

6.23 SUMMARY

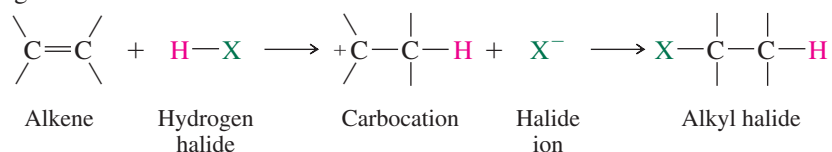
Alkenes are **unsaturated hydrocarbons** and react with substances that add to the double bond.

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.

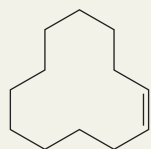
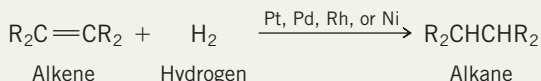
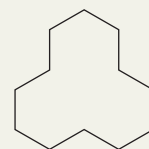
Sections 6.4–6.7 See Table 6.6. Hydrogen halide addition to alkenes proceeds by electrophilic attack of the reagent on the π electrons of the double bond. Carbocations are intermediates. Addition to unsymmetrical alkenes is regioselective.



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

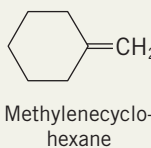
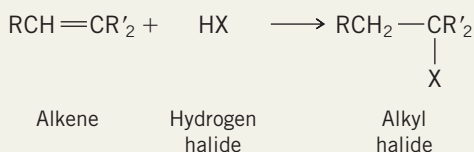
TABLE 6.6 Addition Reactions of Alkenes**Reaction (section) and comments**

Catalytic hydrogenation (Sections 6.1–6.3) Alkenes react with hydrogen in the presence of a platinum, palladium, rhodium, or nickel catalyst to form the corresponding alkane.

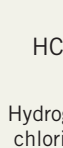
General equation and specific example*cis*-Cyclododecene

Cyclododecane (100%)

Addition of hydrogen halides (Sections 6.4–6.7) 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.

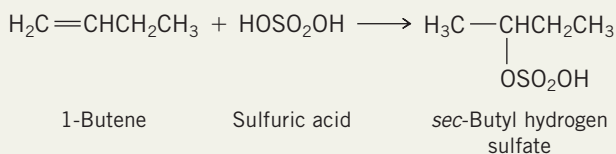
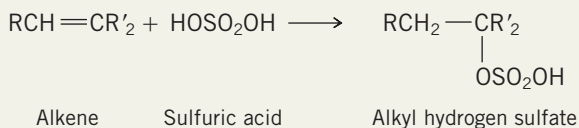


Methylenecyclohexane



1-Chloro-1-methylcyclohexane (75–80%)

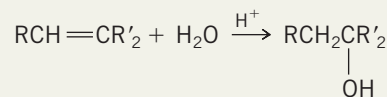
Addition of sulfuric acid (Section 6.9) Alkenes react with sulfuric acid to form alkyl hydrogen sulfates. A proton and a hydrogen sulfate ion add to the double bond in accordance with Markovnikov's rule. Alkenes that yield tertiary carbocations on protonation tend to polymerize in concentrated sulfuric acid (Section 6.22).



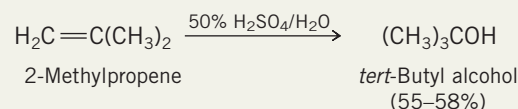
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TABLE 6.6 Addition Reactions of Alkenes (*Continued*)**Reaction (section) and comments****General equation and specific example****Acid-catalyzed hydration (Section 6.10)**

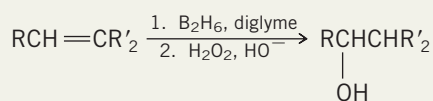
Addition of water to the double bond of an alkene takes place in aqueous acid. Addition occurs according to Markovnikov's rule. A carbocation is an intermediate and is captured by a molecule of water acting as a nucleophile.



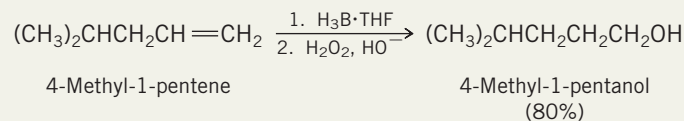
Alkene Water Alcohol

**Hydroboration–oxidation (Sections**

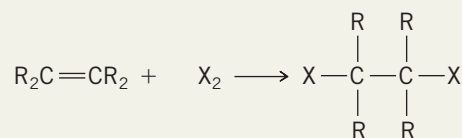
6.12–6.14) This two-step sequence achieves hydration of alkenes in a stereospecific syn manner, with a regioselectivity opposite to Markovnikov's rule. An organoborane is formed by electrophilic addition of diborane to an alkene. Oxidation of the organoborane intermediate with hydrogen peroxide completes the process. Rearrangements do not occur.



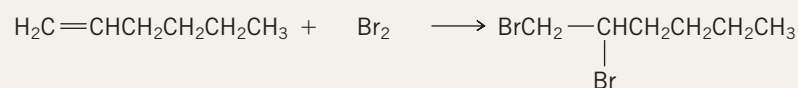
Alkene Alcohol

**Addition of halogens (Sections**

6.15–6.17) Bromine and chlorine add to alkenes to form vicinal dihalides. A cyclic halonium ion is an intermediate. Anti addition is observed.



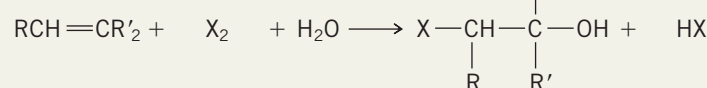
Alkene Halogen Vicinal dihalide



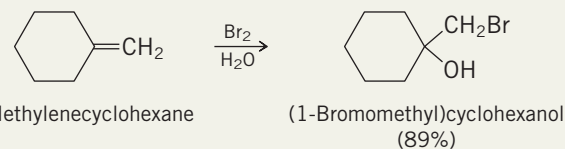
1-Hexene Bromine 1,2-Dibromohexane (100%)

Halohydrin formation (Section 6.18)

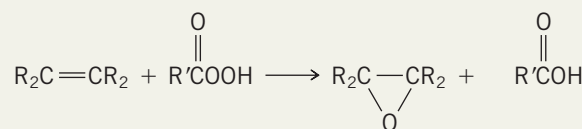
When treated with bromine or chlorine in aqueous solution, alkenes are converted to vicinal halohydrins. A halonium ion is an intermediate. The halogen adds to the carbon that has the greater number of hydrogens. Addition is anti.



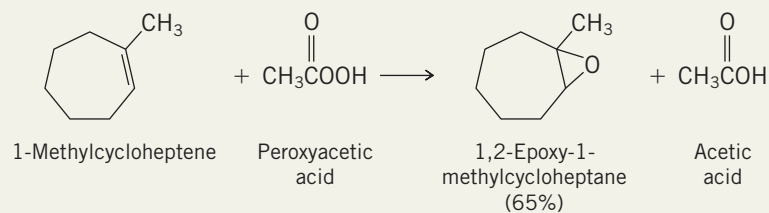
Alkene Halogen Water Vicinal halohydrin Hydrogen halide



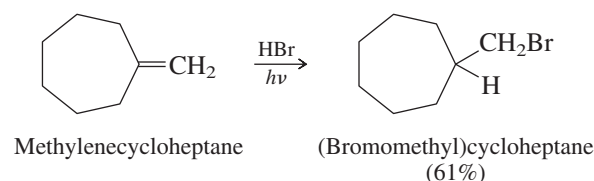
Epoxidation (Section 6.19) Peroxy acids transfer oxygen to the double bond of alkenes to yield epoxides. The reaction is a stereospecific syn addition.



Alkene Peroxy acid Epoxide Carboxylic acid



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 6.9–6.10 See Table 6.6

Section 6.11 Addition and elimination reactions are often reversible, and proceed spontaneously in the direction in which the free energy G decreases. The reaction is at equilibrium when $\Delta G = 0$. Free energy is related to enthalpy (H) and entropy (S) by the equations

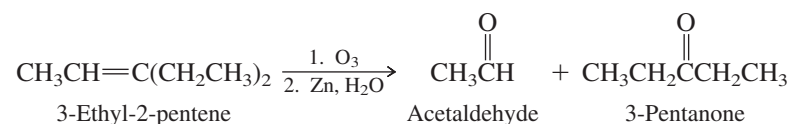
$$G = H - TS \quad \text{and} \quad \Delta G = \Delta H - T\Delta S$$

The standard free energy change ΔG° is related to the equilibrium constant K by the equation

$$\Delta G^\circ = -RT \ln K$$

Sections 6.12–6.20 See Table 6.6

Section 6.20 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 6.21 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 6.36 at the end of this chapter provide some opportunities for practice.

Section 6.22 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

