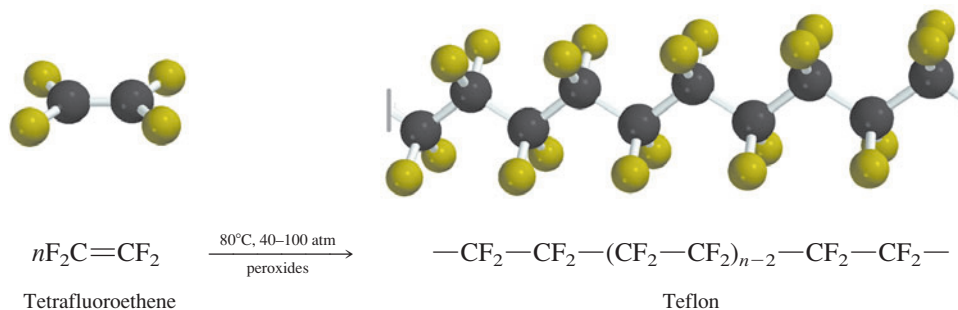


Teflon is made in a similar way by free-radical polymerization of tetrafluoroethene.



Carbon–fluorine bonds are quite strong (slightly stronger than C–H bonds), and like polyethylene, Teflon is a very stable, inert material. We are all familiar with the most characteristic property of Teflon, its “nonstick” surface. This can be understood by comparing Teflon and polyethylene. The high electronegativity of fluorine makes C–F bonds less polarizable than C–H bonds, causing the dispersion forces in Teflon to be less than those in polyethylene. Thus, the surface of Teflon is even less “sticky” than the already slick surface of polyethylene.

A large number of compounds with carbon–carbon double bonds have been polymerized to yield materials having useful properties. Some of the more important or familiar of these are listed in Table 6.5. Not all these monomers are effectively polymerized under free-radical conditions, and much research has been carried out to develop alternative polymerization techniques. One of these, **coordination polymerization**, employs novel transition-metal catalysts. Polyethylene produced by coordination polymerization has a higher density than that produced by free-radical polymerization and somewhat different—in many applications, more desirable—properties. Coordination polymerization was developed independently by Karl Ziegler in Germany and Giulio Natta in Italy in the early 1950s. They shared the Nobel Prize in chemistry in 1963 for this work. Coordination polymerization gives a form of **polypropylene** suitable for plastics and fibers. When propene is polymerized under free-radical conditions, the polypropylene has physical properties (such as a low melting point) that make it useless for most applications.

Coordination polymerization is described in more detail in Sections 7.15 and 14.15.

## 6.22 SUMMARY

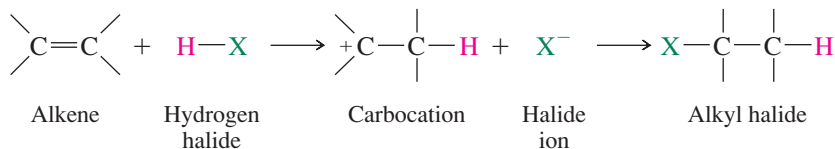
Alkenes are **unsaturated hydrocarbons** and react with substances that add to the double bond.

Section 6.1 See Table 6.6.

Section 6.2 Hydrogenation of alkenes is exothermic. Heats of hydrogenation can be measured and used to assess the stability of various types of double bonds. The information parallels that obtained from heats of combustion.

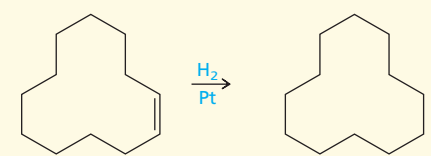
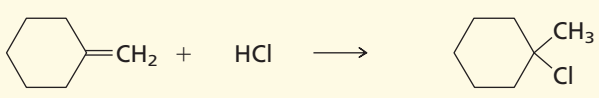
Section 6.3 Hydrogenation of alkenes is a syn addition.

Sections 6.4–6.7 See Table 6.6. Hydrogen halide addition to alkenes proceeds by electrophilic attack of the reagent on the  $\pi$  electrons of the double bond. Carbocations are intermediates.



Protonation of the double bond occurs in the direction that gives the more stable of two possible carbocations.

**TABLE 6.6** Addition Reactions of Alkenes

Reaction (section) and comments	General equation and specific example
<b>Catalytic hydrogenation (Sections 6.1–6.3)</b> Alkenes react with hydrogen in the presence of a platinum, palladium, rhodium, or nickel catalyst to form the corresponding alkane.	$\begin{array}{ccc} \text{R}_2\text{C}=\text{CR}_2 + \text{H}_2 & \xrightarrow{\text{Pt, Pd, Rh, or Ni}} & \text{R}_2\text{CHCHR}_2 \\ \text{Alkene} & \text{Hydrogen} & \text{Alkane} \end{array}$  <p><i>cis</i>-Cyclododecene      Cyclododecane (100%)</p>
<b>Addition of hydrogen halides (Sections 6.4–6.7)</b> A proton and a halogen add to the double bond of an alkene to yield an alkyl halide. Addition proceeds in accordance with Markovnikov's rule; hydrogen adds to the carbon that has the greater number of hydrogens, halide to the carbon that has the fewer hydrogens.	$\begin{array}{ccc} \text{RCH}=\text{CR}'_2 + \text{HX} & \longrightarrow & \text{RCH}_2-\text{CR}'_2 \\ \text{Alkene} & \text{Hydrogen} & \text{Alkyl} \\ & \text{halide} & \text{halide} \end{array}$  <p>Methylenecyclohexane      Hydrogen chloride      1-Chloro-1-methylcyclohexane (75–80%)</p>
<b>Addition of sulfuric acid (Section 6.9)</b> Alkenes react with sulfuric acid to form alkyl hydrogen sulfates. A proton and a hydrogen sulfate ion add to the double bond in accordance with Markovnikov's rule. Alkenes that yield tertiary carbocations on protonation tend to polymerize in concentrated sulfuric acid (Section 6.21).	$\begin{array}{ccc} \text{RCH}=\text{CR}'_2 + \text{HOSO}_2\text{OH} & \longrightarrow & \text{RCH}_2-\text{CR}'_2 \\ \text{Alkene} & \text{Sulfuric acid} & \text{Alkyl hydrogen sulfate} \\ & &   \\ & & \text{OSO}_2\text{OH} \end{array}$ $\begin{array}{ccc} \text{H}_2\text{C}=\text{CHCH}_2\text{CH}_3 + \text{HOSO}_2\text{OH} & \longrightarrow & \text{CH}_3-\text{CHCH}_2\text{CH}_3 \\ \text{1-Butene} & \text{Sulfuric acid} & \text{sec-Butyl hydrogen sulfate} \\ & &   \\ & & \text{OSO}_2\text{OH} \end{array}$
<b>Acid-catalyzed hydration (Section 6.10)</b> Addition of water to the double bond of an alkene takes place in aqueous acid. Addition occurs according to Markovnikov's rule. A carbocation is an intermediate and is captured by a molecule of water acting as a nucleophile.	$\begin{array}{ccc} \text{RCH}=\text{CR}'_2 + \text{H}_2\text{O} & \xrightarrow{\text{H}^+} & \text{RCH}_2-\text{CR}'_2 \\ \text{Alkene} & \text{Water} & \text{Alcohol} \\ & &   \\ & & \text{OH} \end{array}$ $\begin{array}{ccc} \text{H}_2\text{C}=\text{C}(\text{CH}_3)_2 & \xrightarrow{50\% \text{ H}_2\text{SO}_4/\text{H}_2\text{O}} & (\text{CH}_3)_3\text{COH} \\ \text{2-Methylpropene} & & \text{tert-Butyl alcohol} \\ & & (55\text{--}58\%) \end{array}$

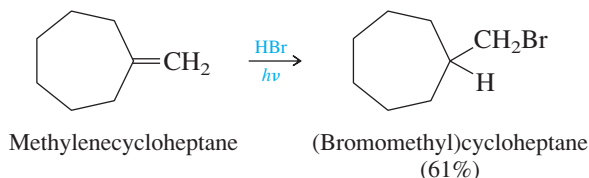
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TABLE 6.6

Addition Reactions of Alkenes (*Continued*)

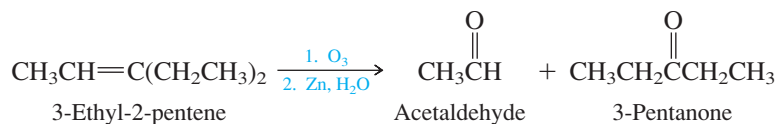
Reaction (section) and comments	General equation and specific example
<p><b>Hydroboration–oxidation (Sections 6.11–6.13)</b> This two-step sequence achieves hydration of alkenes in a stereospecific syn manner, with a regioselectivity opposite to Markovnikov's rule. An organoborane is formed by electrophilic addition of diborane to an alkene. Oxidation of the organoborane intermediate with hydrogen peroxide completes the process. Rearrangements do not occur.</p>	$\text{RCH}=\text{CR}'_2 \xrightarrow[2. \text{H}_2\text{O}_2, \text{HO}^-]{1. \text{B}_2\text{H}_6, \text{diglyme}} \begin{array}{c} \text{RCHCHR}'_2 \\   \\ \text{OH} \end{array}$ <p>Alkene <span style="margin-left: 150px;"></span> Alcohol</p> $(\text{CH}_3)_2\text{CHCH}_2\text{CH}=\text{CH}_2 \xrightarrow[2. \text{H}_2\text{O}_2, \text{HO}^-]{1. \text{H}_3\text{B}\cdot\text{THF}} (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{OH}$ <p>4-Methyl-1-pentene <span style="margin-left: 150px;"></span> 4-Methyl-1-pentanol (80%)</p>
<p><b>Addition of halogens (Sections 6.14–6.16)</b> Bromine and chlorine add to alkenes to form vicinal dihalides. A cyclic halonium ion is an intermediate. Stereospecific anti addition is observed.</p>	$\text{R}_2\text{C}=\text{CR}_2 + \text{X}_2 \longrightarrow \begin{array}{c} \text{R} \quad \text{R} \\   \quad   \\ \text{X}-\text{C}-\text{C}-\text{X} \\   \quad   \\ \text{R} \quad \text{R} \end{array}$ <p>Alkene <span style="margin-left: 50px;">Halogen</span> <span style="margin-left: 50px;">Vicinal dihalide</span></p> $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Br}_2 \longrightarrow \begin{array}{c} \text{BrCH}_2-\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\   \\ \text{Br} \end{array}$ <p>1-Hexene <span style="margin-left: 100px;">Bromine</span> <span style="margin-left: 50px;">1,2-Dibromohexane (100%)</span></p>
<p><b>Halohydrin formation (Section 6.17)</b> When treated with bromine or chlorine in aqueous solution, alkenes are converted to vicinal halohydrins. A halonium ion is an intermediate. The halogen adds to the carbon that has the greater number of hydrogens. Addition is anti.</p>	$\text{RCH}=\text{CR}'_2 + \text{X}_2 + \text{H}_2\text{O} \longrightarrow \begin{array}{c} \text{R}' \\   \\ \text{X}-\text{CH}-\text{C}-\text{OH} \\   \quad   \\ \text{R} \quad \text{R}' \end{array} + \text{HX}$ <p>Alkene <span style="margin-left: 50px;">Halogen</span> <span style="margin-left: 50px;">Water</span> <span style="margin-left: 50px;">Vicinal halohydrin</span> <span style="margin-left: 50px;">Hydrogen halide</span></p> $\text{Cyclohexane ring}-\text{CH}_2 \xrightarrow[\text{H}_2\text{O}]{\text{Br}_2} \begin{array}{c} \text{CH}_2\text{Br} \\   \\ \text{Cyclohexane ring}-\text{OH} \end{array}$ <p>Methylenecyclohexane <span style="margin-left: 150px;">(1-Bromomethyl)cyclohexanol (89%)</span></p>
<p><b>Epoxidation (Section 6.18)</b> Peroxy acids transfer oxygen to the double bond of alkenes to yield epoxides. The reaction is a stereospecific syn addition.</p>	$\text{R}_2\text{C}=\text{CR}_2 + \text{R}'\text{COOH} \longrightarrow \begin{array}{c} \text{O} \\ // \quad // \\ \text{R}_2\text{C}-\text{CR}_2 \end{array} + \text{R}'\text{COH}$ <p>Alkene <span style="margin-left: 50px;">Peroxy acid</span> <span style="margin-left: 50px;">Epoxide</span> <span style="margin-left: 50px;">Carboxylic acid</span></p> $\text{1-Methylcycloheptene} + \text{CH}_3\text{COOH} \longrightarrow \begin{array}{c} \text{CH}_3 \\   \\ \text{Cycloheptane ring}-\text{O} \end{array} + \text{CH}_3\text{COH}$ <p>1-Methylcycloheptene <span style="margin-left: 50px;">Peroxyacetic acid</span> <span style="margin-left: 50px;">1-Methyl-1,2-epoxycycloheptane (65%)</span> <span style="margin-left: 50px;">Acetic acid</span></p>

Section 6.8 Hydrogen bromide is unique among the hydrogen halides in that it can add to alkenes either by electrophilic or free-radical addition. Under photochemical conditions or in the presence of peroxides, free-radical addition is observed, and HBr adds to the double bond with a regioselectivity opposite to that of Markovnikov's rule.



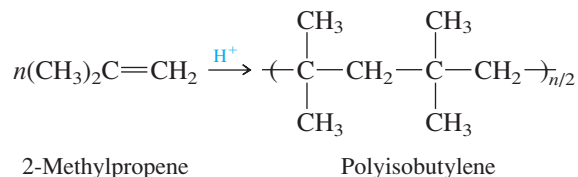
Sections 6.9–6.18 See Table 6.6.

Section 6.19 Alkenes are cleaved to carbonyl compounds by **ozonolysis**. This reaction is useful both for synthesis (preparation of aldehydes, ketones, or carboxylic acids) and analysis. When applied to analysis, the carbonyl compounds are isolated and identified, allowing the substituents attached to the double bond to be deduced.



Section 6.20 The reactions described so far can be carried out sequentially to prepare compounds of prescribed structure from some given starting material. The best way to approach a synthesis is to reason backward from the desired target molecule and to always use reactions that you are sure will work. The 11 exercises that make up Problem 6.32 at the end of this chapter provide some opportunities for practice.

Section 6.21 In their **polymerization**, many individual alkene molecules combine to give a high-molecular-weight product. Among the methods for alkene polymerization, *cationic polymerization*, *coordination polymerization*, and *free-radical polymerization* are the most important. An example of cationic polymerization is:



## PROBLEMS

6.22 Write the structure of the major organic product formed in the reaction of 1-pentene with each of the following:

- Hydrogen chloride
- Hydrogen bromide
- Hydrogen bromide in the presence of peroxides