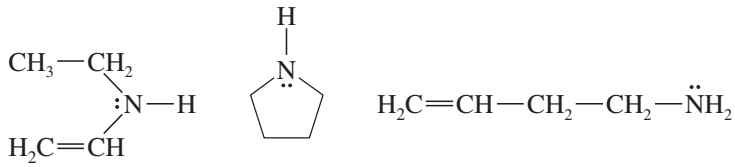
Oxygen An oxygen atom can be added to the chain (or added to a C—H bond to make a C—OH group) without changing the number of hydrogen atoms or carbon atoms. In calculating the number of elements of unsaturation, *ignore the oxygen atoms*.



Nitrogen A nitrogen atom can take the place of a carbon atom in the chain, but nitrogen is trivalent, having only one additional hydrogen atom, compared with two hydrogens for each additional carbon atom. In computing the elements of unsaturation, *count nitrogen as half a carbon atom.*



The formula C_4H_9N is like a formula with $4\frac{1}{2}$ carbon atoms, with saturated formula $C_{4.5}H_{9+2}$. The formula C_4H_9N has one element of unsaturation, because it is two hydrogen atoms short of the saturated formula.



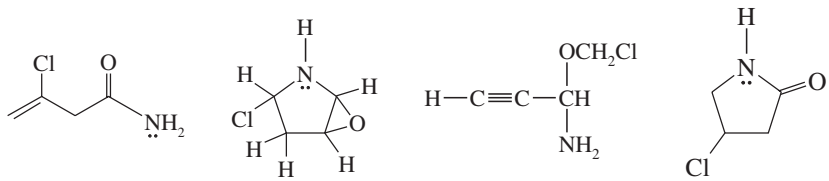
examples of formula C_4H_9N, one element of unsaturation

SOLVED PROBLEM 7-1

Draw at least four compounds of formula C_4H_6NOCl.

SOLUTION

Counting the nitrogen as $\frac{1}{2}$ carbon, ignoring the oxygen, and counting chlorine as a hydrogen shows the formula is equivalent to $C_{4.5}H_7$. The saturated formula for 4.5 carbon atoms is $C_{4.5}H_{11}$, so C_4H_6NOCl has two elements of unsaturation. These could be two double bonds, two rings, one triple bond, or a ring and a double bond. There are many possibilities, four of which are listed here.



two double bonds | two rings | one triple bond | one ring, one double bond

Problem-solving Hint

In figuring elements of unsaturation:
- Count halogens as hydrogens.
- Ignore oxygen.
- Count nitrogen as half a carbon.

PROBLEM 7-3

Draw five more compounds of formula C_4H_6NOCl.

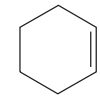
PROBLEM 7-4

For each of the following molecular formulas, determine the number of elements of unsaturation, and draw three examples.

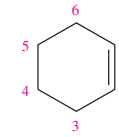
(a) $C_4H_4Cl_2$ **(b)** C_4H_8O **(c)** $C_6H_8O_2$ **(d)** $C_5H_5NO_2$ **(e)** C_6H_3NClBr

7-4 Nomenclature of Alkenes

Simple alkenes are named much like alkanes, using the root name of the longest chain containing the double bond. The ending is changed from *-ane* to *-ene*. For example, "ethane" becomes "ethene," "propane" becomes "propene," and "cyclohexane" becomes "cyclohexene."

	$CH_2{=}CH_2$	$CH_2{=}CH{-}CH_3$	
IUPAC names:	ethene	propene	cyclohexene
Common names:	ethylene	propylene	

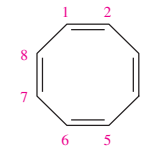
When the chain contains more than three carbon atoms, a number is used to give the location of the double bond. The chain is numbered starting from the end closest to the double bond, and the double bond is given the *lower* number of its two double-bonded carbon atoms. Cycloalkenes are assumed to have the double bond in the number 1 position.

	$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H_2{-}\overset{4}{C}H_3$	$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H_2{-}\overset{4}{C}H_2{-}\overset{5}{C}H_3$	
old IUPAC names:	1-butene	1-pentene	cyclohexene
new IUPAC names:	but-1-ene	pent-1-ene	

	$\overset{1}{C}H_3{-}\overset{2}{C}H{=}\overset{3}{C}H{-}\overset{4}{C}H_3$	$\overset{1}{C}H_3{-}\overset{2}{C}H{=}\overset{3}{C}H{-}\overset{4}{C}H_2{-}\overset{5}{C}H_3$
old IUPAC names:	2-butene	2-pentene
new IUPAC names:	but-2-ene	pent-2-ene

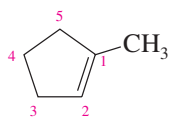
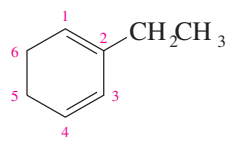
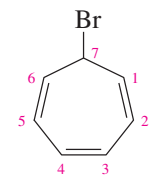
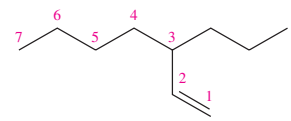
In 1993, the IUPAC recommended a logical change in the positions of the numbers used in names. Instead of placing the numbers before the root name (1-butene), they recommended placing them immediately before the part of the name they locate (but-1-ene). The new placement is helpful for clarifying the names of compounds containing multiple functional groups. You should be prepared to recognize names using either placement of the numbers, because both are widely used. In this section, names using the old number placement are printed in blue, and those using the new number placement are printed in green. Throughout this book, we will generally use the new number placement.

A compound with two double bonds is a **diene.** A **triene** has three double bonds, and a **tetraene** has four. Numbers are used to specify the locations of the double bonds.

	$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H{=}\overset{4}{C}H_2$	$\overset{7}{C}H_3{-}\overset{6}{C}H{=}\overset{5}{C}H{-}\overset{4}{C}H{=}\overset{3}{C}H{-}\overset{2}{C}H{=}\overset{1}{C}H_2$	
old IUPAC names:	1,3-butadiene	1,3,5-heptatriene	1,3,5,7-cyclooctatetraene
new IUPAC names:	buta-1,3-diene	hepta-1,3,5-triene	cycloocta-1,3,5,7-tetraene

Each alkyl group attached to the main chain is listed with a number to give its location. Note that the double bond is still given preference in numbering, however.

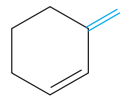
$\overset{4}{C}H_3{-}\overset{3}{C}H{=}\overset{2}{C}(CH_3){-}\overset{1}{C}H_3$	$\overset{4}{C}H_3{-}\overset{3}{C}H(CH_3){-}\overset{2}{C}H{=}\overset{1}{C}H_2$	$\overset{1}{C}H_3{-}\overset{2}{C}H{=}\overset{3}{C}(CH_3){-}\overset{4}{C}H_2{-}\overset{5}{C}H_2{-}\overset{6}{C}H(CH_3){-}\overset{7}{C}H_3$
2-methyl-2-butene	3-methyl-1-butene	3,6-dimethyl-2-heptene
2-methylbut-2-ene	3-methylbut-1-ene	3,6-dimethylhept-2-ene

			
1-methylcyclopentene	2-ethyl-1,3-cyclohexadiene	7-bromo-1,3,5-cycloheptatriene	3-propyl-1-heptene
1-methylcyclopentene	2-ethylcyclohexa-1,3-diene	7-bromocyclohepta-1,3,5-triene	3-propylhept-1-ene

Alkenes as Substituents Alkenes named as substituents are called *alkenyl groups*. They can be named systematically (ethenyl, propenyl, etc.), or by common names. Common alkenyl substituents are the vinyl, allyl, methylene, and phenyl groups. The phenyl group (Ph) is different from the others because it is aromatic (see Chapter 16) and does not undergo the typical reactions of alkenes.

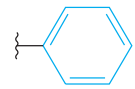
$\wr{=}CH_2$
methylene group
(methylidene group)

$\wr{-}CH{=}CH_2$
vinyl group
(ethenyl group)

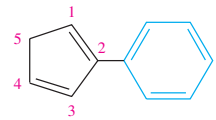

3-methylenecyclohexene

$CH_2{=}CHCH(CH{=}CH_2)CH_2CH{=}CH_2$
3-vinyl-1,5-hexadiene
3-vinylhexa-1,5-diene

$\wr{-}CH_2{-}CH{=}CH_2$
allyl group
2-propenyl group


phenyl group
(Ph)

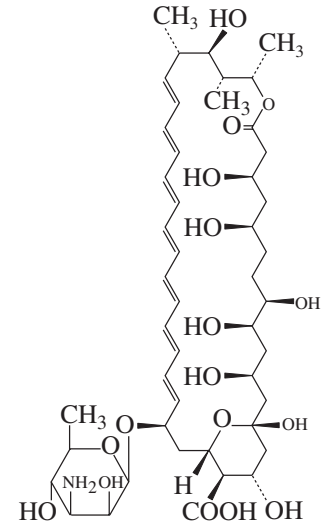
$CH_2{=}CH{-}CH_2{-}Cl$
allyl chloride
3-chloropropene



2-phenyl-1,3-cyclopentadiene
2-phenylcyclopenta-1,3-diene

Application: Antifungal Drugs
The polyene antifungals are a group of drugs with a nonpolar region consisting of 4–7 sets of alternating single and double bonds. They insert themselves in the cell membranes of fungi, causing disruption and leakiness that results in fungal cell death.

The best-known polyene antifungal drug is Amphotericin B, whose structure is shown below.



Amphotericin B

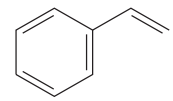
Common Names Most alkenes are conveniently named by the IUPAC system, but common names are sometimes used for the simplest compounds.

IUPAC names:	ethene	propene
common name:	ethylene	propylene

$CH_2{=}CH_2$ $CH_2{=}CH{-}CH_3$

$CH_2{=}C(CH_3){-}CH_3$
2-methylpropene
isobutylene

$CH_2{=}C(CH_3){-}CH{=}CH_2$
2-methylbuta-1,3-diene
isoprene

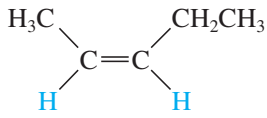

ethenylbenzene
styrene
(vinylbenzene)

7-5 Nomenclature of Cis-Trans Isomers

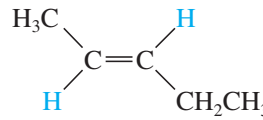
7-5A Cis-Trans Nomenclature

In Chapters 2 and 5, we saw how the rigidity and lack of rotation of carbon–carbon double bonds give rise to **cis-trans isomerism,** also called **geometric isomerism.** If two similar groups bonded to the carbons of the double bond are on the same side of

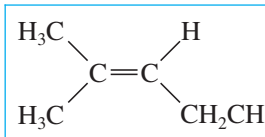
the bond, the alkene is the **cis** isomer. If the similar groups are on opposite sides of the bond, the alkene is **trans.** Not all alkenes are capable of showing cis-trans isomerism. If either carbon of the double bond holds two identical groups, the molecule cannot have cis and trans forms. Following are some cis and trans alkenes and some alkenes that cannot show cis-trans isomerism.



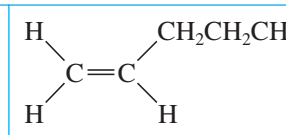
cis-2-pentene
cis-pent-2-ene



trans-2-pentene
trans-pent-2-ene



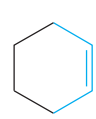
2-methyl-2-pentene
2-methylpent-2-ene



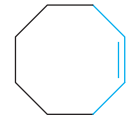
1-pentene
pent-1-ene

(neither cis nor trans)

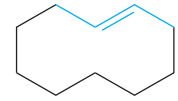
Trans cycloalkenes are unstable unless the ring is large enough (at least eight carbon atoms) to accommodate the trans double bond (Section 7-7D). Therefore, all cycloalkenes are assumed to be cis unless they are specifically named trans. The cis name is rarely used with cycloalkenes, except to distinguish a large cycloalkene from its trans isomer.



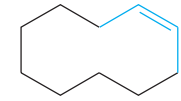
cyclohexene



cyclooctene



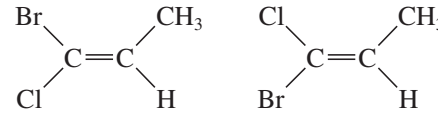
trans-cyclodecene



cis-cyclodecene

7-5B *E-Z* Nomenclature

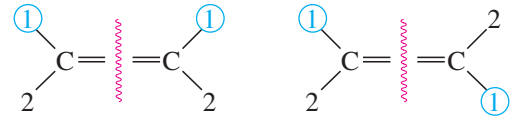
The cis-trans nomenclature for geometric isomers sometimes gives an ambiguous name. For example, the isomers of 1-bromo-1-chloropropene are not clearly cis or trans because it is not obvious which substituents are referred to as being cis or trans.



geometric isomers of 1-bromo-1-chloropropene

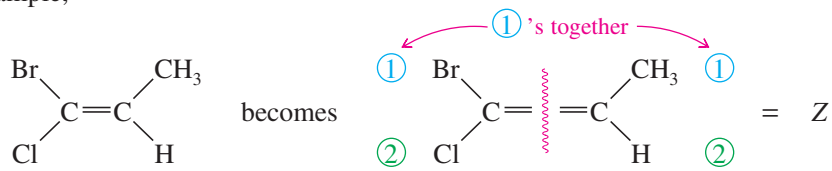
To deal with this problem, we use the ***E-Z* system** of nomenclature (pun intended) for cis-trans isomers, which is patterned after the Cahn–Ingold–Prelog convention for asymmetric carbon atoms (Section 5-3). It assigns a unique configuration of either *E* or *Z* to any double bond capable of geometric isomerism.

To name an alkene by the *E-Z* system, mentally separate the double bond into its two ends. Remember how you used the Cahn–Ingold–Prelog rules (page 181) to assign relative priorities to groups on an asymmetric carbon atom so you could name it (*R*) or (*S*). Consider each end of the double bond separately, and use those same rules to assign first and second priorities to the two substituent groups on that end. Do the same for the other end of the double bond. If the two first-priority atoms are *together (cis)* on the same side of the double bond, you have the ***Z*** isomer, from the German word *zusammen*, "together." If the two first-priority atoms are on *opposite (trans)* sides of the double bond, you have the ***E*** isomer, from the German word *entgegen*, "opposite."



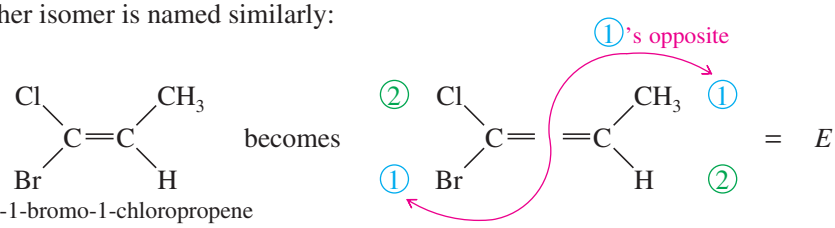
Zusammen Entgegen

For example,



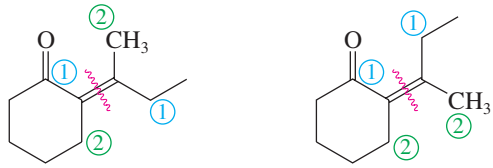
(*Z*)-1-bromo-1-chloropropene

The other isomer is named similarly:



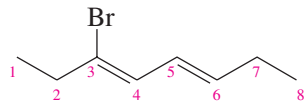
(*E*)-1-bromo-1-chloropropene

The following example shows the use of the *E*-*Z* nomenclature with cyclic stereoisomers that are not clearly cis or trans.



(*E*) isomer (*Z*) isomer

If the alkene has more than one double bond, the stereochemistry about each double bond should be specified. The following compound is properly named (3*Z*,5*E*)-3-bromoocta-3,5-diene:



(3*Z*,5*E*)-3-bromoocta-3,5-diene

The use of *E*-*Z* names (rather than cis and trans) is always an option, but it is required whenever a double bond is not clearly cis or trans. Most trisubstituted and tetrasubstituted double bonds are more clearly named *E* or *Z* rather than cis or trans.

SUMMARY Rules for Naming Alkenes

The following rules summarize the IUPAC system for naming alkenes:

1. Select the longest chain or largest ring that contains the *largest possible number of double bonds*, and name it with the *-ene* suffix. If there are two double bonds, the suffix is *-diene*; for three, *-triene*; for four, *-tetraene*; and so on.
2. Number the chain from the end closest to the double bond(s). Number a ring so that the double bond is between carbons 1 and 2. Place the numbers giving the locations of the double bonds in front of the root name (old system) or in front of the suffix *-ene, -diene*, etc. (new system).
3. Name substituent groups as in alkanes, indicating their locations by the number of the main-chain carbon to which they are attached. The ethenyl group and the propenyl group are usually called the *vinyl* group and the *allyl* group, respectively.
4. For compounds that show geometric isomerism, add the appropriate prefix: *cis*- or *trans*-, or *E*- or *Z*-. Cycloalkenes are assumed to be cis unless named otherwise.

PROBLEM 7-5

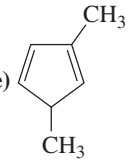
Give the systematic (IUPAC) names of the following alkenes.

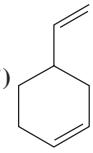
(a) $CH_2{=}CH{-}CH_2{-}CH(CH_3)_2$

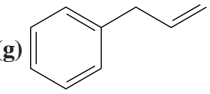
(b) $CH_3(CH_2)_3{-}C(=CH_2){-}CH_2CH_3$

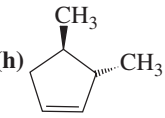
(c) $CH_2{=}CH{-}CH_2{-}CH{=}CH_2$

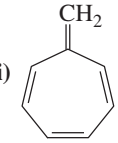
(d) $CH_2{=}C{=}CH{-}CH{=}CH_2$

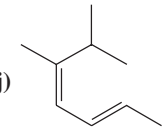
(e) 

(f) 

(g) 

(h) 

(i) 

(j) 

Problem-solving Hint

To see whether a compound can have cis and trans isomers, draw the structure, then draw it again with the groups on one end of the double bond reversed. See if you can describe a difference between the two.

PROBLEM 7-6

1. Determine which of the following compounds show cis-trans isomerism.
2. Draw and name the cis and trans (or *Z* and *E*) isomers of those that do.

(a) hex-3-ene **(b)** buta-1,3-diene **(c)** hexa-2,4-diene
(d) 3-methylpent-2-ene **(e)** 2,3-dimethylpent-2-ene **(f)** 3,4-dibromocyclopentene

PROBLEM 7-7

The following names are all incorrect. Draw the structure represented by the incorrect name (or a consistent structure if the name is ambiguous), and give your drawing the correct name.

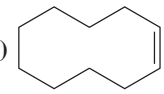
(a) *cis*-2,3-dimethyl-2-pentene **(b)** 3-vinylhex-4-ene
(c) 2-methylcyclopentene **(d)** 6-chlorocyclohexadiene
(e) 2,5-dimethylcyclohexene **(f)** *cis*-2,5-dibromo-3-ethylpent-2-ene

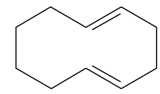
PROBLEM 7-8

Some of the following examples can show geometric isomerism, and some cannot. For the ones that can, draw all the geometric isomers, and assign complete names using the *E*-*Z* system.

(a) 3-bromo-2-chloropent-2-ene **(b)** 3-ethylhexa-2,4-diene
(c) 3-bromo-2-methylhex-3-ene **(d)** penta-1,3-diene
(e) 3-ethyl-5-methyloct-3-ene **(f)** 3,7-dichloroocta-2,5-diene

(g)
cyclohexene

(h) 
cyclodecene

(i) 
cyclodeca-1,5-diene

7-6 Commercial Importance of Alkenes

Because the carbon–carbon double bond is readily converted to other functional groups, alkenes are important intermediates in the synthesis of polymers, drugs, pesticides, and other valuable chemicals.

Ethylene is the organic compound produced in the largest volume, at around 160 billion pounds per year worldwide. Most of this ethylene is polymerized to form about 90 billion pounds of polyethylene per year. The remainder is used to synthesize a wide variety of organic chemicals including ethanol, acetic acid, ethylene

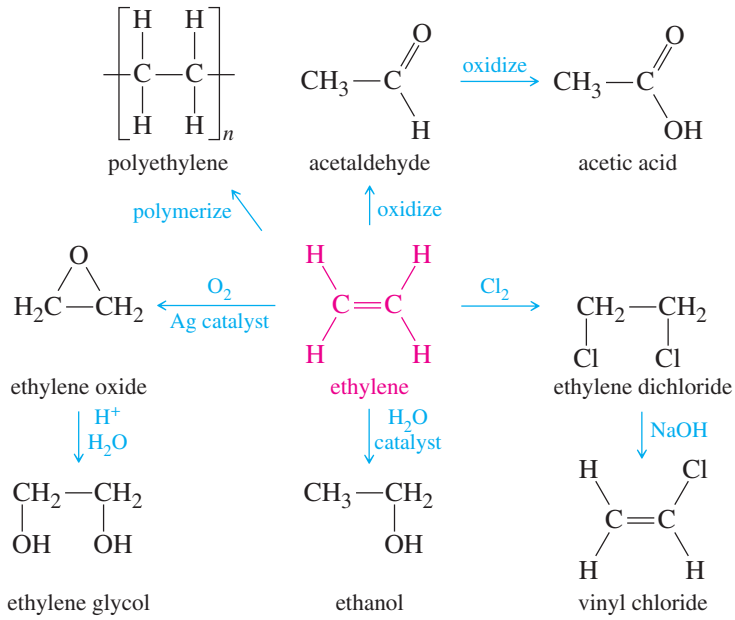


FIGURE 7-3
Uses of ethylene. Ethylene is the largest-volume industrial organic chemical. Most of the 160 billion pounds produced each year is polymerized to make polyethylene. Much of the rest is used to produce a variety of useful two-carbon compounds.

glycol, and vinyl chloride (Figure 7-3). Ethylene also serves as a plant hormone, accelerating the ripening of fruit. For example, tomatoes are harvested and shipped while green, then treated with ethylene to make them ripen and turn red just before they are placed on display.

Propylene is produced at the rate of about 90 billion pounds per year worldwide, with much of that going to make about 40 billion pounds of polypropylene. The rest is used to make propylene glycol, acetone, isopropyl alcohol, and a variety of other useful organic chemicals (Figure 7-4).

Many common polymers are made by polymerizing alkenes. These polymers are used in consumer products from shoes to plastic bags to car bumpers. A **polymer** (Greek, *poly*, "many," and *meros*, "parts") is a large molecule made up of many **monomer** (Greek, *mono*, "one") molecules. An alkene monomer can **polymerize** by a chain reaction where additional alkene molecules add to the end of the growing polymer chain. Because these polymers result from addition of many individual alkene units, they are called **addition polymers. Polyolefins** are polymers made from monofunctional (single functional group) alkenes such as ethylene and propylene. Figure 7-5 shows some addition polymers made from simple alkenes and haloalkenes. We discuss polymerization reactions in Chapters 8 and 26.

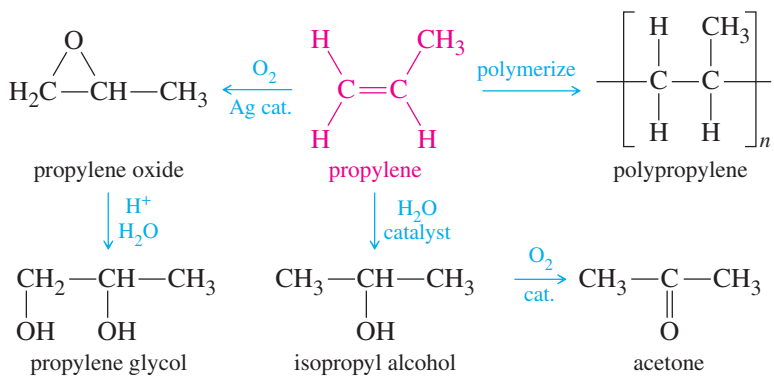


FIGURE 7-4
Uses of propylene. Most propylene is polymerized to make polypropylene. It is also used to make several important three-carbon compounds.

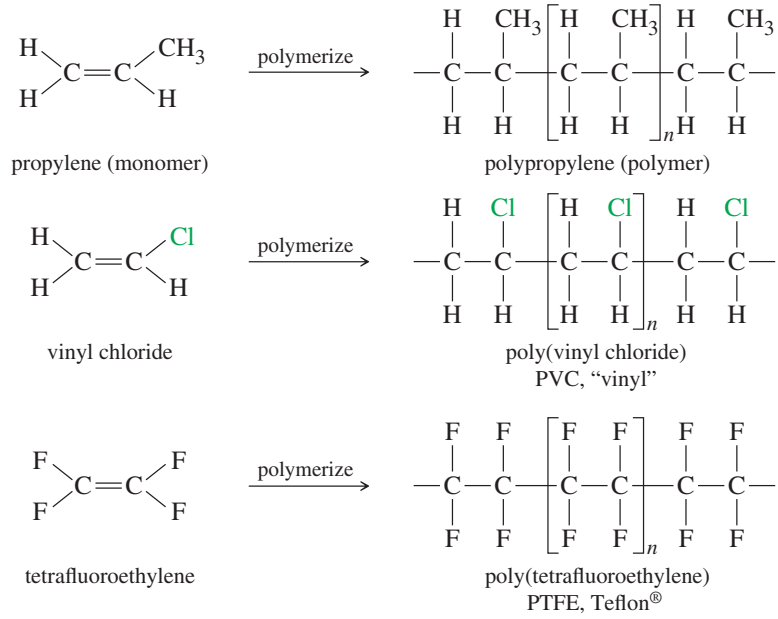


FIGURE 7-5
Addition polymers. Alkenes polymerize to form addition polymers. Many common polymers are produced this way.

7-7 Stability of Alkenes

In making alkenes, we often find that the major product is the most stable alkene. Many reactions also provide opportunities for double bonds to rearrange to more stable isomers. Therefore, we need to know how the stability of an alkene depends on its structure. Stabilities can be compared by converting different compounds to a common product and comparing the amounts of heat given off. One possibility would be to measure heats of combustion from converting alkenes to CO_2 and H_2O. Heats of combustion are large numbers (thousands of kJ per mole), and measuring small differences in these large numbers is difficult. Instead, alkene energies are often compared by measuring the **heat of hydrogenation:** the heat given off ($\Delta H°$) during catalytic hydrogenation. Heats of hydrogenation can be measured about as easily as heats of combustion, yet they are smaller numbers and provide more accurate energy differences.

7-7A Heats of Hydrogenation

When an alkene is treated with hydrogen in the presence of a platinum catalyst, hydrogen adds to the double bond, reducing the alkene to an alkane. Hydrogenation is mildly exothermic, evolving about 80 to 120 kJ (20 to 30 kcal) of heat per mole of hydrogen consumed. Consider the hydrogenation of but-1-ene and *trans*-but-2-ene:

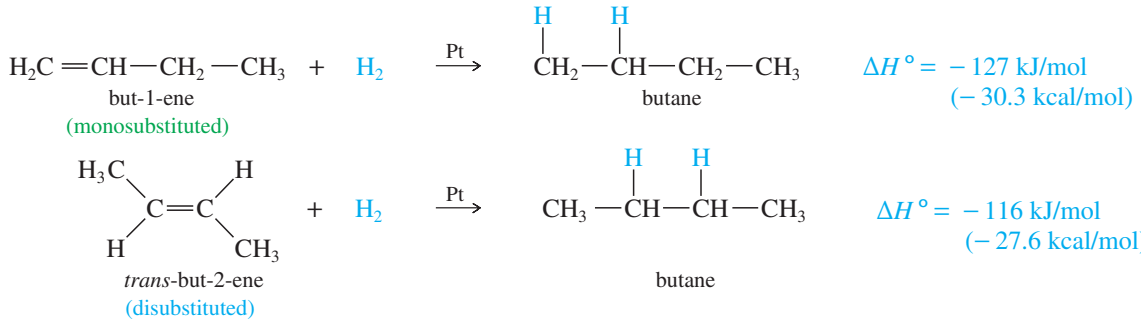


Figure 7-6 shows these heats of hydrogenation on a reaction-energy diagram. The difference in the stabilities of but-1-ene and *trans*-but-2-ene is the difference in their heats of hydrogenation. *trans*-But-2-ene is more stable by

$$126.8\ \text{kJ/mol} - 115.6\ \text{kJ/mol} = 11.2\ \text{kJ/mol}\ (2.7\ \text{kcal/mol})$$

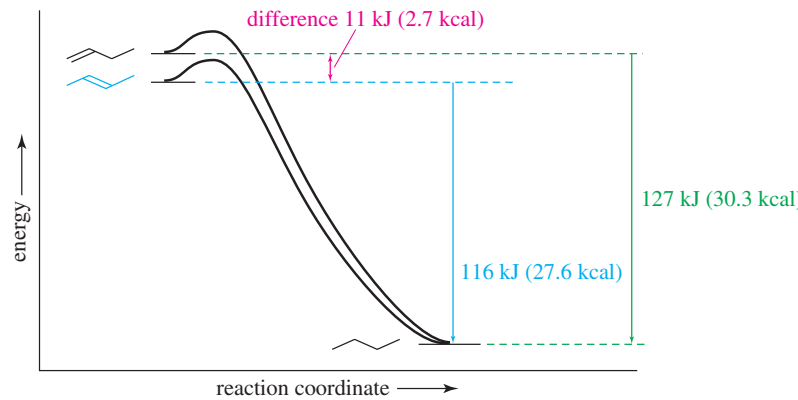
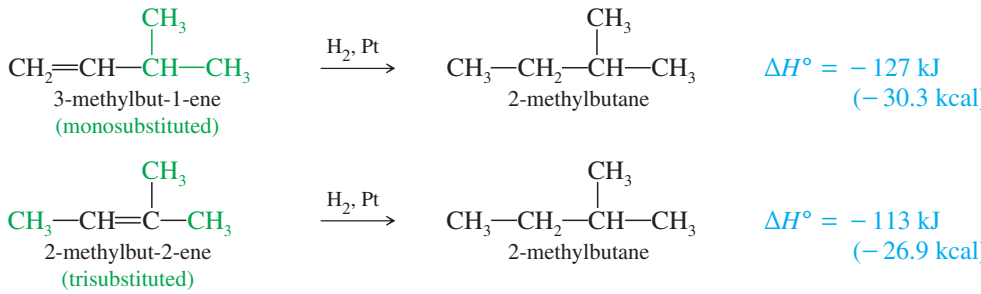


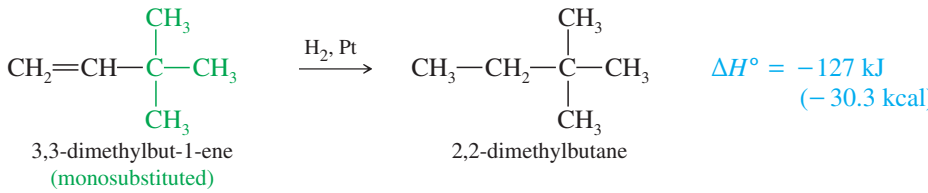
FIGURE 7-6
Relative heats of hydrogenation. *trans*-But-2-ene is more stable than but-1-ene by 11 kJ/mol (2.7 kcal/mol).

7-7B Substitution Effects

An 11 kJ/mol (2.7 kcal/mol) stability difference is typical between a monosubstituted alkene (but-1-ene) and a trans-disubstituted alkene (*trans*-but-2-ene). In the following equations, we compare the monosubstituted double bond of 3-methylbut-1-ene with the trisubstituted double bond of 2-methylbut-2-ene. The trisubstituted alkene is more stable by 14 kJ/mol (3.4 kcal/mol).



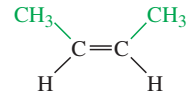
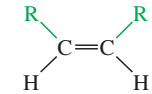
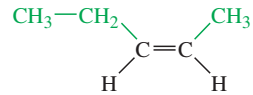
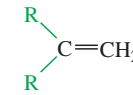
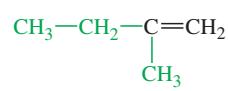
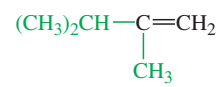
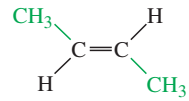
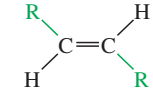
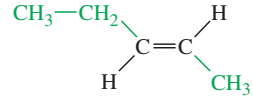
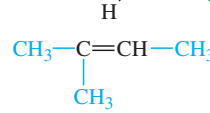
To be completely correct, we should compare heats of hydrogenation only for compounds that give the same alkane, as 3-methylbut-1-ene and 2-methylbut-2-ene do. However, most alkenes with similar substitution patterns give similar heats of hydrogenation. For example, 3,3-dimethylbut-1-ene (below) hydrogenates to give a different alkane than does 3-methylbut-1-ene or but-1-ene (above); yet these three monosubstituted alkenes have similar heats of hydrogenation because the alkanes formed have similar energies. In effect, the heat of hydrogenation is a measure of the energy content of the pi bond.



In practice, we can use heats of hydrogenation to compare the stabilities of different alkenes as long as they hydrogenate to give alkanes of similar energies. Most acyclic alkanes and unstrained cycloalkanes have similar energies, and we can use this approximation. Table 7-1 shows the heats of hydrogenation of a variety of alkenes with different substitution. The compounds are ranked in decreasing order of their heats of hydrogenation, that is, from the least stable double bonds to the most stable. Note that the values are similar for alkenes with similar substitution patterns.

The most stable double bonds are those with the most alkyl groups attached. For example, hydrogenation of ethylene (no alkyl groups attached) evolves 137 kJ/mol, while propene and pent-1-ene (one alkyl group for each) give off 126 kJ/mol. Double bonds with two alkyl groups hydrogenate to produce about 116–120 kJ/mol. Three or

TABLE 7-1 Molar Heats of Hydrogenation of Alkenes

Name	Structure	Molar Heat of Hydrogenation ($-\Delta H°$) kJ	kcal	General Structure
ethene (ethylene)	$H_2C{=}CH_2$	137	32.8	unsubstituted
propene (propylene)	$CH_3{-}CH{=}CH_2$	126	30.1	monosubstituted $R{-}CH{=}CH_2$
but-1-ene	$CH_3{-}CH_2{-}CH{=}CH_2$	127	30.3	
pent-1-ene	$CH_3{-}CH_2{-}CH_2{-}CH{=}CH_2$	126	30.1	
hex-1-ene	$CH_3{-}(CH_2)_3{-}CH{=}CH_2$	126	30.1	
3-methylbut-1-ene	$(CH_3)_2CH{-}CH{=}CH_2$	127	30.3	
3,3-dimethylbut-1-ene	$(CH_3)_3C{-}CH{=}CH_2$	127	30.3	
cis-but-2-ene		120	28.6	disubstituted (cis) 
cis-pent-2-ene		120	28.6	
2-methylpropene (isobutylene)	$(CH_3)_2C{=}CH_2$	117	28.0	disubstituted (geminal) 
2-methylbut-1-ene		119	28.5	
2,3-dimethylbut-1-ene		117	28.0	
trans-but-2-ene		116	27.6	disubstituted (trans) 
trans-pent-2-ene		116	27.6	
2-methylbut-2-ene		113	26.9	trisubstituted $R_2C{=}CHR$
2,3-dimethylbut-2-ene	$(CH_3)_2C{=}C(CH_3)_2$	111	26.6	tetrasubstituted $R_2C{=}CR_2$

Note: A lower heat of hydrogenation corresponds to lower energy and greater stability of the alkene.

four alkyl substituents further stabilize the double bond, as with 2-methylbut-2-ene (trisubstituted, 113 kJ/mol) and 2,3-dimethylbut-2-ene (tetrasubstituted, 111 kJ/mol).

The values in Table 7-1 confirm **Zaitsev's rule (Saytzeff's rule):**

> *More substituted double bonds are usually more stable.*

In other words, the alkyl groups attached to the double-bonded carbons stabilize the alkene.

Two factors are probably responsible for the stabilizing effect of alkyl groups on a double bond. Alkyl groups are electron-donating, and they contribute electron density to the pi bond. In addition, bulky substituents like alkyl groups are best situated as far apart as possible. In an alkane, they are separated by the tetrahedral bond angle, about 109.5°. A double bond increases this separation to about 120°. In general, alkyl groups are separated best by the most highly substituted double bond. This steric effect is illustrated in Figure 7-7 for two **double-bond isomers** (isomers that differ only in the position of the double bond). The isomer with the monosubstituted double bond separates the alkyl groups by only 109.5°, while the trisubstituted double bond separates them by about 120°.

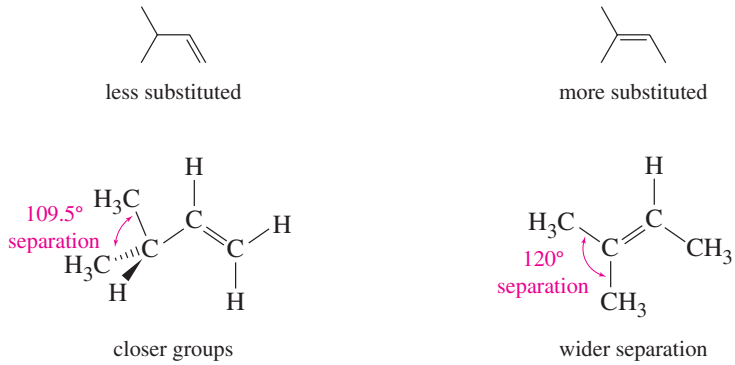


FIGURE 7-7
Bond angles in double-bond isomers. The isomer with the more substituted double bond has a larger angular separation between the bulky alkyl groups.

PROBLEM 7-9

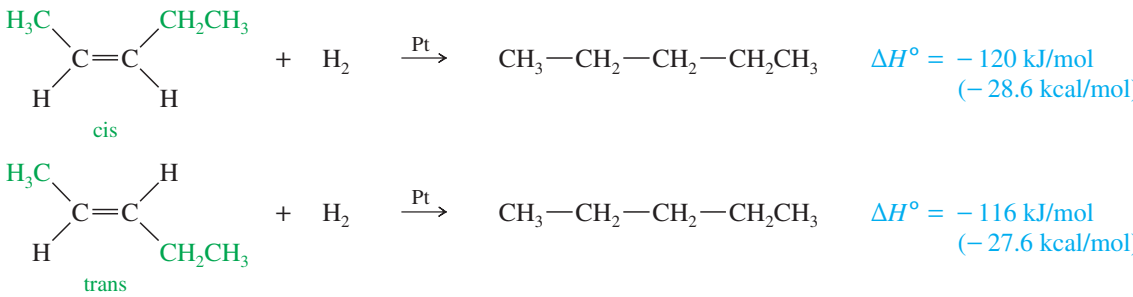
Use the data in Table 7-1 to predict the energy difference between 2,3-dimethyl-but-1-ene and 2,3-dimethylbut-2-ene. Which of these double-bond isomers is more stable?

Problem-solving Hint

Heats of hydrogenation are usually exothermic. A larger amount of heat given off implies a less stable alkene, because the less stable alkene starts from a higher potential energy.

7-7C Energy Differences in cis-trans Isomers

The heats of hydrogenation in Table 7-1 show that trans isomers are generally more stable than the corresponding cis isomers. This trend seems reasonable because the alkyl substituents are separated farther in trans isomers than they are in cis isomers. The greater stability of the trans isomer is evident in the pent-2-enes, which show a 4 kJ/mol (1.0 kcal/mol) difference between the cis and trans isomers.



A 4 kJ/mol difference between cis and trans isomers is typical for disubstituted alkenes. Figure 7-8 summarizes the relative stabilities of alkenes, comparing them with

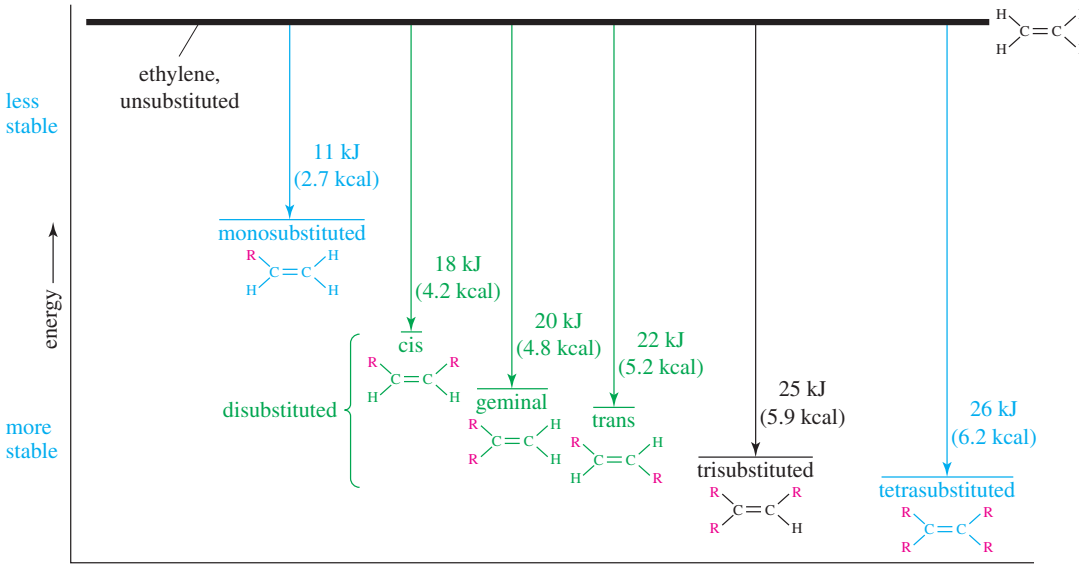


FIGURE 7-8
Relative energies of typical π bonds compared with ethylene. (The numbers are approximate.)

ethylene, the least stable of the simple alkenes. Geminal isomers, $CR_2{=}CH_2$, tend to fall between the cis and trans isomers in energy, but the differences are not as predictable as the cis/trans differences.

PROBLEM 7-10

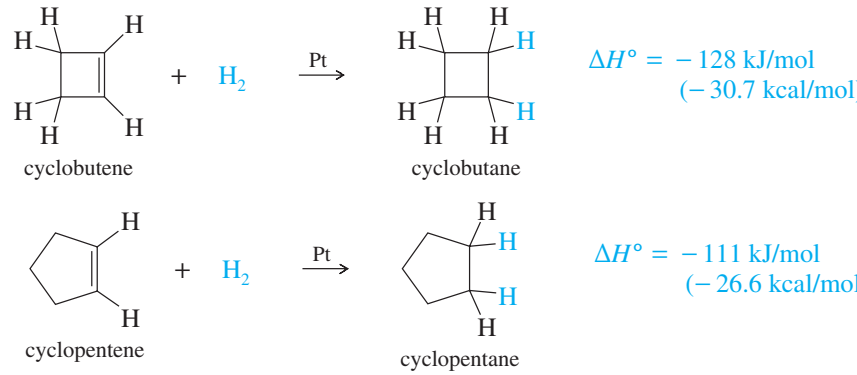
Using Table 7-1 as a guide, predict which member of each pair is more stable, and by about how many kJ/mol or kcal/mol.

(a) *cis,cis*-hexa-2,4-diene or *trans,trans*-hexa-2,4-diene
(b) 2-methylbut-1-ene or 3-methylbut-1-ene
(c) 2-methylbut-1-ene or 2-methylbut-2-ene
(d) 2,3-dimethylbut-1-ene or 2,3-dimethylbut-2-ene

7-7D Stability of Cycloalkenes

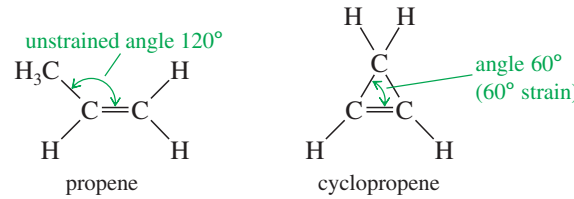
Most cycloalkenes react like acyclic (noncyclic) alkenes. The presence of a ring makes a major difference only if there is ring strain, either because of a small ring or because of a trans double bond. Rings that are five-membered or larger can easily accommodate double bonds, and these cycloalkenes react much like straight-chain alkenes. Three- and four-membered rings show evidence of ring strain, however.

Cyclobutene Cyclobutene has a heat of hydrogenation of −128 kJ/mol (−30.7 kcal/mol), compared with −111 kJ/mol (−26.6 kcal/mol) for cyclopentene.



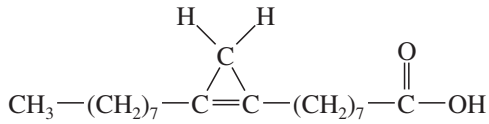
The double bond in cyclobutene has about 17 kJ/mol of *extra* ring strain (in addition to the ring strain in cyclobutane) by virtue of the small ring. The 90° bond angles in cyclobutene compress the angles of the sp^2 hybrid carbons (normally 120°) more than they compress the sp^3 hybrid angles (normally 109.5°) in cyclobutane. The extra ring strain in cyclobutene makes its double bond more reactive than a typical double bond.

Cyclopropene Cyclopropene has bond angles of about 60°, compressing the bond angles of the carbon–carbon double bond to half their usual value of 120°. The double bond in cyclopropene is highly strained.



Many chemists once believed that a cyclopropene could never be made because it would snap open (or polymerize) immediately from the large ring strain. Cyclopropene was eventually synthesized, however, and it can be stored in the cold. Cyclopropenes were still considered to be strange, highly unusual compounds. Natural-product chemists were surprised when they found that the kernel oil of *Sterculia foelida*, a tropical tree, contains *sterculic acid*, a carboxylic acid with a cyclopropene ring.

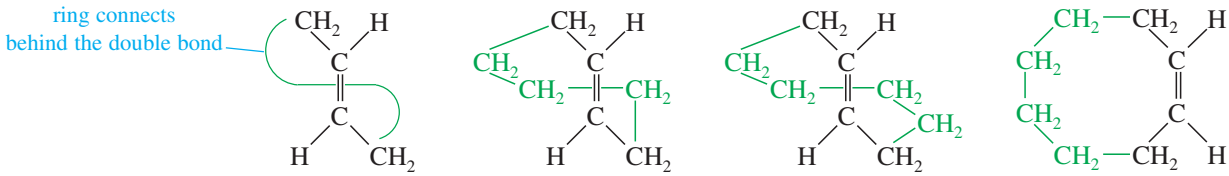
Application: Toxicology
Sterculic acid is a potent inhibitor of several desaturases, which are the enzymes responsible for the formation of double bonds in long-chain acids used as fuels, membrane components, and other critical biological molecules. Consequently, vegetable oils containing sterculic acid must be hydrogenated or processed at high temperatures to reduce or destroy the cyclopropene ring.



sterculic acid

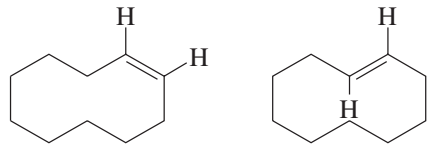
Trans Cycloalkenes Another difference between cyclic and acyclic alkenes is the relationship between cis and trans isomers. In acyclic alkenes, the trans isomers are usually more stable; but the trans isomers of small cycloalkenes are rare, and those with fewer than eight carbon atoms are unstable at room temperature. The problem with making a trans cycloalkene lies in the geometry of the trans double bond. The two alkyl groups on a trans double bond are so far apart that several carbon atoms are needed to complete the ring.

Try to make a model of *trans*-cyclohexene, being careful that the large amount of ring strain does not break your models. *trans*-Cyclohexene is too strained to be isolated, but *trans*-cycloheptene can be isolated at low temperatures. *trans*-Cyclooctene is stable at room temperature, although its cis isomer is still more stable.



trans cyclic system | *trans*-cycloheptene marginally stable | *trans*-cyclooctene stable | *cis*-cyclooctene more stable

Once a cycloalkene contains at least ten or more carbon atoms, it can easily accommodate a trans double bond. For cyclodecene and larger cycloalkenes, the trans isomer is nearly as stable as the cis isomer.



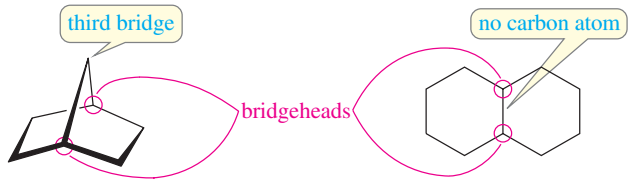
cis-cyclodecene | *trans*-cyclodecene

7-7E Bredt's Rule

We have seen that a trans cycloalkene is not stable unless there are at least eight carbon atoms in the ring. An interesting extension of this principle is called **Bredt's rule.**

> BREDT'S RULE: A bridged bicyclic compound cannot have a double bond at a bridgehead position unless one of the rings contains at least eight carbon atoms.

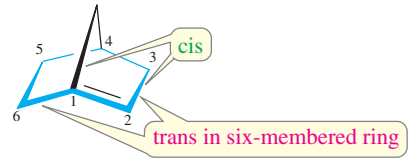
Let's review exactly what Bredt's rule means. A **bicyclic** compound is one that contains two rings. The **bridgehead carbon atoms** are part of both rings, with three links connecting them. A **bridged bicyclic** compound has at least one carbon atom in each of the three links between the bridgehead carbons. In the following examples, the bridgehead carbon atoms are circled in red.



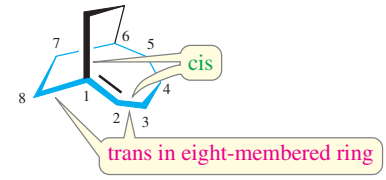
norbornane
a bridged bicyclic compound

decalin
a fused bicyclic compound

If there is a double bond at the bridgehead carbon of a bridged bicyclic system, one of the two rings contains a cis double bond and the other must contain a trans double bond. For example, the following structures show that norbornane contains a five-membered ring and a six-membered ring. If there is a double bond at the bridgehead carbon atom, the five-membered ring contains a cis double bond and the six-membered ring contains a trans double bond. This unstable arrangement is called a "Bredt's rule violation." If the larger ring contains at least eight carbon atoms, then it can contain a trans double bond and the bridgehead double bond is stable.



Bredt's rule violation

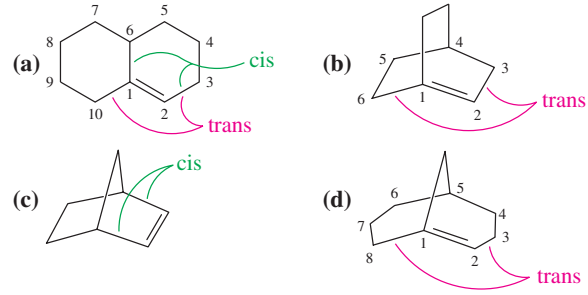


Stable: trans in an eight-membered ring

In general, compounds that violate Bredt's rule are not stable at room temperature. In a few cases, such compounds (usually with seven carbon atoms in the largest ring) have been synthesized at low temperatures.

SOLVED PROBLEM 7-2

Which of the following alkenes are stable?



SOLUTION

Compound (a) is stable. Although the double bond is at a bridgehead, it is not a bridged bicyclic system. The trans double bond is in a 10-membered ring. Compound (b) is a Bredt's rule violation and is not stable. The largest ring contains six carbon atoms, and the trans double bond cannot be stable in this bridgehead position.

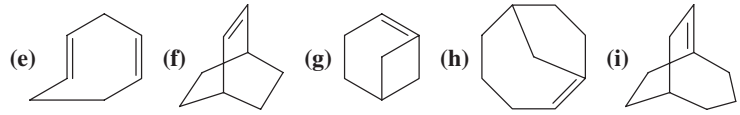
Compound (c) (norbornene) is stable. The (cis) double bond is not at a bridgehead carbon.

Compound (d) is stable. Although the double bond is at the bridgehead of a bridged bicyclic system, there is an eight-membered ring to accommodate the trans double bond.

PROBLEM 7-11

Explain why each of the following alkenes is stable or unstable.

(a) 1,2-dimethylcyclopentene
(b) *trans*-1,2-dimethylcyclopentene
(c) *trans*-3,4-dimethylcyclopentene
(d) *trans*-1,2-dimethylcyclodecene



7-8 Physical Properties of Alkenes

7-8A Boiling Points and Densities

Most physical properties of alkenes are similar to those of the corresponding alkanes. For example, the boiling points of but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene, and *n*-butane

are all close to 0 °C. Also like the alkanes, alkenes have densities around 0.6 or 0.7 g/cm^3. The boiling points and densities of some representative alkenes are listed in Table 7-2. The table shows that boiling points of alkenes increase smoothly with molecular weight. As with alkanes, increased branching leads to greater volatility and lower boiling points. For example, 2-methylpropene (isobutylene) has a boiling point of −7 °C, which is lower than the boiling point of any of the unbranched butenes.

7-8B Polarity

Like alkanes, alkenes are relatively nonpolar. They are insoluble in water but soluble in nonpolar solvents such as hexane, gasoline, halogenated solvents, and ethers. Alkenes tend to be slightly more polar than alkanes, however, for two reasons: The more weakly held electrons in the pi bond are more polarizable (contributing to instantaneous dipole moments), and the vinylic bonds tend to be slightly polar (contributing to a permanent dipole moment).

Alkyl groups are slightly electron-donating toward a double bond, helping to stabilize it. This donation slightly polarizes the vinylic bond, with a small partial positive charge on the alkyl group and a small negative charge on the double-bond carbon atom. For example, propene has a small dipole moment of 0.35 D.

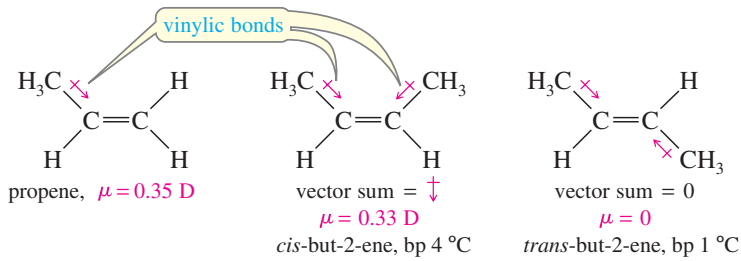
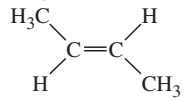
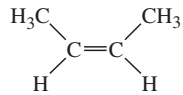
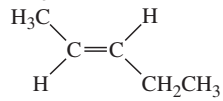
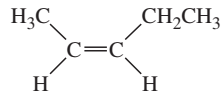


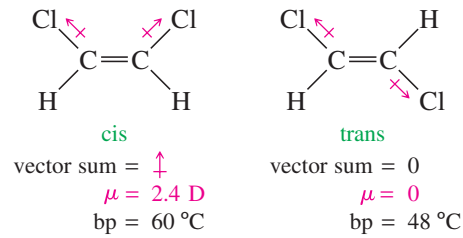
TABLE 7-2 Physical Properties of Some Representative Alkenes

Name	Structure	Carbons	Boiling Point (°C)	Density (g/cm^3)
ethene (ethylene)	$CH_2{=}CH_2$	2	−104	
propene (propylene)	$CH_3CH{=}CH_2$	3	−47	0.52
2-methylpropene (isobutylene)	$(CH_3)_2C{=}CH_2$	4	−7	0.59
but-1-ene	$CH_3CH_2CH{=}CH_2$	4	−6	0.59
trans-but-2-ene		4	1	0.60
cis-but-2-ene		4	4	0.62
3-methylbut-1-ene	$(CH_3)_2CH{-}CH{=}CH_2$	5	25	0.65
pent-1-ene	$CH_3CH_2CH_2{-}CH{=}CH_2$	5	30	0.64
trans-pent-2-ene		5	36	0.65
cis-pent-2-ene		5	37	0.66
2-methylbut-2-ene	$(CH_3)_2C{=}CH{-}CH_3$	5	39	0.66
hex-1-ene	$CH_3(CH_2)_3{-}CH{=}CH_2$	6	64	0.68
2,3-dimethylbut-2-ene	$(CH_3)_2C{=}C(CH_3)_2$	6	73	0.71
hept-1-ene	$CH_3(CH_2)_4{-}CH{=}CH_2$	7	93	0.70
oct-1-ene	$CH_3(CH_2)_5{-}CH{=}CH_2$	8	122	0.72
non-1-ene	$CH_3(CH_2)_6{-}CH{=}CH_2$	9	146	0.73
dec-1-ene	$CH_3(CH_2)_7{-}CH{=}CH_2$	10	171	0.74

In a cis-disubstituted alkene, the vector sum of the two dipole moments is directed perpendicular to the double bond. In a trans-disubstituted alkene, the two dipole moments tend to cancel out. If an alkene is symmetrically trans disubstituted, the dipole moment is zero. For example, *cis*-but-2-ene has a nonzero dipole moment, but *trans*-but-2-ene has no measurable dipole moment.

Compounds with permanent dipole moments engage in dipole–dipole attractions, while those without permanent dipole moments engage only in van der Waals attractions. *cis*-But-2-ene and *trans*-but-2-ene have similar van der Waals attractions, but only the cis isomer has dipole–dipole attractions. Because of its increased intermolecular attractions, *cis*-but-2-ene must be heated to a slightly higher temperature (4 °C versus 1 °C) before it begins to boil.

The effect of bond polarity is even more apparent in the 1,2-dichloroethenes, with their strongly polar carbon–chlorine bonds. The cis isomer has a large dipole moment (2.4 D), giving it a boiling point 12 degrees higher than the trans isomer, with zero dipole moment.



PROBLEM 7-12

For each pair of compounds, predict the one with a higher boiling point. Which compounds have zero dipole moments?

(a) *cis*-1,2-dichloroethene or *cis*-1,2-dibromoethene
(b) *cis*- or *trans*-2,3-dichlorobut-2-ene
(c) cyclohexene or 1,2-dichlorocyclohexene

7-9 Alkene Synthesis by Elimination of Alkyl Halides

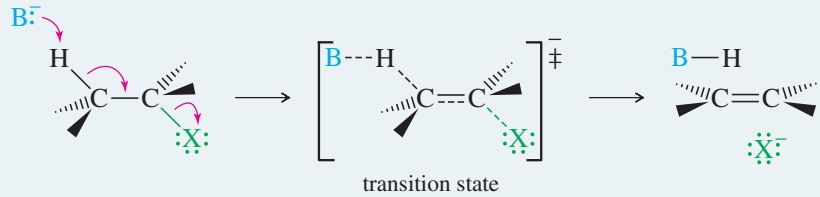
Dehydrohalogenation is the elimination of a hydrogen and a halogen from an alkyl halide to form an alkene. In Sections 6-17 through 6-21 we saw how dehydrohalogenation can take place by the E1 and E2 mechanisms. The second-order elimination (E2) is usually better for synthetic purposes because the E1 has more competing reactions.

7-9A Dehydrohalogenation by the E2 Mechanism

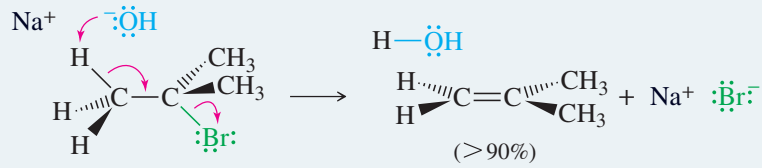
Second-order elimination is a reliable synthetic reaction, especially if the alkyl halide is a poor S_N2 substrate. E2 dehydrohalogenation takes place in one step, in which a strong base abstracts a proton from one carbon atom as the leaving group leaves the adjacent carbon.

MECHANISM 7-1 Dehydrohalogenation by the E2 Mechanism

E2 elimination takes place by a concerted one-step reaction.
A strong base abstracts a proton on a carbon next to the one bearing a halogen.
The leaving group (halide) leaves simultaneously.

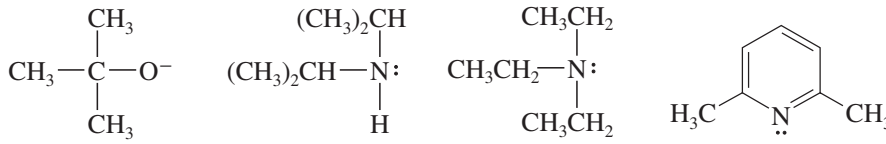


EXAMPLE: E2 elimination of *tert*-butyl bromide with sodium hydroxide.



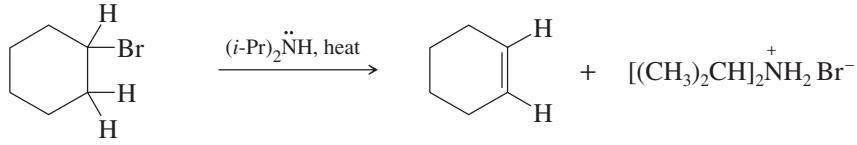
The E2 dehydrohalogenation gives excellent yields with bulky secondary and tertiary alkyl halides, such as *tert*-butyl bromide in the preceding example. A strong base forces second-order elimination (E2) by abstracting a proton. The molecule's bulkiness hinders second-order substitution (S_N2), and a relatively pure elimination product results. Tertiary halides are the best E2 substrates because they are prone to elimination and cannot undergo S_N2 substitution.

Use of a Bulky Base If the substrate is prone to substitution, a bulky base can minimize the amount of substitution. Large alkyl groups on a bulky base hinder its approach to attack a carbon atom (substitution), yet it can easily abstract a proton (elimination). Some of the bulky strong bases commonly used for elimination are *tert*-butoxide ion, diisopropylamine, triethylamine, and 2,6-dimethylpyridine.



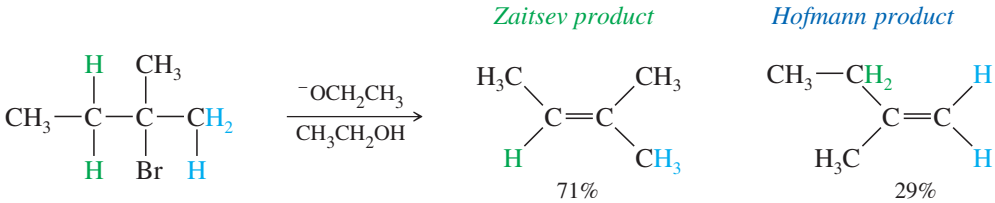
tert-butoxide diisopropylamine triethylamine 2,6-dimethylpyridine

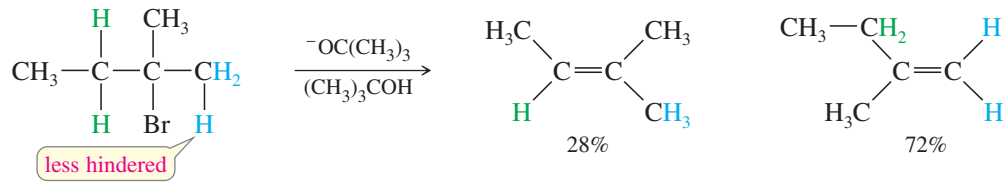
The dehydrohalogenation of bromocyclohexane illustrates the use of a bulky base for elimination. Bromocyclohexane, a secondary alkyl halide, can undergo both substitution and elimination. Elimination (E2) is favored over substitution (S_N2) by using a bulky base such as diisopropylamine. Diisopropylamine is too bulky to be a good nucleophile, but it acts as a strong base to abstract a proton.



bromocyclohexane cyclohexene (93%)

Formation of the Hofmann Product Bulky bases can also accomplish dehydrohalogenations that do not follow the Zaitsev rule. Steric hindrance often prevents a bulky base from abstracting the proton that leads to the most highly substituted alkene. In these cases, it abstracts a less hindered proton, often the one that leads to formation of the least highly substituted product, called the **Hofmann product.** The following reaction gives mostly the **Zaitsev product** with the relatively unhindered ethoxide ion, but mostly the Hofmann product with the bulky *tert*-butoxide ion.





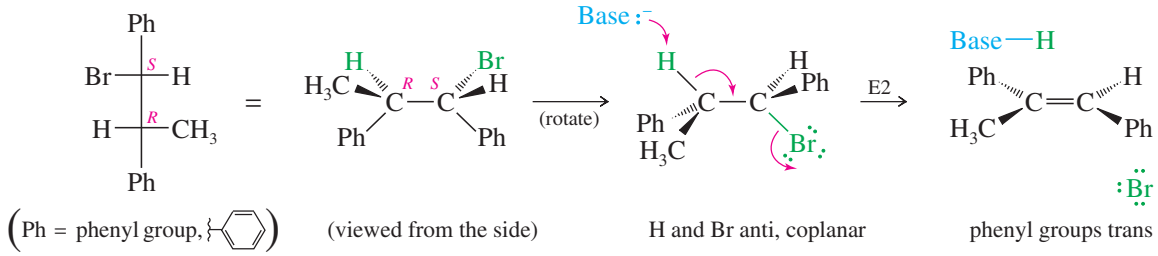
PROBLEM 7-13

For each reaction, decide whether substitution or elimination (or both) is possible, and predict the products you expect. Label the major products.

(a) 1-bromo-1-methylcyclohexane + NaOH in acetone
(b) 1-bromo-1-methylcyclohexane + triethylamine (Et_3N:)
(c) chlorocyclohexane + $NaOCH_3$ in CH_3OH
(d) chlorocyclohexane + $NaOC(CH_3)_3$ in $(CH_3)_3COH$

7-9B Stereospecific E2 Reactions

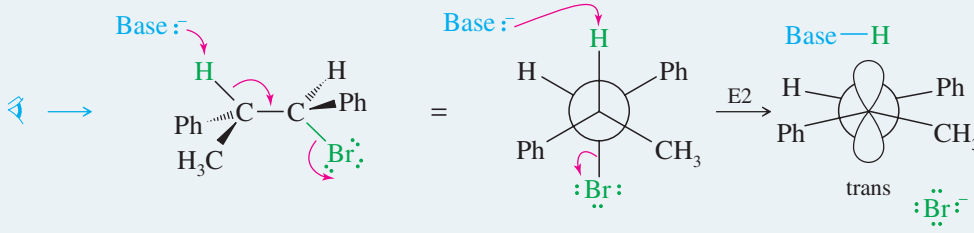
Like the S_N2 reaction (Section 6-12), the E2 is **stereospecific:** Different stereoisomers of the reactant give different stereoisomers of the product. The E2 is stereospecific because it normally goes through an anti and coplanar transition state. The products are alkenes, and different diastereomers of starting materials commonly give different diastereomers of alkenes. In Problem 6-38, you showed why the E2 elimination of one diastereomer of 1-bromo-1,2-diphenylpropane gives only the trans isomer of the alkene product.



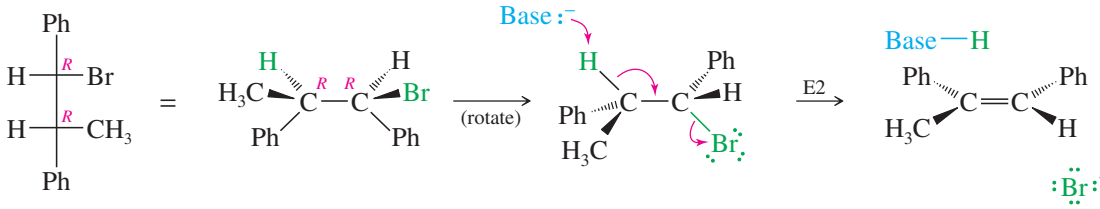
If we make a model and look at this reaction from the left end of the molecule, the anti and coplanar arrangement of the H and Br is apparent.

MECHANISM 7-2 Stereochemistry of the E2 Reaction

Most E2 reactions go through an anti-coplanar transition state. This geometry is most apparent if we view the reaction sighting down the carbon–carbon bond between the hydrogen and leaving group. Viewed from the left:

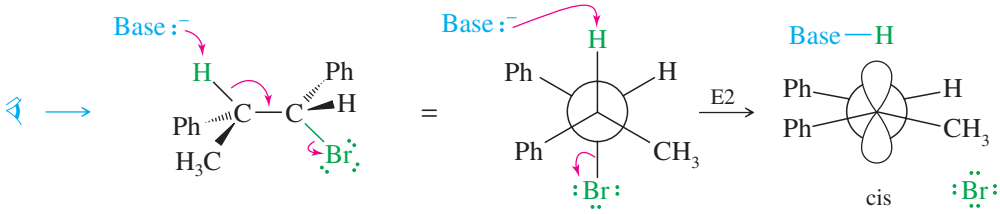


The following reaction shows how the anti-coplanar elimination of the other diastereomer (*R,R*) gives only the cis isomer of the product. In effect, the two different diastereomers of the reactant give two different diastereomers of the product: a stereospecific result.



(viewed from the side) H and Br anti, coplanar phenyl groups cis

Viewed from the left end of the molecule:



PROBLEM 7-14

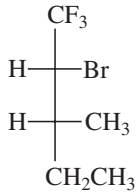
Show that the (*S,S*) enantiomer of this (*R,R*) diastereomer of 1-bromo-1,2-diphenylpropane also undergoes E2 elimination to give the cis diastereomer of the product. (We do not expect these achiral reagents to distinguish between enantiomers.)

Problem-solving Hint

Don't try to memorize your way through these reactions. Look at each one, and consider what it might do. Use your models for the ones that involve stereochemistry.

PROBLEM 7-15

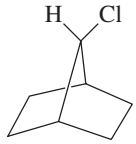
Make models of the following compounds, and predict the products formed when they react with the strong bases shown.

(a) 

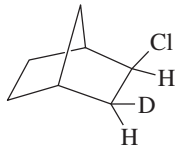
+ KOH ⟶ (substitution and elimination)

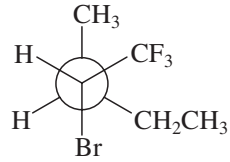
(b) *meso*-1,2-dibromo-1,2-diphenylethane + $(CH_3CH_2)_3N$:

(c) (*d,l*)-1,2-dibromo-1,2-diphenylethane + $(CH_3CH_2)_3N$:

(d) 

+ NaOH in acetone

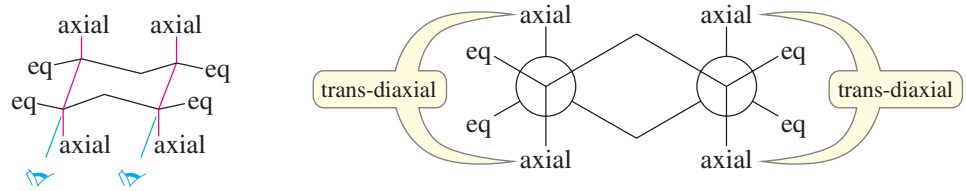
(e) 

+ $(CH_3)_3CO^-$ **(f)** 

+ $NaOCH(CH_3)_2$

7-9C E2 Reactions in Cyclohexane Systems

Nearly all cyclohexanes are most stable in chair conformations. In the chair, all the carbon–carbon bonds are staggered, and any two adjacent carbon atoms have axial bonds in an anti-coplanar conformation, ideally oriented for the E2 reaction. (As drawn in the following figure, the axial bonds are vertical.) On any two adjacent carbon atoms, one has its axial bond pointing up and the other has its axial bond pointing down. These two bonds are trans to each other, and we refer to their geometry as **trans-diaxial.**



perspective view Newman projection

An E2 elimination can take place on this chair conformation only if the proton and the leaving group can get into a trans-diaxial arrangement. Figure 7-9 shows the E2 dehydrohalogenation of bromocyclohexane. The molecule must flip into the chair conformation with the bromine atom axial before elimination can occur.

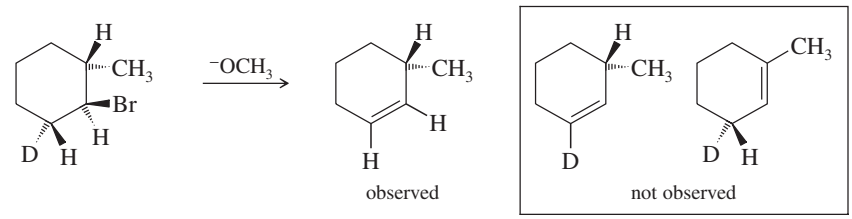
(You should make models of the structures in the following examples and problems so you can follow along more easily.)

Problem-solving Hint

In a chair conformation of a cyclohexane ring, a trans-diaxial arrangement places the two groups anti and coplanar.

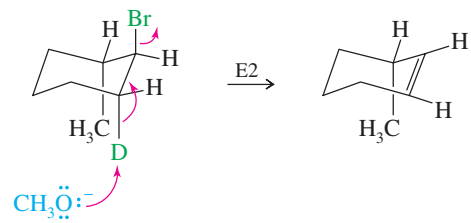
SOLVED PROBLEM 7-3

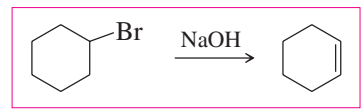
Explain why the following deuterated 1-bromo-2-methylcyclohexane undergoes dehydrohalogenation by the E2 mechanism, to give only the indicated product. Two other alkenes are not observed.



SOLUTION

In an E2 elimination, the hydrogen atom and the leaving group must have a trans-diaxial relationship. In this compound, only one hydrogen atom—the deuterium—is trans to the bromine atom. When the bromine atom is axial, the adjacent deuterium is also axial, providing a trans-diaxial arrangement.





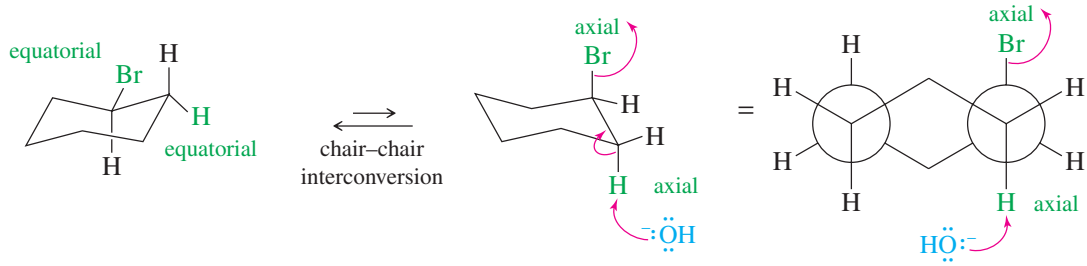


FIGURE 7-9
E2 eliminations on cyclohexane rings. E2 elimination of bromocyclohexane requires that both the proton and the leaving group be trans and both be axial.

PROBLEM 7-16

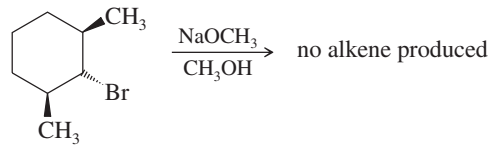
Predict the elimination products of the following reactions, and label the major products.

(a) *cis*-1-bromo-2-methylcyclohexane + $NaOCH_3$ in CH_3OH

(b) *trans*-1-bromo-2-methylcyclohexane + $NaOCH_3$ in CH_3OH

PROBLEM 7-17

When the following stereoisomer of 2-bromo-1,3-dimethylcyclohexane is treated with sodium methoxide, no E2 reaction is observed. Explain why this compound cannot undergo the E2 reaction in the chair conformation.

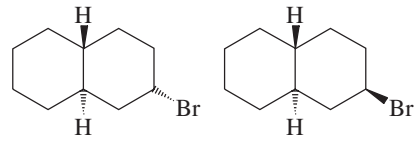


Problem-solving Hint

Look for a hydrogen trans to the leaving group; then see if the hydrogen and the leaving group can become diaxial.

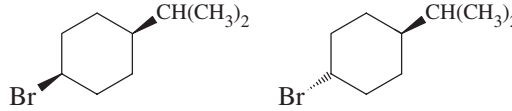
PROBLEM 7-18

(a) Two stereoisomers of a bromodecalin are shown. Although the difference between these stereoisomers may seem trivial, one isomer undergoes elimination with KOH much faster than the other. Predict the products of these eliminations, and explain the large difference in the ease of elimination.



fast elimination slow elimination

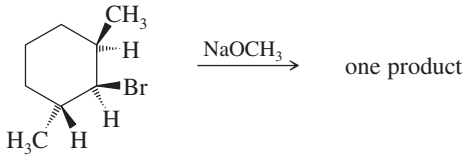
(b) Predict which of the following compounds will undergo elimination with KOH faster, and explain why. Predict the major product that will be formed.



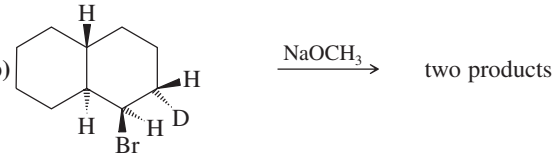
PROBLEM 7-19

Give the expected product(s) of E2 elimination for each reaction. (*Hint*: Use models!)

(a)

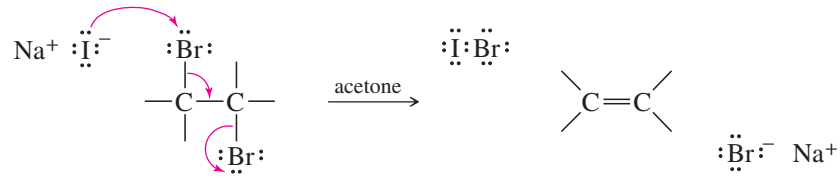


(b)



7-9D Debromination of Vicinal Dibromides

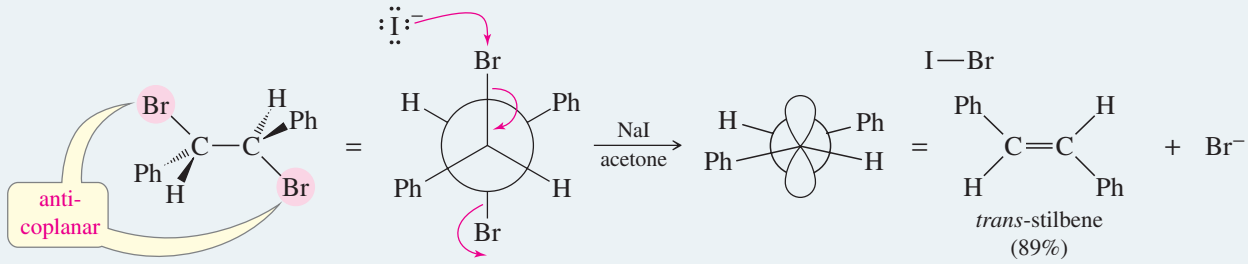
Vicinal dibromides (two bromines on adjacent carbon atoms) are converted to alkenes by reduction with iodide ion in acetone. This **debromination** is rarely an important synthetic reaction, because the most likely origin of a vicinal dibromide is from bromination of an alkene (Section 8-10). We discuss this reaction with dehydrohalogenation because the mechanisms are similar.



Debromination is formally a reduction because a molecule of Br_2 (an oxidizing agent) is removed. The reaction with iodide takes place by the E2 mechanism, with the same geometric constraints as the E2 dehydrohalogenation. Elimination usually takes place through an anti-coplanar arrangement, as shown in Mechanism 7-3. Acetone serves as a convenient solvent that dissolves most alkyl halides and sodium iodide.

MECHANISM 7-3 E2 Debromination of a Vicinal Dibromide

E2 debromination takes place by a concerted, stereospecific mechanism. Iodide ion removes one bromine atom, and the other bromine leaves as bromide ion.



meso-1,2-dibromo-1,2-diphenylethane

Use your models to show that only the trans isomer of stilbene is formed in this example by elimination through the anti-coplanar transition state.

PROBLEM 7-20

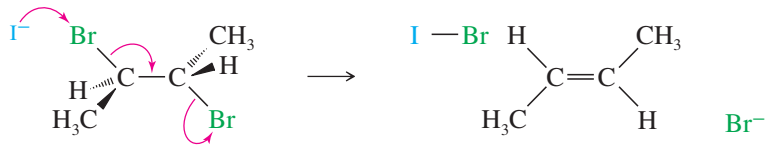
The preceding example shows *meso*-1,2-dibromo-1,2-diphenylethane reacting with iodide ion to give *trans*-stilbene. Show how the other diastereomer of the starting material gives a different stereoisomer of the product.

SOLVED PROBLEM 7-4

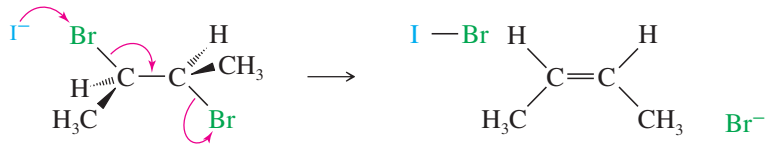
Show that the dehalogenation of 2,3-dibromobutane by iodide ion is stereospecific by showing that the two diastereomers of the starting material give different diastereomers of the product.

SOLUTION

Rotating *meso*-2,3-dibromobutane into a conformation where the bromine atoms are anti and coplanar, we find that the product will be *trans*-but-2-ene. A similar conformation of either enantiomer of the (±) diastereomer shows that the product will be *cis*-but-2-ene. (*Hint*: Your models will be helpful.)



meso-2,3-dibromobutane *trans*-but-2-ene



(R,R)-2,3-dibromobutane *cis*-but-2-ene

PROBLEM 7-21

Solved Problem 7-4 showed that the debromination of (*R*,*R*)-2,3-dibromobutane gives *cis*-but-2-ene. Draw the same reaction using the (*S*,*S*) enantiomer and show that it gives the same diastereomer of the product.

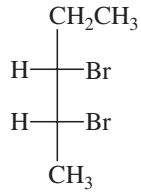
PROBLEM 7-22

Predict the elimination products formed by debromination of the following compounds with iodide ion in acetone. Include stereochemistry, and give a correct name for each product.

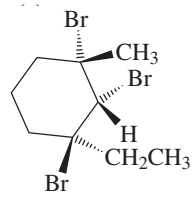
(a) *trans*-1,2-dibromocyclohexane

(b) (3*R*,4*R*)-3,4-dibromoheptane

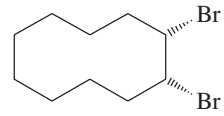
(c)



(d)



(e)

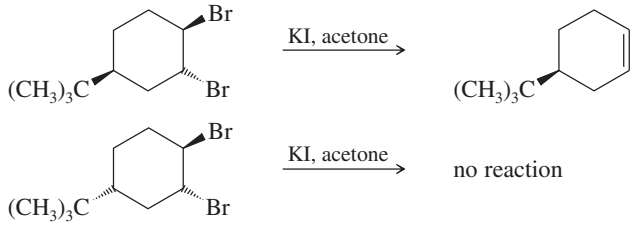


Problem-solving Hint

Make a model of each compound, and place it in the conformation where the groups to be eliminated are anti and coplanar. The positions of the other groups will be near their positions in the alkene product.

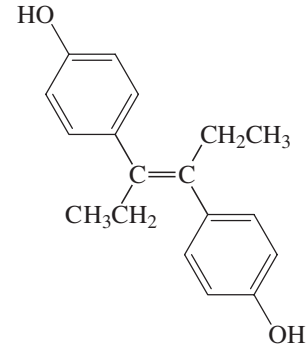
PROBLEM 7-23

The following compounds show different rates of debromination. One reacts quite fast, and the other seems not to react at all. Explain this surprising difference in rates.



Application: Drug Side Effects

A derivative of *trans*-stilbene known as diethylstilbestrol, or DES, was once taken by women during pregnancy to prevent miscarriages. The use of DES was discontinued because studies showed that DES increases the risk of cervical cancer in the children of women who take it.



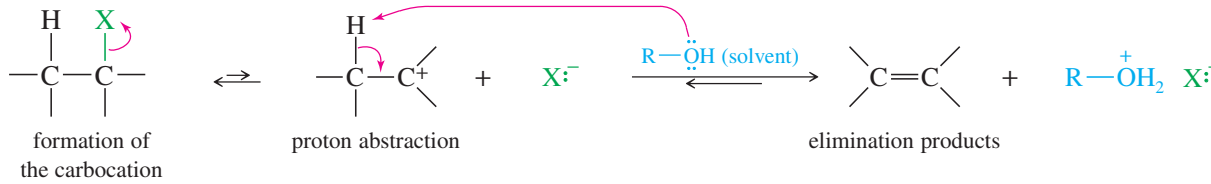
diethylstilbestrol (DES)

7-9E Dehydrohalogenation by the E1 Mechanism

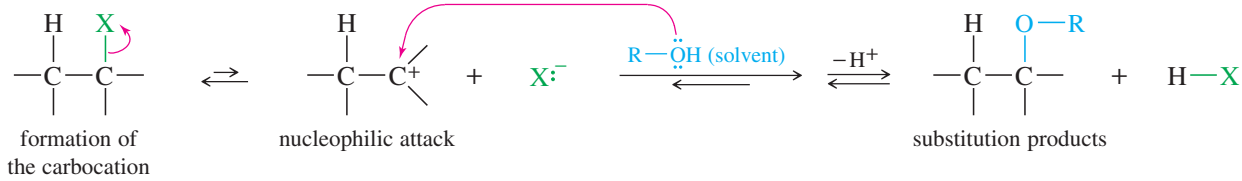
First-order dehydrohalogenation usually takes place in a good ionizing solvent (such as an alcohol or water), without a strong nucleophile or base to force second-order kinetics. The substrate is usually a secondary or tertiary alkyl halide. First-order elimination requires ionization to form a carbocation, which loses a proton to a weak base

(usually the solvent). El dehydrohalogenation is generally accompanied by S_N1 substitution, because the nucleophilic solvent can also attack the carbocation directly to form the substitution product.

Elimination by the E1 mechanism



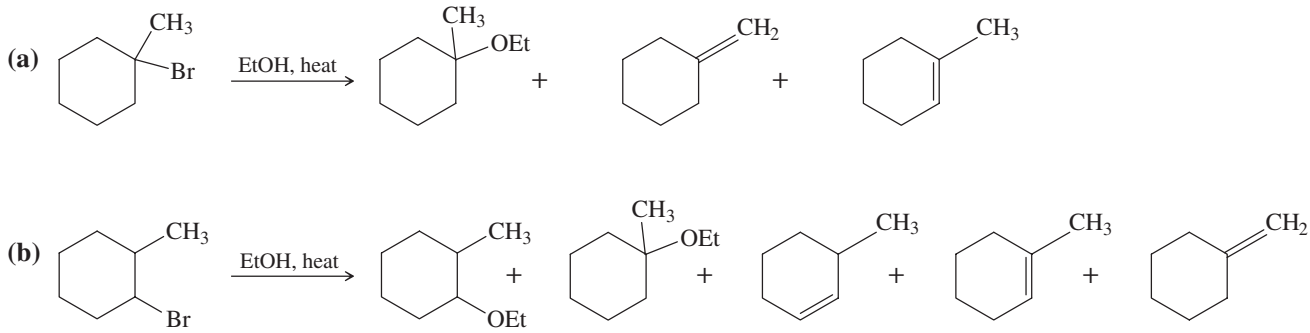
Accompanied by S_N1 substitution



Like all reactions involving carbocation intermediates, E1 dehydrohalogenations are prone to rearrangement, as shown in Problem 7-24.

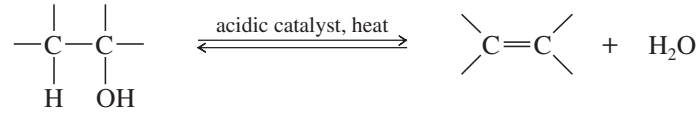
PROBLEM 7-24

Propose mechanisms for the following reactions.



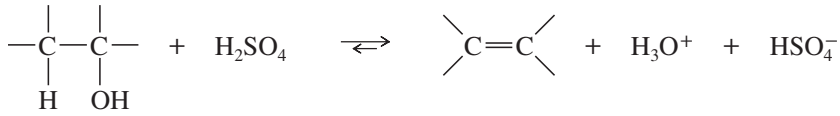
7-10 Alkene Synthesis by Dehydration of Alcohols

Dehydration of alcohols is a common method for making alkenes. The word *dehydration* literally means "removal of water."



Dehydration is reversible, and in most cases the equilibrium constant is not large. In fact, the reverse reaction (hydration) is a method for converting alkenes to alcohols (see Section 8-4). Dehydration can be forced to completion by removing the products from the reaction mixture as they form. The alkene boils at a lower temperature than the alcohol because the alcohol is hydrogen bonded. A carefully controlled distillation removes the alkene while leaving the alcohol in the reaction mixture.

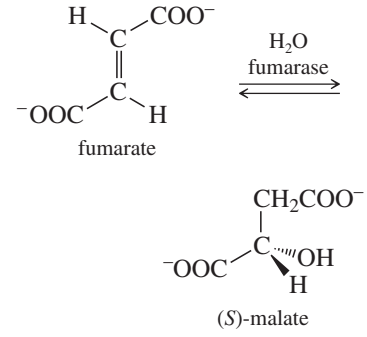
Concentrated sulfuric acid and/or concentrated phosphoric acid are often used as reagents for dehydration because these acids act both as acidic catalysts and as dehydrating agents. Hydration of these acids is strongly exothermic. The overall reaction (using sulfuric acid) is



The mechanism of dehydration resembles the E1 mechanism introduced in Chapter 6 (Mechanism 6-8, p. 258). The hydroxyl group of the alcohol is a poor leaving group (^{-}OH), but protonation by the acidic catalyst converts it to a good leaving group (H_2O). In the second step, loss of water from the protonated alcohol gives a carbocation. The carbocation is a very strong acid: Any weak base such as H_2O or HSO_4^- can abstract the proton in the final step to give the alkene.

Application: Biochemistry

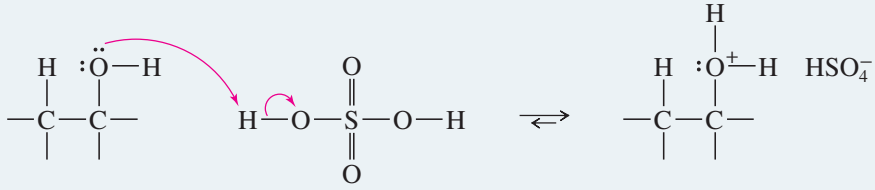
Hydration and dehydration reactions are common in biological pathways. The enzyme fumarase catalyzes the reversible addition of water to the double bond of fumarate to form malate. In contrast to the harsh conditions used in the chemical reaction, the enzymatic reaction takes place at neutral pH and at 37 °C.



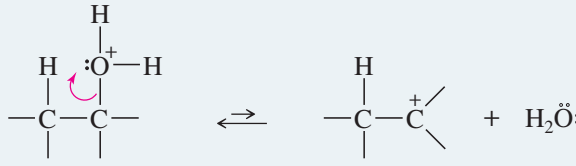
KEY MECHANISM 7-4 Acid-Catalyzed Dehydration of an Alcohol

Alcohol dehydrations usually involve E1 elimination of the protonated alcohol.

Step 1: Protonation of the hydroxyl group (fast equilibrium).



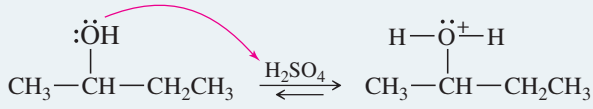
Step 2: Ionization to a carbocation (slow; rate limiting).



Step 3: Deprotonation to give the alkene (fast).

EXAMPLE: Acid-catalyzed dehydration of butan-2-ol

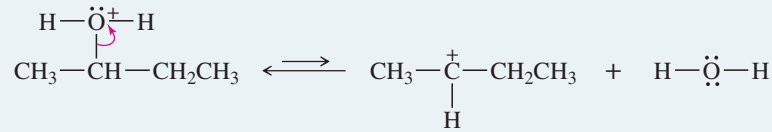
Step 1: Protonation of the hydroxyl group (fast equilibrium).



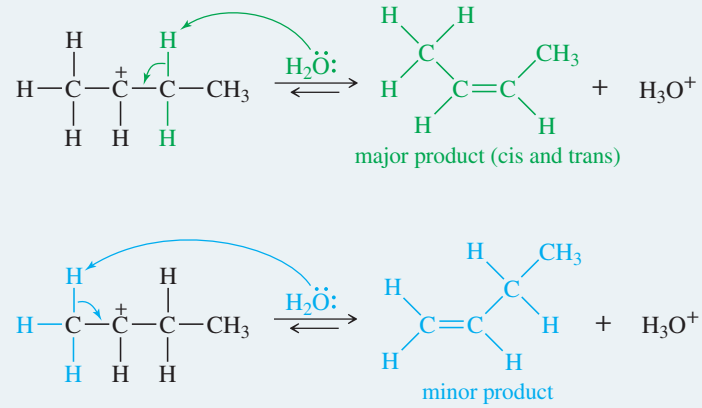
Problem-solving Hint

In acid-catalyzed mechanisms, the first step is often addition of H^+, and the last step is often loss of H^+.

Step 2: Ionization to a carbocation (slow; rate limiting).



Step 3: Deprotonation to give the alkene (fast).



Like other E1 reactions, alcohol dehydration follows an order of reactivity that reflects carbocation stability: 3° alcohols react faster than 2° alcohols, and 1° alcohols are the least reactive. Rearrangements of the carbocation intermediates are common in alcohol dehydrations. In most cases, Zaitsev's rule applies: The major product is usually the one with the most substituted double bond.

Problem-solving Hint

Alcohol dehydrations usually go through E1 elimination of the protonated alcohol.

Reactivity is: 3° > 2° ≫ 1°

Rearrangements are common.

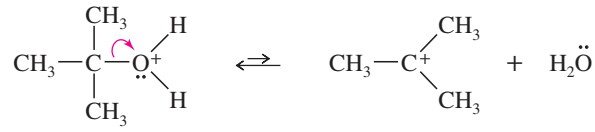
SOLVED PROBLEM 7-5

Propose a mechanism for the sulfuric acid–catalyzed dehydration of *tert*-butyl alcohol.

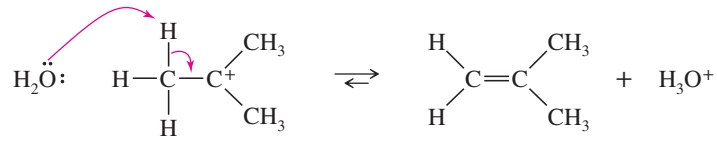
SOLUTION

The first step is protonation of the hydroxyl group, which converts it to a good leaving group.

The second step is ionization of the protonated alcohol to give a carbocation.

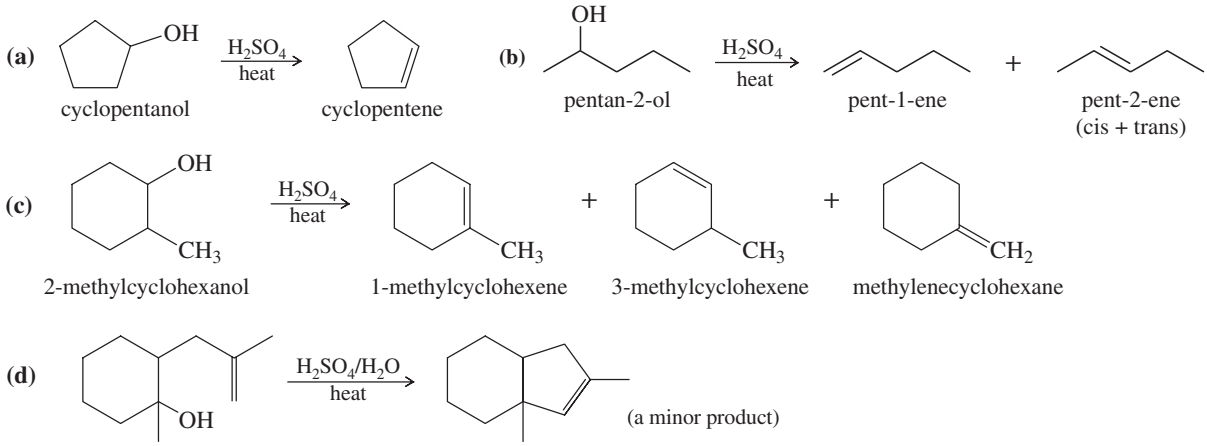


Abstraction of a proton completes the mechanism.



PROBLEM 7-25

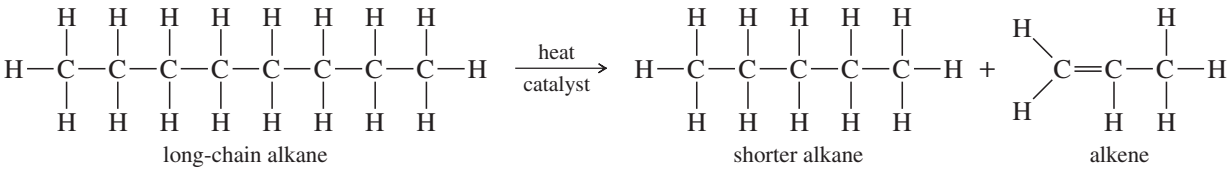
Propose mechanisms for the following reactions.



7-11 Alkene Synthesis by High-Temperature Industrial Methods

7-11A Catalytic Cracking of Alkanes

The least expensive way to make alkenes on a large scale is by the **catalytic cracking** of petroleum: heating a mixture of alkanes in the presence of a catalyst (usually aluminosilicates). Alkenes are formed by bond cleavage to give an alkene and a shortened alkane.



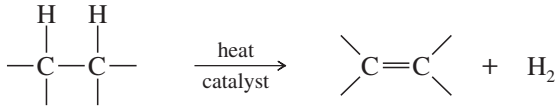
Cracking is used primarily to make small alkenes, up to about six carbon atoms. Its value depends on having a market for all the different alkenes and alkanes produced. The average molecular weight and the relative amounts of alkanes and alkenes can be controlled by varying the temperature, catalyst, and concentration of hydrogen in the cracking process. A careful distillation on a huge column separates the mixture into its pure components, ready to be packaged and sold.

Because the products are always mixtures, catalytic cracking is unsuitable for laboratory synthesis of alkenes. Better methods are available for synthesizing relatively pure alkenes from a variety of other functional groups. Several of these methods are discussed in Sections 7-9, 7-10, and later sections listed in the summary on page 320.

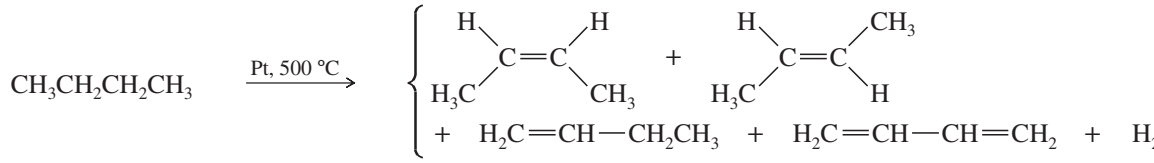
This plant in Tokuyama, Japan, passes ethane rapidly over a hot catalyst. The products are ethylene and hydrogen.

7-11B Dehydrogenation of Alkanes

Dehydrogenation is the removal of H_2 from a molecule, just the reverse of hydrogenation. Dehydrogenation of an alkane gives an alkene. This reaction has an unfavorable enthalpy change but a favorable entropy change.



$\Delta H^\circ = +80$ to $+120$ kJ/mol ($+20$ to $+30$ kcal/mol) $\Delta S^\circ = +125$ J/kelvin-mol



The hydrogenation of alkenes (Section 7-7) is exothermic, with values of $\Delta H°$ around -80 to -120 kJ/mol (-20 to -30 kcal/mol). Therefore, dehydrogenation is endothermic and has an unfavorable (positive) value of $\Delta H°$. The entropy change for dehydrogenation is strongly favorable ($\Delta S° = +120$ J/kelvin-mol), however, because one alkane molecule is converted into two molecules (the alkene and hydrogen), and two molecules are more disordered than one.

The equilibrium constant for the hydrogenation–dehydrogenation equilibrium depends on the change in free energy, $\Delta G = \Delta H - T\Delta S$. At room temperature, the enthalpy term predominates and hydrogenation is favored. When the temperature is raised, however, the entropy term ($-T\Delta S$) becomes larger and eventually dominates the expression. At a sufficiently high temperature, dehydrogenation is favored.

PROBLEM 7-26

The dehydrogenation of butane to *trans*-but-2-ene has $\Delta H° = +116$ kJ/mol (+27.6 kcal/mol) and $\Delta S° = +117$ J/kelvin-mol (+28.0 cal/kelvin-mol).

(a) Compute the value of $\Delta G°$ for dehydrogenation at room temperature (25 °C or 298 °K). Is dehydrogenation favored or disfavored?

(b) Compute the value of ΔG for dehydrogenation at 1000 °C, assuming ΔS and ΔH are constant. Is dehydrogenation favored or disfavored?

In many ways, dehydrogenation is similar to catalytic cracking. In both cases, a catalyst lowers the activation energy, and both reactions use high temperatures to increase a favorable entropy term ($-T\Delta S$) and overcome an unfavorable enthalpy term (ΔH). Unfortunately, dehydrogenation and catalytic cracking also share a tendency to produce mixtures of products, and neither reaction is well suited for the laboratory synthesis of alkenes.

PROBLEM-SOLVING STRATEGY

Proposing Reaction Mechanisms

At this point, we have seen examples of three major classes of reaction mechanisms:

- Those involving strong bases and strong nucleophiles
- Those involving strong acids and strong electrophiles
- Those involving free radicals

Many students have difficulty proposing mechanisms. We can use some general principles to approach this process, however, by breaking it down into a series of logical steps. Using a systematic approach, we can usually come up with a mechanism that is at least possible and that explains the products, without requiring any unusual steps. Appendix 3A contains more complete methods for approaching mechanism problems.

First, Classify the Reaction

Before you begin to propose a mechanism, you must determine what kind of reaction you are dealing with. Examine what you know about the reactants and the reaction conditions:

A free-radical initiator such as chlorine, bromine, or a peroxide (with heat or light) suggests that a free-radical chain reaction is most likely. Free-radical reactions were discussed in detail in Chapter 4.

Strong acids or strong electrophiles (or a reactant that can dissociate to give a strong electrophile) suggest mechanisms such as the S_N1, E1, alcohol dehydration, etc. that involve carbocations and other strongly acidic intermediates.

Strong bases or strong nucleophiles suggest mechanisms such as the S_N2 or E2, involving attack by the strong base or nucleophile on a substrate.

General Principles for Drawing Mechanisms

Once you have decided which type of mechanism is most likely (acidic, basic, or free-radical), some general principles can guide you in proposing the mechanism. Some principles for free-radical reactions were discussed in Chapter 4. Now we consider reactions that involve either strong nucleophiles or strong electrophiles as intermediates. In later chapters, we will apply these principles to more complex mechanisms.

Whenever you start to work out a mechanism, **draw all the bonds** and all the substituents of each carbon atom affected throughout the mechanism. Three-bonded carbon atoms are likely to be the reactive intermediates. If you attempt to draw condensed formulas or line–angle formulas, you will likely misplace a hydrogen atom and show the wrong carbon atom as a radical, cation, or anion.

Show only one step at a time; never combine steps, unless two or more bonds really do change position in one step (as in the E2 reaction, for example). Protonation of an alcohol and loss of water to give a carbocation, for example, must be shown as two steps. You must not simply circle the hydroxyl and the proton to show water falling off.

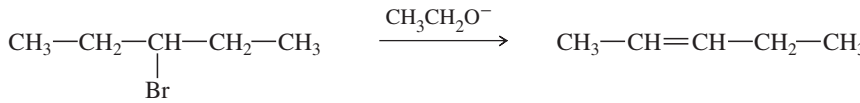
Use curved arrows to show the movement of electrons in each step of the reaction. This movement is always *from* the nucleophile (electron donor) to the electrophile (electron acceptor). For example, protonation of an alcohol must show the arrow going from the electrons of the hydroxyl oxygen to the proton—never from the proton to the hydroxyl group. *Don't* use curved arrows to try to "point out" where the proton (or other reagent) goes.

Reactions Involving Strong Nucleophiles

When a strong base or nucleophile is present, we expect to see intermediates that are also strong bases and strong nucleophiles; anionic intermediates are common. Acids and electrophiles in such a reaction are generally weak. Avoid drawing carbocations, H_3O^+, and other strong acids. They are unlikely to coexist with strong bases and strong nucleophiles.

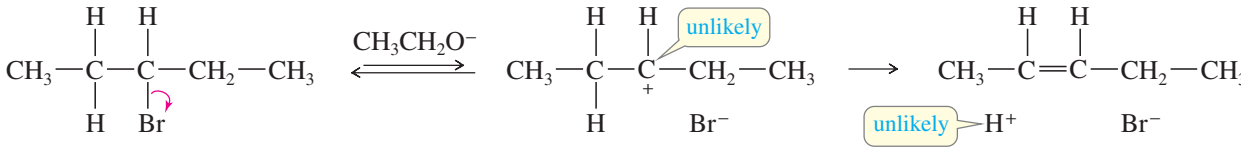
Functional groups are often converted to alkoxides, carbanions, or other strong nucleophiles by deprotonation or reaction with a strong nucleophile. Then the carbanion or other strong nucleophile reacts with a weak electrophile such as a carbonyl group or an alkyl halide.

Consider, for example, the mechanism for the dehydrohalogenation of 3-bromopentane.



Someone who has not read Chapter 6 or these guidelines for classifying mechanisms might propose an ionization, followed by loss of a proton:

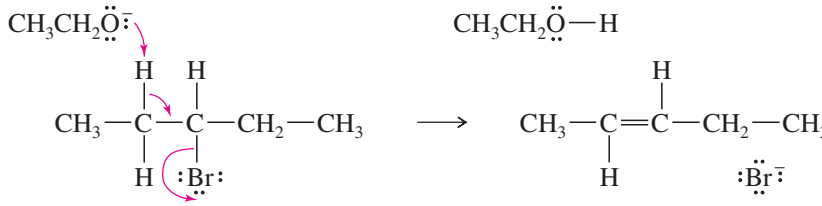
Incorrect mechanism



This mechanism would violate several general principles of proposing mechanisms. First, in the presence of ethoxide ion (a strong base), both the carbocation and the H^+ ion are unlikely. Second, the mechanism fails to explain why the strong base is required; the rate of ionization would be unaffected by the presence of ethoxide ion. Also, H^+ doesn't just fall off (even in an acidic reaction); it must be removed by a base.

The presence of ethoxide ion (a strong base and a strong nucleophile) in the reaction suggests that the mechanism involves only strong bases and nucleophiles and not any strongly acidic intermediates. As shown in Section 7-9A, the reaction occurs by the E2 mechanism, an example of a reaction involving a strong nucleophile. In this concerted reaction, ethoxide ion removes a proton as the electron pair left behind forms a pi bond and expels bromide ion.

Correct mechanism



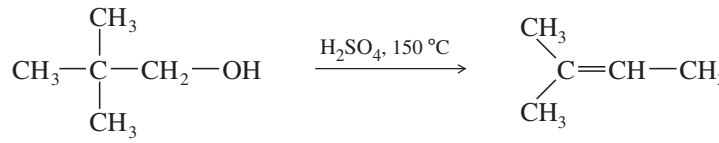
(Continued)

Reactions Involving Strong Electrophiles

When a strong acid or electrophile is present, expect to see intermediates that are also strong acids and strong electrophiles. Cationic intermediates are common, but avoid drawing any species with more than one + charge. Bases and nucleophiles in such a reaction are generally weak. Avoid drawing carbanions, alkoxide ions, and other strong bases. They are unlikely to coexist with strong acids and strong electrophiles.

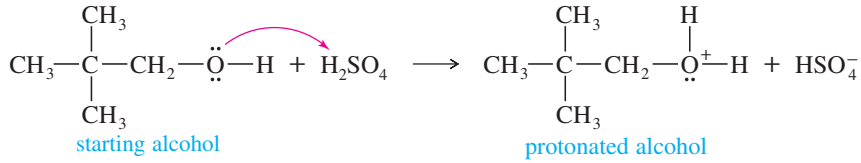
Functional groups are often converted to carbocations or other strong electrophiles by protonation or by reaction with a strong electrophile; then the carbocation or other strong electrophile reacts with a weak nucleophile such as an alkene or the solvent.

For example, consider the dehydration of 2,2-dimethylpropan-1-ol:



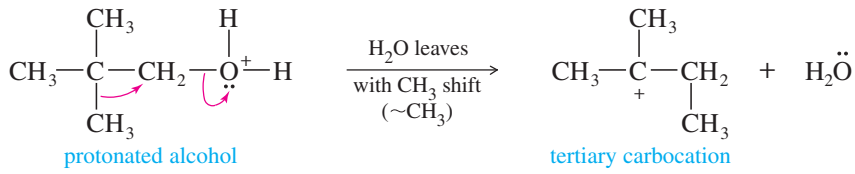
The presence of sulfuric acid indicates that the reaction is acidic and should involve strong electrophiles. The carbon skeleton of the product is different from the reactant. Under these acidic conditions, formation and rearrangement of a carbocation would be likely. The hydroxyl group is a poor leaving group; it certainly cannot ionize to give a carbocation and ^{-}OH (and we do not expect to see a strong base like ^{-}OH in this acidic reaction). The hydroxyl group is weakly basic, however, and it can become protonated in the presence of a strong acid. The protonated OH group becomes a good leaving group.

Step 1: Protonation of the hydroxyl group



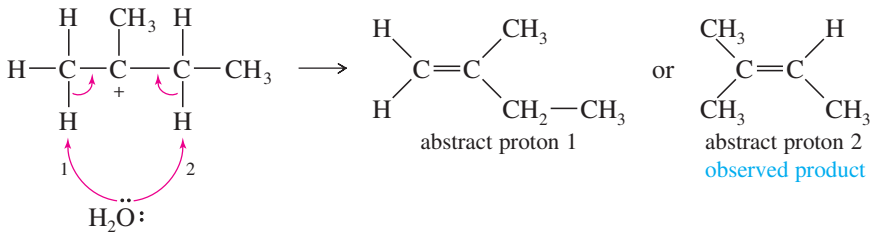
The protonated hydroxyl group $—\overset{+}{O}H_2$ is a good leaving group. A simple ionization to a carbocation would form a primary carbocation. Primary carbocations, however, are very unstable. Thus, a methyl shift occurs as water leaves, so a primary carbocation is never formed. A tertiary carbocation results. (You can visualize this as two steps if you prefer.)

Step 2: Ionization with rearrangement



The final step is loss of a proton to a weak base, such as HSO_4^- or H_2O (but *not* ^{-}OH, which is incompatible with the acidic solution). Either of two types of protons, labeled 1 and 2 in the following figure, could be lost to give alkenes. Loss of proton 2 gives the required product.

Step 3: Abstraction of a proton to form the required product



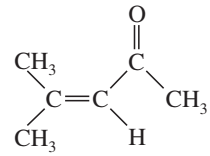
Because abstraction of proton 2 gives the more highly substituted (therefore more stable) product, Zaitsev's rule predicts it will be the major product. Note that in other problems, however, you may be asked to propose mechanisms to explain unusual compounds that are only minor products.

PROBLEM 7-27

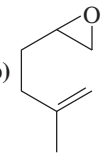
For practice in recognizing mechanisms, classify each reaction according to the type of mechanism you expect:

1. Free-radical chain reaction
2. Reaction involving strong bases and strong nucleophiles
3. Reaction involving strong acids and strong electrophiles

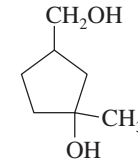
(a) $2\ CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \xrightarrow{Ba(OH)_2}$



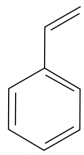
(b)



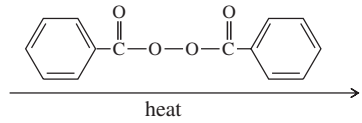
$\xrightarrow[H_2O]{H^+}$



(c)



styrene



heat

polystyrene

(d) ethylene $\xrightarrow{BF_3}$ polyethylene

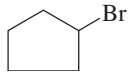
PROBLEM 7-28

Propose mechanisms for the following reactions. Additional products may be formed, but your mechanism only needs to explain the products shown.

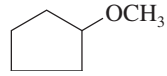
(a) $CH_3{-}CH_2{-}CH_2{-}CH_2{-}OH \xrightarrow{H_2SO_4,\ 140\,°C} CH_3{-}CH{=}CH{-}CH_3 + CH_2{=}CH{-}CH_2CH_3$

(*Hint*: Hydride shift)

(b)



$\xrightarrow{NaOCH_3}$



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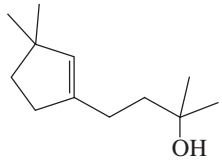
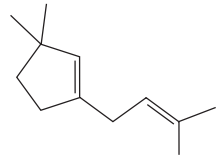
(c)



$\xrightarrow[heat]{H_2SO_4}$



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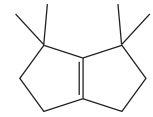
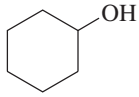


PROBLEM 7-29

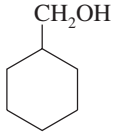
Propose mechanisms for the following reactions.

(a)

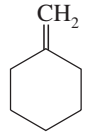


$\xrightarrow[heat]{H_3PO_4}$

(b)



$\xrightarrow[heat]{H_2SO_4}$



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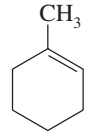

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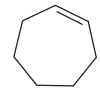

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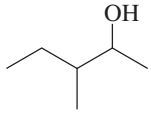
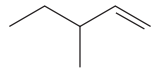


$\xrightarrow[heat]{H_2SO_4}$



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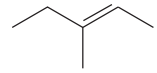

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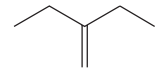
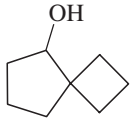
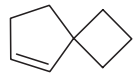


(d)



$\xrightarrow[heat]{H_2SO_4}$



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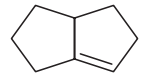

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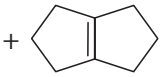
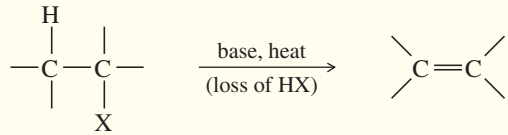


Problem-solving Hint

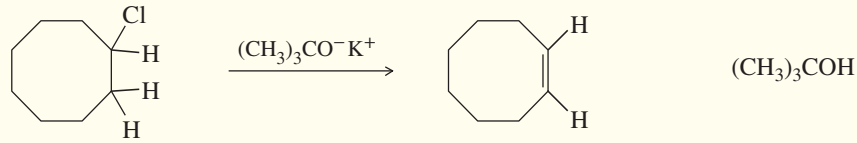
Alcohol dehydrations usually go through E1 elimination of the protonated alcohol, with a carbocation intermediate. Rearrangements are common.

SUMMARY Methods for Synthesis of Alkenes

1. *Dehydrohalogenation of alkyl halides* (Section 7-9)

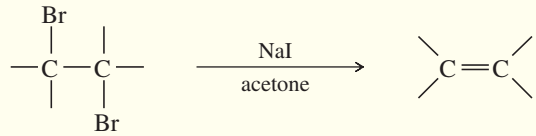


Example

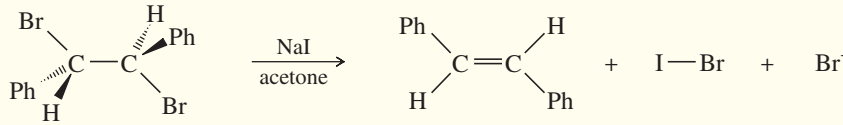


chlorocyclooctane cyclooctene

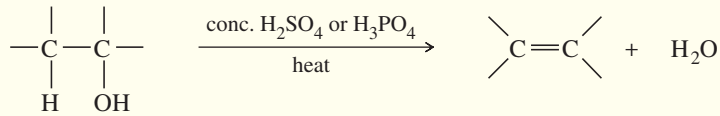
2. *Dehalogenation of vicinal dibromides* (Section 7-9D)



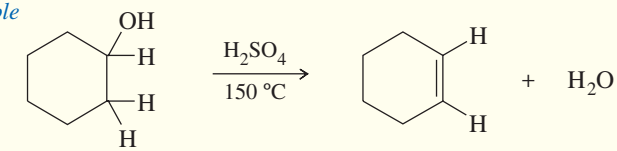
Example



3. *Dehydration of alcohols* (Section 7-10)

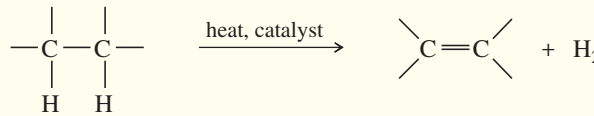


Example



cyclohexanol cyclohexene

4. *Dehydrogenation of alkanes* (Section 7-11B)

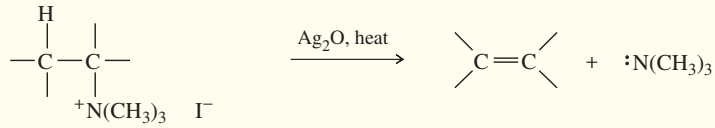


(Industrial prep, useful only for small alkenes; commonly gives mixtures.)

Example

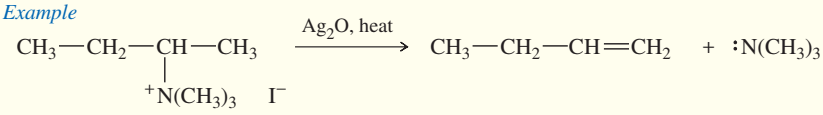
$CH_3CH_2CH_2CH_3 \xrightarrow{\text{Pt, 500 °C}}$ { but-1-ene + *cis*- and *trans*-but-2-ene + buta-1,3-diene + H_2

5. *Hofmann and Cope eliminations* (Sections 19-14 and 19-15)

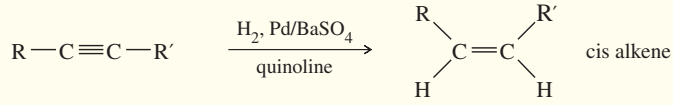


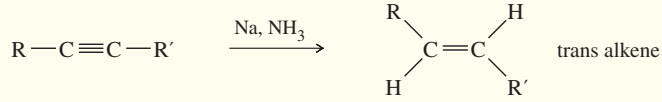
(Usually gives the least substituted alkene.)

Example

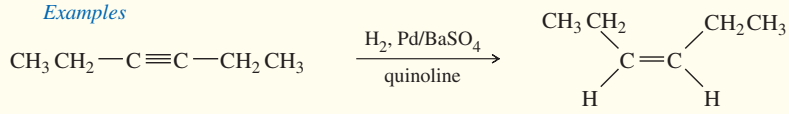


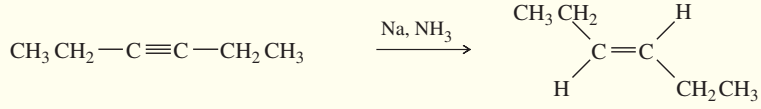
6. *Reduction of alkynes* (Section 9-9)



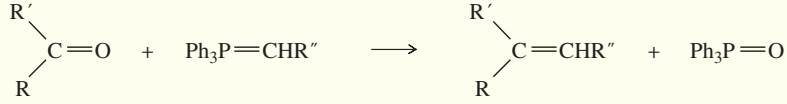


Examples

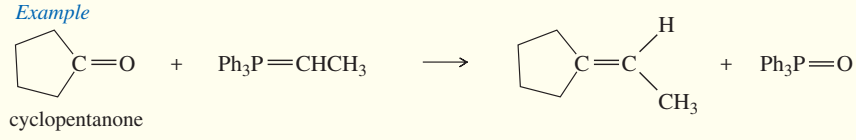




7. *Wittig reaction* (Section 18-12)



Example



cyclopentanone

ESSENTIAL PROBLEM-SOLVING SKILLS IN CHAPTER 7

Each skill is followed by problem numbers exemplifying that particular skill.

1 Draw and name alkenes, and calculate the elements of unsaturation.	**Problems 7-31, 32, and 34**
2 Predict the relative stabilities of alkenes and cycloalkenes, based on their structure and stereochemistry.	**Problems 7-44, 51, 52, and 56**
3 Name geometric isomers using both the *E*-*Z* and cis-trans systems, and compare their stabilities.	**Problems 7-31, 32, 33, 34, 35, and 36**

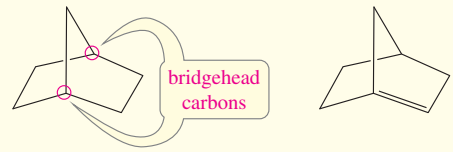
4 Predict the major and minor products of dehydrohalogenation of alkyl halides, dehalogenation of dibromides, and dehydration of alcohols.	**Problems 7-38, 39, 41, and 44**
5 Propose logical mechanisms for dehydrohalogenation, dehalogenation, and dehydration reactions.	**Problems 7-43, 45, 47, and 48**
6 Predict and explain the stereochemistry of E2 eliminations to form alkenes. Predict the products of E2 reactions on cyclohexane systems.	**Problems 7-46, 50, 53, 54, and 57**
7 Propose effective single-step and multistep syntheses of alkenes.	**Problems 7-40 and 42**

ESSENTIAL TERMS

alkene — **(olefin)** A hydrocarbon with one or more carbon–carbon double bonds. (p. 285)
- **diene:** A compound with two carbon–carbon double bonds. (p. 290)
- **triene:** A compound with three carbon–carbon double bonds. (p. 290)
- **tetraene:** A compound with four carbon–carbon double bonds. (p. 290)

allyl group — A vinyl group plus a methylene group: $CH_2{=}CH{-}CH_2{-}$ (p. 291)

Bredt's rule — A stable bridged bicyclic compound cannot have a double bond at a bridgehead position unless one of the rings contains at least eight carbon atoms. (p. 301)
- **bicyclic:** Containing two rings.
- **bridged bicyclic:** Having at least one carbon atom in each of the three links connecting the bridgehead carbons. (p. 301)
- **bridgehead carbons:** Those carbon atoms that are part of both rings, with three bridges of bonds connecting them.

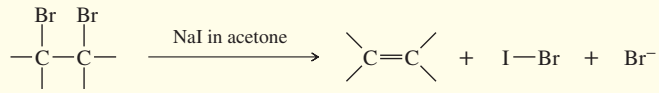


a bridged bicyclic compound a Bredt's rule violation

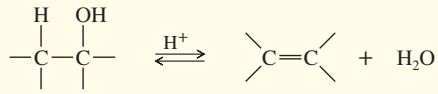
catalytic cracking — The heating of petroleum products in the presence of a catalyst (usually an aluminosilicate mineral), causing bond cleavage to form alkenes and alkanes of lower molecular weight. (p. 315)

cis-trans isomers — **(geometric isomers)** Isomers that differ in their cis-trans arrangement on a ring or double bond. Cis-trans isomers are a subclass of diastereomers. (p. 291)
- **cis:** Having similar groups on the same side of a double bond or a ring.
- **trans:** Having similar groups on opposite sides of a double bond or a ring.
- ***Z*:** Having the higher-priority groups on the same side of a double bond.
- ***E*:** Having the higher-priority groups on opposite sides of a double bond.

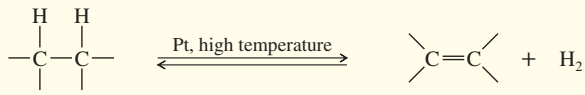
dehalogenation — The elimination of a halogen (X_2) from a compound. Dehalogenation is formally a reduction. An example is **debromination**. (p. 310)



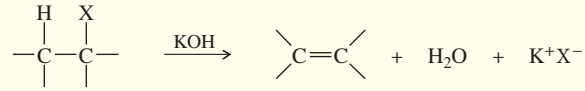
dehydration — The elimination of water from a compound; usually acid-catalyzed. (p. 312)



dehydrogenation — The elimination of hydrogen (H_2) from a compound; usually done in the presence of a catalyst. (p. 315)



dehydrohalogenation The elimination of a hydrogen halide (HX) from a compound; usually base-promoted. (p. 304)



double-bond isomers Constitutional isomers that differ only in the position of a double bond. Double-bond isomers hydrogenate to give the same alkane. (p. 298)

element of unsaturation A structural feature that results in two fewer hydrogen atoms in the molecular formula. A double bond or a ring is one element of unsaturation; a triple bond is two elements of unsaturation. (p. 287)

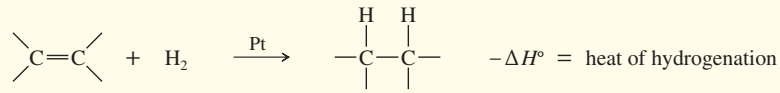
geminal dihalide A compound with two halogen atoms on the same carbon atom.

geometric isomers See **cis-trans isomers.** (p. 291)

heteroatom Any atom other than carbon or hydrogen. (p. 288)

Hofmann product The least highly substituted alkene product. (p. 305)

hydrogenation Addition of hydrogen to a molecule. The most common hydrogenation is the addition of H_2 across a double bond in the presence of a catalyst (*catalytic hydrogenation*). The value of $(-\Delta H^\circ)$ for this reaction is called the **heat of hydrogenation.** (p. 296)



olefin An alkene. (p. 285)

polymer A substance of high molecular weight made by linking many small molecules, called **monomers.** (p. 295)

- **addition polymer:** A polymer formed by simple addition of monomer units.
- **polyolefin:** A type of addition polymer with an olefin (alkene) serving as the monomer.

saturated Having only single bonds; incapable of undergoing addition reactions. (p. 288)

Saytzeff Alternate spelling of Zaitsev.

stereospecific reaction A reaction in which different stereoisomers react to give different stereoisomers of the product. (p. 306)

trans-diaxial An anti and coplanar arrangement allowing E2 elimination of two adjacent substituents on a cyclohexane ring. The substituents must be trans to each other, and both must be in axial positions on the ring. (p. 307)

unsaturated Having multiple bonds that can undergo addition reactions. (p. 287)

vicinal dihalide A compound with two halogens on adjacent carbon atoms. (p. 310)

vinyl group An ethenyl group, $CH_2{=}CH{-}$. (p. 291)

Zaitsev's rule **(Saytzeff's rule)** An elimination usually gives the most stable alkene product, commonly the most substituted alkene. Zaitsev's rule does not always apply, especially with a bulky base or a bulky leaving group. (pp. 298, 305)

- **Zaitsev elimination:** An elimination that gives the Zaitsev product.
- **Zaitsev product:** The most substituted alkene product.

STUDY PROBLEMS

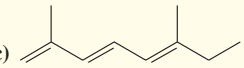
7-30 Using cyclohexane as your starting material, show how you would synthesize each of the following compounds. (Once you have shown how to synthesize a compound, you may use it as the starting material in any later parts of this problem.)

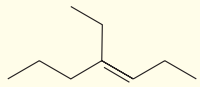
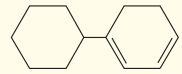
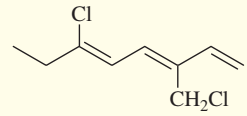
(a) bromocyclohexane **(b)** cyclohexene **(c)** ethoxycyclohexane
(d) 3-bromocyclohex-1-ene **(e)** cyclohexa-1,3-diene **(f)** cyclohexanol

7-31 Draw a structure for each compound (includes old and new names).

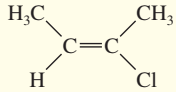
(a) 3-methylpent-1-ene **(b)** *cis*-3-methyl-3-hexene **(c)** 3,4-dibromobut-1-ene
(d) 1,3-cyclohexadiene **(e)** cycloocta-1,4-diene **(f)** (*Z*)-3-methyl-2-octene
(g) vinylcyclopropane **(h)** (*Z*)-2-bromo-2-pentene **(i)** (*3Z,6E*)-1,3,6-octatriene

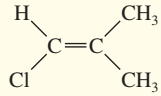
7-32 Give a correct name for each compound.

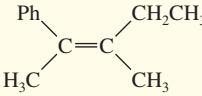
(a) $CH_3—CH_2—C(=CH_2)—CH_2—CH_2—CH_3$ **(b)** $(CH_3CH_2)_2C{=}CHCH_3$ **(c)** 

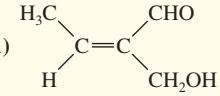
(d)  **(e)**  **(f)** 

7-33 Label each structure as *Z, E*, or neither.

(a) 

(b) 

(c) 

(d) 

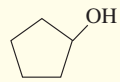
7-34 **(a)** Draw and name all five isomers of formula C_3H_5F.
(b) Draw all 12 acyclic (no rings) isomers of formula C_4H_7Br. Include stereoisomers.
(c) Cholesterol, $C_{27}H_{46}O$, has only one pi bond. With no additional information, what else can you say about its structure?

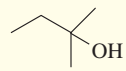
7-35 Draw and name all stereoisomers of 3-chlorohepta-2,4-diene
(a) Using the cis-trans nomenclature.
(b) Using the *E-Z* nomenclature.

7-36 Determine which compounds show cis-trans isomerism. Draw and label the isomers, using both the cis-trans and *E-Z* nomenclatures where applicable.
(a) pent-1-ene
(b) pent-2-ene
(c) hex-3-ene
(d) 1,1-dibromopropene
(e) 1,2-dibromopropene
(f) 1-bromo-1-chlorohexa-1,3-diene

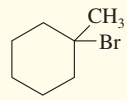
7-37 For each alkene, indicate the direction of the dipole moment. For each pair, determine which compound has the larger dipole moment.
(a) *cis*-1,2-difluoroethene or *trans*-1,2-difluoroethene
(b) *cis*-1,2-dibromoethene or *trans*-2,3-dibromobut-2-ene
(c) *cis*-1,2-dibromo-1,2-dichloroethene or *cis*-1,2-dichloroethene

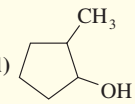
7-38 Predict the products of the following reactions. When more than one product is expected, predict which will be the major product.

(a) 

$\xrightarrow[\text{heat}]{H_2SO_4}$ **(b)** 

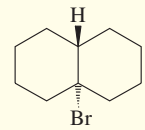
$\xrightarrow[\text{heat}]{H_3PO_4}$

(c) 

$\xrightarrow{NaOCH_3}$ **(d)** 

$\xrightarrow[\text{heat}]{H_2SO_4}$

7-39 Write a balanced equation for each reaction.

(a) $CH_3—CH_2—CH(OH)—CH_3 \xrightarrow{H_2SO_4,\ \text{heat}}$ **(b)** 

$\xrightarrow{NaOC(CH_3)_3}$

(c) $CH_3—CH(Br)—CH(Br)—CH_3 \xrightarrow[\text{acetone}]{NaI}$ **(d)** $CH_3—CH(CH_3)—C(CH_3)(Br)—CH_3 \xrightarrow{NaOH,\ \text{heat}}$

7-40 Show how you would prepare cyclopentene from each compound.
(a) *trans*-1,2-dibromocyclopentane **(b)** cyclopentanol
(c) cyclopentyl bromide **(d)** cyclopentane (not by dehydrogenation)

7-41 Predict the products formed by sodium hydroxide-promoted dehydrohalogenation of the following compounds. In each case, predict which will be the major product.

(a) 1-bromobutane **(b)** 2-chlorobutane **(c)** 3-bromopentane
(d) *cis*-1-bromo-2-methylcyclohexane **(e)** *trans*-1-bromo-2-methylcyclohexane

7-42 What halides would undergo dehydrohalogenation to give the following pure alkenes?

(a) hex-1-ene **(b)** isobutylene **(c)** pent-2-ene
(d) methylenecyclohexane **(e)** 4-methylcyclohexene

7-43 In the dehydrohalogenation of alkyl halides, a strong base such as *tert*-butoxide usually gives the best results via the E2 mechanism.

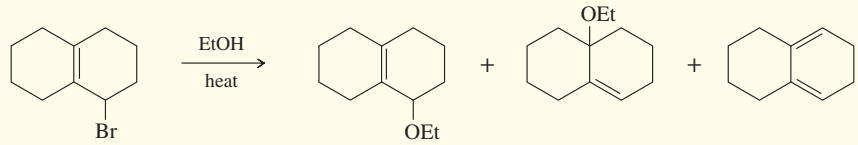
(a) Explain why a strong base such as *tert*-butoxide cannot dehydrate an alcohol through the E2 mechanism.
(b) Explain why strong acid, used in the dehydration of an alcohol, is not effective in the dehydrohalogenation of an alkyl halide.

7-44 Predict the major products of acid-catalyzed dehydration of the following alcohols.

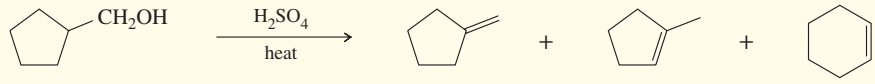
(a) pentan-2-ol **(b)** 1-methylcyclopentanol
(c) 2-methylcyclohexanol **(d)** 2,2-dimethylpropan-1-ol

7-45 Propose mechanisms for the following reactions. Additional products may be formed, but your mechanism only needs to explain the products shown.

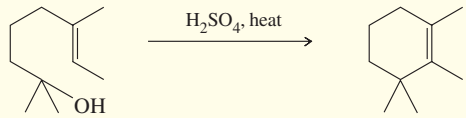
(a)



(b)



(c)



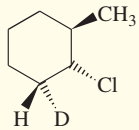
7-46 Predict the dehydrohalogenation product(s) that result when the following alkyl halides are heated in alcoholic KOH. When more than one product is formed, predict the major and minor products.

(a) $(CH_3)_2CH—C(CH_3)_2$ (Br)

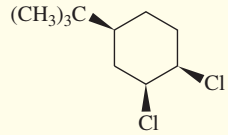
(b) $(CH_3)_2CH—CH(Br)—CH_3$

(c) $(CH_3)_2C(Br)—CH_2—CH_3$

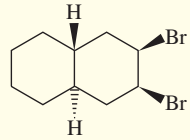
(d)



(e)

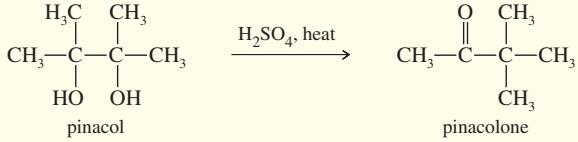


(f)



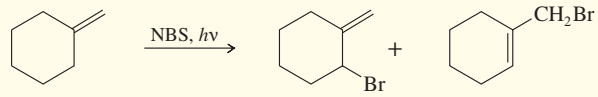
7-47 E1 eliminations of alkyl halides are rarely useful for synthetic purposes because they give mixtures of substitution and elimination products. Explain why the sulfuric acid-catalyzed dehydration of cyclohexanol gives a good yield of cyclohexene even though the reaction goes by an E1 mechanism. (*Hint*: What are the nucleophiles in the reaction mixture? What products are formed if these nucleophiles attack the carbocation? What further reactions can these substitution products undergo?)

***7-48** The following reaction is called the *pinacol rearrangement*. The reaction begins with an acid-promoted ionization to give a carbocation. This carbocation undergoes a methyl shift to give a more stable, resonance-stabilized cation. Loss of a proton gives the observed product. Propose a mechanism for the pinacol rearrangement.



pinacol pinacolone

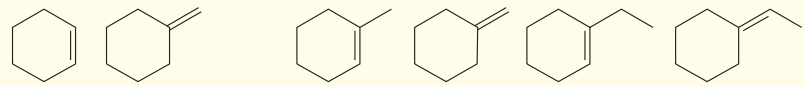
7-49 Propose a mechanism to explain the formation of two products in the following reaction.



7-50 A chemist allows some pure (2*S*,3*R*)-3-bromo-2,3-diphenylpentane to react with a solution of sodium ethoxide ($NaOCH_2CH_3$) in ethanol. The products are two alkenes: **A** (cis-trans mixture) and **B,** a single pure isomer. Under the same conditions, the reaction of (2*S*,3*S*)-3-bromo-2,3-diphenylpentane gives two alkenes, **A** (cis-trans mixture) and **C.** Upon catalytic hydrogenation, all three of these alkenes (**A, B,** and **C**) give 2,3-diphenylpentane. Determine the structures of **A, B,** and **C,** give equations for their formation, and explain the stereospecificity of these reactions.

7-51 The energy difference between *cis*- and *trans*-but-2-ene is about 4 kJ/mol; however, the trans isomer of 4,4-dimethylpent-2-ene is nearly 16 kJ/mol more stable than the cis isomer. Explain this large difference.

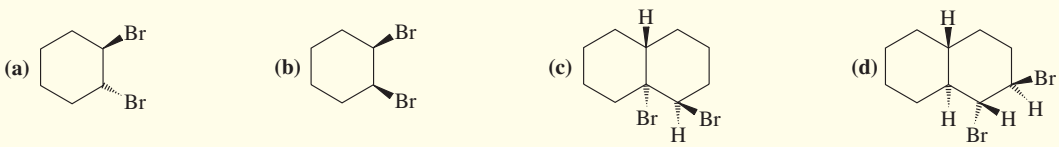
7-52 A double bond in a six-membered ring is usually more stable in an endocyclic position than in an exocyclic position. Hydrogenation data on two pairs of compounds follow. One pair suggests that the energy difference between endocyclic and exocyclic double bonds is about 9 kJ/mol. The other pair suggests an energy difference of about 5 kJ/mol. Which number do you trust as being more representative of the actual energy difference? Explain your answer.



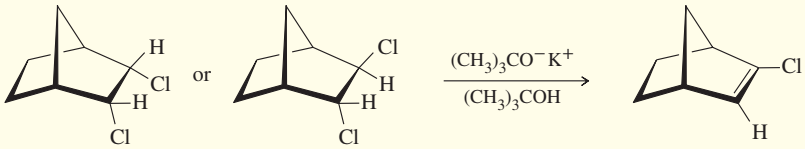
endocyclic exocyclic 107 116 105 110

heats of hydrogenation (kJ/mol)

7-53 Predict the products of the following eliminations of vicinal dibromides with potassium iodide. Remember to consider the geometric constraints of the E2 reaction.

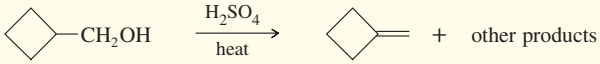


***7-54** One of the following dichloronorbornanes undergoes elimination much faster than the other. Determine which one reacts faster, and explain the large difference in rates.



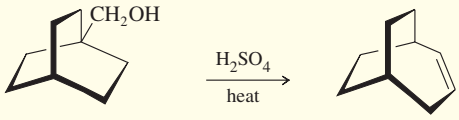
cis trans

***7-55** A graduate student wanted to make methylenecyclobutane, and he tried the following reaction. Propose structures for the other products, and give mechanisms to account for their formation.



methylenecyclobutane (minor)

***7-56** Write a mechanism that explains the formation of the following product. In your mechanism, explain the cause of the rearrangement, and explain the failure to form the Zaitsev product.



*7-57 When 2-bromo-3-phenylbutane is treated with sodium methoxide, two alkenes result (by E2 elimination). The Zaitsev product predominates.

(a) Draw the reaction, showing the major and minor products.

(b) When one pure stereoisomer of 2-bromo-3-phenylbutane reacts, one pure stereoisomer of the major product results. For example, when (*2R,3R*)-2-bromo-3-phenylbutane reacts, the product is the stereoisomer with the methyl groups cis. Use your models to draw a Newman projection of the transition state to show why this stereospecificity is observed.

(c) Use a Newman projection of the transition state to predict the major product of elimination of (*2S,3R*)-2-bromo-3-phenylbutane.

(d) Predict the major product from elimination of (*2S,3S*)-2-bromo-3-phenylbutane. This prediction can be made without drawing any structures, by considering the results in part (b).

7-58 A student adds NBS to a solution of 1-methylcyclohexene and irradiates the mixture with a sunlamp until all the NBS has reacted. After a careful distillation, the product mixture contains two major products of formula $C_7H_{11}Br$.

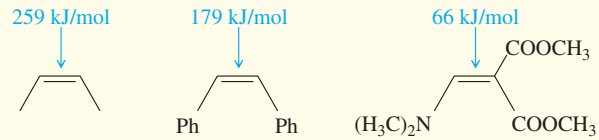
(a) Draw the resonance forms of the three possible allylic free radical intermediates.

(b) Rank these three intermediates from least stable to most stable.

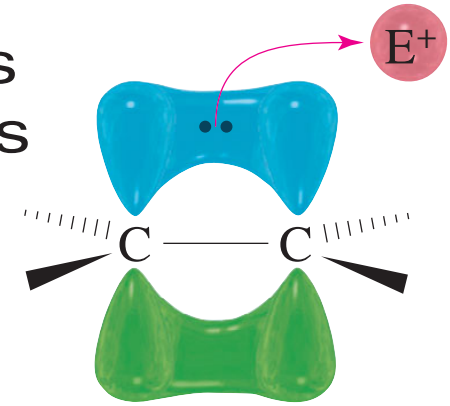
(c) Draw the products obtained from each free-radical intermediate.

(d) The two major products are the ones with the most stable double bonds that result from the two most stable intermediates. Indicate the compounds that are likely to be the major products.

*7-59 Explain the dramatic difference in rotational energy barriers of the following three alkenes. (*Hint:* Consider what the transition states must look like.)



8 Reactions of Alkenes



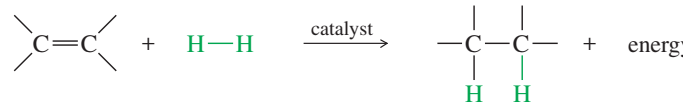
GOALS FOR CHAPTER 8

1. Explain why electrophilic additions are among the most common reactions of alkenes.
2. Predict the products of the reactions of alkenes, including the orientation of the reaction (regiochemistry) and the stereochemistry.
3. Propose mechanisms to explain the observed products of alkene reactions.
4. Use retrosynthetic analysis to solve multistep synthesis problems with alkenes as reagents, intermediates, or products.

All alkenes have a common feature: a carbon–carbon double bond. The reactions of alkenes arise from the reactivity of the carbon–carbon double bond. Once again, the concept of the functional group helps to organize and simplify the study of chemical reactions. By studying the characteristic reactions of the double bond, we can predict the reactions of alkenes we have never seen before.

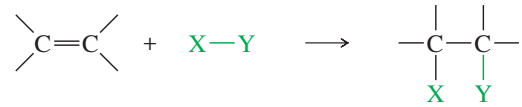
8-1 Reactivity of the Carbon–Carbon Double Bond

Because single bonds (sigma bonds) are more stable than pi bonds, the most common reactions of double bonds transform the pi bond into a sigma bond. For example, catalytic hydrogenation converts the C═C pi bond and the H—H sigma bond into two C—H sigma bonds (Section 7-7). The reaction is exothermic (ΔH° = about −80 to −120 kJ/mol or about −20 to −30 kcal/mol), showing that the product is more stable than the reactants.

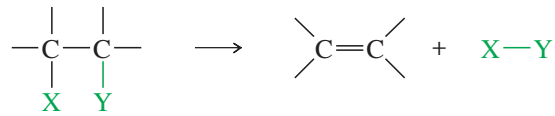


Hydrogenation of an alkene is an example of an **addition,** one of the three major reaction types we have studied: addition, elimination, and substitution. In an addition, two molecules combine to form one product molecule. When an alkene undergoes addition, two groups add to the carbon atoms of the double bond and the carbons become saturated. In many ways, addition is the reverse of **elimination,** in which one molecule splits into two fragment molecules. In a **substitution,** one fragment replaces another fragment in a molecule.

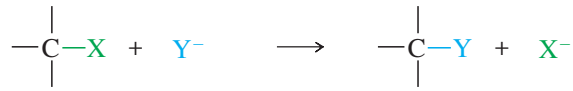
Addition



Elimination



Substitution



Addition is the most common reaction of alkenes, and in this chapter we consider additions to alkenes in detail. A wide variety of functional groups can be formed by adding suitable reagents to the double bonds of alkenes.

8-2 Electrophilic Addition to Alkenes

In principle, many different reagents could add to a double bond to form more stable products; that is, the reactions are energetically favorable. Not all of these reactions have convenient rates, however. For example, the reaction of ethylene with hydrogen (to give ethane) is strongly exothermic, but the rate is very slow. A mixture of ethylene and hydrogen can remain for years without appreciable reaction. Adding a catalyst such as platinum, palladium, or nickel allows the reaction to take place at a rapid rate.

Some reagents react with carbon–carbon double bonds without the aid of a catalyst. To understand what types of reagents react with double bonds, consider the structure of the pi bond. Although the electrons in the sigma bond framework are tightly held, the pi bond is delocalized above and below the sigma bond (Figure 8-1). The pi-bonding electrons are spread farther from the carbon nuclei, and they are more loosely held. A strong electrophile has an affinity for these loosely held electrons. It can pull them away to form a new bond (Figure 8-2), leaving one of the carbon atoms with only three bonds and a positive charge: a carbocation. In effect, the double bond has reacted as a nucleophile, donating a pair of electrons to the electrophile.

Most addition reactions involve a second step in which a nucleophile attacks the carbocation (as in the second step of the S_N1 reaction), forming a stable addition product. In the product, both the electrophile and the nucleophile are bonded to the carbon atoms that were connected by the double bond. This reaction is outlined in Key Mechanism 8-1, identifying the electrophile as E^+ and the nucleophile as Nuc:$^-$. This type of reaction requires a strong electrophile to attract the electrons of the pi bond and generate a carbocation in the rate-limiting step. Most alkene reactions fall into this large class of **electrophilic additions** to alkenes.

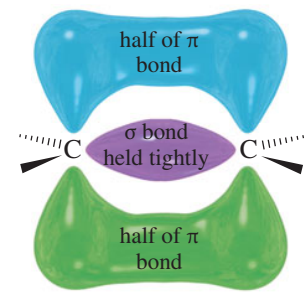


FIGURE 8-1
The electrons in the pi bond are spread farther from the carbon nuclei and are more loosely held than the sigma electrons.

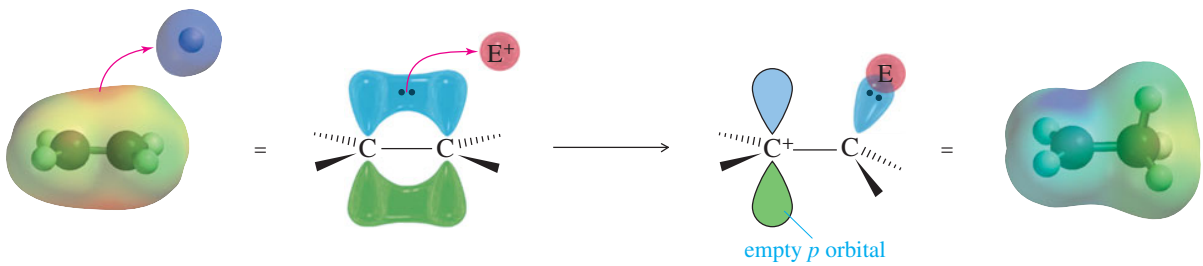
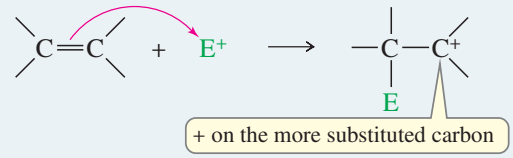


FIGURE 8-2
The pi bond as a nucleophile. A strong electrophile attracts the electrons out of the pi bond to form a new sigma bond, generating a carbocation. The (red) curved arrow shows the movement of electrons, from the electron-rich pi bond to the electron-poor electrophile.

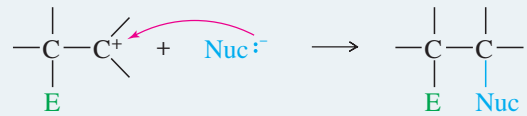
KEY MECHANISM 8-1 Electrophilic Addition to Alkenes

A wide variety of electrophilic additions involve similar mechanisms. First, a strong electrophile attracts the loosely held electrons from the pi bond of an alkene. The electrophile forms a sigma bond to one of the carbons of the (former) double bond, while the other carbon becomes a carbocation. The carbocation (a strong electrophile) reacts with a nucleophile (often a weak nucleophile) to form another sigma bond.

Step 1: Attack of the pi bond on the electrophile forms a carbocation.



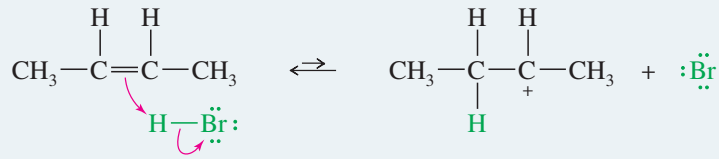
Step 2: Attack by a nucleophile gives the addition product.



EXAMPLE: Ionic addition of HBr to but-2-ene

This example shows what happens when gaseous HBr adds to but-2-ene. The proton in HBr is electrophilic; it reacts with the alkene to form a carbocation. Bromide ion reacts rapidly with the carbocation to give a stable product in which the elements of HBr have added to the ends of the double bond.

Step 1: Protonation of the double bond forms a carbocation.



Step 2: Bromide ion attacks the carbocation.

PROBLEM: Explain why the + charge of the carbocation always appears at the carbon of the (former) double bond that has NOT bonded to the electrophile.

We will consider several types of additions to alkenes, using a wide variety of reagents: water, borane, hydrogen, carbenes, halogens, oxidizing agents, and even other alkenes. Most, but not all, of these will be electrophilic additions. Table 8-1 summarizes the classes of additions we will cover. Note that the table shows what elements have added across the double bond in the final product, but it says nothing about reagents or mechanisms. As we study these reactions, you should note the **regiochemistry** of each reaction, also called the *orientation of addition*, meaning which part of the reagent adds to which end of the double bond. Also note the *stereochemistry* if the reaction is stereospecific.

TABLE 8-1 Types of Additions to Alkenes

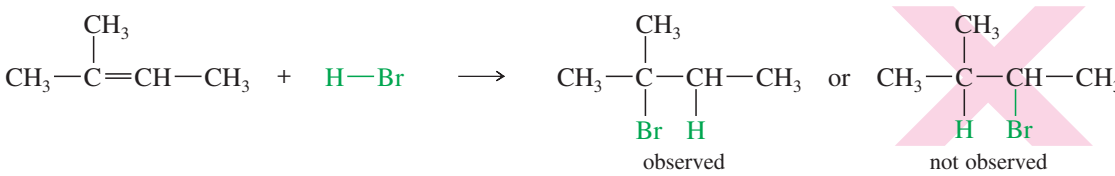
C=C → Type of Addition [Elements Added][a]	Product	C=C → Type of Addition [Elements Added][a]	Product
hydration [H_2O]	H, OH	halogenation [X_2], an oxidation	X, X
hydrogenation [H_2], a reduction	H, H	halohydrin formation [HOX], an oxidation	X, OH
dihydroxylation [HOOH], an oxidation	OH, OH	HX addition [HX] (hydrohalogenation)	H, X
oxidative cleavage [O_2], an oxidation	C=O, O=C	cyclopropanation [CH_2]	H, H
epoxidation [O], an oxidation	O		

[a]These are not the reagents used but simply the groups that appear in the product.

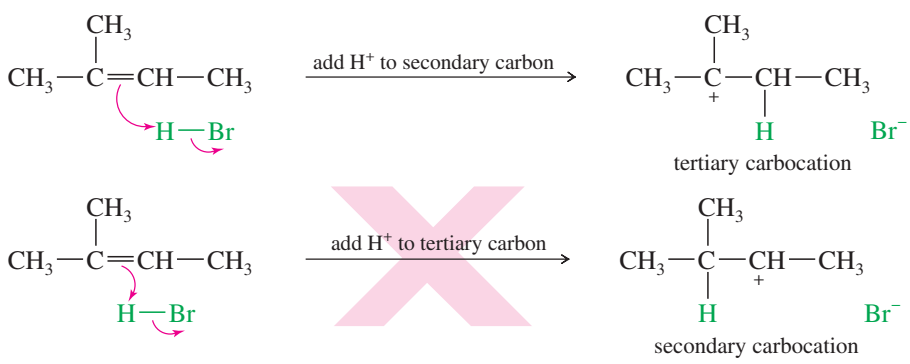
8-3 Addition of Hydrogen Halides to Alkenes

8-3A Orientation of Addition: Markovnikov's Rule

The simple mechanism shown for addition of HBr to but-2-ene applies to a large number of electrophilic additions. We can use this mechanism to predict the outcome of some fairly complicated reactions. For example, the addition of HBr to 2-methylbut-2-ene could lead to either of two products, yet only one is observed.



The first step is protonation of the double bond. If the proton adds to the secondary carbon, the product will be different from the one formed if the proton adds to the tertiary carbon.



When the proton adds to the secondary carbon, a tertiary carbocation results. When the proton adds to the tertiary carbon atom, a secondary carbocation results. The tertiary carbocation is more stable (see Section 4-16A), so the first reaction is favored.

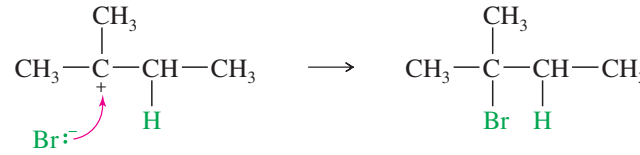
Problem-solving Hint

Stability of carbocations:

$3^\circ > 2^\circ > 1^\circ > {}^+CH_3$

An electrophile adds to a double bond to give the most stable carbocation in the intermediate.

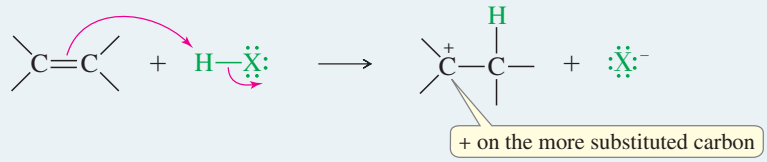
The second half of the mechanism produces the final product of the addition of HBr to 2-methylbut-2-ene.



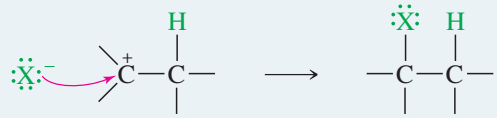
Note that protonation of one carbon atom of a double bond gives a carbocation on the carbon atom that was *not* protonated. Therefore, the proton adds to the end of the double bond that is *less* substituted to give the *more substituted carbocation* (the more stable carbocation).

MECHANISM 8-2 Ionic Addition of HX to an Alkene

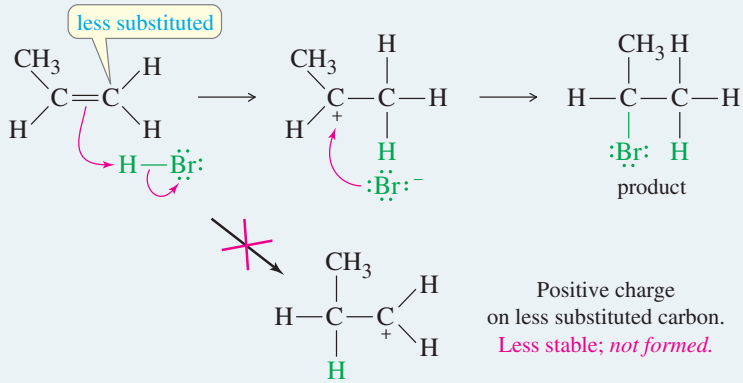
Step 1: Protonation of the pi bond forms a carbocation.



Step 2: Attack by the halide ion gives the addition product.



EXAMPLE: The ionic addition of HBr to propene shows protonation of the less substituted carbon to give the more substituted carbocation. Reaction with bromide ion completes the addition.



There are many examples of reactions where the proton adds to the less substituted carbon atom of the double bond in order to produce the more substituted carbocation. The addition of HBr (and other hydrogen halides) is said to be **regioselective** because in each case, one of the two possible orientations of addition results preferentially over the other.

Markovnikov's Rule A Russian chemist, Vladimir Markovnikov, first showed the orientation of addition of HBr to alkenes in 1869. Markovnikov stated:

> MARKOVNIKOV'S RULE: The addition of a proton acid to the double bond of an alkene results in a product with the acid proton bonded to the carbon atom that already holds the greater number of hydrogen atoms.

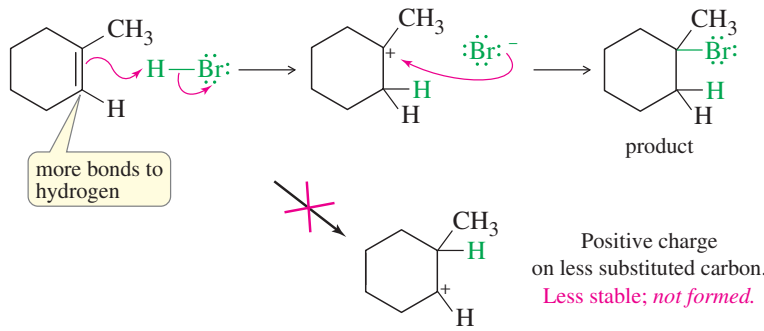


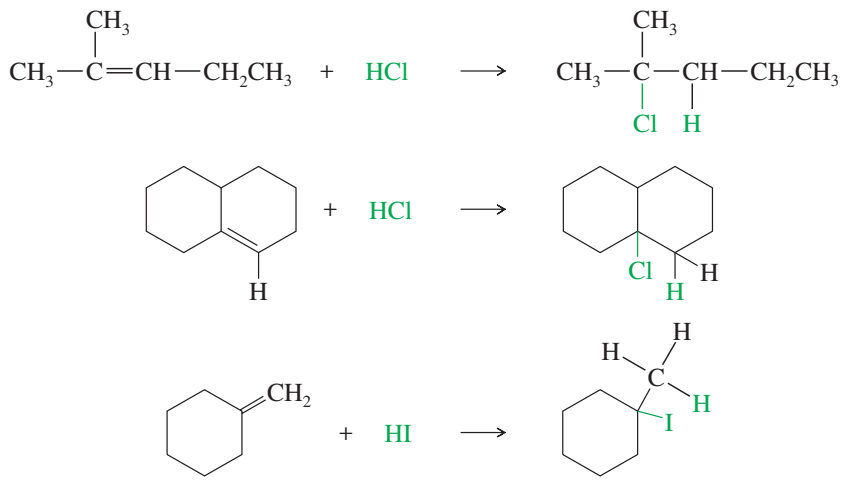
FIGURE 8-3
An electrophile adds to the less substituted end of the double bond to give the more substituted (and therefore more stable) carbocation.

This is the original statement of **Markovnikov's rule.** Reactions that follow this rule are said to follow **Markovnikov orientation** and give the **Markovnikov product.** We are often interested in adding electrophiles other than proton acids to the double bonds of alkenes. Markovnikov's rule can be extended to include a wide variety of other additions, based on the addition of the electrophile in such a way as to produce the most stable carbocation.

> MARKOVNIKOV'S RULE (extended): In an electrophilic addition to an alkene, the electrophile adds in such a way as to generate the most stable intermediate.

Figure 8-3 shows how HBr adds to 1-methylcyclohexene to give the product with an additional hydrogen bonded to the carbon that already had the most bonds to hydrogen (one) in the alkene. Note that this orientation results from addition of the proton in the way that generates the more stable carbocation.

Like HBr, both HCl and HI add to the double bonds of alkenes, and they also follow Markovnikov's rule; for example,



PROBLEM 8-1

Predict the major products of the following reactions, and propose mechanisms to support your predictions.

(a) pent-1-ene + HCl
(b) 2-methylpropene + HCl
(c) 1-methylcyclohexene + HI
(d) 4-methylcyclohexene + HBr

PROBLEM 8-2

(a) When 1 mol of buta-1,3-diene reacts with 1 mol of HBr, both 3-bromobut-1-ene and 1-bromobut-2-ene are formed. Propose a mechanism to account for this mixture of products.
(b) When 1-chlorocyclohexene reacts with HBr, the major product is 1-bromo-1-chlorocyclohexane. Propose a mechanism for this reaction, and explain why your proposed intermediate is more stable than the other possible intermediate.

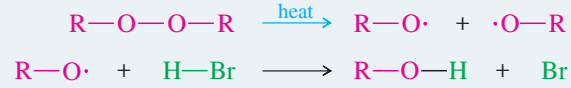
8-3B Free-Radical Addition of HBr: Anti-Markovnikov Addition

In 1933, M. S. Kharasch and F. W. Mayo found that some additions of HBr (but not HCl or HI) to alkenes gave products that were opposite to those expected from Markovnikov's rule. These **anti-Markovnikov** reactions were most likely when the reagents or solvents came from old supplies that had accumulated peroxides from exposure to the air. Peroxides give rise to free radicals that initiate the addition, causing it to occur by a radical mechanism. The oxygen–oxygen bond in peroxides is rather weak, so it can break to give two alkoxy radicals.

Alkoxy radicals (R—O·) initiate the anti-Markovnikov addition of HBr. The mechanism of this free-radical chain reaction is shown in Mechanism 8-3.

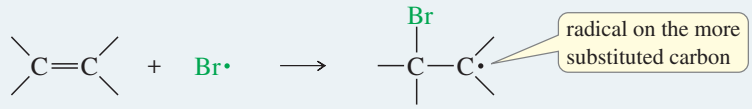
MECHANISM 8-3 Free-Radical Addition of HBr to Alkenes

Initiation: Formation of radicals.



Propagation: A radical reacts to generate another radical.

Step 1: A bromine radical adds to the double bond to generate an alkyl radical on the more substituted carbon atom.

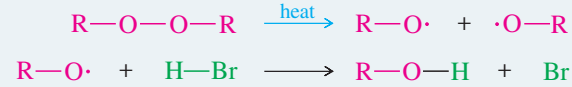


Step 2: The alkyl radical abstracts a hydrogen atom from HBr to generate the product and a bromine radical.

The bromine radical generated in Step 2 goes on to react with another molecule of alkene in Step 1, continuing the chain.

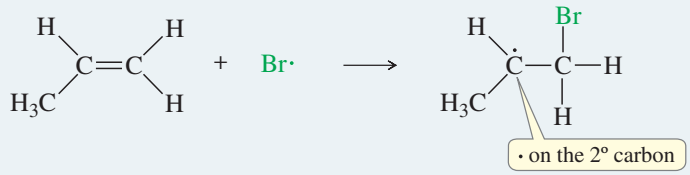
EXAMPLE: Free-radical addition of HBr to propene.

Initiation: Radicals are formed.

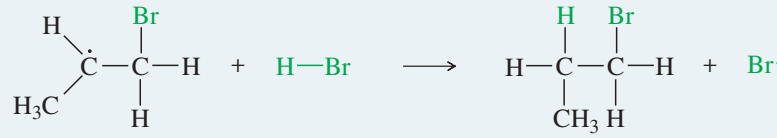


Propagation: A radical reacts to generate another radical.

Step 1: A bromine radical adds to the double bond to generate an alkyl radical on the secondary carbon atom.

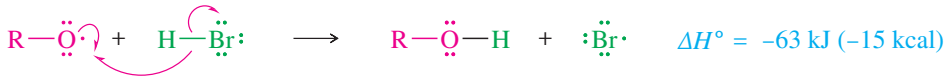


Step 2: The alkyl radical abstracts a hydrogen atom from HBr to generate the product and a bromine radical.

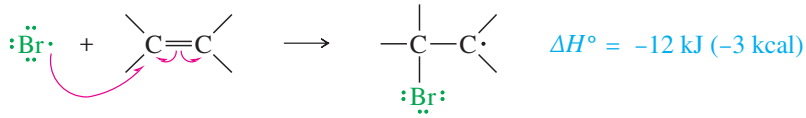


The bromine radical generated in Step 2 goes on to react in Step 1, continuing the chain.

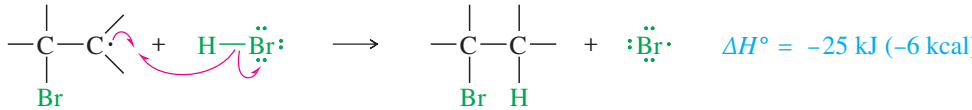
Let's consider the individual steps. In the initiation step, free radicals generated from the peroxide react with HBr to form bromine radicals.



The bromine radical lacks an octet of electrons in its valence shell, making it electron-deficient and electrophilic. It adds to a double bond, forming a new free radical with the odd electron on a carbon atom.

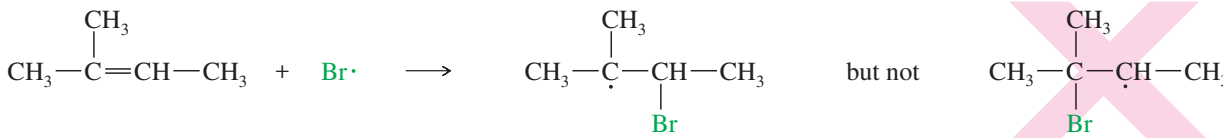


This free radical reacts with an HBr molecule to form a C—H bond and generate another bromine radical.



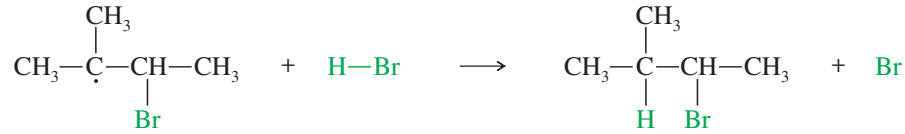
The regenerated bromine radical reacts with another molecule of the alkene, continuing the chain reaction. Both of the propagation steps are moderately exothermic, allowing them to proceed faster than the termination steps. Note that each propagation step starts with one free radical and ends with another free radical. The number of free radicals is constant, until the reactants are consumed, and free radicals come together and terminate the chain reaction.

Radical Addition of HBr to Unsymmetrical Alkenes Now we must explain the anti-Markovnikov orientation found in the products of the peroxide-catalyzed reaction. With an unsymmetrical alkene like 2-methylbut-2-ene, adding the bromine radical to the secondary end of the double bond forms a tertiary radical.



tertiary radical (more stable) secondary radical (less stable)

As we saw in the protonation of an alkene, the electrophile (in this case, Br·) adds to the less substituted end of the double bond, and the unpaired electron appears on the more substituted carbon to give the more stable free radical. This intermediate reacts with HBr to give the anti-Markovnikov product, in which H has added to the more substituted end of the double bond: the end that started with *fewer* hydrogens.



anti-Markovnikov product

Problem-solving Hint

Stability of radicals:

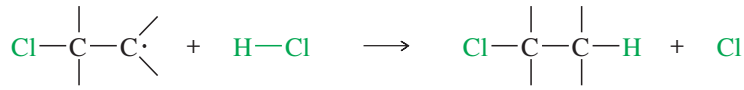
$3^\circ > 2^\circ > 1^\circ > \cdot CH_3$

A radical adds to a double bond to give the most stable radical in the intermediate.

Note that *both* mechanisms for the addition of HBr to an alkene (with and without peroxides) follow our extended statement of Markovnikov's rule: In both cases, the electrophile adds to the less substituted end of the double bond to give the more stable intermediate, either a carbocation or a free radical. In the ionic reaction, the electrophile is H^+. In the peroxide-catalyzed free-radical reaction, $Br\cdot$ is the electrophile.

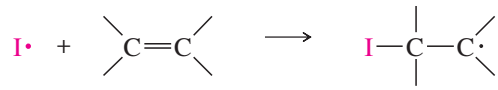
Many students wonder why the reaction with Markovnikov orientation does not take place in the presence of peroxides, together with the free-radical chain reaction. It actually does take place, but the peroxide-catalyzed reaction is faster. If just a tiny bit of peroxide is present, a mixture of Markovnikov and anti-Markovnikov products results. If an appreciable amount of peroxide is present, the radical chain reaction is so much faster than the uncatalyzed ionic reaction that only the anti-Markovnikov product is observed.

The reversal of orientation in the presence of peroxides is called the **peroxide effect.** It occurs only with the addition of HBr to alkenes. The peroxide effect is not seen with HCl because the reaction of an alkyl radical with HCl is strongly endothermic.



$\Delta H^\circ = +42$ kJ (+10 kcal)

Similarly, the peroxide effect is not observed with HI because the reaction of an iodine atom with an alkene is strongly endothermic. Only HBr has just the right reactivity for each step of the free-radical chain reaction to take place.



$\Delta H^\circ = +54$ kJ (+13 kcal)

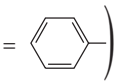
Problem-solving Hint

Remember to write out complete structures, including all bonds and charges, when writing a mechanism or determining the course of a reaction.

PROBLEM 8-3

Predict the major products of the following reactions, and propose mechanisms to support your predictions.

(a) 1-methylcyclopentene + HBr + $CH_3-C(=O)-O-O-C(=O)-CH_3$

(b) 1-phenylpropene + HBr + di-*tert*-butyl peroxide (phenyl = Ph = )

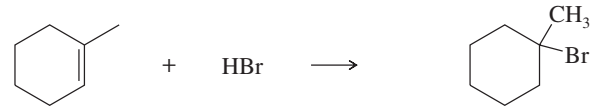
SOLVED PROBLEM 8-1

Show how you would accomplish the following synthetic conversions.

(a) Convert 1-methylcyclohexene to 1-bromo-1-methylcyclohexane.

SOLUTION

This synthesis requires the addition of HBr to an alkene with Markovnikov orientation. Ionic addition of HBr gives the correct product.

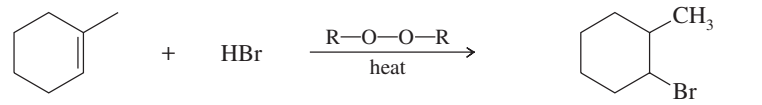


1-methylcyclohexene 1-bromo-1-methylcyclohexane

(b) Convert 1-methylcyclohexanol to 1-bromo-2-methylcyclohexane.

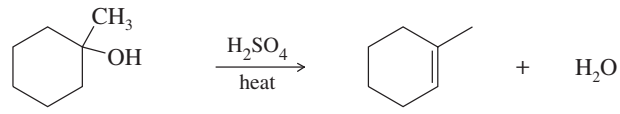
SOLUTION

This synthesis requires the conversion of an alcohol to an alkyl bromide with the bromine atom at the neighboring carbon atom. This is the anti-Markovnikov product, which could be formed by the radical-catalyzed addition of HBr to 1-methylcyclohexene.



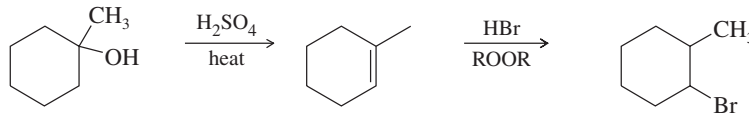
1-methylcyclohexene 1-bromo-2-methylcyclohexane

1-Methylcyclohexene is easily synthesized by the dehydration of 1-methylcyclohexanol. The most substituted alkene is the desired product.



1-methylcyclohexanol 1-methylcyclohexene

The two-step synthesis is summarized as follows:



1-methylcyclohexanol 1-methylcyclohexene 1-bromo-2-methylcyclohexane

PROBLEM 8-4

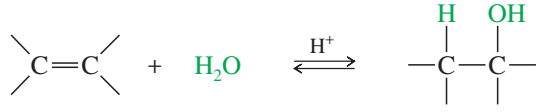
Show how you would accomplish the following synthetic conversions.

(a) but-1-ene ⟶ 1-bromobutane
(b) but-1-ene ⟶ 2-bromobutane
(c) 2-methylcyclohexanol ⟶ 1-bromo-1-methylcyclohexane
(d) 2-methylbutan-2-ol ⟶ 2-bromo-3-methylbutane

8-4 Addition of Water: Hydration of Alkenes

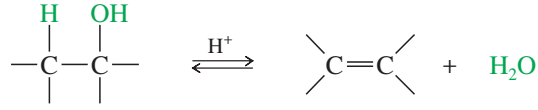
An alkene may react with water in the presence of a strongly acidic catalyst to form an alcohol. Formally, this reaction is a **hydration** (the addition of water), with a hydrogen atom adding to one carbon and a hydroxyl group adding to the other. Hydration of an alkene is the reverse of the dehydration of alcohols we studied in Section 7-10.

Hydration of an alkene



alkene alcohol
(Markovnikov orientation)

Dehydration of an alcohol



alcohol alkene

For dehydrating alcohols, a concentrated dehydrating acid (such as H_2SO_4 or H_3PO_4) is used to drive the equilibrium to favor the alkene. Hydration of an alkene, on the other hand, is accomplished by adding excess water to drive the equilibrium toward the alcohol.

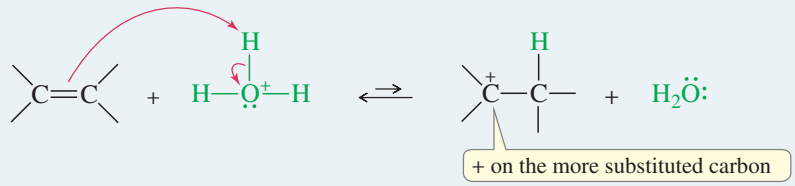
8-4A Mechanism of Hydration

The *principle of microscopic reversibility* states that a forward reaction and a reverse reaction taking place under the same conditions (as in an equilibrium) must follow the same reaction pathway in microscopic detail. The hydration and dehydration reactions are the two complementary reactions in an equilibrium; therefore, they must follow the same reaction pathway. It makes sense that the lowest-energy transition states and intermediates for the reverse reaction are the same as those for the forward reaction, except in reverse order.

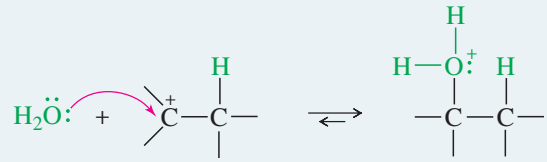
According to the principle of microscopic reversibility, we can write the hydration mechanism by reversing the order of the steps of the dehydration (Section 7-10). Protonation of the double bond forms a carbocation. Nucleophilic attack by water, followed by loss of a proton, gives the alcohol.

MECHANISM 8-4 Acid-Catalyzed Hydration of an Alkene

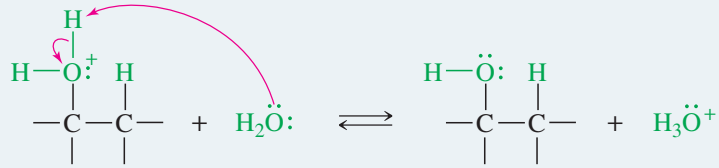
Step 1: Protonation of the double bond forms a carbocation.



Step 2: Nucleophilic attack by water gives a protonated alcohol.

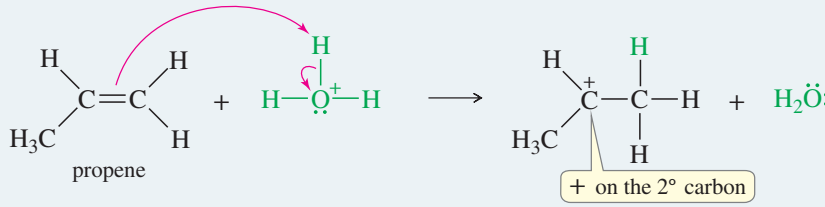


Step 3: Deprotonation gives the alcohol.

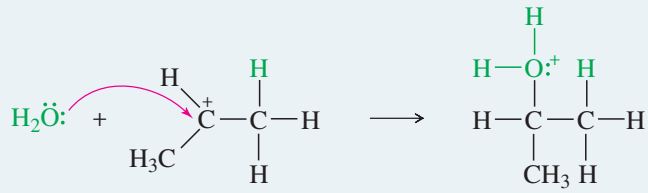


EXAMPLE: Acid-catalyzed hydration of propene.

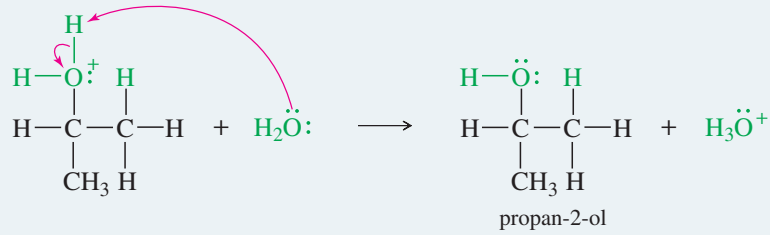
Step 1: Protonation of the double bond forms a secondary carbocation.



Step 2: Nucleophilic attack by water gives a protonated alcohol.

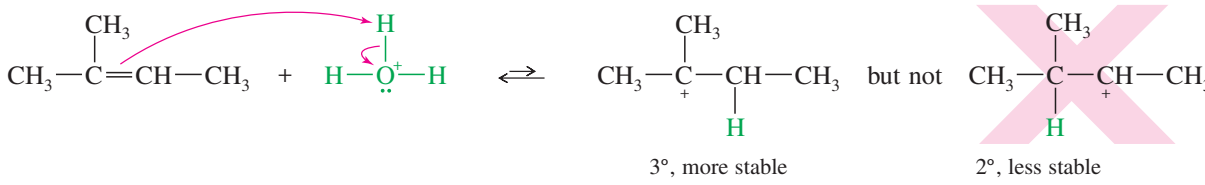


Step 3: Deprotonation gives the alcohol.

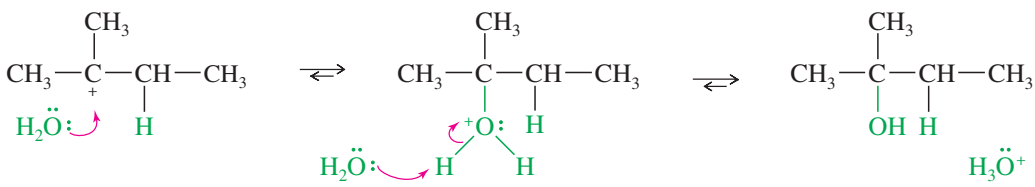


8-4B Orientation of Hydration

Step 1 of the hydration mechanism is similar to the first step in the addition of HBr. The proton adds to the *less* substituted end of the double bond to form the *more* substituted carbocation. Water attacks the carbocation to give (after loss of a proton) the alcohol with the —OH group on the more substituted carbon. Like the addition of hydrogen halides, hydration is *regioselective*: It follows Markovnikov's rule, giving a product in which the new hydrogen has added to the less substituted end of the double bond. Consider the hydration of 2-methylbut-2-ene:

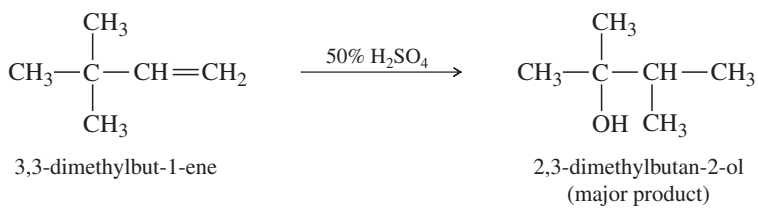


The proton adds to the less substituted end of the double bond, so the positive charge appears at the more substituted end. Water attacks the carbocation to give the protonated alcohol.



The reaction follows Markovnikov's rule. The proton has added to the end of the double bond that already had more hydrogens (that is, the less substituted end), and the —OH group has added to the more substituted end.

Like other reactions that involve carbocation intermediates, hydration may take place with rearrangement. For example, when 3,3-dimethylbut-1-ene undergoes acid-catalyzed hydration, the major product results from rearrangement of the carbocation intermediate.



PROBLEM 8-5

Propose a mechanism to show how 3,3-dimethylbut-1-ene reacts with dilute aqueous H_2SO_4 to give 2,3-dimethylbutan-2-ol and a small amount of 3,3-dimethylbut-2-ene.

Problem-solving Hint

When predicting products for electrophilic additions, first draw the structure of the carbocation (or other intermediate) that results from electrophilic attack.

PROBLEM 8-6

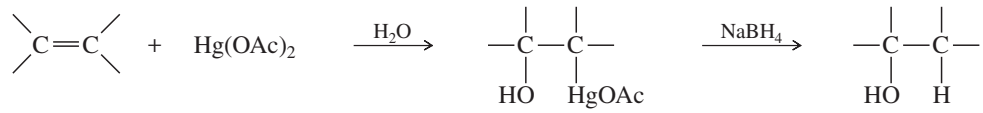
Predict the products of the following hydration reactions.
(a) 1-methylcyclopentene + dilute acid
(b) 2-phenylpropene + dilute acid
(c) 1-phenylcyclohexene + dilute acid

8-5 Hydration by Oxymercuration–Demercuration

Many alkenes do not easily undergo hydration in aqueous acid. Some alkenes are nearly insoluble in aqueous acid, and others undergo side reactions such as rearrangement, polymerization, or charring under these strongly acidic conditions. In some cases, the overall equilibrium favors the alkene rather than the alcohol. No amount of catalysis can cause a reaction to occur if the energetics are unfavorable.

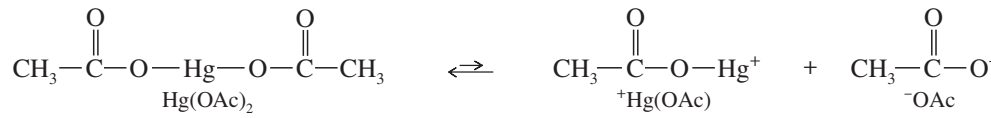
Oxymercuration–demercuration is another method for converting alkenes to alcohols with Markovnikov orientation. Oxymercuration–demercuration works with many alkenes that do not easily undergo direct hydration, and it takes place under milder conditions. No free carbocation is formed, so there is no opportunity for rearrangements or polymerization.

Oxymercuration–Demercuration



(Markovnikov orientation)

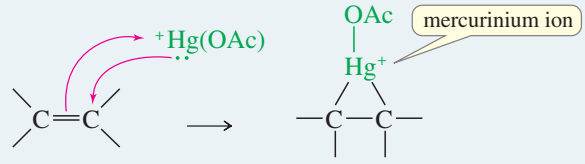
The reagent for mercuration is mercuric acetate, $Hg(OCOCH_3)_2$, abbreviated $Hg(OAc)_2$. There are several theories as to how this reagent acts as an electrophile; the simplest one is that mercuric acetate dissociates slightly to form a positively charged mercury species, $^{+}Hg(OAc)$.



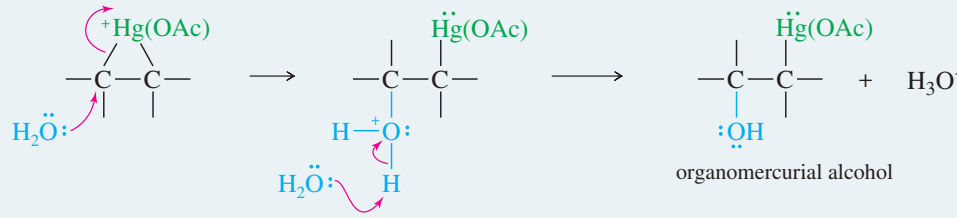
Oxymercuration involves an electrophilic attack on the double bond by the positively charged mercury species. The product is a *mercurinium ion*, an organometallic cation containing a three-membered ring. In the second step, water from the solvent attacks the mercurinium ion to give (after deprotonation) an organomercurial alcohol. A subsequent reaction is **demercuration,** to remove the mercury. Sodium borohydride ($NaBH_4$, a reducing agent) replaces the mercuric acetate fragment with a hydrogen atom.

MECHANISM 8-5 Oxymercuration of an Alkene

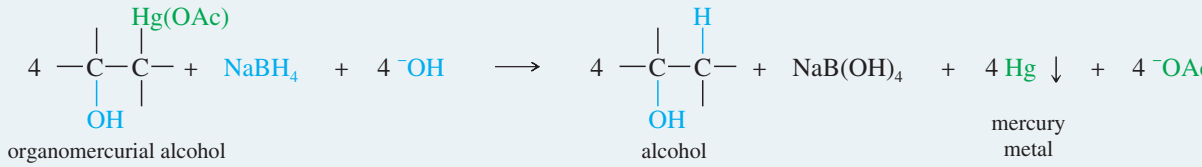
Step 1: Electrophilic attack forms a mercurinium ion.



Step 2: Water opens the ring to give an organomercurial alcohol.

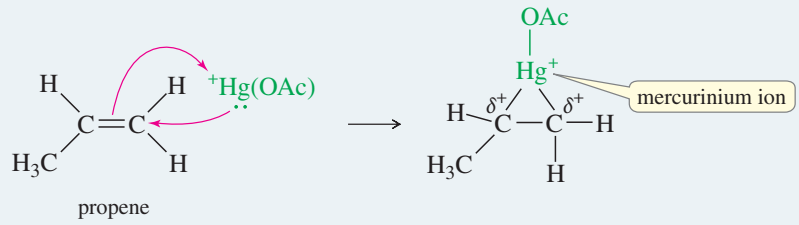


Demercuration replaces the mercuric fragment with hydrogen to give the alcohol.

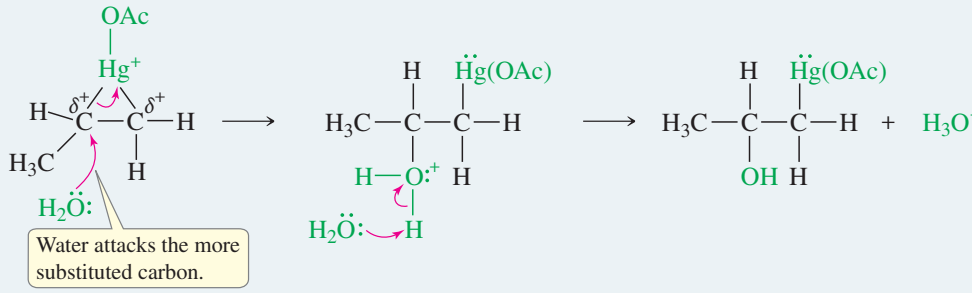


EXAMPLE: Oxymercuration–demercuration of propene.

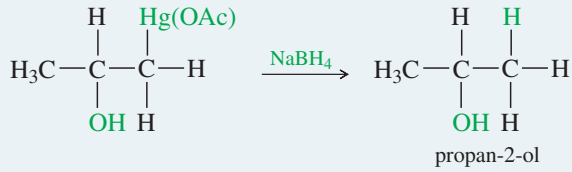
Step 1: Electrophilic attack forms a mercurinium ion.



Step 2: Water opens the ring to give an organomercurial alcohol.



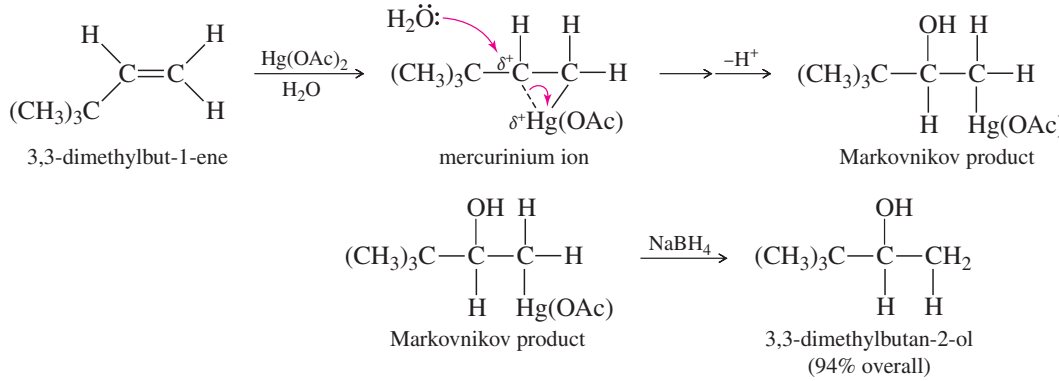
Demercuration replaces the mercuric fragment with hydrogen to give the alcohol.



Oxymercuration–demercuration of an unsymmetrical alkene generally gives Markovnikov orientation of addition, as shown by the oxymercuration of propene in the preceding example. The mercurinium ion has a considerable amount of positive charge on both of its carbon atoms, but there is more of a positive charge on the more substituted carbon atom, where it is more stable. Attack by water occurs on this more electrophilic carbon, giving Markovnikov orientation. The electrophile, $^{+}Hg(OAc)$, remains

bonded to the less substituted end of the double bond. Reduction of the organomercurial alcohol gives the Markovnikov alcohol: propan-2-ol.

Similarly, oxymercuration–demercuration of 3,3-dimethylbut-1-ene gives the Markovnikov product, 3,3-dimethylbutan-2-ol, in excellent yield. Contrast this unrearranged product with the rearranged product formed in the acid-catalyzed hydration of the same alkene in Section 8-4B. Oxymercuration–demercuration reliably adds water across the double bond of an alkene with Markovnikov orientation and without rearrangement.



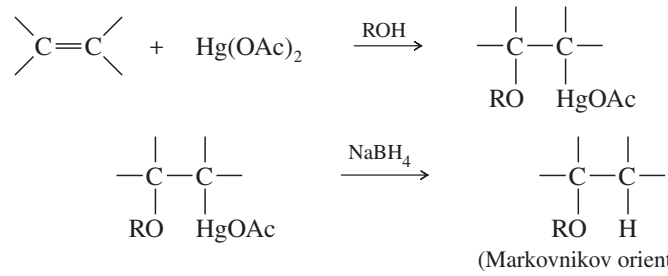
Of the methods we have seen for Markovnikov hydration of alkenes, oxymercuration–demercuration is most commonly used in the laboratory. It gives better yields than direct acid-catalyzed hydration, it avoids the possibility of rearrangements, and it does not involve harsh conditions. There are also disadvantages, however. Organomercurial compounds are highly toxic. They must be used with great care and then must be disposed of properly.

8-6 Alkoxymercuration–Demercuration

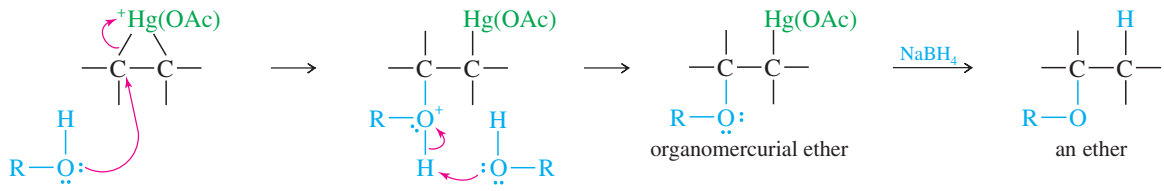
When mercuration takes place in an alcohol solvent, the alcohol serves as a nucleophile to attack the mercurinium ion. The resulting product contains an alkoxy (—O—R) group. In effect, **alkoxymercuration**–demercuration converts alkenes to ethers by adding an alcohol across the double bond of the alkene.

Application: Toxicology

Mercury and its compounds were used for centuries as ingredients in antibacterial drugs, skin creams, and antiseptics. Mercury compounds are quite toxic, however. In the body, mercury combines with the thiol groups of critical enzymes, inactivating them. Mercury poisoning causes brain and kidney damage, often leading to death.



As we have seen, an alkene reacts to form a mercurinium ion that is attacked by the nucleophilic solvent. Attack by an alcohol solvent gives an organomercurial ether that can be reduced to the ether.



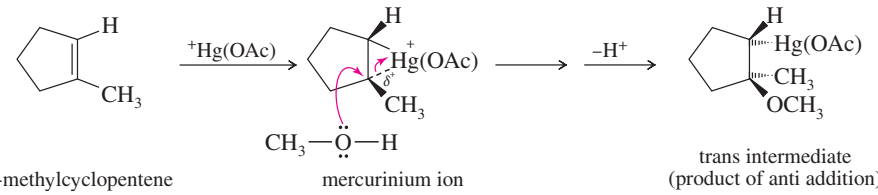
The solvent attacks the mercurinium ion at the *more* substituted end of the double bond (where there is more δ^+ charge), giving Markovnikov orientation of addition. The Hg(OAc) group appears at the *less* substituted end of the double bond. Reduction gives the Markovnikov product, with hydrogen at the less substituted end of the double bond.

SOLVED PROBLEM 8-2

Show the intermediates and products that result from alkoxymercuration–demercuration of 1-methylcyclopentene, using methanol as the solvent.

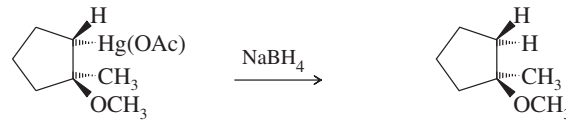
SOLUTION

Mercuric acetate adds to 1-methylcyclopentene to give the cyclic mercurinium ion. This ion has a considerable amount of positive charge on the more substituted tertiary carbon atom. Methanol attacks this carbon from the opposite side, leading to ***anti* addition:** The reagents (HgOAc and OCH_3) have added to opposite faces of the double bond.



1-methylcyclopentene — mercurinium ion — trans intermediate (product of anti addition)

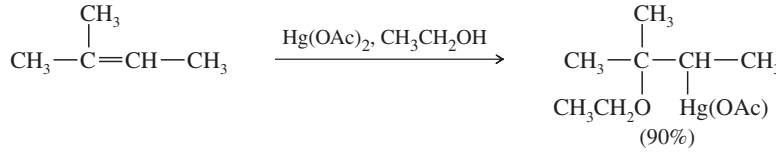
Reduction of the intermediate gives the Markovnikov product, 1-methoxy-1-methylcyclopentane.



intermediate — 1-methoxy-1-methylcyclopentane

PROBLEM 8-7

(a) Propose a mechanism for the following reaction.



(b) Give the structure of the product that results when this intermediate is reduced by sodium borohydride.

PROBLEM 8-8

Predict the major products of the following reactions.

(a) 1-methylcyclohexene + aqueous $Hg(OAc)_2$

(b) the product from part (a), treated with $NaBH_4$

(c) 4-chlorocycloheptene + $Hg(OAc)_2$ in CH_3OH

(d) the product from part (c), treated with $NaBH_4$

PROBLEM 8-9

Show how you would accomplish the following synthetic conversions.

(a) but-1-ene → 2-methoxybutane

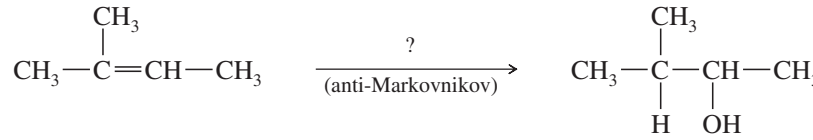
(b) 1-iodo-2-methylcyclopentane → 1-methylcyclopentanol

(c) 3-methylpent-1-ene → 3-methylpentan-2-ol

Explain why acid-catalyzed hydration would be a poor choice for the reaction in (c).

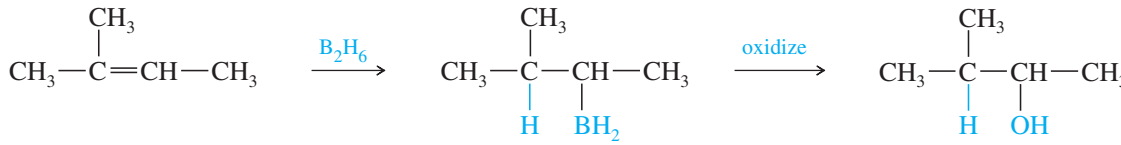
8-7 Hydroboration of Alkenes

We have seen two methods for hydrating an alkene with Markovnikov orientation. What if we need to convert an alkene to the anti-Markovnikov alcohol? For example, the following transformation cannot be accomplished using the hydration procedures covered thus far.



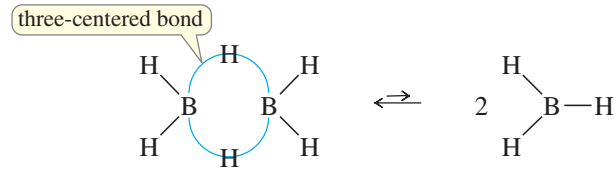
2-methylbut-2-ene 3-methylbutan-2-ol

Such an anti-Markovnikov hydration was impossible until H. C. Brown, of Purdue University, discovered that diborane (B_2H_6) adds to alkenes with anti-Markovnikov orientation to form alkylboranes, which can be oxidized to give anti-Markovnikov alcohols. This discovery led to the development of a large field of borane chemistry, for which Brown received the Nobel Prize in Chemistry in 1979.



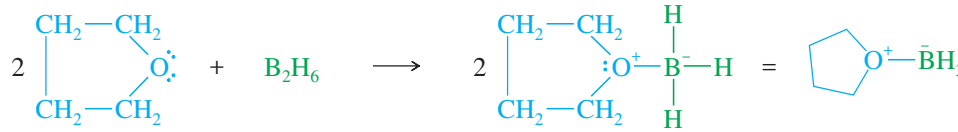
2-methylbut-2-ene an alkylborane 3-methylbutan-2-ol (>90%)

Diborane (B_2H_6) is a dimer composed of two molecules of borane (BH_3). The bonding in diborane is unconventional, using three-centered (banana-shaped) bonds with protons in the middle of them. Diborane is in equilibrium with a small amount of borane (BH_3), a strong Lewis acid with only six valence electrons.



diborane borane

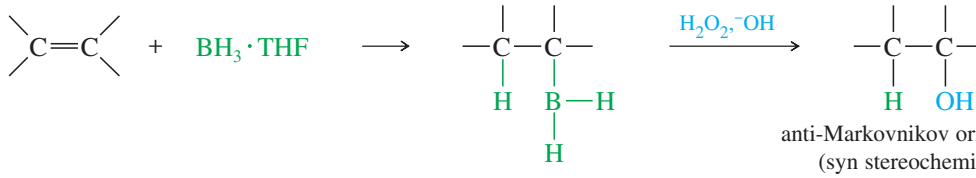
Diborane is an inconvenient reagent. It is a toxic, flammable, and explosive gas. It is more easily used as a complex with tetrahydrofuran (THF), a cyclic ether. This complex reacts like diborane, yet the solution is easily measured and transferred.



tetrahydrofuran (THF) diborane borane–THF complex = $BH_3 \cdot THF$

The $BH_3 \cdot THF$ reagent is the form of borane commonly used in organic reactions. BH_3 adds to the double bond of an alkene to give an alkylborane. Basic hydrogen peroxide oxidizes the alkylborane to an alcohol. In effect, hydroboration–oxidation converts alkenes to alcohols by adding water across the double bond, with anti-Markovnikov orientation.

Hydroboration–oxidation:



anti-Markovnikov orientation (syn stereochemistry)

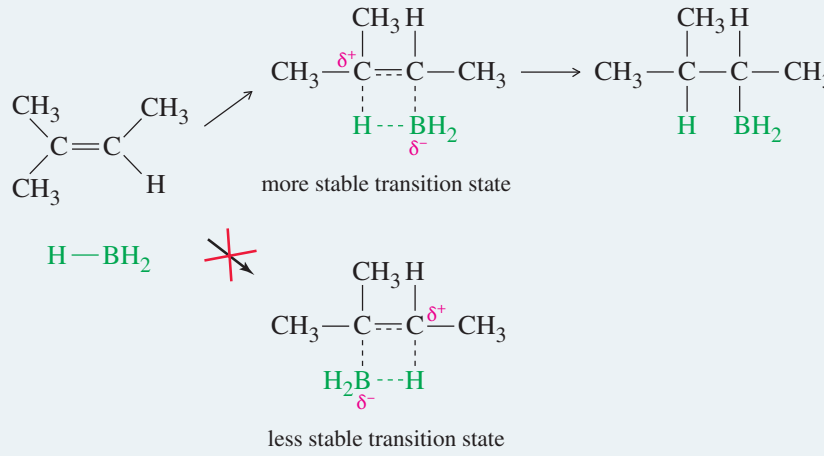
8-7A Mechanism of Hydroboration

Borane is an electron-deficient compound. It has only six valence electrons, so the boron atom in BH_3 cannot have an octet. Acquiring an octet is the driving force for the unusual bonding structures ("banana" bonds, for example) found in boron compounds. As an electron-deficient compound, BH_3 is a strong electrophile, capable of adding to a double bond. This **hydroboration** of the double bond is thought to occur in one step, with the boron atom adding to the less substituted end of the double bond, as shown in Mechanism 8-6.

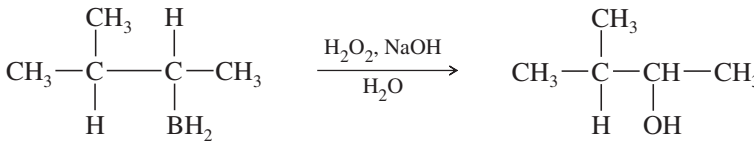
In the transition state, the electrophilic boron atom withdraws electrons from the pi bond, and the carbon at the other end of the double bond acquires a partial positive charge. This partial charge is more stable on the more substituted carbon atom. The product shows boron bonded to the less substituted end of the double bond and hydrogen bonded to the more substituted end. Also, steric hindrance favors boron adding to the less hindered, less substituted end of the double bond.

MECHANISM 8-6 Hydroboration of an Alkene

Borane adds to the double bond in a single step. Boron adds to the less hindered, less substituted carbon, and hydrogen adds to the more substituted carbon.



The boron atom is removed by oxidation, using aqueous sodium hydroxide and hydrogen peroxide (HOOH or H_2O_2) to replace the boron atom with a hydroxyl (—OH) group. The oxidation does not affect the orientation of the product, because the anti-Markovnikov orientation was established in the first step, the addition of BH_3.



This hydration of an alkene by hydroboration–oxidation is another example of a reaction that does not follow the original statement of Markovnikov's rule (the product is anti-Markovnikov), but still follows our understanding of the reasoning behind Markovnikov's rule. The electrophilic boron atom adds to the *less* substituted end of the double bond, placing the positive charge (and the hydrogen atom) at the more substituted end.

Problem-solving Hint

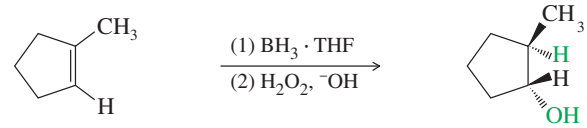
Work backward on multistep syntheses.

SOLVED PROBLEM 8-3

Show how you would convert 1-methylcyclopentanol to 2-methylcyclopentanol.

SOLUTION

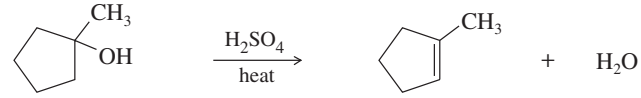
Working backward, use hydroboration–oxidation to form 2-methyl-cyclopentanol from 1-methylcyclopentene. The use of (1) and (2) above and below the reaction arrow indicates individual steps in a two-step sequence.



1-methylcyclopentene *trans*-2-methylcyclopentanol

The 2-methylcyclopentanol that results from this synthesis is the pure trans isomer. This stereochemical result is discussed in Section 8-7C.

1-Methylcyclopentene is the most substituted alkene that results from dehydration of 1-methylcyclopentanol. Dehydration of the alcohol would give the correct alkene.



1-methylcyclopentanol 1-methylcyclopentene

PROBLEM 8-10

Predict the major products of the following reactions.

(a) propene + $BH_3 \cdot THF$
(b) the product from part (a) + H_2O_2/OH^-
(c) 2-methylpent-2-ene + $BH_3 \cdot THF$
(d) the product from part (c) + H_2O_2/OH^-
(e) 1-methylcyclohexene + $BH_3 \cdot THF$
(f) the product from part (e) + H_2O_2/OH^-

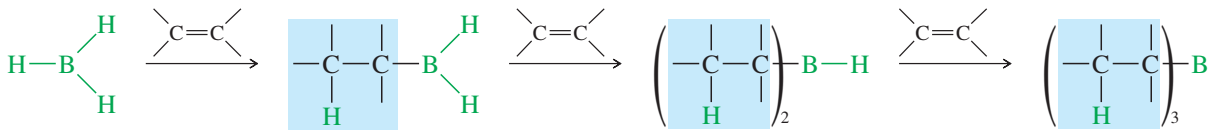
PROBLEM 8-11

Show how you would accomplish the following synthetic conversions.

(a) but-1-ene → butan-1-ol
(b) but-1-ene → butan-2-ol
(c) 2-bromo-2,4-dimethylpentane → 2,4-dimethylpentan-3-ol

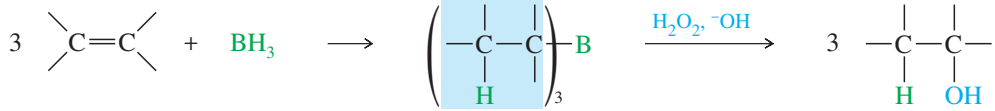
8-7B Stoichiometry of Hydroboration

For simplicity, we have neglected the fact that 3 moles of an alkene can react with each mole of BH_3. Each B—H bond in BH_3 can add across the double bond of an alkene. The first addition forms an alkylborane, the second a dialkylborane, and the third a trialkylborane.



alkylborane dialkylborane trialkylborane

Summary



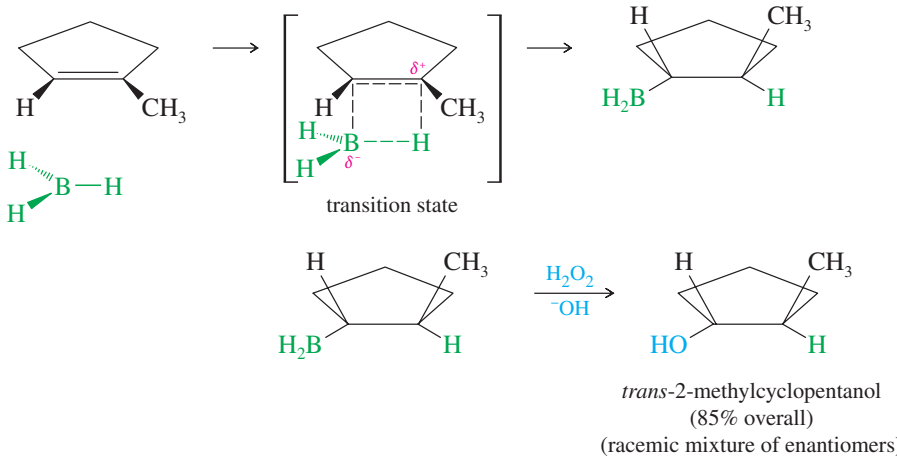
Trialkylboranes react exactly as we have discussed, and they oxidize to give anti-Markovnikov alcohols. Trialkylboranes are quite bulky, further reinforcing the preference for boron to add to the less hindered carbon atom of the double bond. Boranes are often

drawn as the 1:1 monoalkylboranes to simplify their structure and emphasize the organic part of the molecule.

8-7C Stereochemistry of Hydroboration

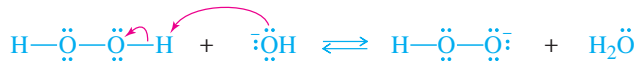
The simultaneous addition of boron and hydrogen to the double bond (as shown in Mechanism 8-6) leads to a **syn addition:** Boron and hydrogen add across the double bond on the *same side* of the molecule. (If they added to opposite sides of the molecule, the process would be an **anti addition.**)

The stereochemistry of the hydroboration–oxidation of 1-methylcyclopentene is shown next. Boron and hydrogen add to the same face of the double bond (syn) to form a trialkylborane. Oxidation of the trialkylborane replaces boron with a hydroxyl group in the same stereochemical position. The product is *trans*-2-methylcyclopentanol. A racemic mixture is expected because a chiral product is formed from achiral reagents.

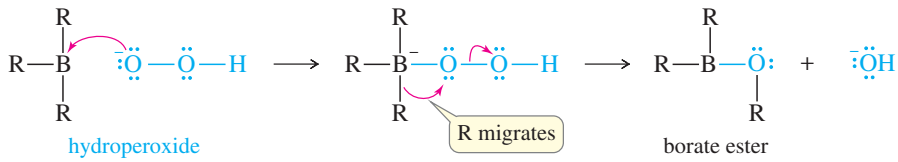


The second step (oxidation of the borane to the alcohol) takes place with retention of configuration. Hydroperoxide ion adds to the borane, causing the alkyl group to migrate from boron to oxygen. The alkyl group migrates with retention of configuration because it moves with its electron pair and does not alter the tetrahedral structure of the migrating carbon atom. Hydrolysis of the borate ester gives the alcohol.

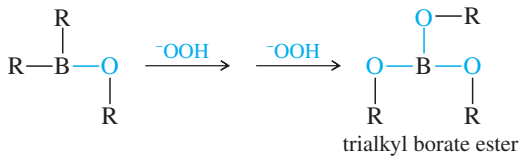
Formation of hydroperoxide ion



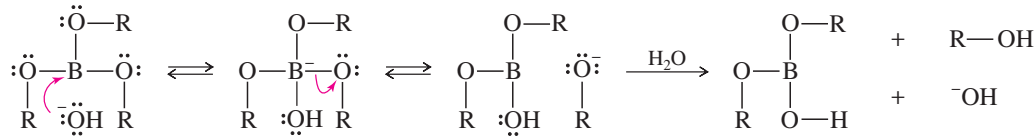
Addition of hydroperoxide and migration of the alkyl group



Twice more to oxidize the other two alkyl groups



Hydrolysis of the borate ester

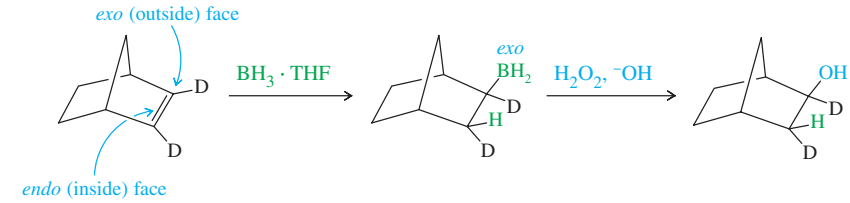


(The other two OR groups hydrolyze similarly.)

Hydroboration of alkenes is another example of a **stereospecific reaction,** in which different stereoisomers of the starting compound react to give different stereoisomers of the product. Problem 8-14 considers the different products formed by the hydroboration–oxidation of two acyclic diastereomers.

SOLVED PROBLEM 8-4

A norbornene molecule labeled with deuterium is subjected to hydroboration–oxidation. Give the structures of the intermediates and products.



deuterium-labeled norbornene — alkylborane — alcohol (racemic mixture)

SOLUTION

The syn addition of BH_3 across the double bond of norbornene takes place mostly from the more accessible outside (exo) face of the double bond. Oxidation gives a product with both the hydrogen atom and the hydroxyl group in exo positions. (The less accessible inner face of the double bond is called the endo face.)

PROBLEM 8-12

In the hydroboration of 1-methylcyclopentene shown in Solved Problem 8-3, the reagents are achiral, and the products are chiral. The product is a racemic mixture of *trans*-2-methylcyclopentanol, but only one enantiomer is shown. Show how the other enantiomer is formed.

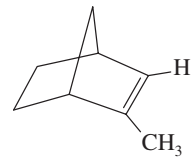
PROBLEM 8-13

Predict the major products of the following reactions. Include stereochemistry where applicable.

(a) 1-methylcycloheptene + $BH_3 \cdot THF$, then H_2O_2, OH^-

(b) *trans*-4,4-dimethylpent-2-ene + $BH_3 \cdot THF$, then H_2O_2, OH^-

(c)



+ $BH_3 \cdot THF$, then H_2O_2, OH^-

PROBLEM 8-14

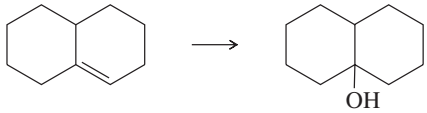
(a) When (*Z*)-3-methylhex-3-ene undergoes hydroboration–oxidation, two isomeric products are formed. Give their structures, and label each asymmetric carbon atom as (*R*) or (*S*). What is the relationship between these isomers?

(b) Repeat part (a) for (*E*)-methylhex-3-ene. What is the relationship between the products formed from (*Z*)-3-methylhex-3-ene and those formed from (*E*)-3-methylhex-3-ene?

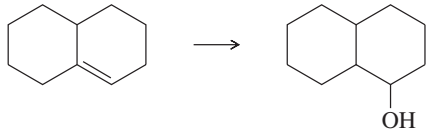
PROBLEM 8-15

Show how you would accomplish the following transformations.

(a)



(b)



(c) 1-methylcycloheptanol → 2-methylcycloheptanol

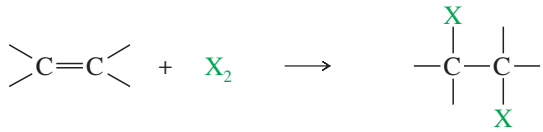
PROBLEM 8-16

(a) When HBr adds across the double bond of 1,2-dimethylcyclopentene, the product is a mixture of the cis and trans isomers. Show why this addition is not stereospecific.

(b) When 1,2-dimethylcyclopentene undergoes hydroboration–oxidation, one diastereomer of the product predominates. Show why this addition is stereospecific, and predict the stereochemistry of the major product.

8-8 Addition of Halogens to Alkenes

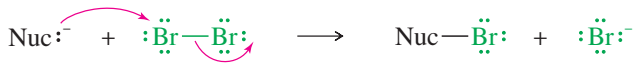
Halogens add to alkenes to form vicinal dihalides.



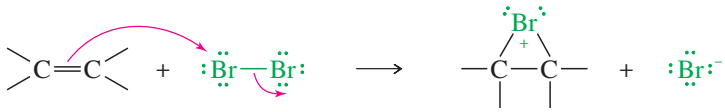
(X_2 = Cl_2, Br_2, sometimes I_2) usually anti addition

8-8A Mechanism of Halogen Addition

A halogen molecule (Br_2, Cl_2, or I_2) is electrophilic; a nucleophile can react with a halogen, displacing a halide ion:



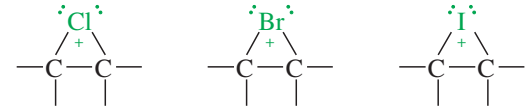
In this example, the nucleophile attacks the electrophilic nucleus of one bromine atom, and the other bromine serves as the leaving group, departing as bromide ion. Many reactions fit this general pattern; for example:



bromonium ion

In the last reaction, the pi electrons of an alkene attack the bromine molecule, expelling bromide ion. A **bromonium ion** results, containing a three-membered ring with a positive charge on the bromine atom. This bromonium ion is similar in structure to the mercurinium ion discussed in Section 8-5. Similar reactions with other halogens form other **halonium ions.** The structures of a **chloronium ion,** a **bromonium ion,** and an **iodonium ion** are shown next.

Examples



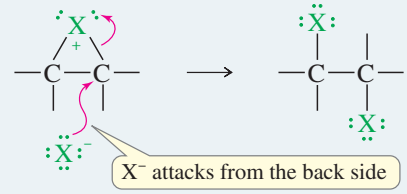
chloronium ion bromonium ion iodonium ion

Unlike a normal carbocation, all the atoms in a halonium ion have filled octets. The three-membered ring has considerable ring strain, however, which, combined with a positive charge on an electronegative halogen atom, makes the halonium ion strongly electrophilic. Attack by a nucleophile, such as a halide ion, opens the halonium ion to give a stable product.

MECHANISM 8-7 Addition of Halogens to Alkenes

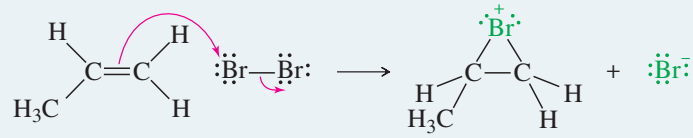
Step 1: Electrophilic attack forms a halonium ion.

Step 2: The halide ion opens the halonium ion.



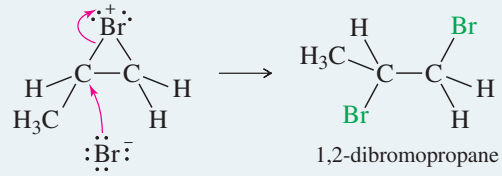
EXAMPLE: Addition of Br_2 to propene.

Step 1: Electrophilic attack forms a bromonium ion.

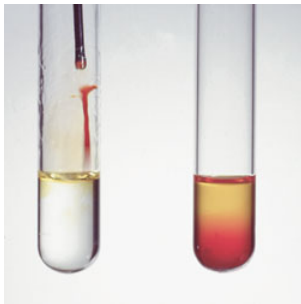


propene bromonium ion

Step 2: Bromide ion opens the bromonium ion.



1,2-dibromopropane



When a solution of bromine (red-brown) is added to cyclohexene, the bromine color quickly disappears because bromine adds across the double bond. When bromine is added to cyclohexane (at right), the color persists because no reaction occurs.

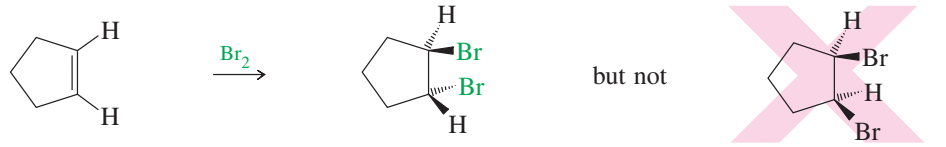
Chlorine and bromine commonly add to alkenes by the halonium ion mechanism. Iodination is used less frequently because diiodide products decompose easily. Any solvents used must be inert to the halogens; methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4) are the most frequent choices.

The addition of bromine has been used as a simple chemical test for the presence of olefinic double bonds. A solution of bromine in carbon tetrachloride is a clear, deep

red color. When this red solution is added to an alkene, the red bromine color disappears (we say it is "decolorized"), and the solution becomes clear and colorless. (Although there are other functional groups that decolorize bromine, few do it as quickly as alkenes.)

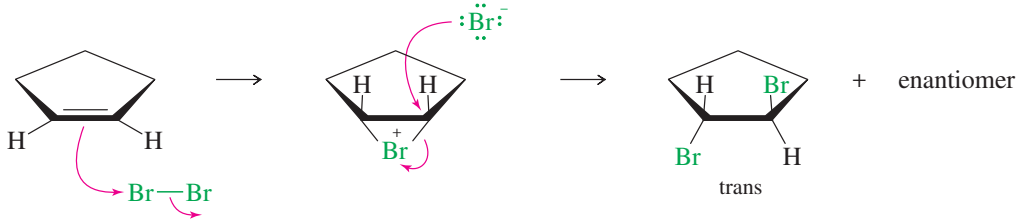
8-8B Stereochemistry of Halogen Addition

The addition of bromine to cyclopentene is a stereospecific **anti addition.**



cyclopentene — *trans*-1,2-dibromocyclopentane (92%) (both enantiomers) — but not — *cis*-1,2-dibromocyclopentane (not formed)

Anti stereochemistry results from the bromonium ion mechanism. When a nucleophile attacks a halonium ion, it must do so from the back side, in a manner similar to the S_N2 displacement. This back-side attack assures anti stereochemistry of addition.



Halogen addition is another example of a stereospecific reaction, in which different stereoisomers of the starting material give different stereoisomers of the product. Figure 8-4 shows additional examples of the anti addition of halogens to alkenes.

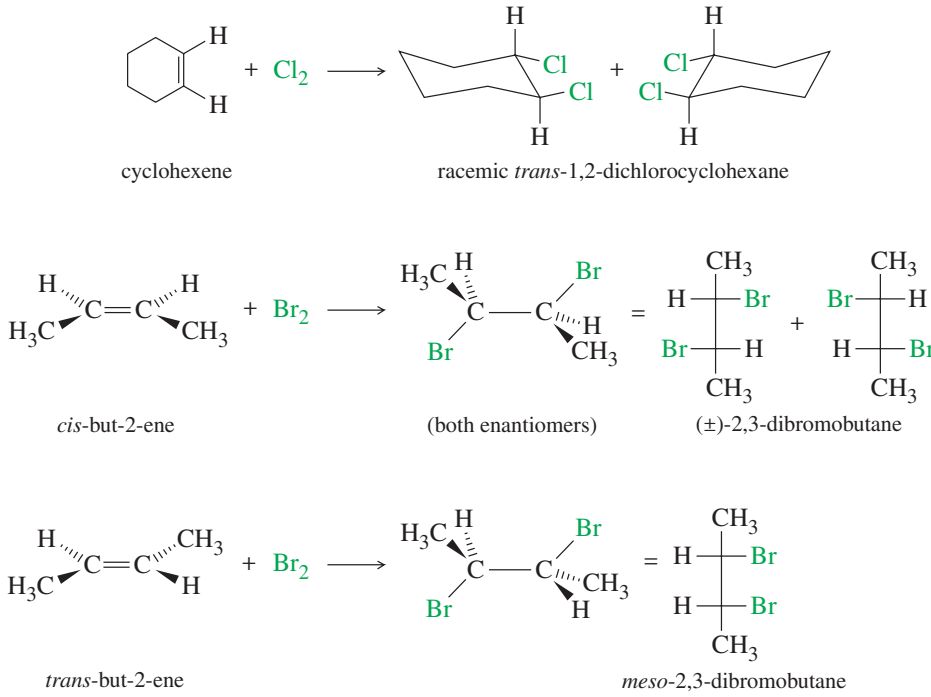


FIGURE 8-4
Examples of the anti addition of halogens to alkenes. The stereospecific anti addition gives predictable stereoisomers of the products.

PROBLEM 8-17

Give mechanisms to account for the stereochemistry of the products observed from the addition of bromine to *cis*- and *trans*-but-2-ene (Figure 8-4). Why are two products formed from the cis isomer but only one from the trans? (Making models will be helpful.)

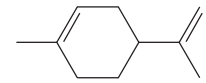
Problem-solving Hint

Models may be helpful whenever stereochemistry is involved. Write complete structures, including all bonds and charges, when writing mechanisms.

PROBLEM 8-18

Propose mechanisms and predict the major products of the following reactions. Include stereochemistry where appropriate.

(a) cycloheptene + Br_2 in CH_2Cl_2

(b)  + 2 Cl_2 in CCl_4

(c) (*E*)-dec-3-ene + Br_2 in CCl_4

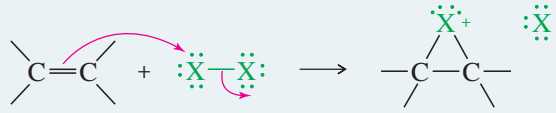
(d) (*Z*)-dec-3-ene + Br_2 in CCl_4

8-9 Formation of Halohydrins

A **halohydrin** is an alcohol with a halogen on the adjacent carbon atom. In the presence of water, halogens add to alkenes to form halohydrins. The electrophilic halogen adds to the alkene to give a halonium ion, which is also electrophilic. Water acts as a nucleophile to open the halonium ion and form the halohydrin.

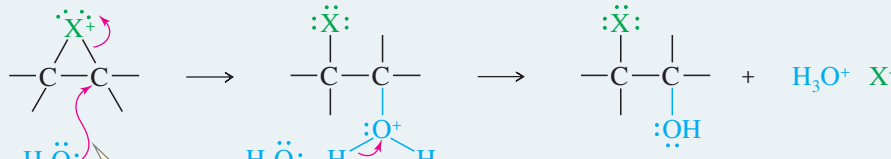
MECHANISM 8-8 Formation of Halohydrins

Step 1: Electrophilic attack forms a halonium ion.



(X = Cl, Br, or I) halonium ion

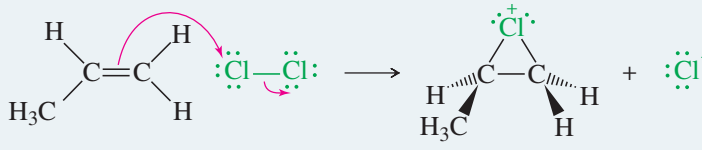
Step 2: Water opens the halonium ion; deprotonation gives the halohydrin.



halohydrin
Markovnikov orientation
anti stereochemistry

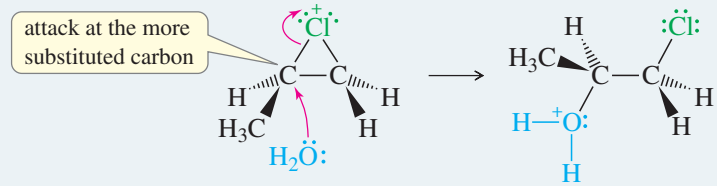
EXAMPLE: Addition of Cl_2 to propene in water.

Step 1: Electrophilic attack forms a chloronium ion.

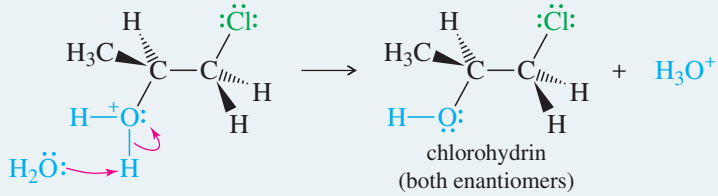


propene chloronium ion

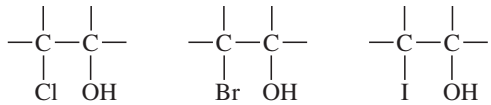
Step 2: Back-side attack by water opens the chloronium ion.



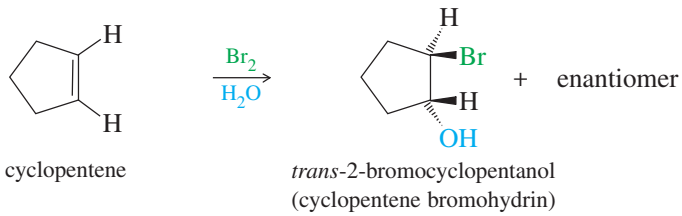
Step 3: Water removes a proton to give the chlorohydrin.



When halogenation takes place with no solvent or with an inert solvent such as carbon tetrachloride (CCl_4) or chloroform ($CHCl_3$), only the halide ion is available as a nucleophile to attack the halonium ion. A dihalide results. But when an alkene reacts with a halogen in the presence of a nucleophilic solvent such as water, a solvent molecule is the most likely nucleophile to attack the halonium ion. When a water molecule attacks the halonium ion, the final product is a halohydrin, with a halogen on one carbon atom and a hydroxyl group on the adjacent carbon. The product may be a *chlorohydrin*, a *bromohydrin*, or an *iodohydrin*, depending on the halogen.



Stereochemistry of Halohydrin Formation Because the mechanism involves a halonium ion, the stereochemistry of addition is anti, as in halogenation. For example, the addition of bromine water to cyclopentene gives *trans*-2-bromocyclopentanol, the product of anti addition across the double bond.



PROBLEM 8-19

Propose a mechanism for the addition of bromine water to cyclopentene, being careful to show why the trans product results and how both enantiomers are formed.

Orientation of Halohydrin Formation Even though a halonium ion is involved, rather than a carbocation, the extended version of Markovnikov's rule applies to halohydrin formation. When propene reacts with chlorine water, the major product has the

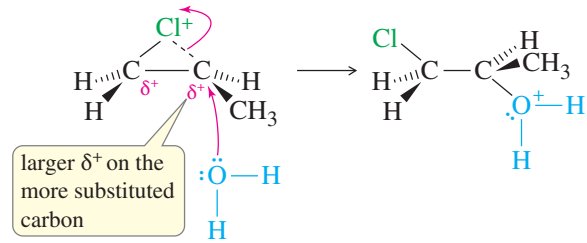
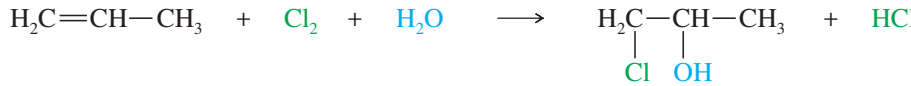


FIGURE 8-5
Orientation of halohydrin formation. The more substituted carbon of the chloronium ion bears more positive charge than the less substituted carbon. Attack by water occurs on the more substituted carbon to give the Markovnikov product.

electrophile (the chlorine atom) bonded to the less substituted carbon of the double bond. The nucleophile (the hydroxyl group) is bonded to the more substituted carbon.



The Markovnikov orientation observed in halohydrin formation is explained by the structure of the halonium ion intermediate. The two carbon atoms bonded to the halogen have partial positive charges, with a larger charge (and a weaker bond to the halogen) on the more substituted carbon atom (Figure 8-5). The nucleophile (water) attacks this more substituted, more electrophilic carbon atom. The result is both anti stereochemistry and Markovnikov orientation.

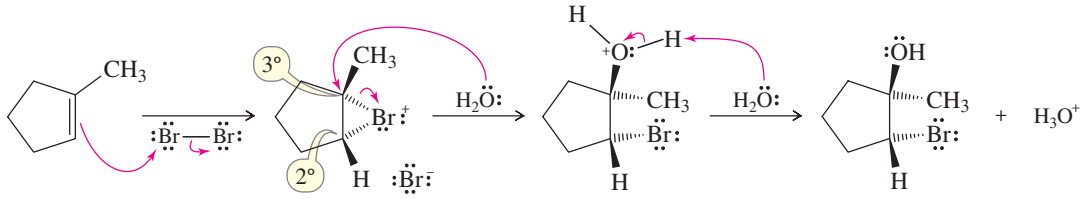
This halonium ion mechanism can be used to explain and predict a wide variety of reactions in both nucleophilic and non-nucleophilic solvents. The halonium ion mechanism is similar to the mercurinium ion mechanism for oxymercuration of an alkene, and both give Markovnikov orientation (Section 8-5).

SOLVED PROBLEM 8-5

Propose a mechanism for the reaction of 1-methylcyclopentene with bromine water.

SOLUTION

1-Methylcyclopentene reacts with bromine to give a bromonium ion. Attack by water could occur at either the secondary carbon or the tertiary carbon of the bromonium ion. Attack actually occurs at the more substituted carbon, which bears more of the positive charge. The product is formed as a racemic mixture.



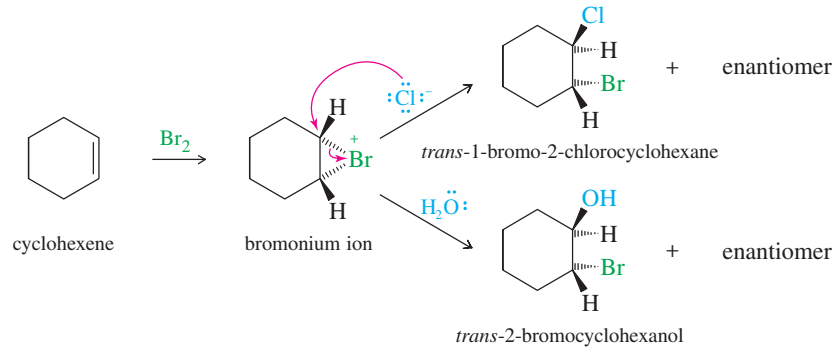
(both enantiomers)

SOLVED PROBLEM 8-6

When cyclohexene is treated with bromine in saturated aqueous sodium chloride, a mixture of *trans*-2-bromocyclohexanol and *trans*-1-bromo-2-chlorocyclohexane results. Propose a mechanism to account for these two products.

SOLUTION

Cyclohexene reacts with bromine to give a bromonium ion, which will react with any available nucleophile. The most abundant nucleophiles in saturated aqueous sodium chloride solution are water and chloride ions. Attack by water gives the bromohydrin, and attack by chloride gives the dihalide. Either of these attacks gives anti stereochemistry.



PROBLEM 8-20

The solutions to Solved Problem 8-5 and Solved Problem 8-6 showed only how one enantiomer of the product is formed. For each product, show how an equally probable reaction forms the other enantiomer.

PROBLEM 8-21

Predict the major product(s) for each reaction. Include stereochemistry where appropriate.

(a) 1-methylcyclohexene + Cl_2/H_2O
(b) 2-methylbut-2-ene + Br_2/H_2O
(c) *cis*-but-2-ene + Cl_2/H_2O
(d) *trans*-but-2-ene + Cl_2/H_2O
(e) 1-methylcyclopentene + Br_2 in saturated aqueous NaCl

PROBLEM 8-22

Show how you would accomplish the following synthetic conversions.

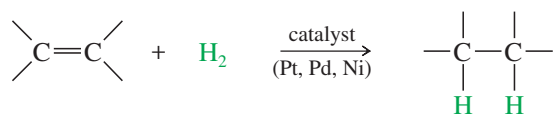
(a) 3-methylpent-2-ene → 2-chloro-3-methylpentan-3-ol
(b) chlorocyclohexane → *trans*-2-chlorocyclohexanol
(c) 1-methylcyclopentanol → 2-chloro-1-methylcyclopentanol

Problem-solving Hint

The opening of a halonium ion is driven by its electrophilic nature. The weak nucleophile attacks the carbon bearing more positive charge.

8-10 Catalytic Hydrogenation of Alkenes

Although we have mentioned **catalytic hydrogenation** before (Sections 7-7 and 8-1), we now consider the mechanism and stereochemistry in more detail. Hydrogenation of an alkene is formally a reduction, with H_2 adding across the double bond to give an alkane. The process usually requires a catalyst containing Pt, Pd, or Ni.

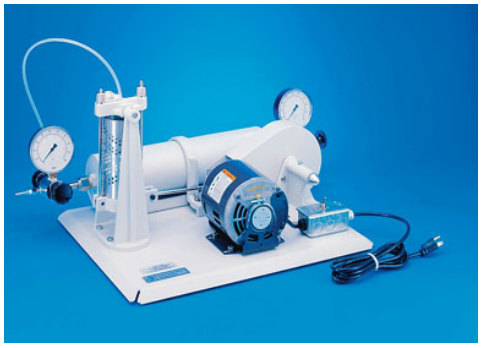


Example

$$CH_3{-}CH{=}CH{-}CH_3 + H_2 \xrightarrow{Pt} CH_3{-}CH_2{-}CH_2{-}CH_3$$

For most alkenes, hydrogenation takes place at room temperature, using hydrogen gas at atmospheric pressure. The alkene is usually dissolved in an alcohol, an alkane, or acetic acid. A small amount of platinum, palladium, or nickel catalyst is added, and the container is shaken or stirred while the reaction proceeds. Hydrogenation actually takes place at the surface of the metal, where the liquid solution of the alkene comes into contact with hydrogen and the catalyst.

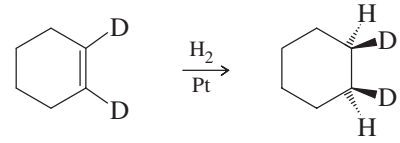
Hydrogen gas is adsorbed onto the surface of these metal catalysts, and the catalyst weakens the H—H bond. In fact, if H_2 and D_2 are mixed in the presence of a



The Parr hydrogenation apparatus shakes the reaction vessel (containing the alkene and the solid catalyst), while a pressurized cylinder supplies hydrogen.

platinum catalyst, the two isotopes quickly scramble to produce a random mixture of HD, H_2, and D_2. (No scrambling occurs in the absence of the catalyst.) Hydrogenation is an example of **heterogeneous catalysis,** because the (solid) catalyst is in a different phase from the reactant solution. In contrast, **homogeneous catalysis** involves reactants and catalyst in the same phase, as in the acid-catalyzed dehydration of an alcohol.

Because the two hydrogen atoms add from a solid surface, they add with **syn** stereochemistry. For example, when 1,2-dideuteriocyclohexene is treated with hydrogen gas over a catalyst, the product is the cis isomer resulting from syn addition (Figure 8-6).



One face of the alkene pi bond binds to the catalyst, which has hydrogen adsorbed on its surface. Hydrogen inserts into the pi bond, and the product is freed from the catalyst. Both hydrogen atoms add to the face of the double bond that is complexed with the catalyst.

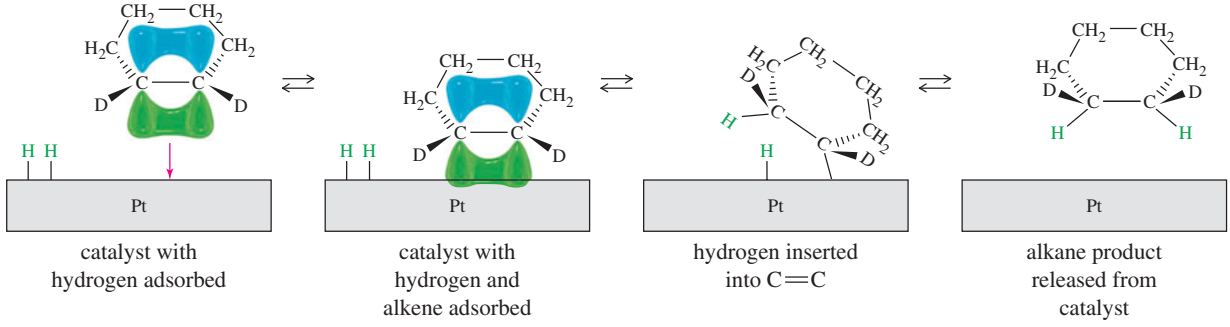
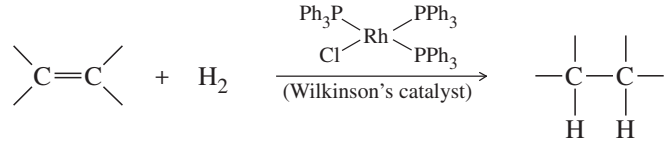


FIGURE 8-6
Syn stereochemistry in catalytic hydrogenation. A solid heterogeneous catalyst adds two hydrogen atoms to the same face of the pi bond (syn stereochemistry).

Soluble homogeneous catalysts, such as *Wilkinson's catalyst*, also catalyze the hydrogenation of carbon–carbon double bonds.



Wilkinson's catalyst is not chiral, but its triphenylphosphine (PPh_3) ligands can be replaced by chiral ligands to give chiral catalysts that are capable of converting optically inactive starting materials to optically active products. Such a process is called **asymmetric induction** or **enantioselective synthesis.** For example, Figure 8-7 shows a chiral ruthenium complex catalyzing an enantioselective hydrogenation of a carbon–carbon double bond to give a large excess of one enantiomer. Because the catalyst is chiral, the transition states leading to the two enantiomers of product are diastereomeric. They have different energies, and the transition state leading to the (*R*) enantiomer is favored. Ryoji Noyori and William Knowles shared the 2001 Nobel Prize in Chemistry for their work on chirally catalyzed hydrogenation reactions.

Enantioselective synthesis is particularly important in the pharmaceutical industry, because only one enantiomer of a chiral drug is likely to have the desired effect. For example, levodopa [(−)-dopa or *l*-dopa] is used in patients with Parkinson's disease to counteract a deficiency of dopamine, one of the neurotransmitters in the brain. Dopamine

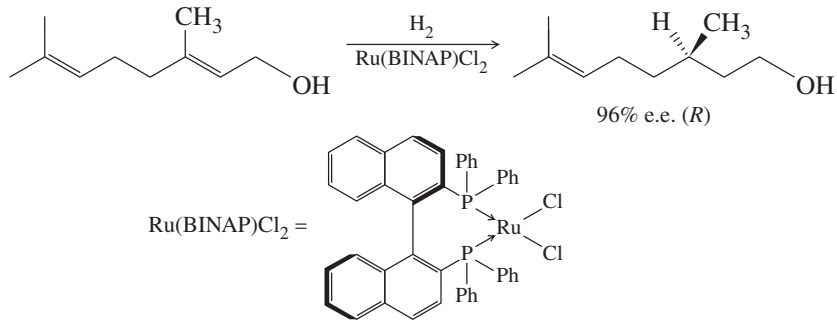
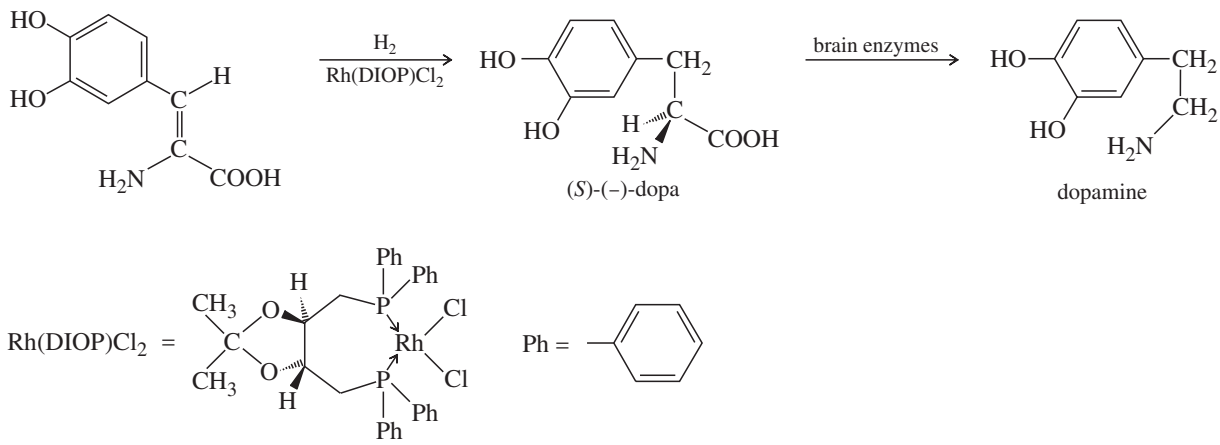


FIGURE 8-7
Chiral hydrogenation catalysts. Rhodium and ruthenium phosphines are effective homogeneous catalysts for hydrogenation. Chiral ligands can be attached to accomplish asymmetric induction, the creation of a new asymmetric carbon as mostly one enantiomer.

itself is useless as a drug because it cannot cross the "blood–brain barrier"; that is, it cannot get into the cerebrospinal fluid from the bloodstream. (−)-Dopa, on the other hand, is an amino acid related to tyrosine. It crosses the blood–brain barrier into the cerebrospinal fluid, where it undergoes enzymatic conversion to dopamine. Only the (−) enantiomer of dopa can be transformed into dopamine; the other enantiomer, (+)-dopa, is toxic to the patient.

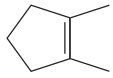
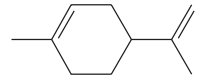
The correct enantiomer can be synthesized from an achiral starting material by catalytic hydrogenation using a complex of rhodium with a chiral ligand called DIOP. Such an enantioselective synthesis is more efficient than making a racemic mixture, resolving it into enantiomers, and discarding the unwanted enantiomer.



PROBLEM 8-23

Give the expected major product for each reaction, including stereochemistry where applicable.

(a) but-1-ene + H_2/Pt **(b)** *cis*-but-2-ene + H_2/Ni

(c)  + H_2/Pt **(d)**  + excess H_2/Pt

PROBLEM 8-24

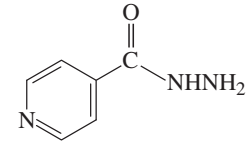
One of the principal components of lemon grass oil is *limonene*, $C_{10}H_{16}$. When limonene is treated with excess hydrogen and a platinum catalyst, the product is an alkane of formula $C_{10}H_{20}$. What can you conclude about the structure of limonene?

PROBLEM 8-25

The chiral BINAP ligand shown in Figure 8-7 contains no asymmetric carbon atoms. Explain how this ligand is chiral.

Application: Antibiotics

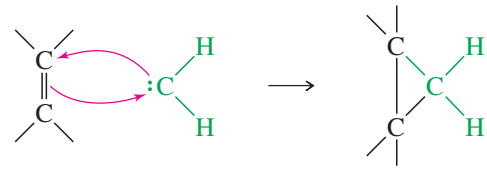
The enzymatic reduction of a double bond is a key step in the formation of a fatty acid that is ultimately incorporated into the cell wall of the bacterium that causes tuberculosis. The antituberculosis drug isoniazid blocks this enzyme, preventing reduction of the double bond. Without an intact cell wall, the bacteria die.



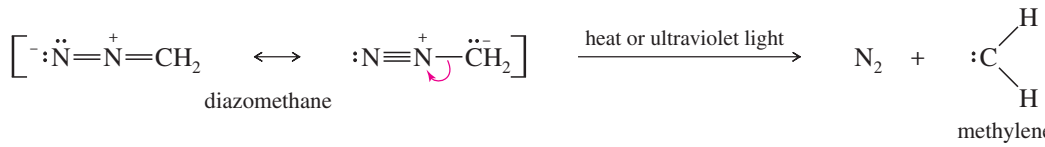
isoniazid

8-11 Addition of Carbenes to Alkenes

Methylene ($:CH_2$) is the simplest of the **carbenes:** uncharged, reactive intermediates that have a carbon atom with two bonds and two nonbonding electrons. Like borane (BH_3), methylene is a potent electrophile because it has an unfilled octet. It adds to the electron-rich pi bond of an alkene to form a cyclopropane.

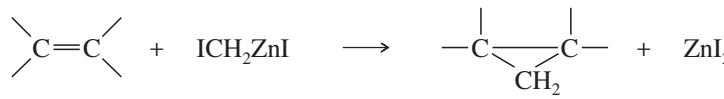


Heating or photolysis of diazomethane gives nitrogen gas and methylene:

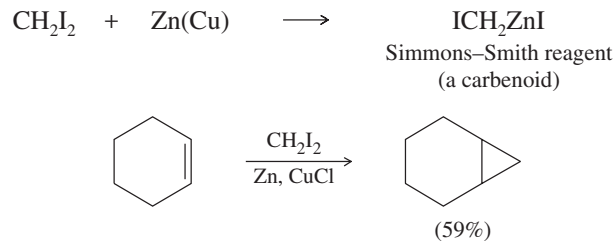


The methylene generated from diazomethane reacts with alkenes to form cyclopropanes, but diazomethane is very toxic and explosive, and the methylene generated is so reactive that it forms many side products. A safer and more reliable way to make cyclopropanes is with the Simmons–Smith reagent.

8-11A The Simmons–Smith Reaction



The **Simmons–Smith reagent,** named for the two DuPont chemists who discovered it, is made by adding methylene iodide to the "zinc–copper couple" (zinc dust that has been activated with an impurity of copper). The reagent probably resembles iodomethyl zinc iodide, ICH_2ZnI. This kind of reagent is called a *carbenoid* because it reacts much like a carbene, but it does not actually contain a divalent carbon atom.

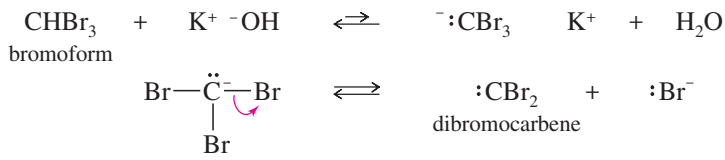


PROBLEM 8-26

Predict the carbenoid addition products of the following reactions.
(a) *trans*-hex-3-ene + CH_2I_2, Zn(Cu) **(b)** *cis*-hept-2-ene + CH_2I_2, Zn(Cu)

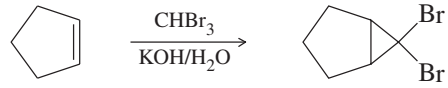
8-11B Formation of Carbenes by Alpha Elimination

Carbenes are also formed by reactions of halogenated compounds with bases. If a carbon atom has bonds to at least one hydrogen and to enough halogen atoms to make the hydrogen slightly acidic, it may be possible to form a carbene. For example, bromoform ($CHBr_3$) reacts with a 50% aqueous solution of potassium hydroxide to form dibromocarbene.

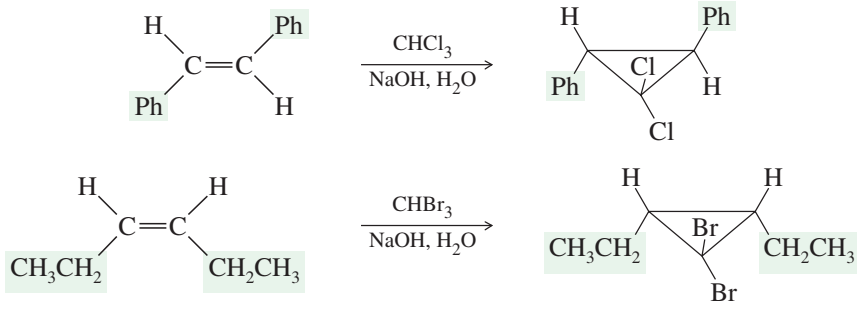


This dehydrohalogenation is called an **alpha elimination** (α elimination) because the hydrogen and the halogen are lost from the same carbon atom. The more common dehydrohalogenations (to form alkenes) are called **beta eliminations** because the hydrogen and the halogen are lost from adjacent carbon atoms.

Dibromocarbene formed from $CHBr_3$ can add to a double bond to form a dibromocyclopropane.



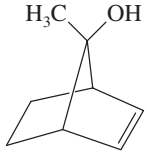
The products of these cyclopropanations retain any cis or trans stereochemistry of the reactants.



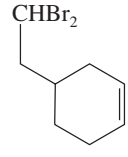
PROBLEM 8-27

Predict the carbene addition products of the following reactions.

(a) cyclohexene + $CHCl_3$, 50% $NaOH/H_2O$

(b) 

+ CH_2I_2, Zn(Cu)

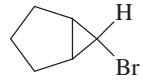
(c) 

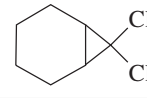
+ 50% $NaOH/H_2O$

PROBLEM 8-28

Show how you would accomplish each of the following synthetic conversions.

(a) *trans*-but-2-ene ⟶ *trans*-1,2-dimethylcyclopropane

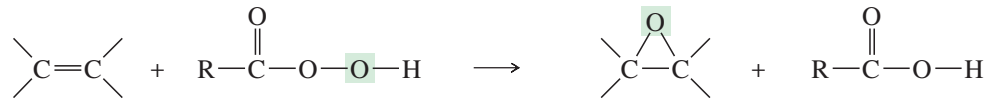
(b) cyclopentene ⟶ 

(c) cyclohexanol ⟶ 

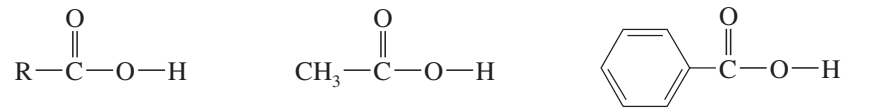
8-12 Epoxidation of Alkenes

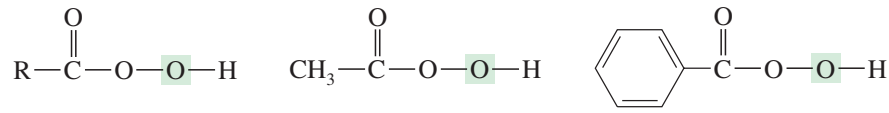
Some of the most important reactions of alkenes involve oxidation. When we speak of oxidation, we usually mean reactions that form carbon–oxygen bonds. (Halogens are oxidizing agents, and the addition of a halogen molecule across a double bond is formally an oxidation as well.) Oxidations are particularly important because many common functional groups contain oxygen, and alkene oxidations are some of the best methods for introducing oxygen into organic molecules. We will consider methods for epoxidation, dihydroxylation, and oxidative cleavage of alkene double bonds.

An **epoxide** is a three-membered cyclic ether, also called an **oxirane.** Epoxides are valuable synthetic intermediates used for converting alkenes to a variety of other functional groups. An alkene is converted to an epoxide by a **peroxyacid,** a carboxylic acid that has an extra oxygen atom in a —O—O— (peroxy) linkage.



The **epoxidation** of an alkene is clearly an oxidation, since an oxygen atom is added. Peroxyacids are highly selective oxidizing agents. Some simple peroxyacids (sometimes called *peracids*) and their corresponding carboxylic acids are shown next.



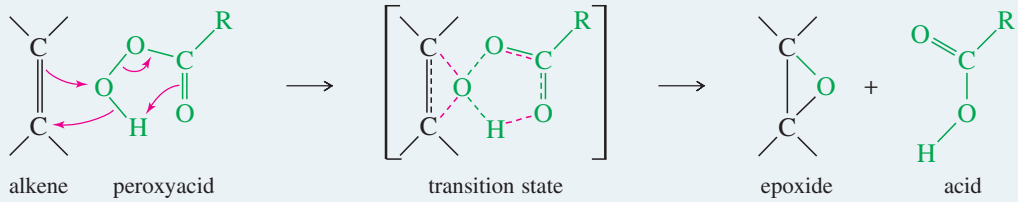


Application: Insecticides
Epoxides are often found as components of natural products that plants use as defense mechanisms against insects. Typically, the epoxide reacts with critical cellular enzymes or DNA, preventing them from carrying out their normal functions. As a result, the insect is killed.

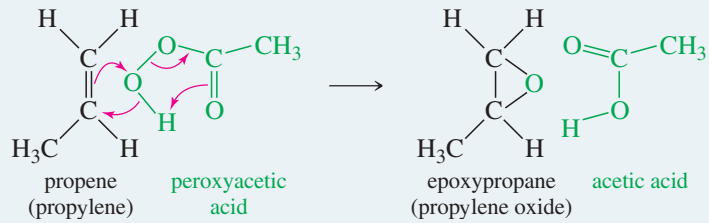
A peroxyacid epoxidizes an alkene by a concerted electrophilic reaction where several bonds are broken and several are formed at the same time. Starting with the alkene and the peroxyacid, a one-step reaction gives the epoxide and the acid directly, without any intermediates.

MECHANISM 8-9 Epoxidation of Alkenes

Peroxyacids epoxidize alkenes in a one-step (concerted) process.

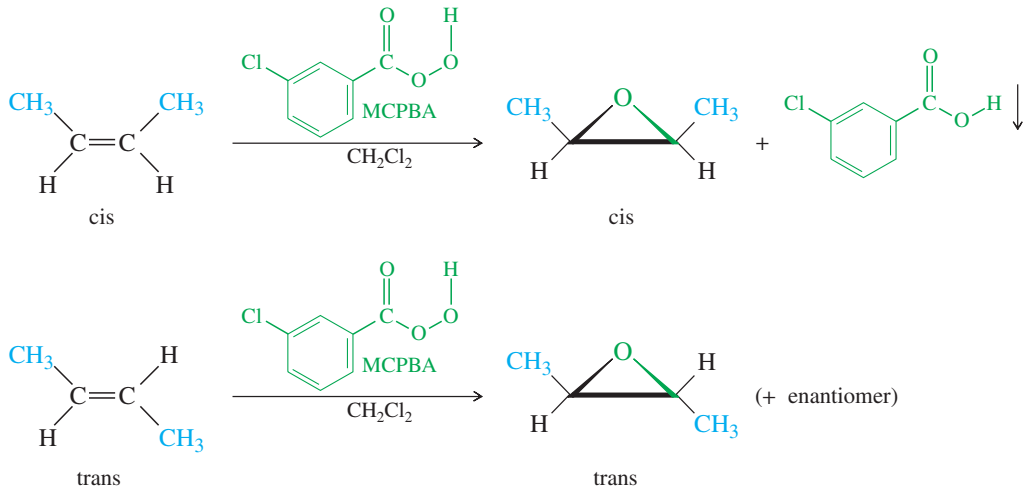


EXAMPLE: Epoxidation of propene by peroxyacetic acid.



Because the epoxidation takes place in one step, there is no opportunity for the alkene molecule to rotate and change its cis or trans geometry. The epoxide retains whatever stereochemistry is present in the alkene.

The following examples use *m*-chloroperoxybenzoic acid (MCPBA), a common epoxidizing reagent, to convert alkenes to epoxides having the same cis or trans stereochemistry. MCPBA is used for its desirable solubility properties: The peroxyacid dissolves, then the spent acid precipitates out of solution.



PROBLEM 8-29

Predict the products, including stereochemistry where appropriate, for the *m*-chloroperoxybenzoic acid epoxidations of the following alkenes.

(a) *cis*-hex-2-ene
(b) *trans*-hex-2-ene
(c) *cis*-cyclodecene
(d) *trans*-cyclodecene

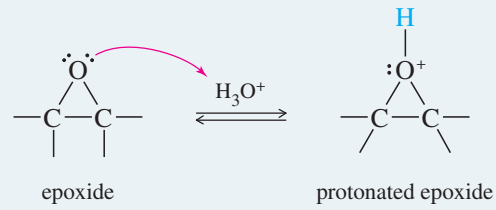
8-13 Acid-Catalyzed Opening of Epoxides

Most epoxides are easily isolated as stable products if the solution is not too acidic. Any moderately strong acid protonates the epoxide, however. Water attacks the protonated epoxide, opening the ring and forming a 1,2-diol, commonly called a **glycol.**

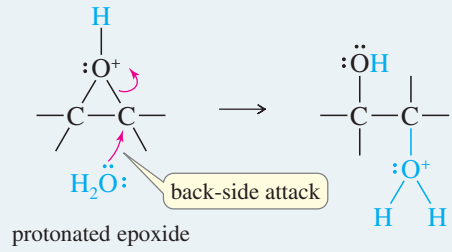
MECHANISM 8-10 Acid-Catalyzed Opening of Epoxides

The crucial step is a back-side attack by the solvent on the protonated epoxide.

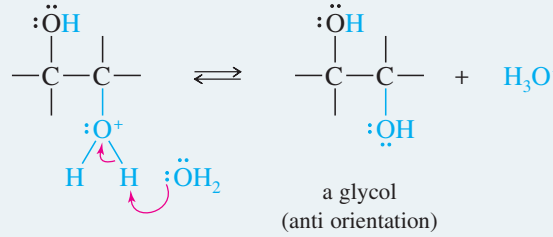
Step 1: Protonation of the epoxide activates it toward nucleophilic attack.



Step 2: Back-side attack by the solvent (water) opens the ring.

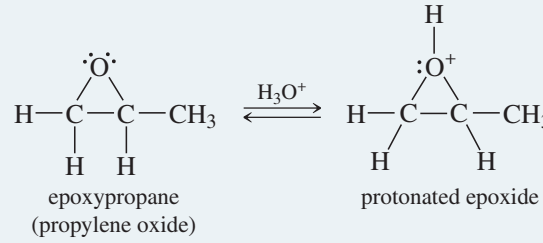


Step 3: Deprotonation gives the diol product.

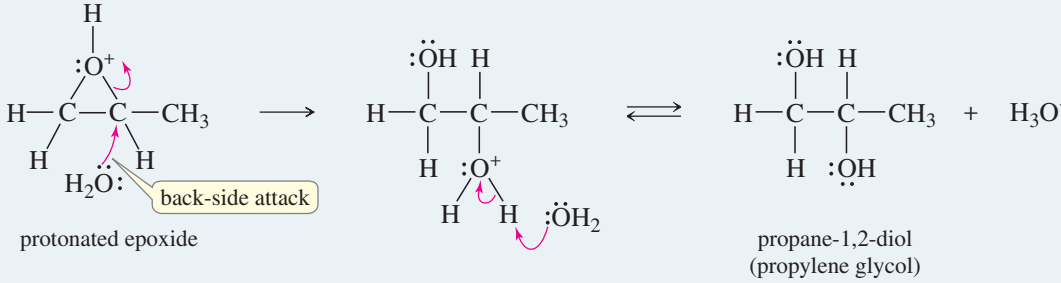


EXAMPLE: Acid-catalyzed hydrolysis of propylene oxide (epoxypropane).

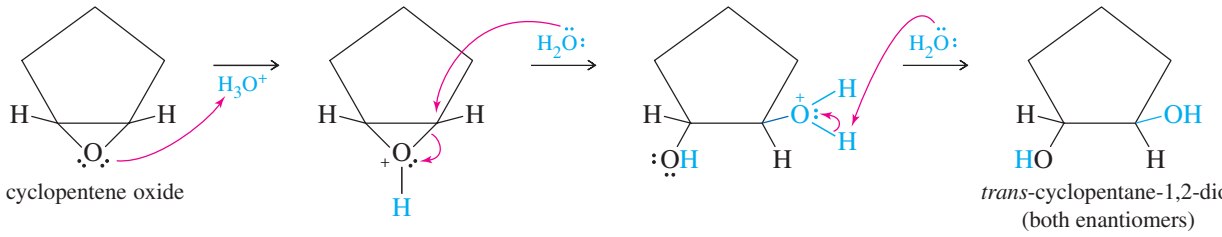
Step 1: Protonation of the epoxide.



Steps 2 and 3: Back-side attack by water, then deprotonation of the product.



Because glycol formation involves a back-side attack on a protonated epoxide, the result is anti orientation of the hydroxyl groups on the double bond. For example, when 1,2-epoxycyclopentane ("cyclopentene oxide") is treated with dilute mineral acid, the product is pure *trans*-cyclopentane-1,2-diol.



cyclopentene oxide

trans-cyclopentane-1,2-diol (both enantiomers)

PROBLEM 8-30

(a) Propose a mechanism for the conversion of *cis*-hex-3-ene to the epoxide (3,4-epoxyhexane) and the ring-opening reaction to give the glycol, hexane-3,4-diol. In your mechanism, pay particular attention to the stereochemistry of the intermediates and products.

(b) Repeat part (a) for *trans*-hex-3-ene. Compare the products obtained from *cis*- and *trans*-hex-3-ene. Is this reaction sequence stereospecific?

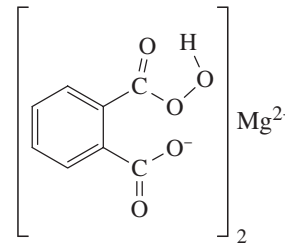
Application: Biochemistry

The body oxidizes the alkene components of drugs and other substances to epoxides, which are then hydrolyzed to diols by an epoxide hydrolase enzyme. The more reactive epoxides are rapidly converted to water-soluble diols and eliminated in the urine. Epoxide hydrolase enzymes are sometimes used in organic synthesis to produce chiral diols.

Epoxidation reagents can be chosen to favor either the epoxide or the glycol. Peroxyacetic acid is used in strongly acidic water solutions. The acidic solution protonates the epoxide and converts it to the glycol. Peroxybenzoic acids are weak acids that can be used in nonnucleophilic solvents such as carbon tetrachloride. *m*-Chloroperoxybenzoic acid in CCl_4 generally gives good yields of epoxides. Figure 8-8 compares the uses of these reagents.

PROBLEM 8-31

Magnesium monoperoxyphthalate (MMPP) epoxidizes alkenes much like MCPBA. MMPP is more stable, however, and it may be safer to use for large-scale and industrial reactions. Propose a mechanism for the reaction of *trans*-2-methylhept-3-ene with MMPP, and predict the structure of the product(s).



Magnesium monoperoxyphthalate, MMPP

PROBLEM 8-32

Predict the major products of the following reactions.

(a) *cis*-hex-2-ene + MCPBA in chloroform

(b) *trans*-hex-3-ene + peroxyacetic acid (CH_3CO_3H) in water

(c) 1-methylcyclohexene + MMPP in ethanol

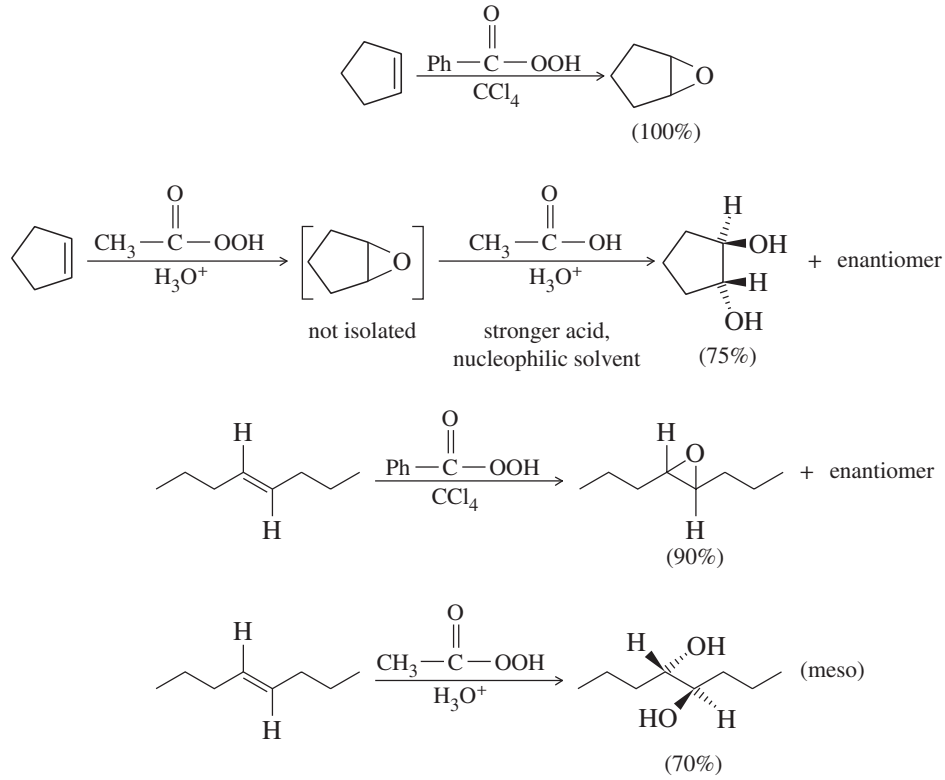
(d) *trans*-cyclodecene + peroxyacetic acid in acidic water

(e) *cis*-cyclodecene + MCPBA in CH_2Cl_2, then dilute aqueous acid

PROBLEM 8-33

When 1,2-epoxycyclohexane (cyclohexene oxide) is treated with anhydrous HCl in methanol, the principal product is *trans*-2-methoxycyclohexanol. Propose a mechanism to account for the formation of this product.

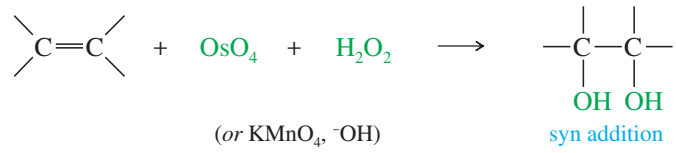
FIGURE 8-8
Reagents for epoxidation. Peroxyacetic acid is used in strongly acidic aqueous solutions. Alkenes are epoxidized, then opened to glycols in one step. Weakly acidic peroxyacids, such as peroxybenzoic acid, can be used in nonaqueous solutions to give good yields of epoxides.



8-14 Syn Dihydroxylation of Alkenes

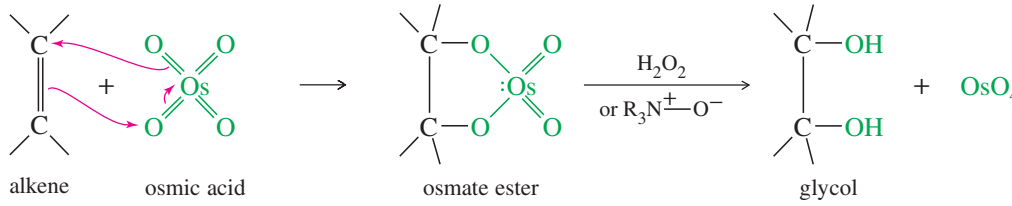
Application: Catalysis
Older dihydroxylation procedures once used a full equivalent of OsO_4 followed by a reducing agent such as $NaHSO_3$ to reduce the osmate ester. These old procedures have been supplanted by methods using only catalytic amounts of OsO_4, an exceptionally toxic and expensive reagent.

Converting an alkene to a glycol requires adding a hydroxyl group to each end of the double bond. This addition is called **dihydroxylation** (or **hydroxylation**) of the double bond. We have seen that epoxidation of an alkene, followed by acidic hydrolysis, gives *anti* dihydroxylation of the double bond. Reagents are also available for the dihydroxylation of alkenes with *syn* stereochemistry. The two most common reagents for this purpose are osmium tetroxide and potassium permanganate.

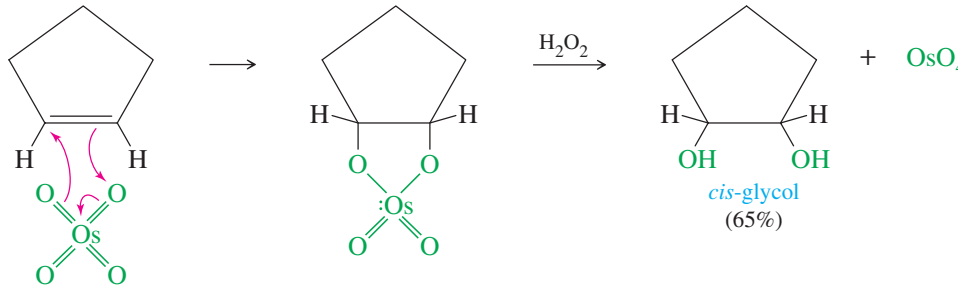


8-14A Osmium Tetroxide Dihydroxylation

Osmium tetroxide (OsO_4, sometimes called *osmic acid*) reacts with alkenes in a concerted step to form a cyclic osmate ester. Oxidizing agents such as hydrogen peroxide (H_2O_2) or tertiary amine oxides ($R_3N^+—O^-$) are used to hydrolyze the osmate ester and reoxidize osmium to osmium tetroxide. The regenerated osmium tetroxide catalyst continues to hydroxylate more molecules of the alkene.

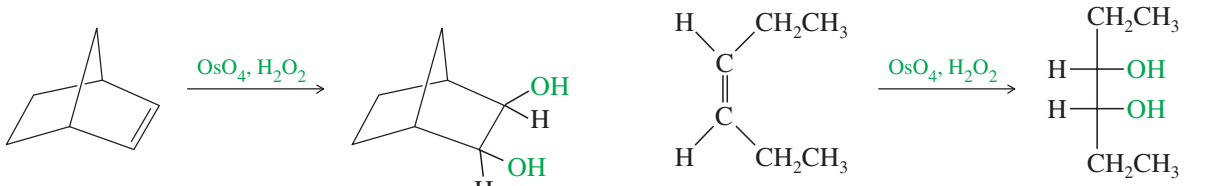


Because the two carbon–oxygen bonds are formed simultaneously with the cyclic osmate ester, the oxygen atoms add to the same face of the double bond; that is, they add with syn stereochemistry. The following reactions show the use of OsO_4 and H_2O_2 for the syn dihydroxylation of alkenes.



cis-glycol
(65%)

concerted formation of osmate ester

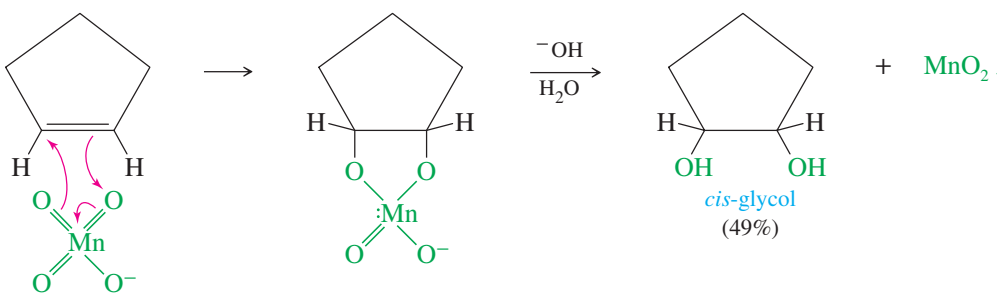


cis-hex-3-ene

meso-hexane-3,4-diol

8-14B Permanganate Dihydroxylation

Osmium tetroxide is expensive, highly toxic, and volatile. A cold, dilute solution of potassium permanganate ($KMnO_4$) also hydroxylates alkenes with syn stereochemistry, with slightly reduced yields in most cases. Like osmium tetroxide, permanganate adds to the alkene double bond to form a cyclic ester: a manganate ester in this case. The basic solution hydrolyzes the manganate ester, liberating the glycol and producing a brown precipitate of manganese dioxide, MnO_2.



cis-glycol
(49%)

concerted formation of manganate ester

In addition to its synthetic value, the permanganate oxidation of alkenes provides a simple chemical test for the presence of an alkene. When an alkene is added to a clear, deep purple aqueous solution of potassium permanganate, the solution loses its purple color and becomes the murky, opaque brown color of MnO_2. (Although there are other functional groups that decolorize permanganate, few do it as quickly as alkenes.)

8-14C Choosing a Reagent

To dihydroxylate an alkene with syn stereochemistry, which is the better reagent: osmium tetroxide or potassium permanganate? Osmium tetroxide gives better yields, but permanganate is cheaper and safer to use. The answer depends on the circumstances.

If the starting material is only 2 mg of a compound 15 steps along in a difficult synthesis, we use osmium tetroxide. The better yield is crucial because the starting material is precious and expensive, and little osmic acid is needed. If the dihydroxylation is the first step in a synthesis and involves 5 kg of the starting material, we use potassium permanganate. The cost of buying enough osmium tetroxide would be prohibitive, and dealing with such a large amount of a volatile, toxic reagent would be inconvenient. On such a large scale, we can accept the lower yield of the permanganate oxidation.

PROBLEM 8-34

Predict the major products of the following reactions, including stereochemistry.

(a) cyclohexene + $KMnO_4/H_2O$ (cold, dilute)
(b) cyclohexene + peroxyacetic acid in water
(c) *cis*-pent-2-ene + OsO_4/H_2O_2
(d) *cis*-pent-2-ene + peroxyacetic acid in water
(e) *trans*-pent-2-ene + OsO_4/H_2O_2
(f) *trans*-pent-2-ene + peroxyacetic acid in water

PROBLEM 8-35

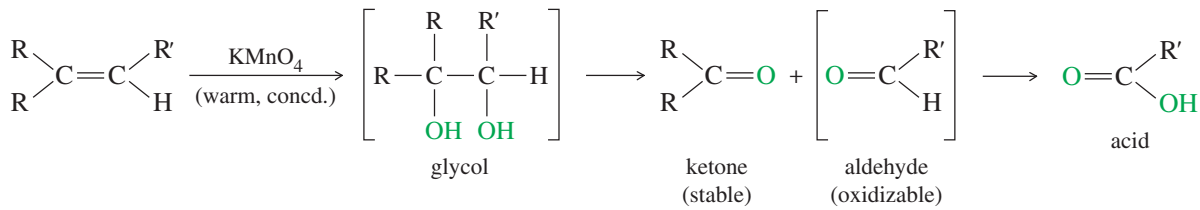
Show how you would accomplish the following conversions.

(a) *cis*-hex-3-ene to *meso*-hexane-3,4-diol
(b) *cis*-hex-3-ene to (*d,l*)-hexane-3,4-diol
(c) *trans*-hex-3-ene to *meso*-hexane-3,4-diol
(d) *trans*-hex-3-ene to (*d,l*)-hexane-3,4-diol

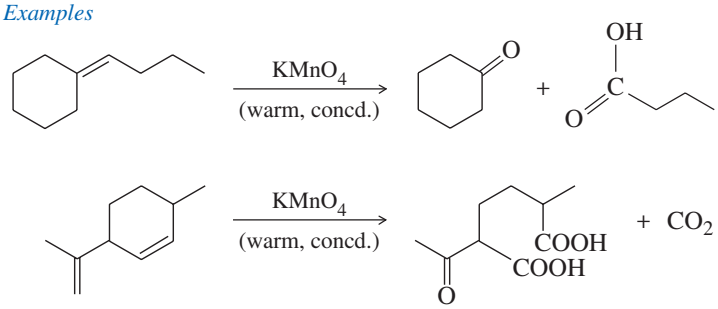
8-15 Oxidative Cleavage of Alkenes

8-15A Cleavage by Permanganate

In a potassium permanganate dihydroxylation, if the solution is warm or acidic or too concentrated, **oxidative cleavage** of the glycol may occur. In effect, the double bond is cleaved to two carbonyl groups. The products are initially ketones and aldehydes, but aldehydes are oxidized to carboxylic acids under these strong oxidizing conditions. If the molecule contains a terminal $=CH_2$ group, that group is oxidized all the way to CO_2 and water.

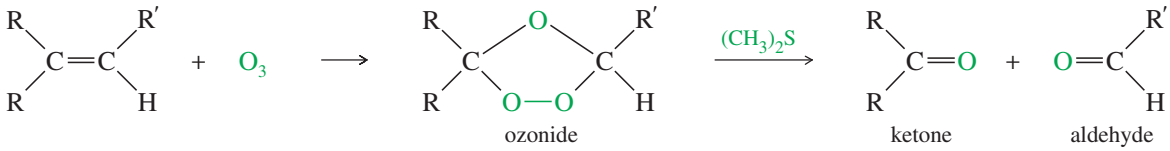


Examples



8-15B Ozonolysis

Like permanganate, ozone cleaves double bonds to give ketones and aldehydes. However, ozonolysis is milder, and both ketones and aldehydes can be recovered without further oxidation.

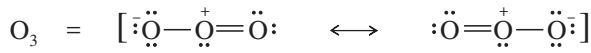


Ozone (O_3) is a high-energy form of oxygen produced when ultraviolet light or an electrical discharge passes through oxygen gas. Ultraviolet light from the sun converts oxygen to ozone in the upper atmosphere. This "ozone layer" shields the earth from some of the high-energy ultraviolet radiation it would otherwise receive.

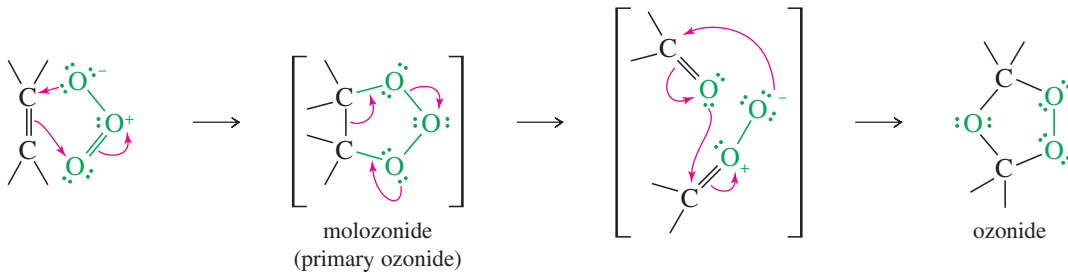
$$\tfrac{3}{2}O_2 + 142\text{ kJ (34 kcal)} \longrightarrow O_3$$

Ozone has 142 kJ/mol of excess energy over oxygen, and it is much more reactive. A Lewis structure of ozone shows that the central oxygen atom bears a positive charge, and each of the outer oxygen atoms bears half a negative charge.

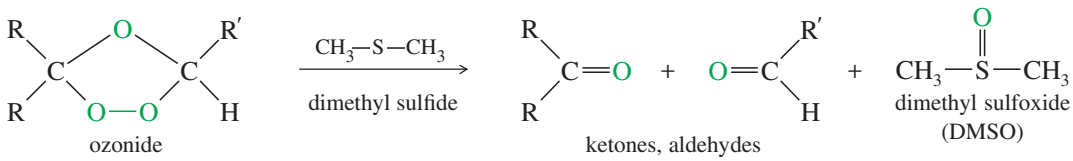
Application: Air Pollution
Ozone is a powerful lung irritant, causing a cough, sore throat, and tiredness. It can also increase a person's sensitivity to allergens. The mechanism may involve oxidation of the double bonds of the fatty acids that make up the surfactants and the membranes of the cells lining the bronchial airways and lungs.

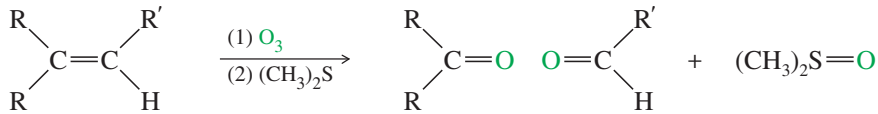


Ozone reacts with an alkene to form a cyclic compound called a *primary ozonide* or *molozonide* (because 1 mole of ozone has been added). The molozonide has two peroxy (—O—O—) linkages, so it is quite unstable. It rearranges rapidly, even at low temperatures, to form an ozonide.

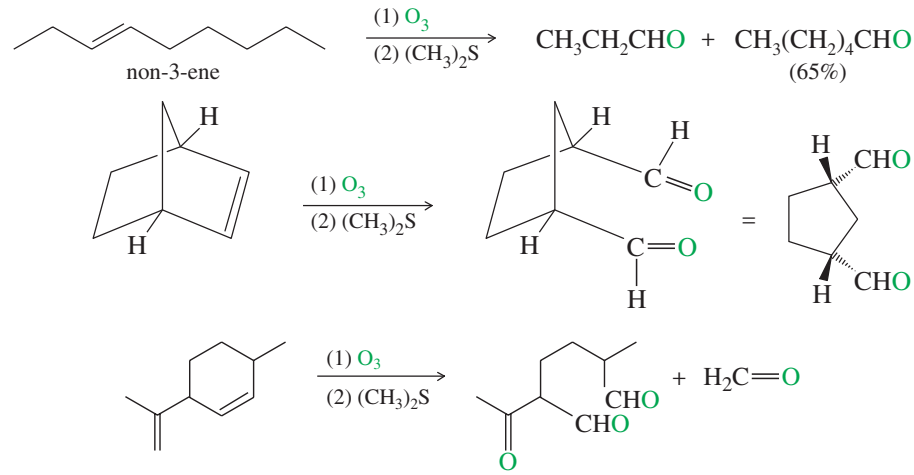


Ozonides are not very stable, and they are rarely isolated. In most cases, they are immediately reduced by a mild reducing agent such as zinc or (more recently) dimethyl sulfide. The products of this reduction are ketones and aldehydes.

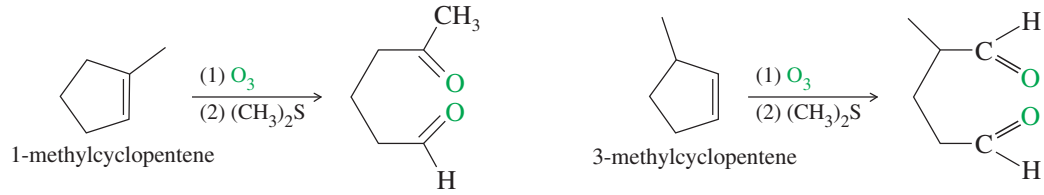




The following reactions show the products obtained from ozonolysis of some representative alkenes. Note how (1) and (2) are used with a single reaction arrow to denote the steps in a two-step sequence.



One of the most common uses of ozonolysis has been for determining the positions of double bonds in alkenes. For example, if we were uncertain of the position of the methyl group in a methylcyclopentene, the products of ozonolysis–reduction would confirm the structure of the original alkene.

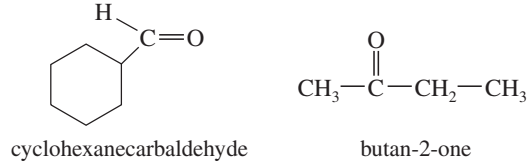


Problem-solving Hint

To predict the products from ozonolysis of an alkene, erase the double bond and add two oxygen atoms as carbonyl (C=O) groups where the double bond used to be.

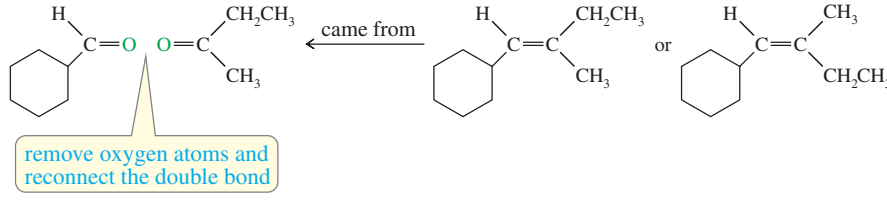
SOLVED PROBLEM 8-7

Ozonolysis–reduction of an unknown alkene gives an equimolar mixture of cyclohexanecarbaldehyde and butan-2-one. Determine the structure of the original alkene.



SOLUTION

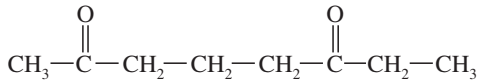
We can reconstruct the alkene by removing the two oxygen atoms of the carbonyl groups (C=O) and connecting the remaining carbon atoms with a double bond. One uncertainty remains, however: The original alkene might be either of two possible geometric isomers.



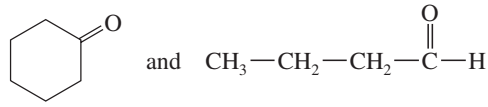
PROBLEM 8-36

Give structures of the alkenes that would give the following products upon ozonolysis–reduction.

(a)

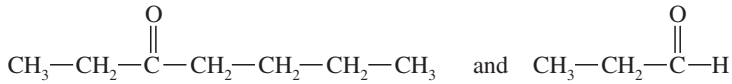


(b)



cyclohexanone

(c)

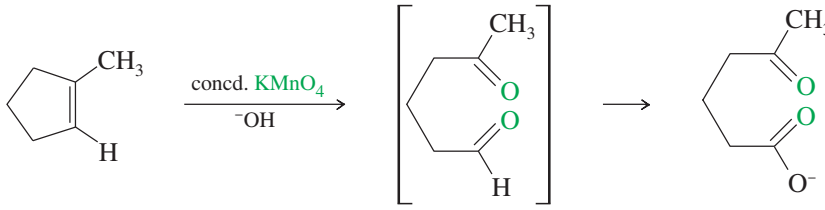


Application: Disinfectant

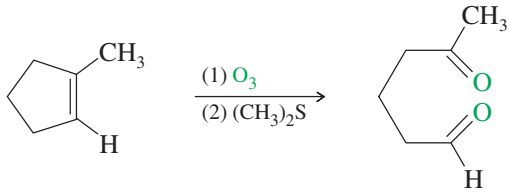
Ozone is a strong oxidizing agent that can be used instead of chlorine to disinfect the water in swimming pools. Ozone oxidizes organic matter, and it kills bacteria and algae. Ozone is used instead of chlorine because it can be generated on-site (rather than storing and using toxic chemicals such as chlorine gas or sodium hypochlorite) and because it doesn't produce as many harmful by-products.

8-15C Comparison of Permanganate Cleavage and Ozonolysis

Both permanganate and ozonolysis break the carbon–carbon double bond and replace it with carbonyl (C═O) groups. In the permanganate cleavage, any aldehyde products are further oxidized to carboxylic acids. In the ozonolysis–reduction procedure, the aldehyde products are generated in the dimethyl sulfide reduction step (and not in the presence of ozone), and they are not oxidized.



(not isolated)

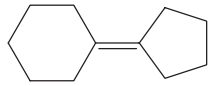


PROBLEM 8-37

Predict the major products of the following reactions.

(a) (*E*)-3-methyloct-3-ene + ozone, then $(CH_3)_2S$

(b) (*Z*)-3-methyloct-3-ene + warm, concentrated $KMnO_4$

(c)  + O_3, then $(CH_3)_2S$

(d) 1-ethylcycloheptene + ozone, then $(CH_3)_2S$

(e) 1-ethylcycloheptene + warm, concentrated $KMnO_4$

(f) 1-ethylcycloheptene + cold, dilute $KMnO_4$

Problem-solving Hint

Osmium tetroxide, cold, dilute $KMnO_4$ and epoxidation oxidize the pi bond of an alkene but leave the sigma bond intact. Either ozone or warm, concentrated $KMnO_4$ breaks the double bond entirely to give carbonyl compounds.

8-16 Polymerization of Alkenes

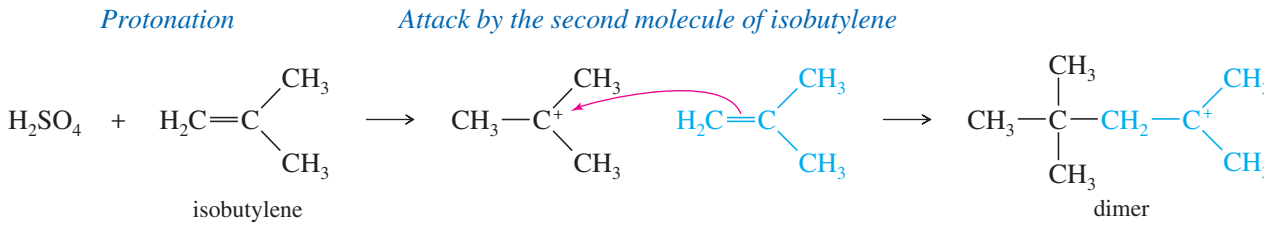
A **polymer** is a large molecule composed of many smaller repeating units (the **monomers**) bonded together. Alkenes serve as monomers for some of the most common polymers, such as polyethylene, polypropylene, polystyrene, poly(vinyl chloride),

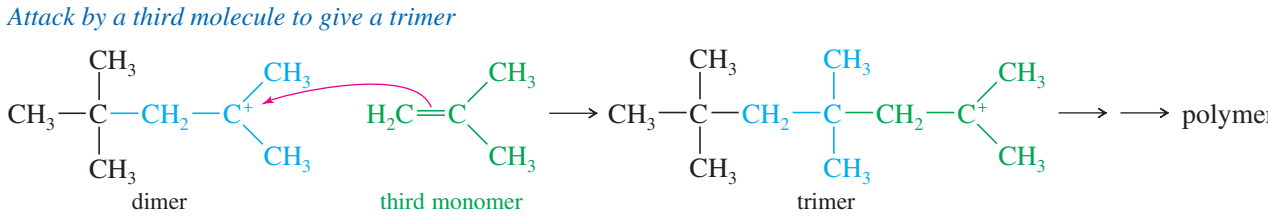
and many others. Alkenes polymerize to give **addition polymers** resulting from repeated addition reactions across their double bonds. Addition polymers generally form by **chain-growth polymerization,** the rapid addition of one molecule at a time to a growing polymer chain. There is generally a reactive intermediate (cation, anion, or radical) at the growing end of the chain.

Many alkenes form addition polymers under the right conditions. The chain-growth mechanism involves addition of the reactive end of the growing chain across the double bond of the alkene monomer. Depending on the conditions and the structure of the monomer, the reactive intermediates may be carbocations, free radicals, or carbanions.

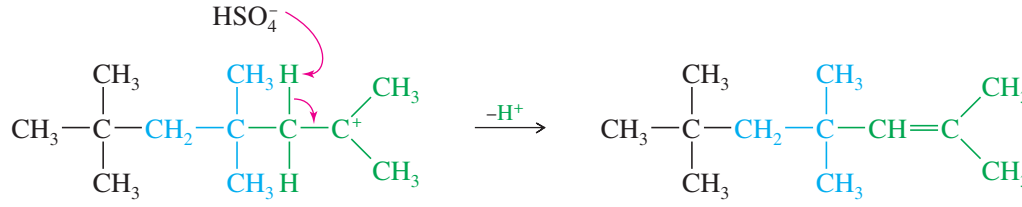
8-16A Cationic Polymerization

Alkenes that easily form carbocations are good candidates for **cationic polymerization,** which is just another example of electrophilic addition to an alkene. Consider what happens when pure isobutylene is treated with a trace of concentrated sulfuric acid. Protonation of the alkene forms a carbocation. If a large concentration of isobutylene is available, another molecule of the alkene may act as the nucleophile and attack the carbocation to form the *dimer* (two monomers joined together) and give another carbocation. If the conditions are right, the growing cationic end of the chain will keep adding across more molecules of the monomer. The polymer of isobutylene is *polyisobutylene*, one of the constituents of *butyl rubber* used in inner tubes and other synthetic rubber products.



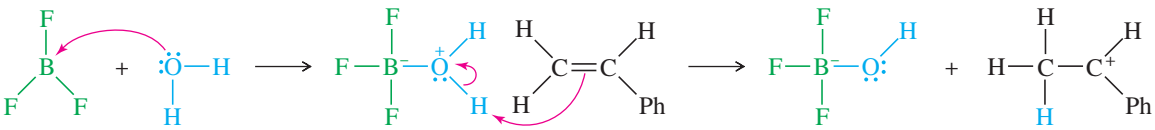


Loss of a proton is the most common side reaction that terminates chain growth:



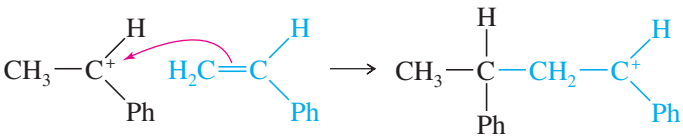
Boron trifluoride (BF_3) is an excellent catalyst for cationic polymerization because it leaves no good nucleophile that might attack a carbocation intermediate and end the polymerization. Boron trifluoride is electron-deficient and a strong Lewis acid. It usually contains a trace of water that acts as a co-catalyst by adding to BF_3 and then protonating the monomer. Protonation occurs at the less substituted end of

an alkene double bond to give the more stable carbocation. Each additional monomer molecule adds with the same orientation, always giving the more stable carbocation. The following reaction shows the polymerization of styrene (vinylbenzene) using BF_3 as the catalyst.

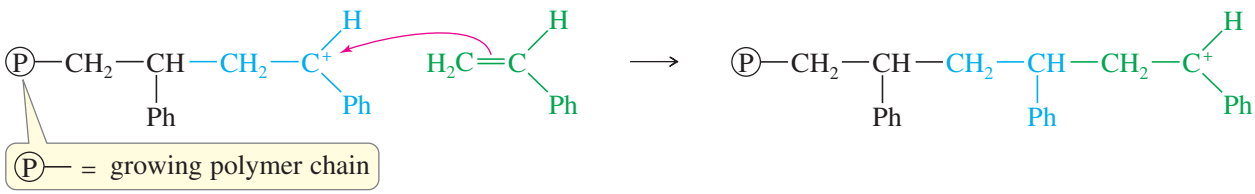


styrene

First chain-lengthening step

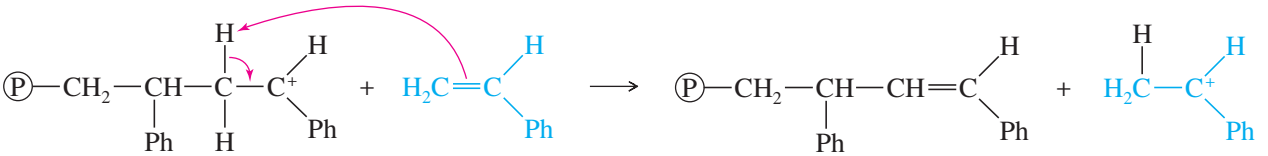


After many steps the polymerization continues



The most likely ending of this BF_3-catalyzed polymerization is the loss of a proton from the carbocation at the end of the chain. This side reaction terminates one chain, but it also protonates another molecule of styrene, initiating a new chain.

Termination of a polymer chain



polystyrene starts another chain

The product of this polymerization is polystyrene: a clear, brittle plastic that is often used for inexpensive lenses, transparent containers, and styrofoam insulation. Polystyrene is also the major component of the resin beads that are used to make synthetic proteins. (See Section 24-11).

PROBLEM 8-38

(a) Propose a mechanism for the following reaction.

$$2\ (CH_3)_2C{=}CH{-}CH_3 + \text{cat. } H^+ \longrightarrow \text{2,3,4,4-tetramethylhex-2-ene}$$

(b) Show the first three steps (as far as the tetramer) in the BF_3-catalyzed polymerization of propylene to form polypropylene.

PROBLEM 8-39

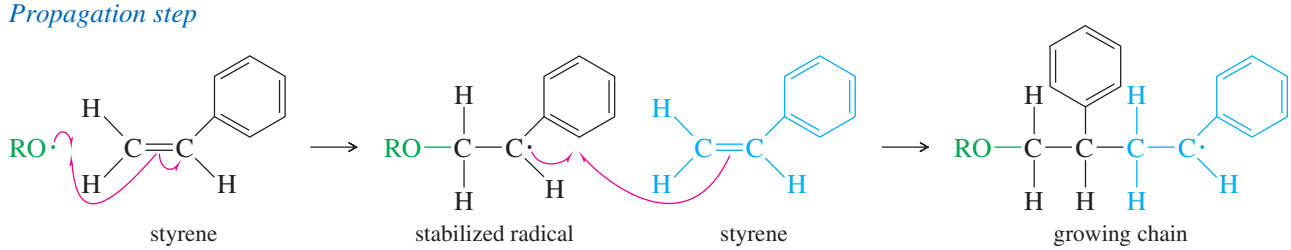
When cyclohexanol is dehydrated to cyclohexene, a gummy green substance forms on the bottom of the flask. Suggest what this residue might be, and propose a mechanism for its formation (as far as the dimer).

8-16B Free-Radical Polymerization

Many alkenes undergo **free-radical polymerization** when they are heated with radical initiators. For example, styrene polymerizes to polystyrene when it is heated to 100 °C with a peroxide initiator. A radical adds to styrene to give a resonance-stabilized radical, which then attacks another molecule of styrene to give an elongated radical.

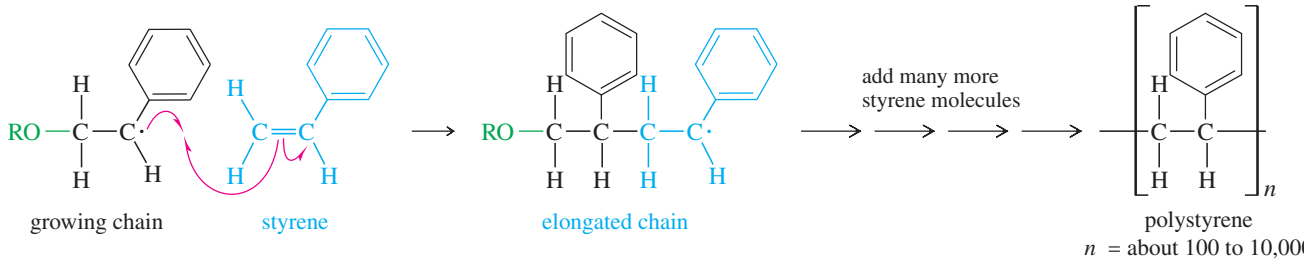
Initiation step $\text{ROOR} \xrightarrow{\text{heat}} 2\ \text{RO}\cdot$

Propagation step



Each propagation step adds another molecule of styrene to the radical end of the growing chain. This addition always takes place with the orientation that gives another resonance-stabilized benzylic (next to a benzene ring) radical.

Propagation step



Chain growth may continue with addition of several hundred or several thousand styrene units. Eventually, the chain reaction stops, either by the coupling of two chains or by reaction with an impurity (such as oxygen) or simply by running out of monomer.

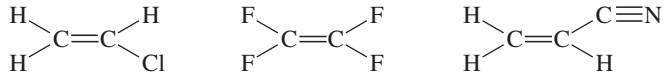
PROBLEM 8-40

Show the intermediate that would result if the growing chain added to the other end of the styrene double bond. Explain why the final polymer has phenyl groups substituted on alternate carbon atoms rather than randomly distributed.

Ethylene is also polymerized by free-radical chain-growth polymerization. With ethylene, the free-radical intermediates are less stable, so stronger reaction conditions are required. Ethylene is commonly polymerized by free-radical initiators at pressures around 3000 atm and temperatures of about 200 °C. The product, called *low-density polyethylene*, is the material commonly used in polyethylene bags.

PROBLEM 8-41

The structures of three monomers are shown. In each case, show the structure of the polymer that would result from polymerization of the monomer. Vinyl chloride is polymerized to "vinyl" plastics and PVC pipe. Tetrafluoroethylene polymerizes to Teflon®, used as non-stick coatings and PTFE valves and gaskets. Acrylonitrile is polymerized to Orlon®, used in sweaters and carpets.



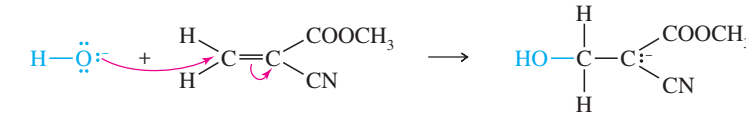
vinyl chloride tetrafluoroethylene acrylonitrile

This 1949 DuPont promotional photo shows how a Teflon rod (on our right, in the model's left hand) resists a hot acid solution compared with a rod made from another plastic. In World War II, Teflon was used for insulation in aircraft wiring and for seals in the equipment used to enrich corrosive uranium hexafluoride.

8-16C Anionic Polymerization

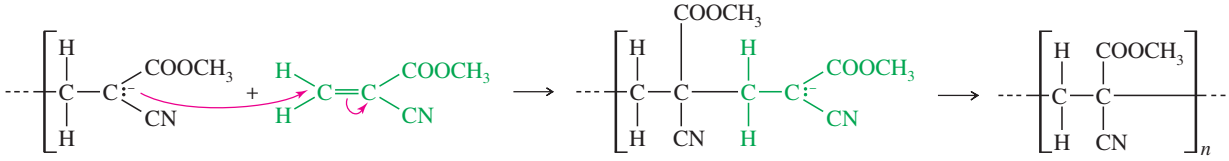
Like cationic polymerization, **anionic polymerization** depends on the presence of a stabilizing group. To stabilize anions, the double bond should have a strong electron-withdrawing group such as a carbonyl group, a cyano group, or a nitro group. Methyl α-cyanoacrylate contains two powerful electron-withdrawing groups, and it undergoes nucleophilic additions very easily. If this liquid monomer is spread in a thin film between two surfaces, traces of basic impurities (metal oxides, etc.) can catalyze its rapid polymerization. The solidified polymer joins the two surfaces. The chemists who first made this monomer noticed how easily it polymerizes and realized that it could serve as a fast-setting glue. Methyl α-cyanoacrylate is sold commercially as Super Glue.

Initiation step



trace of base Super Glue highly stabilized anion

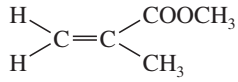
Chain-lengthening step



growing chain monomer elongated chain polymer

PROBLEM 8-42

Draw a mechanism for a base-catalyzed polymerization of methyl α-methacrylate to give the Plexiglas® polymer.



methyl α-methacrylate

8-17 Olefin Metathesis

The double bond is the strongest bond in an alkene, yet it is also the most reactive bond. Imagine how useful it would be if we could break molecules at their double bonds and reassemble them as we please. That is the goal of olefin metathesis. We can think of an alkene as two **alkylidene groups** (=CHR) held together by the double

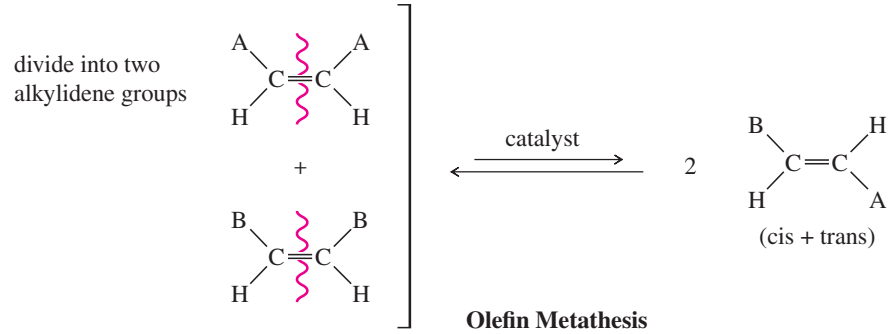


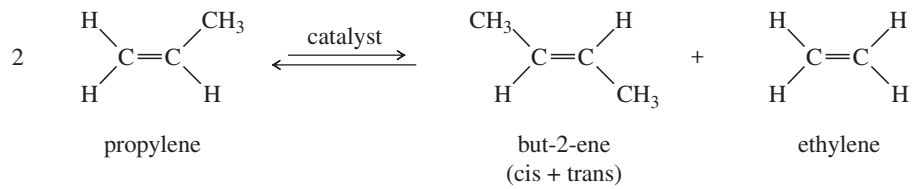
FIGURE 8-9
Olefin metathesis. During metathesis, the alkylidene groups of the reactant olefins trade partners and rearrange to give new combinations of alkenes in the products.

bond, and mentally divide it up just like we divide the molecule when we go to name it as *E* or *Z* (Section 7-5B). **Olefin metathesis** is any reaction that trades and interchanges these alkylidene groups. The word *metathesis* comes from the Greek words *meta* (change) and *thesis* (position), meaning that the alkylidene groups change their positions in the products. Figure 8-9 shows the trading of alkylidene groups that takes place during olefin metathesis.

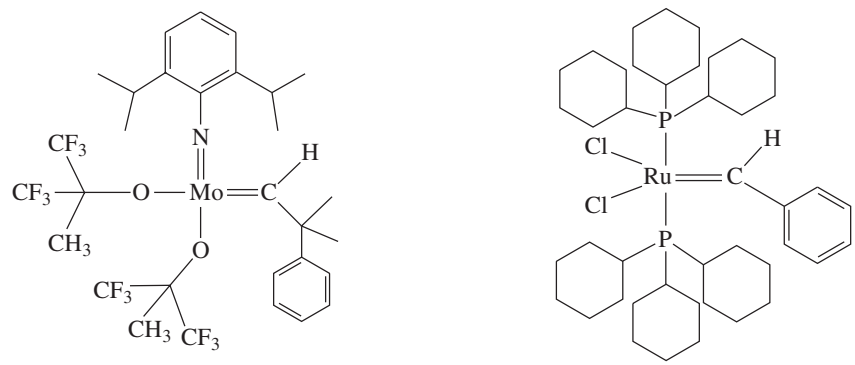
The 2005 Nobel Prize in Chemistry was awarded to Yves Chauvin (French Petroleum Institute), Robert Grubbs (Caltech), and Richard Schrock (MIT) for developing effective ways to induce alkenes to undergo metathesis.

8-17A Catalysts for Olefin Metathesis

Olefin metathesis was first observed in the 1950s, and was used in industry to convert propylene to a mixture of but-2-ene and ethylene. This *Phillips Triolefin Process* used an aluminum/molybdenum catalyst whose exact structure was unknown.



Around 1990, Richard Schrock developed versatile molybdenum and tungsten catalysts for olefin metathesis that tolerate a wide range of functional groups in the alkylidene fragments of the olefins. The Schrock catalyst shown in Figure 8-10a is now commercially available. The Schrock catalysts tend to be air- and moisture-sensitive, which limits their use in commercial processes.



(a) Schrock **(b) Grubbs**

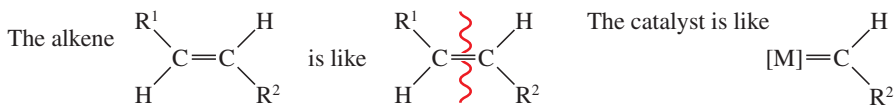
FIGURE 8-10
(a) One of the Schrock molybdenum metathesis catalysts. (b) One of the Grubbs ruthenium metathesis catalysts.

In 1992, Robert Grubbs developed a ruthenium phosphine catalyst (Figure 8-10b) that is less sensitive to oxygen and moisture than the Schrock catalysts, and tolerates even more functional groups in the alkylidene fragments of the olefins. Both the Schrock and Grubbs catalysts have a metal atom that is double-bonded to an alkylidene (═CHR) group. They can be symbolized [M]═CHR, where the [M] in brackets signifies that the metal atom has other ligands that fine-tune its reactivity.

Figure 8-11 shows some examples of useful reactions that are catalyzed by the Schrock and Grubbs catalysts. One important aspect of these metathesis reactions is that they are all reversible, so they form equilibrium mixtures of the reactants and all possible products unless something is done to drive the reaction toward the desired products. The first two examples in Figure 8-11 use the most common method, formation of ethylene gas. Ethylene bubbles off as it forms, effectively driving the reaction to completion. The ring-opening metathesis polymerization is exothermic and naturally goes to products because the ring strain in the bicyclic norbornene is released when the ring opens to form the polymer.

8-17B Mechanism of Olefin Metathesis

Several mechanisms were proposed to explain the catalytic metathesis reactions, but the mechanism published by Yves Chauvin in 1971 has come to be accepted as correct. We can think of an alkene as two alkylidene groups bonded together. Similarly, the Schrock and Grubbs catalysts are like a metal atom bonded to one alkylidene group.



Chauvin proposed that the metal-alkylidene catalyst forms an intermediate four-membered ring with an alkene, as shown in Mechanism 8-11. Then the ring breaks apart, either to give the starting alkene and catalyst or to give a new alkene that has traded one alkylidene group with the catalyst.

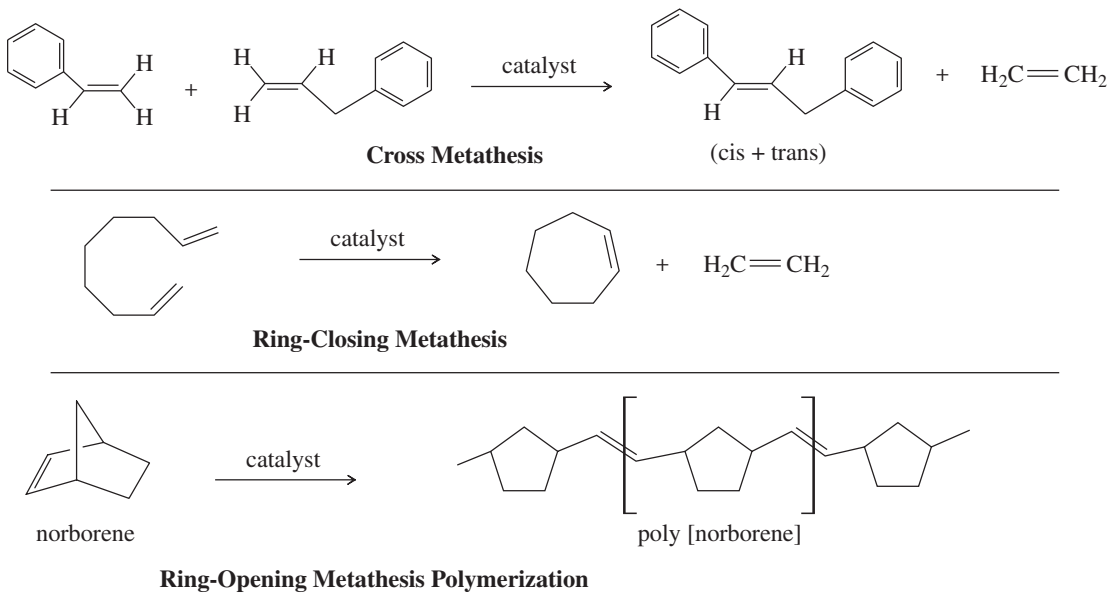
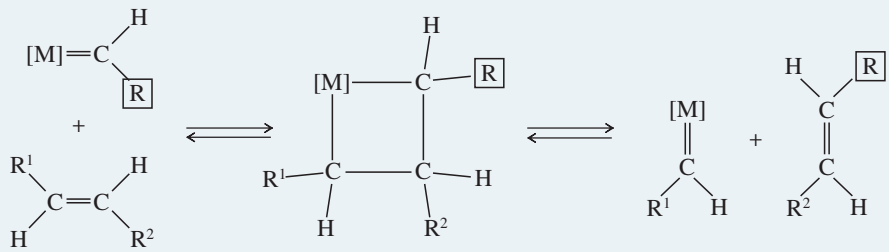


FIGURE 8-11
Useful examples of metathesis reactions.

This mechanism allows the alkylidene groups to change partners back and forth with the catalytic metal until a thermodynamic equilibrium is reached. As we saw earlier, good yields of products result if there is an effective driving force (such as formation of a gaseous by-product or release of ring strain) to push the equilibrium toward the desired products.

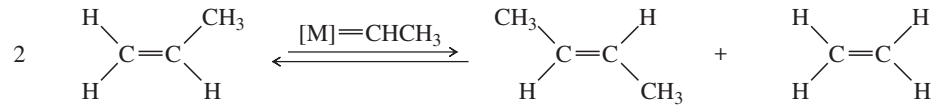
MECHANISM 8-11 Olefin Metathesis



The omnivorous leafroller (OLR) feeds on a wide variety of fruits, vegetables, and ornamentals. Vineyards use pheromone traps to monitor the OLR populations and determine when control methods are needed.

PROBLEM 8-43

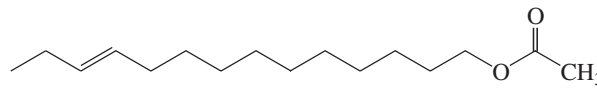
Propose a mechanism for the triolefin process using a metal alkylidene as the catalyst.



propylene — but-2-ene (cis + trans) — ethylene

PROBLEM 8-44

Show what reagents would be needed to synthesize the pheromone of the omnivorous leafroller (OLR) using olefin metathesis to assemble the molecule at the double bond.



OLR pheromone (cis + trans)

PROBLEM-SOLVING STRATEGY

Organic Synthesis

Alkyl halides and alkenes are readily made from other compounds, and they are easily converted to other functional groups. This flexibility makes them useful as reagents and intermediates for organic synthesis. Alkenes are particularly important for industrial syntheses because they are inexpensive and available in large quantities from cracking and dehydrogenation of petroleum fractions.

Organic synthesis is the preparation of desired compounds from readily available materials. Synthesis is one of the major areas of organic chemistry, and nearly every chapter of this book involves organic synthesis in some way. A synthesis may be a simple one-step reaction, or it may involve many steps and incorporate a subtle strategy for assembling the correct carbon skeleton with all the functional groups in the right positions.

Many of the problems in this book are synthesis problems. In some synthesis problems, you are asked to show how to convert a given starting material to the desired product. There are obvious one-step answers to some of these problems, but others may require several steps and there may be many correct answers. In solving multistep synthetic problems, it is often helpful to analyze the problem backward: Begin with the desired product (called the *target compound*) and see how it might be mentally changed or broken down to give the starting materials. This backward approach to synthesis is called a **retrosynthetic analysis.**

Some problems allow you to begin with any compounds that meet a certain restriction. For example, you might be allowed to use any alcohols containing no more than four carbon atoms. A retrosynthetic analysis can be used to break down the target compound into fragments no larger than four carbon atoms; then those fragments could be formed from the appropriate alcohols by functional group chemistry.

The following suggestions should help you solve synthesis problems:

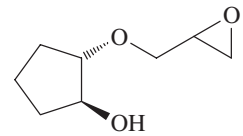
1. Do not guess a starting material and try every possible reaction to convert it to the target compound. Rather, begin with the target compound and use a retrosynthetic analysis to simplify it.
2. Use simple equations, with reagents written above and below the arrows, to show the reactions. The equations do not have to be balanced, but they should include all the reagents and conditions that are important to the success of the reaction.

$$\text{A} \xrightarrow{\text{Br}_2\text{, light}} \text{B} \xrightarrow[\text{heat}]{\text{NaOH, alcohol}} \text{C} \xrightarrow{\text{H}^+\text{, H}_2\text{O}} \text{D}$$

3. Focus on the functional groups, since that is generally where reactions occur. Do not use any reagents that react with a functional group that you don't intend to modify.

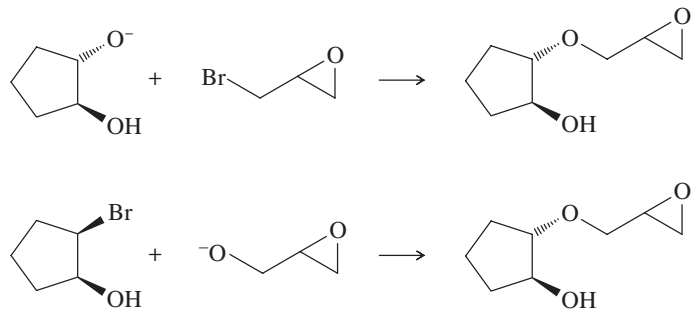
In solving multistep synthesis problems, you will rarely be able to "see" the solution immediately. These problems are best approached systematically, working backward and considering alternative routes. To illustrate a systematic approach that can guide you in solving synthesis problems, we will work through the synthesis of a complex ether starting from alkenes. The problem-solving method described here will be extended in future chapters to multistep syntheses based on the reactions of additional functional groups.

A systematic retrosynthetic analysis begins with an examination of the structure of the product. We will consider the synthesis of the following compound from alkenes containing up to five carbon atoms.

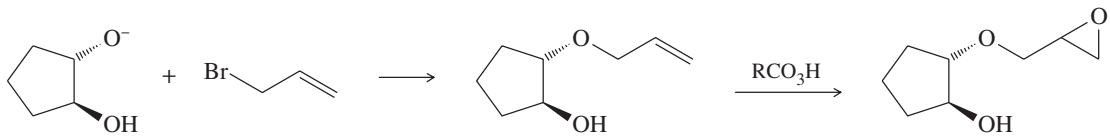


1. **Review the functional groups and carbon skeleton of the target compound.**
   The target compound is an ether. One alkyl group is a five-carbon cyclopentane ring with two oxygen atoms situated trans. The other group has three carbons containing a reactive epoxide ring.
2. **Review the functional groups and carbon skeletons of the starting materials (if specified), and see how their skeletons might fit together in the target compound.**
   The synthesis is to begin with alkenes containing up to five carbon atoms, so all the functional groups in the product must be derived from alkenes. Most likely, we will start with cyclopentene to give the five-carbon ring and propene to give the three-carbon chain.
3. **Compare methods for synthesizing the functional groups in the target compound, and select the reactions that are most likely to give the correct product.**
   This step may require writing several possible reactions and evaluating them.

   Ethers can be synthesized by nucleophilic reactions between alkyl halides and alkoxides (Section 6-9). The target compound might be formed by S_N2 attack of an alkoxide ion on an alkyl halide in either of two ways as shown below:



   The first reaction is better because the S_N2 attack is on a primary alkyl halide, while the second is on a secondary halide. Also, in the second reaction the alkoxide might simply deprotonate the alcohol on the left and cause the reaction to fail.
4. **In general, reactive functional groups are best put into place toward the end of a synthesis.**
   The target compound contains a reactive epoxide ring. Epoxides react with acids and bases, and the epoxide might not survive the crucial ether-forming reaction just shown. Perhaps the epoxide is best added after formation of the ether. That gives us the following final two steps in the synthesis:



(Continued)

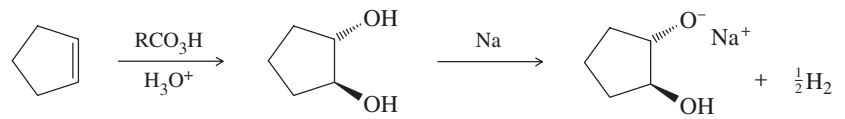
5. Working backward through as many steps as necessary, compare methods for synthesizing the reactants needed for the final step.

This process may require writing several possible reaction sequences and evaluating them, keeping in mind the specified starting materials.

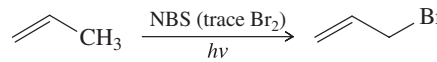
Two reactants are needed to form the ether: an allylic halide and an alkoxide ion. Alkoxide ions are commonly formed by the reaction of an alcohol with sodium metal:

$$R{-}O{-}H + Na \longrightarrow Na^+\ {}^-O{-}R + \tfrac{1}{2}H_2\uparrow$$

The alkoxide needed to make the ether is formed by adding sodium to a trans diol as shown below. Trans diols are formed by epoxidation and hydrolysis of alkenes (Section 8-13).



The other piece we need is an allylic bromide. Allylic bromides are formed by allylic bromination of alkenes (Section 6-6B).



6. Summarize the complete synthesis in the forward direction, including all steps and all reagents, and check it for errors and omissions.

This summary is left to you as a review of both the chemistry involved in the synthesis and the method used to develop multistep syntheses.

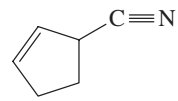
PROBLEM: Summarize the synthesis outlined in the problem-solving strategy. This summary should be in the synthetic (forward) direction, showing each step and all reagents.

Problem 8-45 requires devising several multistep syntheses. As practice in working such problems, we suggest that you proceed in order through the five steps just outlined.

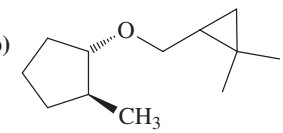
PROBLEM 8-45

Show how you would synthesize each compound, starting with alkenes or cycloalkenes that contain no more than six carbon atoms. You may use any additional reagents you need.

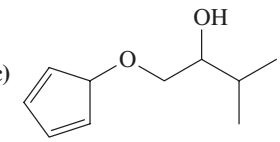
(a)



(b)



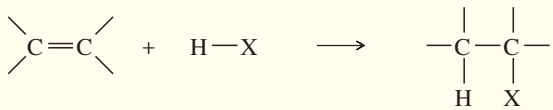
(c)



SUMMARY Reactions of Alkenes

1. *Electrophilic Additions*

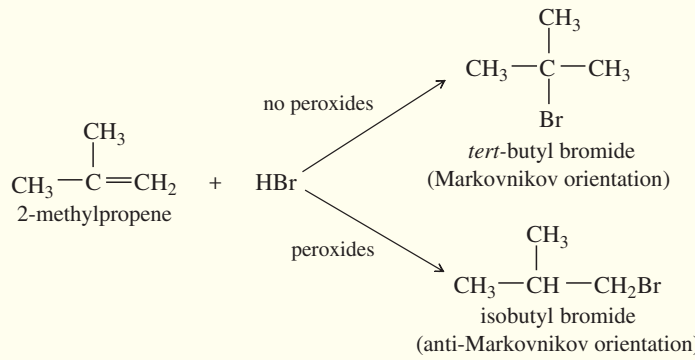
a. *Addition of hydrogen halides* (Section 8-3)



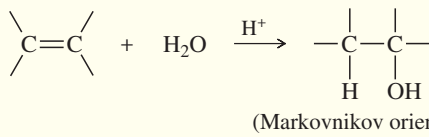
(HX = HCl, HBr, or HI)

Markovnikov orientation
(anti-Markovnikov with HBr and peroxides)

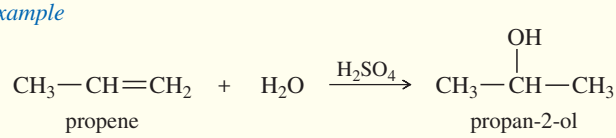
Example



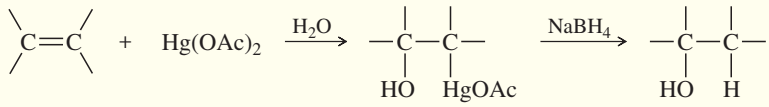
b. *Acid-catalyzed hydration* (Section 8-4)



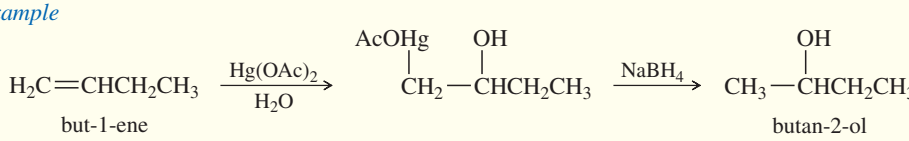
Example



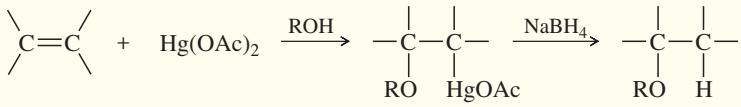
c. *Oxymercuration–demercuration* (Section 8-5)



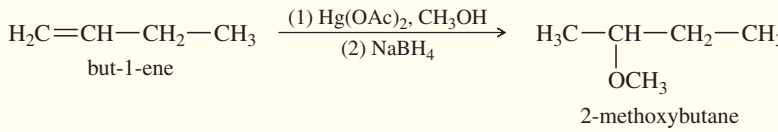
Example



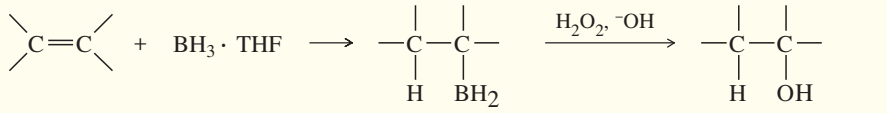
d. *Alkoxymercuration–demercuration* (Section 8-6)



Example

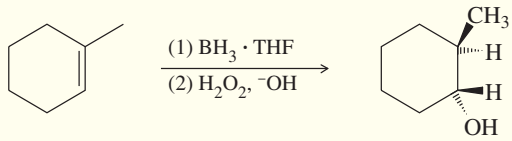


e. *Hydroboration–oxidation* (Section 8-7)

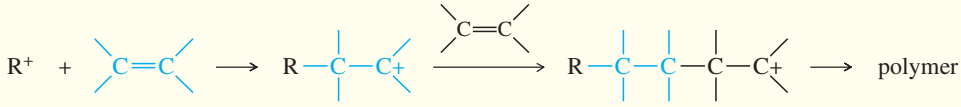


(Continued)

Example

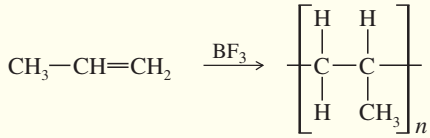


f. *Polymerization* (Section 8-16)



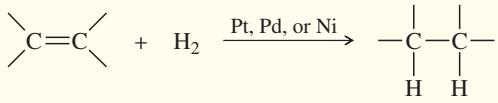
(also radical and anionic polymerization)

Example



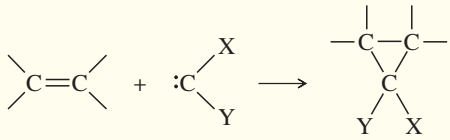
propylene polypropylene

2. *Reduction: Catalytic Hydrogenation* (Section 8-10)



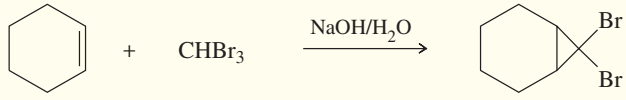
(syn addition)

3. *Addition of Carbenes: Cyclopropanation* (Section 8-11)



(X,Y = H, Cl, Br, I, or —COOEt)

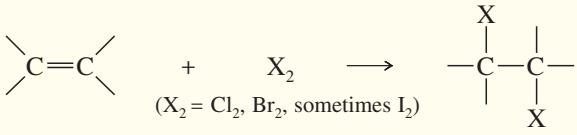
Example



cyclohexene

4. *Oxidative Additions*

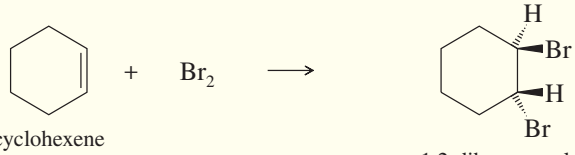
a. *Addition of halogens* (Section 8-8)



(X_2 = Cl_2, Br_2, sometimes I_2)

(anti addition)

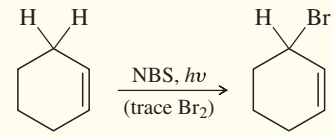
Example



cyclohexene

trans-1,2-dibromocyclohexane

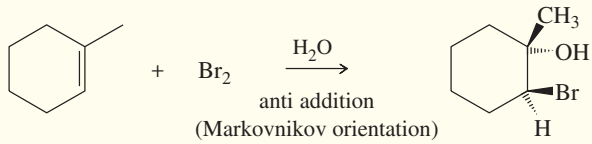
(or substitution)



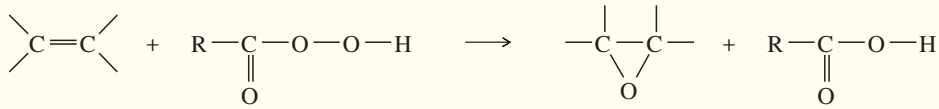
cyclohexene 3-bromocyclohexene

At low concentrations of Br_2, an allylic substitution may be observed. NBS provides a trace of Br_2 that (with light as initiator) allows radical substitution to proceed faster than the ionic addition. (Section 6-6B)

b. *Halohydrin formation* (Section 8-9)

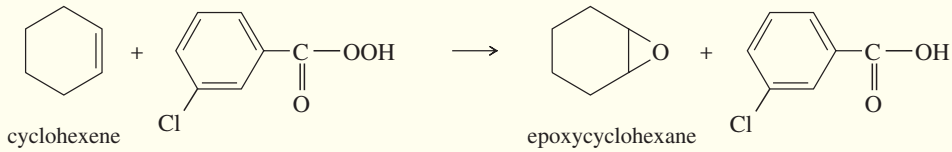


c. *Epoxidation* (Section 8-12)



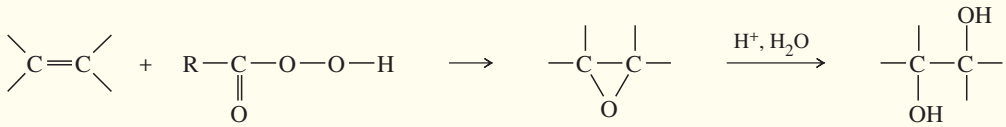
alkene peroxyacid syn addition

Example



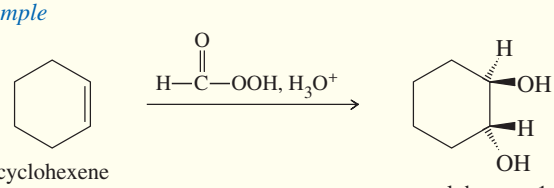
cyclohexene epoxycyclohexane (cyclohexene oxide)

d. *Anti dihydroxylation* (Section 8-13)



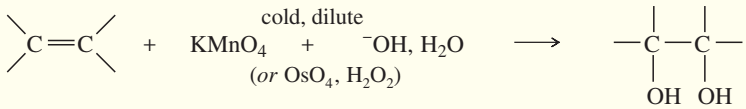
(anti addition)

Example



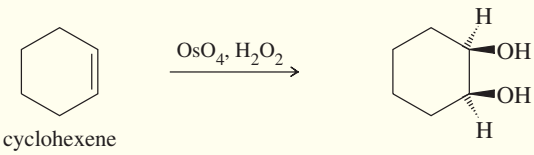
cyclohexene *trans*-cyclohexane-1,2-diol

e. *Syn dihydroxylation* (Section 8-14)



(syn addition)

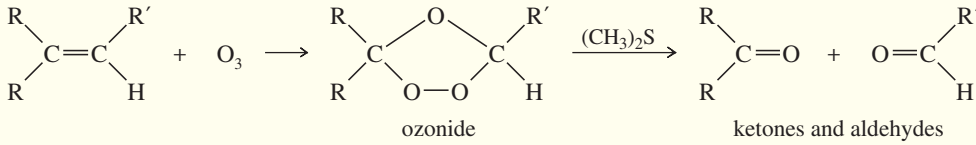
Example



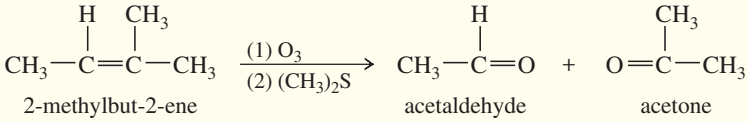
cyclohexene *cis*-cyclohexane-1,2-diol

5. *Oxidative Cleavage of Alkenes* (Section 8-15)

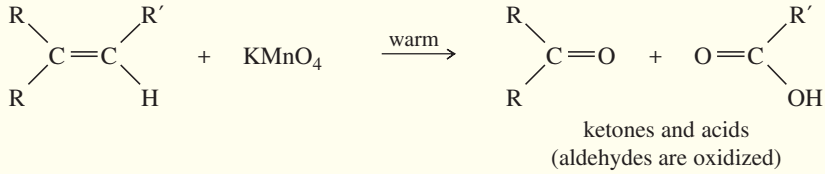
a. *Ozonolysis*



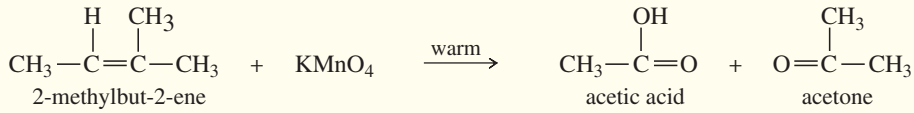
Example



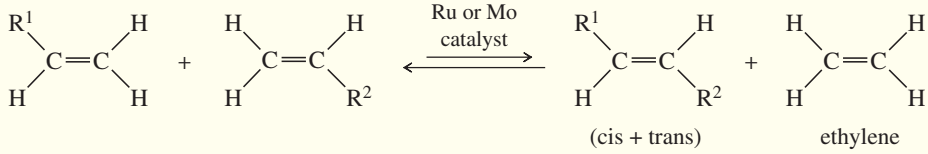
b. *Potassium permanganate*



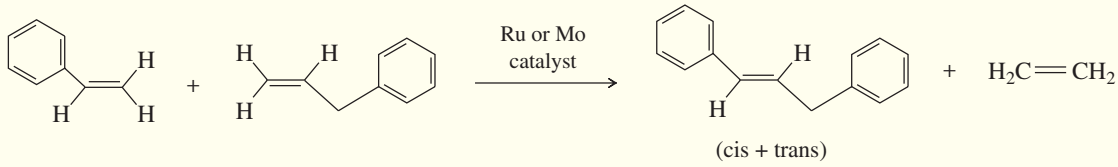
Example

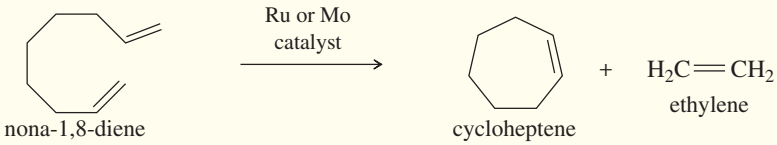


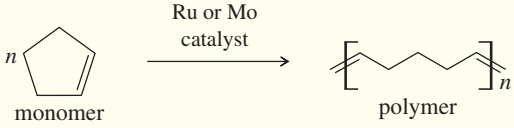
6. *Olefin (Alkene) Metathesis* (Section 8-17)



Examples







metathesis polymerization

ESSENTIAL PROBLEM-SOLVING SKILLS IN CHAPTER 8

Each skill is followed by problem numbers exemplifying that particular skill.

1 Use the extended version of Markovnikov's rule to predict the regiochemistry (orientation) of electrophilic additions to alkenes.	**Problems 8-46, 47, and 50**
2 Show how we can control the stereochemistry and regiochemistry (orientation) of additions to alkenes to obtain the products we want.	**Problems 8-46, 47, 59, and 65**
3 Show how we can control the hydration of alkenes to give alcohols with either Markovnikov or anti-Markovnikov orientation, depending on the reagents.	**Problems 8-46, 47, 49, and 59**
4 Predict the products of halogenations, oxidations, reductions, and cleavages of alkenes, including the orientation (regiochemistry) and the stereochemistry of the reaction.	**Problems 8-47, 50, and 61**
5 Predict the stereochemistry observed in the hydroboration, halogenation, and dihydroxylation reactions of alkenes.	**Problems 8-46, 47, 49, and 66**
6 Propose logical mechanisms to explain the observed products of alkene reactions, including regiochemistry and stereochemistry.	**Problems 8-48, 56, 57, 64, 66, 67, 70, 71, and 72**
7 Use retrosynthetic analysis to solve multistep synthesis problems with alkenes as reagents, intermediates, or products.	**Problems 8-46, 49, 59**
8 Use clues provided by the products of reactions, such as ozonolysis, to determine the structure of an unknown alkene.	**Problems 8-58, 60, 61, 62, 63, 68**
9 Show how metathesis interchanges the alkylidene (=CHR) groups in alkenes, forming new and different alkenes.	**Problems 8-47, 54, 55**
10 Given a particular monomer unit, draw the structure of the resulting polymer.	**Problems 8-52 and 53**

In studying these reaction-intensive chapters, students ask whether they should "memorize" all the reactions. Doing organic chemistry is like speaking a foreign language, and the reactions are our vocabulary. Without knowing the words, how can you construct sentences? Making flash cards often helps students to learn the reactions.

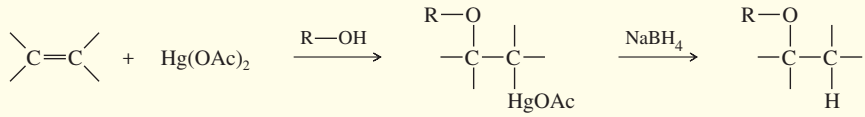
In organic chemistry, the mechanisms, regiochemistry, and stereochemistry are our grammar. You must develop *facility* with the reactions, as you develop facility with the words and grammar you use in speaking. Problems and multistep syntheses are the sentences of organic chemistry. You must *practice* combining all aspects of your vocabulary in solving these problems.

Students who fail organic chemistry exams often do so because they have memorized the vocabulary, but they have not practiced enough problems. Others fail because they think they can do problems, but they lack the vocabulary. If you understand the reactions and can do the end-of-chapter problems without looking back in the chapter, then you should do well on your exams.

ESSENTIAL TERMS

addition	A reaction involving an increase in the number of groups attached to the alkene and a decrease in the number of elements of unsaturation. (p. 328)
anti addition:	An addition in which two groups add to opposite faces of the double bond (as in addition of Br_2). (p. 351)
electrophilic addition:	An addition in which the electrophile (electron-pair acceptor) bonds to one of the double-bonded carbons first, followed by the nucleophile. (p. 329)
syn addition:	An addition in which two groups add to the same face of the double bond (as in osmium tetroxide **dihydroxylation**). (p. 347)
addition polymer	A polymer that results from the addition reactions of alkenes, dienes, or other compounds with double and triple bonds. Most addition polymers form by a chain-growth process. (p. 370)
alkoxy group	**(alkoxyl group)** (**—O—R**) An alkyl group bonded through an oxygen atom, as in an ether. (p. 342)

alkoxymercuration The addition of mercuric acetate to an alkene in an alcohol solution, forming an alkoxymercurial intermediate. Demercuration gives an ether. (p. 342)



alkylidene group One of the carbon atoms at either end of a double bond, together with its two substituents. Most commonly $=CH_2$ or $=CHR$ or $=CR_2$. (p. 373)

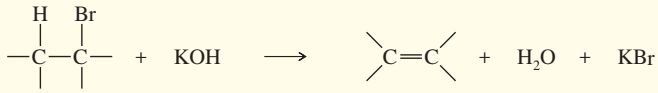
alpha elimination **(α elimination)** The elimination of two atoms or groups from the same carbon atom. Alpha eliminations can be used to form carbenes. (p. 359)

$$CHBr_3 + KOH \longrightarrow :CBr_2 + H_2O + KBr$$

anionic polymerization The process of forming an addition polymer by chain-growth polymerization involving an anion at the end of the growing chain. (p. 373)

asymmetric induction **(enantioselective synthesis)** The formation of an optically active product from an optically inactive starting material. Such a process requires the use of an optically active reagent or catalyst. (p. 356)

beta elimination **(β elimination)** The elimination of two atoms or groups from adjacent carbon atoms. This is the most common type of elimination. (p. 359)



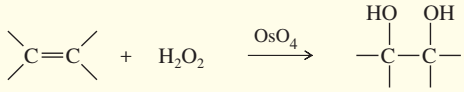
carbene A reactive intermediate with a neutral carbon atom having only two bonds and two nonbonding electrons. Methylene $(:CH_2)$ is the simplest carbene. (p. 358)

cationic polymerization The process of forming an addition polymer by chain-growth polymerization involving a cation at the end of the growing chain. (p. 370)

chain-growth polymer A polymer that results from the rapid addition of one monomer at a time to a growing polymer chain, usually with a reactive intermediate (cation, radical, or anion) at the growing end of the chain. Most chain-growth polymers are addition polymers of alkenes and dienes. (p. 370)

demercuration The removal of a mercury species from a molecule. Demercuration of the products of oxymercuration and alkoxymercuration is usually accomplished using sodium borohydride. (p. 340)

dihydroxylation **(hydroxylation)** The addition of two hydroxyl groups, one at each carbon of the double bond; formally, an oxidation. (p. 364)



epoxide **(oxirane)** A three-membered cyclic ether. (p. 360)

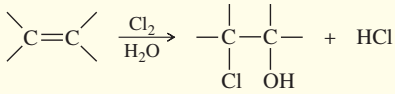
epoxidation: Formation of an epoxide, usually from an alkene. A peroxyacid is generally used for alkene epoxidations. (p. 360)

free-radical polymerization The process of forming an addition polymer by chain-growth polymerization involving a free radical at the end of the growing chain. (p. 372)

glycol A 1,2-diol. (p. 361)

halogenation The addition of a halogen (X_2) to a molecule, or the free-radical substitution of a halogen for a hydrogen. (p. 349)

halohydrin A beta-haloalcohol, with a halogen and a hydroxyl group on adjacent carbon atoms. (p. 352)



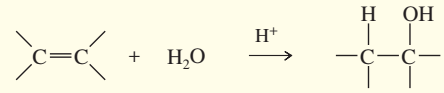
a chlorohydrin

halonium ion A reactive, cationic intermediate with a three-membered ring containing a halogen atom; usually, a **chloronium ion,** a **bromonium ion,** or an **iodonium ion.** (p. 349)

heterogeneous catalysis Use of a catalyst that is in a separate phase from the reactants. For example, a platinum hydrogenation catalyst is a solid, a separate phase from the liquid alkene. (p. 356)

homogeneous catalysis Use of a catalyst that is in the same phase as the reactants. For example, the acid catalyst in hydration is in the liquid phase with the alkene. (p. 356)

hydration The addition of water to a molecule. Hydration of an alkene forms an alcohol. (p. 337)



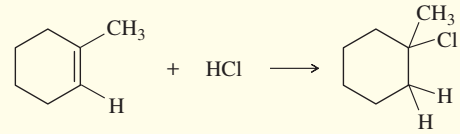
hydroboration The addition of borane (BH_3) or one of its derivatives ($BH_3 \cdot THF$, for example) to a molecule. (p. 343)

hydrogenation The addition of hydrogen to a molecule. The most common hydrogenation is the addition of H_2 across a double bond in the presence of a catalyst (**catalytic hydrogenation** or **catalytic reduction**). (p. 355)

hydroxylation See **dihydroxylation.**

Markovnikov's rule (*original statement*) When a proton acid adds to the double bond of an alkene, the proton bonds to the carbon atom that already has more hydrogen atoms. (p. 332)

Markovnikov's rule (*extended statement*) In an electrophilic addition to an alkene, the electrophile adds in such a way as to generate the most stable intermediate. (p. 333)



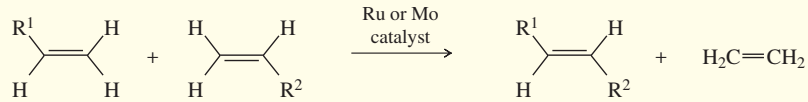
Markovnikov product

Markovnikov orientation: An orientation of addition that obeys the original statement of Markovnikov's rule; one that gives the **Markovnikov product.** (p. 333)

anti-Markovnikov orientation: An orientation of addition that is the opposite of that predicted by the original statement of Markovnikov's rule; one that gives the **anti-Markovnikov product.** (p. 334)

MCPBA (*meta*-chloroperoxybenzoic acid) A common reagent for epoxidizing alkenes. MCPBA dissolves in common solvents such as dichloromethane. As the epoxidation takes place, the *m*-chlorobenzoic acid by-product precipitates out of solution. (p. 361)

metathesis **(olefin metathesis)** Any reaction that trades and interchanges the alkylidene groups of an alkene. (p. 374)



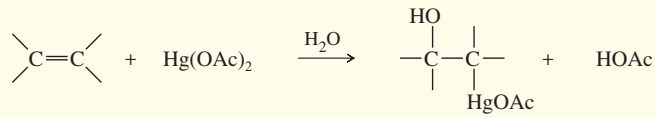
olefin metathesis (cis + trans) ethylene

monomer One of the small molecules that bond together to form a polymer. (p. 369)

organic synthesis The preparation of desired organic compounds from readily available materials. (p. 376)

oxidative cleavage The cleavage of a carbon–carbon bond through oxidation. Carbon–carbon double bonds are commonly cleaved by ozonolysis/reduction or by warm, concentrated permanganate. (p. 366)

oxymercuration The addition of aqueous mercuric acetate to an alkene. (p. 340)



ozonolysis The use of ozone, usually followed by reduction, to cleave a double bond. (p. 367)

peroxide effect The reversal of orientation of HBr addition to alkenes in the presence of peroxides. A free-radical mechanism is responsible for the peroxide effect. (p. 336)

peroxyacid (peracid) A carboxylic acid with an extra oxygen atom and a peroxy (—O—O—) linkage. The general formula is RCO_3H. (p. 360)

polymer A high-molecular-weight compound composed of many molecules of a smaller, simpler compound called the **monomer.** (p. 369)

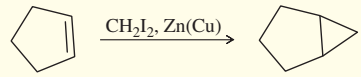
polymerization: The reaction of monomer molecules to form a polymer. (p. 370)

regiochemistry The orientation of a chemical reaction on an unsymmetrical substrate. In additions to alkenes, the regiochemistry of the addition involves which part of the reagent adds to which end of an unsymmetrical alkene. (p. 330)

regioselective reaction A reaction in which one direction of bond making or bond breaking occurs preferentially over all other directions. For example, the addition of HCl is regioselective, predicted by Markovnikov's rule. Hydroboration–oxidation is regioselective because it consistently gives anti-Markovnikov orientation. (p. 332)

retrosynthetic analysis A method of working backward to solve multistep synthetic problems. (p. 376)

Simmons–Smith reaction A cyclopropanation of an alkene using the carbenoid reagent generated from diiodomethane and the zinc–copper couple. (p. 358)

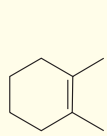


Simmons–Smith reaction

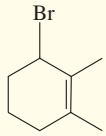
stereospecific reaction A reaction that converts different stereoisomers of the starting material into different stereoisomers of the product. (p. 348)

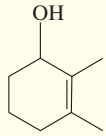
STUDY PROBLEMS

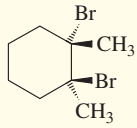
8-46 Using 1,2-dimethylcyclohexene as your starting material, show how you would synthesize the following compounds. (Once you have shown how to synthesize a compound, you may use it as the starting material in any later parts of this problem.) If a chiral product is shown, assume it is part of a racemic mixture.

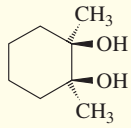


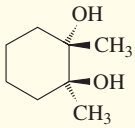
1,2-dimethylcyclohexene

(a) 

(b) 

(c) 

(d) 

(e) 

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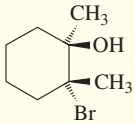
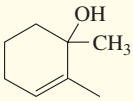
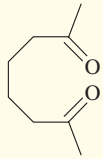
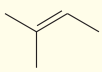
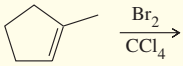
(g) 

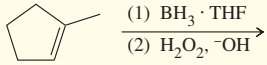
(h) 

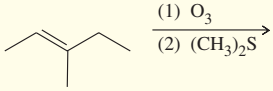
(i) 

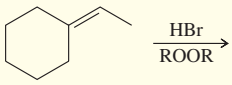
8-47 Predict the major products of the following reactions, and give the structures of any intermediates. Include stereochemistry where appropriate.

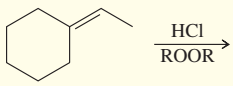
(a) 

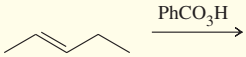
(b) 

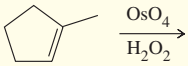
(c) 

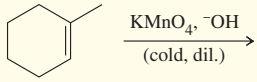
(d) 

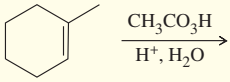
(e) 

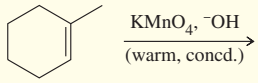
(f) 

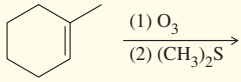
(g) 

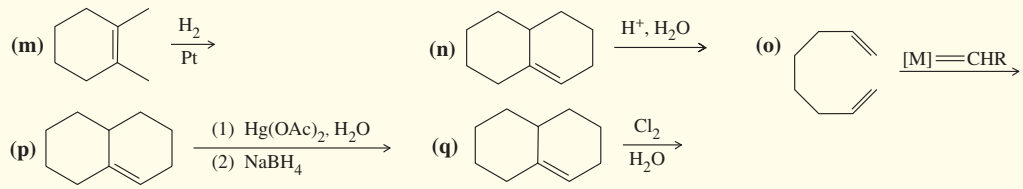
(h) 

(i) 

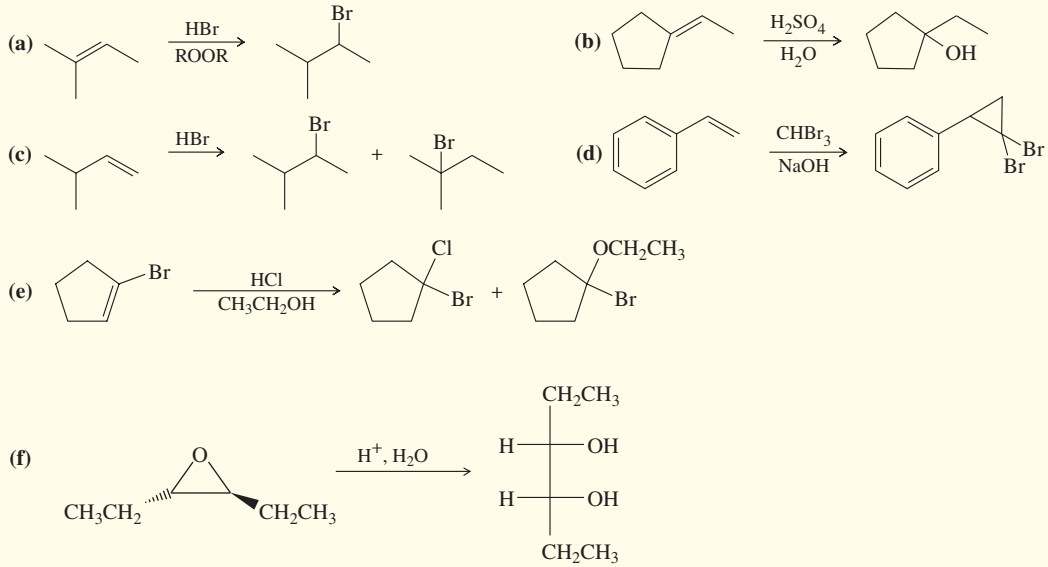
(j) 

(k) 

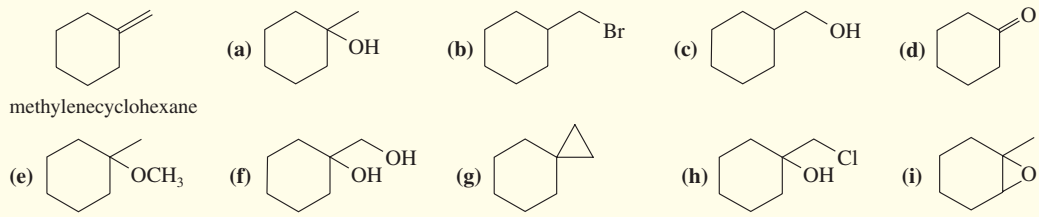
(l) 



8-48 Propose mechanisms consistent with the following reactions.

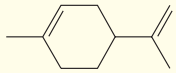


8-49 Show how you would synthesize each compound using methylenecyclohexane as your starting material.



methylenecyclohexane

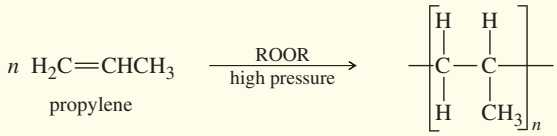
8-50 Limonene is one of the compounds that give lemons their tangy odor. Show the structures of the products expected when limonene reacts with an excess of each of these reagents.



limonene

(a) borane in tetrahydrofuran, followed by basic hydrogen peroxide
(b) *m*-chloroperoxybenzoic acid
(c) ozone, then dimethyl sulfide
(d) a mixture of osmic acid and hydrogen peroxide
(e) hot, concentrated potassium permanganate
(f) peroxyacetic acid in acidic water
(g) hydrogen and a platinum catalyst
(h) hydrogen bromide gas
(i) hydrogen bromide gas in a solution containing dimethyl peroxide
(j) bromine water
(k) chlorine gas
(l) mercuric acetate in methanol, followed by sodium borohydride
(m) $CHBr_3$ and 50% aq. NaOH

8-51 Propose a mechanism for reaction of the first three propylene units in the polymerization of propylene in the presence of a peroxide.



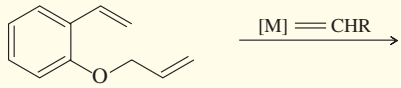
polypropylene

***8-52** When styrene (vinylbenzene) is commercially polymerized, about 1–3% of 1,4-divinylbenzene is often added to the styrene. The incorporation of some divinylbenzene gives a polymer with more strength and better resistance to organic solvents. Explain how a very small amount of divinylbenzene has a marked effect on the properties of the polymer.

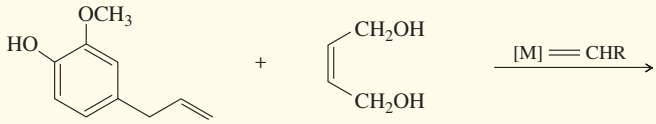
8-53 The cationic polymerization of isobutylene (2-methylpropene) is shown in Section 8-16A. Isobutylene is often polymerized under free-radical conditions. Propose a mechanism for the free-radical polymerization of isobutylene.

8-54 Show what products you would expect from the following metathesis reactions, using the Schrock or Grubbs catalysts.

(a)

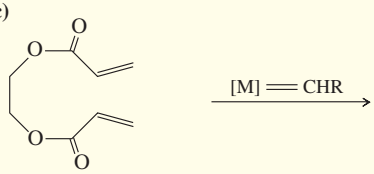


(b)



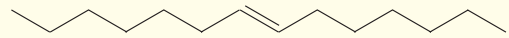
eugenol

(c)



8-55 Show how you might use olefin metathesis to assemble the following alkenes from smaller units:

(a)



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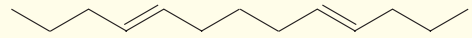
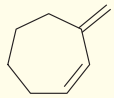


8-56 Cyclohexene is dissolved in a solution of lithium chloride in chloroform. To this solution is added one equivalent of bromine. The material isolated from this reaction contains primarily a mixture of *trans*-1,2-dibromocyclohexane and *trans*-1-bromo-2-chlorocyclohexane. Propose a mechanism to show how these compounds are formed.

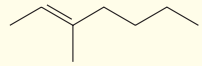
8-57 Draw a reaction-energy diagram for the propagation steps of the free-radical addition of HBr to isobutylene. Draw curves representing the reactions leading to both the Markovnikov and the anti-Markovnikov products. Compare the values of $\Delta G°$ and E_a for the rate-limiting steps, and explain why only one of these products is observed.

8-58 Give the products expected when the following compounds are ozonized and reduced.

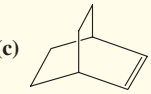
(a)



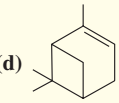
(b)



(c)

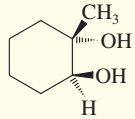


(d)



8-59 Show how you would make the following compounds from a suitable cyclic alkene.

(a)



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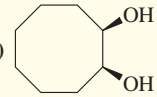

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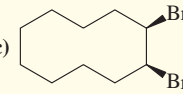

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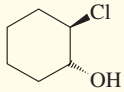
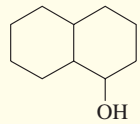


(e)



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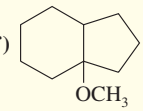
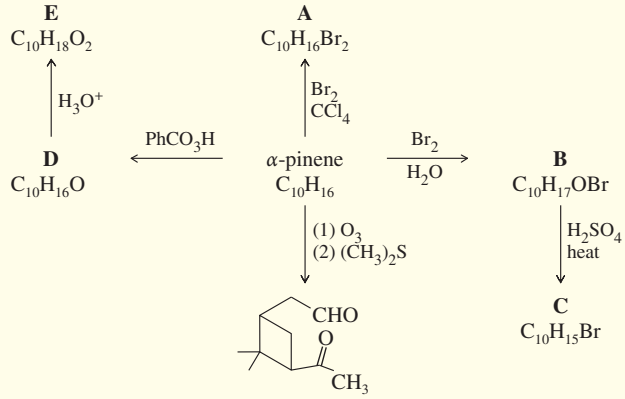


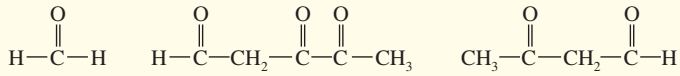
8-60 Unknown **X,** C_5H_9Br, does not react with bromine or with dilute $KMnO_4$. Upon treatment with potassium *tert*-butoxide, **X** gives only one product, **Y,** C_5H_8. Unlike **X, Y** decolorizes bromine and changes $KMnO_4$ from purple to brown. Catalytic hydrogenation of **Y** gives methylcyclobutane. Ozonolysis–reduction of **Y** gives dialdehyde **Z,** $C_5H_8O_2$. Propose consistent structures for **X, Y,** and **Z.** Is there any aspect of the structure of **X** that is still unknown?

8-61 One of the constituents of turpentine is α-pinene, formula $C_{10}H_{16}$. The following scheme (called a "road map") gives some reactions of α-pinene. Determine the structure of α-pinene and of the reaction products **A** through **E.**



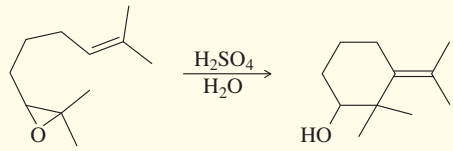
8-62 The sex attractant of the housefly has the formula $C_{23}H_{46}$. When treated with warm potassium permanganate, this pheromone gives two products: $CH_3(CH_2)_{12}COOH$ and $CH_3(CH_2)_7COOH$. Suggest a structure for this sex attractant. Explain which part of the structure is uncertain.

8-63 In contact with a platinum catalyst, an unknown alkene reacts with 3 equivalents of hydrogen gas to give 1-isopropyl-4-methylcyclohexane. When the unknown alkene is ozonized and reduced, the products are the following:

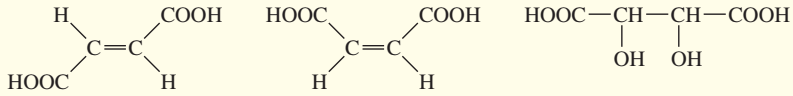


Deduce the structure of the unknown alkene.

***8-64** Propose a mechanism for the following reaction.



8-65 The two butenedioic acids are called *fumaric acid* (trans) and *maleic acid* (cis). 2,3-Dihydroxybutanedioic acid is called *tartaric acid*.



fumaric acid maleic acid tartaric acid

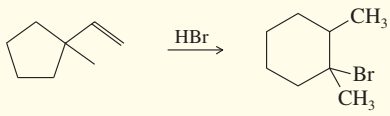
Show how you would convert

(a) fumaric acid to (±)-tartaric acid. **(b)** fumaric acid to *meso*-tartaric acid.

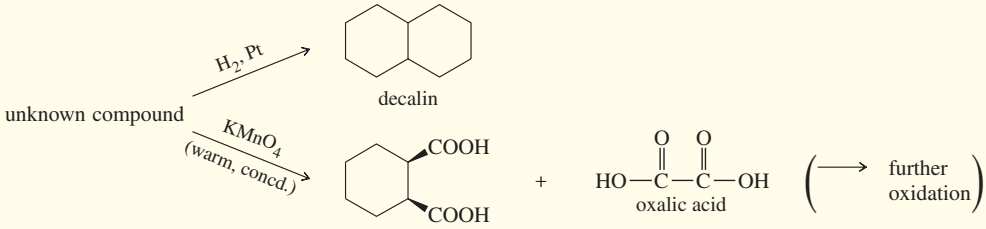
(c) maleic acid to (±)-tartaric acid. **(d)** maleic acid to *meso*-tartaric acid.

8-66 The compound BD_3 is a deuterated form of borane. Predict the product formed when 1-methylcyclohexene reacts with $BD_3 \cdot THF$, followed by basic hydrogen peroxide.

8-67 A routine addition of HBr across the double bond of a vinylcyclopentane gave a small amount of an unexpected rearranged product. Propose a mechanism for the formation of this product, and explain why the rearrangement occurs.



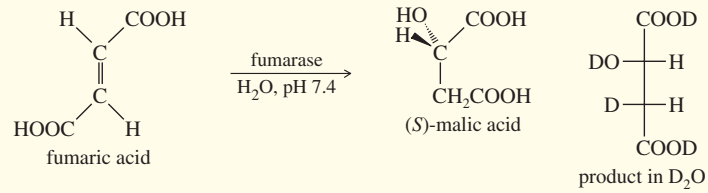
8-68 An unknown compound decolorizes bromine in carbon tetrachloride, and it undergoes catalytic reduction to give decalin. When treated with warm, concentrated potassium permanganate, this compound gives *cis*-cyclohexane-1,2-dicarboxylic acid and oxalic acid. Propose a structure for the unknown compound.



cis-cyclohexane-1,2-dicarboxylic acid

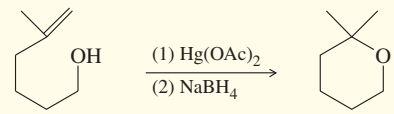
***8-69** Many enzymes catalyze reactions that are similar to reactions we might use for organic synthesis. Enzymes tend to be stereospecific in their reactions, and asymmetric induction is common. The following reaction, part of the tricarboxylic

acid cycle of cell respiration, resembles a reaction we might use in the laboratory; however, the enzyme-catalyzed reaction gives only the (*S*) enantiomer of the product, malic acid.



(a) What type of reaction does fumarase catalyze?
(b) Is fumaric acid chiral? Is malic acid chiral? In the enzyme-catalyzed reaction, is the product (malic acid) optically active?
(c) If we could run the preceding reaction in the laboratory using sulfuric acid as the catalyst, would the product (malic acid) be optically active?
(d) Do you expect the fumarase enzyme to be a chiral molecule?
(e) When the enzyme-catalyzed reaction takes place in D_2O, the *only* product is the stereoisomer just pictured. No enantiomer or diastereomer of this compound is formed. Is the enzyme-catalyzed reaction a syn or anti addition?
(f) Assume we found conditions to convert fumaric acid to deuterated malic acid using hydroboration with $BD_3 \cdot THF$, followed by oxidation with D_2O_2 and NaOD. Use Fischer projections to show the stereoisomer(s) of deuterated malic acid you would expect to be formed.

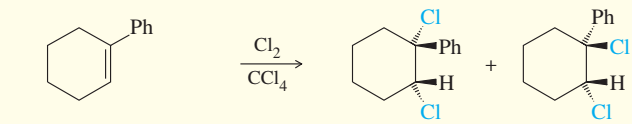
***8-70** **(a)** The following cyclization has been observed in the oxymercuration–demercuration of this unsaturated alcohol. Propose a mechanism for this reaction.



(b) Predict the product of formula $C_7H_{13}BrO$ from the reaction of this same unsaturated alcohol with bromine. Propose a mechanism to support your prediction.

***8-71** An inexperienced graduate student treated dec-5-ene with borane in THF, placed the flask in a refrigerator, and left for a party. When he returned from the party, he discovered that the refrigerator was broken, and it had gotten quite warm inside. Although all the THF had evaporated from the flask, he treated the residue with basic hydrogen peroxide. To his surprise, he recovered a fair yield of decan-1-ol. Use a mechanism to show how this reaction might have occurred. (*Hint*: The addition of BH_3 is reversible.)

***8-72** We have seen many examples where halogens add to alkenes with anti stereochemistry via the halonium ion mechanism. However, when 1-phenylcyclohexene reacts with chlorine in carbon tetrachloride, a mixture of the cis and trans isomers of the product is recovered. Propose a mechanism, and explain this lack of stereospecificity.



1-phenylcyclohexene

cis- and *trans*-
1,2-dichloro-1-phenylcyclohexane