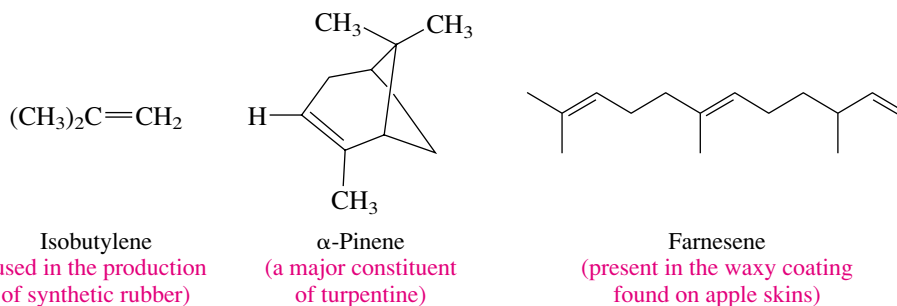


CHAPTER 5

STRUCTURE AND PREPARATION OF ALKENES: ELIMINATION REACTIONS

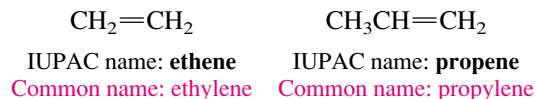
Alkenes are hydrocarbons that contain a carbon-carbon double bond. A carbon-carbon double bond is both an important structural unit and an important functional group in organic chemistry. The shape of an organic molecule is influenced by the presence of this bond, and the double bond is the site of most of the chemical reactions that alkenes undergo. Some representative alkenes include *isobutylene* (an industrial chemical), α -*pinene* (a fragrant liquid obtained from pine trees), and *farnesene* (a naturally occurring alkene with three double bonds).



This chapter is the first of two dealing with alkenes; it describes their structure, bonding, and preparation. Chapter 6 discusses their chemical reactions.

5.1 ALKENE NOMENCLATURE

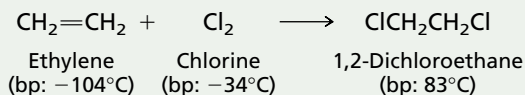
We give alkenes IUPAC names by replacing the *-ane* ending of the corresponding alkane with *-ene*. The two simplest alkenes are **ethene** and **propene**. Both are also well known by their common names *ethylene* and *propylene*.



Ethylene is an acceptable synonym for *ethene* in the IUPAC system. *Propylene*, *isobutylene*, and other common names ending in *-ylene* are not acceptable IUPAC names.

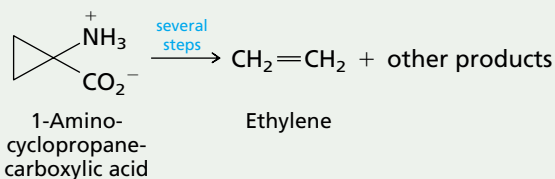
ETHYLENE

Ethylene was known to chemists in the eighteenth century and isolated in pure form in 1795. An early name for ethylene was *gaz oléfiante* (French for “oil-forming gas”), a term suggested to describe the fact that an oily liquid product is formed when two gases—ethylene and chlorine—react with each other.



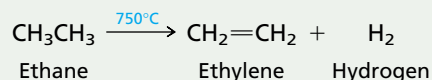
The term *gaz oléfiante* was the forerunner of the general term *olefin*, formerly used as the name of the class of compounds we now call *alkenes*.

Ethylene occurs naturally in small amounts as a plant hormone. Hormones are substances that act as messengers and play regulatory roles in biological processes. Ethylene is involved in the ripening of many fruits, in which it is formed in a complex series of steps from a compound containing a cyclopropane ring:



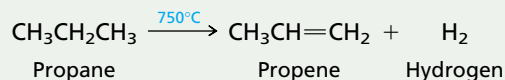
Even minute amounts of ethylene can stimulate ripening, and the rate of ripening increases with the concentration of ethylene. This property is used to advantage, for example, in the marketing of bananas. Bananas are picked green in the tropics, kept green by being stored with adequate ventilation to limit the amount of ethylene present, and then induced to ripen at their destination by passing ethylene over the fruit.*

Ethylene is the cornerstone of the world’s mammoth petrochemical industry and is produced in vast quantities. In a typical year the amount of ethylene produced in the United States (5×10^{10} lb) exceeds the combined weight of all of its people. In one process, ethane from natural gas is heated to bring about its dissociation into ethylene and hydrogen:



This reaction is known as **dehydrogenation** and is simultaneously both a source of ethylene and one of the methods by which hydrogen is prepared on an industrial scale. Most of the hydrogen so generated is subsequently used to reduce nitrogen to ammonia for the preparation of fertilizer.

Similarly, dehydrogenation of propane gives propene:



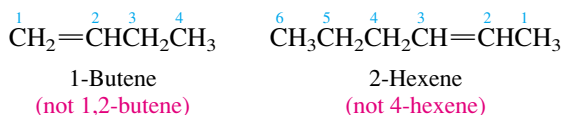
Propene is the second most important petrochemical and is produced on a scale about half that of ethylene.

Almost any hydrocarbon can serve as a starting material for production of ethylene and propene. Cracking of petroleum (Section 2.13) gives ethylene and propene by processes involving cleavage of carbon–carbon bonds of higher molecular weight hydrocarbons.

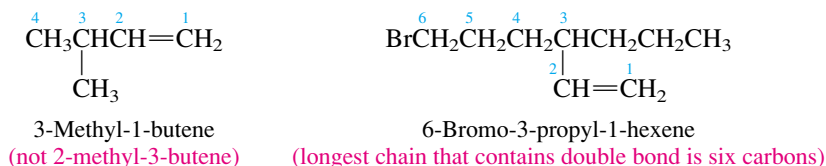
The major uses of ethylene and propene are as starting materials for the preparation of polyethylene and polypropylene plastics, fibers, and films. These and other applications will be described in Chapter 6.

*For a review, see “Ethylene—An Unusual Plant Hormone” in the April 1992 issue of the *Journal of Chemical Education* (pp. 315–318).

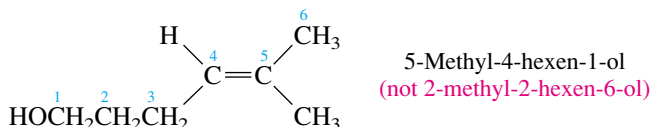
The longest continuous chain that includes the double bond forms the base name of the alkene, and the chain is numbered in the direction that gives the doubly bonded carbons their lower numbers. The locant (or numerical position) of only one of the doubly bonded carbons is specified in the name; it is understood that the other doubly bonded carbon must follow in sequence.



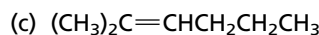
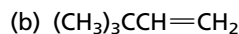
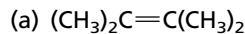
Carbon-carbon double bonds take precedence over alkyl groups and halogens in determining the main carbon chain and the direction in which it is numbered.



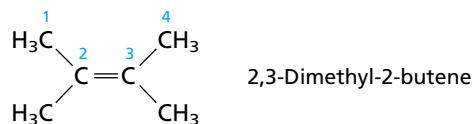
Hydroxyl groups, however, outrank the double bond. Compounds that contain both a double bond and a hydroxyl group use the combined suffix *-en* + *-ol* to signify that both functional groups are present.



PROBLEM 5.1 Name each of the following using IUPAC nomenclature:



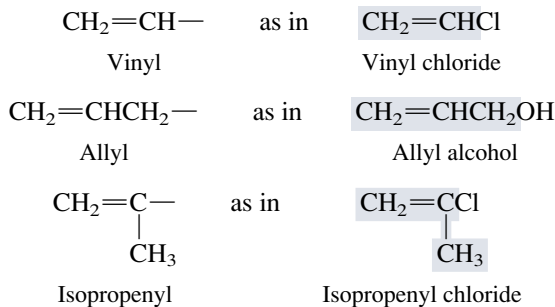
SAMPLE SOLUTION (a) The longest continuous chain in this alkene contains four carbon atoms. The double bond is between C-2 and C-3, and so it is named as a derivative of 2-butene.



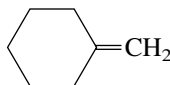
Identifying the alkene as a derivative of 2-butene leaves two methyl groups to be accounted for as substituents attached to the main chain. This alkene is 2,3-dimethyl-2-butene. (It is sometimes called *tetramethylethylene*, but that is a common name, not an IUPAC name.)

We noted in Section 2.10 that the common names of certain frequently encountered *alkyl* groups, such as isopropyl and *tert*-butyl, are acceptable in the IUPAC system. Three *alkenyl* groups—**vinyl**, **allyl**, and **isopropenyl**—are treated the same way.

Vinyl chloride is an industrial chemical produced in large amounts (10^{10} lb/year in the United States) and is used in the preparation of poly(vinyl chloride). Poly(vinyl chloride), often called simply *vinyl*, has many applications, including siding for houses, wall coverings, and PVC piping.

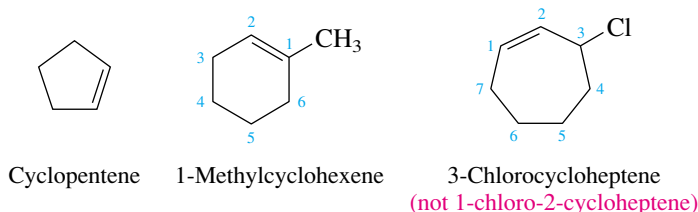


When a CH_2 group is doubly bonded to a ring, the prefix *methylene* is added to the name of the ring.



Methylenecyclohexane

Cycloalkenes and their derivatives are named by adapting cycloalkane terminology to the principles of alkene nomenclature.



No locants are needed in the absence of substituents; it is understood that the double bond connects C-1 and C-2. Substituted cycloalkenes are numbered beginning with the double bond, proceeding through it, and continuing in sequence around the ring. The direction of numbering is chosen so as to give the lower of two possible locants to the substituent.



PROBLEM 5.2 Write structural formulas or build molecular models and give the IUPAC names of all the monochloro-substituted derivatives of cyclopentene.

5.2 STRUCTURE AND BONDING IN ALKENES

The structure of ethylene and the orbital hybridization model for the double bond were presented in Section 1.17. To review, Figure 5.1 depicts the planar structure of ethylene, its bond distances, and its bond angles. Each of the carbon atoms is sp^2 -hybridized, and the double bond possesses a σ component and a π component. The σ component results when an sp^2 orbital of one carbon, oriented so that its axis lies along the internuclear axis, overlaps with a similarly disposed sp^2 orbital of the other carbon. Each sp^2 orbital contains one electron, and the resulting σ bond contains two of the four electrons of the double bond. The π bond contributes the other two electrons and is formed by a “side-by-side” overlap of singly occupied p orbitals of the two carbons.

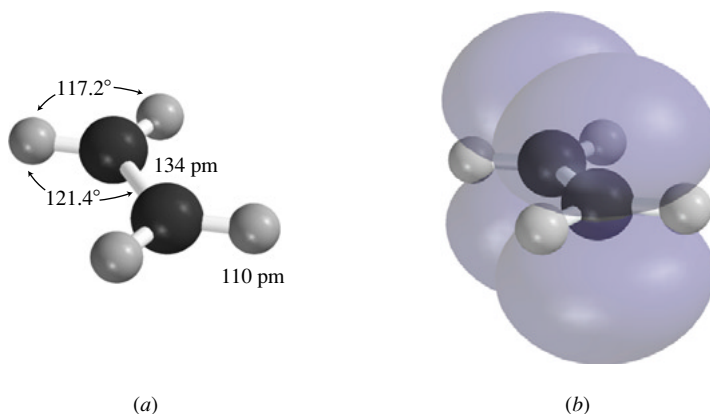
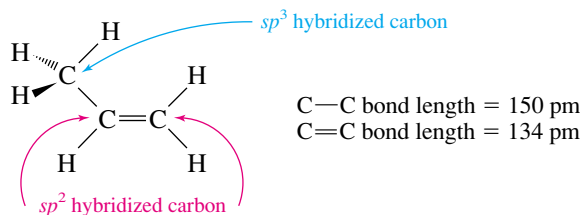


FIGURE 5.1 (a) The framework of σ bonds in ethylene showing bond distances in picometers and bond angles in degrees. All six atoms are coplanar. The carbon-carbon bond is a double bond made up of the σ component shown and the π component illustrated in *b*. (b) The p orbitals of two sp^2 hybridized carbons overlap to produce a π bond. An electron pair in the π bond is shared by the two carbons.

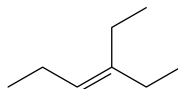
The double bond in ethylene is stronger than the C—C single bond in ethane, but it is not twice as strong. The C=C bond energy is 605 kJ/mol (144.5 kcal/mol) in ethylene versus 368 kJ/mol (88 kcal/mol) for the C—C bond in ethane. Chemists do not agree on exactly how to apportion the total C=C bond energy between its σ and π components, but all agree that the π bond is weaker than the σ bond.

There are two different types of carbon-carbon bonds in propene, $\text{CH}_3\text{CH}=\text{CH}_2$. The double bond is of the $\sigma + \pi$ type, and the bond to the methyl group is a σ bond formed by sp^3 - sp^2 overlap.



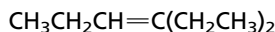
The simplest arithmetic approach subtracts the C—C σ bond energy of ethane (368 kJ/mol; 88 kcal/mol) from the C=C bond energy of ethylene (605 kJ/mol; 144.5 kcal/mol). This gives a value of 237 kJ/mol (56.5 kcal/mol) for the π bond energy.

PROBLEM 5.3 We can use bond-line formulas to represent alkenes in much the same way that we use them to represent alkanes. Consider the following alkene:



- What is the molecular formula of this alkene?
- What is its IUPAC name?
- How many carbon atoms are sp^2 -hybridized in this alkene? How many are sp^3 -hybridized?
- How many σ bonds are of the sp^2 - sp^3 type? How many are of the sp^3 - sp^3 type?

SAMPLE SOLUTION (a) Recall when writing bond-line formulas for hydrocarbons that a carbon occurs at each end and at each bend in a carbon chain. The appropriate number of hydrogens are attached so that each carbon has four bonds. Thus the compound shown is

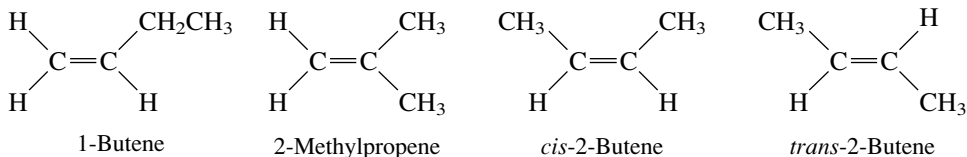


The general molecular formula for an alkene is C_nH_{2n} . Ethylene is C_2H_4 ; propene is C_3H_6 . Counting the carbons and hydrogens of the compound shown (C_8H_{16}) reveals that it, too, corresponds to C_nH_{2n} .

5.3 ISOMERISM IN ALKENES

Although ethylene is the only two-carbon alkene, and propene the only three-carbon alkene, there are *four* isomeric alkenes of molecular formula C_4H_8 :

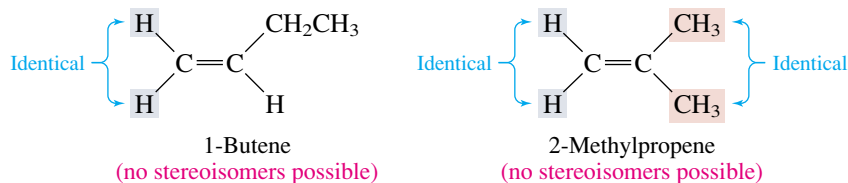
Make molecular models of *cis*- and *trans*-2-butene to verify that they are different.



1-Butene has an unbranched carbon chain with a double bond between C-1 and C-2. It is a constitutional isomer of the other three. Similarly, 2-methylpropene, with a branched carbon chain, is a constitutional isomer of the other three.

The pair of isomers designated *cis*- and *trans*-2-butene have the same constitution; both have an unbranched carbon chain with a double bond connecting C-2 and C-3. They differ from each other, however, in that the *cis* isomer has both of its methyl groups on the same side of the double bond, but the methyl groups in the *trans* isomer are on opposite sides of the double bond. Recall from Section 3.12 that isomers that have the same constitution but differ in the arrangement of their atoms in space are classified as *stereoisomers*. *cis*-2-Butene and *trans*-2-butene are stereoisomers, and the terms “*cis*” and “*trans*” specify the *configuration* of the double bond.

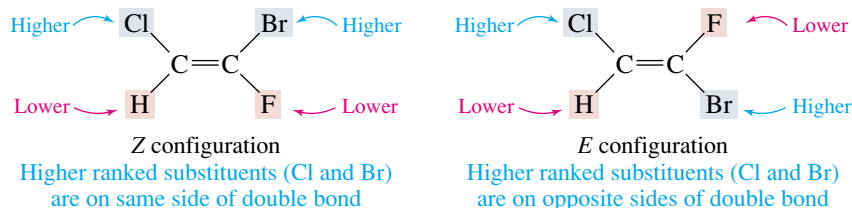
Cis-trans stereoisomerism in alkenes is not possible when one of the doubly bonded carbons bears two identical substituents. Thus, neither 1-butene nor 2-methylpropene can have stereoisomers.



The activation energy for rotation about a typical carbon-carbon double bond is very high—on the order of 250 kJ/mol (about 60 kcal/mol). This quantity may be taken as a measure of the π bond contribution to the total C=C bond strength of 605 kJ/mol (144.5 kcal/mol) in ethylene and compares closely with the value estimated by manipulation of thermochemical data on page 171.

PROBLEM 5.4 How many alkenes have the molecular formula C_5H_{10} ? Write their structures and give their IUPAC names. Specify the configuration of stereoisomers as *cis* or *trans* as appropriate.

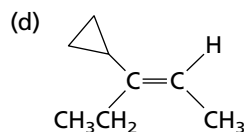
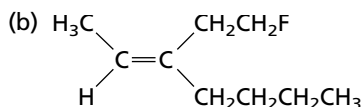
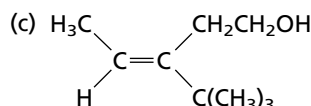
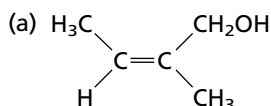
In principle, *cis*-2-butene and *trans*-2-butene may be interconverted by rotation about the C-2=C-3 *double* bond. However, unlike rotation about the C-2—C-3 *single* bond in butane, which is quite fast, interconversion of the stereoisomeric 2-butenes does not occur under normal circumstances. It is sometimes said that rotation about a carbon-carbon double bond is *restricted*, but this is an understatement. Conventional laboratory sources of heat do not provide enough thermal energy for rotation about the double bond in alkenes to take place. As shown in Figure 5.2, rotation about a double bond requires the *p* orbitals of C-2 and C-3 to be twisted from their stable parallel alignment—in effect, the π component of the double bond must be broken at the transition state.



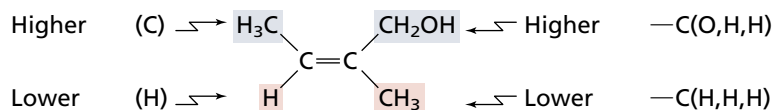
The priority rules were developed by R. S. Cahn and Sir Christopher Ingold (England) and Vladimir Prelog (Switzerland) in the context of a different aspect of organic stereochemistry; they will appear again in Chapter 7.

The substituent groups on the double bonds of most alkenes are, of course, more complicated than in this example. The rules for ranking substituents, especially alkyl groups, are described in Table 5.1.

PROBLEM 5.6 Determine the configuration of each of the following alkenes as *Z* or *E* as appropriate:



SAMPLE SOLUTION (a) One of the doubly bonded carbons bears a methyl group and a hydrogen. According to the rules of Table 5.1, methyl outranks hydrogen. The other carbon atom of the double bond bears a methyl and a $\text{—CH}_2\text{OH}$ group. The $\text{—CH}_2\text{OH}$ group is of higher priority than methyl.



Higher ranked substituents are on the same side of the double bond; the configuration is *Z*.

A table on the inside back cover (right page) lists some of the more frequently encountered atoms and groups in order of increasing precedence. You should not attempt to memorize this table, but should be able to derive the relative placement of one group versus another.

5.5 PHYSICAL PROPERTIES OF ALKENES

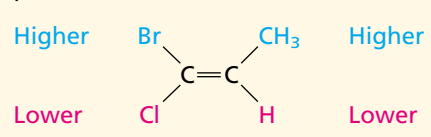
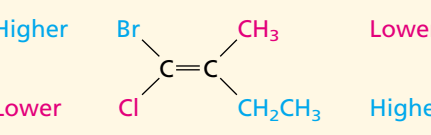
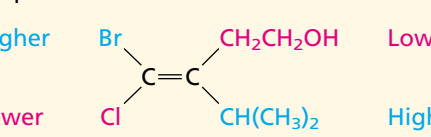
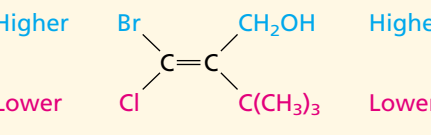

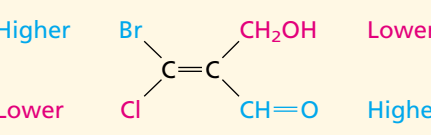
Alkenes resemble alkanes in most of their physical properties. The lower molecular weight alkenes through C_4H_8 are gases at room temperature and atmospheric pressure.

The dipole moments of most alkenes are quite small. Among the C_4H_8 isomers, 1-butene, *cis*-2-butene, and 2-methylpropene have dipole moments in the 0.3–0.5 D range; *trans*-2-butene has no dipole moment. Nevertheless, we can learn some things about alkenes by looking at the effect of substituents on dipole moments.

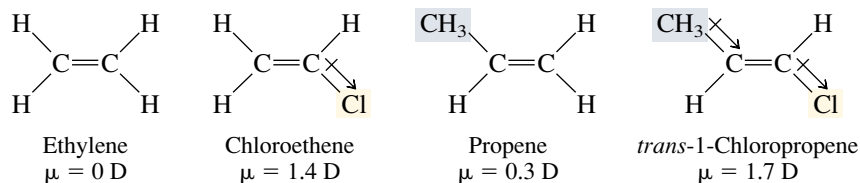
Experimental measurements of dipole moments give size, but not direction. We normally deduce the overall direction by examining the directions of individual bond

The physical properties of selected alkenes are collected in Appendix 1.

TABLE 5.1 Cahn–Ingold–Prelog Priority Rules

Rule	Example
<p>1. Higher atomic number takes precedence over lower. Bromine (atomic number 35) outranks chlorine (atomic number 17). Methyl (C, atomic number 6) outranks hydrogen (atomic number 1).</p>	<p>The compound</p>  <p>has the <i>Z</i> configuration. Higher ranked atoms (Br and C of CH₃) are on the same side of the double bond.</p>
<p>2. When two atoms directly attached to the double bond are identical, compare the atoms attached with these two on the basis of their atomic numbers. Precedence is determined at the first point of difference:</p> <p>Ethyl [—C(C,H,H)] outranks methyl [—C(H,H,H)]</p> <p>Similarly, <i>tert</i>-butyl outranks isopropyl, and isopropyl outranks ethyl:</p> $-C(CH_3)_3 > -CH(CH_3)_2 > -CH_2CH_3$ $-C(C,C,C) > -C(C,C,H) > -C(C,H,H)$	<p>The compound</p>  <p>has the <i>E</i> configuration.</p>
<p>3. Work outward from the point of attachment, comparing all the atoms attached to a particular atom before proceeding further along the chain:</p> <p>—CH(CH₃)₂ [—C(C,C,H)] outranks —CH₂CH₂OH [—C(C,H,H)]</p>	<p>The compound</p>  <p>has the <i>E</i> configuration.</p>
<p>4. When working outward from the point of attachment, always evaluate substituent atoms one by one, never as a group. Since oxygen has a higher atomic number than carbon,</p> <p>—CH₂OH [—C(O,H,H)] outranks —C(CH₃)₃ [—C(C,C,C)]</p>	<p>The compound</p>  <p>has the <i>Z</i> configuration.</p>
<p>5. An atom that is multiply bonded to another atom is considered to be replicated as a substituent on that atom:</p> <p> is treated as if it were —C(O,O,H)</p> <p>The group —CH=O [—C(O,O,H)] outranks —CH₂OH [—C(O,H,H)]</p>	<p>The compound</p>  <p>has the <i>E</i> configuration.</p>

dipoles. With alkenes the basic question concerns the alkyl groups attached to $C=C$. *Does an alkyl group donate electrons to or withdraw electrons from a double bond?* This question can be approached by comparing the effect of an alkyl group, methyl for example, with other substituents.

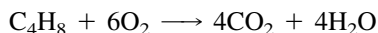


Ethylene, of course, has no dipole moment. Replacing one of its hydrogens by chlorine gives chloroethene, which has a dipole moment of 1.4 D. The effect is much smaller when one of the hydrogens is replaced by methyl; $CH_3CH=CH_2$ has a dipole moment of only 0.3 D. Now place CH_3 and Cl *trans* to each other on the double bond. If methyl releases electrons better than H, then the dipole moment of *trans*- $CH_3CH=CHCl$ should be larger than that of $CH_2=CHCl$, because the effects of CH_3 and Cl reinforce each other. If methyl is electron attracting, the opposite should occur, and the dipole moment of *trans*- $CH_3CH=CHCl$ will be smaller than 1.4 D. In fact, the dipole moment of *trans*- $CH_3CH=CHCl$ is larger than that of $CH_2=CHCl$, indicating that a methyl group is an electron-donating substituent on the double bond.

A methyl group releases electrons to a double bond in much the same way that it releases electrons to the positively charged carbon of a carbocation—by an inductive effect and by hyperconjugation (Figure 5.3). Other alkyl groups behave similarly and, as we go along, we'll see several ways in which the electron-releasing effects of alkyl substituents influence the properties of alkenes. The first is described in the following section.

5.6 RELATIVE STABILITIES OF ALKENES

Earlier (Sections 2.15, 3.12) we saw how to use heats of combustion to compare the stabilities of isomeric alkanes. We can do the same thing with isomeric alkenes. Consider the heats of combustion of the four isomeric alkenes of molecular formula C_4H_8 . All undergo combustion according to the equation



When the heats of combustion of the isomers are plotted on a common scale as in Figure 5.4, we see that the isomer of highest energy (the least stable one) is 1-butene, $CH_2=CHCH_2CH_3$. The isomer of lowest energy (most stable) is 2-methylpropene $(CH_3)_2C=CH_2$.

sp^2 -hybridized carbons of an alkene are more electronegative than sp^3 -hybridized carbon and are stabilized by electron-donating substituents.

Methyl group is a better electron-donating substituent than hydrogen.

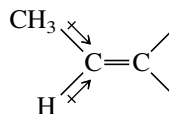


FIGURE 5.3 Alkyl groups donate electrons to sp^2 -hybridized carbons of an alkene.

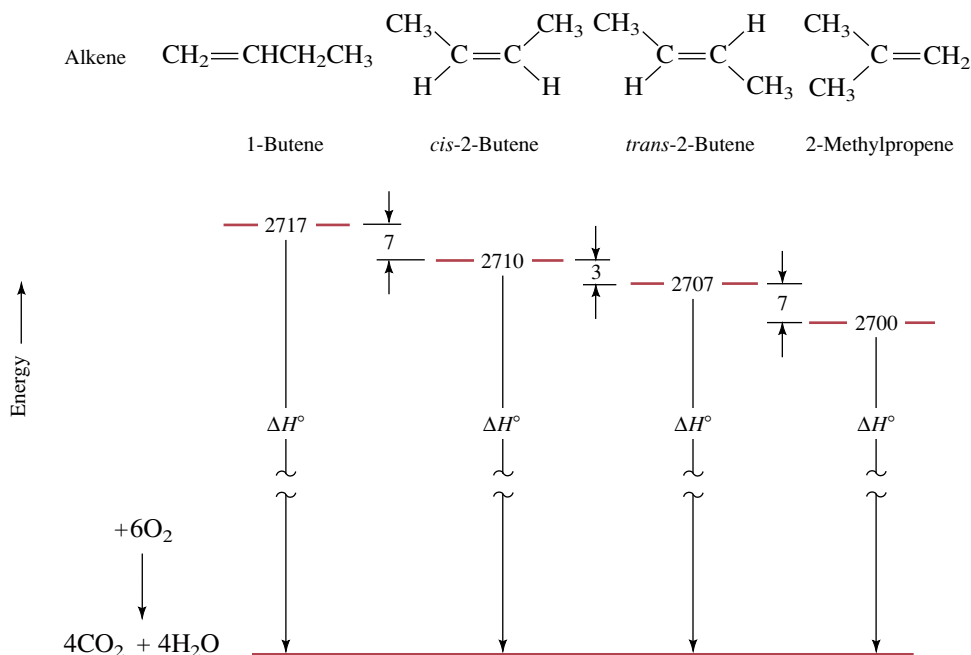


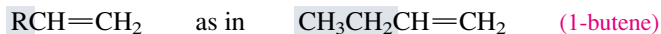
FIGURE 5.4 Heats of combustion of C₄H₈ alkene isomers plotted on a common scale. All energies are in kilojoules per mole. (An energy difference of 3 kJ/mol is equivalent to 0.7 kcal/mol; 7 kJ/mol is equivalent to 1.7 kcal/mol.)

Analogous data for a host of alkenes tell us that the most important factors governing alkene stability are:

1. *Degree of substitution* (alkyl substituents stabilize a double bond)
2. *Van der Waals strain* (destabilizing when alkyl groups are *cis* to each other)

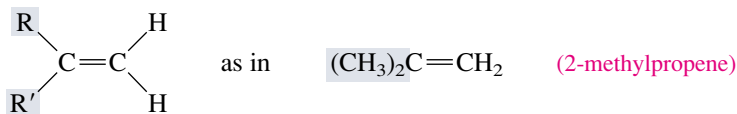
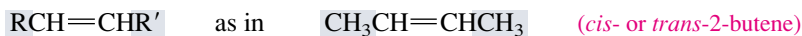
Degree of substitution. We classify double bonds as **monosubstituted**, **disubstituted**, **trisubstituted**, or **tetrasubstituted** according to the number of carbon atoms that are *directly* attached to the C=C structural unit.

Monosubstituted alkenes:



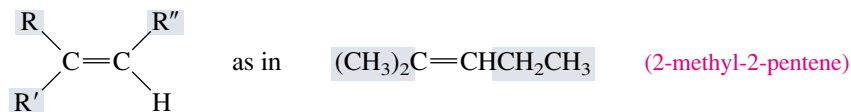
Disubstituted alkenes:

(R and R' may be the same or different)



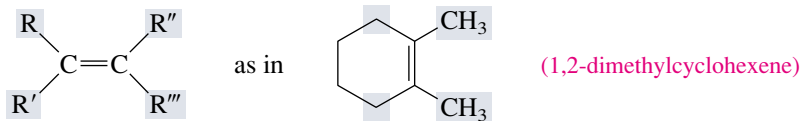
Trisubstituted alkenes:

(R, R', and R'' may be the same or different)



Tetrasubstituted alkenes:

(R, R', R'', and R''' may be the same or different)

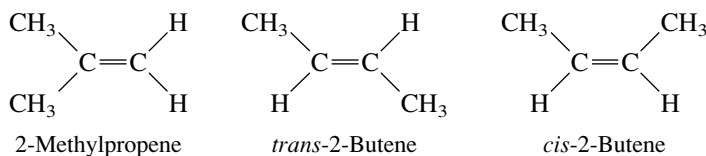


In the example shown, each of the highlighted ring carbons counts as a separate substituent on the double bond.

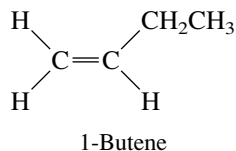


PROBLEM 5.7 Write structural formulas or build molecular models and give the IUPAC names for all the alkenes of molecular formula C_6H_{12} that contain a trisubstituted double bond. (Don't forget to include stereoisomers.)

From the heats of combustion of the C_4H_8 alkenes in Figure 5.5 we see that each of the disubstituted alkenes



is more stable than the monosubstituted alkene



In general, alkenes with more highly substituted double bonds are more stable than isomers with less substituted double bonds.



PROBLEM 5.8 Give the structure or make a molecular model of the most stable C_6H_{12} alkene.

Like the sp^2 -hybridized carbons of carbocations and free radicals, the sp^2 -hybridized carbons of double bonds are electron attracting, and alkenes are stabilized by substituents that release electrons to these carbons. As we saw in the preceding section, alkyl groups are better electron-releasing substituents than hydrogen and are, therefore, better able to stabilize an alkene.

An effect that results when two or more atoms or groups interact so as to alter the electron distribution in a system is called an **electronic effect**. The greater stability of more highly substituted alkenes is an example of an electronic effect.

van der Waals strain. Alkenes are more stable when large substituents are *trans* to each other than when they are *cis*. As was seen in Figure 5.4, *trans*-2-butene has a lower heat of combustion and is more stable than *cis*-2-butene. The energy difference between the two is 3 kJ/mol (0.7 kcal/mol). The source of this energy difference is illustrated in

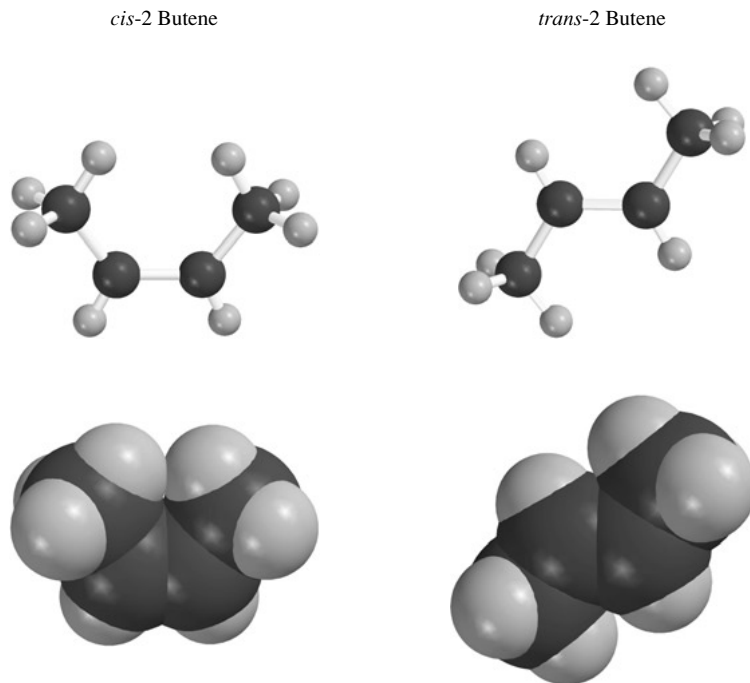
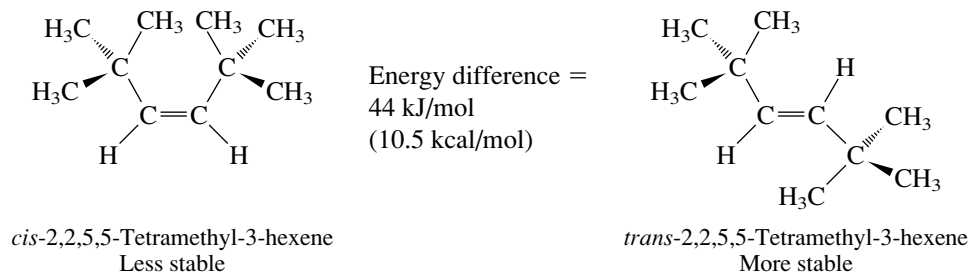


FIGURE 5.5 Ball-and-spoke and space-filling models of *cis*- and *trans*-2-butene. The space-filling model shows the serious van der Waals strain between two of the hydrogens in *cis*-2-butene. The molecule adjusts by expanding those bond angles that increase the separation between the crowded atoms. The combination of angle strain and van der Waals strain makes *cis*-2-butene less stable than *trans*-2-butene.

Figure 5.5, where it is seen that methyl groups approach each other very closely in *cis*-2-butene, but the *trans* isomer is free of strain. An effect that results when two or more atoms are close enough in space that a repulsion occurs between them is one type of **steric effect**. The greater stability of *trans* alkenes compared with their *cis* counterparts is an example of a steric effect.

PROBLEM 5.9 Arrange the following alkenes in order of decreasing stability: 1-pentene; (*E*)-2-pentene; (*Z*)-2-pentene; 2-methyl-2-butene.

The difference in stability between stereoisomeric alkenes is even more pronounced with larger alkyl groups on the double bond. A particularly striking example compares *cis*- and *trans*-2,2,5,5-tetramethyl-3-hexene, in which the heat of combustion of the *cis* stereoisomer is 44 kJ/mol (10.5 kcal/mol) higher than that of the *trans*. The *cis* isomer is destabilized by the large van der Waals strain between the bulky *tert*-butyl groups on the same side of the double bond.



A similar steric effect was seen in Section 3.12, where van der Waals strain between methyl groups on the same side of the ring made *cis*-1,2-dimethylcyclopropane less stable than its *trans* stereoisomer.

The common names of these alkenes are *cis*- and *trans*-di-*tert*-butylethylene. In cases such as this the common names are somewhat more convenient than the IUPAC names because they are more readily associated with molecular structure.

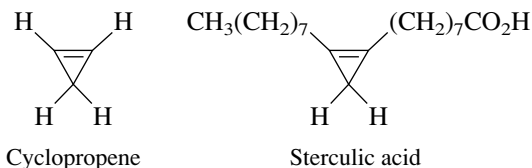


PROBLEM 5.10 Despite numerous attempts, the alkene 3,4-di-*tert*-butyl-2,2,5,5-tetramethyl-3-hexene has never been synthesized. Can you explain why? Try making a space-filling model of this compound.

5.7 CYCLOALKENES

Double bonds are accommodated by rings of all sizes. The simplest cycloalkene, cyclopropene, was first synthesized in 1922. A cyclopropene ring is present in sterculic acid, a substance derived from one of the components of the oil present in the seeds of a tree (*Sterculia foelida*) that grows in the Philippines and Indonesia.

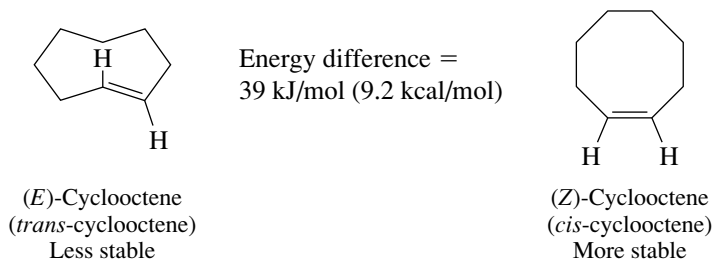
Sterculic acid and related substances are the subject of an article in the July 1982 issue of *Journal of Chemical Education* (pp. 539–543).



As we saw in Section 3.9, cyclopropane is destabilized by angle strain because its 60° bond angles are much smaller than the normal 109.5° angles associated with sp^3 -hybridized carbon. Cyclopropene is even more strained because the deviation of the bond angles at its doubly bonded carbons from the normal sp^2 hybridization value of 120° is greater still. Cyclobutene has, of course, less angle strain than cyclopropene, and the angle strain of cyclopentene, cyclohexene, and higher cycloalkenes is negligible.

So far we have represented cycloalkenes by structural formulas in which the double bonds are of the *cis* configuration. If the ring is large enough, however, a *trans* stereoisomer is also possible. The smallest *trans* cycloalkene that is stable enough to be isolated and stored in a normal way is *trans*-cyclooctene.

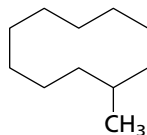
Make molecular models of (*E*) and (*Z*)-cyclooctene and compare their H—C=C—H dihedral angles.



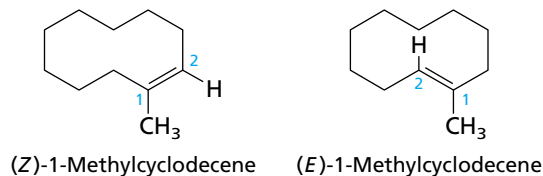
trans-Cycloheptene has been prepared and studied at low temperature (-90°C) but is too reactive to be isolated and stored at room temperature. Evidence has also been presented for the fleeting existence of the even more strained *trans*-cyclohexene as a reactive intermediate in certain reactions.

PROBLEM 5.11 Place a double bond in the carbon skeleton shown so as to represent

- | | |
|--------------------------------------|--------------------------------------|
| (a) (<i>Z</i>)-1-Methylcyclodecene | (d) (<i>E</i>)-3-Methylcyclodecene |
| (b) (<i>E</i>)-1-Methylcyclodecene | (e) (<i>Z</i>)-5-Methylcyclodecene |
| (c) (<i>Z</i>)-3-Methylcyclodecene | (f) (<i>E</i>)-5-Methylcyclodecene |



SAMPLE SOLUTION (a) and (b) Since the methyl group must be at C-1, there are only two possible places to put the double bond:

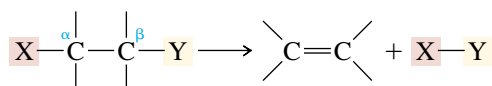


In the *Z* stereoisomer the two lower priority substituents—the methyl group and the hydrogen—are on the same side of the double bond. In the *E* stereoisomer these substituents are on opposite sides of the double bond. The ring carbons are the higher ranking substituents at each end of the double bond.

Because larger rings have more carbons with which to span the ends of a double bond, the strain associated with a trans cycloalkene decreases with increasing ring size. The strain eventually disappears when a 12-membered ring is reached and *cis* and *trans*-cyclododecene are of approximately equal stability. When the rings are larger than 12 membered, trans cycloalkenes are more stable than *cis*. In these cases, the ring is large enough and flexible enough that it is energetically similar to a noncyclic alkene. As in noncyclic *cis* alkenes, van der Waals strain between carbons on the same side of the double bond destabilizes a *cis* cycloalkene.

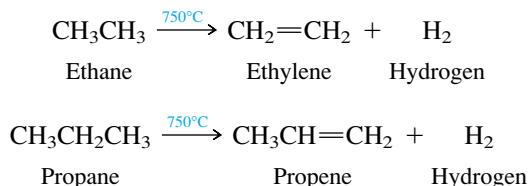
5.8 PREPARATION OF ALKENES: ELIMINATION REACTIONS

The rest of this chapter describes how alkenes are prepared by reactions of the type:



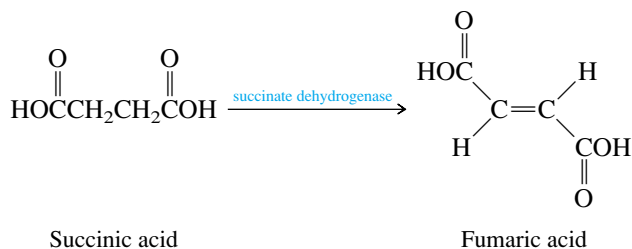
Alkene formation requires that *X* and *Y* be substituents on adjacent carbon atoms. By making *X* the reference atom and identifying the carbon attached to it as the α carbon, we see that atom *Y* is a substituent on the β carbon. Carbons successively more remote from the reference atom are designated γ , δ , and so on. Only β elimination reactions will be discussed in this chapter. [Beta (β) elimination reactions are also known as *1,2 eliminations*.]

You are already familiar with one type of β elimination, having seen in Section 5.1 that ethylene and propene are prepared on an industrial scale by the high-temperature *dehydrogenation* of ethane and propane. Both reactions involve β elimination of H_2 .



Many reactions classified as dehydrogenations occur within the cells of living systems at 25°C . H_2 is not one of the products, however. Instead, the hydrogens are lost in separate steps of an enzyme-catalyzed process. The enzyme indicated in the reaction:

A quote from a biochemistry text is instructive here. "This is not an easy reaction in organic chemistry. It is, however, a very important type of reaction in metabolic chemistry and is an integral step in the oxidation of carbohydrates, fats, and several amino acids." G. L. Zubay, *Biochemistry*, 4th ed., William C. Brown Publishers, 1996, p. 333.

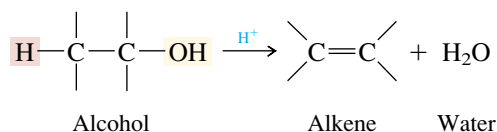


is a special kind, known as a *flavoprotein*.

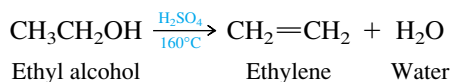
Dehydrogenation of alkanes is not a practical *laboratory* synthesis for the vast majority of alkenes. The principal methods by which alkenes are prepared in the laboratory are two other β eliminations: the **dehydration of alcohols** and the **dehydrohalogenation of alkyl halides**. A discussion of these two methods makes up the remainder of this chapter.

5.9 DEHYDRATION OF ALCOHOLS

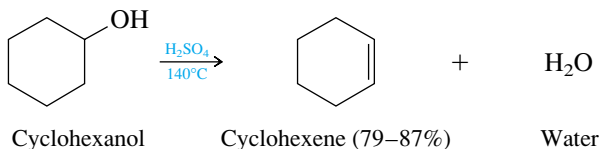
In the dehydration of alcohols, the H and OH are lost from adjacent carbons. An acid catalyst is necessary.



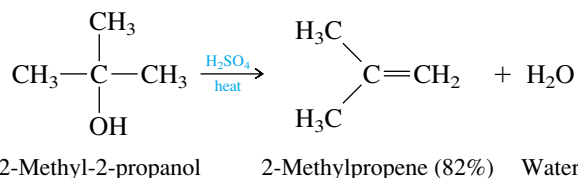
Before dehydrogenation of ethane became the dominant method, ethylene was prepared by heating ethyl alcohol with sulfuric acid.



Other alcohols behave similarly. Secondary alcohols undergo elimination at lower temperatures than primary alcohols,



and tertiary alcohols at lower temperatures than secondary alcohols.



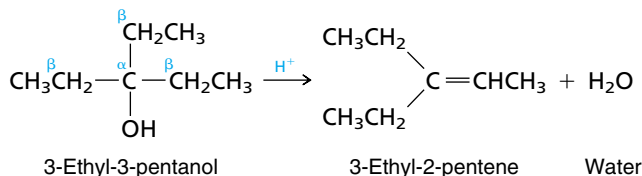
HSO_4^- and H_3PO_4 are very similar in acid strength. Both are much weaker than H_2SO_4 , which is a strong acid.

Sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) are the acids most frequently used in alcohol dehydrations. Potassium hydrogen sulfate (KHSO_4) is also often used.

PROBLEM 5.12 Identify the alkene obtained on dehydration of each of the following alcohols:

- (a) 3-Ethyl-3-pentanol (c) 2-Propanol
 (b) 1-Propanol (d) 2,3,3-Trimethyl-2-butanol

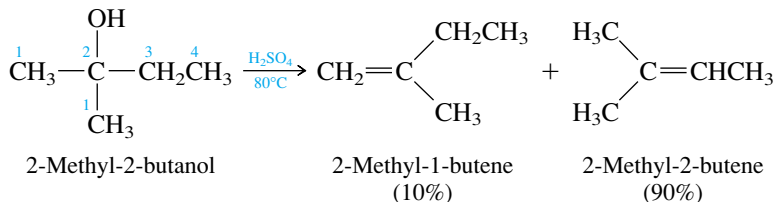
SAMPLE SOLUTION (a) The hydrogen and the hydroxyl are lost from adjacent carbons in the dehydration of 3-ethyl-3-pentanol.



The hydroxyl group is lost from a carbon that bears three equivalent ethyl substituents. Beta elimination can occur in any one of three equivalent directions to give the same alkene, 3-ethyl-2-pentene.

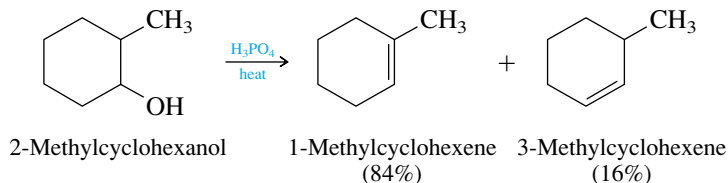
5.10 REGIOSELECTIVITY IN ALCOHOL DEHYDRATION: THE ZAITSEV RULE

In the preceding examples, including those of Problem 5.12, only a single alkene could be formed from each alcohol by β elimination. What about elimination in alcohols such as 2-methyl-2-butanol, in which dehydration can occur in two different directions to give alkenes that are constitutional isomers? Here, a double bond can be generated between C-1 and C-2 or between C-2 and C-3. Both processes occur but not nearly to the same extent. Under the usual reaction conditions 2-methyl-2-butene is the major product, and 2-methyl-1-butene the minor one.



Dehydration of this alcohol is selective in respect to its *direction*. Elimination occurs in the direction that leads to the double bond between C-2 and C-3 more than between C-2 and C-1. Reactions that can proceed in more than one direction, but in which one direction is preferred, are said to be *regioselective*.

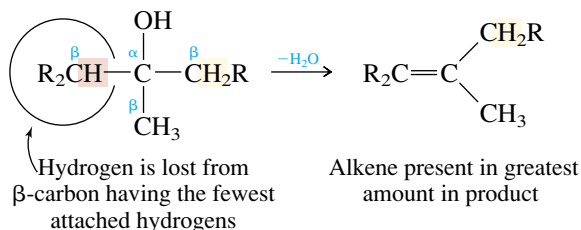
As a second example, consider the regioselective dehydration of 2-methylcyclohexanol to yield a mixture of 1-methylcyclohexene (major) and 3-methylcyclohexene (minor).



The term "regioselective" was coined by Alfred Hassner, then at the University of Colorado, in a paper published in the *Journal of Organic Chemistry* in 1968.

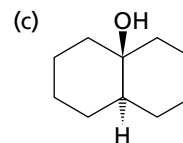
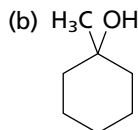
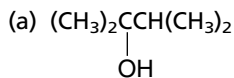
Although Russian, Zaitsev published most of his work in German scientific journals, where his name was transliterated as Saytzeff. The spelling used here (Zaitsev) corresponds to the currently preferred style.

In 1875, Alexander M. Zaitsev of the University of Kazan (Russia) set forth a generalization describing the regioselectivity β -eliminations. **Zaitsev's rule** summarizes the results of numerous experiments in which alkene mixtures were produced by β elimination. In its original form, Zaitsev's rule stated that *the alkene formed in greatest amount is the one that corresponds to removal of the hydrogen from the β carbon having the fewest hydrogens*.

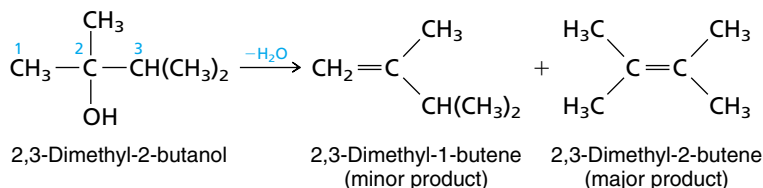


Zaitsev's rule as applied to the acid-catalyzed dehydration of alcohols is now more often expressed in a different way: *β elimination reactions of alcohols yield the most highly substituted alkene as the major product*. Since, as was discussed in Section 5.6, the most highly substituted alkene is also normally the most stable one, Zaitsev's rule is sometimes expressed as a preference for *predominant formation of the most stable alkene that could arise by β elimination*.

PROBLEM 5.13 Each of the following alcohols has been subjected to acid-catalyzed dehydration and yields a mixture of two isomeric alkenes. Identify the two alkenes in each case, and predict which one is the major product on the basis of the Zaitsev rule.



SAMPLE SOLUTION (a) Dehydration of 2,3-dimethyl-2-butanol can lead to either 2,3-dimethyl-1-butene by removal of a C-1 hydrogen or to 2,3-dimethyl-2-butene by removal of a C-3 hydrogen.

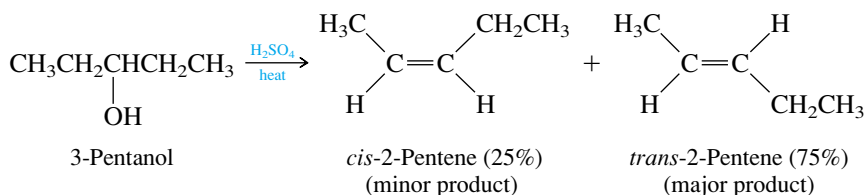


The major product is 2,3-dimethyl-2-butene. It has a tetrasubstituted double bond and is more stable than 2,3-dimethyl-1-butene, which has a disubstituted double bond. The major alkene arises by loss of a hydrogen from the β carbon that has fewer attached hydrogens (C-3) rather than from the β carbon that has the greater number of hydrogens (C-1).

5.11 STEREOSELECTIVITY IN ALCOHOL DEHYDRATION

In addition to being regioselective, alcohol dehydrations are **stereoselective**. A stereoselective reaction is one in which a single starting material can yield two or more stereoisomeric products, but gives one of them in greater amounts than any other.

Alcohol dehydrations tend to produce the more stable stereoisomer of an alkene. Dehydration of 3-pentanol, for example, yields a mixture of *trans*-2-pentene and *cis*-2-pentene in which the more stable *trans* stereoisomer predominates.



PROBLEM 5.14 What three alkenes are formed in the acid-catalyzed dehydration of 2-pentanol?

The biological dehydrogenation of succinic acid described in Section 5.8 is 100% stereoselective. Only fumaric acid, which has a *trans* double bond, is formed. High levels of stereoselectivity are characteristic of enzyme-catalyzed reactions.

5.12 THE MECHANISM OF ACID-CATALYZED DEHYDRATION OF ALCOHOLS

The dehydration of alcohols and the conversion of alcohols to alkyl halides by treatment with hydrogen halides (Section 4.8) are similar in two important ways:

1. Both reactions are promoted by acids.
2. The relative reactivity of alcohols decreases in the order tertiary > secondary > primary.

These common features suggest that carbocations are key intermediates in alcohol dehydration, just as they are in the conversion of alcohols to alkyl halides. Figure 5.6 portrays a three-step mechanism for the sulfuric acid-catalyzed dehydration of *tert*-butyl alcohol. Steps 1 and 2 describe the generation of *tert*-butyl cation by a process similar to that which led to its formation as an intermediate in the reaction of *tert*-butyl alcohol with hydrogen chloride. Step 3 in Figure 5.6, however, is new to us and is the step in which the double bond is formed.

Step 3 is an acid-base reaction in which the carbocation acts as a Brønsted acid, transferring a proton to a Brønsted base (water). This is the property of carbocations that is of the most significance to elimination reactions. Carbocations are strong acids; they are the conjugate acids of alkenes and readily lose a proton to form alkenes. Even weak bases such as water are sufficiently basic to abstract a proton from a carbocation.

Step 3 in Figure 5.6 shows water as the base which abstracts a proton from the carbocation. Other Brønsted bases present in the reaction mixture that can function in the same way include *tert*-butyl alcohol and hydrogen sulfate ion.

PROBLEM 5.15 Write a structural formula for the carbocation intermediate formed in the dehydration of each of the alcohols in Problem 5.13 (Section 5.10). Using curved arrows, show how each carbocation is deprotonated by water to give a mixture of alkenes.

SAMPLE SOLUTION (a) The carbon that bears the hydroxyl group in the starting alcohol is the one that becomes positively charged in the carbocation.

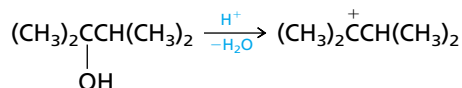
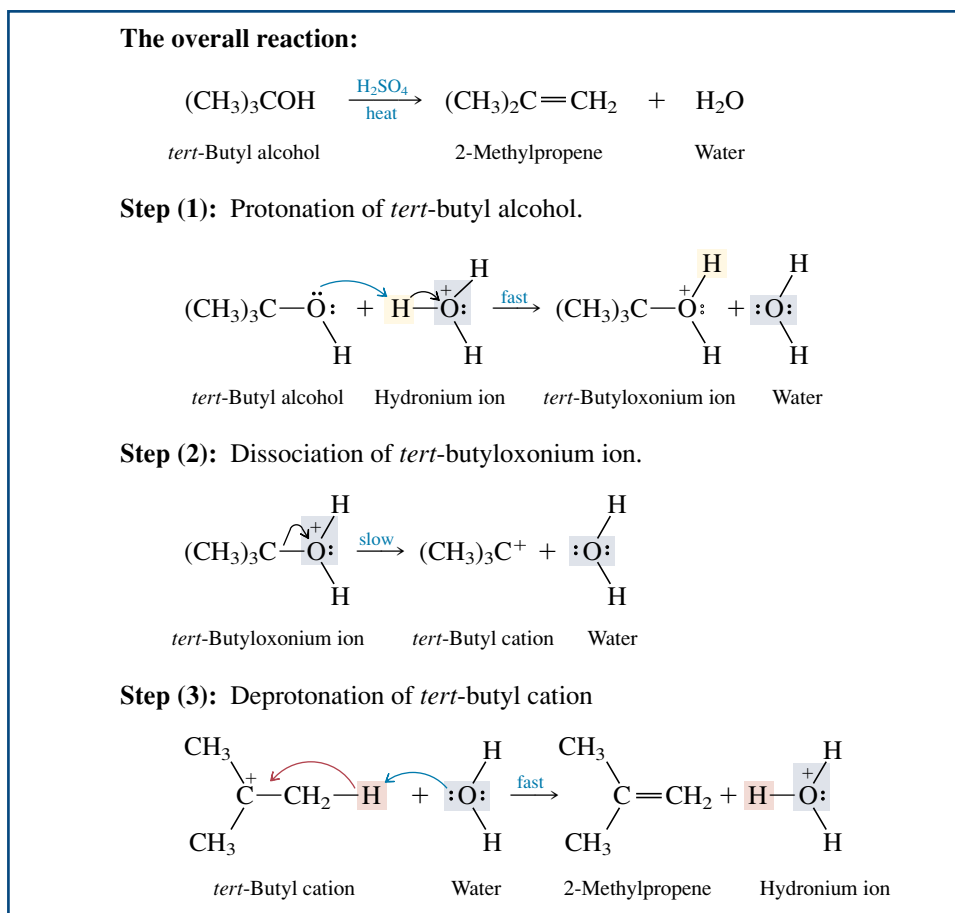
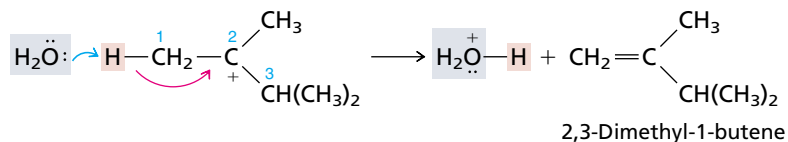


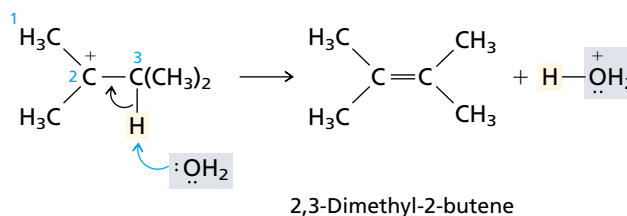
FIGURE 5.6 The mechanism for the acid-catalyzed dehydration of *tert*-butyl alcohol.



Water may remove a proton from either C-1 or C-3 of this carbocation. Loss of a proton from C-1 yields the minor product 2,3-dimethyl-1-butene. (This alkene has a disubstituted double bond.)

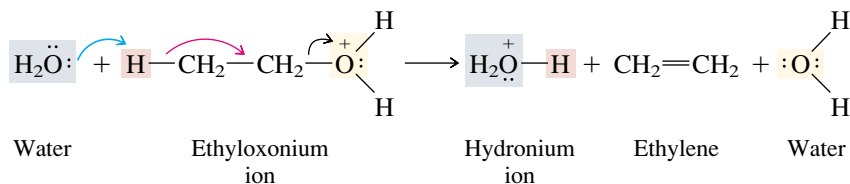


Loss of a proton from C-3 yields the major product 2,3-dimethyl-2-butene. (This alkene has a tetrasubstituted double bond.)



As noted earlier (Section 4.13) primary carbocations are too high in energy to be intermediates in most chemical reactions. If primary alcohols don't form primary car-

bocations, then how do they undergo elimination? A modification of our general mechanism for alcohol dehydration offers a reasonable explanation. For primary alcohols it is believed that a proton is lost from the alkyloxonium ion in the same step in which carbon–oxygen bond cleavage takes place. For example, the rate-determining step in the sulfuric acid-catalyzed dehydration of ethanol may be represented as:

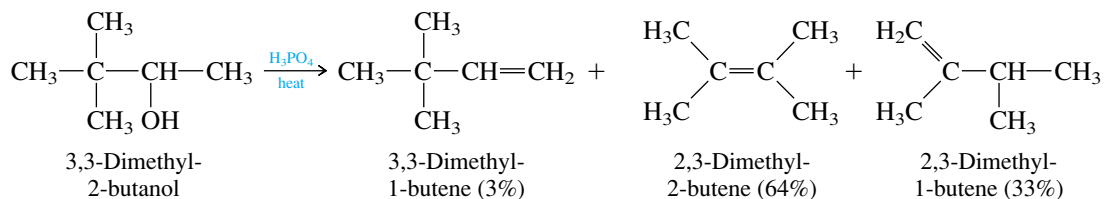


Like tertiary alcohols, secondary alcohols normally undergo dehydration by way of carbocation intermediates.

In Chapter 4 you learned that carbocations could be captured by halide anions to give alkyl halides. In the present chapter, a second type of carbocation reaction has been introduced—a carbocation can lose a proton to form an alkene. In the next section a third aspect of carbocation behavior will be described, the *rearrangement* of one carbocation to another.

5.13 REARRANGEMENTS IN ALCOHOL DEHYDRATION

Some alcohols undergo dehydration to yield alkenes having carbon skeletons different from the starting alcohols. Not only has elimination taken place, but the arrangement of atoms in the alkene is different from that in the alcohol. A **rearrangement** is said to have occurred. An example of an alcohol dehydration that is accompanied by rearrangement is the case of 3,3-dimethyl-2-butanol. This is one of many such experiments carried out by F. C. Whitmore and his students at Pennsylvania State University in the 1930s as part of a general study of rearrangement reactions.



A mixture of three alkenes was obtained in 80% yield, having the composition shown. The alkene having the same carbon skeleton as the starting alcohol, 3,3-dimethyl-1-butene, constituted only 3% of the alkene mixture. The two alkenes present in greatest amount, 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene, both have carbon skeletons different from that of the starting alcohol.

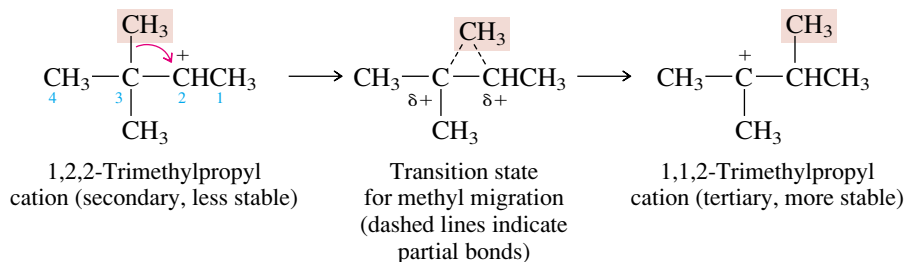
Whitmore proposed that the carbon skeleton rearrangement occurred in a separate step following carbocation formation. Once the alcohol was converted to the corresponding carbocation, that carbocation could either lose a proton to give an alkene having the same carbon skeleton or rearrange to a different carbocation, as shown in Figure 5.7. The rearranged alkenes arise by loss of a proton from the rearranged carbocation.

Why do carbocations rearrange? The answer is straightforward once we recall that tertiary carbocations are more stable than secondary carbocations (Section 4.10). Thus, rearrangement of a secondary to a tertiary carbocation is energetically favorable. As shown in Figure 5.7, the carbocation that is formed first in the dehydration of

To simplify the accompanying discussion, the carbons of the carbocation are numbered so as to correspond to their positions in the starting alcohol 3,3-dimethyl-2-butanol. These numbers are different from the locants in the IUPAC cation names, which are given under the structural formulas.

3,3-dimethyl-2-butanol is secondary; the rearranged carbocation is tertiary. Rearrangement occurs, and almost all of the alkene products come from the tertiary carbocation.

How do carbocations rearrange? To understand this we need to examine the structural change that takes place at the transition state. Again referring to the initial (secondary) carbocation intermediate in the dehydration of 3,3-dimethyl-2-butanol, rearrangement occurs when a methyl group shifts from C-3 to the positively charged carbon. The methyl group migrates with the pair of electrons that made up its original σ bond to C-3. In the curved arrow notation for this methyl migration, the arrow shows the movement of both the methyl group and the electrons in the σ bond.



At the transition state for rearrangement, the methyl group is partially bonded both to its point of origin and to the carbon that will be its destination.

This rearrangement is shown in orbital terms in Figure 5.8. The relevant orbitals of the secondary carbocation are shown in structure (a), those of the transition state for rearrangement in (b), and those of the tertiary carbocation in (c). Delocalization of the electrons of the C—CH₃ σ bond into the vacant *p* orbital of the positively charged carbon by hyperconjugation is present in both (a) and (c), requires no activation energy, and stabilizes each carbocation. Migration of the atoms of the methyl group, however, occurs only when sufficient energy is absorbed by (a) to achieve the transition state (b). The activation energy is modest, and carbocation rearrangements are normally quite fast.

Once a carbocation is formed, anything that happens afterward happens rapidly.

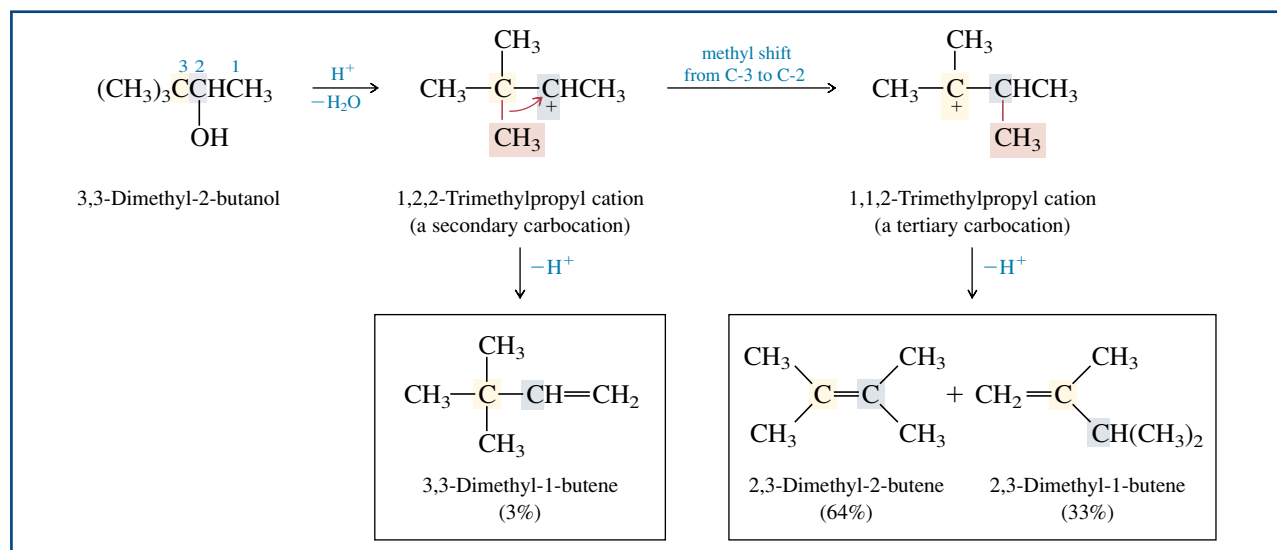


FIGURE 5.7 The first formed carbocation from 3,3-dimethyl-2-butanol is secondary and rearranges to a more stable tertiary carbocation by a methyl migration. The major portion of the alkene products is formed by way of the tertiary carbocation.

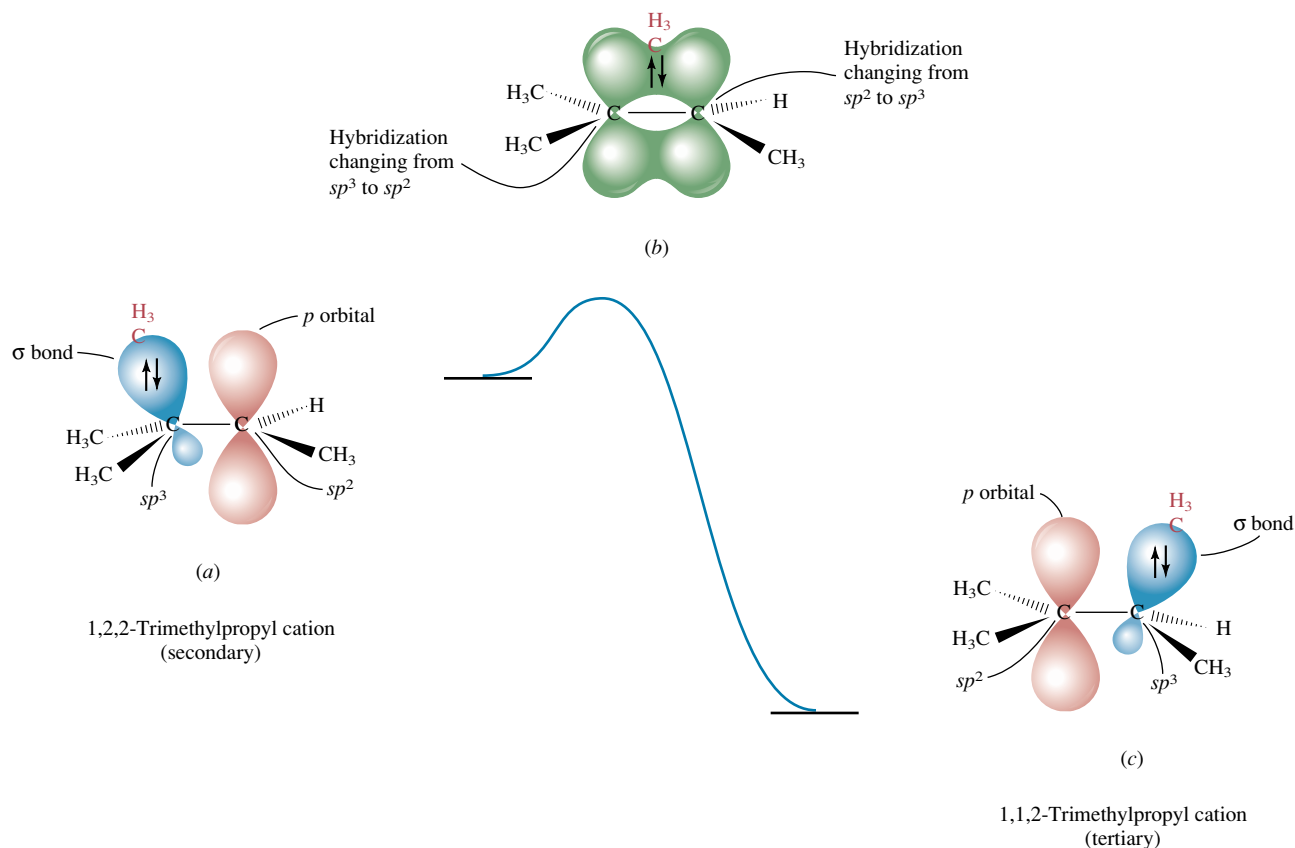
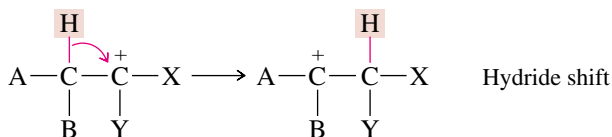


FIGURE 5.8 An orbital representation of methyl migration in 1,2,2-trimethylpropyl cation. Structure (a) is the initial secondary carbocation; structure (b) is the transition state for methyl migration, and structure (c) is the final tertiary carbocation.

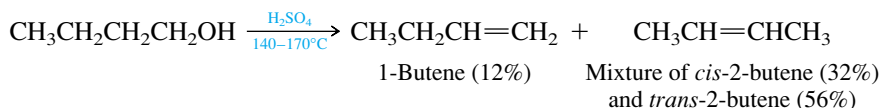
PROBLEM 5.16 The alkene mixture obtained on dehydration of 2,2-dimethylcyclohexanol contains appreciable amounts of 1,2-dimethylcyclohexene. Give a mechanistic explanation for the formation of this product.

Alkyl groups other than methyl can also migrate to a positively charged carbon.

Many carbocation rearrangements involve migration of a hydrogen. These are called **hydride shifts**. The same requirements apply to hydride shifts as to alkyl group migrations; they proceed in the direction that leads to a more stable carbocation; the origin and destination of the migrating hydrogen are adjacent carbons, one of which must be positively charged; and the hydrogen migrates with a pair of electrons.



Hydride shifts often occur during the dehydration of primary alcohols. Thus, although 1-butene would be expected to be the only alkene formed on dehydration of 1-butanol, it is in fact only a minor product. The major product is a mixture of *cis*- and *trans*-2-butene.

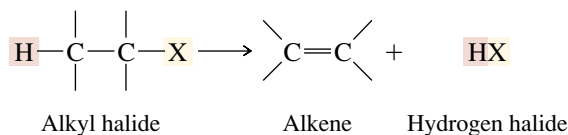


A mechanism for the formation of these three alkenes is shown in Figure 5.9. Dissociation of the primary alkyloxonium ion is accompanied by a shift of hydride from C-2 to C-1. This avoids the formation of a primary carbocation, leading instead to a secondary carbocation in which the positive charge is at C-2. Deprotonation of this carbocation yields the observed products. (Some 1-butene may also arise directly from the primary alkyloxonium ion.)

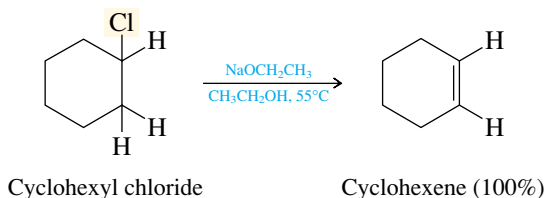
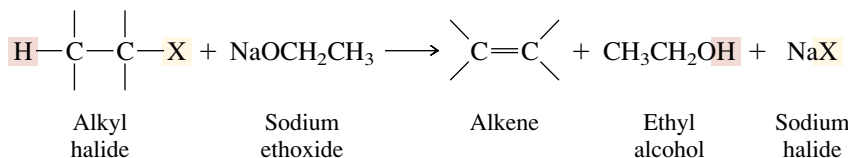
This concludes discussion of our second functional group transformation involving *alcohols*: the first was the conversion of alcohols to alkyl halides (Chapter 4), and the second the conversion of alcohols to alkenes. In the remaining sections of the chapter the conversion of *alkyl halides* to alkenes by dehydrohalogenation is described.

5.14 DEHYDROHALOGENATION OF ALKYL HALIDES

Dehydrohalogenation is the loss of a hydrogen and a halogen from an alkyl halide. It is one of the most useful methods for preparing alkenes by β elimination.



When applied to the preparation of alkenes, the reaction is carried out in the presence of a strong base, such as sodium ethoxide ($\text{NaOCH}_2\text{CH}_3$) in ethyl alcohol as solvent.



Sodium ethoxide is prepared by the reaction of sodium metal with ethanol.

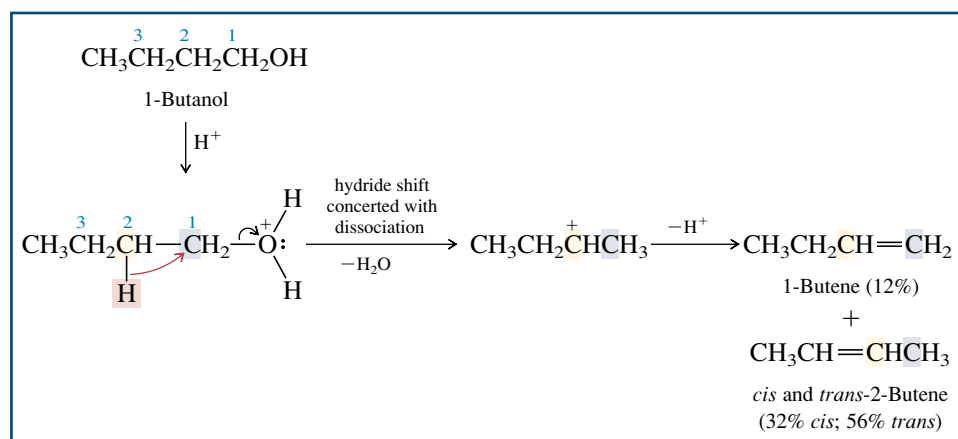
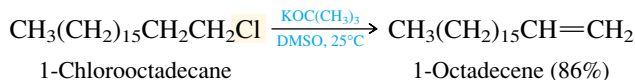
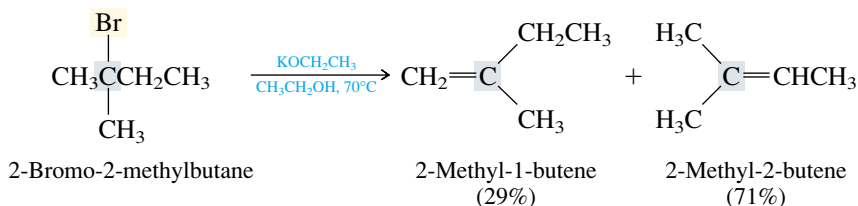


FIGURE 5.9 Dehydration of 1-butanol is accompanied by a hydride shift from C-2 to C-1.

Similarly, sodium methoxide (NaOCH₃) is a suitable base and is used in methyl alcohol. Potassium hydroxide in ethyl alcohol is another base–solvent combination often employed in the dehydrohalogenation of alkyl halides. Potassium *tert*-butoxide [KOC(CH₃)₃] is the preferred base when the alkyl halide is primary; it is used in either *tert*-butyl alcohol or dimethyl sulfoxide as solvent.



The regioselectivity of dehydrohalogenation of alkyl halides follows the Zaitsev rule; β elimination predominates in the direction that leads to the more highly substituted alkene.

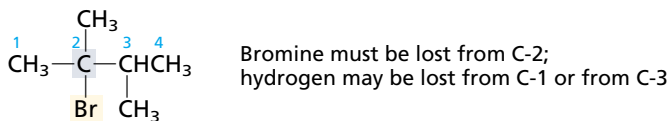


Dimethyl sulfoxide has the structure (CH₃)₂S=O and is commonly referred to as DMSO. It is a relatively inexpensive solvent, obtained as a byproduct in paper manufacture.

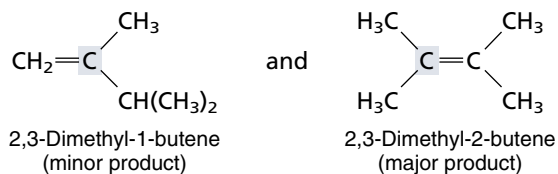
PROBLEM 5.17 Write the structures of all the alkenes that can be formed by dehydrohalogenation of each of the following alkyl halides. Apply the Zaitsev rule to predict the alkene formed in greatest amount in each case.

- | | |
|---------------------------------|--------------------------------|
| (a) 2-Bromo-2,3-dimethylbutane | (d) 2-Bromo-3-methylbutane |
| (b) <i>tert</i> -Butyl chloride | (e) 1-Bromo-3-methylbutane |
| (c) 3-Bromo-3-ethylpentane | (f) 1-Iodo-1-methylcyclohexane |

SAMPLE SOLUTION (a) First analyze the structure of 2-bromo-2,3-dimethylbutane with respect to the number of possible β elimination pathways.

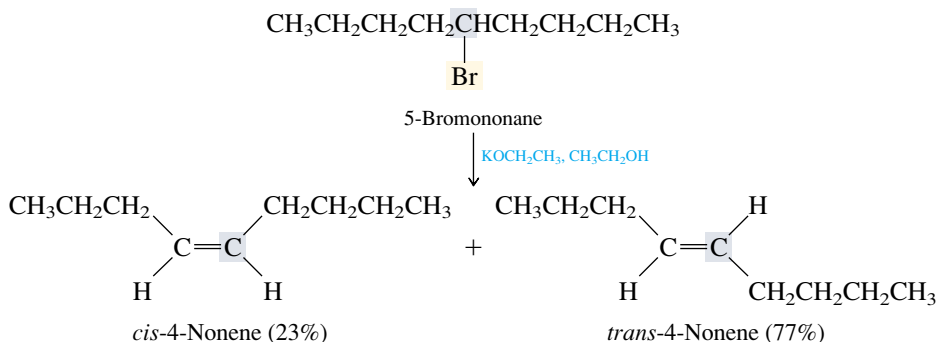


The two possible alkenes are



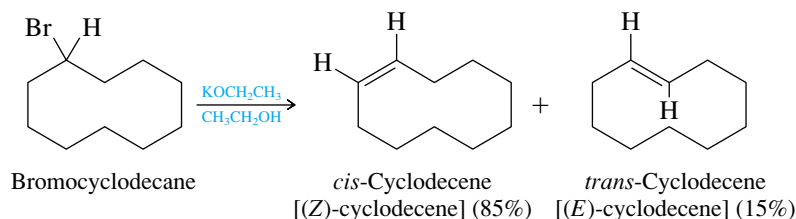
The major product, predicted on the basis of Zaitsev's rule, is 2,3-dimethyl-2-butene. It has a tetrasubstituted double bond. The minor alkene has a disubstituted double bond.

In addition to being regioselective, dehydrohalogenation of alkyl halides is stereoselective and favors formation of the more stable stereoisomer. Usually, as in the case of 5-bromononane, the *trans* (or *E*) alkene is formed in greater amounts than its *cis* (or *Z*) stereoisomer.



PROBLEM 5.18 Write structural formulas for all the alkenes that can be formed in the reaction of 2-bromobutane with potassium ethoxide.

Dehydrohalogenation of cycloalkyl halides lead exclusively to cis cycloalkenes when the ring has fewer than ten carbons. As the ring becomes larger, it can accommodate either a cis or a trans double bond, and large-ring cycloalkyl halides give mixtures of cis and trans cycloalkenes.



5.15 MECHANISM OF THE DEHYDROHALOGENATION OF ALKYL HALIDES: THE E₂ MECHANISM

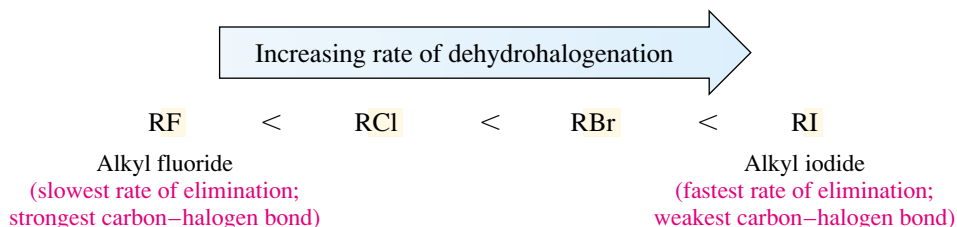
In the 1920s, Sir Christopher Ingold proposed a mechanism for dehydrohalogenation that is still accepted as a valid description of how these reactions occur. Some of the information on which Ingold based his mechanism included these facts:

1. The reaction exhibits second-order kinetics; it is first-order in alkyl halide and first-order in base.

$$\text{Rate} = k[\text{alkyl halide}][\text{base}]$$

Doubling the concentration of either the alkyl halide or the base doubles the reaction rate. Doubling the concentration of both reactants increases the rate by a factor of 4.

2. The rate of elimination depends on the halogen, the reactivity of alkyl halides increasing with decreasing strength of the carbon-halogen bond.

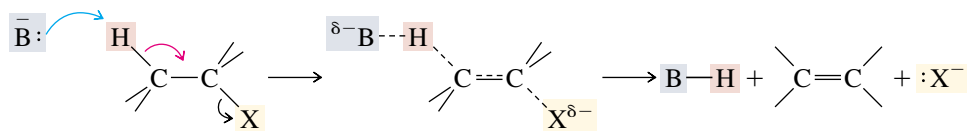


Cyclohexyl bromide, for example, is converted to cyclohexene by sodium ethoxide in ethanol over 60 times faster than cyclohexyl chloride. Iodide is the best **leaving group** in a dehydrohalogenation reaction, fluoride the poorest leaving group. Fluoride is such a poor leaving group that alkyl fluorides are rarely used as starting materials in the preparation of alkenes.

What are the implications of second-order kinetics? Ingold reasoned that second-order kinetics suggest a bimolecular rate-determining step involving both a molecule of the alkyl halide and a molecule of base. He concluded that proton removal from the β carbon by the base occurs during the rate-determining step rather than in a separate step following the rate-determining step.

What are the implications of the effects of the various halide leaving groups? Since it is the halogen with the weakest bond to carbon that reacts fastest, Ingold concluded that the carbon–halogen bond breaks in the rate-determining step. The weaker the carbon–halogen bond, the easier it breaks.

On the basis of these observations, Ingold proposed a concerted (one-step) mechanism for dehydrohalogenation and gave it the mechanistic symbol **E2**, standing for **elimination bimolecular**.



Transition state for bimolecular elimination

In the E2 mechanism the three key elements

1. C–H bond breaking
2. C=C π bond formation
3. C–X bond breaking

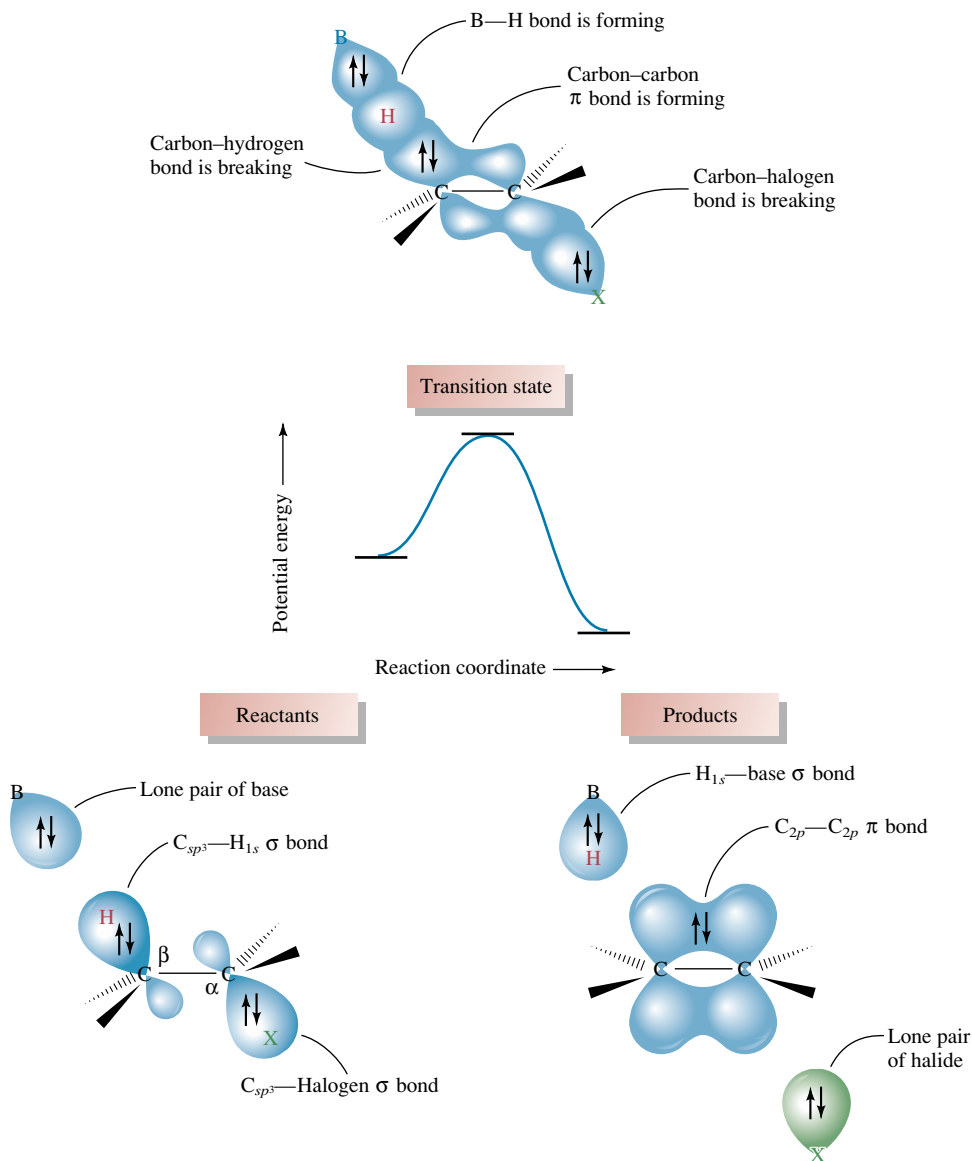
are all taking place at the same transition state. The carbon–hydrogen and carbon–halogen bonds are in the process of being broken, the base is becoming bonded to the hydrogen, a π bond is being formed, and the hybridization of carbon is changing from sp^3 to sp^2 . An energy diagram for the E2 mechanism is shown in Figure 5.10.

PROBLEM 5.19 Use curved arrows to track electron movement in the dehydrohalogenation of *tert*-butyl chloride by sodium methoxide by the E2 mechanism.

The regioselectivity of elimination is accommodated in the E2 mechanism by noting that a partial double bond develops at the transition state. Since alkyl groups stabilize double bonds, they also stabilize a partially formed π bond in the transition state. The more stable alkene therefore requires a lower energy of activation for its formation and predominates in the product mixture because it is formed faster than a less stable one.

Ingold was a pioneer in applying quantitative measurements of reaction rates to the understanding of organic reaction mechanisms. Many of the reactions to be described in this text were studied by him and his students during the period of about 1920 to 1950. The facts disclosed by Ingold's experiments have been verified many times. His interpretations, although considerably refined during the decades that followed his

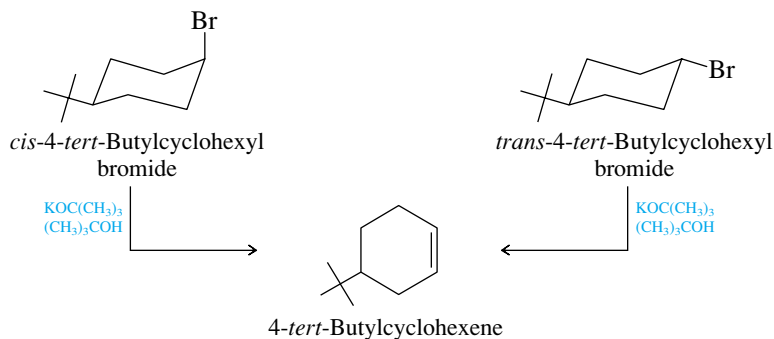
FIGURE 5.10 Potential energy diagram for concerted E2 elimination of an alkyl halide.



original reports, still serve us well as a starting point for understanding how the fundamental processes of organic chemistry take place. Beta-elimination of alkyl halides by the E2 mechanism is one of those fundamental processes.

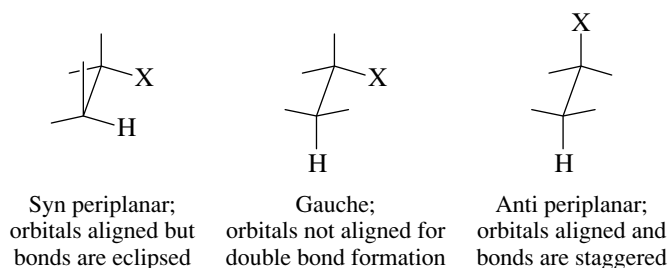
5.16 ANTI ELIMINATION IN E2 REACTIONS: STEREOELECTRONIC EFFECTS

Further insight into the E2 mechanism comes from stereochemical studies. One such experiment compares the rates of elimination of the *cis* and *trans* isomers of 4-*tert*-butylcyclohexyl bromide.



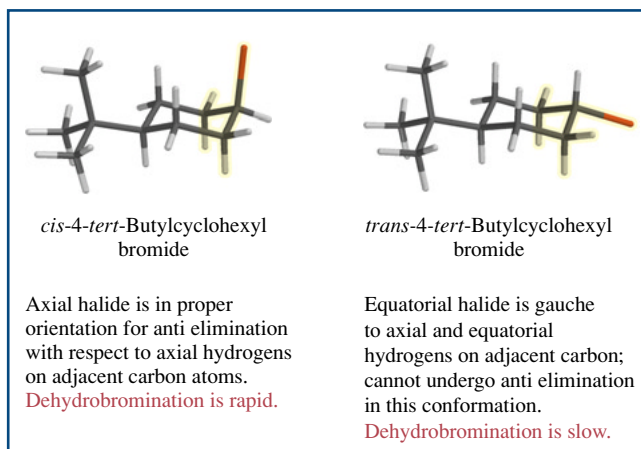
Although both stereoisomers yield 4-*tert*-butylcyclohexene as the only alkene, they do so at quite different rates. The *cis* isomer reacts over 500 times faster than the *trans*.

The difference in reaction rate results from different degrees of π bond development in the E2 transition state. Since π overlap of p orbitals requires their axes to be parallel, π bond formation is best achieved when the four atoms of the H—C—C—X unit lie in the same plane at the transition state. The two conformations that permit this relationship are termed *syn periplanar* and *anti periplanar*.



Because adjacent bonds are eclipsed when the H—C—C—X unit is *syn periplanar*, a transition state having this geometry is less stable than one that has an *anti periplanar* relationship between the proton and the leaving group.

As Figure 5.11 shows, bromine is axial in the most stable conformation of *cis*-4-*tert*-butylcyclohexyl bromide, but it is equatorial in the *trans* stereoisomer. An axial bromine is *anti periplanar* with respect to the axial hydrogens at C-2 and C-6, and so



The *peri*- in *periplanar* means "almost" or "nearly." Although coplanarity of the p orbitals is the best geometry for the E2 process, modest deviations from this ideal can be tolerated.

FIGURE 5.11 Conformations of *cis*- and *trans*-4-*tert*-butylcyclohexyl bromide and their relationship to the preference for an *anti periplanar* arrangement of a proton and leaving group.

the proper geometry between the proton and the leaving group is already present in the *cis* bromide, which undergoes E2 elimination rapidly. The less reactive stereoisomer, the *trans* bromide, has an equatorial bromine in its most stable conformation. An equatorial bromine is not anti periplanar with respect to any of the hydrogens that are β to it. The relationship between an equatorial leaving group and all the C-2 and C-6 hydrogens is *gauche*. In order to undergo E2 elimination, the *trans* bromide must adopt a geometry in which the ring is strained. The transition state for its elimination is therefore higher in energy, and reaction is slower.

PROBLEM 5.20 Use curved arrow notation to show the bonding changes in the reaction of *cis*-4-*tert*-butylcyclohexyl bromide with potassium *tert*-butoxide. Be sure your drawing correctly represents the spatial relationship between the leaving group and the proton that is lost.

Effects that arise because one spatial arrangement of electrons (or orbitals or bonds) is more stable than another are called **stereoelectronic effects**. *There is a stereoelectronic preference for the anti periplanar arrangement of proton and leaving group in E2 reactions.*

5.17 A DIFFERENT MECHANISM FOR ALKYL HALIDE ELIMINATION: THE E1 MECHANISM

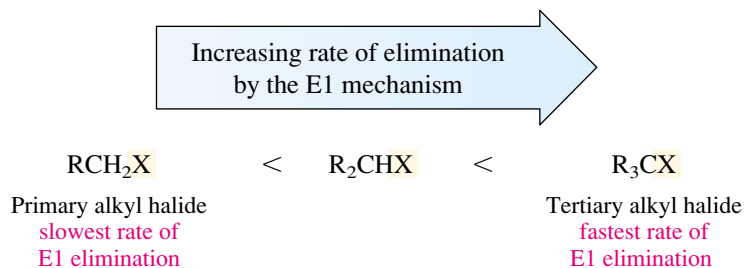
The E2 mechanism is a concerted process in which the carbon–hydrogen and carbon–halogen bonds both break in the same elementary step. What if these bonds break in separate steps?

One possibility is the two-step mechanism of Figure 5.12, in which the carbon–halogen bond breaks first to give a carbocation intermediate, followed by deprotonation of the carbocation in a second step.

The alkyl halide, in this case 2-bromo-2-methylbutane, ionizes to a carbocation and a halide anion by a heterolytic cleavage of the carbon–halogen bond. Like the dissociation of an alkyloxonium ion to a carbocation, this step is rate-determining. Because the rate-determining step is unimolecular—it involves only the alkyl halide and not the base—this mechanism is known by the symbol **E1**, standing for **elimination unimolecular**. It exhibits first-order kinetics.

$$\text{Rate} = k[\text{alkyl halide}]$$

Typically, elimination by the E1 mechanism is observed only for tertiary and some secondary alkyl halides, and then only when the base is weak or in low concentration. The reactivity order parallels the ease of carbocation formation.



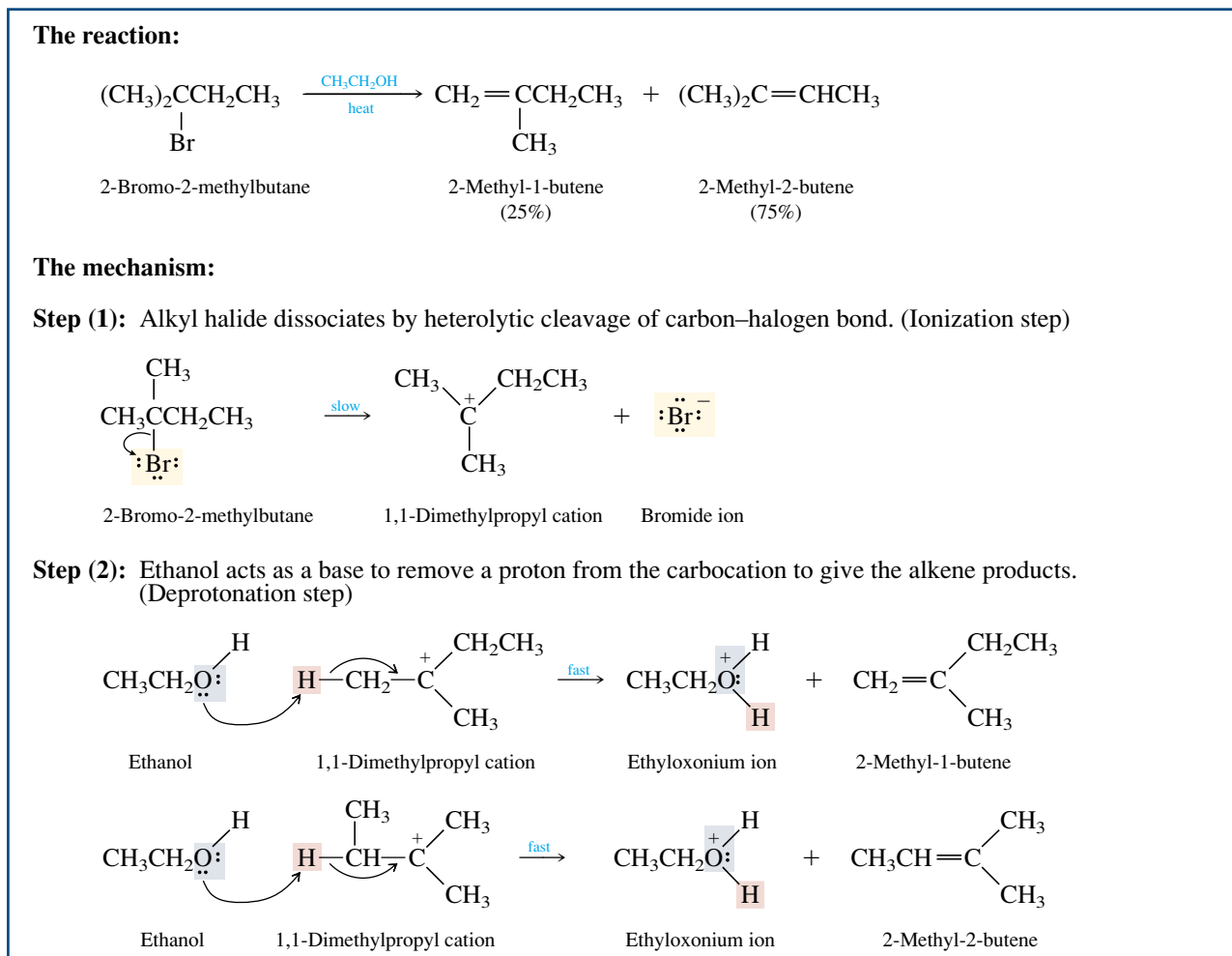
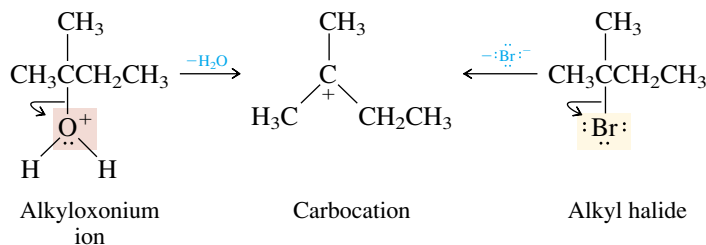


FIGURE 5.12 The E1 mechanism for the dehydrohalogenation of 2-bromo-2-methylbutane in ethanol.

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.

The best examples of E1 eliminations are those carried out in the absence of added base. In the example cited in Figure 5.12, 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.

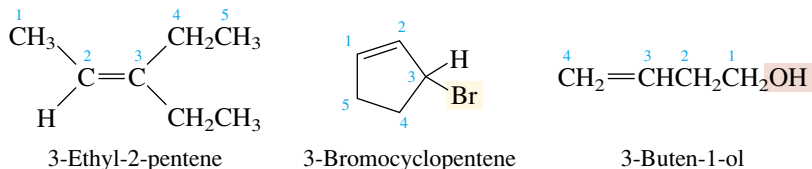
There is a strong similarity between the mechanism shown in Figure 5.12 and the one shown for alcohol dehydration in Figure 5.6. Indeed, we can describe the acid-catalyzed dehydration of alcohols as an E1 elimination of their conjugate acids. The main difference between the dehydration of 2-methyl-2-butanol 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.



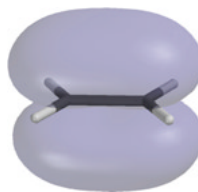
Like alcohol dehydrations, E1 reactions of alkyl halides can be accompanied by carbocation rearrangements. Eliminations by the E2 mechanism, on the other hand, normally proceed without rearrangement. Consequently, if one wishes to prepare an alkene from an alkyl halide, conditions favorable to E2 elimination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

5.18 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 the hydroxyl group.

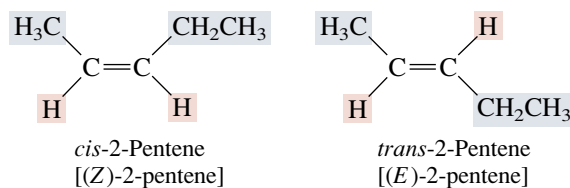


Section 5.2 Bonding in alkenes is described according to an sp^2 orbital hybridization model. The double bond unites two sp^2 -hybridized carbon atoms and is made of a σ component and a π component. The σ bond arises by overlap of an sp^2 hybrid orbital on each carbon. The π bond is weaker than the σ 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 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.



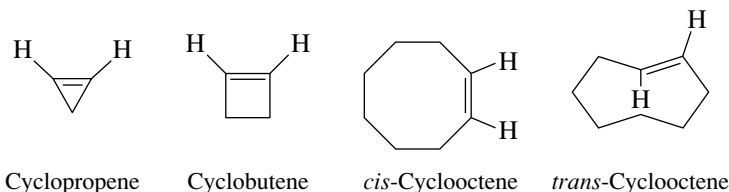
Section 5.5 Alkenes are relatively nonpolar. Alkyl substituents donate electrons to an sp^2 -hybridized carbon to which they are attached slightly better than hydrogen does.

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 11 carbons. Terminally disubstituted alkenes ($\text{R}_2\text{C}=\text{CH}_2$) may be slightly more or less stable than $\text{RCH}=\text{CHR}$, depending on their substituents.
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**.

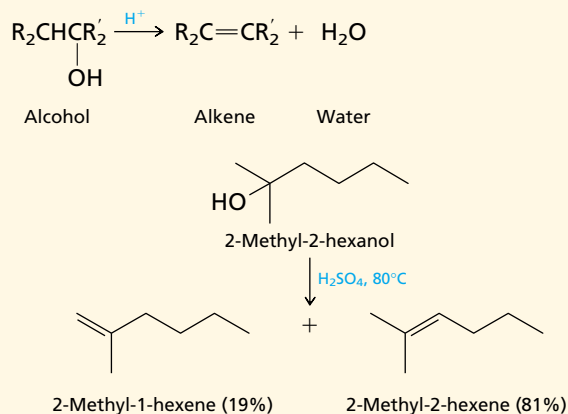
Section 5.7 Cycloalkenes that have *trans* double bonds in rings smaller than 12 members are less stable than their *cis* stereoisomers. *trans*-Cyclooctene can be isolated and stored at room temperature, but *trans*-cycloheptene is not stable above -30°C .



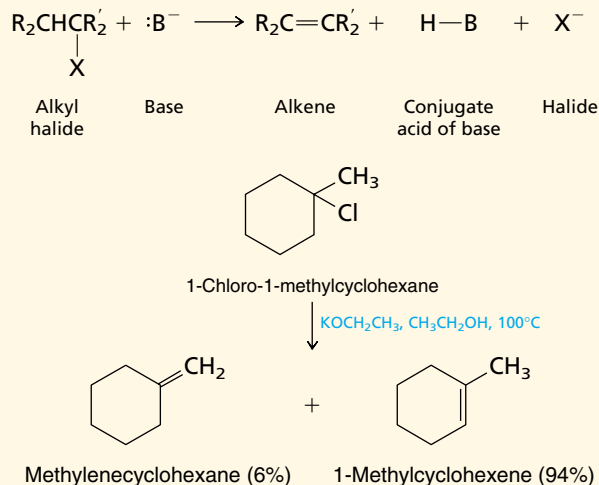
Section 5.8 Alkenes are prepared by **β elimination** of alcohols and alkyl halides. These reactions are summarized with examples in Table 5.2. In both cases, β elimination proceeds in the direction that yields the more highly substituted double bond (**Zaitsev's rule**).

TABLE 5.2 Preparation of Alkenes by Elimination Reactions of Alcohols and Alkyl Halides**Reaction (section) and comments****General equation and specific example**

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. A carbocation intermediate is involved, and sometimes rearrangements take place during elimination.

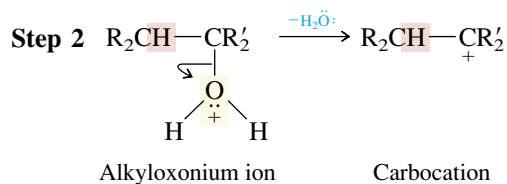
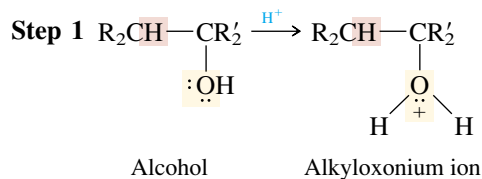


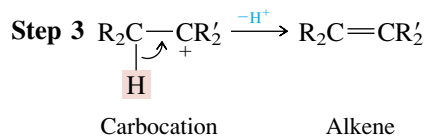
Dehydrohalogenation of alkyl halides (Sections 5.14–5.16) Strong bases cause a proton and a halide to be lost from adjacent carbons of an alkyl halide to yield an alkene. Regioselectivity is in accord with the Zaitsev rule. The order of halide reactivity is $\text{I} > \text{Br} > \text{Cl} > \text{F}$.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



Sections 5.9–5.11 See Table 5.2.

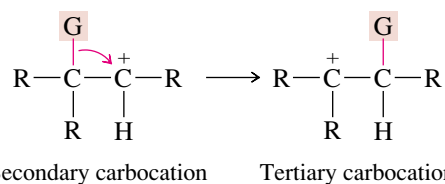
Section 5.12 Secondary and tertiary alcohols undergo **dehydration** by way of carbocation intermediates.





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.

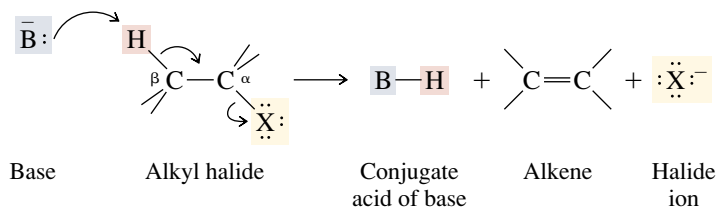
Section 5.13 Alkene synthesis via alcohol dehydration is complicated by **carbocation rearrangements**. A less stable carbocation can rearrange to a more stable one by an alkyl group migration or by a hydride shift, opening the possibility for alkene formation from two different carbocations.



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

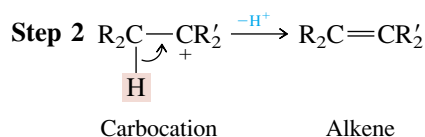
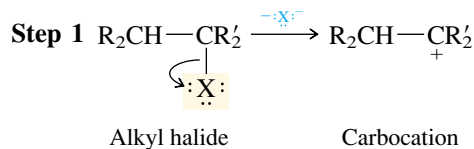
Section 5.14 See Table 5.2.

Section 5.15 **Dehydrohalogenation** of alkyl halides by alkoxide bases is not complicated by rearrangements, because carbocations are not intermediates. The **bimolecular (E2) mechanism** 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 periplanar** relationship that is required for elimination by the E2 mechanism.

Section 5.17 In the absence of a strong base, alkyl halides eliminate by the **unimolecular (E1) mechanism**. The E1 mechanism involves rate-determining ionization of the alkyl halide to a carbocation, followed by deprotonation of the carbocation.



PROBLEMS

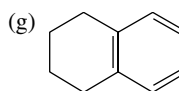
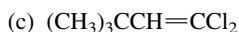
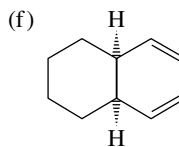
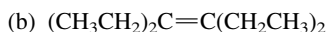
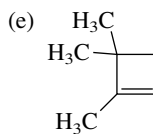
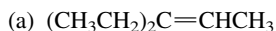
5.21 Write structural formulas for each of the following:

- | | |
|---|---|
| (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 |



5.22 Write a structural formula or build a molecular model and give a correct IUPAC name for each alkene of molecular formula C_7H_{14} that has a *tetrasubstituted* double bond.

5.23 Give the IUPAC names for each of the following compounds:



(d)



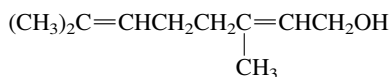
5.24 (a) A hydrocarbon isolated from fish oil and from plankton was identified as 2,6,10,14-tetramethyl-2-pentadecene. Write its structure.

(b) Alkyl isothiocyanates are compounds of the type $RN=C=S$. Write a structural formula for *allyl isothiocyanate*, a pungent-smelling compound isolated from mustard.



5.25 (a) The sex attractant of the Mediterranean fruit fly is (*E*)-6-nonen-1-ol. Write a structural formula or build a molecular model for this compound, showing the stereochemistry of the double bond.

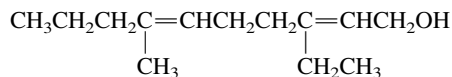
(b) Geraniol is a naturally occurring substance present in the fragrant oil of many plants. It has a pleasing, roselike odor. Geraniol is the *E* isomer of



Write a structural formula or build a molecular model for geraniol, showing its stereochemistry.

(c) Nerol is a naturally occurring substance that is a stereoisomer of geraniol. Write its structure or build a molecular model.

(d) The sex attractant of the codling moth is the *2Z, 6E* stereoisomer of

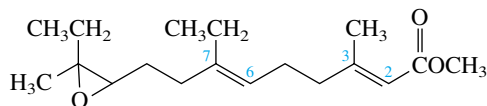


Write the structure of this substance or build a molecular model in a way that clearly shows its stereochemistry.

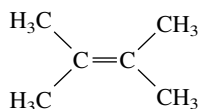
- (e) The sex pheromone of the honeybee is the *E* stereoisomer of the compound shown. Write a structural formula or build a molecular model for this compound.



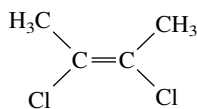
- (f) A growth hormone from the cecropia moth has the structure shown. Express the stereochemistry of the double bonds according to the *E-Z* system.



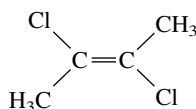
- 5.26 Which one of the following has the largest dipole moment (is the most polar)? Compare your answer with the calculated dipole moments on the *Learning By Modeling* CD.



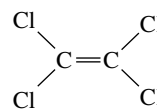
A



B



C



D

- 5.27 Match each alkene with the appropriate heat of combustion:

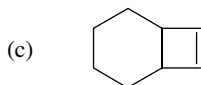
Heats of combustion (kJ/mol): 5293; 4658; 4650; 4638; 4632

Heats of combustion (kcal/mol): 1264.9; 1113.4; 1111.4; 1108.6; 1107.1

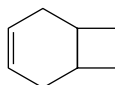
- (a) 1-Heptene
 (b) 2,4-Dimethyl-1-pentene
 (c) 2,4-Dimethyl-2-pentene
 (d) (*Z*)-4,4-Dimethyl-2-pentene
 (e) 2,4,4-Trimethyl-2-pentene

- 5.28 Choose the more stable alkene in each of the following pairs. Explain your reasoning.

- (a) 1-Methylcyclohexene or 3-methylcyclohexene
 (b) Isopropenylcyclopentane or allylcyclopentane



or

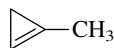


Bicyclo[4.2.0]oct-7-ene

Bicyclo[4.2.0]oct-3-ene

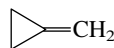
- (d) (*Z*)-Cyclononene or (*E*)-cyclononene
 (e) (*Z*)-Cyclooctadecene or (*E*)-cyclooctadecene

- 5.29 (a) Suggest an explanation for the fact that 1-methylcyclopropene is some 42 kJ/mol (10 kcal/mol) less stable than methylenecyclopropane.



1-Methylcyclopropene

is less stable than



Methylenecyclopropane

- (b) On the basis of your answer to part (a), compare the expected stability of 3-methylcyclopropene with that of 1-methylcyclopropene and that of methylenecyclopropane.

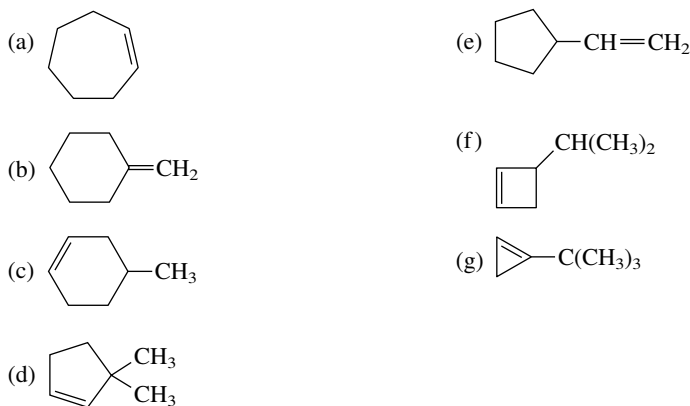
5.30 How many alkenes would you expect to be formed from each of the following alkyl bromides under conditions of E2 elimination? Identify the alkenes in each case.

- | | |
|-----------------------------|--------------------------------|
| (a) 1-Bromohexane | (e) 2-Bromo-3-methylpentane |
| (b) 2-Bromohexane | (f) 3-Bromo-2-methylpentane |
| (c) 3-Bromohexane | (g) 3-Bromo-3-methylpentane |
| (d) 2-Bromo-2-methylpentane | (h) 3-Bromo-2,2-dimethylbutane |

5.31 Write structural formulas for all the alkene products that could reasonably be formed from each of the following compounds under the indicated reaction conditions. Where more than one alkene is produced, specify the one that is the major product.

- 1-Bromo-3,3-dimethylbutane (potassium *tert*-butoxide, *tert*-butyl alcohol, 100°C)
- 1-Methylcyclopentyl chloride (sodium ethoxide, ethanol, 70°C)
- 3-Methyl-3-pentanol (sulfuric acid, 80°C)
- 2,3-Dimethyl-2-butanol (phosphoric acid, 120°C)
- 3-Iodo-2,4-dimethylpentane (sodium ethoxide, ethanol, 70°C)
- 2,4-Dimethyl-3-pentanol (sulfuric acid, 120°C)

5.32 Choose the compound of molecular formula $C_7H_{13}Br$ that gives each alkene shown as the *exclusive* product of E2 elimination.



5.33 Give the structures of two different alkyl bromides both of which yield the indicated alkene as the *exclusive* product of E2 elimination.

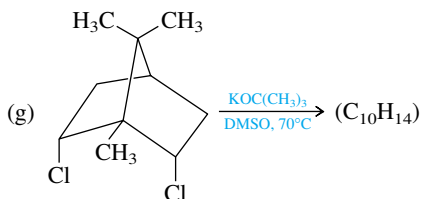
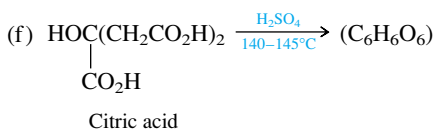
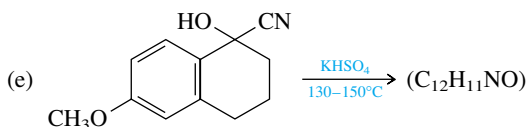
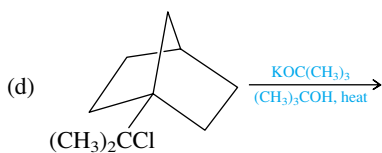
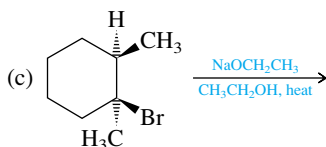
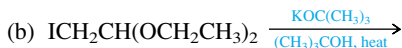
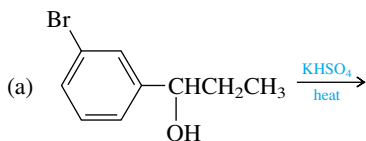


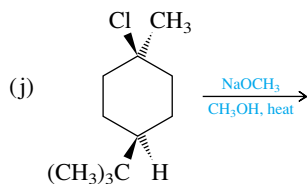
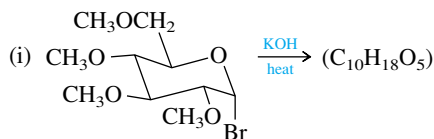
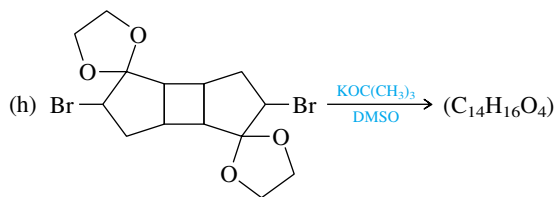
- 5.34**
- Write the structures or build molecular models of all the isomeric alkyl bromides having the molecular formula $C_5H_{11}Br$.
 - Which one undergoes E1 elimination at the fastest rate?
 - Which one is incapable of reacting by the E2 mechanism?
 - Which ones can yield only a single alkene on E2 elimination?
 - For which isomer does E2 elimination give two alkenes which are not constitutional isomers?
 - Which one yields the most complex mixture of alkenes on E2 elimination?

- 5.35 (a) Write the structures or build molecular models of all the isomeric alcohols having the molecular formula $C_5H_{12}O$.
- (b) Which one will undergo acid-catalyzed dehydration most readily?
- (c) Write the structure of the most stable C_5H_{11} carbocation.
- (d) Which alkenes may be derived from the carbocation in part (c)?
- (e) Which alcohols can yield the carbocation in part (c) by a process involving a hydride shift?
- (f) Which alcohols can yield the carbocation in part (c) by a process involving a methyl shift?

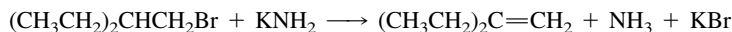


5.36 Predict the major organic product of each of the following reactions. In spite of the structural complexity of some of the starting materials, the functional group transformations are all of the type described in this chapter.





5.37 Evidence has been reported in the chemical literature that the reaction



proceeds by the E2 mechanism. Use curved arrow notation to represent the flow of electrons for this process.

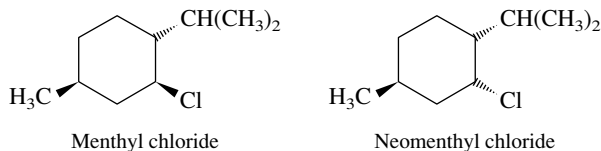
5.38 The rate of the reaction



is first-order in (CH₃)₃CCl and first-order in NaSCH₂CH₃. Give the symbol (E1 or E2) for the most reasonable mechanism, and use curved arrow notation to represent the flow of electrons.



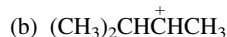
5.39 Menthyl chloride and neomenthyl chloride have the structures shown. One of these stereoisomers undergoes elimination on treatment with sodium ethoxide in ethanol much more readily than the other. Which reacts faster, menthyl chloride or neomenthyl chloride? Why? (Molecular models will help here.)

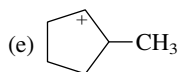
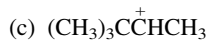


5.40 The stereoselectivity of elimination of 5-bromononane on treatment with potassium ethoxide was described in Section 5.14. Draw Newman projections or make molecular models of 5-bromononane showing the conformations that lead to *cis*-4-nonene and *trans*-4-nonene, respectively. Identify the proton that is lost in each case, and suggest a mechanistic explanation for the observed stereoselectivity.

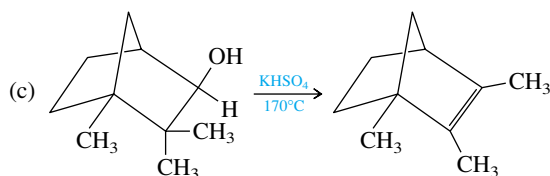
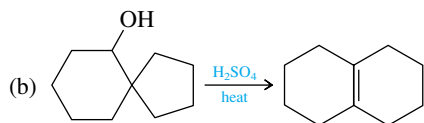
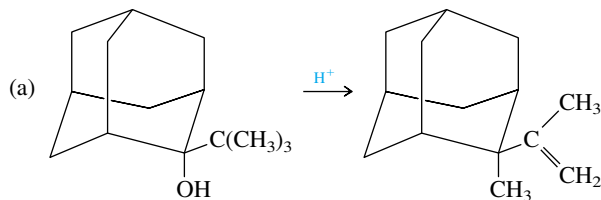
5.41 In the acid-catalyzed dehydration of 2-methyl-1-propanol, what carbocation would be formed if a hydride shift accompanied cleavage of the carbon–oxygen bond in the alkyloxonium ion? What ion would be formed as a result of a methyl shift? Which pathway do you think will predominate, a hydride shift or a methyl shift?

5.42 Each of the following carbocations has the potential to rearrange to a more stable one. Write the structure of the rearranged carbocation.

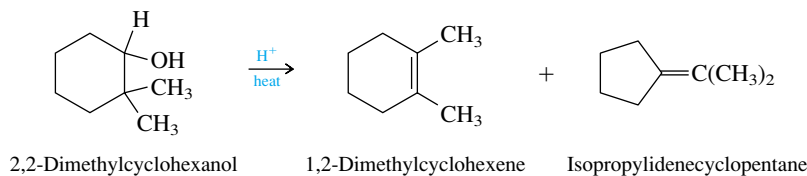




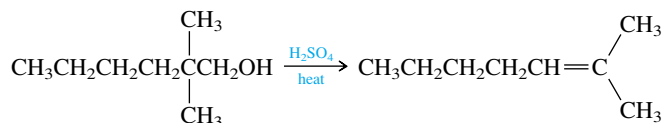
5.43 Write a sequence of steps depicting the mechanisms of each of the following reactions:



5.44 In Problem 5.16 (Section 5.13) we saw that acid-catalyzed dehydration of 2,2-dimethylcyclohexanol afforded 1,2-dimethylcyclohexene. To explain this product we must write a mechanism for the reaction in which a methyl shift transforms a secondary carbocation to a tertiary one. Another product of the dehydration of 2,2-dimethylcyclohexanol is isopropylidenecyclopentane. Write a mechanism to rationalize its formation.



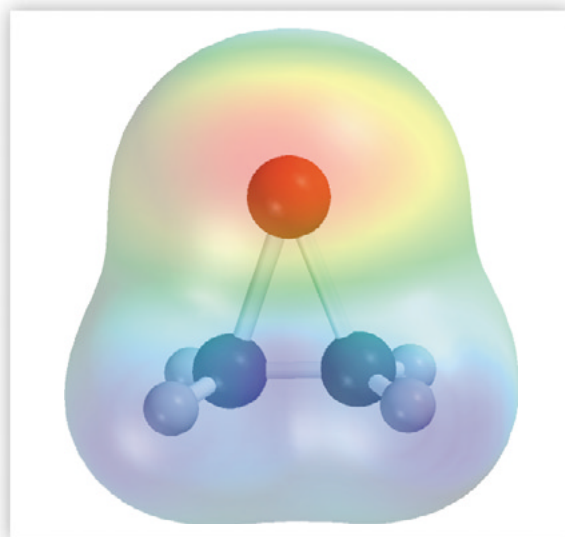
5.45 Acid-catalyzed dehydration of 2,2-dimethyl-1-hexanol gave a number of isomeric alkenes including 2-methyl-2-heptene as shown in the following formula.



- (a) Write a stepwise mechanism for the formation of 2-methyl-2-heptene.
 (b) What other alkenes do you think are formed in this reaction?

5.46 Compound A (C_4H_{10}) gives two different monochlorides on photochemical chlorination. Treatment of either of these monochlorides with potassium *tert*-butoxide in dimethyl sulfoxide gives the same alkene B (C_4H_8) as the only product. What are the structures of compound A, the two monochlorides, and alkene B?

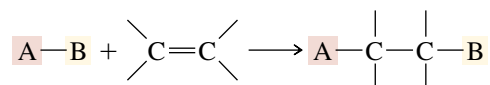
5.47 Compound A (C_6H_{14}) gives three different monochlorides on photochemical chlorination. One of these monochlorides is inert to E2 elimination. The other two monochlorides yield the same alkene B (C_6H_{12}) on being heated with potassium *tert*-butoxide in *tert*-butyl alcohol. Identify compound A, the three monochlorides, and alkene B.



CHAPTER 6

REACTIONS OF ALKENES: ADDITION REACTIONS

Now that we're familiar with the structure and preparation of alkenes, let's look at their chemical reactions. The characteristic reaction of alkenes is **addition** to the double bond according to the general equation:



The range of compounds represented as A—B in this equation is quite large, and their variety offers a wealth of opportunity for converting alkenes to a number of other functional group types.

Alkenes are commonly described as **unsaturated hydrocarbons** because they have the capacity to react with substances which add to them. Alkanes, on the other hand, are said to be **saturated** hydrocarbons and are incapable of undergoing addition reactions.

6.1 HYDROGENATION OF ALKENES

The relationship between reactants and products in addition reactions can be illustrated by the *hydrogenation* of alkenes to yield alkanes. **Hydrogenation** is the addition of H₂ to a multiple bond. An example is the reaction of hydrogen with ethylene to form ethane.

