

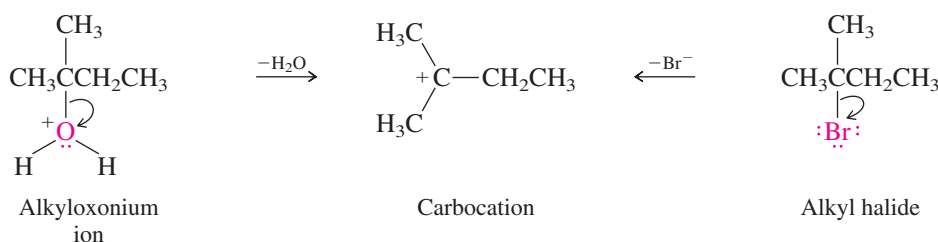
Because the carbon–halogen bond breaks in the slow step, the rate of the reaction depends on the leaving group. Alkyl iodides have the weakest carbon–halogen bond and are the most reactive; alkyl fluorides have the strongest carbon–halogen bond and are the least reactive.

PROBLEM 5.24

Based on the E1 process shown for it in Mechanism 5.5, would you expect elimination in 2-bromo-2-methylbutane to exhibit a kinetic isotope effect?

The best examples of E1 eliminations are those carried out in the absence of added base. In the example cited in Mechanism 5.5, the base that abstracts the proton from the carbocation intermediate is a very weak one; it is a molecule of the solvent, ethyl alcohol. At even modest concentrations of strong base, elimination by the E2 mechanism is much faster than E1 elimination.

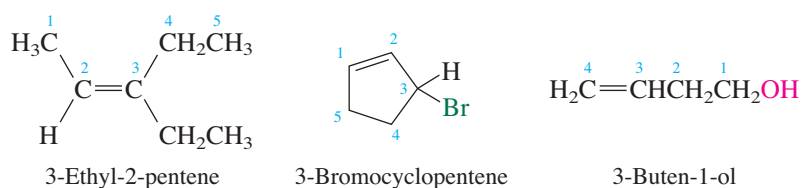
There is a strong similarity between the process shown in Mechanism 5.5 and the one shown for alcohol dehydration in Mechanism 5.1. The main difference between the dehydration of 2-methyl-2-butanol and the dehydrohalogenation of 2-bromo-2-methylbutane is the source of the carbocation. When the alcohol is the substrate, it is the corresponding alkyloxonium ion that dissociates to form the carbocation. The alkyl halide ionizes directly to the carbocation.



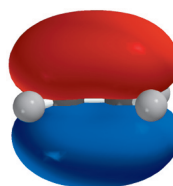
Like alcohol dehydrations, E1 reactions of alkyl halides can be accompanied by carbocation rearrangements. Eliminations by the E2 mechanism, on the other hand, normally proceed without rearrangement. Consequently, if one wishes to prepare an alkene from an alkyl halide, conditions favorable to E2 elimination should be chosen. In practice this simply means carrying out the reaction in the presence of a strong base.

5.19 SUMMARY

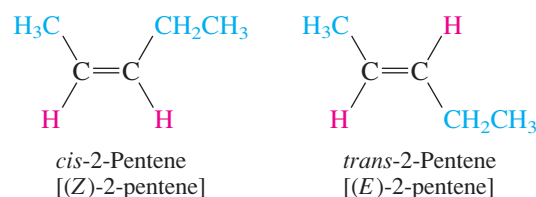
Section 5.1 Alkenes and cycloalkenes contain carbon–carbon double bonds. According to **IUPAC nomenclature**, alkenes are named by substituting *-ene* for the *ane* suffix of the alkane that has the same number of carbon atoms as the longest continuous chain that includes the double bond. The chain is 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 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.



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 π component of the double bond. Stereoisomeric alkenes do not interconvert under normal conditions. Their configurations 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.

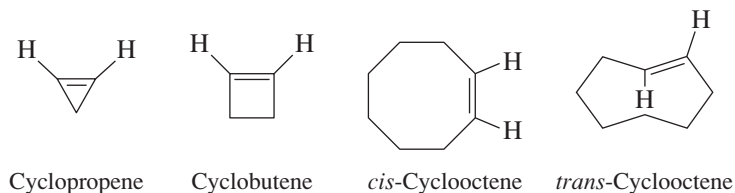
Section 5.6 Electron release from alkyl substituents stabilizes a double bond. In general, the order of alkene stability is:

1. Tetrasubstituted alkenes ($\text{R}_2\text{C}=\text{CR}_2$) are the most stable.
2. Trisubstituted alkenes ($\text{R}_2\text{C}=\text{CHR}$) are next.
3. Among disubstituted alkenes, *trans*- $\text{RCH}=\text{CHR}$ is normally more stable than *cis*- $\text{RCH}=\text{CHR}$. Exceptions are cycloalkenes, cis cycloalkenes being more stable than trans when the ring contains fewer than 12 carbons.
4. Monosubstituted alkenes ($\text{RCH}=\text{CH}_2$) 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 .



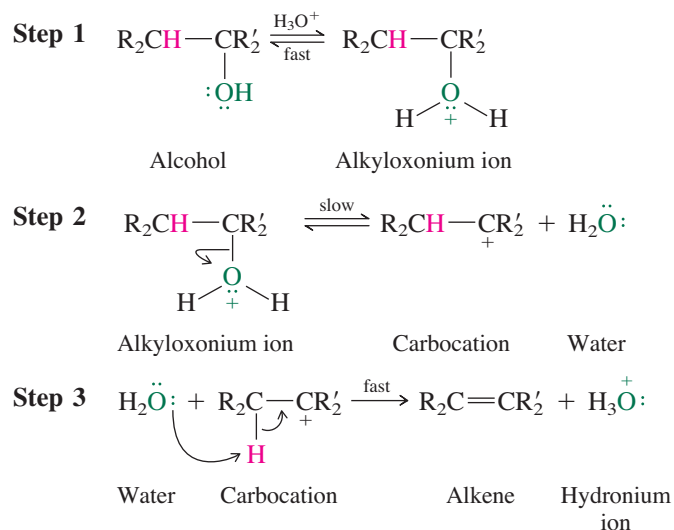
Section 5.8 Alkenes are prepared by **β elimination** of alcohols and alkyl halides. These reactions are summarized with examples in Table 5.2. In both cases, β elimination proceeds in the direction that yields the more highly substituted double bond (**Zaitsev's rule**).

Sections 5.9–5.11 See Table 5.2.

TABLE 5.2 Preparation of Alkenes by Elimination Reactions of Alcohols and Alkyl Halides

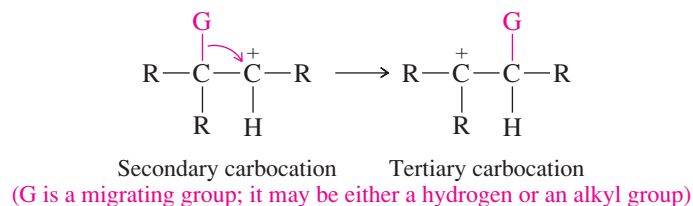
Reaction (section) and comments	General equation and specific example
<p>Dehydration of alcohols (Sections 5.9–5.13) Dehydration requires an acid catalyst; the order of reactivity of alcohols is tertiary > secondary > primary. Elimination is regioselective and proceeds in the direction that produces 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.</p>	$\text{R}_2\text{CHCR}_2 \xrightarrow{\text{H}^+} \text{R}_2\text{C}=\text{CR}_2 + \text{H}_2\text{O}$ <p style="text-align: center;">Alcohol Alkene Water</p> <p style="text-align: center;">2-Methyl-2-hexanol \downarrow $\text{H}_2\text{SO}_4, 80^{\circ}\text{C}$ 2-Methyl-1-hexene (19%) + 2-Methyl-2-hexene (81%)</p>
<p>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 $\text{I} > \text{Br} > \text{Cl} > \text{F}$. 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.</p>	$\text{R}_2\text{CHCR}_2 + \text{:B}^- \longrightarrow \text{R}_2\text{C}=\text{CR}_2 + \text{H-B} + \text{X}^-$ <p style="text-align: center;">Alkyl halide Base Alkene Conjugate Halide acid of base</p> <p style="text-align: center;">1-Chloro-1-methylcyclohexane \downarrow $\text{KOCH}_2\text{CH}_3, \text{CH}_3\text{CH}_2\text{OH}, 100^{\circ}\text{C}$ Methylenecyclohexane (6%) + 1-Methylcyclohexene (94%)</p>

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



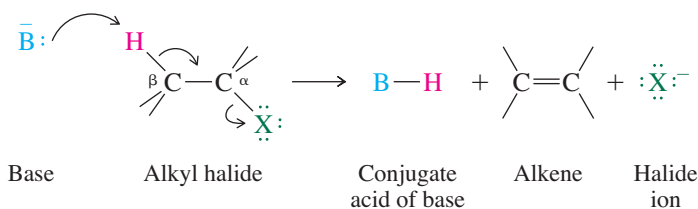
Primary alcohols do not dehydrate as readily as secondary or tertiary alcohols, and their dehydration does not involve a primary carbocation. A proton is lost from the β carbon in the same step in which carbon–oxygen bond cleavage occurs. The mechanism is E2.

Section 5.13 Alkene synthesis via alcohol dehydration is sometimes accompanied by carbocation **rearrangement**. 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.

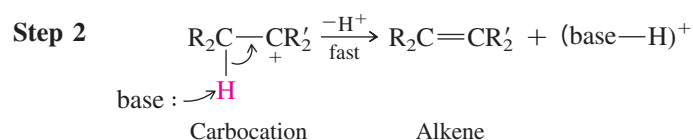
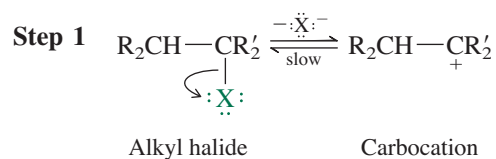
Section 5.15 **Dehydrohalogenation** of alkyl halides by alkoxide bases is not complicated by rearrangements, because carbocations are not intermediates. The mechanism is E2. It is a concerted process in which the base abstracts a proton from the β carbon while the bond between the halogen and the α 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 A β C–D bond is broken more slowly in the E2 dehydrohalogenation of alkyl halides than a β C–H bond. The ratio of the rate constants $k_{\text{H}}/k_{\text{D}}$ is a measure of the **deuterium isotope effect** and has a value in the range 3–8 when a carbon–hydrogen bond breaks in the rate-determining step of a reaction.

Section 5.18 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.



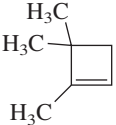
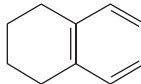
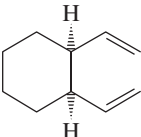

PROBLEMS

5.25 Write structural formulas for each of the following:

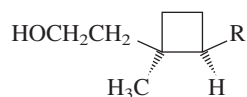
- | | |
|---|---|
| (a) 1-Heptene | (g) 1-Bromo-3-methylcyclohexene |
| (b) 3-Ethyl-2-pentene | (h) 1-Bromo-6-methylcyclohexene |
| (c) <i>cis</i> -3-Octene | (i) 4-Methyl-4-penten-2-ol |
| (d) <i>trans</i> -1,4-Dichloro-2-butene | (j) Vinylcycloheptane |
| (e) (<i>Z</i>)-3-Methyl-2-hexene | (k) 1,1-Diallylcyclopropane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

5.26 Write a structural formula and give two acceptable IUPAC names for each alkene of molecular formula C_7H_{14} that has a *tetrasubstituted* double bond.

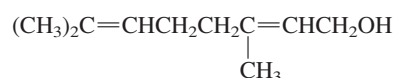
5.27 Give an IUPAC name for each of the following compounds:

- | | | |
|---|---|--|
| (a) $(\text{CH}_3\text{CH}_2)_2\text{C}=\text{CHCH}_3$ | (e)  | (g)  |
| (b) $(\text{CH}_3\text{CH}_2)_2\text{C}=\text{C}(\text{CH}_2\text{CH}_3)_2$ | (f)  | |
| (c) $(\text{CH}_3)_3\text{CCH}=\text{CCl}_2$ | | |
| (d)  | | |

- 5.28 (a) A hydrocarbon isolated from fish oil and from plankton was identified as 2,6,10,14-tetramethyl-2-pentadecene. Write its structure.
- (b) Alkyl isothiocyanates are compounds of the type $\text{RN}=\text{C}=\text{S}$. Write a structural formula for *allyl isothiocyanate*, a pungent-smelling compound isolated from mustard.
- (c) Grandisol is one component of the sex attractant of the boll weevil. Write a structural formula for grandisol given that R in the structure shown is an isopropenyl group.



- 5.29 (a) The sex attractant of the Mediterranean fruit fly is (*E*)-6-nonen-1-ol. Write a structural formula for this compound, showing the stereochemistry of the double bond.
- (b) Geraniol is a naturally occurring substance present in the fragrant oil of many plants. It has a pleasing, rose-like odor. Geraniol is the *E* isomer of



Write a structural formula for geraniol, showing its stereochemistry.

- (c) Nerol is a naturally occurring substance that is a stereoisomer of geraniol. Write its structure.