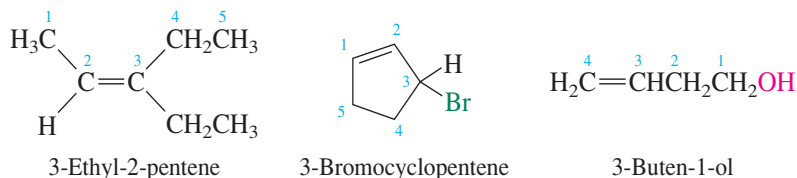
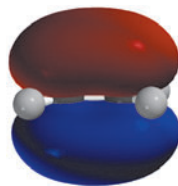


## 5.18 SUMMARY

Section 5.1 Alkenes and cycloalkenes contain carbon–carbon double bonds. According to **IUPAC nomenclature**, alkenes are named by substituting *-ene* for the *-ane* suffix of the alkane that has the same number of carbon atoms as the longest continuous chain that includes the double bond. The chain is numbered in the direction that gives the lower number to the first-appearing carbon of the double bond. The double bond takes precedence over alkyl groups and halogens in dictating the direction of numbering, but is outranked by a hydroxyl group.

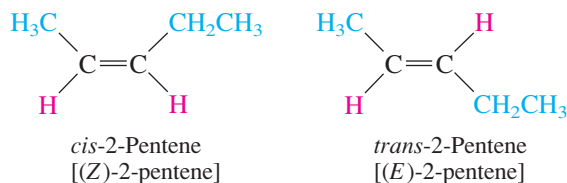


Section 5.2 Bonding in alkenes is described according to an  $sp^2$  orbital hybridization model. The double bond unites two  $sp^2$ -hybridized carbon atoms and is made of a  $\sigma$  component and a  $\pi$  component. The  $\sigma$  bond arises by overlap of an  $sp^2$  hybrid orbital on each carbon. The  $\pi$  bond is weaker than the  $\sigma$  bond and results from a side-by-side overlap of  $p$  orbitals.



Sections 5.3–5.4

Isomeric alkenes may be either **constitutional isomers** or **stereoisomers**. There is a sizable barrier to rotation about a carbon–carbon double bond, which corresponds to the energy required to break the  $\pi$  component of the double bond. Stereoisomeric alkenes are configurationally stable under normal conditions. The **configurations** of stereoisomeric alkenes are described according to two notational systems. One system adds the prefix *cis-* to the name of the alkene when similar substituents are on the same side of the double bond and the prefix *trans-* when they are on opposite sides. The other ranks substituents according to a system of rules based on atomic number. The prefix *Z* is used for alkenes that have higher ranked substituents on the same side of the double bond; the prefix *E* is used when higher ranked substituents are on opposite sides.



Section 5.5 Alkenes are relatively nonpolar. Alkyl substituents donate electrons to an  $sp^2$ -hybridized carbon to which they are attached slightly better than hydrogen does.



TABLE 5.2

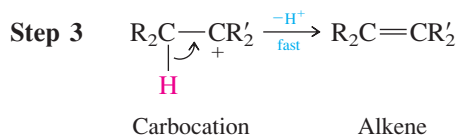
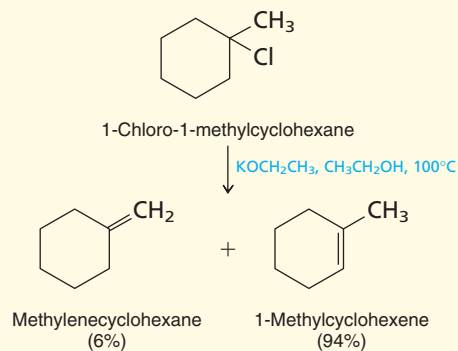
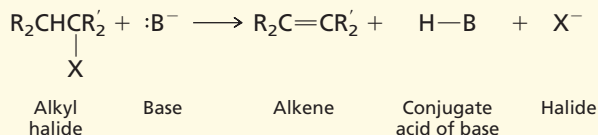
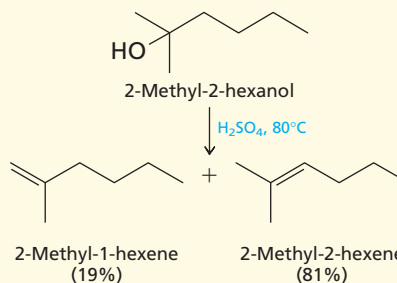
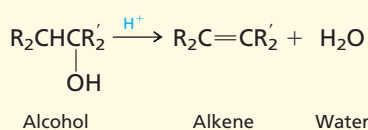
## Preparation of Alkenes by Elimination Reactions of Alcohols and Alkyl Halides

## Reaction (section) and comments

**Dehydration of alcohols (Sections 5.9–5.13)** Dehydration requires an acid catalyst; the order of reactivity of alcohols is tertiary > secondary > primary. Elimination is regioselective and proceeds in the direction that produces the most highly substituted double bond. When stereoisomeric alkenes are possible, the more stable one is formed in greater amounts. An E1 (elimination unimolecular) mechanism via a carbocation intermediate is followed with secondary and tertiary alcohols. Primary alcohols react by an E2 (elimination bimolecular) mechanism. Sometimes elimination is accompanied by rearrangement.

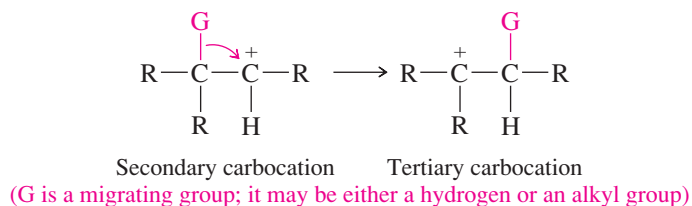
**Dehydrohalogenation of alkyl halides (Sections 5.14–5.16)** Strong bases cause a proton and a halide to be lost from adjacent carbons of an alkyl halide to yield an alkene. Regioselectivity is in accord with the Zaitsev rule. The order of halide reactivity is  $I > Br > Cl > F$ . A concerted E2 reaction pathway is followed, carbocations are not involved, and rearrangements do not occur. An anti coplanar arrangement of the proton being removed and the halide being lost characterizes the transition state.

## General equation and specific example



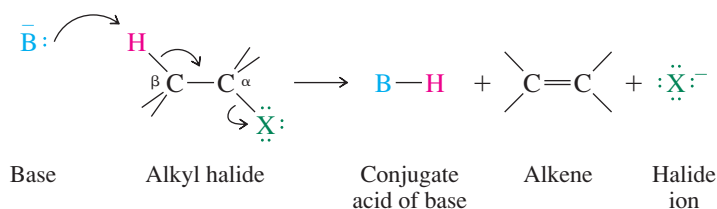
Primary alcohols do not dehydrate as readily as secondary or tertiary alcohols, and their dehydration does not involve a primary carbocation. A proton is lost from the  $\beta$  carbon in the same step in which carbon–oxygen bond cleavage occurs. The mechanism is E2.

Section 5.13 Alkene synthesis via alcohol dehydration is complicated by **carbocation rearrangements**. A less stable carbocation can rearrange to a more stable one by an alkyl group migration or by a hydride shift, opening the possibility for alkene formation from two different carbocations.



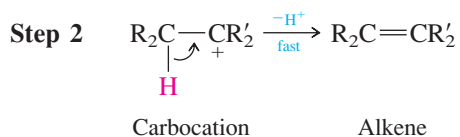
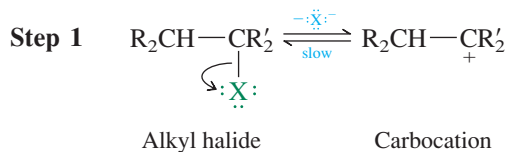
Section 5.14 See Table 5.2.

Section 5.15 **Dehydrohalogenation** of alkyl halides by alkoxide bases is not complicated by rearrangements, because carbocations are not intermediates. The mechanism is E2. It is a concerted process in which the base abstracts a proton from the  $\beta$  carbon while the bond between the halogen and the  $\alpha$  carbon undergoes heterolytic cleavage.



Section 5.16 The preceding equation shows the proton H and the halogen X in the **anti coplanar** relationship that is required for elimination by the E2 mechanism.

Section 5.17 In the absence of a strong base, alkyl halides eliminate by an E1 mechanism. Rate-determining ionization of the alkyl halide to a carbocation is followed by deprotonation of the carbocation.



## PROBLEMS

5.22 Write structural formulas for each of the following:

- |   |   |
|---|---|
| (a) 1-Heptene                           | (g) 1-Bromo-3-methylcyclohexene                     |
| (b) 3-Ethyl-2-pentene                   | (h) 1-Bromo-6-methylcyclohexene                     |
| (c) <i>cis</i> -3-Octene                | (i) 4-Methyl-4-penten-2-ol                          |
| (d) <i>trans</i> -1,4-Dichloro-2-butene | (j) Vinylcycloheptane                               |
| (e) ( <i>Z</i> )-3-Methyl-2-hexene      | (k) 1,1-Diallylcyclopropane                         |
| (f) ( <i>E</i> )-3-Chloro-2-hexene      | (l) <i>trans</i> -1-Isopropenyl-3-methylcyclohexane |