7

Alkenes: Reactions and Synthesis

Alkene addition reactions occur widely, both in the laboratory and in living organisms. Although we've studied only the addition of HX thus far, many closely related reactions also take place. In this chapter, we'll see briefly how alkenes are prepared, we'll discuss many further examples of alkene addition reactions, and we'll see the wide variety of compounds that can be made from alkenes.
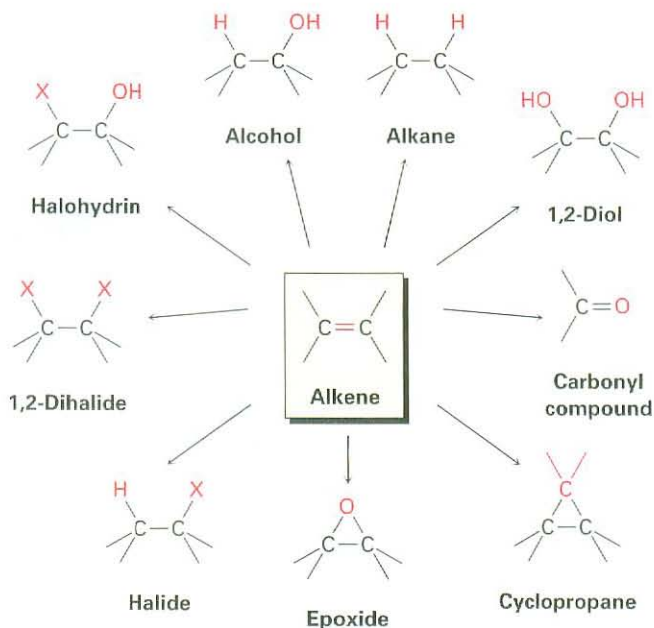

WHY THIS CHAPTER?

Much of the background needed to understand organic reactions has now been covered, and it's time to begin a systematic description of the major functional groups. Both in this chapter on alkenes and in future chapters on other

functional groups, we'll discuss a variety of reactions but try to focus on the general principles and patterns of reactivity that tie organic chemistry together. There are no shortcuts: you have to know the reactions to understand organic chemistry.

7.1 Preparation of Alkenes: A Preview of Elimination Reactions

Before getting to the main subject of this chapter—the reactions of alkenes—let's take a brief look at how alkenes are prepared. The subject is a bit complex, though, so we'll return in Chapter 11 for a more detailed study. For the present, it's enough to realize that alkenes are readily available from simple precursors—usually alcohols in biological systems and either alcohols or alkyl halides in the laboratory.

Just as the chemistry of alkenes is dominated by addition reactions, the preparation of alkenes is dominated by elimination reactions. Additions and eliminations are, in many respects, two sides of the same coin. That is, an addition reaction might involve the addition of HBr or H_2O to an alkene to form an alkyl halide or alcohol, whereas an elimination reaction might involve the loss of HBr or H_2O from an alkyl halide or alcohol to form an alkene.
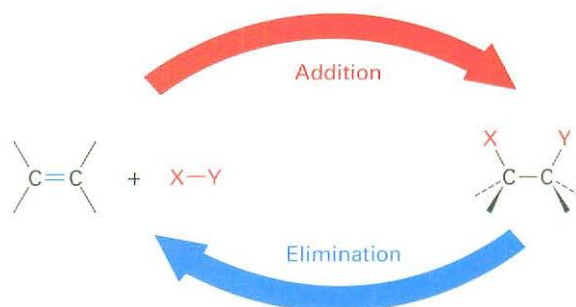
The two most common elimination reactions are *dehydrohalogenation*—the loss of HX from an alkyl halide—and *dehydration*—the loss of water from an alcohol. Dehydrohalogenation usually occurs by reaction of an alkyl halide with strong base such as potassium hydroxide. For example, bromocyclohexane yields cyclohexene when treated with KOH in ethanol solution.

**Bromocyclohexane**   **Cyclohexene (81%)**
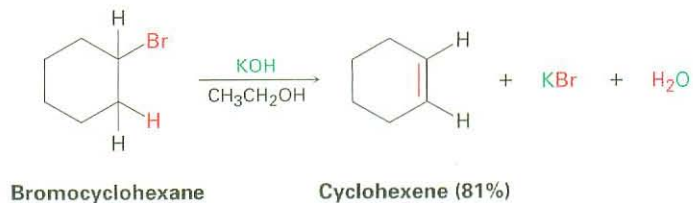
Dehydration is often carried out by treatment of an alcohol with a strong acid. For example, loss of water occurs and 1-methylcyclohexene is formed

when 1-methylcyclohexanol is warmed with aqueous sulfuric acid in tetra-hydrofuran (THF) solvent.


1-Methylcyclohexanol   **1-Methylcyclohexene (91%)**

Tetrahydrofuran (THF)—a common solvent

In biological pathways, dehydrations rarely occur with isolated alcohols but instead normally take place on substrates in which the −OH is positioned two carbons away from a carbonyl group. In the biosynthesis of fats, for instance, β-hydroxybutyryl ACP is converted by dehydration to *trans*-crotonyl ACP, where ACP is an abbreviation for *acyl carrier protein*. We'll see the reason for this requirement in Section 11.10.

β-Hydroxybutyryl ACP   ***trans*-Crotonyl ACP**
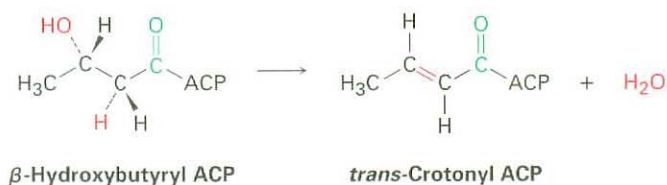
Problem 7.1 One problem with elimination reactions is that mixtures of products are often formed. For example, treatment of 2-bromo-2-methylbutane with KOH in ethanol yields a mixture of two alkene products. What are their likely structures?

Problem 7.2 How many alkene products, including *E,Z* isomers, might be obtained by dehydration of 3-methyl-3-hexanol with aqueous sulfuric acid?

$$CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}CH_2CH_3 \xrightarrow{H_2SO_4} ?$$

3-Methyl-3-hexanol
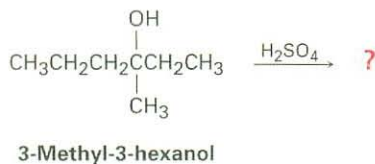
7.2 Addition of Halogens to Alkenes

Bromine and chlorine add rapidly to alkenes to yield 1,2-dihalides, a process called *halogenation*. For example, approximately 6 million tons per year of 1,2-dichloroethane (ethylene dichloride) are synthesized industrially by addition

of Cl_2 to ethylene. The product is used both as a solvent and as starting material for the manufacture of poly(vinyl chloride), PVC. Fluorine is too reactive and difficult to control for most laboratory applications, and iodine does not react with most alkenes.
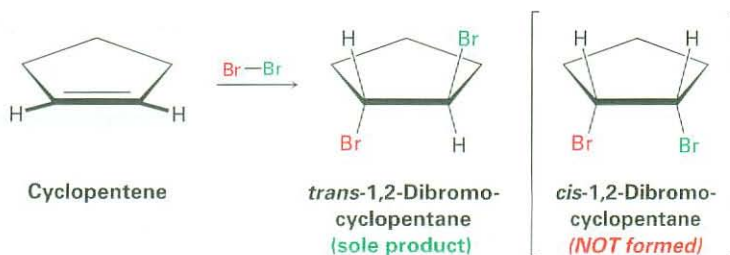

Ethylene

**1,2-Dichloroethane
(ethylene dichloride)**
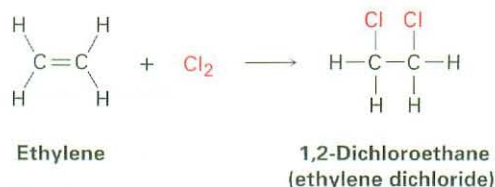
Based on what we've seen thus far, a possible mechanism for the reaction of bromine with alkenes might involve electrophilic addition of Br^+ to the alkene, giving a carbocation that could undergo further reaction with Br^- to yield the dibromo addition product.
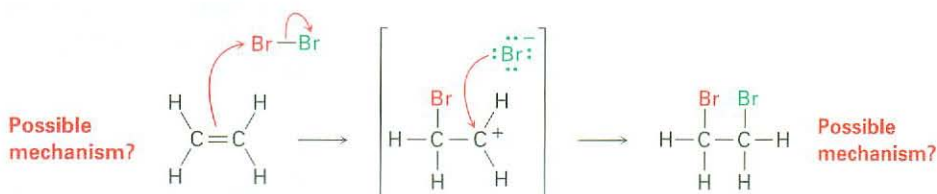
Although this mechanism seems plausible, it's not fully consistent with known facts. In particular, it doesn't explain the *stereochemistry* of the addition reaction. That is, the mechanism doesn't tell which product stereoisomer is formed.

When the halogenation reaction is carried out on a cycloalkene, such as cyclopentene, only the *trans* stereoisomer of the dihalide addition product is formed rather than the mixture of cis and trans isomers that might have been expected if a planar carbocation intermediate were involved. We say that the reaction occurs with **anti stereochemistry**, meaning that the two bromine atoms come from opposite faces of the double bond—one from the top face and one from the bottom face.

Cyclopentene

**trans-1,2-Dibromo-
cyclopentane
(sole product)**

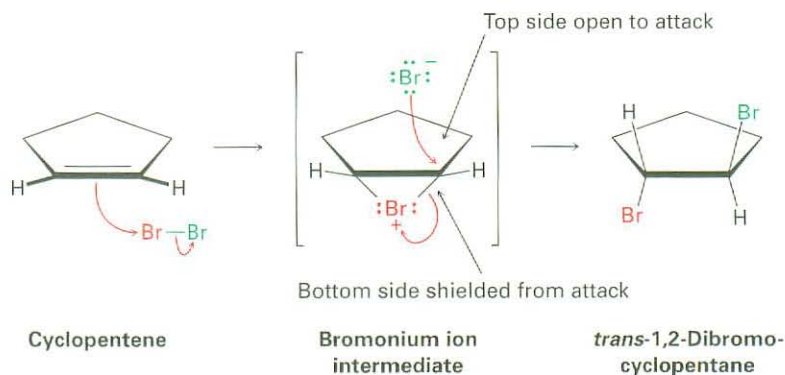**cis-1,2-Dibromo-
cyclopentane
(NOT formed)**

An explanation for the observed anti stereochemistry of addition was suggested in 1937 by George Kimball and Irving Roberts, who proposed that the

reaction intermediate is not a carbocation but is instead a **bromonium ion**, R_2Br^+, formed by addition of Br^+ to the alkene. (Similarly, a *chloronium ion* contains a positively charged divalent chlorine, R_2Cl^+.) The bromonium ion is formed in a single step by interaction of the alkene with Br_2 and simultaneous loss of Br^-.

ThomsonNOW   Click *Organic Process* to view an animation of the bromonium ion intermediate and product formation in this reaction.
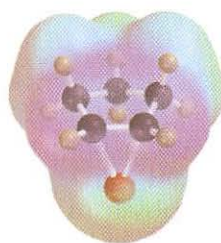

An alkene   A bromonium ion
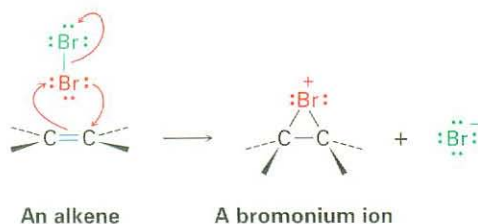
How does the formation of a bromonium ion account for the observed anti stereochemistry of addition to cyclopentene? If a bromonium ion is formed as an intermediate, we can imagine that the large bromine atom might "shield" one side of the molecule. Reaction with Br^- ion in the second step could then occur only from the opposite, unshielded side to give trans product.

Top side open to attack

Bottom side shielded from attack

Cyclopentene   Bromonium ion intermediate   *trans*-1,2-Dibromo-cyclopentane

George Andrew Olah

George Andrew Olah (1927–) was born in Budapest, Hungary, and received a doctorate in 1949 at the Technical University of Budapest. During the Hungarian revolution in 1956, he immigrated to Canada and joined the Dow Chemical Company. After moving to the United States, he was professor of chemistry at Case Western Reserve University (1965–1977) and then at the University of Southern California (1977–). He received the 1994 Nobel Prize in chemistry for his work on carbocations.


The bromonium ion postulate, made more than 75 years ago to explain the stereochemistry of halogen addition to alkenes, is a remarkable example of deductive logic in chemistry. Arguing from experimental results, chemists were able to make a hypothesis about the intimate mechanistic details of alkene electrophilic reactions. Subsequently, strong evidence supporting the mechanism came from the work of George Olah, who prepared and studied *stable*

solutions of cyclic bromonium ions in liquid SO_2. There's no question that bromonium ions exist.

Bromonium ion
(stable in SO_2 solution)

Alkene halogenation reactions occur in nature just as they do in the laboratory but are limited primarily to marine organisms, which live in a halide-rich environment. The reactions are carried out by enzymes called *haloperoxidases*, which use H_2O_2 to oxidize Br^- or Cl^- ions to a biological equivalent of Br^+ or Cl^+. Electrophilic addition to the double bond of a substrate molecule then yields a bromonium or chloronium ion intermediate just as in the laboratory, and reaction with another halide ion completes the process. For example, the following tetrahalide, isolated from the red alga *Plocamium cartilagineum*, is thought to arise from β-ocimene by twofold addition of BrCl through the corresponding bromonium ions.


β-Ocimene
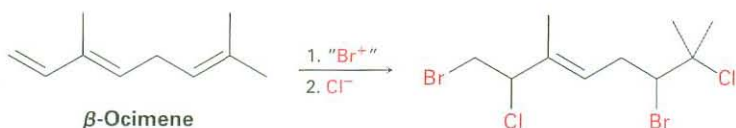
Problem 7.3 | What product would you expect to obtain from addition of Cl_2 to 1,2-dimethylcyclohexene? Show the stereochemistry of the product.

Problem 7.4 | Addition of HCl to 1,2-dimethylcyclohexene yields a mixture of two products. Show the stereochemistry of each, and explain why a mixture is formed.

7.3 | Addition of Hypohalous Acids to Alkenes: Halohydrin Formation
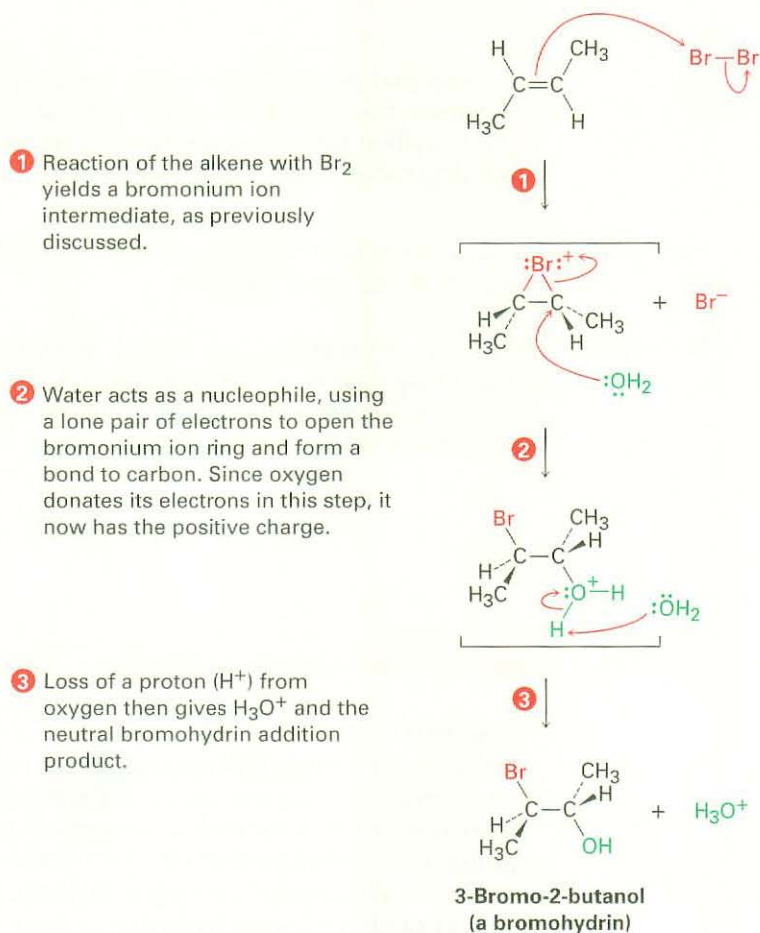
Yet another example of an electrophilic addition is the reaction of alkenes with the hypohalous acids HO−Cl or HO−Br to yield 1,2-halo alcohols, called **halohydrins.** Halohydrin formation doesn't take place by direct reaction of an alkene with HOBr or HOCl, however. Rather, the addition is done indirectly by reaction of the alkene with either Br_2 or Cl_2 in the presence of water.

An alkene   **A halohydrin**
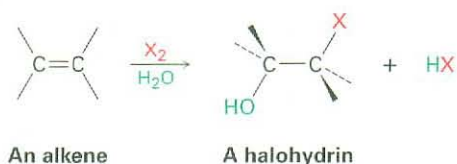
We saw in the previous section that when Br_2 reacts with an alkene, th cyclic bromonium ion intermediate reacts with the only nucleophile present Br^- ion. If the reaction is carried out in the presence of an additional nucle phile, however, the intermediate bromonium ion can be intercepted by th added nucleophile and diverted to a different product. In the presence of water for instance, water competes with Br^- ion as nucleophile and reacts with th bromonium ion intermediate to yield a *bromohydrin*. The net effect is addition of $HO-Br$ to the alkene by the pathway shown in Figure 7.1.

Figure 7.1 MECHANISM:
Mechanism of bromohydrin formation by reaction of an alkene with Br_2 in the presence of water. Water acts as a nucleophile to react with the intermediate bromonium ion.

1 Reaction of the alkene with Br_2 yields a bromonium ion intermediate, as previously discussed.

2 Water acts as a nucleophile, using a lone pair of electrons to open the bromonium ion ring and form a bond to carbon. Since oxygen donates its electrons in this step, it now has the positive charge.

3 Loss of a proton (H^+) from oxygen then gives H_3O^+ and the neutral bromohydrin addition product.

3-Bromo-2-butanol (a bromohydrin)

© John McMurry

In practice, few alkenes are soluble in water, and bromohydrin formation is often carried out in a solvent such as aqueous dimethyl sulfoxide, CH_3SOCH_3 (DMSO), using a reagent called *N*-bromosuccinimide (NBS) as a source of Br_2. NBS is a stable, easily handled compound that slowly decomposes in water to yield Br_2 at a controlled rate. Bromine itself can also be used

in the addition reaction, but it is more dangerous and more difficult to handle than NBS.

Styrene

H_2O, CH_3SOCH_3 (DMSO)

2-Bromo-1-phenylethanol
(70%)
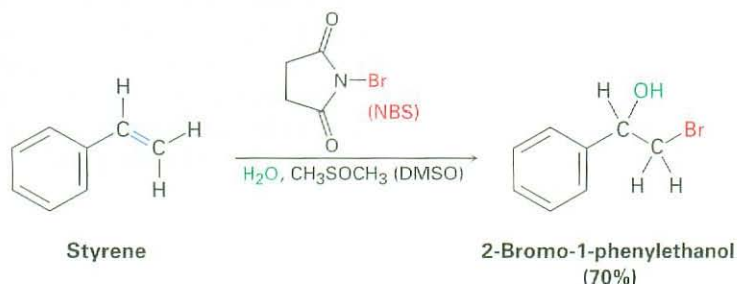
Note that the aromatic ring in the preceding example does not react with Br_2 under the conditions used, even though it appears to contain three carbon–carbon double bonds. As we'll see in Chapter 15, aromatic rings are a good deal more stable than might be expected.

Problem 7.5   What product would you expect from the reaction of cyclopentene with NBS and water? Show the stereochemistry.
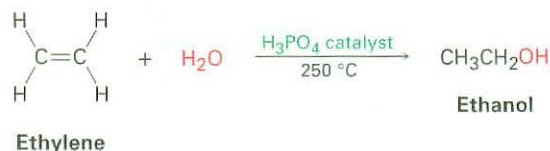
Problem 7.6   When an unsymmetrical alkene such as propene is treated with N-bromosuccinimide in aqueous dimethyl sulfoxide, the major product has the bromine atom bonded to the less highly substituted carbon atom. Is this Markovnikov or non-Markovnikov orientation? Explain.

$$CH_3CH=CH_2 \xrightarrow{Br_2, H_2O} \underset{\overset{|}{OH}}{CH_3CHCH_2Br}$$
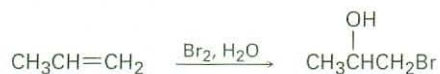
7.4 | Addition of Water to Alkenes: Oxymercuration

Water adds to alkenes to yield alcohols, a process called *hydration*. The reaction takes place on treatment of the alkene with water and a strong acid catalyst (HA) by a mechanism similar to that of HX addition. Thus, protonation of an alkene double bond yields a carbocation intermediate, which reacts with water to yield a protonated alcohol product (ROH_2^+). Loss of H^+ from this protonated alcohol gives the neutral alcohol and regenerates the acid catalyst (Figure 7.2).

Acid-catalyzed alkene hydration is particularly suited to large-scale industrial procedures, and approximately 300,000 tons of ethanol are manufactured each year in the United States by hydration of ethylene. The reaction is of little value in the typical laboratory, however, because it requires high temperatures—250 °C in the case of ethylene—and strongly acidic conditions.

$$\underset{\text{Ethylene}}{\overset{H}{\underset{H}{\smash{}}}C=C\overset{H}{\underset{H}{\smash{}}}} + H_2O \xrightarrow[250 \, °C]{H_3PO_4 \text{ catalyst}} CH_3CH_2OH$$

Ethanol

Figure 7.2 MECHANISM:
Mechanism of the acid-catalyzed hydration of an alkene to yield an alcohol. Protonation of the alkene gives a carbocation intermediate that reacts with water.
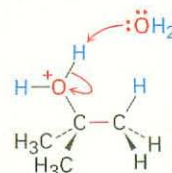
1 A hydrogen atom on the electrophile H_3O^+ is attacked by π electrons from the nucleophilic double bond, forming a new C–H bond. This leaves the other carbon atom with a + charge and a vacant p orbital. Simultaneously, two electrons from the H–O bond move onto oxygen, giving neutral water.
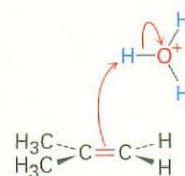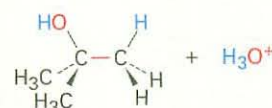
2-Methylpropene
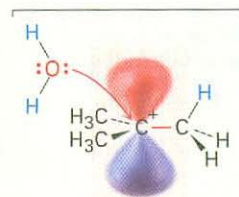
Carbocation

**2** The nucleophile H_2O donates an electron pair to the positively charged carbon atom, forming a C–O bond and leaving a positive charge on oxygen in the protonated alcohol addition product.

Protonated alcohol

3 Water acts as a base to remove H^+, regenerating H_3O^+ and yielding the neutral alcohol addition product.

2-Methyl-2-propanol

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Acid-catalyzed hydration of isolated double bonds is also uncommon in biological pathways. More frequently, biological hydrations require that the double bond be adjacent to a carbonyl group for reaction to proceed. Fumarate, for instance, is hydrated to give malate as one step in the citric acid cycle of food metabolism. Note that the requirement for an adjacent carbonyl group in the addition of water is the same as that we saw in Section 7.1 for the elimination of water. We'll see the reason for the requirement in Section 19.13, but might note for now that the reaction is not an electrophilic addition but instead occurs

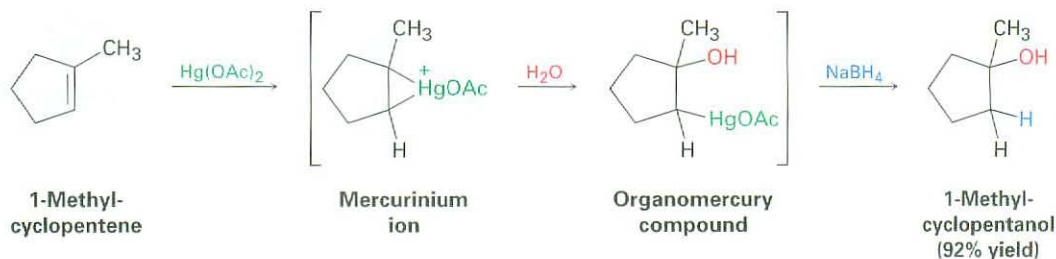through a mechanism that involves formation of an anion intermediate followed by protonation by an acid HA.
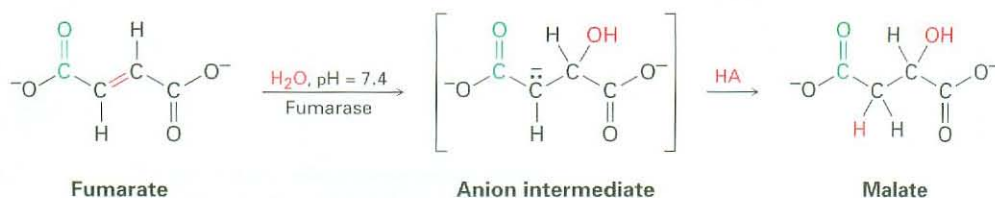
Fumarate   **Anion intermediate**   **Malate**

In the laboratory, alkenes are often hydrated by the **oxymercuration** procedure. When an alkene is treated with mercury(II) acetate [$Hg(O_2CCH_3)_2$, usually abbreviated $Hg(OAc)_2$] in aqueous tetrahydrofuran (THF) solvent, electrophilic addition of Hg^{2+} to the double bond rapidly occurs. The intermediate *organomercury* compound is then treated with sodium borohydride, $NaBH_4$, and an alcohol is produced. For example:

1-Methylcyclopentene   **1-Methylcyclopentanol**
   **(92%)**
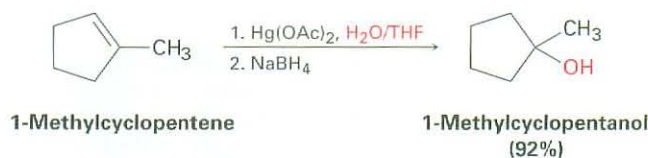
Alkene oxymercuration is closely analogous to halohydrin formation. The reaction is initiated by electrophilic addition of Hg^{2+} (mercuric) ion to the alkene to give an intermediate *mercurinium ion*, whose structure resembles that of a bromonium ion (Figure 7.3). Nucleophilic addition of water as in halohydrin formation, followed by loss of a proton, then yields a stable organomercury product. The final step, reaction of the organomercury compound with sodium borohydride, is complex and appears to involve radicals. Note that the regiochemistry of the reaction corresponds to Markovnikov addition of water; that is, the −OH group attaches to the more highly substituted carbon atom, and the −H attaches to the less highly substituted carbon.

**1-Methyl-   Mercurinium   Organomercury   1-Methyl-
cyclopentene   ion   compound   cyclopentanol
                                                                 (92% yield)**

Figure 7.3 Mechanism of the oxymercuration of an alkene to yield an alcohol. The reaction involves a mercurinium ion intermediate and proceeds by a mechanism similar to that of halohydrin formation. The product of the reaction is the more highly substituted alcohol, corresponding to Markovnikov regiochemistry.

Problem 7.7   What products would you expect from oxymercuration of the following alkenes?

(a) $CH_3CH_2CH_2CH=CH_2$ (b) CH_3
                                          |
                                   $CH_3C=CHCH_2CH_3$
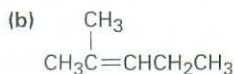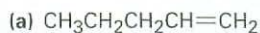
Problem 7.8 | What alkenes might the following alcohols have been prepared from?

(a)

$$CH_3\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2CH_2CH_2CH_3$$

(b)
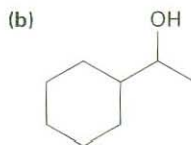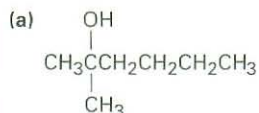
7.5 | Addition of Water to Alkenes: Hydroboration

In addition to the oxymercuration method, which yields the Markovnikov product, a complementary method that yields the non-Markovnikov product is also useful. Discovered in 1959 by H. C. Brown and called **hydroboration**, the reaction involves addition of a B—H bond of borane, BH_3, to an alkene to yield an organoborane intermediate, RBH_2. Oxidation of the organoborane by reaction with basic hydrogen peroxide, H_2O_2, then gives an alcohol. For example:

**2-Methyl-2-pentene**   **Organoborane intermediate**   **2-Methyl-3-pentanol**
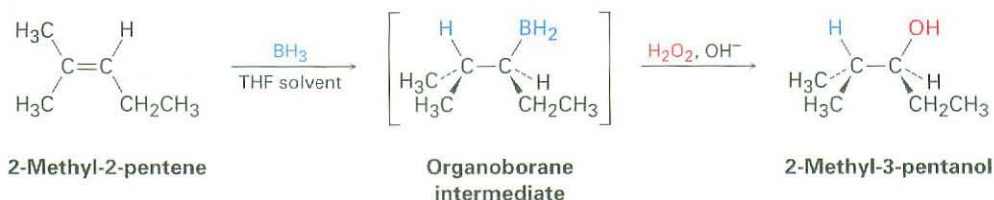
Herbert Charles Brown

Herbert Charles Brown (1912–2004) was born in London to Ukrainian parents and brought to the United States in 1914. Brown received his Ph.D. in 1938 from the University of Chicago, taught at Chicago and at Wayne State University, and then became professor of chemistry at Purdue University. The author of more than 1000 scientific papers, he received the 1979 Nobel Prize in chemistry for his work on organoboranes.

Borane is very reactive because the boron atom has only six electrons in its valence shell. In tetrahydrofuran solution, BH_3 accepts an electron pair from a solvent molecule in a Lewis acid–base reaction to complete its octet and form a stable BH_3–THF complex.

Borane   **THF**   **BH_3 –THF complex**
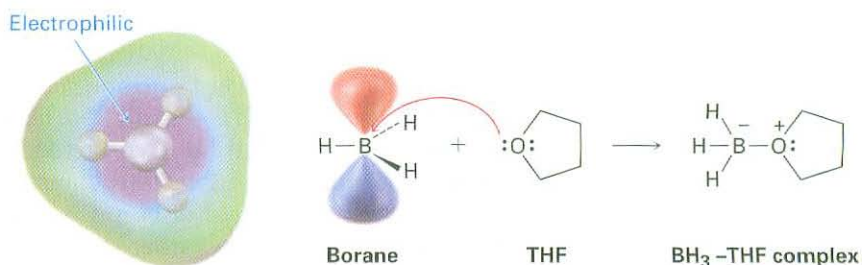
When an alkene reacts with BH_3 in THF solution, rapid addition to the double bond occurs three times and a *trialkylborane*, R_3B, is formed. For example, 1 molar equivalent of BH_3 adds to 3 molar equivalents of cyclohexene to yield tricyclohexylborane. When tricyclohexylborane is then treated with aqueous hydrogen peroxide (H_2O_2) in basic solution, an oxidation takes place. The three C—B bonds are broken, —OH groups bond to the three carbons, and 3 equivalents of cyclohexanol are produced. The net effect of the

two-step hydroboration/oxidation sequence is hydration of the alkene double bond.

Cyclohexene

Tricyclohexylborane

Cyclohexanol
(87%)
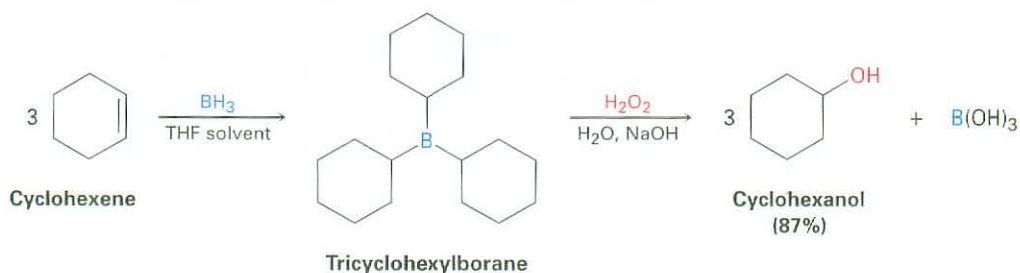
One of the features that makes the hydroboration reaction so useful is the regiochemistry that results when an unsymmetrical alkene is hydroborated. For example, hydroboration/oxidation of 1-methylcyclopentene yields *trans*-2-methylcyclopentanol. Boron and hydrogen both add to the alkene from the same face of the double bond—that is, with **syn stereochemistry**, the opposite of anti—with boron attaching to the less highly substituted carbon. During the oxidation step, the boron is replaced by an −OH with the same stereochemistry, resulting in an overall syn non-Markovnikov addition of water. This stereochemical result is particularly useful because it is complementary to the Markovnikov regiochemistry observed for oxymercuration.

1-Methyl-
cyclopentene

Organoborane
intermediate

trans-2-Methyl-
cyclopentanol
(85% yield)
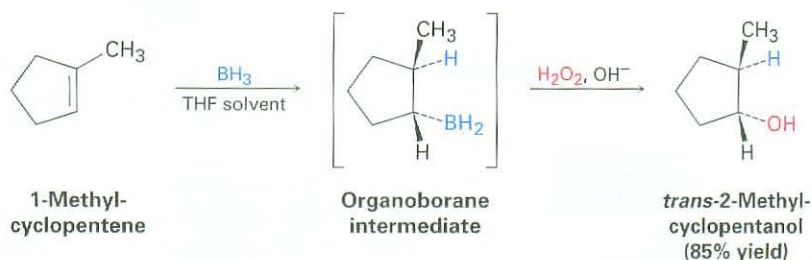
Why does alkene hydroboration take place with non-Markovnikov regiochemistry, yielding the less highly substituted alcohol? Hydroboration differs from many other alkene addition reactions in that it occurs in a single step through a four-center, cyclic transition state without a carbocation intermediate (Figure 7.4). Because both C−H and C−B bonds form at the same time and from the same face of the alkene, syn stereochemistry results. This mechanism accounts not only for the syn stereochemistry of the reaction but also for the regiochemistry. Attachment of boron is favored at the less sterically hindered carbon atom of the alkene, rather than at the more hindered carbon, because there is less steric crowding in the resultant transition state.


WORKED EXAMPLE 7.1   *Predicting the Products Formed in a Reaction*

What products would you obtain from reaction of 2,4-dimethyl-2-pentene with:
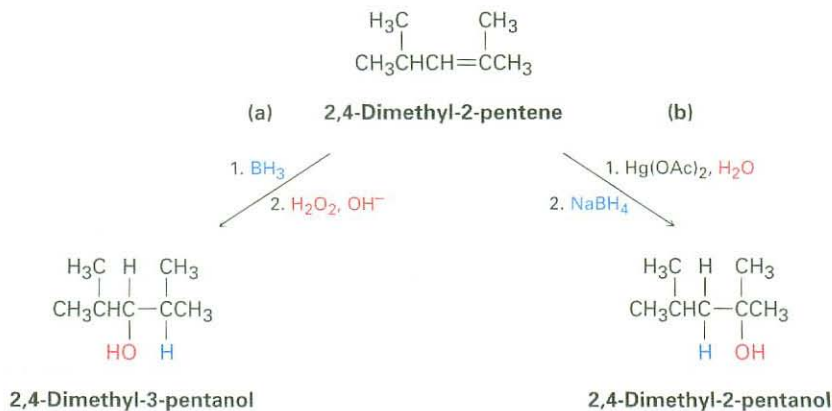(a) BH_3, followed by H_2O_2, OH^- (b) $Hg(OAc)_2$, followed by $NaBH_4$

Strategy   When predicting the product of a reaction, you have to recall what you know about the kind of reaction being carried out and then apply that knowledge to the specific case you're dealing with. In the present instance, recall that the two methods of

1-Methyl-cyclopentene

Steric crowding here

NOT formed

trans-2-Methyl-cyclopentanol
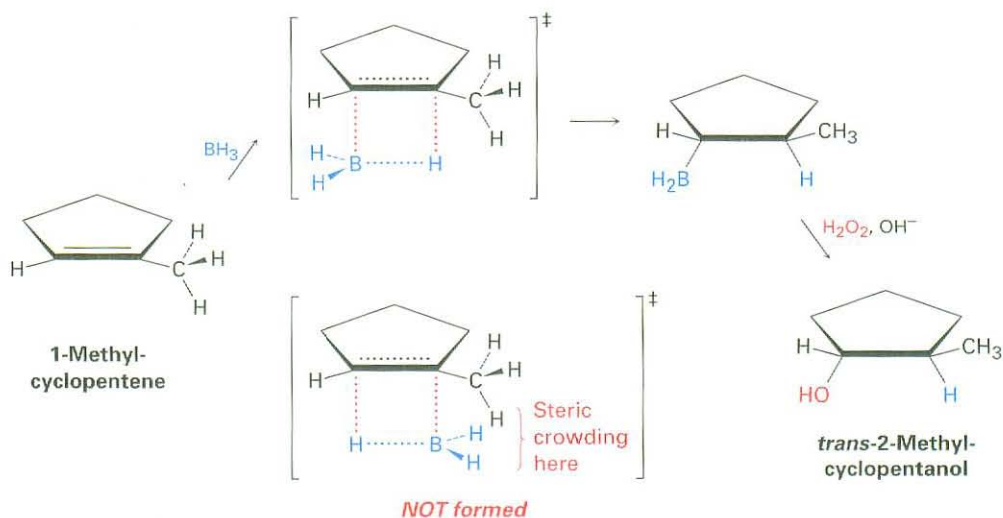
Active Figure 7.4 Mechanism of alkene hydroboration. The reaction occurs in a single step in which both C–H and C–B bonds form at the same time and on the same face of the double bond. The lower energy, more rapidly formed transition state is the one with less steric crowding, leading to non-Markovnikov regiochemistry. *Sign in at* **www.thomsonedu.com** *to see a simulation based on this figure and to take a short quiz.*

hydration—hydroboration/oxidation and oxymercuration—give complementary products. Hydroboration/oxidation occurs with syn stereochemistry and gives the non-Markovnikov addition product; oxymercuration gives the Markovnikov product.

Solution

(a)   **2,4-Dimethyl-2-pentene**   (b)

1. BH₃
2. H₂O₂, OH⁻

1. Hg(OAc)₂, H₂O
2. NaBH₄

2,4-Dimethyl-3-pentanol

2,4-Dimethyl-2-pentanol

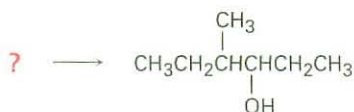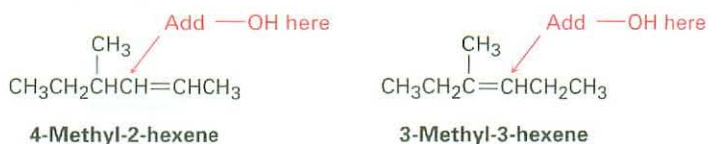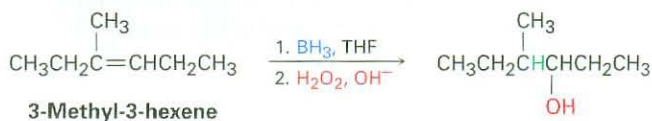**WORKED EXAMPLE 7.2**   *Choosing a Reactant to Synthesize a Specific Compound*

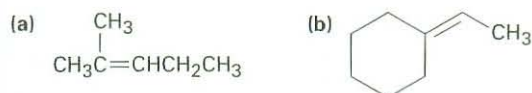How might you prepare the following alcohol?

Strategy   Problems that require the synthesis of a specific target molecule should always be worked backward. Look at the target, identify its functional group(s), and ask yourself "What are the methods for preparing this functional group?" In the present instance, the target molecule is a secondary alcohol (R_2CHOH), and we've seen that alcohols can be prepared from alkenes by either hydroboration/oxidation or oxymercuration. The $-OH$ bearing carbon in the product must have been a double-bond carbon in the alkene reactant, so there are two possibilities: 4-methyl-2-hexene and 3-methyl-3-hexene.

Add —OH here   Add —OH here

CH_3 CH_3
| |
$CH_3CH_2CHCH{=}CHCH_3$ $CH_3CH_2C{=}CHCH_2CH_3$

4-Methyl-2-hexene   **3-Methyl-3-hexene**

4-Methyl-2-hexene has a disubstituted double bond, $RCH{=}CHR'$, and would probably give a mixture of two alcohols with either hydration method since Markovnikov's rule does not apply to symmetrically substituted alkenes. 3-Methyl-3-hexene, however, has a trisubstituted double bond, and would give only the desired product on non-Markovnikov hydration using the hydroboration/oxidation method.

Solution

CH_3 CH_3
| |
$CH_3CH_2C{=}CHCH_2CH_3$ $\xrightarrow[\text{2. } H_2O_2, OH^-]{\text{1. } BH_3, \text{ THF}}$ $CH_3CH_2CHCHCH_2CH_3$
                                                                     |
3-Methyl-3-hexene   OH

Problem 7.9   Show the structures of the products you would obtain by hydroboration/oxidation of the following alkenes:

(a) CH_3
        |
       $CH_3C{=}CHCH_2CH_3$

(b) CH_3

Problem 7.10   What alkenes might be used to prepare the following alcohols by hydroboration/oxidation?

(a) CH_3
        |
       $CH_3CHCH_2CH_2OH$

(b) H_3C OH
 | |
       $CH_3CHCHCH_3$

(c) CH_2OH
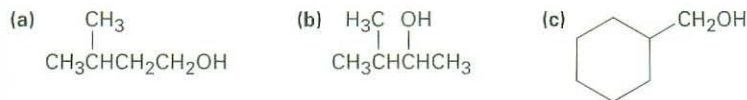
Problem 7.11   The following cycloalkene gives a mixture of two alcohols on hydroboration followed by oxidation. Draw the structures of both, and explain the result.
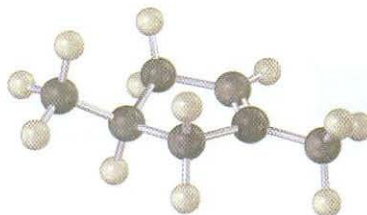
7.6 | Addition of Carbenes to Alkenes: Cyclopropane Synthesis

Yet another kind of alkene addition is the reaction of a *carbene* with an alkene to yield a cyclopropane. A **carbene**, R_2C:, is a neutral molecule containing a divalent carbon with only six electrons in its valence shell. It is therefore highly reactive and is generated only as a reaction intermediate, rather than as an isolable molecule. Because they're electron-deficient, carbenes behave as electrophiles and react with nucleophilic C=C bonds. The reaction occurs in a single step without intermediates.


An alkene   A carbene   A cyclopropane
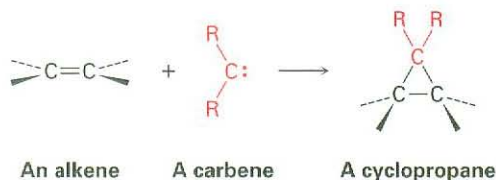
One of the simplest methods for generating a substituted carbene is by treatment of chloroform, $CHCl_3$, with a strong base such as KOH. Loss of a proton from $CHCl_3$ gives the trichloromethanide anion, $^-$:CCl_3, which expels a Cl^- ion to yield dichlorocarbene, :CCl_2 (Figure 7.5).

Figure 7.5 MECHANISM:
Mechanism of the formation of dichlorocarbene by reaction of chloroform with strong base.
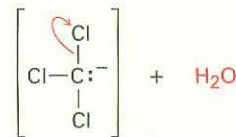
Chloroform

① Base abstracts the hydrogen from chloroform, leaving behind the electron pair from the C–H bond and forming the trichloromethanide anion.
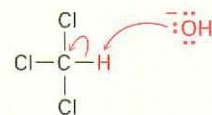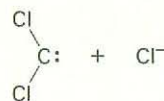
Trichloromethanide anion

**②** Spontaneous loss of chloride ion then yields the neutral dichlorocarbene.

Dichlorocarbene

The dichlorocarbene carbon atom is sp^2-hybridized, with a vacant p orbital extending above and below the plane of the three atoms and with an unshared pair of electrons occupying the third sp^2 lobe. Note that this electronic description of dichlorocarbene is similar to that for a carbocation (Section 6.9) with respect to both the sp^2 hybridization of carbon and the vacant p orbital. Electrostatic potential maps further show this similarity (Figure 7.6).
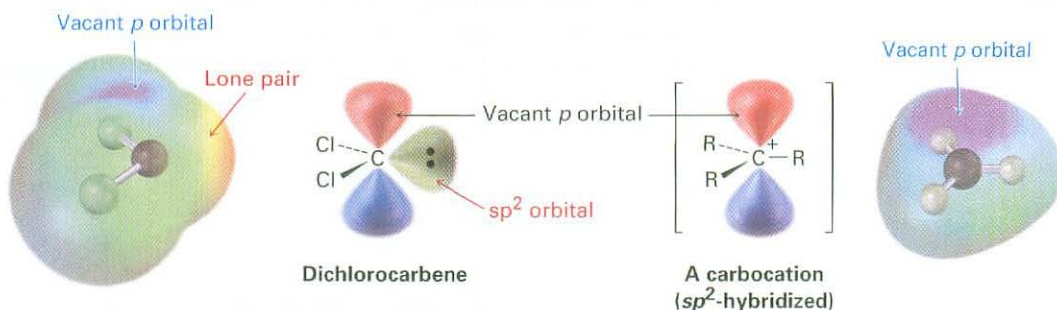
Figure 7.6 The structure of dichlorocarbene. Electrostatic potential maps show how the positive region (blue) coincides with the empty p orbital in both dichlorocarbene and a carbocation (CH_3^+). The negative region (red) in the dichlorocarbene map coincides with the lone-pair electrons.
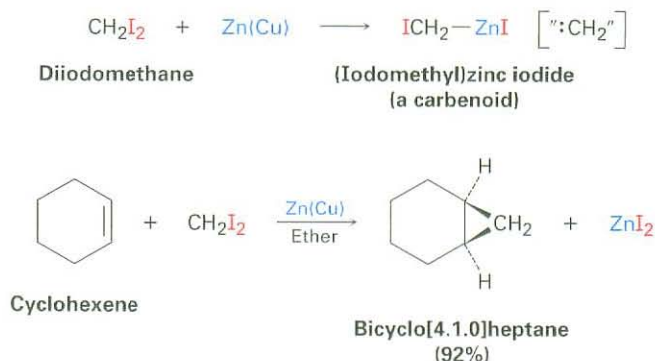
If dichlorocarbene is generated in the presence of an alkene, addition to the double bond occurs and a dichlorocyclopropane is formed. As the reaction of dichlorocarbene with *cis*-2-pentene demonstrates, the addition is **stereospecific**, meaning that only a single stereoisomer is formed as product. Starting from a cis alkene, for instance, only cis-disubstituted cyclopropane is produced; starting from a trans alkene, only trans-disubstituted cyclopropane is produced.
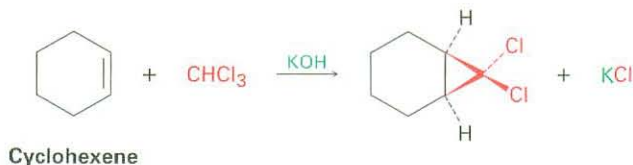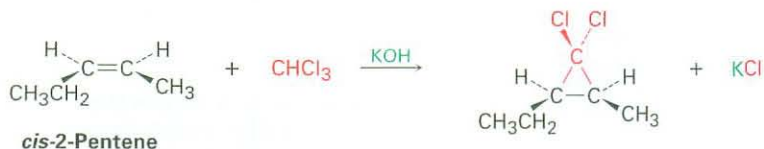
The best method for preparing nonhalogenated cyclopropanes is by a process called the **Simmons–Smith reaction**. First investigated at the DuPont company, this reaction does not involve a free carbene. Rather, it utilizes a *carbenoid*—a metal-complexed reagent with carbene-like reactivity. When diiodomethane is treated with a specially prepared zinc–copper mix, (iodomethyl)zinc iodide, ICH_2ZnI, is formed. In the presence of an alkene, (iodomethyl)zinc iodide transfers a CH_2 group to the double bond and yields the cyclopropane. For example, cyclohexene reacts cleanly and in good yield to give the corresponding cyclopropane. Although we won't discuss the mechanistic details, carbene addition to

an alkene is one of a general class of reactions called *cycloadditions*, which we'll study more carefully in Chapter 30.

$$CH_2I_2 \quad + \quad Zn(Cu) \quad \longrightarrow \quad ICH_2-ZnI \quad \left[\text{":CH}_2\text{"} \right]$$

Diiodomethane   **(Iodomethyl)zinc iodide**
                                          (a carbenoid)

Cyclohexene   **Bicyclo[4.1.0]heptane**
                                          (92%)

Problem 7.12 | What products would you expect from the following reactions?

(a)

$$+ \quad CHCl_3 \quad \xrightarrow{\text{KOH}} \quad ?$$

(b)
$$\begin{array}{c} CH_3 \\ | \\ CH_3CHCH_2CH=CHCH_3 \end{array} \quad + \quad CH_2I_2 \quad \xrightarrow{\text{Zn(Cu)}} \quad ?$$
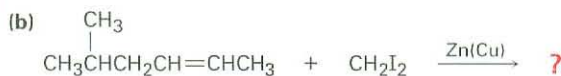
7.7 | Reduction of Alkenes: Hydrogenation

Alkenes react with H_2 in the presence of a metal catalyst to yield the corresponding saturated alkane addition products. We describe the result by saying that the double bond has been **hydrogenated**, or *reduced*. Note that the words *oxidation* and *reduction* are used somewhat differently in organic chemistry from what you might have learned previously. In general chemistry, a reduction is defined as the gain of one or more electrons by an atom. In organic chemistry, however, a **reduction** is a reaction that results in a gain of electron density by carbon, caused either by bond formation between carbon and a less electronegative atom or by bond-breaking between carbon and a more electronegative atom. We'll explore the topic in more detail in Section 10.9.

Reduction   Increases electron density on carbon by:

– forming this: $C-H$

– or breaking one of these: $C-O$ $C-N$ $C-X$

A reduction:
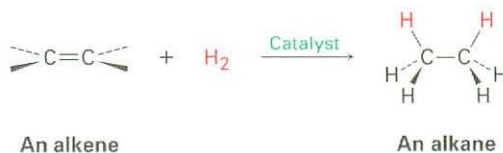
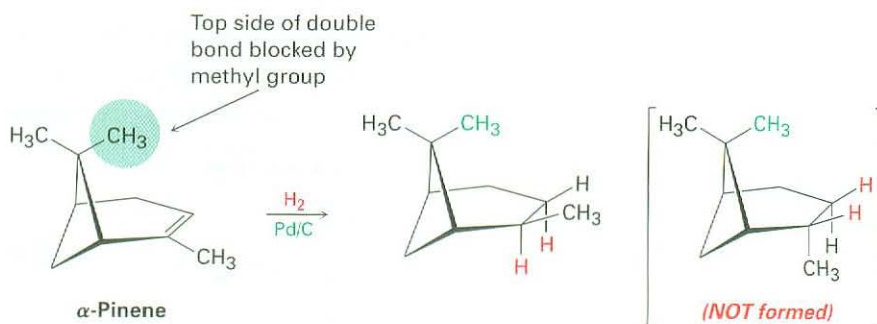**An alkene**   **An alkane**

Platinum and palladium are the most common catalysts for alkene hydrogenations. Palladium is normally used as a very fine powder "supported" on an inert material such as charcoal (Pd/C) to maximize surface area. Platinum is normally used as PtO_2, a reagent called *Adams' catalyst* after its discoverer, Roger Adams.
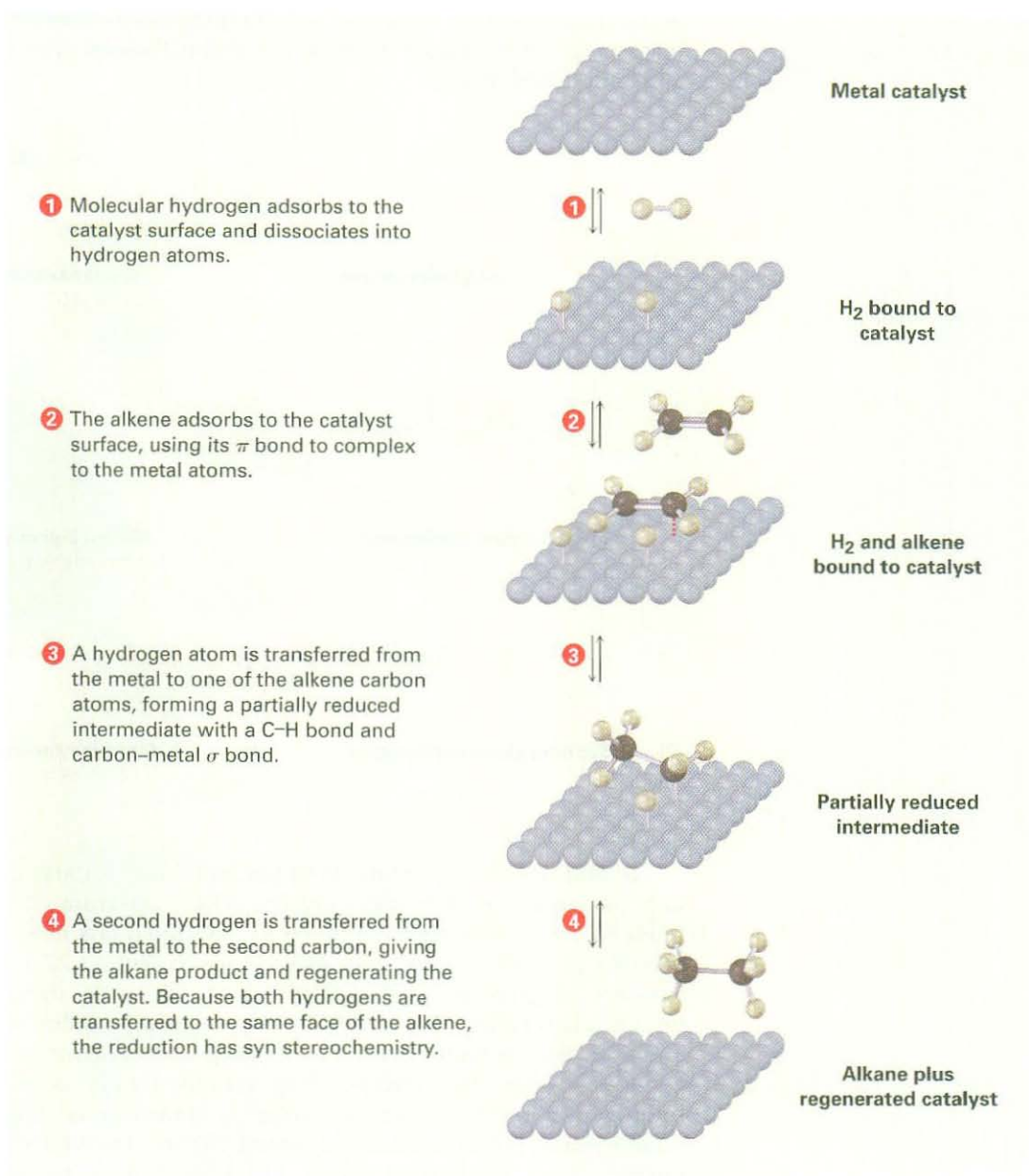
Catalytic hydrogenation, unlike most other organic reactions, is a *heterogeneous* process rather than a homogeneous one. That is, the hydrogenation reaction does not occur in a homogeneous solution but instead takes place on the surface of insoluble catalyst particles. Hydrogenation usually occurs with syn stereochemistry—both hydrogens add to the double bond from the same face.

1,2-Dimethyl-cyclohexene → *cis*-1,2-Dimethyl-cyclohexane (82%)
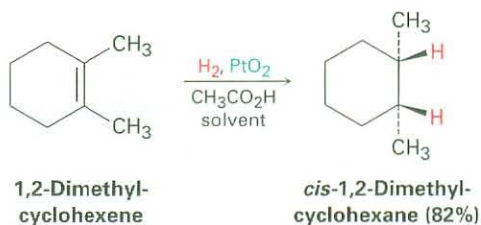
The first step in the reaction is adsorption of H_2 onto the catalyst surface. Complexation between catalyst and alkene then occurs as a vacant orbital on the metal interacts with the filled alkene π orbital. In the final steps, hydrogen is inserted into the double bond and the saturated product diffuses away from the catalyst (Figure 7.7). The stereochemistry of hydrogenation is syn because both hydrogens add to the double bond from the same catalyst surface.

An interesting feature of catalytic hydrogenation is that the reaction is extremely sensitive to the steric environment around the double bond. As a result, the catalyst often approaches only the more accessible face of an alkene, giving rise to a single product. In α-pinene, for example, one of the methyl groups attached to the four-membered ring hangs over the top face of the double bond and blocks approach of the hydrogenation catalyst from that side. Reduction therefore occurs exclusively from the bottom face to yield the product shown.

Top side of double bond blocked by methyl group

α-Pinene   *(NOT formed)*

Metal catalyst

1 Molecular hydrogen adsorbs to the catalyst surface and dissociates into hydrogen atoms.

H₂ bound to catalyst

2 The alkene adsorbs to the catalyst surface, using its π bond to complex to the metal atoms.

H₂ and alkene bound to catalyst

3 A hydrogen atom is transferred from the metal to one of the alkene carbon atoms, forming a partially reduced intermediate with a C–H bond and carbon–metal σ bond.

Partially reduced intermediate

4 A second hydrogen is transferred from the metal to the second carbon, giving the alkane product and regenerating the catalyst. Because both hydrogens are transferred to the same face of the alkene, the reduction has syn stereochemistry.

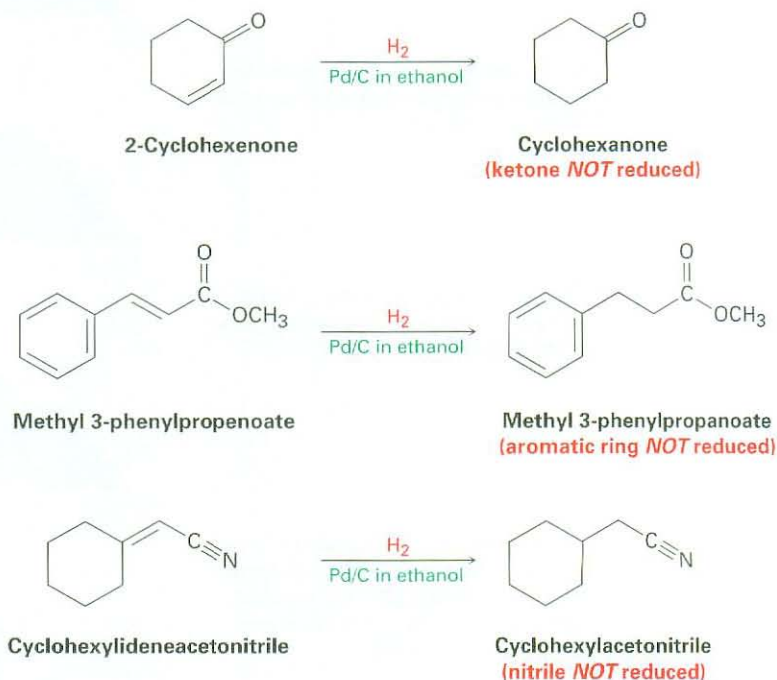**Alkane plus regenerated catalyst**

© John McMurry

Figure 7.7 MECHANISM: Mechanism of alkene hydrogenation. The reaction takes place with syn stereochemistry on the surface of insoluble catalyst particles.

Alkenes are much more reactive than most other unsaturated functional groups toward catalytic hydrogenation, and the reaction is therefore quite selective. Other functional groups such as aldehydes, ketones, esters, and nitriles survive normal alkene hydrogenation conditions unchanged, although reaction with these groups does occur under more vigorous conditions. Note particularly

in the hydrogenation of methyl 3-phenylpropenoate shown below that the aromatic ring is not reduced by hydrogen and palladium even though it contains apparent double bonds.

2-Cyclohexenone

Cyclohexanone
(ketone *NOT* reduced)

Methyl 3-phenylpropenoate

Methyl 3-phenylpropanoate
(aromatic ring *NOT* reduced)

Cyclohexylideneacetonitrile

Cyclohexylacetonitrile
(nitrile *NOT* reduced)

In addition to its usefulness in the laboratory, catalytic hydrogenation is also important in the food industry, where unsaturated vegetable oils are reduced on a vast scale to produce the saturated fats used in margarine and cooking products (Figure 7.8). As we'll see in Section 27.1, vegetable oils are triesters of glycerol, $HOCH_2CH(OH)CH_2OH$, with three long-chain carboxylic acids called *fatty acids*. The fatty acids are generally polyunsaturated, and their double bonds invariably have cis stereochemistry. Complete hydrogenation yields the corresponding saturated fatty acids, but incomplete hydrogenation often results in partial cis–trans isomerization of a remaining double bond. When eaten and digested, the free trans fatty acids are released, raising blood cholesterol levels and contributing to potential coronary problems.

Problem 7.13 | What product would you obtain from catalytic hydrogenation of the following alkenes?

(a) CH_3
         |
     $CH_3C{=}CHCH_2CH_3$

(b)
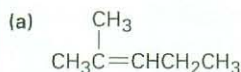
Figure 7.8 Catalytic hydrogenation of polyunsaturated fats leads to saturated products, along with a small amount of isomerized trans fats.

A vegetable oil

A polyunsaturated fatty acid in vegetable oil

2 H$_2$, Pd/C

A saturated fatty acid in margarine

A trans fatty acid
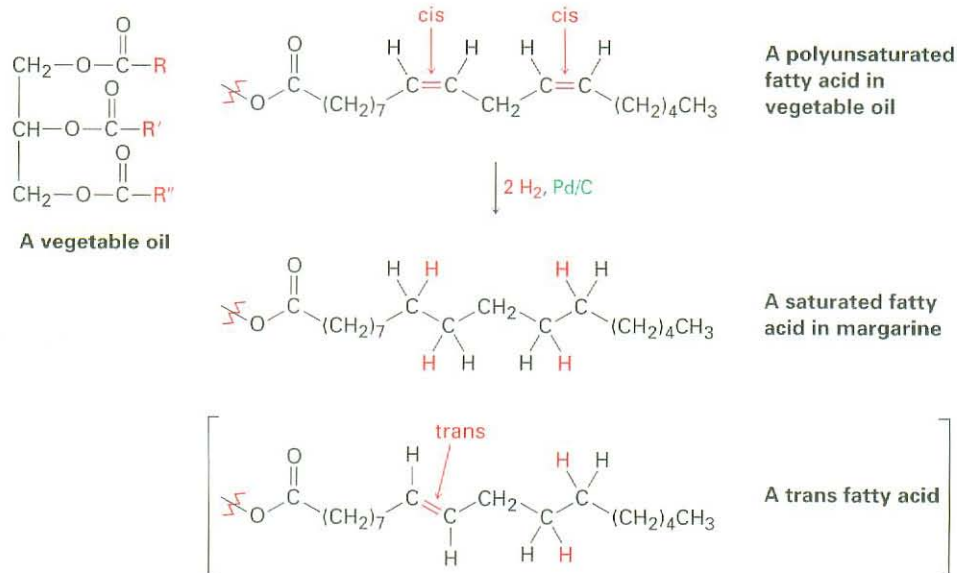
7.8 | Oxidation of Alkenes: Epoxidation and Hydroxylation

Like the word *reduction* used in the previous section for addition of hydrogen to a double bond, the word *oxidation* has a slightly different meaning in organic chemistry from what you might have previously learned. In general chemistry, an oxidation is defined as the loss of one or more electrons by an atom. In organic chemistry, however, an **oxidation** is a reaction that results in a loss of electron density by carbon, caused either by bond formation between carbon and a more electronegative atom—usually oxygen, nitrogen, or a halogen—or by bond-breaking between carbon and a less electronegative atom—usually hydrogen. Note that an *oxidation* often adds oxygen, while a *reduction* often adds hydrogen.

Oxidation   Decreases electron density on carbon by:

– forming one of these: C–O   C–N   C–X

– or breaking this: C–H

Alkenes are oxidized to give *epoxides* on treatment with a peroxyacid (RCO$_3$H), such as *meta*-chloroperoxybenzoic acid. An **epoxide**, also called an *oxirane*, is a cyclic ether with an oxygen atom in a three-membered ring. For example:


Cycloheptene   *meta*-Chloroperoxy-   1,2-Epoxy-   *meta*-Chloro-
                    benzoic acid   cycloheptane   benzoic acid
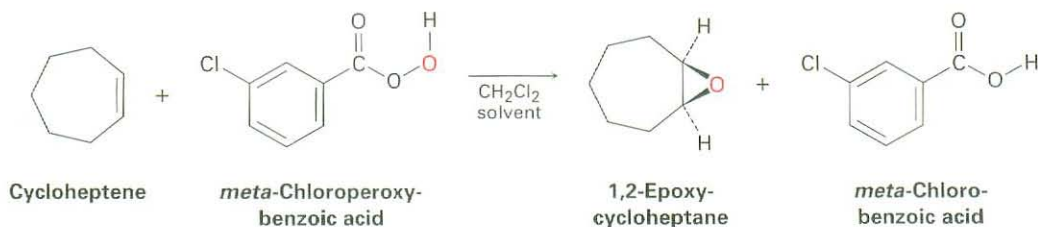
Peroxyacids transfer an oxygen atom to the alkene with syn stereo-chemistry—both C–O bonds form on the same face of the double bond—through a one-step mechanism without intermediates. The oxygen atom farthest from the carbonyl group is the one transferred.

| Alkene | Peroxyacid | Epoxide | Acid |
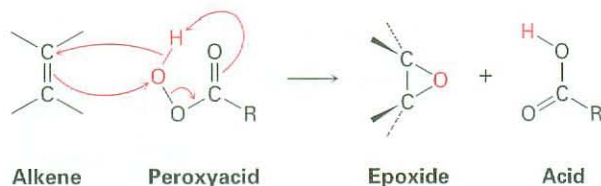
Another method for the synthesis of epoxides is through the use of halohydrins, prepared by electrophilic addition of HO–X to alkenes (Section 7.3). When a halohydrin is treated with base, HX is eliminated and an epoxide is produced.
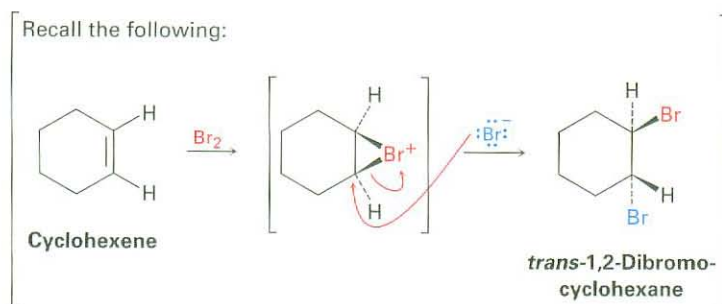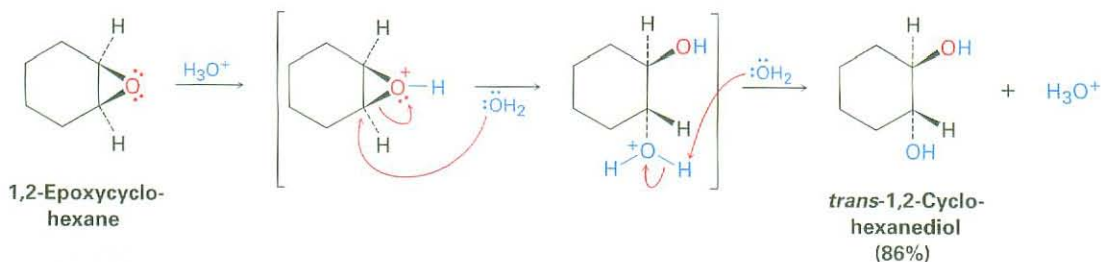

| Cyclohexene | *trans*-2-Chloro-cyclohexanol | 1,2-Epoxycyclohexane (73%) |
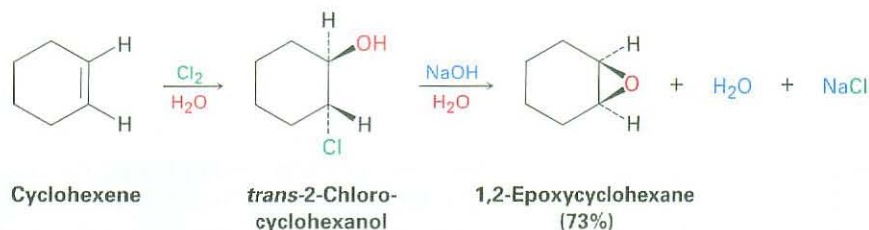
Epoxides undergo an acid-catalyzed ring-opening reaction with water (a *hydrolysis*) to give the corresponding dialcohol *(diol)*, also called a **glycol**. Thus, the net result of the two-step alkene epoxidation/hydrolysis is **hydroxylation**—the addition of an –OH group to each of the two double-bond carbons. In fact, more than 3 million tons of ethylene glycol, $HOCH_2CH_2OH$, most of it used for automobile antifreeze, is produced each year in the United States by epoxidation of ethylene followed by hydrolysis.


| An alkene | An epoxide | A 1,2-diol |
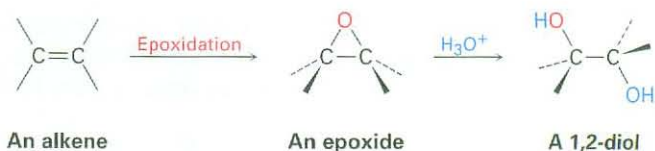
Acid-catalyzed epoxide opening takes place by protonation of the epoxide to increase its reactivity, followed by nucleophilic addition of water. This nucleophilic addition is analogous to the final step of alkene bromination, in which a cyclic bromonium ion is opened by a nucleophile (Section 7.2). That is,

a *trans*-1,2-diol results when an epoxycycloalkane is opened by aqueous acid, just as a *trans*-1,2-dibromide results when a cycloalkene is halogenated. We'll look at epoxide chemistry in more detail in Section 18.6.
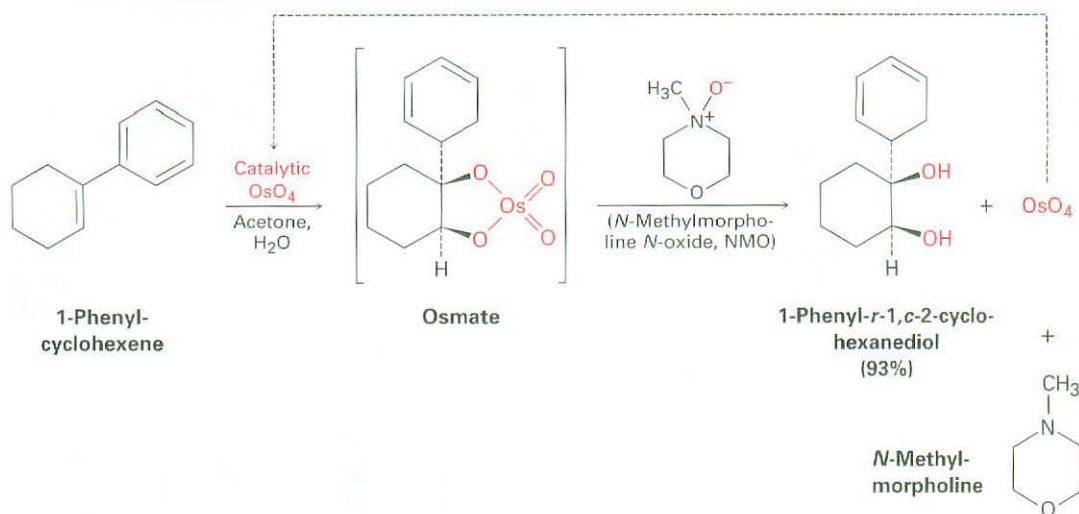

1,2-Epoxycyclo-hexane

trans-**1,2-Cyclo-hexanediol**
(86%)

Recall the following:

Cyclohexene

trans-**1,2-Dibromo-cyclohexane**

Hydroxylation can be carried out directly without going through the intermediate epoxide by treating an alkene with osmium tetroxide, OsO_4. The reaction occurs with syn stereochemistry and does not involve a carbocation intermediate. Instead, it takes place through an intermediate cyclic *osmate*, which is formed in a single step by addition of OsO_4 to the alkene. This cyclic osmate is then cleaved using aqueous sodium bisulfite, $NaHSO_3$.

1,2-Dimethylcyclopentene

A cyclic osmate intermediate

cis-**1,2-Dimethyl-1,2-cyclo-pentanediol (87%)**
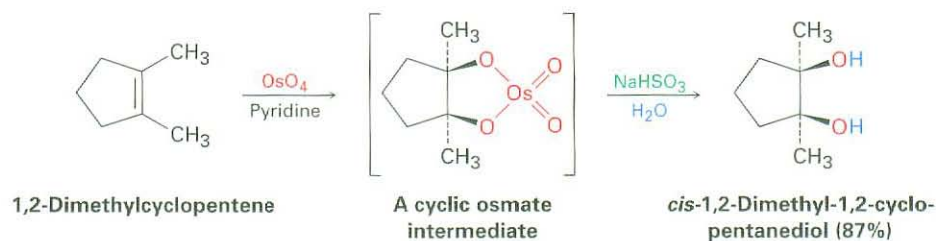
Unfortunately, a serious problem with the osmium tetroxide reaction is that OsO_4 is both very expensive and *very* toxic. As a result, the reaction is usually carried out using only a small, catalytic amount of OsO_4 in the presence of a stoichiometric amount of a safe and inexpensive co-oxidant such as *N*-methylmorpholine *N*-oxide, abbreviated NMO. The initially formed osmate intermediate reacts rapidly with NMO to yield the product diol plus
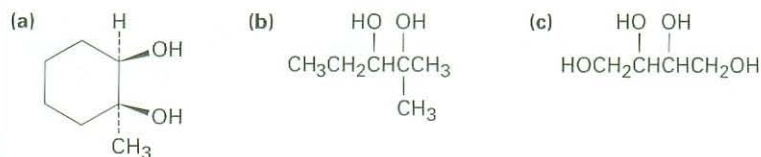
N-methylmorpholine and reoxidized OsO_4. The OsO_4 then reacts with more alkene in a catalytic cycle.

1-Phenyl-cyclohexene

Osmate

1-Phenyl-*r*-1,*c*-2-cyclo-hexanediol (93%)

(*N*-Methylmorpho-line *N*-oxide, NMO)

N-Methyl-morpholine

Note that a *cis-* or *trans-* prefix would be ambiguous when naming the diol derived from 1-phenylcyclohexene because the ring has three substituents. In such a case, the substituent with the lowest number is taken as the reference substituent, denoted *r*, and the other substituents are identified as being cis *(c)* or trans *(t)* to that reference. When two substituents share the same lowest number, the one with the highest priority by the Cahn–Ingold–Prelog sequence rules (Section 6.5) is taken as the reference. In the case of 1-phenyl-1,2-cyclohexane-diol, the −OH group at C1 is the reference (*r*-1), and the −OH at C2 is either cis *(c-2)* or trans *(t-2)* to that reference. Thus, the diol resulting from cis hydroxy-lation is named 1-phenyl-*r*-1,*c*-2-cyclohexanediol, and its isomer resulting from trans hydroxylation would be named 1-phenyl-*r*-1,*t*-2-cyclohexanediol.

Problem 7.14   What product would you expect from reaction of *cis*-2-butene with *meta*-chloro-peroxybenzoic acid? Show the stereochemistry.

**Problem 7.15**   How would you prepare each of the following compounds starting with an alkene?

(a)

(b)   HO OH
        | |
CH₃CH₂CHCCH₃
        |
        CH₃

$CH_3CH_2CHCCH_3$

(c)   HO OH
        | |
HOCH₂CHCHCH₂OH

$HOCH_2CHCHCH_2OH$

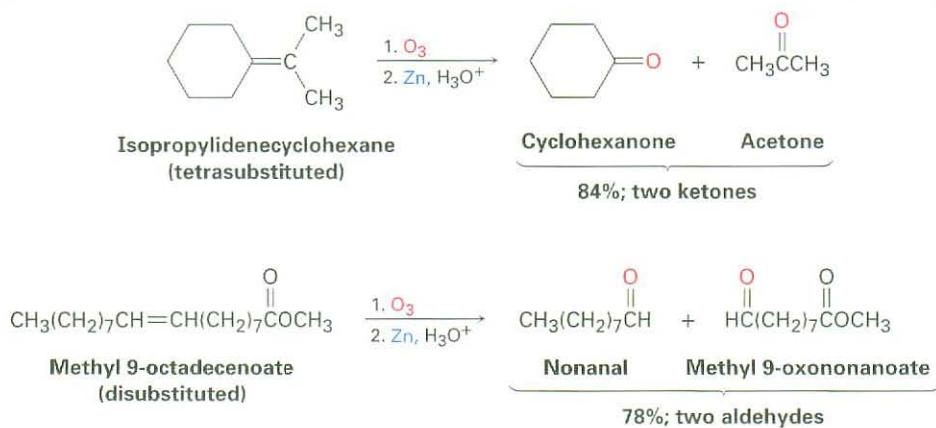## 7.9   Oxidation of Alkenes: Cleavage to Carbonyl Compounds

In all the alkene addition reactions we've seen thus far, the carbon–carbon dou-ble bond has been converted into a single bond but the carbon skeleton has been left intact. There are, however, powerful oxidizing reagents that will cleave C=C bonds and produce two carbonyl-containing fragments.

Ozone (O_3) is perhaps the most useful double-bond cleavage reagent. Prepared by passing a stream of oxygen through a high-voltage electrical discharge, ozone adds rapidly to an alkene at low temperature to give a cyclic intermediate called a *molozonide*. Once formed, the molozonide then spontaneously rearranges to form an **ozonide**. Although we won't study the mechanism of this rearrangement in detail, it involves the molozonide coming apart into two fragments that then recombine in a different way.

$$3\,O_2 \xrightarrow[\text{discharge}]{\text{Electric}} 2\,O_3$$

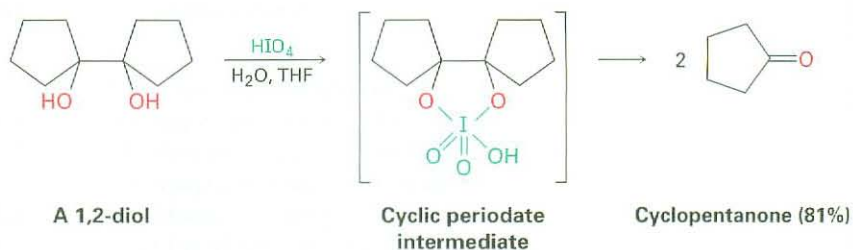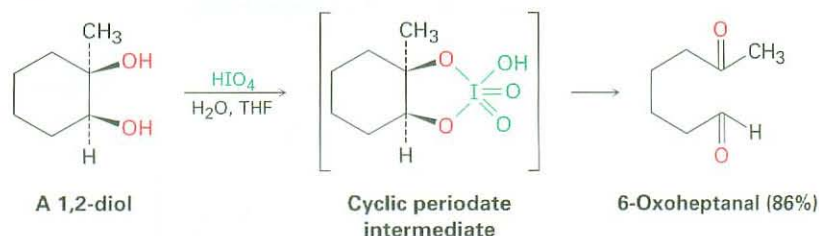An alkene   A molozonide   An ozonide
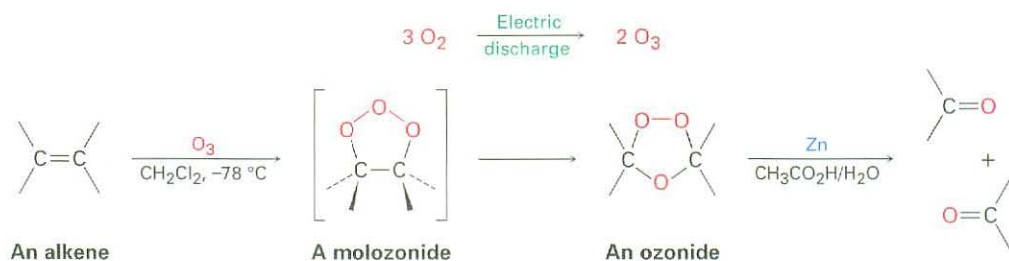
Low-molecular-weight ozonides are explosive and are therefore not isolated. Instead, the ozonide is immediately treated with a reducing agent such as zinc metal in acetic acid to convert it to carbonyl compounds. The net result of the ozonolysis/reduction sequence is that the C=C bond is cleaved and oxygen becomes doubly bonded to each of the original alkene carbons. If an alkene with a tetrasubstituted double bond is ozonized, two ketone fragments result; if an alkene with a trisubstituted double bond is ozonized, one ketone and one aldehyde result; and so on.

Isopropylidenecyclohexane   **Cyclohexanone**   **Acetone**
(tetrasubstituted)   84%; two ketones

Methyl 9-octadecenoate   **Nonanal**   **Methyl 9-oxononanoate**
(disubstituted)   78%; two aldehydes

Several oxidizing reagents other than ozone also cause double-bond cleavage. For example, potassium permanganate ($KMnO_4$) in neutral or acidic solution cleaves alkenes to give carbonyl-containing products. If hydrogens are present on the double bond, carboxylic acids are produced; if two hydrogens are present on one carbon, CO_2 is formed.


3,7-Dimethyl-1-octene   **2,6-Dimethylheptanoic acid (45%)**
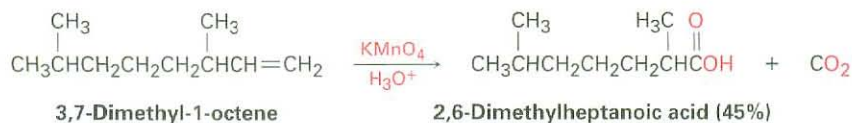
In addition to direct cleavage with ozone or $KMnO_4$, an alkene can also be cleaved by initial hydroxylation to a 1,2-diol followed by treatment with periodic acid, HIO_4. If the two $-OH$ groups are in an open chain, two carbonyl compounds result. If the two $-OH$ groups are on a ring, a single, open-chain dicarbonyl compound is formed. As indicated in the following examples, the cleavage reaction takes place through a cyclic periodate intermediate.

A 1,2-diol   Cyclic periodate   6-Oxoheptanal (86%)
                    intermediate

A 1,2-diol   Cyclic periodate   Cyclopentanone (81%)
                    intermediate

**WORKED EXAMPLE 7.3**   *Predicting the Reactant in an Ozonolysis Reaction*

What alkene would yield a mixture of cyclopentanone and propanal on treatment with ozone followed by reduction with zinc?
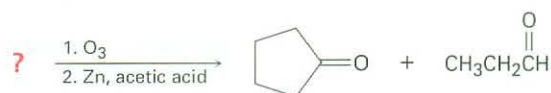
Strategy   Reaction of an alkene with ozone, followed by reduction with zinc, cleaves the carbon–carbon double bond and gives two carbonyl-containing fragments. That is, the C=C bond becomes two C=O bonds. Working backward from the carbonyl-containing products, the alkene precursor can be found by removing the oxygen from each product and joining the two carbon atoms to form a double bond.

Solution
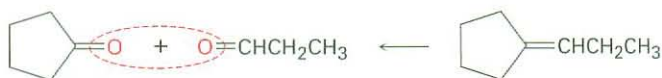
Problem 7.16   What products would you expect from reaction of 1-methylcyclohexene with the following reagents?
(a) Aqueous acidic $KMnO_4$ (b) O_3, followed by Zn, CH_3CO_2H

Problem 7.17   Propose structures for alkenes that yield the following products on reaction with ozone followed by treatment with Zn:
(a) $(CH_3)_2C=O + H_2C=O$ (b) 2 equiv $CH_3CH_2CH=O$

# 7.10 | Radical Additions to Alkenes: Polymers

We had a brief introduction to radical reactions in Section 5.3 and said at that time that radicals can add to alkene double bonds, taking one electron from the double bond and leaving one behind to yield a new radical. Let's now look at the process in more detail, focusing on the industrial synthesis of alkene polymers.

A **polymer** is simply a large—sometimes *very* large—molecule built up by repetitive bonding together of many smaller molecules, called **monomers**. Nature makes wide use of biological polymers. Cellulose, for instance, is a polymer built of repeating glucose monomer units; proteins are polymers built of repeating amino acid monomers; and nucleic acids are polymers built of repeating nucleotide monomers. Synthetic polymers, such as polyethylene, are chemically much simpler than biopolymers, but there is still a great diversity to their structures and properties, depending on the identity of the monomers and on the reaction conditions used for polymerization.
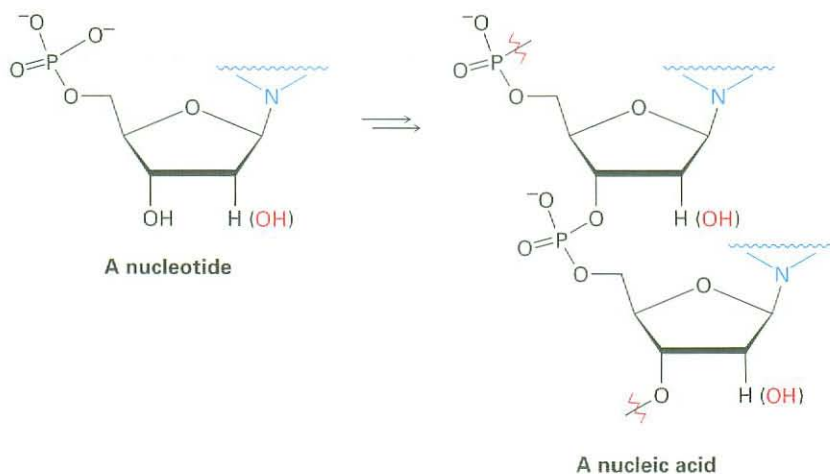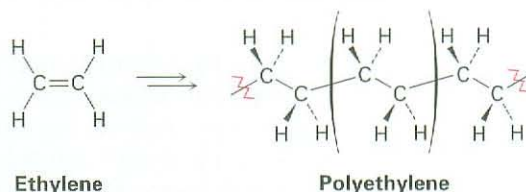
Cellulose—a glucose polymer

Glucose

Cellulose
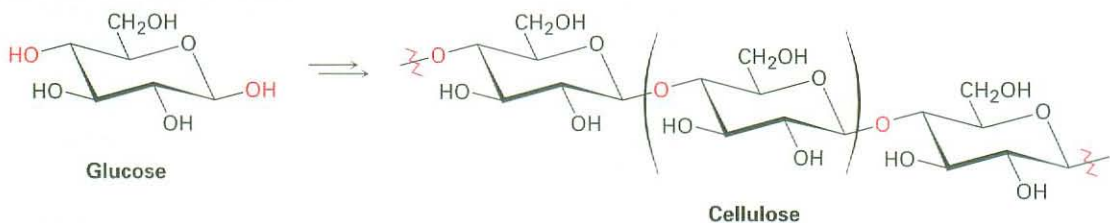
Protein—an amino acid polymer

An amino acid

A protein
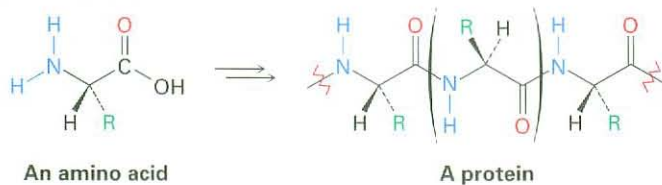
Nucleic acid—a nucleotide polymer

A nucleotide

A nucleic acid

Polyethylene—a synthetic alkene polymer

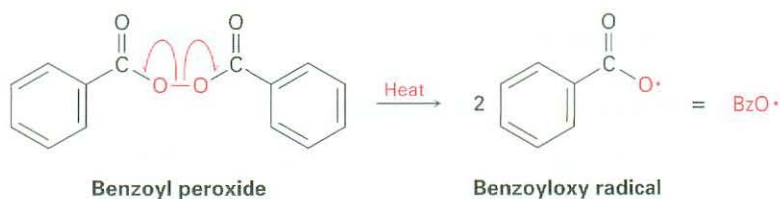Ethylene   Polyethylene

The simplest synthetic polymers are those that result when an alkene is treated with a small amount of a radical as catalyst. Ethylene, for example, yields polyethylene, an enormous alkane that may have up to *200,000* monomer units incorporated into a gigantic hydrocarbon chain. Approximately 14 million tons per year of polyethylene is manufactured in the United States alone.
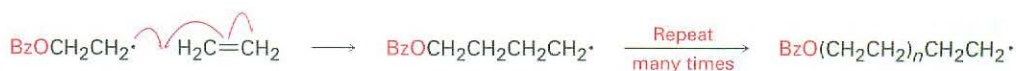
Historically, ethylene polymerization was carried out at high pressure (1000–3000 atm) and high temperature (100–250 °C) in the presence of a catalyst such as benzoyl peroxide, although other catalysts and reaction conditions are now more often used. The key step is the addition of a radical to the ethylene double bond, a reaction similar in many respects to what takes place in the addition of an electrophile. In writing the mechanism, recall that a curved half-arrow, or "fishhook" ⌒, is used to show the movement of a single electron, as opposed to the full curved arrow used to show the movement of an electron pair in a polar reaction.

▌ **Initiation** The polymerization reaction is initiated when a few radicals are generated on heating a small amount of benzoyl peroxide catalyst to break the weak O−O bond. A benzoyloxy radical then adds to the C=C bond of ethylene to generate a carbon radical. One electron from the C=C bond pairs up with the odd electron on the benzoyloxy radical to form a C−O bond, and the other electron remains on carbon.

Benzoyl peroxide   Benzoyloxy radical

▌ **Propagation** Polymerization occurs when the carbon radical formed in the initiation step adds to another ethylene molecule to yield another radical.
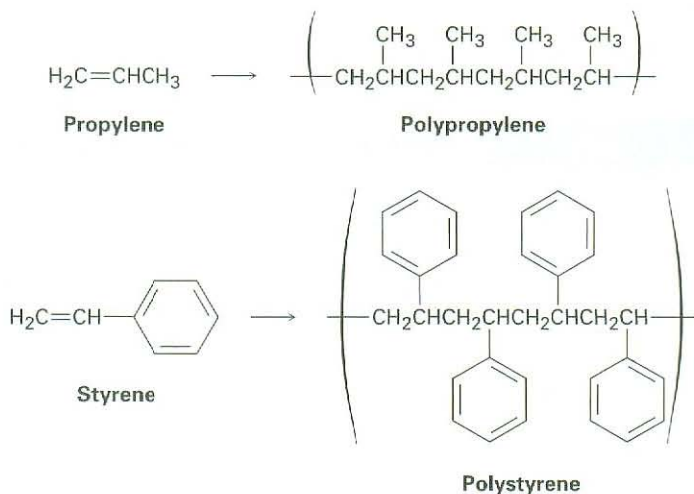
Repetition of the process for hundreds or thousands of times builds the polymer chain.
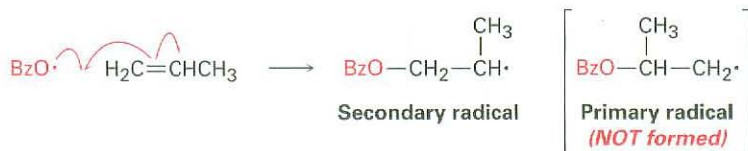
$$BzOCH_2CH_2\cdot \quad H_2C=CH_2 \longrightarrow BzOCH_2CH_2CH_2CH_2\cdot \xrightarrow[\text{many times}]{\text{Repeat}} BzO(CH_2CH_2)_nCH_2CH_2\cdot$$

❚ **Termination** The chain process is eventually ended by a reaction that consumes the radical. Combination of two growing chains is one possible chain-terminating reaction.

$$2\ R-CH_2CH_2\cdot \longrightarrow R-CH_2CH_2CH_2CH_2-R$$

Ethylene is not unique in its ability to form a polymer. Many substituted ethylenes, called *vinyl monomers,* also undergo polymerization to yield polymers with substituent groups regularly spaced on alternating carbon atoms along the chain. Propylene, for example, yields polypropylene, and styrene yields polystyrene.

$$H_2C=CHCH_3 \longrightarrow$$

Propylene

$$\left(\!\!\begin{array}{c} CH_3 \quad CH_3 \quad CH_3 \quad CH_3 \\ | \qquad | \qquad | \qquad | \\ -CH_2CHCH_2CHCH_2CHCH_2CH- \end{array}\!\!\right)$$

Polypropylene

$$H_2C=CH-\bigcirc \longrightarrow$$

Styrene

$$\left(\!-CH_2CHCH_2CHCH_2CHCH_2CH-\!\right)$$

Polystyrene

When an unsymmetrically substituted vinyl monomer such as propylene or styrene is polymerized, the radical addition steps can take place at either end of the double bond to yield either a primary radical intermediate ($RCH_2\cdot$) or a secondary radical ($R_2CH\cdot$). Just as in electrophilic addition reactions, however, we find that only the more highly substituted, secondary radical is formed.

$$BzO\cdot \quad H_2C=CHCH_3 \longrightarrow BzO-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}H\cdot \qquad \left[\ BzO-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2\cdot\ \right]$$

Secondary radical   **Primary radical**
(NOT formed)

Table 7.1 shows some commercially important alkene polymers, their uses, and the vinyl monomers from which they are made.

Table 7.1   Some Alkene Polymers and Their Uses

Monomer	Formula	Trade or common name of polymer	Uses
Ethylene	$H_2C{=}CH_2$	Polyethylene	Packaging, bottles
Propene (propylene)	$H_2C{=}CHCH_3$	Polypropylene	Moldings, rope, carpets
Chloroethylene (vinyl chloride)	$H_2C{=}CHCl$	Poly(vinyl chloride) Tedlar	Insulation, films, pipes
Styrene	$H_2C{=}CHC_6H_5$	Polystyrene	Foam, moldings
Tetrafluoroethylene	$F_2C{=}CF_2$	Teflon	Gaskets, nonstick coatings
Acrylonitrile	$H_2C{=}CHCN$	Orlon, Acrilan	Fibers
Methyl methacrylate	$\underset{H_2C{=}CCO_2CH_3}{\overset{CH_3}{|}}$	Plexiglas, Lucite	Paint, sheets, moldings
Vinyl acetate	$H_2C{=}CHOCOCH_3$	Poly(vinyl acetate)	Paint, adhesives, foams

---

WORKED EXAMPLE 7.4   *Predicting the Structure of a Polymer*

Show the structure of poly(vinyl chloride), a polymer made from $H_2C{=}CHCl$, by drawing several repeating units.

Strategy   Mentally break the carbon–carbon double bond in the monomer unit, and form single bonds by connecting numerous units together.

Solution   The general structure of poly(vinyl chloride) is

$$\left(\!\!-CH_2\overset{\overset{\displaystyle Cl}{|}}{CH}-CH_2\overset{\overset{\displaystyle Cl}{|}}{CH}-CH_2\overset{\overset{\displaystyle Cl}{|}}{CH}-\!\!\right)$$

Problem 7.18   Show the monomer units you would use to prepare the following polymers:

(a)

$$\left(\!\!-CH_2-\overset{\overset{\displaystyle OCH_3}{|}}{CH}-CH_2-\overset{\overset{\displaystyle OCH_3}{|}}{CH}-CH_2-\overset{\overset{\displaystyle OCH_3}{|}}{CH}-\!\!\right)$$

(b)

$$\left(\!\!-\overset{\overset{\displaystyle Cl}{|}}{CH}-\overset{\overset{\displaystyle Cl}{|}}{CH}-\overset{\overset{\displaystyle Cl}{|}}{CH}-\overset{\overset{\displaystyle Cl}{|}}{CH}-\overset{\overset{\displaystyle Cl}{|}}{CH}-\overset{\overset{\displaystyle Cl}{|}}{CH}-\!\!\right)$$

Problem 7.19 One of the chain-termination steps that sometimes occurs to interrupt polymerization is the following reaction between two radicals. Propose a mechanism for the reaction, using fishhook arrows to indicate electron flow.

$$2 \quad \text{—CH}_2\dot{\text{C}}\text{H}_2 \quad \longrightarrow \quad \text{—CH}_2\text{CH}_3 \quad + \quad \text{—CH}=\text{CH}_2$$

7.11 | Biological Additions of Radicals to Alkenes

The same high reactivity of radicals that makes possible the alkene polymerization we saw in the previous section also makes it difficult to carry out controlled radical reactions on complex molecules. As a result, there are severe limitations on the usefulness of radical addition reactions in the laboratory. In contrast to an *electrophilic* addition, where reaction occurs once and the reactive cation intermediate is rapidly quenched in the presence of a nucleophile, the reactive intermediate in a *radical* reaction is not usually quenched, so it reacts again and again in a largely uncontrollable way.

Electrophilic addition
(Intermediate is quenched,
so reaction stops.)
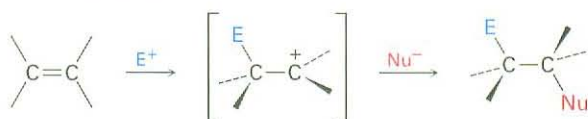
Radical addition
(Intermediate is not quenched,
so reaction does not stop.)
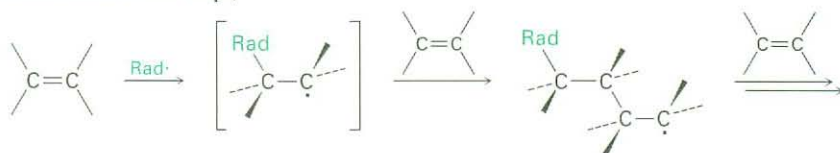
In biological reactions, the situation is different from that in the laboratory. Only one substrate molecule at a time is present in the active site of the enzyme where reaction takes place, and that molecule is held in a precise position, with coenzymes and other necessary reacting groups nearby. As a result, biological radical reactions are both more controlled and more common than laboratory or industrial radical reactions. A particularly impressive example occurs in the biosynthesis of prostaglandins from arachidonic acid, where a sequence of four radical additions take place. The reaction mechanism was discussed briefly in Section 5.3.

Prostaglandin biosynthesis begins with abstraction of a hydrogen atom from C13 of arachidonic acid by an iron–oxy radical (Figure 7.9, step 1) to give a carbon radical that reacts with O_2 at C11 through a resonance form (step 2). The oxygen radical that results adds to the C8–C9 double bond (step 3) to give

a carbon radical at C8, which then adds to the C12–C13 double bond and gives a carbon radical at C13 (step 4). A resonance form of this carbon radical adds at C15 to a second O_2 molecule (step 5), completing the prostaglandin skeleton, and reduction of the O–O bond then gives prostaglandin H_2 (step 6). The pathway looks complicated, but the entire process is catalyzed with exquisite control by just one enzyme.
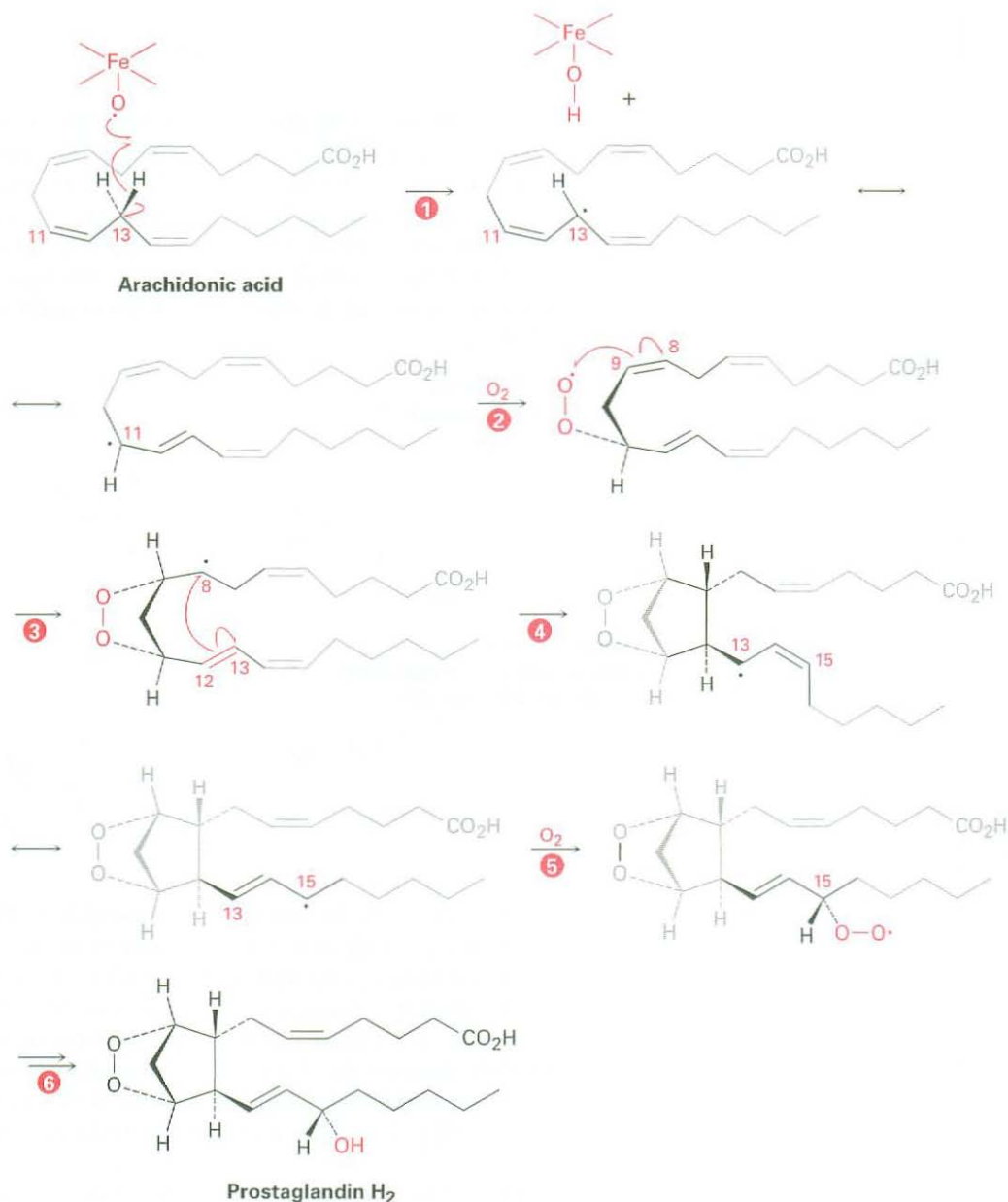
Figure 7.9 Pathway for the biosynthesis of prostaglandins from arachidonic acid. Steps 2 and 5 are radical addition reactions to O_2; steps 3 and 4 are radical additions to carbon–carbon double bonds.

Focus On . . .

Natural Rubber
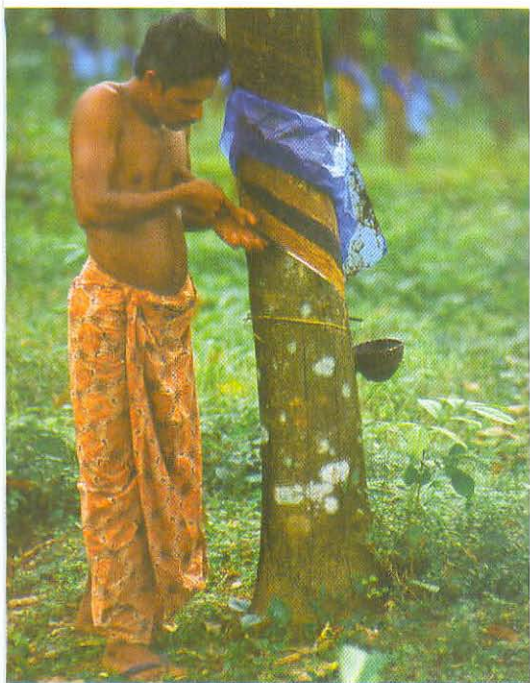
Natural rubber is obtained from the bark of the rubber tree, *Hevea brasiliensis,* grown on enormous plantations in Southeast Asia.

Rubber—an unusual name for an unusual substance—is a naturally occurring alkene polymer produced by more than 400 different plants. The major source is the so-called rubber tree, *Hevea brasiliensis,* from which the crude material is harvested as it drips from a slice made through the bark. The name *rubber* was coined by Joseph Priestley, the discoverer of oxygen and early researcher of rubber chemistry, for the simple reason that one of rubber's early uses was to rub out pencil marks on paper.

Unlike polyethylene and other simple alkene polymers, natural rubber is a polymer of a *diene,* isoprene (2-methyl-1,3-butadiene). The polymerization takes place by addition of isoprene monomer units to the growing chain, leading to formation of a polymer that still contains double bonds spaced regularly at four-carbon intervals. As the following structure shows, these double bonds have *Z* stereochemistry:

Many isoprene units

Z geometry

A segment of natural rubber
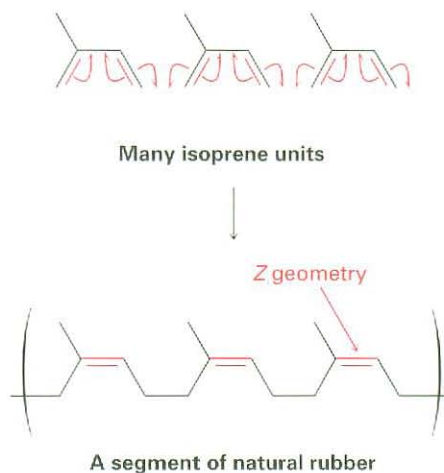
Crude rubber, called *latex,* is collected from the tree as an aqueous dispersion that is washed, dried, and coagulated by warming in air. The resultant polymer has chains that average about 5000 monomer units in length and have molecular weights of 200,000 to 500,000 amu. This crude coagulate is too soft and tacky to be useful until it is hardened by heating with elemental sulfur, a process called *vulcanization.* By mechanisms that are still not fully understood, vulcanization cross-links the rubber chains together by forming

carbon–sulfur bonds between them, thereby hardening and stiffening the polymer. The exact degree of hardening can be varied, yielding material soft enough for automobile tires or hard enough for bowling balls (*ebonite*).

The remarkable ability of rubber to stretch and then contract to its original shape is due to the irregular shapes of the polymer chains caused by the double bonds. These double bonds introduce bends and kinks into the polymer chains, thereby preventing neighboring chains from nestling together. When stretched, the randomly coiled chains straighten out and orient along the direction of the pull but are kept from sliding over one another by the cross-links. When the stretch is released, the polymer reverts to its original random state.

SUMMARY AND KEY WORDS

anti stereochemistry, 216

bromonium ion, 217

carbene, 227

epoxide, 233

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halohydrin, 218

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Simmons–Smith reaction, 228

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syn stereochemistry, 224

Alkenes are generally prepared by an *elimination reaction*, such as *dehydrohalogenation*, the elimination of HX from an alkyl halide, or *dehydration*, the elimination of water from an alcohol.

HCl, HBr, and HI add to alkenes by a two-step electrophilic addition mechanism. Initial reaction of the nucleophilic double bond with H^+ gives a carbocation intermediate, which then reacts with halide ion. Bromine and chlorine add to alkenes via three-membered-ring **bromonium ion** or chloronium ion intermediates to give addition products having **anti stereochemistry**. If water is present during the halogen addition reaction, a **halohydrin** is formed.

Hydration of an alkene—the addition of water—is carried out by either of two procedures, depending on the product desired. **Oxymercuration** involves electrophilic addition of Hg^{2+} to an alkene, followed by trapping of the cation intermediate with water and subsequent treatment with $NaBH_4$. **Hydroboration** involves addition of borane (BH_3) followed by oxidation of the intermediate organoborane with alkaline H_2O_2. The two hydration methods are complementary: oxymercuration gives the product of Markovnikov addition, whereas hydroboration/oxidation gives the product with non-Markovnikov **syn stereochemistry**.

A **carbene**, R_2C:, is a neutral molecule containing a divalent carbon with only six valence electrons. Carbenes are highly reactive toward alkenes, adding to give cyclopropanes. Nonhalogenated cyclopropanes are best prepared by treatment of the alkene with CH_2I_2 and zinc–copper, a process called the **Simmons–Smith reaction**.

Alkenes are **reduced** by addition of H_2 in the presence of a catalyst such as platinum or palladium to yield alkanes, a process called **catalytic hydrogenation**. Alkenes are also **oxidized** by reaction with a peroxyacid to give **epoxides**, which can be converted into trans-1,2-diols by acid-catalyzed epoxide hydrolysis. The corresponding cis-1,2-diols can be made directly from alkenes by **hydroxylation** with OsO_4. Alkenes can also be cleaved to produce carbonyl compounds by reaction with ozone, followed by reduction with zinc metal.

Alkene **polymers**—large molecules resulting from repetitive bonding together of many hundreds or thousands of small **monomer** units—are formed by reaction of simple alkenes with a radical initiator at high temperature and

pressure. Polyethylene, polypropylene, and polystyrene are common examples. As a general rule, radical addition reactions are not common in the laboratory but occur much more frequently in biological pathways.

What's seven times nine? Sixty-three, of course. You didn't have to stop and figure it out; you knew the answer immediately because you long ago learned the multiplication tables. Learning the reactions of organic chemistry requires the same approach: reactions have to be learned for immediate recall if they are to be useful.

Different people take different approaches to learning reactions. Some people make flash cards; others find studying with friends to be helpful. To help guide your study, most chapters in this book end with a summary of the reactions just presented. In addition, the accompanying *Study Guide and Solutions Manual* has several appendixes that organize organic reactions from other viewpoints. Fundamentally, though, there are no shortcuts. Learning organic chemistry does take effort.

SUMMARY OF REACTIONS

Note: No stereochemistry is implied unless specifically indicated with wedged, solid, and dashed lines.

1. Addition reactions of alkenes
   (a) Addition of HCl, HBr, and HI (Sections 6.7 and 6.8)

   Markovnikov regiochemistry occurs, with H adding to the less highly substituted alkene carbon and halogen adding to the more highly substituted carbon.
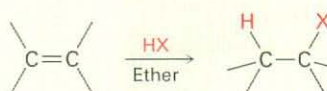
   (b) Addition of halogens Cl_2 and Br_2 (Section 7.2)

   Anti addition is observed through a halonium ion intermediate.
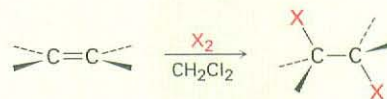
   (c) Halohydrin formation (Section 7.3)

   Markovnikov regiochemistry and anti stereochemistry occur.
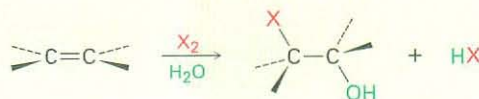
(d) Addition of water by oxymercuration (Section 7.4)
Markovnikov regiochemistry occurs.

$$\ce{C=C} \quad \xrightarrow[\text{2. NaBH}_4]{\text{1. Hg(OAc)}_2,\ \text{H}_2\text{O/THF}} \quad \overset{\text{HO}\qquad\text{H}}{\ce{C-C}}$$
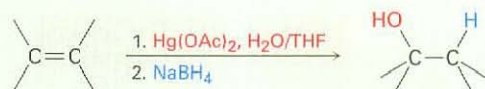
(e) Addition of water by hydroboration/oxidation (Section 7.5)
Non-Markovnikov syn addition occurs.

$$\ce{C=C} \quad \xrightarrow[\text{2. H}_2\text{O}_2,\ \text{OH}^-]{\text{1. BH}_3,\ \text{THF}} \quad \overset{\text{H}\qquad\text{OH}}{\ce{C-C}}$$
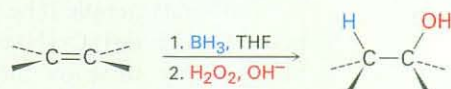
(f) Addition of carbenes to yield cyclopropanes (Section 7.6)
(1) Dichlorocarbene addition

$$\ce{C=C} \ +\ \text{CHCl}_3 \quad \xrightarrow{\text{KOH}} \quad \overset{\text{Cl}\quad\text{Cl}}{\underset{\ce{C-C}}{\ce{C}}}$$

(2) Simmons–Smith reaction

$$\ce{C=C} \ +\ \text{CH}_2\text{I}_2 \quad \xrightarrow[\text{Ether}]{\text{Zn(Cu)}} \quad \overset{\text{H}\quad\text{H}}{\underset{\ce{C-C}}{\ce{C}}}$$
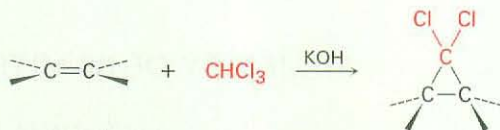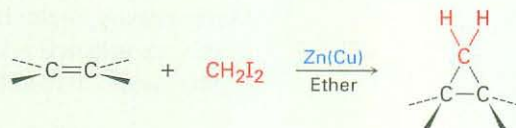
(g) Catalytic hydrogenation (Section 7.7)
Syn addition occurs.

$$\ce{C=C} \quad \xrightarrow[\text{Pd/C or PtO}_2]{\text{H}_2} \quad \overset{\text{H}\qquad\text{H}}{\ce{C-C}}$$
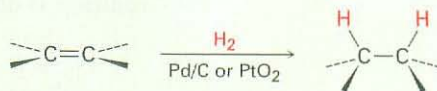
(h) Epoxidation with a peroxyacid (Section 7.8)
Syn addition occurs.

$$\ce{C=C} \quad \xrightarrow{\overset{\text{O}}{\overset{\|}{\text{RCOOH}}}} \quad \overset{\text{O}}{\ce{C-C}}$$
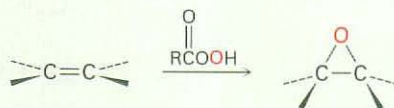
(i) Hydroxylation by acid-catalyzed epoxide hydrolysis (Section 7.8)
Anti stereochemistry occurs.
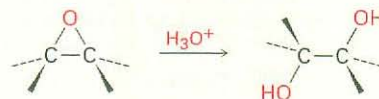
(j) Hydroxylation with OsO_4 (Section 7.8)
Syn addition occurs.
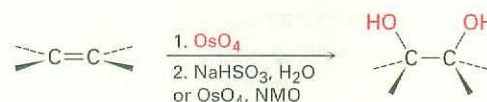
(k) Radical polymerization (Section 7.10)
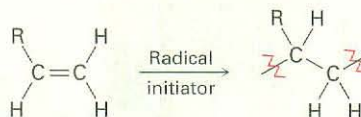
2. Oxidative cleavage of alkenes (Section 7.9)
(a) Reaction with ozone followed by zinc in acetic acid
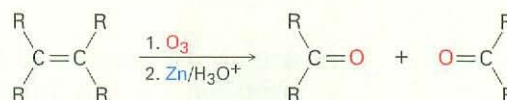
(b) Reaction with $KMnO_4$ in acidic solution
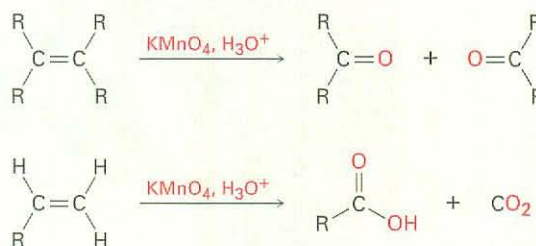
3. Cleavage of 1,2-diols (Section 7.9)
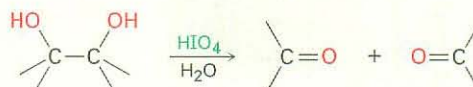
EXERCISES

VISUALIZING CHEMISTRY

(Problems 7.1–7.19 appear within the chapter.)

7.20 ■ Name the following alkenes, and predict the products of their reaction with (i) *meta*-chloroperoxybenzoic acid, (ii) KMnO₄ in aqueous acid, and (iii) O₃, followed by Zn in acetic acid:
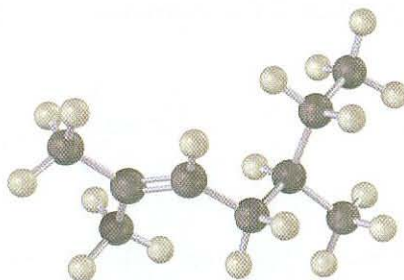
(a)   (b)
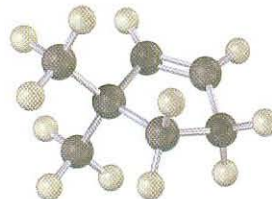
7.21 ■ Draw the structures of alkenes that would yield the following alcohols on hydration (red = O). Tell in each case whether you would use hydroboration/oxidation or oxymercuration.
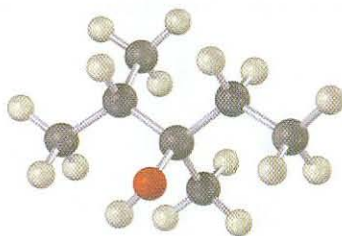
(a)   (b)
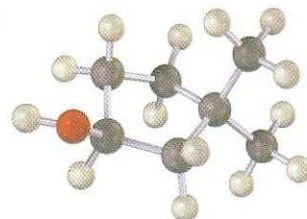
7.22 The following alkene undergoes hydroboration/oxidation to yield a single product rather than a mixture. Explain the result, and draw the product showing its stereochemistry.
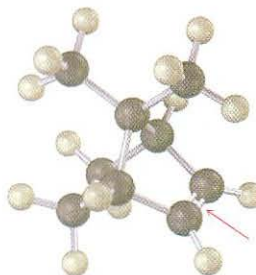
7.23 ■ From what alkene was the following 1,2-diol made, and what method was used, epoxide hydrolysis or OsO_4?
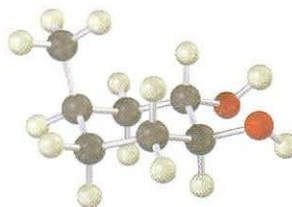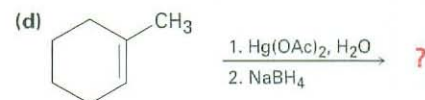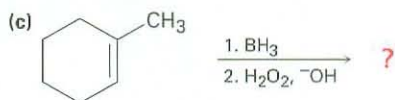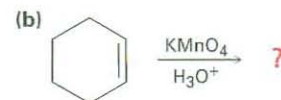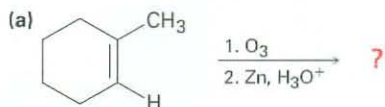

ADDITIONAL PROBLEMS

7.24 ■ Predict the products of the following reactions (the aromatic ring is unreactive in all cases). Indicate regiochemistry when relevant.

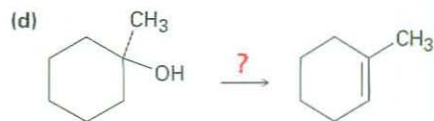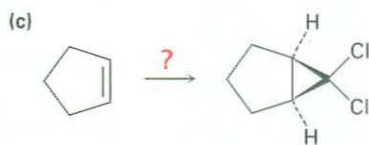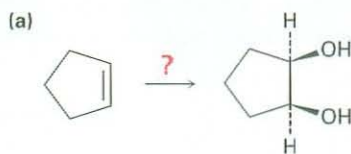|		
(a)	H_2/Pd	?
(b)	Br_2	?
(c)	OsO_4 / NMO	?
(d)	Cl_2, H_2O	?
(e)	CH_2I_2, Zn/Cu	?
(f)	*meta*-Chloroperoxybenzoic acid	?
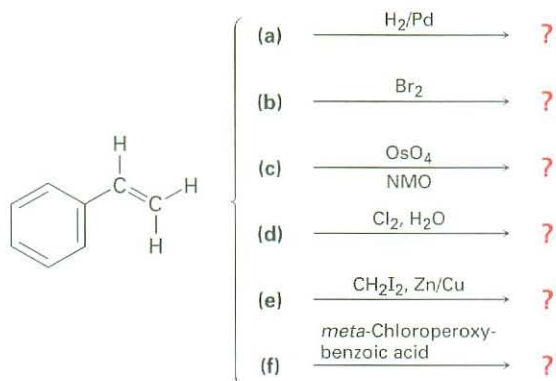
7.25 ■ Suggest structures for alkenes that give the following reaction products. There may be more than one answer for some cases.

(a)

? $\xrightarrow{\text{H}_2/\text{Pd}}$ CH$_3$CHCH$_2$CH$_2$CH$_2$CH$_3$ (with CH$_3$ branch)

(b)

? $\xrightarrow{\text{H}_2/\text{Pd}}$ (cyclohexane with CH$_3$, CH$_3$ groups)

(c)

? $\xrightarrow{\text{Br}_2}$ CH$_3$CHCHCH$_2$CHCH$_3$ (with Br, CH$_3$, Br substituents)

(d)

? $\xrightarrow{\text{HCl}}$ CH$_3$CHCHCH$_2$CH$_2$CH$_2$CH$_3$ (with Cl, CH$_3$ substituents)

(e)

? $\xrightarrow[\text{2. NaBH}_4]{\text{1. Hg(OAc)}_2, \text{H}_2\text{O}}$ CH$_3$CH$_2$CH$_2$CHCH$_3$ (with OH)

(f)

? $\xrightarrow{\text{CH}_2\text{I}_2, \text{Zn/Cu}}$ (spiro compound)
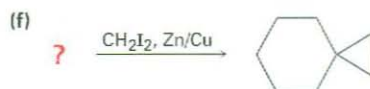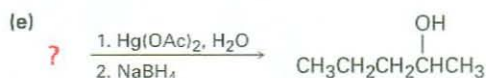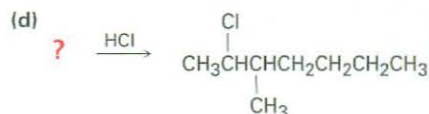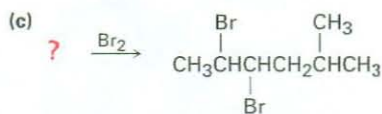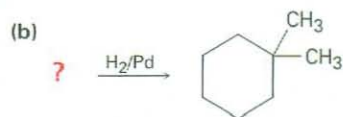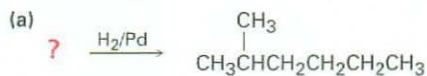
7.26 ■ Predict the products of the following reactions, showing both regiochemistry and stereochemistry where appropriate:

(a)

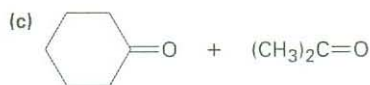(cyclohexene with CH$_3$, H) $\xrightarrow[\text{2. Zn, H}_3\text{O}^+]{\text{1. O}_3}$?

(b)

(cyclohexene) $\xrightarrow[\text{H}_3\text{O}^+]{\text{KMnO}_4}$?

(c)

(methylcyclohexene) $\xrightarrow[\text{2. H}_2\text{O}_2, \text{ }^-\text{OH}]{\text{1. BH}_3}$?

(d)

(methylcyclohexene) $\xrightarrow[\text{2. NaBH}_4]{\text{1. Hg(OAc)}_2, \text{H}_2\text{O}}$?

7.27 ■ How would you carry out the following transformations? Tell the reagents you would use in each case.

(a)

(cyclopentene) $\xrightarrow{?}$ (cyclopentane diol, cis H, OH, OH, H)

(b)

(cyclopentene) $\xrightarrow{?}$ (cyclopentanol, OH)

(c)

(cyclopentene) $\xrightarrow{?}$ (bicyclic with H, Cl, Cl, H)

(d)

(cyclohexane with CH$_3$, OH) $\xrightarrow{?}$ (methylcyclohexene, CH$_3$)

(e)

CH$_3$CH=CHCHCH$_3$ (with CH$_3$) $\xrightarrow{?}$ CH$_3$CH (with O) + CH$_3$CHCH (with H$_3$C, O)

(f)

CH$_3$C=CH$_2$ (with CH$_3$) $\xrightarrow{?}$ CH$_3$CHCH$_2$OH (with CH$_3$)
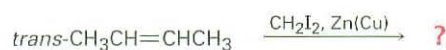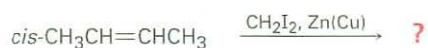

■ Assignable in OWL

7.28 Which reaction would you expect to be faster, addition of HBr to cyclohexene or to 1-methylcyclohexene? Explain.

7.29 What product will result from hydroboration/oxidation of 1-methylcyclopentene with deuterated borane, BD_3? Show both the stereochemistry (spatial arrangement) and the regiochemistry (orientation) of the product.

7.30 ■ Draw the structure of an alkene that yields only acetone, $(CH_3)_2C{=}O$, on ozonolysis followed by treatment with Zn.

7.31 ■ Show the structures of alkenes that give the following products on oxidative cleavage with $KMnO_4$ in acidic solution:

(a) $CH_3CH_2CO_2H$ + CO_2 (b) $(CH_3)_2C{=}O$ + $CH_3CH_2CH_2CO_2H$

(c) $={=}O$ + $(CH_3)_2C{=}O$

(d)
$$\overset{\displaystyle O}{\overset{\displaystyle \|}{CH_3CH_2CCH_2CH_2CH_2CH_2CO_2H}}$$

7.32 ■ Compound A has the formula $C_{10}H_{16}$. On catalytic hydrogenation over palladium, it reacts with only 1 molar equivalent of H_2. Compound A also undergoes reaction with ozone, followed by zinc treatment, to yield a symmetrical diketone, B ($C_{10}H_{16}O_2$).
(a) How many rings does A have?
(b) What are the structures of A and B?
(c) Write the reactions.

7.33 An unknown hydrocarbon A with the formula C_6H_{12} reacts with 1 molar equivalent of H_2 over a palladium catalyst. Hydrocarbon A also reacts with OsO_4 to give diol B. When oxidized with $KMnO_4$ in acidic solution, A gives two fragments. One fragment is propanoic acid, $CH_3CH_2CO_2H$, and the other fragment is ketone C. What are the structures of A, B, and C? Write all reactions, and show your reasoning.

7.34 Using an oxidative cleavage reaction, explain how you would distinguish between the following two isomeric dienes:

and

7.35 Compound A, $C_{10}H_{18}O$, undergoes reaction with dilute H_2SO_4 at 50 °C to yield a mixture of two alkenes, $C_{10}H_{16}$. The major alkene product, B, gives only cyclopentanone after ozone treatment followed by reduction with zinc in acetic acid. Identify A and B, and write the reactions.

7.36 The cis and trans isomers of 2-butene give different cyclopropane products in the Simmons–Smith reaction. Show the structure of each, and explain the difference.

$cis\text{-}CH_3CH{=}CHCH_3$ $\xrightarrow{\text{CH}_2\text{I}_2,\ \text{Zn(Cu)}}$ **?**

$trans\text{-}CH_3CH{=}CHCH_3$ $\xrightarrow{\text{CH}_2\text{I}_2,\ \text{Zn(Cu)}}$ **?**

■ Assignable in OWL

7.37 Iodine azide, IN_3, adds to alkenes by an electrophilic mechanism similar to that of bromine. If a monosubstituted alkene such as 1-butene is used, only one product results:

$$CH_3CH_2CH=CH_2 \quad + \quad I-N=N=N \quad \longrightarrow \quad CH_3CH_2\overset{\overset{\displaystyle N=N=N}{|}}{C}HCH_2I$$
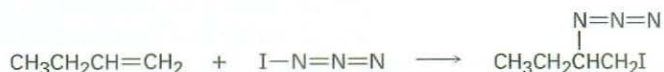
(a) Add lone-pair electrons to the structure shown for IN_3, and draw a second resonance form for the molecule.

(b) Calculate formal charges for the atoms in both resonance structures you drew for IN_3 in part (a).

(c) In light of the result observed when IN_3 adds to 1-butene, what is the polarity of the $I-N_3$ bond? Propose a mechanism for the reaction using curved arrows to show the electron flow in each step.

7.38 ■ 10-Bromo-α-chamigrene, a compound isolated from marine algae, is thought to be biosynthesized from γ-bisabolene by the following route:
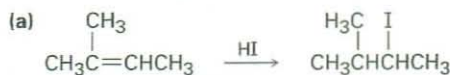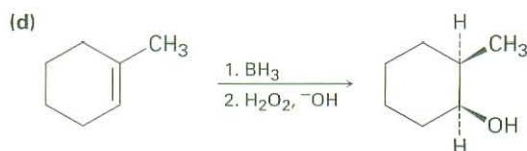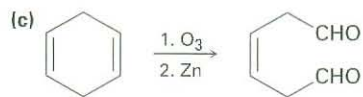

γ-Bisabolene

10-Bromo-α-chamigrene
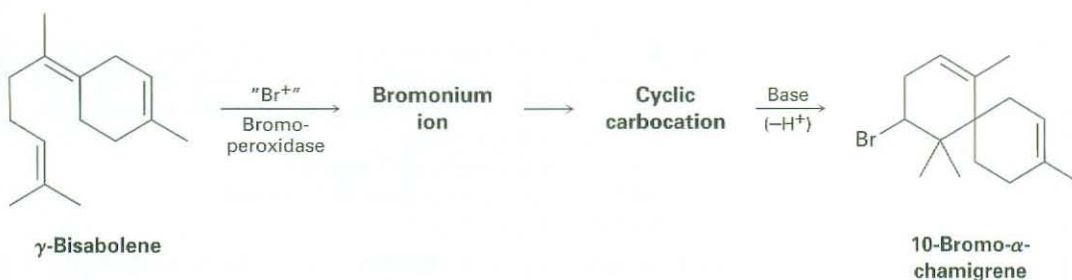
Draw the structures of the intermediate bromonium and cyclic carbocation, and propose mechanisms for all three steps.

7.39 ■ Draw the structure of a hydrocarbon that absorbs 2 molar equivalents of H_2 on catalytic hydrogenation and gives only butanedial on ozonolysis.

$$\overset{\overset{\displaystyle O}{||}}{H}CCH_2CH_2\overset{\overset{\displaystyle O}{||}}{C}H \qquad \textbf{Butanedial}$$
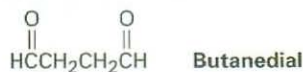
7.40 Simmons–Smith reaction of cyclohexene with diiodomethane gives a single cyclopropane product, but the analogous reaction of cyclohexene with 1,1-diiodoethane gives (in low yield) a mixture of two isomeric methyl-cyclopropane products. What are the two products, and how do they differ?

7.41 In planning the synthesis of one compound from another, it's just as important to know what *not* to do as to know what to do. The following reactions all have serious drawbacks to them. Explain the potential problems of each.
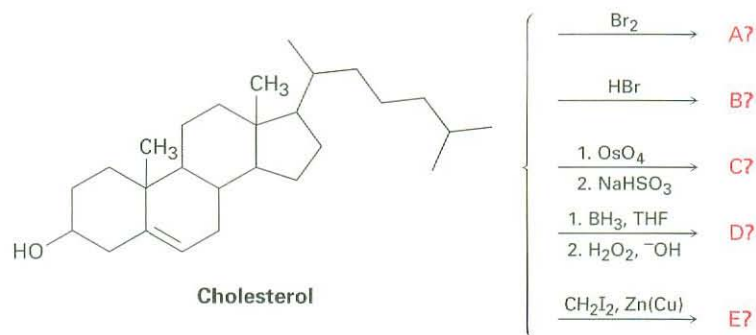
(a)

$$\underset{\underset{\displaystyle CH_3}{|}}{CH_3C}=CHCH_3 \quad \xrightarrow{\text{HI}} \quad CH_3\underset{\underset{\displaystyle I}{|}}{\overset{\overset{\displaystyle H_3C}{|}}{C}}HCHCH_3$$

(b)

(c)

$$\xrightarrow[\text{2. Zn}]{\text{1. O}_3}$$

CHO
CHO

(d)

CH₃

$$\xrightarrow[\text{2. H}_2\text{O}_2, \text{ }^-\text{OH}]{\text{1. BH}_3}$$

H
CH₃
OH
H
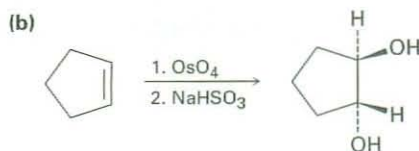
7.42 Which of the following alcohols could *not* be made selectively by hydroboration/oxidation of an alkene? Explain.

(a)

OH
|
$CH_3CH_2CH_2CHCH_3$

(b)

OH
|
$(CH_3)_2CHC(CH_3)_2$

(c)

H
CH₃
OH
H

(d)

OH
CH₃
H
H
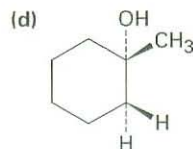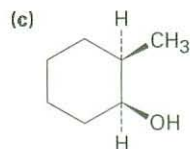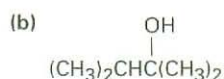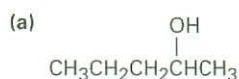
7.43 ■ Predict the products of the following reactions. Don't worry about the size of the molecule; concentrate on the functional groups.


CH₃
CH₃
HO

Cholesterol

$$\xrightarrow{\text{Br}_2} \text{A?}$$

$$\xrightarrow{\text{HBr}} \text{B?}$$

$$\xrightarrow[\text{2. NaHSO}_3]{\text{1. OsO}_4} \text{C?}$$

$$\xrightarrow[\text{2. H}_2\text{O}_2, \text{ }^-\text{OH}]{\text{1. BH}_3, \text{ THF}} \text{D?}$$

$$\xrightarrow{\text{CH}_2\text{I}_2, \text{ Zn(Cu)}} \text{E?}$$

7.44 The sex attractant of the common housefly is a hydrocarbon with the formula $C_{23}H_{46}$. On treatment with aqueous acidic $KMnO_4$, two products are obtained, $CH_3(CH_2)_{12}CO_2H$ and $CH_3(CH_2)_7CO_2H$. Propose a structure.

7.45 Compound A has the formula C_8H_8. It reacts rapidly with $KMnO_4$ to give CO_2 and a carboxylic acid, B ($C_7H_6O_2$), but reacts with only 1 molar equivalent of H_2 on catalytic hydrogenation over a palladium catalyst. On hydrogenation under conditions that reduce aromatic rings, 4 equivalents of H_2 are taken up and hydrocarbon C (C_8H_{16}) is produced. What are the structures of A, B, and C? Write the reactions.

■ Assignable in OWL

7.46 ■ Plexiglas, a clear plastic used to make many molded articles, is made by polymerization of methyl methacrylate. Draw a representative segment of Plexiglas.


Methyl methacrylate
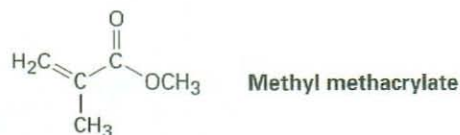
7.47 ■ Poly(vinyl pyrrolidone), prepared from *N*-vinylpyrrolidone, is used both in cosmetics and as a synthetic blood substitute. Draw a representative segment of the polymer.

N-Vinylpyrrolidone
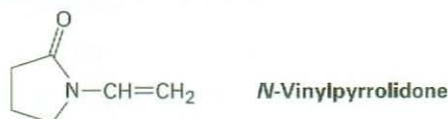
7.48 Reaction of 2-methylpropene with CH_3OH in the presence of H_2SO_4 catalyst yields methyl *tert*-butyl ether, $CH_3OC(CH_3)_3$, by a mechanism analogous to that of acid-catalyzed alkene hydration. Write the mechanism, using curved arrows for each step.

7.49 ■ Isolated from marine algae, prelaureatin is thought to be biosynthesized from laurediol by the following route. Propose a mechanism.

**Laurediol**   **Prelaureatin**
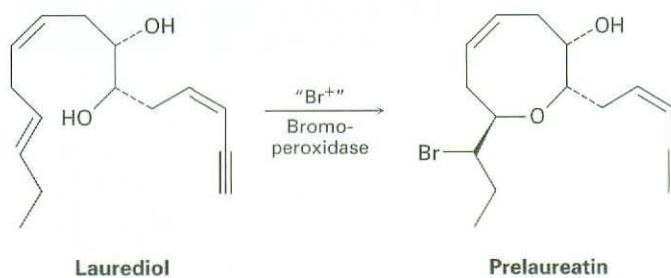
7.50 How would you distinguish between the following pairs of compounds using simple chemical tests? Tell what you would do and what you would see.
(a) Cyclopentene and cyclopentane   (b) 2-Hexene and benzene

7.51 Dichlorocarbene can be generated by heating sodium trichloroacetate. Propose a mechanism for the reaction, and use curved arrows to indicate the movement of electrons in each step. What relationship does your mechanism bear to the base-induced elimination of HCl from chloroform?
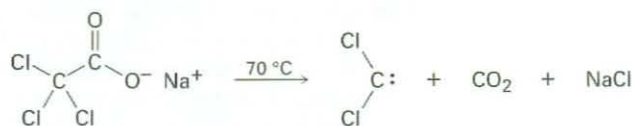
7.52 ■ α-Terpinene, $C_{10}H_{16}$, is a pleasant-smelling hydrocarbon that has been iso-lated from oil of marjoram. On hydrogenation over a palladium catalyst, α-terpinene reacts with 2 molar equivalents of H_2 to yield a hydrocarbon, $C_{10}H_{20}$. On ozonolysis, followed by reduction with zinc and acetic acid, α-terpinene yields two products, glyoxal and 6-methyl-2,5-heptanedione.
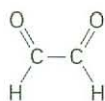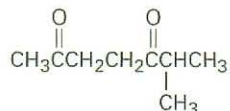

Glyoxal   **6-Methyl-2,5-heptanedione**

(a) How many degrees of unsaturation does α-terpinene have?
(b) How many double bonds and how many rings does it have?
(c) Propose a structure for α-terpinene.

7.53 Evidence that cleavage of 1,2-diols by HIO_4 occurs through a five-membered cyclic periodate intermediate is based on *kinetic data*—the measurement of reaction rates. When diols A and B were prepared and the rates of their reac-tion with HIO_4 were measured, it was found that diol A cleaved approximately 1 million times faster than diol B. Make molecular models of A and B and of potential cyclic periodate intermediates, and then explain the kinetic results.
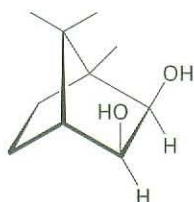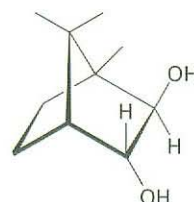
A   B
(*cis* diol)   (*trans* diol)

7.54 ■ Reaction of HBr with 3-methylcyclohexene yields a mixture of four prod-ucts: *cis-* and *trans*-1-bromo-3-methylcyclohexane and *cis-* and *trans*-1-bromo-2-methylcyclohexane. The analogous reaction of HBr with 3-bromocyclohexene yields *trans*-1,2-dibromocyclohexane as the sole product. Draw structures of the possible intermediates, and then explain why only a single product is formed in the reaction of HBr with 3-bromocyclohexene.


cis, trans   cis, trans
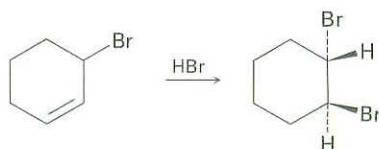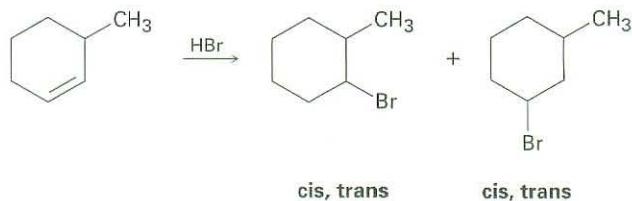
7.55 Reaction of cyclohexene with mercury(II) acetate in CH_3OH rather than H_2O, followed by treatment with $NaBH_4$, yields cyclohexyl methyl ether rather than cyclohexanol. Suggest a mechanism.

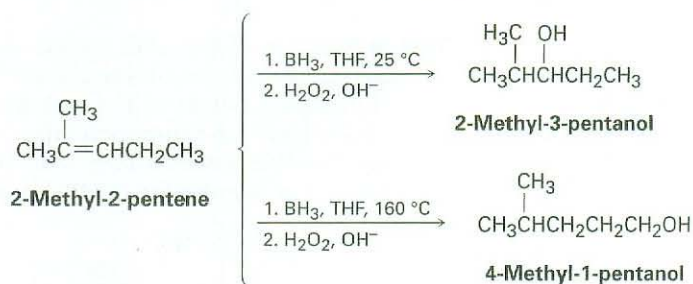**Cyclohexene**   **Cyclohexyl methyl ether**
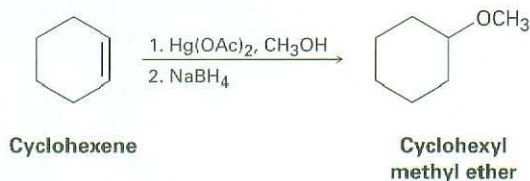
7.56 Use your general knowledge of alkene chemistry to suggest a mechanism for the following reaction:
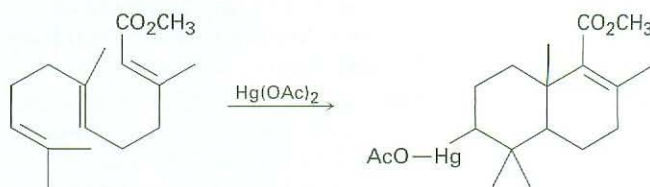
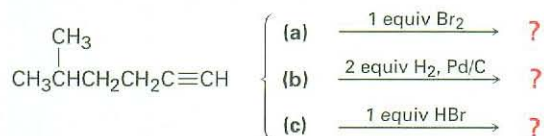**7.57** ■ Treatment of 4-penten-1-ol with aqueous Br_2 yields a cyclic bromo ether rather than the expected bromohydrin. Suggest a mechanism, using curved arrows to show electron movement.

4-Penten-1-ol   **2-(Bromomethyl)tetrahydrofuran**
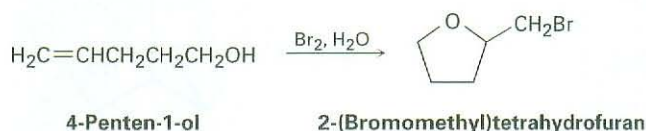
7.58 Hydroboration of 2-methyl-2-pentene at 25 °C followed by oxidation with alkaline H_2O_2 yields 2-methyl-3-pentanol, but hydroboration at 160 °C followed by oxidation yields 4-methyl-1-pentanol. Suggest a mechanism.

$$CH_3\overset{CH_3}{\underset{|}{C}}=CHCH_2CH_3$$

2-Methyl-2-pentene

1. BH_3, THF, 25 °C
2. H_2O_2, OH^-

$$CH_3\overset{H_3C}{\underset{|}{CH}}\overset{OH}{\underset{|}{CH}}CH_2CH_3$$

2-Methyl-3-pentanol

1. BH_3, THF, 160 °C
2. H_2O_2, OH^-

$$CH_3\overset{CH_3}{\underset{|}{CH}}CH_2CH_2CH_2OH$$

4-Methyl-1-pentanol

7.59 We'll see in the next chapter that alkynes undergo many of the same reactions that alkenes do. What product might you expect from each of the following reactions?

$$CH_3\overset{CH_3}{\underset{|}{CH}}CH_2CH_2C{\equiv}CH$$

(a) $\xrightarrow{\text{1 equiv } Br_2}$?

(b) $\xrightarrow{\text{2 equiv } H_2,\ Pd/C}$?

(c) $\xrightarrow{\text{1 equiv HBr}}$?

7.60 Hydroxylation of *cis*-2-butene with OsO_4 yields a different product than hydroxylation of *trans*-2-butene. Draw the structure, show the stereochemistry of each product, and explain the difference between them.