

V

valence bond (VB) theory **15**
valence shell **13**
van der Waals forces **58**

vinyl group **212**

Z

Z configuration **215**
Zaitsev's rule **362**

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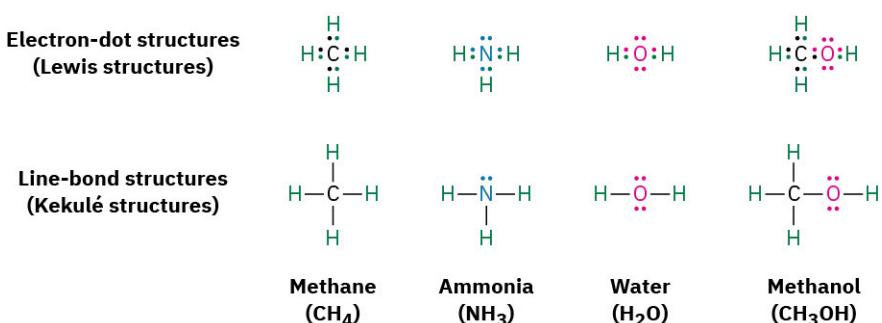
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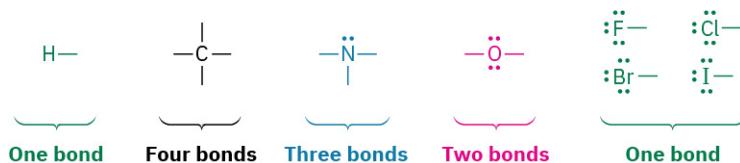
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Reactions of Alkyl Halides: Nucleophilic Substitutions and Eliminations 341

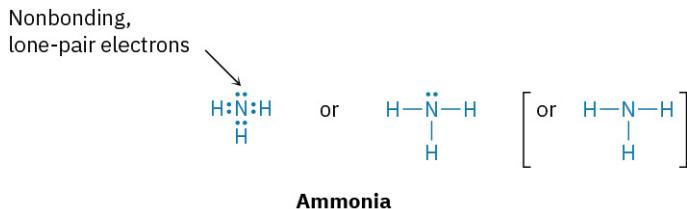
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The number of covalent bonds an atom forms depends on how many additional valence electrons it needs to reach a noble-gas configuration. Hydrogen has one valence electron ($1s$) and needs only one more to reach the helium configuration ($1s^2$), so it forms one bond. Carbon has four valence electrons ($2s^2 2p^2$) and needs four more to reach the neon configuration ($2s^2 2p^6$), so it forms four bonds. Nitrogen has five valence electrons ($2s^2 2p^3$), needs three more, and forms three bonds; oxygen has six valence electrons ($2s^2 2p^4$), needs two more, and forms two bonds; and the halogens have seven valence electrons, need one more, and form one bond.



Valence electrons that are not used for bonding remain as dots in structures and are called **lone-pair electrons**, or **nonbonding electrons**. The nitrogen atom in ammonia, NH_3 , for instance, shares six valence electrons in three covalent bonds and has its remaining two valence electrons as two dots in a nonbonding lone pair. As a time-saving shorthand, nonbonding electrons are often omitted when drawing line-bond structures, but you still have to keep them in mind since they're often crucial in chemical reactions.



WORKED EXAMPLE 1.1

Predicting the Number of Bonds Formed by Atoms in Molecules

How many hydrogen atoms does phosphorus bond to in forming phosphine, PH_3 ?

Strategy

Identify the periodic group of phosphorus, and find from that how many electrons (bonds) are needed to make an octet.

Solution

Phosphorus is in group 5A of the periodic table and has five valence electrons. It thus needs to share three more electrons to make an octet and therefore bonds to three hydrogen atoms, giving PH_3 .



WORKED EXAMPLE 1.2

Drawing Electron-Dot and Line-Bond Structures

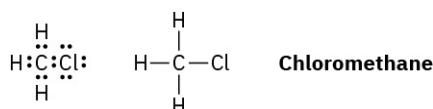
Draw both electron-dot and line-bond structures for chloromethane, CH_3Cl .

Strategy

Remember that a covalent bond—that is, a pair of shared electrons—is represented as a line between atoms.

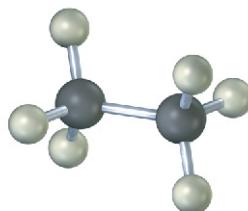
Solution

Hydrogen has one valence electron, carbon has four valence electrons, and chlorine has seven valence electrons. Thus, chloromethane is represented as



PROBLEM Draw a molecule of chloroform, CHCl_3 , using solid, wedged, and dashed lines to show its tetrahedral geometry.
1-3

PROBLEM Convert the following representation of ethane, C_2H_6 , into a conventional drawing that uses solid, wedged, and dashed lines to indicate tetrahedral geometry around each carbon (black = C, gray = H).



Ethane

PROBLEM What are likely formulas for the following substances?

- 1-5 (a) $\text{CCl}_?$ (b) $\text{AlH}_?$ (c) $\text{CH}_?\text{Cl}_2$ (d) SiF (e) $\text{CH}_3\text{NH}_?$

PROBLEM Write line-bond structures for the following substances, showing all nonbonding electrons:

- 1-6 (a) CHCl_3 , chloroform (b) H_2S , hydrogen sulfide (c) CH_3NH_2 , methylamine
(d) CH_3Li , methyl lithium

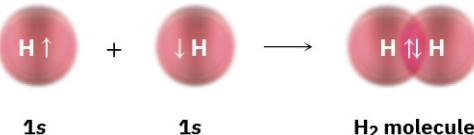
PROBLEM Why can't an organic molecule have the formula C_2H_7 ?

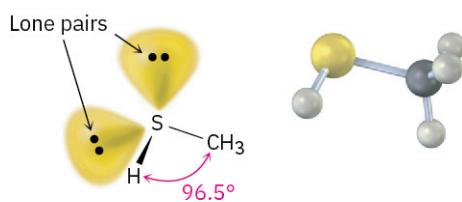
1-7

1.5 Describing Chemical Bonds: Valence Bond Theory

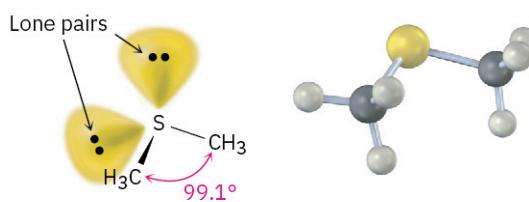
How does electron sharing lead to bonding between atoms? Two models have been developed to describe covalent bonding: *valence bond theory* and *molecular orbital theory*. Each model has its strengths and weaknesses, and chemists tend to use them interchangeably depending on the circumstances. Valence bond theory is the more easily visualized of the two, so most of the descriptions we'll use in this book derive from that approach.

According to **valence bond (VB) theory**, a covalent bond forms when two atoms approach each other closely and a singly occupied orbital on one atom *overlaps* a singly occupied orbital on the other atom. The electrons are now paired in the overlapping orbitals and are attracted to the nuclei of both atoms, thus bonding the atoms together. In the H_2 molecule, for instance, the H–H bond results from the overlap of two singly occupied hydrogen 1s orbitals.





Methanethiol

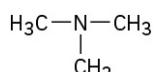


Dimethyl sulfide

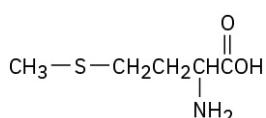
PROBLEM Identify all nonbonding lone pairs of electrons in the following molecules, and tell what geometry

1-14 you expect for each of the indicated atoms.

- (a) The oxygen atom in dimethyl ether, CH_3OCH_3 (b) The nitrogen atom in trimethylamine,



- (c) The phosphorus atom in phosphine, PH_3
 (d) The sulfur atom in the amino acid methionine,



1.11 Describing Chemical Bonds: Molecular Orbital Theory

We said in [Section 1.5](#) that chemists use two models for describing covalent bonds: valence bond theory and molecular orbital theory. Having now seen the valence bond approach, which uses hybrid atomic orbitals to account for geometry and assumes the overlap of atomic orbitals to account for electron sharing, let's look briefly at the molecular orbital approach to bonding. We'll return to this topic in Chapters 14, 15, and 30 for a more in-depth discussion.

Molecular orbital (MO) theory describes covalent bond formation as arising from a mathematical combination of atomic orbitals (wave functions) on different atoms to form *molecular orbitals*, so called because they belong to the entire molecule rather than to an individual atom. Just as an *atomic orbital*, whether unhybridized or hybridized, describes a region of space around an *atom* where an electron is likely to be found, so a *molecular orbital* describes a region of space in a *molecule* where electrons are most likely to be found.

Like an atomic orbital, a molecular orbital has a specific size, shape, and energy. In the H_2 molecule, for example, two singly occupied $1s$ atomic orbitals combine to form two molecular orbitals. There are two ways for the orbital combination to occur—an additive way and a subtractive way. The additive combination leads to formation of a molecular orbital that is lower in energy and roughly egg-shaped, while the subtractive combination leads to a molecular orbital that is higher in energy and has a node between nuclei ([FIGURE 1.18](#)). Note that the additive combination is a single, egg-shaped, molecular orbital; it is not the same as the two overlapping $1s$ atomic orbitals of the valence bond description. Similarly, the subtractive combination is a single molecular orbital with the shape of an elongated dumbbell.

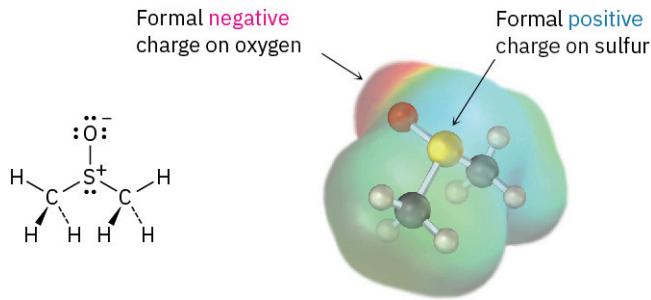
PROBLEM Ethylene glycol, HOCH₂CH₂OH, may look nonpolar when drawn, but an internal hydrogen bond between the two –OH groups results in a dipole moment. Explain.

PROBLEM Make three-dimensional drawings of the following molecules, and predict whether each has a dipole moment. If you expect a dipole moment, show its direction.

- (a) H₂C=CH₂ (b) CHCl₃ (c) CH₂Cl₂ (d) H₂C=CCl₂

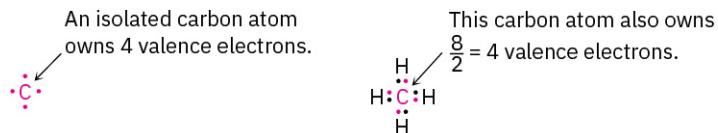
2.3 Formal Charges

Closely related to the ideas of bond polarity and dipole moment is the assignment of *formal charges* to specific atoms within a molecule, particularly atoms that have an apparently “abnormal” number of bonds. Look at dimethyl sulfoxide (CH₃SOCH₃), for instance, a solvent commonly used for preserving biological cell lines at low temperature. The sulfur atom in dimethyl sulfoxide has three bonds rather than the usual two and has a formal positive charge. The oxygen atom, by contrast, has one bond rather than the usual two and has a formal negative charge. Note that an electrostatic potential map of dimethyl sulfoxide shows the oxygen as negative (red) and the sulfur as relatively positive (blue), in accordance with the formal charges.

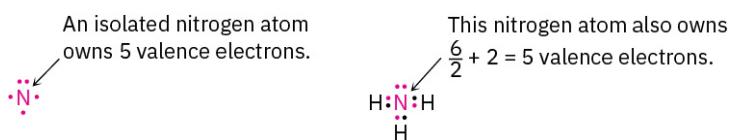


Dimethyl sulfoxide

Formal charges, as the name suggests, are a formalism and don't imply the presence of actual ionic charges in a molecule. Instead, they're a device for electron “bookkeeping” and can be thought of in the following way: A typical covalent bond is formed when each atom donates one electron. Although the bonding electrons are shared by both atoms, each atom can still be considered to “own” one electron for bookkeeping purposes. In methane, for instance, the carbon atom owns one electron in each of the four C–H bonds. Because a neutral, isolated carbon atom has four valence electrons, and because the carbon atom in methane still owns four, the methane carbon atom is neutral and has no formal charge.



The same is true for the nitrogen atom in ammonia, which has three covalent N–H bonds and two nonbonding electrons (a lone pair). Atomic nitrogen has five valence electrons, and the ammonia nitrogen also has five—one in each of three shared N–H bonds plus two in the lone pair. Thus, the nitrogen atom in ammonia has no formal charge.



The situation is different in dimethyl sulfoxide. Atomic sulfur has six valence electrons, but the dimethyl sulfoxide sulfur owns only five—one in each of the two S–C single bonds, one in the S–O single bond, and two in a lone pair. Thus, the sulfur atom has formally lost an electron and therefore has a positive formal charge. A similar calculation for the oxygen atom shows that it has formally gained an electron and has a negative charge. Atomic oxygen has six valence electrons, but the oxygen in dimethyl sulfoxide has seven—one in the O–S bond and two in each of three lone pairs. Thus, the oxygen has formally gained an electron and has a negative formal charge.



CHEMISTRY MATTERS

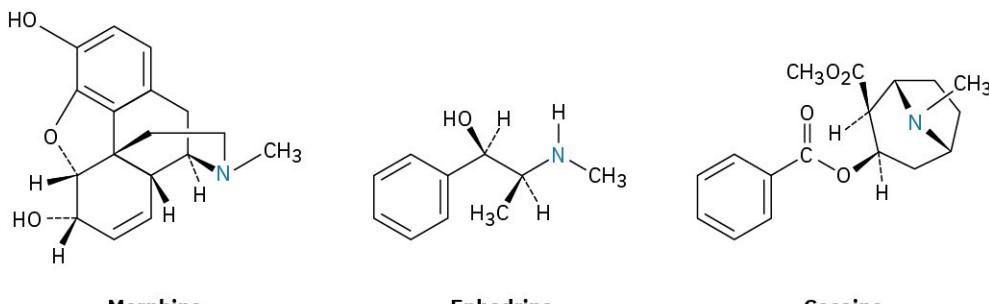
Alkaloids: From Cocaine to Dental Anesthetics

Just as ammonia (NH_3) is a weak base, there are a large number of nitrogen-containing organic compounds called amines that are also weak bases. In the early days of organic chemistry, basic amines derived from natural sources were known as vegetable alkali, but they are now called **alkaloids**. More than 20,000 alkaloids are known. Their study provided much of the impetus for the growth of organic chemistry in the nineteenth century and remains today an active and fascinating area of research.



FIGURE 2.9 The coca bush *Erythroxylon coca*, native to upland rain forest areas of Colombia, Ecuador, Peru, Bolivia, and western Brazil, is the source of the alkaloid cocaine. (credit: "Erythroxylum coca" by Danna Guevara/Wikimedia Commons, CC BY 4.0)

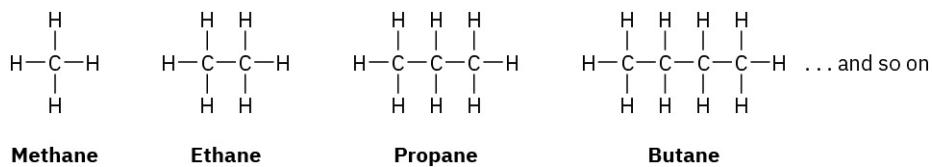
Many alkaloids have pronounced biological properties, and approximately 50% of pharmaceutical agents used today are derived from naturally occurring amines. As just three examples, morphine, an analgesic agent (painkiller), is obtained from the opium poppy *Papaver somniferum*. Ephedrine, a bronchodilator, decongestant, and appetite suppressant, is obtained from *Ephedra sinica*, an evergreen shrub native to Mongolia and northeastern China. Cocaine, both an anesthetic and a stimulant, is obtained from the coca bush *Erythroxylon coca*, endemic to the upland rain forest areas of central South America. (And yes, there really was a small amount of cocaine in the original Coca-Cola recipe, although it was removed in 1906.)



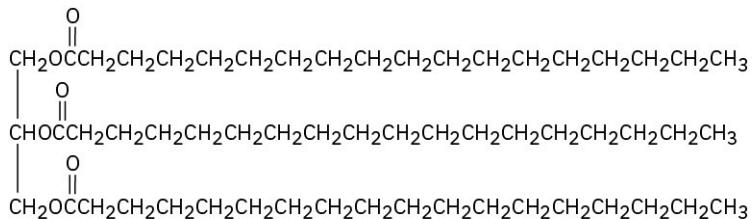
Cocaine itself is rarely used medically because it is too addictive, but its anesthetic properties provoked a long search for related but nonaddictive compounds. This search ultimately resulted in the synthesis of the “caine” anesthetics that are commonly used today in dental and surgical anesthesia. Procaine, the first such compound, was synthesized in 1898 and marketed under the name Novocain. It was rapidly adopted and remains in use today as a topical anesthetic. Other related compounds with different activity profiles followed: Lidocaine, marketed as Xylocaine, was introduced in 1943, and mepivacaine (Carbocaine) in the early 1960s. More recently, bupivacaine (Marcaine) and prilocaine (Citanest) have gained popularity. Both are quick-acting, but the effects of bupivacaine last for 3 to 6 hours while those of prilocaine fade after 45 minutes. Notice some structural similarity of all the caines to cocaine itself.

3.2 Alkanes and Alkane Isomers

Before beginning a systematic study of the different functional groups, let's look first at the simplest family of molecules to develop some general ideas that apply to all families. We saw in [Section 1.7](#) that the carbon–carbon single bond in ethane results from σ (head-on) overlap of carbon sp^3 hybrid orbitals. If we imagine joining three, four, five, or even more carbon atoms by C–C single bonds, we can generate the large family of molecules called **alkanes**.

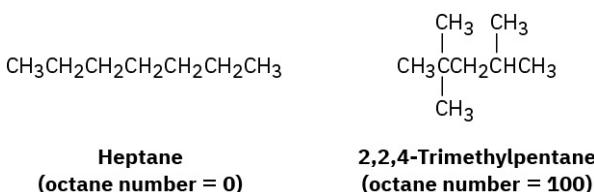


Alkanes are often described as *saturated hydrocarbons*: **hydrocarbons** because they contain only carbon and hydrogen; **saturated** because they have only C–C and C–H single bonds and thus contain the maximum possible number of hydrogens per carbon. They have the general formula C_nH_{2n+2} , where n is an integer. Alkanes are also occasionally called **aliphatic** compounds, a name derived from the Greek *aleiphas*, meaning “fat.” We'll see in [Section 27.1](#) that many animal fats contain long carbon chains similar to alkanes.



Think about the ways that carbon and hydrogen might combine to make alkanes. With one carbon and four hydrogens, only one structure is possible: methane, CH_4 . Similarly, there is only one combination of two carbons with six hydrogens (ethane, CH_3CH_3) and only one combination of three carbons with eight hydrogens (propane, $CH_3CH_2CH_3$). When larger numbers of carbons and hydrogens combine, however, more than one structure is possible. For example, there are two substances with the formula C_4H_{10} : the four carbons can all be in a row (butane), or they can branch (isobutane). Similarly, there are three C_5H_{12} molecules, and so on for larger alkanes.

The *octane number* of a fuel is the measure by which its antiknock properties are judged. It was recognized long ago that straight-chain hydrocarbons are far more prone to inducing engine knock than highly branched compounds. Heptane, a particularly bad fuel, is assigned a base value of 0 octane number, and 2,2,4-trimethylpentane, commonly known as iso-octane, has a rating of 100.



Because straight-run gasoline burns so poorly in engines, petroleum chemists have devised numerous methods for producing higher-quality fuels. One of these methods, *catalytic cracking*, involves taking the high-boiling kerosene cut ($\text{C}_{11}\text{--C}_{14}$) and “cracking” it into smaller branched molecules suitable for use in gasoline. Another process, called *reforming*, is used to convert $\text{C}_6\text{--C}_8$ alkanes to aromatic compounds such as benzene and toluene, which have substantially higher octane numbers than alkanes. The final product that goes in your tank has an approximate composition of 15% $\text{C}_4\text{--C}_8$ straight-chain alkanes, 25% to 40% $\text{C}_4\text{--C}_{10}$ branched-chain alkanes, 10% cyclic alkanes, 10% straight-chain and cyclic alkenes, and 25% arenes (aromatics).

Key Terms

- alcohol
- aldehyde
- aliphatic
- alkane
- alkene
- alkyl group
- alkyl halide
- alkyne
- amide
- amine
- anti conformation
- arene
- branched-chain alkane
- carbonyl group
- carboxylic acid
- conformation
- conformational isomer
- conformer
- constitutional isomer
- eclipsed conformation
- ester
- ether
- functional group
- gauche conformation
- hydrocarbon
- isomer
- ketone
- Newman projection
- nitrile
- R group
- saturated
- sawhorse representation
- staggered conformation
- stereochemistry
- steric strain
- straight-chain alkane
- substituent
- sulfid
- thiol
- torsional strain

Summary

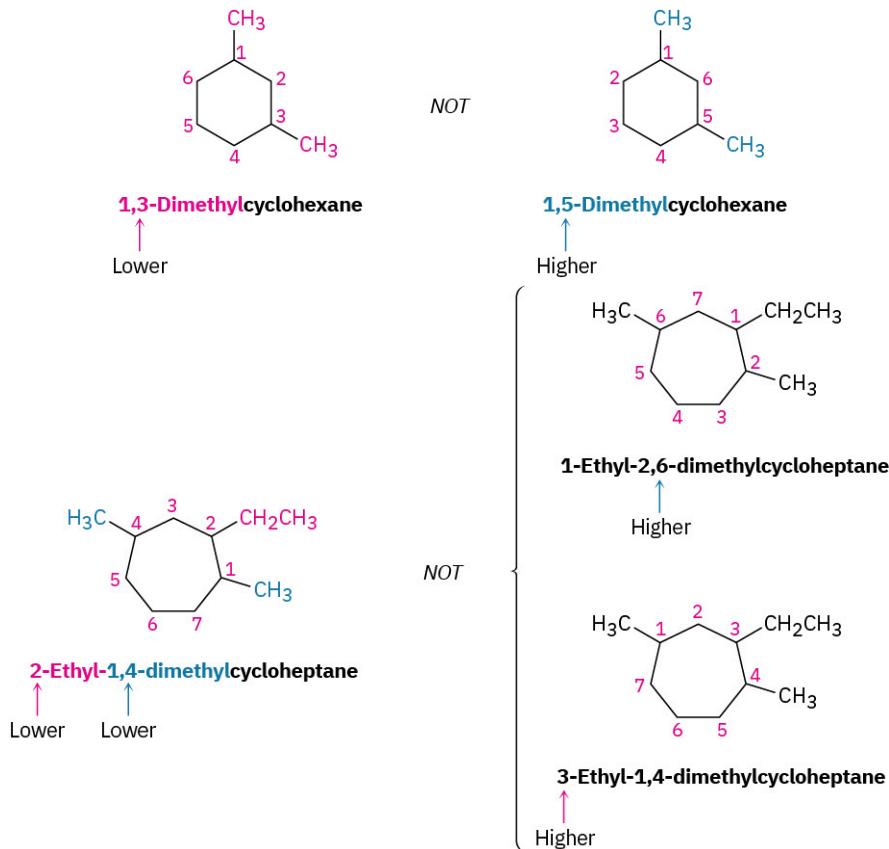
Alkanes are relatively unreactive and rarely involved in chemical reactions, but they nevertheless provide a useful vehicle for introducing some important general ideas. In this chapter, we’ve used alkanes to introduce the basic approach to naming organic compounds and to take an initial look at some of the three-dimensional aspects of molecules.

A **functional group** is a group of atoms within a larger molecule that has a characteristic chemical reactivity. Because functional groups behave in approximately the same way in all molecules where they occur, the chemical reactions of an organic molecule are largely determined by its functional groups.

Alkanes are a class of **saturated hydrocarbons** with the general formula $\text{C}_n\text{H}_{2n+2}$. They contain no functional groups, are relatively inert, and can be either **straight-chain** (*normal*) or **branched**. Alkanes are named by a series of IUPAC rules of nomenclature. Compounds that have the same chemical formula but different

STEP 2**Number the substituents, and write the name.**

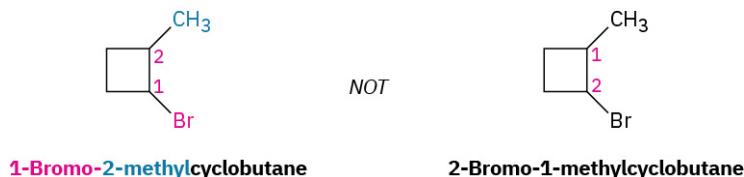
For an alkyl- or halo-substituted cycloalkane, choose a point of attachment as carbon 1 and number the substituents on the ring so that the *second* substituent has as low a number as possible. If ambiguity still exists, number so that the third or fourth substituent has as low a number as possible, until a point of difference is found.



(a) When two or more different alkyl groups are present that could potentially take the same numbers, number them by alphabetical priority, ignoring numerical prefixes such as di- and tri-.



(b) If halogens are present, treat them just like alkyl groups.

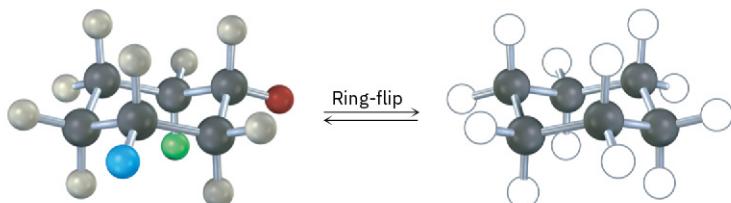


Some additional examples follow:

PROBLEM Draw two different chair conformations of cyclohexanol (hydroxycyclohexane), showing all **4-12** hydrogen atoms. Identify each position as axial or equatorial.

PROBLEM Draw two different chair conformations of *trans*-1,4-dimethylcyclohexane, and label all positions **4-13** as axial or equatorial.

PROBLEM Identify each of the colored positions—red, blue, and green—as axial or equatorial. Then carry out a **4-14** ring-flip, and show the new positions occupied by each color.



4.7 Conformations of Monosubstituted Cyclohexanes

Even though cyclohexane rings flip rapidly between chair conformations at room temperature, the two conformations of a monosubstituted cyclohexane aren't equally stable. In methylcyclohexane, for instance, the equatorial conformation is more stable than the axial conformation by 7.6 kJ/mol (1.8 kcal/mol). The same is true of other monosubstituted cyclohexanes: a substituent is almost always more stable in an equatorial position than in an axial position.

You might recall from your general chemistry course that it's possible to calculate the percentages of two isomers at equilibrium using the equation $\Delta E = -RT \ln K$, where ΔE is the energy difference between isomers, R is the gas constant [8.315 J/(K·mol)], T is the Kelvin temperature, and K is the equilibrium constant between isomers. For example, an energy difference of 7.6 kJ/mol means that about 95% of methylcyclohexane molecules have an equatorial methyl group at any given instant while only 5% have an axial methyl group. **FIGURE 4.13** plots the relationship between energy and isomer percentages.

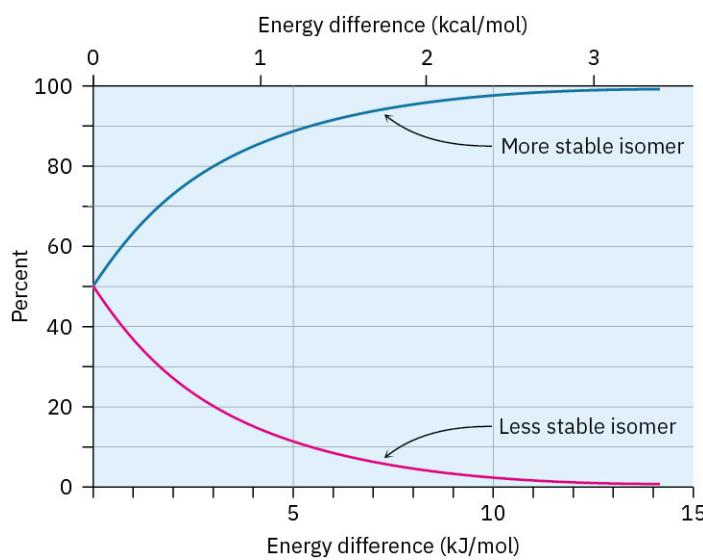


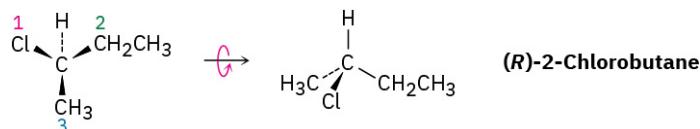
FIGURE 4.13 A plot of the percentages of two isomers at equilibrium versus the energy difference between them. The curves are calculated using the equation $\Delta E = -RT \ln K$.

The energy difference between axial and equatorial conformations is due to steric strain caused by **1,3-diaxial interactions**. The axial methyl group on C1 is too close to the axial hydrogens three carbons away on C3 and C5, resulting in 7.6 kJ/mol of steric strain (**FIGURE 4.14**).

Strategy

Begin by ranking the four substituents bonded to the chirality center: (1) $-\text{Cl}$, (2) $-\text{CH}_2\text{CH}_3$, (3) $-\text{CH}_3$, (4) $-\text{H}$. To draw a tetrahedral representation of the molecule, orient the lowest-ranked group ($-\text{H}$) away from you and imagine that the other three groups are coming out of the page toward you. Then, place the remaining three substituents such that the direction of travel $1 \rightarrow 2 \rightarrow 3$ is clockwise (right turn), and tilt the molecule toward you to bring the rear hydrogen into view. Using molecular models is a real help in working problems of this sort.

Solution



PROBLEM Which member in each of the following sets ranks higher?

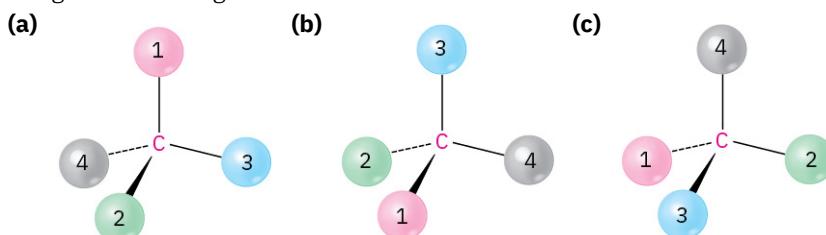
- 5-7 (a) $-\text{H}$ or $-\text{Br}$ (b) $-\text{Cl}$ or $-\text{Br}$ (c) $-\text{CH}_3$ or $-\text{CH}_2\text{CH}_3$ (d) $-\text{NH}_2$ or $-\text{OH}$ (e) $-\text{CH}_2\text{OH}$ or $-\text{CH}_3$
 (f) $-\text{CH}_2\text{OH}$ or $-\text{CH}=\text{O}$

PROBLEM Rank each of the following sets of substituents:

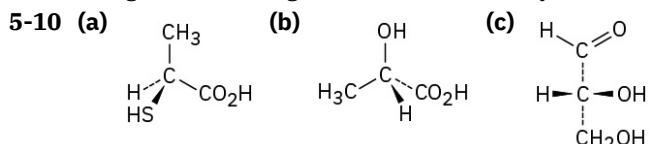
- 5-8 (a) $-\text{H}$, $-\text{OH}$, $-\text{CH}_2\text{CH}_3$, $-\text{CH}_2\text{CH}_2\text{OH}$ (b) $-\text{CO}_2\text{H}$, $-\text{CO}_2\text{CH}_3$, $-\text{CH}_2\text{OH}$, $-\text{OH}$
 (c) $-\text{CN}$, $-\text{CH}_2\text{NH}_2$, $-\text{CH}_2\text{NHCH}_3$, $-\text{NH}_2$ (d) $-\text{SH}$, $-\text{CH}_2\text{SCH}_3$, $-\text{CH}_3$, $-\text{SSCH}_3$

PROBLEM Orient each of the following drawings so that the lowest-ranked group is toward the rear, and then

- 5-9 assign *R* or *S* configuration:



PROBLEM Assign *R* or *S* configuration to the chirality center in each of the following molecules:

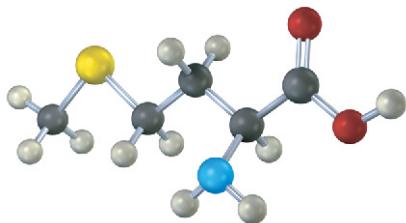


PROBLEM Draw a tetrahedral representation of *(S)*-2-pentanol (2-hydroxypentane).

5-11

PROBLEM Assign *R* or *S* configuration to the chirality center in the following molecular model of the amino

5-12 acid methionine (blue = N, yellow = S):



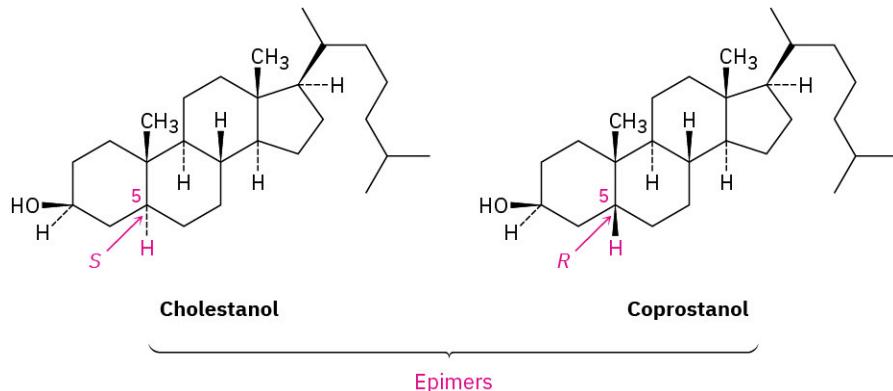
5.6 Diastereomers

Molecules like lactic acid, alanine, and glyceraldehyde are relatively simple because each has only one chirality center and thus only two stereoisomers. The situation becomes more complex, however, with molecules that have more than one chirality center. As a general rule, a molecule with *n* chirality centers can have up to

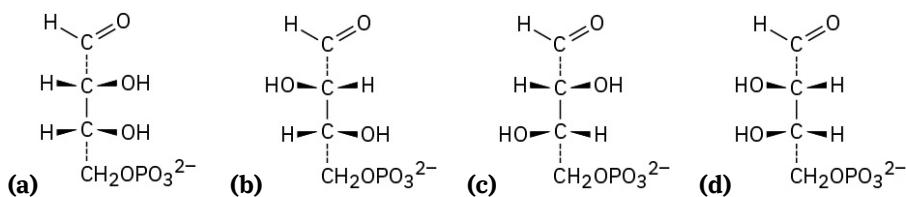
TABLE 5.2 Relationships among the Four Stereoisomers of Threonine

Stereoisomer	Enantiomer	Diastereomer
2R,3S	2S,3R	2R,3R and 2S,3S
2S,3R	2R,3S	2R,3R and 2S,3S

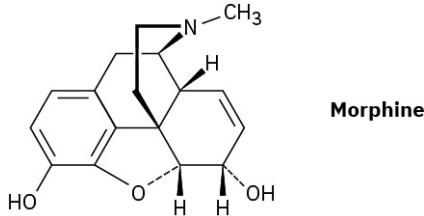
In the special case where two diastereomers differ at only one chirality center but are the same at all others, we say that the compounds are **epimers**. Cholestanol and coprostanol, for instance, are both found in human feces, and both have nine chirality centers. Eight of the nine are identical, but the one at C5 is different. Thus, cholestanol and coprostanol are *epimeric* at C5.



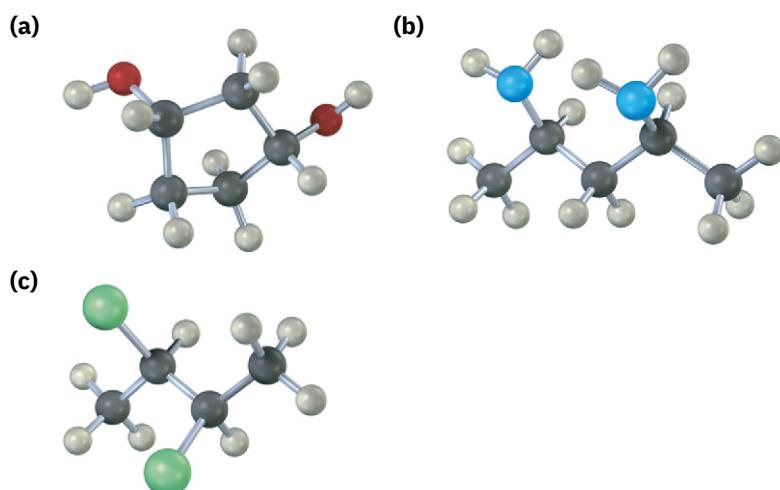
PROBLEM One of the following molecules **(a)**–**(d)** is D-erythrose 4-phosphate, an intermediate in the Calvin
5-13 photosynthetic cycle by which plants incorporate CO₂ into carbohydrates. If D-erythrose 4-phosphate has R stereochemistry at both chirality centers, which of the structures is it? Which of the remaining three structures is the enantiomer of D-erythrose 4-phosphate, and which are diastereomers?



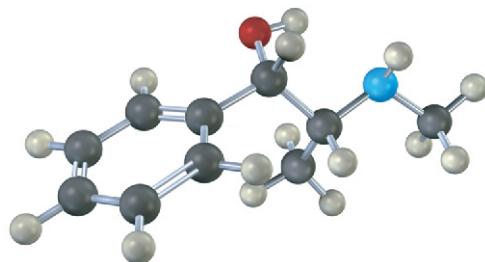
PROBLEM How many chirality centers does morphine have? How many stereoisomers of morphine are
5-14 possible in principle?



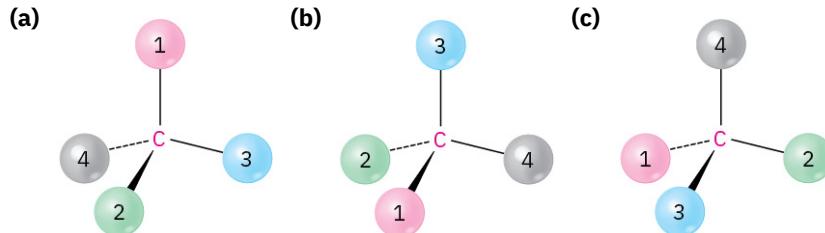
PROBLEM Assign R or S configuration to each chirality center in the following molecular model of the amino
5-15 acid isoleucine (blue = N):



PROBLEM Assign *R* or *S* configuration to each chirality center in pseudoephedrine, an over-the-counter decongestant found in cold remedies (blue = N).



PROBLEM Orient each of the following drawings so that the lowest-ranked group is toward the rear, and then assign *R* or *S* configuration:



Chirality and Optical Activity

PROBLEM Which of the following objects are chiral?

- 5-31 (a) A basketball (b) A fork (c) A wine glass (d) A golf club (e) A spiral staircase
 (f) A snowflake

PROBLEM Which of the following compounds are chiral? Draw them, and label the chirality centers.

- 5-32 (a) 2,4-Dimethylheptane (b) 5-Ethyl-3,3-dimethylheptane (c) *cis*-1,4-Dichlorocyclohexane

PROBLEM Draw chiral molecules that meet the following descriptions:

- 5-33 (a) A chloroalkane, $C_5H_{11}Cl$ (b) An alcohol, $C_6H_{14}O$ (c) An alkene, C_6H_{12}
 (d) An alkane, C_8H_{18}

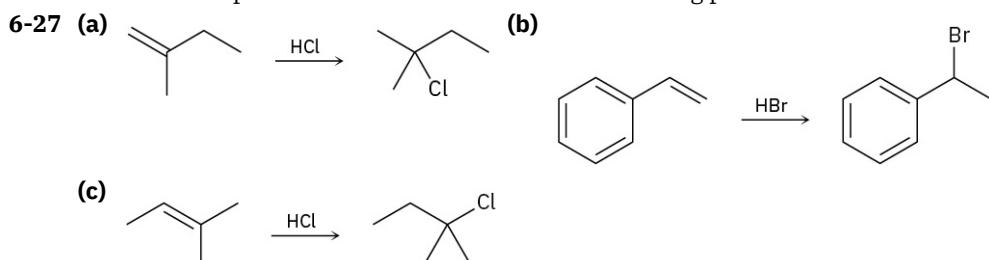
PROBLEM Eight alcohols have the formula $C_5H_{12}O$. Draw them. Which are chiral?

- 5-34

PROBLEM Draw compounds that fit the following descriptions:

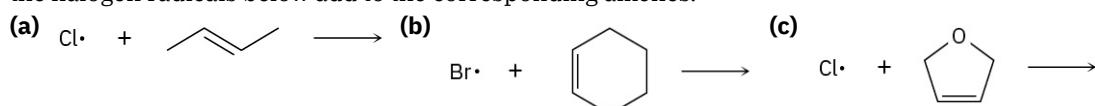
- 5-35 (a) A chiral alcohol with four carbons (b) A chiral carboxylic acid with the formula $C_5H_{10}O_2$

PROBLEM Draw the complete mechanism for each of the following polar reactions.



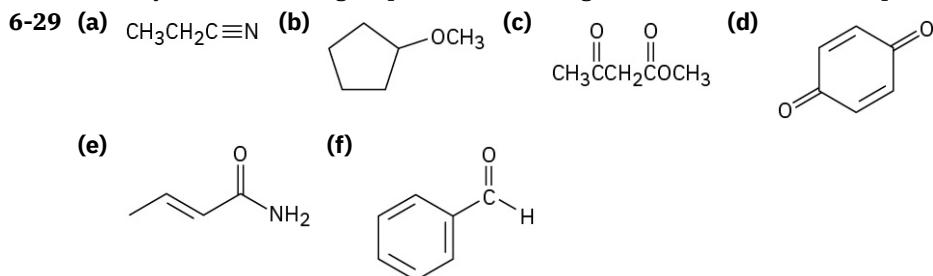
PROBLEM Use curved arrows to show the flow of electrons, and draw the carbon radical that is formed when

6-28 the halogen radicals below add to the corresponding alkenes.

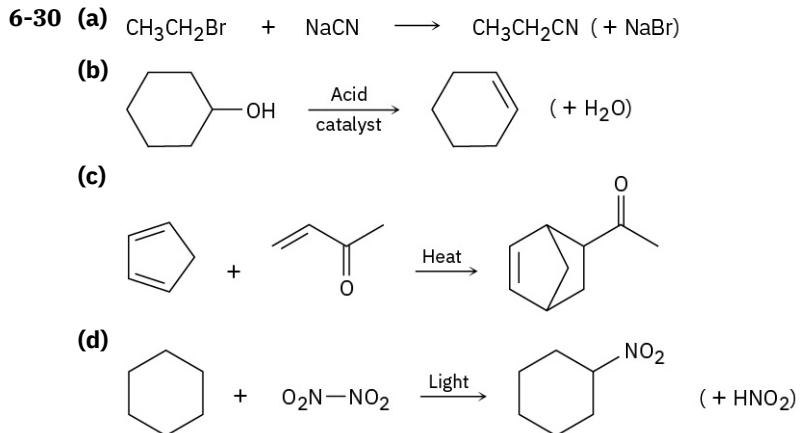


Polar Reactions

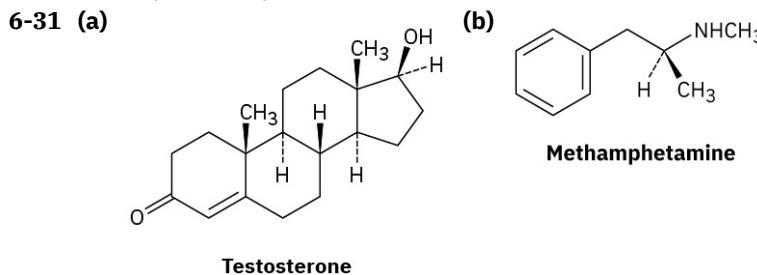
PROBLEM Identify the functional groups in the following molecules, and show the polarity of each:



PROBLEM Identify the following reactions as additions, eliminations, substitutions, or rearrangements:



PROBLEM Identify the likely electrophilic and nucleophilic sites in each of the following molecules:



Testosterone

PROBLEM Identify the electrophile and the nucleophile.

6-32



CHEMISTRY MATTERS

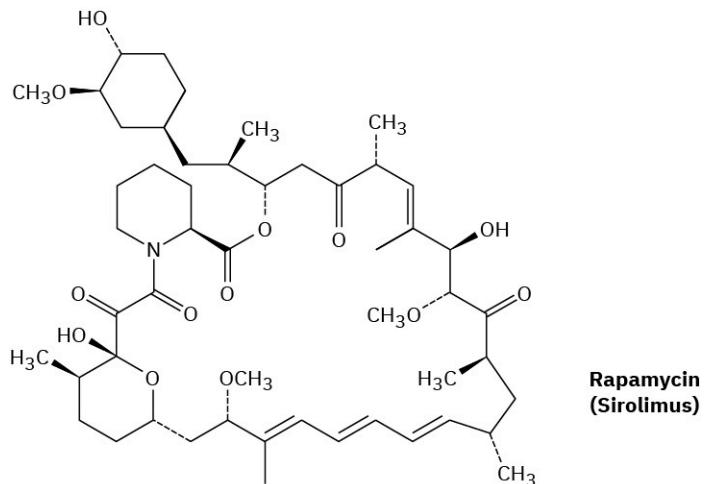
Bioprospecting: Hunting for Natural Products

Most people know the names of the common classes of biomolecules—proteins, carbohydrates, lipids, and nucleic acids—but there are many more kinds of compounds in living organisms than just those four. All living organisms also contain a vast diversity of substances usually grouped under the heading *natural products*. The term **natural product** really refers to any naturally occurring substance but is generally taken to mean a so-called secondary metabolite—a small molecule that is not essential to the growth and development of the producing organism and is not classified by structure.



FIGURE 7.18 Rapamycin, an immunosuppressant natural product used during organ transplants, was originally isolated from a soil sample found on Rapa Nui (Easter Island), an island 2200 miles off the coast of Chile known for its giant Moai statues. (credit: modification of work "Moai facing inland at Ahu Tongariki" by Ian Sewell/Wikimedia Commons, CC BY 2.5)

It has been estimated that well over 300,000 secondary metabolites exist, and it's thought that their primary function is to increase the likelihood of an organism's survival by repelling or attracting other organisms. Alkaloids, such as morphine; antibiotics, such as erythromycin and the penicillins; and immunosuppressive agents, such as rapamycin (sirolimus) prescribed for liver transplant recipients, are examples.



Where do these natural products come from, and how are they found? Although most chemists and biologists spend their working time in the laboratory, a few spend their days scuba diving on South Pacific islands or trekking through the rainforests of South America and Southeast Asia at work as bioprospectors. Their job is to

8.7 Oxidation of Alkenes: Epoxidation and Hydroxylation

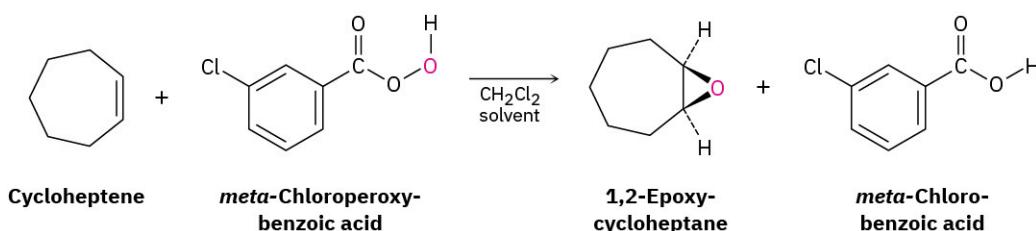
Like the word *reduction* used in the previous section for the addition of hydrogen to a double bond, the word *oxidation* has a slightly different meaning in organic chemistry than what you might have previously learned. In general chemistry, an oxidation is defined as the loss of one or more electrons by an atom. In organic chemistry, however, an **oxidation** is a reaction that results in a loss of electron density for carbon, caused either by bond formation between carbon and a more electronegative atom—usually oxygen, nitrogen, or a halogen—or by bond-breaking between carbon and a less electronegative atom—usually hydrogen. Note that an *oxidation* often adds oxygen, while a *reduction* often adds hydrogen.

Oxidation

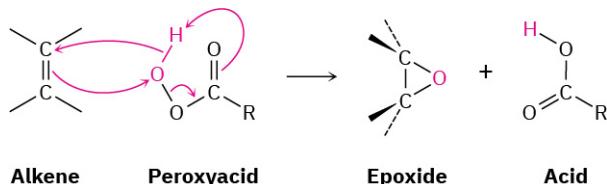
Decreases electron density on carbon by:

- forming one of these: C–O C–N C–X
- or breaking this: C–H

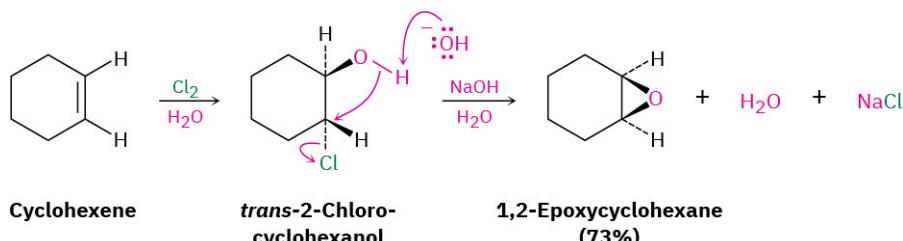
In the laboratory, alkenes are oxidized to give *epoxides* on treatment with a *peroxyacid*, RCO_3H , such as *meta*-chloroperoxybenzoic acid. An **epoxide**, also called an **oxirane**, is a cyclic ether with an oxygen atom in a three-membered ring. For example:



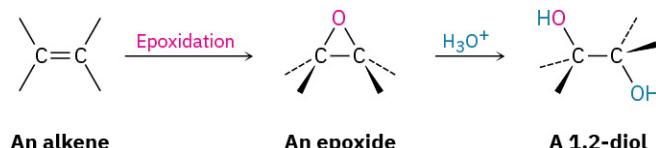
Peroxyacids transfer an oxygen atom to the alkene with *syn* stereochemistry—both C–O bonds form on the same face of the double bond—through a one-step mechanism without intermediates. The oxygen atom farthest from the carbonyl group is the one transferred.

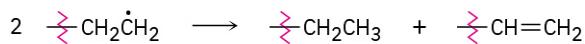


Another method for the synthesis of epoxides involves the use of halohydrins, prepared by electrophilic addition of $\text{HO}-\text{X}$ to alkenes (Section 8.3). When a halohydrin is treated with base, HX is eliminated and an epoxide is produced.



Epoxides undergo an acid-catalyzed ring-opening reaction with water (a hydrolysis) to give the corresponding 1,2-dialcohol, or *diol*, also called a **glycol**. Thus, the net result of the two-step alkene epoxidation/hydrolysis is **hydroxylation**—the addition of an $-\text{OH}$ group to each of the two double-bond carbons. In fact, approximately 204 million tons of ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$, most of it used for automobile antifreeze, are produced worldwide each year by the epoxidation of ethylene and subsequent hydrolysis.

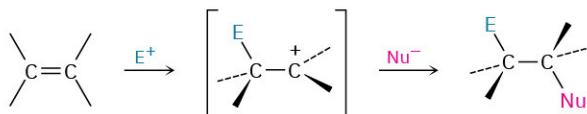




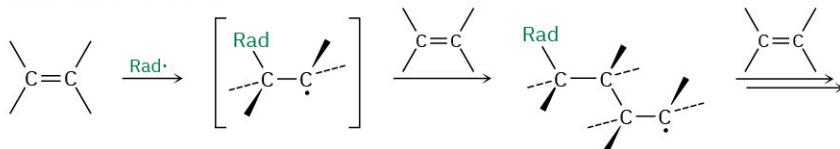
8.11 Biological Additions of Radicals to Alkenes

The same high reactivity of radicals that enables the alkene polymerization we saw in the previous section also makes it difficult to carry out controlled radical reactions on complex molecules. As a result, there are severe limitations on the usefulness of radical addition reactions in the laboratory. In contrast to an electrophilic addition, where reaction occurs once and the reactive cation intermediate is rapidly quenched by a nucleophile, the reactive intermediate in a radical reaction is not usually quenched. Instead, it reacts again and again in a largely uncontrollable way.

Electrophilic addition
**(Intermediate is quenched,
so reaction stops.)**



Radical addition
**(Intermediate is not quenched,
so reaction does not stop.)**

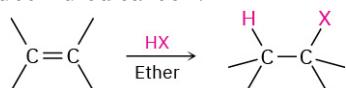


In biological reactions, the situation is different from that in the laboratory. Only one substrate molecule at a time is present in the active site of an enzyme, and that molecule is held in a precise position, with other necessary reacting groups nearby. As a result, biological radical reactions are more controlled and more common than laboratory or industrial radical reactions. A particularly impressive example occurs in the biosynthesis of prostaglandins from arachidonic acid, where a sequence of four radical additions take place. Its reaction mechanism was discussed briefly in [Section 6.6](#).

As shown in [FIGURE 8.12](#), prostaglandin biosynthesis begins with abstraction of a hydrogen atom from C13 of arachidonic acid by an iron–oxy radical to give a carbon radical that reacts with O₂ at C11 through a resonance form. The oxygen radical that results adds to the C8–C9 double bond to give a carbon radical at C8, which adds to the C12–C13 double bond and gives a carbon radical at C13. A resonance form of this carbon radical adds at C15 to a second O₂ molecule, completing the prostaglandin skeleton. Reduction of the O–O bond then gives prostaglandin H₂, called PGH₂. The pathway looks complicated, but the entire process is catalyzed with exquisite control by a single enzyme.

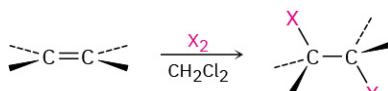
a. Addition of HCl, HBr, and HI ([Section 7.7](#) and [Section 7.8](#))

Markovnikov regiochemistry occurs, with H adding to the less highly substituted alkene carbon and halogen adding to the more highly substituted carbon.



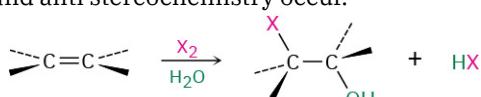
b. Addition of halogens Cl₂ and Br₂ ([Section 8.2](#))

Anti addition is observed through a halonium ion intermediate.



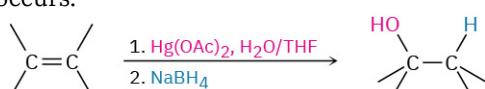
c. Halohydrin formation ([Section 8.3](#))

Markovnikov regiochemistry and anti stereochemistry occur.



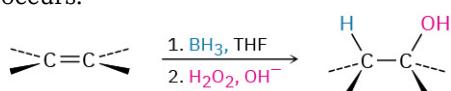
d. Addition of water by oxymercuration–demercuration ([Section 8.4](#))

Markovnikov regiochemistry occurs.



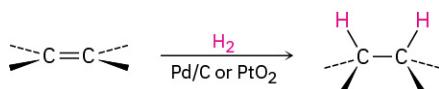
e. Addition of water by hydroboration–oxidation ([Section 8.5](#))

Non-Markovnikov syn addition occurs.



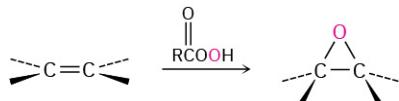
f. Catalytic hydrogenation ([Section 8.6](#))

Syn addition occurs.



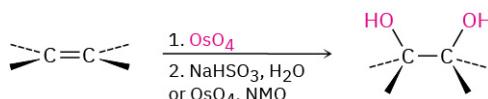
g. Epoxidation with a peroxyacid ([Section 8.7](#))

Syn addition occurs.



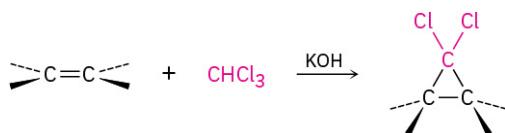
h. Hydroxylation with OsO₄ ([Section 8.7](#))

Syn addition occurs.

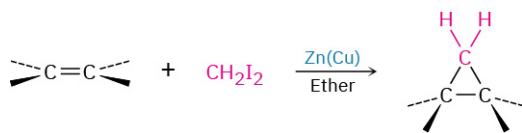


i. Addition of carbenes to yield cyclopropanes ([Section 8.9](#))

(1) Dichlorocarbene addition



(2) Simmons–Smith reaction





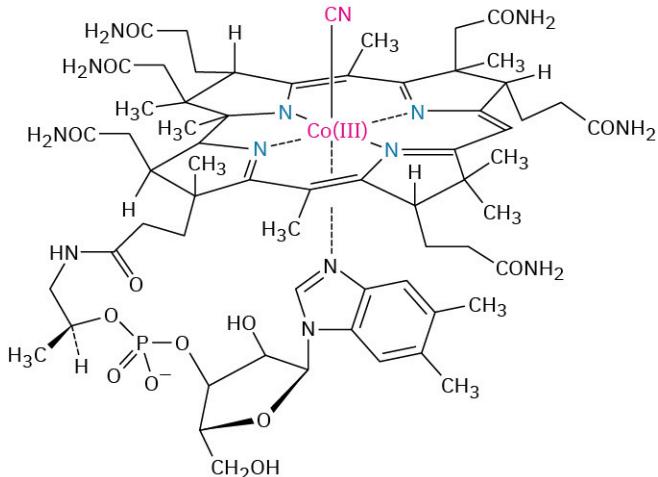
CHEMISTRY MATTERS

The Art of Organic Synthesis



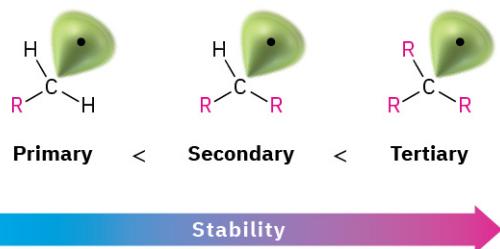
FIGURE 9.8 Vitamin B₁₂ has been synthesized from scratch in the laboratory, but the bacteria growing on sludge from municipal sewage plants do a much better job. (credit: “Aeration and sludge-wasting” by U.S. Department of Agriculture/Flickr, Public Domain)

If you think some of the synthesis problems at the end of this chapter are difficult, try devising a synthesis of vitamin B₁₂ starting only from simple substances you can buy in a chemical catalog. This extraordinary achievement was reported in 1973 as the culmination of a collaborative effort headed by Robert B. Woodward of Harvard University and Albert Eschenmoser of the Swiss Federal Institute of Technology in Zürich. More than 100 graduate students and postdoctoral associates contributed to the work, which took more than a decade to complete.



Vitamin B₁₂

Why put such extraordinary effort into the laboratory synthesis of a molecule so easily obtained from natural sources? There are many reasons. On a basic human level, a chemist might be motivated primarily by the challenge, much as a climber might be challenged by the ascent of a difficult peak. Beyond the pure challenge, the completion of a difficult synthesis is also valuable in that it establishes new standards and raises the field to a new level. If vitamin B₁₂ can be made, then why can't any molecule found in nature be made? Indeed, the decades that have passed since the work of Woodward and Eschenmoser have seen the laboratory synthesis of many enormously complex and valuable substances. Sometimes these substances—for instance, the anticancer compound paclitaxel, trade named Taxol—are not easily available in nature, so laboratory synthesis is the only



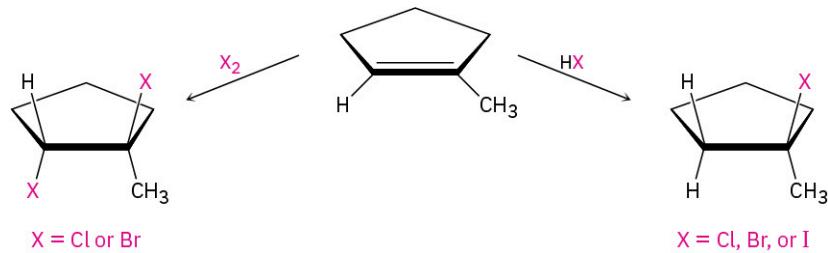
PROBLEM Draw and name all monochloro products you would expect to obtain from radical chlorination of **10-3** 2-methylpentane. Which, if any, are chiral?

PROBLEM Taking the relative reactivities of 1° , 2° , and 3° hydrogen atoms into account, what product(s) would

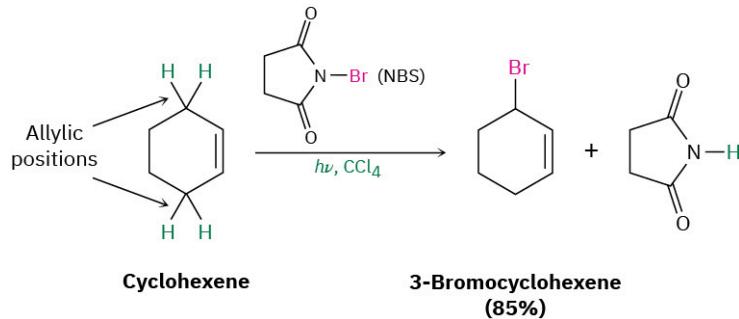
10-4 you expect to obtain from monochlorination of 2-methylbutane? What would the approximate percentage of each product be? (Don't forget to take into account the number of each kind of hydrogen.)

10.3 Preparing Alkyl Halides from Alkenes: Allylic Bromination

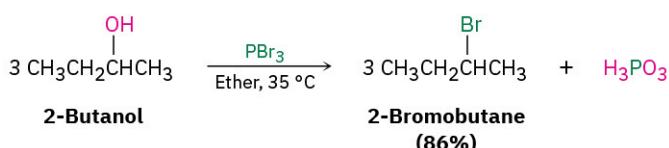
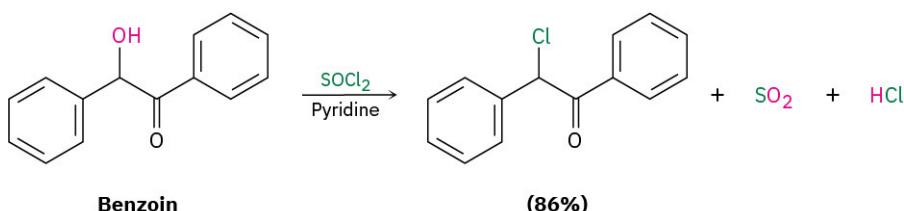
We've already seen several methods for preparing alkyl halides from alkenes, including the reactions of HX and X_2 with alkenes in electrophilic addition reactions ([Section 7.7](#) and [Section 8.2](#)). The hydrogen halides HCl , HBr , and HI react with alkenes by a polar mechanism to give the product of Markovnikov addition. Bromine and chlorine undergo anti addition through halonium ion intermediates to give 1,2-dihalogenated products.



Another laboratory method for preparing alkyl halides from alkenes is by reaction with *N*-bromosuccinimide (abbreviated NBS), in the presence of ultraviolet light, to give products resulting from substitution of hydrogen by bromine at the position next to the double bond—the **allylic** position. Cyclohexene, for example, gives 3-bromocyclohexene.

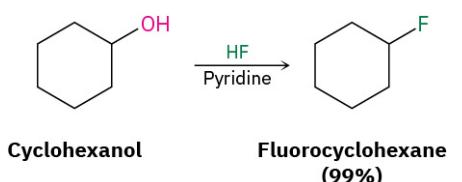


This allylic bromination with NBS is analogous to the alkane chlorination reaction discussed in the previous section and occurs by a radical chain-reaction pathway ([FIGURE 10.3](#)). As in alkane halogenation, a $\text{Br}\cdot$ radical abstracts an allylic hydrogen atom, forming an allylic radical plus HBr . The HBr then reacts with NBS to form Br_2 , which in turn reacts with the allylic radical to yield the brominated product and a $\text{Br}\cdot$ radical that cycles back into the first step and carries on the chain.



As the preceding examples indicate, the yields of these SOCl_2 and PBr_3 reactions are generally high and other functional groups such as ethers, carbonyls, and aromatic rings don't usually interfere. We'll look at the mechanisms of these and other related substitution reactions in **Section 11.3**.

Alkyl fluorides can also be prepared from alcohols. Numerous alternative reagents are used for such reactions, including diethylaminosulfur trifluoride [$(CH_3CH_2)_2NSF_3$] and HF in pyridine solvent.

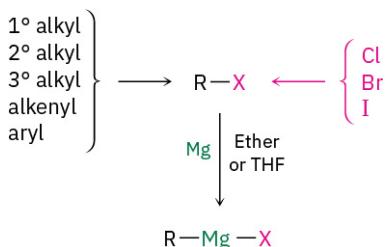


PROBLEM How would you prepare the following alkyl halides from the corresponding alcohols?

- 10-8 (a)**  **(b)**  **(c)** 

10.6 Reactions of Alkyl Halides: Grignard Reagents

Alkyl halides, RX, react with magnesium metal in ether or tetrahydrofuran (THF) solvent to yield alkylmagnesium halides, RMgX. The products, called **Grignard reagents** (**RMgX**) after their discoverer, Francois Auguste Victor Grignard, who received the 1912 Nobel Prize in Chemistry, are examples of **organometallic** compounds because they contain a carbon–metal bond. In addition to alkyl halides, Grignard reagents can also be made from alkenyl (vinylic) and aryl (aromatic) halides. The halogen can be Cl, Br, or I, although chlorides are less reactive than bromides and iodides. Organofluorides rarely react with magnesium.



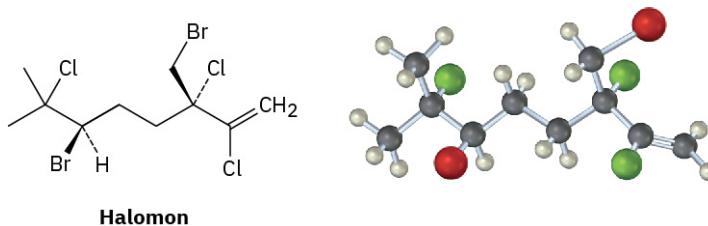
As you might expect from the discussion of electronegativity and bond polarity in [Section 6.3](#), the carbon–magnesium bond is polarized, making the carbon atom of Grignard reagents both nucleophilic and basic. An electrostatic potential map of methylmagnesium iodide, for instance, indicates the electron-rich (red) character of the carbon bonded to magnesium.



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Naturally Occurring Organohalides

Just forty years ago in 1980, only about 30 naturally occurring organohalides were known. It was simply assumed that chloroform, halogenated phenols, chlorinated aromatic compounds called PCBs, and other such substances found in the environment were industrial pollutants. Now, less than half a century later, the situation is quite different. More than 5000 organohalides have been found to occur naturally, and tens of thousands more surely exist. From a simple compound like chloromethane to an extremely complex one like the antibiotic vancomycin, a remarkably diverse range of organohalides exists in plants, bacteria, and animals. Many even have valuable physiological activity. The pentahalogenated alkene halomon, for instance, has been isolated from the red alga *Portieria hornemannii* and found to have anticancer activity against several human tumor cell lines.



Halomon

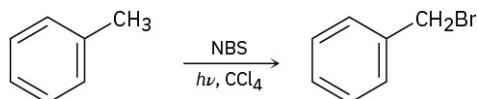
Some naturally occurring organohalides are produced in massive quantities. Forest fires, volcanic eruptions, and marine kelp release up to 5 million tons of CH_3Cl per year, for example, while annual industrial emissions total about 26,000 tons. Termites are thought to release as much as 10^8 kg of chloroform per year. A detailed examination of the Okinawan acorn worm *Ptychoderma flava* found that the 64 million worms living in a 1 km^2 study area excreted nearly 8000 pounds per year of bromophenols and bromoindoles, compounds previously thought to be non-natural pollutants.

Why do organisms produce organohalides, many of which are undoubtedly toxic? The answer seems to be that many organisms use organohalogen compounds for self-defense, either as feeding deterrents, irritants to predators, or natural pesticides. Marine sponges, coral, and sea hares, for example, release foul-tasting organohalides that deter fish, starfish, and other predators. Even humans appear to produce halogenated compounds as part of their defense against infection. The human immune system contains a peroxidase enzyme capable of carrying out halogenation reactions on fungi and bacteria, thereby killing the pathogen. And most remarkable of all, even free chlorine— Cl_2 —has been found to be present in humans.



FIGURE 10.8 Marine corals secrete organohalogen compounds that act as a feeding deterrent to fish. (credit: "Coral reef" by Qui Nguyen, United Nations Environment Programme/Flickr, Public Domain)

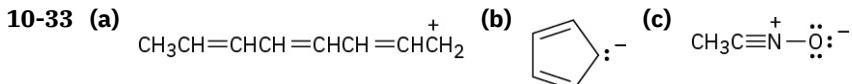
substitution has occurred at the position next to the aromatic ring (the *benzylic* position). Explain, based on the bond dissociation energies in Table 6.3.



PROBLEM Draw resonance structures for the benzyl radical, $C_6H_5CH_2\cdot$, the intermediate produced in the NBS

10-32 bromination reaction of toluene (Problem 10-31).

PROBLEM Draw resonance structures for the following species:



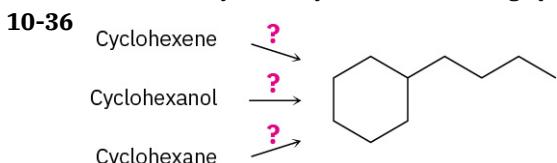
PROBLEM (*S*)-3-Methylhexane undergoes radical bromination to yield optically inactive

10-34 3-bromo-3-methylhexane as the major product. Is the product chiral? What conclusions can you draw about the radical intermediate?

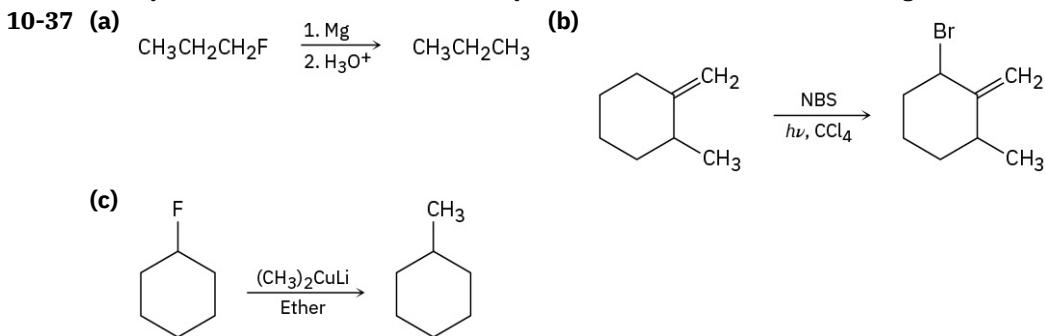
PROBLEM Assume that you have carried out a radical chlorination reaction on (*R*)-2-chloropentane and have

10-35 isolated (in low yield) 2,4-dichloropentane. How many stereoisomers of the product are formed, and in what ratio? Are any of the isomers optically active? (See Problem 10-34.)

PROBLEM How would you carry out the following syntheses?



PROBLEM The syntheses shown here are unlikely to occur as written. What is wrong with each?



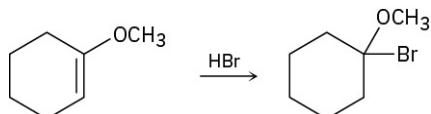
PROBLEM Why do you suppose it's not possible to prepare a Grignard reagent from a bromo alcohol such

10-38 as 4-bromo-1-pentanol? Give another example of a molecule that is unlikely to form a Grignard reagent.



PROBLEM Addition of HBr to a double bond with an ether (-OR) substituent occurs regiospecifically to give

10-39 a product in which the -Br and -OR are bonded to the same carbon. Draw the two possible carbocation intermediates in this electrophilic addition reaction, and explain using resonance why the observed product is formed.

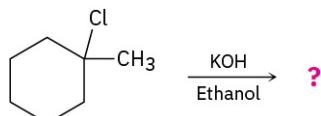




WORKED EXAMPLE 11.3

Predicting the Product of an Elimination Reaction

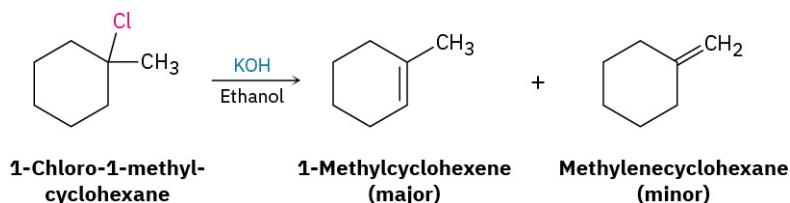
What product would you expect from reaction of 1-chloro-1-methylcyclohexane with KOH in ethanol?



Strategy

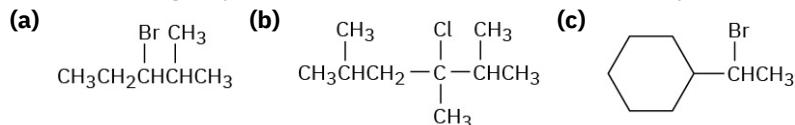
Treatment of an alkyl halide with a strong base such as KOH yields an alkene. To find the products in a specific case, locate the hydrogen atoms on each carbon next to the leaving group, and then generate the potential alkene products by removing HX in as many ways as possible. The major product will be the one that has the most highly substituted double bond—in this case, 1-methylcyclohexene.

Solution

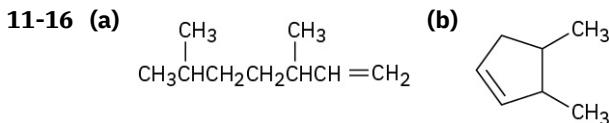


PROBLEM Ignoring double-bond stereochemistry, what products would you expect from elimination reactions

11-15 of the following alkyl halides? Which product will be the major product in each case?



PROBLEM What alkyl halides might the following alkenes have been made from?



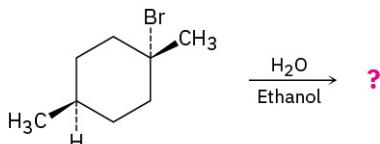
11.8 The E2 Reaction and the Deuterium Isotope Effect

The **E2 reaction** (for *elimination, bimolecular*) occurs when an alkyl halide is treated with a strong base, such as hydroxide ion or alkoxide ion (RO^-). It is the most commonly occurring pathway for elimination and can be formulated as shown in **FIGURE 11.18**.



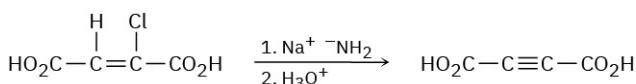
PROBLEM Predict the product(s) of the following reaction, indicating stereochemistry where necessary:

11-62



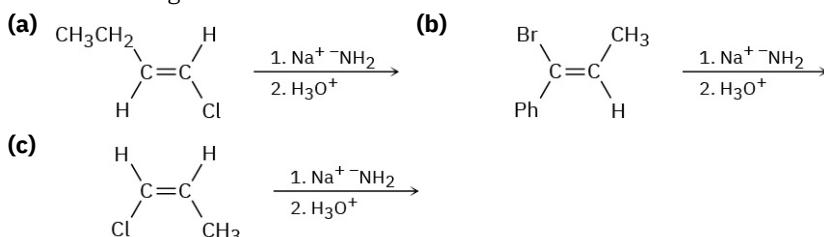
PROBLEM Alkynes can be made by dehydrohalogenation of vinylic halides in a reaction that is essentially

11-63 an E2 process. In studying the stereochemistry of this elimination, it was found that (*Z*)-2-chloro-2-butenedioic acid reacts 50 times as fast as the corresponding *E* isomer. What conclusion can you draw about the stereochemistry of eliminations in vinylic halides? How does this result compare with eliminations of alkyl halides?



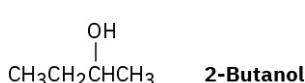
PROBLEM Based on your answer to Problem 11-63, predict the product(s) and show the mechanism for each

11-64 of the following reactions.



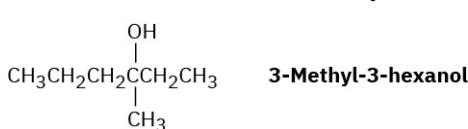
PROBLEM (*S*)-2-Butanol slowly racemizes on standing in dilute sulfuric acid. Explain.

11-65



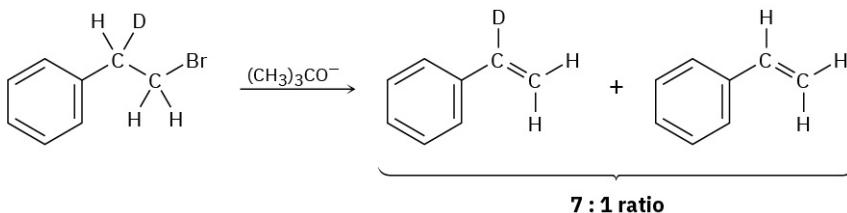
PROBLEM Reaction of HBr with (*R*)-3-methyl-3-hexanol leads to racemic 3-bromo-3-methylhexane. Explain.

11-66



PROBLEM Treatment of 1-bromo-2-deutero-2-phenylethane with strong base leads to a mixture of

11-67 deuterated and nondeuterated phenylethylenes in an approximately 7 : 1 ratio. Explain.



PROBLEM Propose a structure for an alkyl halide that gives only (*E*)-3-methyl-2-phenyl-2-pentene on E2

11-68 elimination. Make sure you indicate the stereochemistry.

TABLE 12.1 Characteristic IR Absorptions of Some Functional Groups

Functional Group	Absorption (cm^{-1})	Intensity	
Carboxylic acid	O—H	2500–3100	Strong, broad
Nitrile	C≡N	2210–2260	Medium
Nitro	NO ₂	1540	Strong

Look at the IR spectra of hexane, 1-hexene, and 1-hexyne in **FIGURE 12.21** to see an example of how IR spectroscopy can be used. Although all three IR spectra contain many peaks, there are characteristic absorptions of C=C and C≡C functional groups that allow the three compounds to be distinguished. Thus, 1-hexene shows a characteristic C=C absorption at 1660 cm^{-1} and a vinylic =C—H absorption at 3100 cm^{-1} , whereas 1-hexyne has a C≡C absorption at 2100 cm^{-1} and a terminal alkyne ≡C—H absorption at 3300 cm^{-1} .

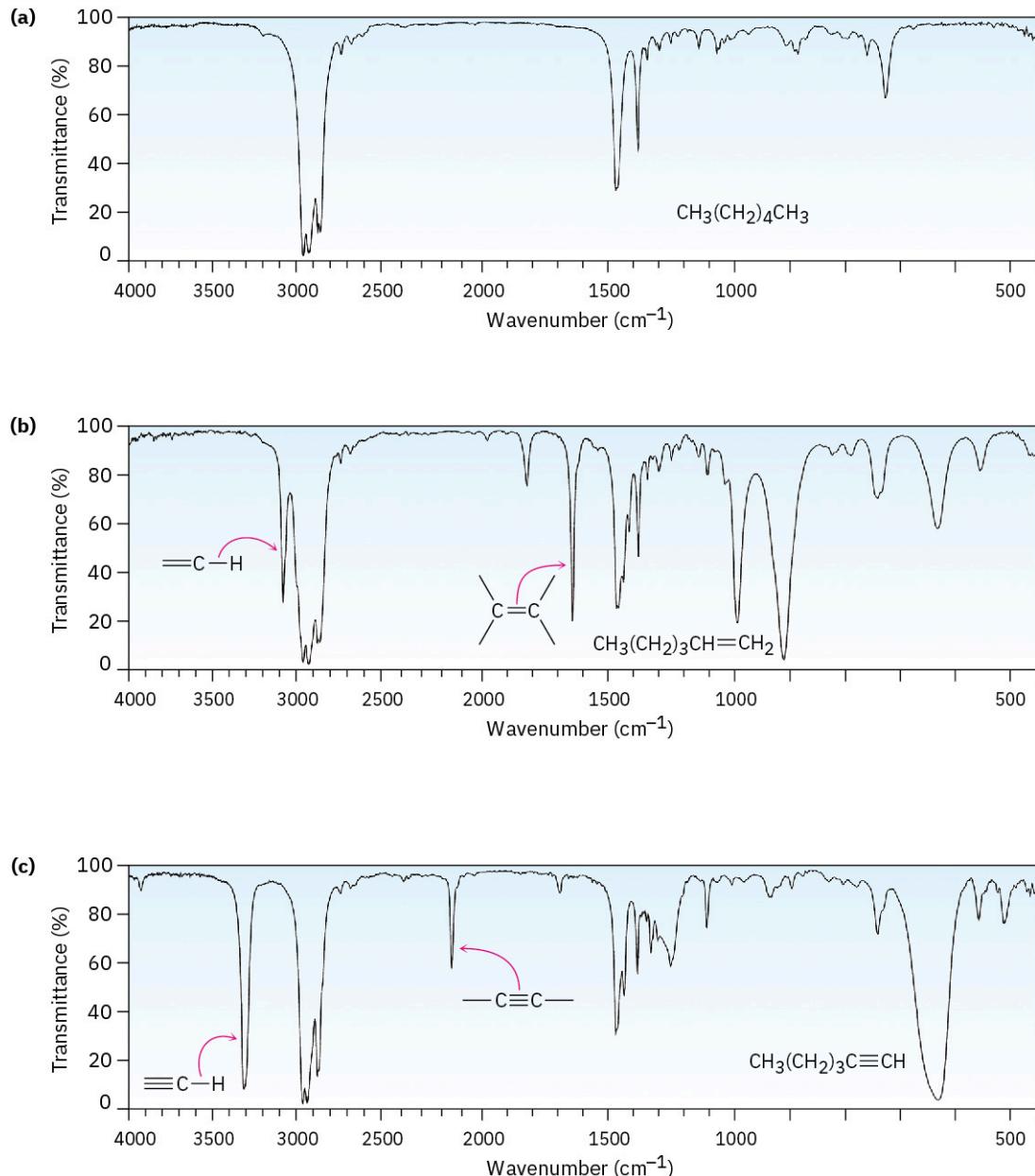


FIGURE 12.21 IR spectra of (a) hexane, (b) 1-hexene, and (c) 1-hexyne. Spectra like these are easily obtained from sub-milligram amounts of material in a few minutes using commercially available instruments.

It helps in remembering the position of specific IR absorptions to divide the IR region from 4000 cm^{-1} to 400 cm^{-1} into four parts, as shown in **FIGURE 12.22**.

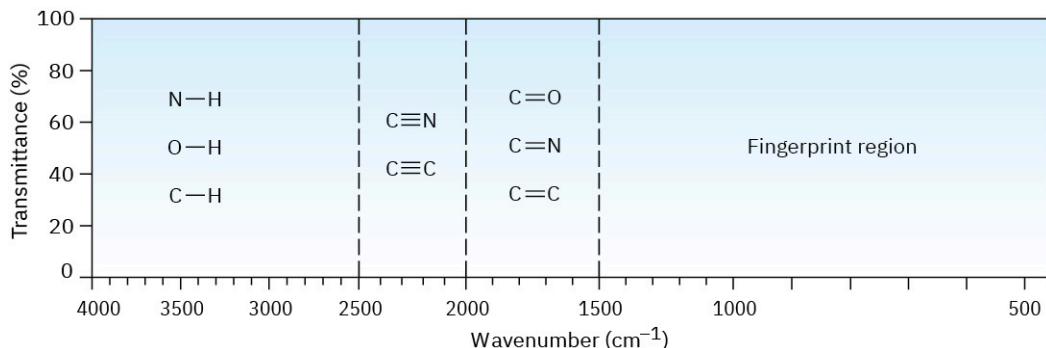


FIGURE 12.22 The four regions of the infrared spectrum: single bonds to hydrogen, triple bonds, double bonds, and fingerprint.

- The region from 4000 to 2500 cm^{-1} corresponds to absorptions caused by N–H, C–H, and O–H single-bond stretching motions. N–H and O–H bonds absorb in the 3300 to 3600 cm^{-1} range; C–H bond stretching occurs near 3000 cm^{-1} .
- The region from 2500 to 2000 cm^{-1} is where triple-bond stretching occurs. Both C≡N and C≡C bonds absorb here.
- The region from 2000 to 1500 cm^{-1} is where double bonds (C=O, C=N, and C=C) absorb. Carbonyl groups generally absorb in the range 1680 to 1750 cm^{-1} , and alkene stretching normally occurs in the narrow range of 1640 to 1680 cm^{-1} .
- The region below 1500 cm^{-1} is the fingerprint portion of the IR spectrum. A large number of absorptions due to a variety of C–C, C–O, C–N, and C–X single-bond vibrations occur here.

Why do different functional groups absorb where they do? As noted previously, a good analogy is that of two weights (atoms) connected by a spring (a bond). Short, strong bonds vibrate at a higher energy and higher frequency than do long, weak bonds, just as a short, strong spring vibrates faster than a long, weak spring. Thus, triple bonds absorb at a higher frequency than double bonds, which in turn absorb at a higher frequency than single bonds. In addition, C–H, O–H, and N–H bonds vibrate at a higher frequency than bonds between heavier C, O, and N atoms.



WORKED EXAMPLE 12.4

Distinguishing Isomeric Compounds by IR Spectroscopy

Acetone (CH_3COCH_3) and 2-propen-1-ol ($\text{H}_2\text{C}=\text{CHCH}_2\text{OH}$) are isomers. How could you distinguish them by IR spectroscopy?

Strategy

Identify the functional groups in each molecule, and refer to **TABLE 12.1**.

Solution

Acetone has a strong C=O absorption at 1715 cm^{-1} , while 2-propen-1-ol has an –OH absorption at 3500 cm^{-1} and a C=C absorption at 1660 cm^{-1} .

PROBLEM What functional groups might the following molecules contain?

- 12-7** (a) A compound with a strong absorption at 1710 cm^{-1}
 (b) A compound with a strong absorption at 1540 cm^{-1}
 (c) A compound with strong absorptions at 1720 cm^{-1} and 2500 to 3100 cm^{-1}

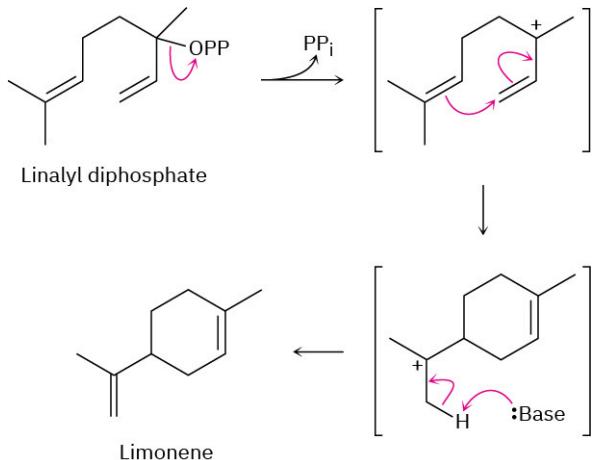
PROBLEM How might you use IR spectroscopy to distinguish between the following pairs of isomers?

- 12-8** (a) $\text{CH}_3\text{CH}_2\text{OH}$ and CH_3OCH_3 (b) Cyclohexane and 1-hexene
 (c) $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ and $\text{HOCH}_2\text{CH}_2\text{CHO}$

TABLE B1

Compound	pK_a
$\text{H}_2\text{C}=\text{CH}_2$	44
CH_4	~60

An acidity list covering more than 5000 organic compounds has been published: E.P. Serjeant and B. Dempsey (eds.), "Ionization Constants of Organic Acids in Aqueous Solution," IUPAC Chemical Data Series No. 23, Pergamon Press, Oxford, 1979.

11-12**PROBLEM (a) S_N1 (b) S_N2****11-13****PROBLEM****11-14****PROBLEM (a)** Major: 2-methyl-2-pentene; minor: 4-methyl-2-pentene**11-15 (b)** Major: 2,3,5-trimethyl-2-hexene; minor: 2,3,5-trimethyl-3-hexene and 2-isopropyl-4-methyl-1-pentene**(c)** Major: ethylenecyclohexane; minor: cyclohexylethylene**PROBLEM (a)** 1-Bromo-3,6-dimethylheptane **(b)** 4-Bromo-1,2-dimethylcyclopentane**11-16****PROBLEM** (*Z*)-1-Bromo-1,2-diphenylethylene**11-17****PROBLEM** (*Z*)-3-Methyl-2-pentene**11-18****PROBLEM** Cis isomer reacts faster because the bromine is axial.**11-19****PROBLEM (a) S_N2 (b) E2 (c) S_N1 (d) E1cB****11-20**

Chapter 12

PROBLEM C₁₉H₂₈O₂**12-1****PROBLEM (a)** 2-Methyl-2-pentene **(b)** 2-Hexene**12-2****PROBLEM (a)** 43, 71 **(b)** 82 **(c)** 58 **(d)** 86**12-3****PROBLEM** 102 (M⁺), 84 (dehydration), 87 (alpha cleavage), 59 (alpha cleavage)**12-4****PROBLEM** X-ray energy is higher; $\lambda = 9.0 \times 10^{-6}$ m is higher in energy.**12-5****PROBLEM (a)** 2.4×10^6 kJ/mol **(b)** 4.0×10^4 kJ/mol **(c)** 2.4×10^3 kJ/mol **(d)** 2.8×10^2 kJ/mol**12-6 (e)** 6.0 kJ/mol **(f)** 4.0×10^{-2} kJ/mol**PROBLEM (a)** Ketone or aldehyde **(b)** Nitro compound **(c)** Carboxylic acid**12-7****PROBLEM (a)** CH₃CH₂OH has an -OH absorption. **(b)** 1-Hexene has a double-bond absorption.**12-8 (c)** CH₃CH₂CO₂H has a very broad -OH absorption.**PROBLEM** 1450–1600 cm⁻¹: aromatic ring; 2100 cm⁻¹: C≡C; 3300 cm⁻¹: C≡C–H**12-9**