5.18 SUMMARY

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 σ component and a π component. The σ bond arises by overlap of an sp^2 hybrid orbital on each carbon. The π bond is weaker than the σ bond and results from a side-by-side overlap of p orbitals.



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 π 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.

$$H_3C$$
 $C=C$
 H
 $C=C$
 H
 $C=C$
 CH_2CH_3
 $C=C$
 H
 $C=C$
 CH_2CH_3
 $C=C$
 CH_2CH_3
 $C=C$
 CH_2CH_3
 $C=C$
 CH_2CH_3
 $C=C$
 $C=$

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.

- Section 5.6 Electron release from alkyl substituents stabilizes a double bond. In general, the order of alkene stability is:
 - 1. Tetrasubstituted alkenes ($R_2C=CR_2$) are the most stable.
 - 2. Trisubstituted alkenes (R₂C=CHR) are next.
 - **3.** Among disubstituted alkenes, *trans*-RCH=CHR is normally more stable than *cis*-RCH=CHR. Exceptions are cycloalkenes, cis cycloalkenes being more stable than trans when the ring contains fewer than 11 carbons.
 - **4.** Monosubstituted alkenes (RCH=CH₂) have a more stabilized double bond than ethylene (unsubstituted) but are less stable than disubstituted alkenes.

The greater stability of more highly substituted double bonds is an example of an **electronic effect**. The decreased stability that results from van der Waals strain between cis substituents is an example of a **steric effect**.

Section 5.7 Cycloalkenes that have trans double bonds in rings smaller than 12 members are less stable than their cis stereoisomers. trans-Cyclooctene can be isolated and stored at room temperature, but trans-cycloheptene is not stable above -30°C.

Carbocation

Section 5.8 Alkenes are prepared by β elimination of alcohols and alkyl halides. These reactions are summarized with examples in Table 5.2. In both cases, β elimination proceeds in the direction that yields the more highly substituted double bond (**Zaitsev's rule**).

Sections 5.9–5.11

See Table 5.2.

Section 5.12 Secondary and tertiary alcohols undergo **dehydration** by an E1 mechanism involving carbocation intermediates.

Step 1
$$R_2CH$$
— $CR'_2 \xrightarrow{H_3O^+}$ R_2CH — $CR'_2 \xrightarrow{I}$ R_2CH — $CR'_2 \xrightarrow{I}$ R_2CH — R

Alkyloxonium ion

ABLE 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

$$R_{2}\mathsf{CHCR}_{2}' \xrightarrow{\mathsf{H}^{+}} R_{2}\mathsf{C} = \mathsf{CR}_{2}' + \mathsf{H}_{2}\mathsf{O}$$

$$\mathsf{Alcohol} \qquad \mathsf{Alkene} \qquad \mathsf{Water}$$

$$\mathsf{HO} \qquad \qquad \mathsf{L}_{2}\mathsf{-Methyl-2-hexanol} \qquad \qquad \mathsf{H}_{2}\mathsf{SO}_{4}, 80^{\circ}\mathsf{C} \qquad \qquad \mathsf{L}_{2}\mathsf{-Methyl-1-hexene} \qquad 2^{-\mathsf{Methyl-2-hexene}} \qquad \mathsf{(81\%)}$$

$$R_{2}\mathsf{CHCR}_{2}' + \mathsf{:B}^{-} \longrightarrow R_{2}\mathsf{C} = \mathsf{CR}_{2}' + \mathsf{H}^{-\mathsf{B}} + \mathsf{X}^{-}$$

$$\mathsf{X}$$

$$\mathsf{Alkyl} \qquad \mathsf{Base} \qquad \mathsf{Alkene} \qquad \mathsf{Conjugate} \qquad \mathsf{Halide} \qquad \mathsf{acid of base}$$

$$\mathsf{LCH}_{3} \qquad \mathsf{LCH}_{2}\mathsf{CH}_{3}, \mathsf{CH}_{3}\mathsf{CH}_{2}\mathsf{OH}, \mathsf{100^{\circ}C} \qquad \mathsf{CH}_{2} \qquad \mathsf{CH}_{3}$$

$$\mathsf{Methylenecyclohexane} \qquad \mathsf{L-Methylcyclohexene} \qquad \mathsf{Methylenecyclohexane} \qquad \mathsf{L-Methylcyclohexene} \qquad \mathsf{$$

Step 3
$$R_2C \xrightarrow{C} CR'_2 \xrightarrow{fast} R_2C = CR'_2$$

H

Carbocation Alkene

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 β carbon in the same step in which carbonoxygen 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.

Problems 223

Secondary carbocation Tertiary carbocation

(G is a migrating group; it may be either a hydrogen or an alkyl group)

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 β carbon while the bond between the halogen and the α 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.

Step 1
$$R_2CH - CR'_2 \xrightarrow[slow]{-:\overset{\cdot}{X}:^{-}} R_2CH - CR'_2$$

Alkyl halide

Carbocation

Step 2
$$R_2C \xrightarrow{R_2} CR_2' \xrightarrow{fast} R_2C = CR_2'$$

Carbocation

Alkene

PROBLEMS

- **5.22** Write structural formulas for each of the following:
 - (a) 1-Heptene
 - (b) 3-Ethyl-2-pentene
 - (c) cis-3-Octene
 - (d) trans-1,4-Dichloro-2-butene
 - (e) (Z)-3-Methyl-2-hexene
 - (f) (E)-3-Chloro-2-hexene

- (g) 1-Bromo-3-methylcyclohexene
- (h) 1-Bromo-6-methylcyclohexene
- (i) 4-Methyl-4-penten-2-ol
- (j) Vinylcycloheptane
- (k) 1,1-Diallylcyclopropane
- (1) trans-1-Isopropenyl-3-methylcyclohexane