19.1 Hydrocarbons

EXPLAIN THIS How is a road like an oil spill?

Organic compounds that contain only carbon and hydrogen atoms are called **hydrocarbons,** which differ from one another by the number of carbon and hydrogen atoms they contain. The simplest hydrocarbon is methane, CH_4, with only one carbon per molecule. Methane is the main component of natural gas. The hydrocarbon octane, C_8H_{18}, has eight carbons per molecule and is a component of gasoline, which is a mixture of many different sorts of hydrocarbons. The hydrocarbon polyethylene contains hundreds of carbon and hydrogen atoms per molecule. Polyethylene is a plastic used to make many familiar items, such as milk containers and plastic bags.

MasteringPhysics®
TUTORIAL: Introduction to Organic Molecules
TUTORIAL: Organic Molecules and Isomers

VIDEO: Organic Compounds


Methane, CH_4


Octane, C_8H_{18}


Polyethylene

Hydrocarbons also differ in the way the carbon atoms connect to one another. Figure 19.1 shows the three hydrocarbons pentane, isopentane, and neopentane. These hydrocarbons have the same molecular formula, C_5H_{12}, but they are structurally different from one another.

We can see the different structural features of pentane, isopentane, and neopentane more clearly by drawing the molecules in two dimensions, as shown in the middle row of Figure 19.1. Alternatively, we can represent them by the

In looking at the stick structures, remember that each corner or end represents a carbon atom and that each carbon atom must be bonded four times. Because hydrogen atoms are assumed, they're not usually depicted.

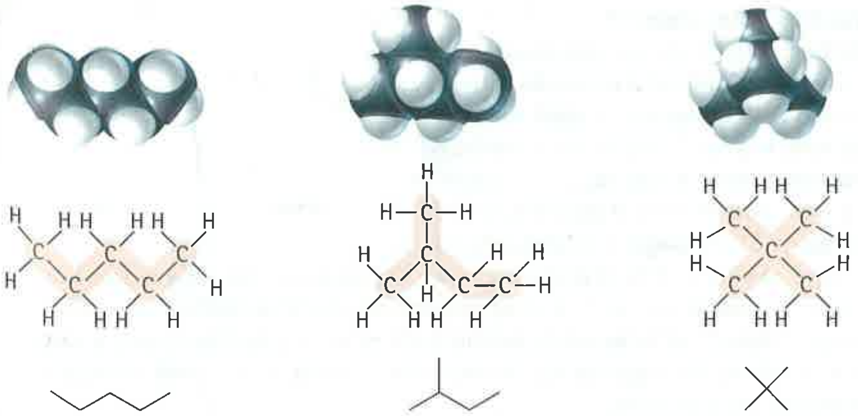

Pentane, C_5H_{12} Isopentane, C_5H_{12} Neopentane, C_5H_{12}

FIGURE 19.1
These three hydrocarbons all have the same molecular formula. We can see their different structural features by highlighting the carbon framework in two dimensions. Easy-to-draw stick structures that use lines for all carbon–carbon covalent bonds are also useful.

stick structures shown in the bottom row. A stick structure is a commonly used shorthand notation for representing an organic molecule. Each line (stick) represents a covalent bond, and carbon atoms are understood to exist at the end of any line or wherever two or more straight lines meet (unless another type of atom is drawn at the end of the line). Any hydrogen atoms bonded to the carbons are also typically not shown. Instead, their presence is only implied, so that the focus can remain on the skeletal structure that is formed by the carbon atoms.

Molecules such as pentane, isopentane, and neopentane have the same molecular formula, which means they have the same number of the same kinds of atoms. The way these atoms are put together, however, is different. We say that they each have their own **configuration,** which refers to how the atoms are connected. Different configurations result in different chemical structures. Molecules with the same molecular formula but different configurations (and hence different structures) are known as **structural isomers.** Structural isomers have different physical and chemical properties. For example, pentane has a boiling point of 36°C, isopentane's boiling point is 30°C, and neopentane's boiling point is 10°C.

The number of possible structural isomers for a chemical formula increases rapidly as the number of carbon atoms increases. There are three structural isomers for compounds that have the formula C_5H_{12}: 18 for C_8H_{18}, 75 for $C_{10}H_{22}$, and a whopping 366,319 for $C_{20}H_{42}$!

A carbon-based molecule can have different spatial orientations called **conformations.** Flex your wrist, elbow, and shoulder joints, and you'll find your arm passing through a range of conformations. Likewise, organic molecules can twist and turn about their carbon–carbon single bonds and thus have a range of conformations. The structures in Figure 19.2, for example, are different conformations of pentane. In the language of organic chemistry, we say that the *configuration* of a molecule, such as pentane, has a broad range of *conformations.* Change the configuration of pentane, however, and you no longer have pentane. Rather, you have a different structural isomer, such as isopentane, which has its own range of different conformations.

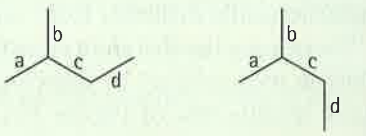
Which is easier to change: the conformation or the configuration of your arm? Does the same hold true for a molecule? The answer is YES!

fyi

- As discussed in Section 18.4, we are placing unusually large amounts of carbon dioxide into the atmosphere by burning fossil fuels. The atmosphere, however, is not the only possible repository for the carbon dioxide we produce. The smokestacks of power plants, for example, can be modified to capture CO_2, which is then liquefied and pumped kilometers deep into the ground. This idea is not so far-fetched. Underground storage of carbon dioxide is already being employed at the Salah natural gas refinery in Algeria. Such a system, however, would have its costs. The price of electricity from a CO_2-capturing coal-fired power plant would rise by about 20%. The long-term costs of not implementing such systems, however, may be even greater.

CHECKPOINT

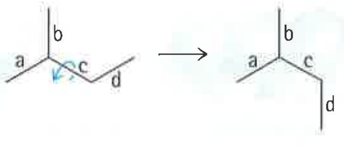
Which carbon–carbon bond was rotated to go from the "before" conformation of isopentane to the "after" conformation?



Before After

Was this your answer?

The best way to answer any question about the conformation of a molecule is to play around with molecular models that you can hold in your hand. In this case, bond c rotates in such a way that the carbon at the right end of bond d comes up out of the plane of the page, momentarily points straight at you, and then plops back into the plane of the page below bond c. This rotation is similar to that of the arm of an arm wrestler who, with the arm just above the table while on the brink of losing, suddenly gets a surge of strength and swings the opponent's arm (and his or her own) through a half-circle arc and wins.



Before After

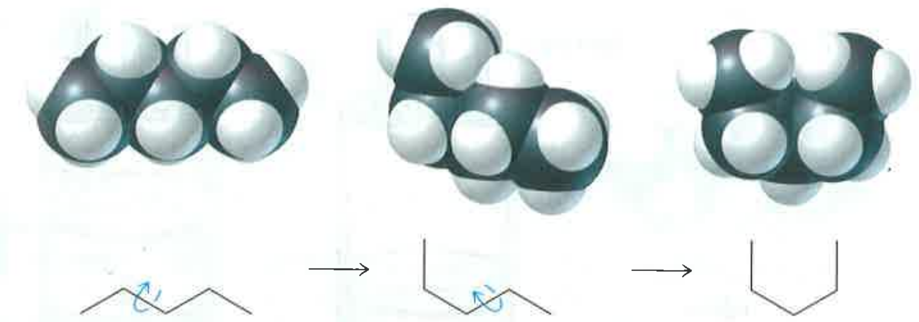


FIGURE 19.2
Three conformations for a molecule of pentane. The molecule looks different in each conformation, but the five-carbon framework is the same in all three conformations. In a sample of liquid pentane, the molecules are found in all conformations—not unlike a bucket of worms.

Hydrocarbons are obtained from fossil fuels, primarily from coal and petroleum and growing amounts of natural gas. Most of the fossil fuels that exist today were formed between 280 million and 395 million years ago when plant and animal matter decayed in the absence of oxygen. At that time, Earth was covered with extensive swamps that, because they were close to sea level, periodically became submerged. The organic matter of the swamps was buried beneath layers of marine sediments and was eventually transformed into coal, petroleum, or natural gas.

Coal is a solid material that contains many large, complex hydrocarbon molecules. Most of the coal mined today is used to produce steel and to generate electricity at coal-burning power plants.

Petroleum, also called crude oil, is a liquid readily separated into its hydrocarbon components through a process known as *fractional distillation,* shown in Figure 19.3. The crude oil is heated in a pipe still to a temperature high enough to vaporize most of the components. The hot vapor flows into the bottom of a fractionating tower, which is warmer at the bottom than at the top. As the vapor rises in the tower and cools, the various components begin to condense. Hydrocarbons that have high boiling points, such as tar and lubricating stocks, condense first at warmer temperatures. Hydrocarbons that have low boiling points, such as gasoline, travel to the cooler regions at the top of the tower before condensing. Pipes drain the various liquid hydrocarbon fractions from the tower. Natural gas, which is primarily methane, does not condense. It remains a gas and is collected at the top of the tower.

The lower the boiling point of the hydrocarbon, the higher it travels up the fractionation tower.

Differences in the strength of molecular attractions explain why different hydrocarbons condense at different temperatures. As discussed in Section 15.8, in our comparison of induced dipole–induced dipole attractions in methane and octane, larger hydrocarbons experience many more of these attractions than smaller hydrocarbons do. For this reason, the larger hydrocarbons condense readily at high temperatures and so are found at the bottom of the tower. Smaller molecules, because they experience fewer attractions to their neighbors, condense only at the cooler temperatures found at the top of the tower.

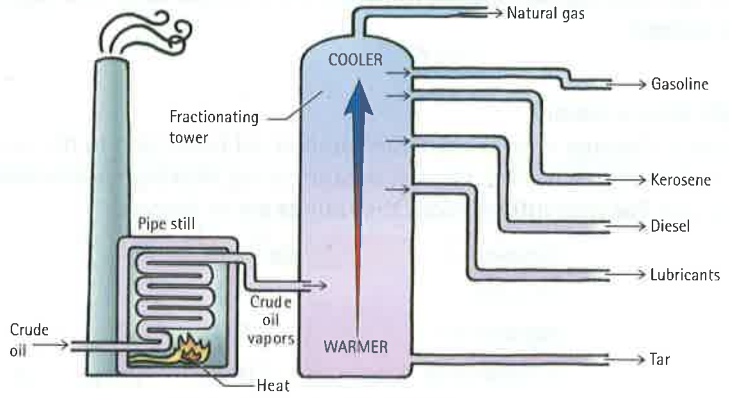


FIGURE 19.3
A schematic for the fractional distillation of petroleum into its useful hydrocarbon components.

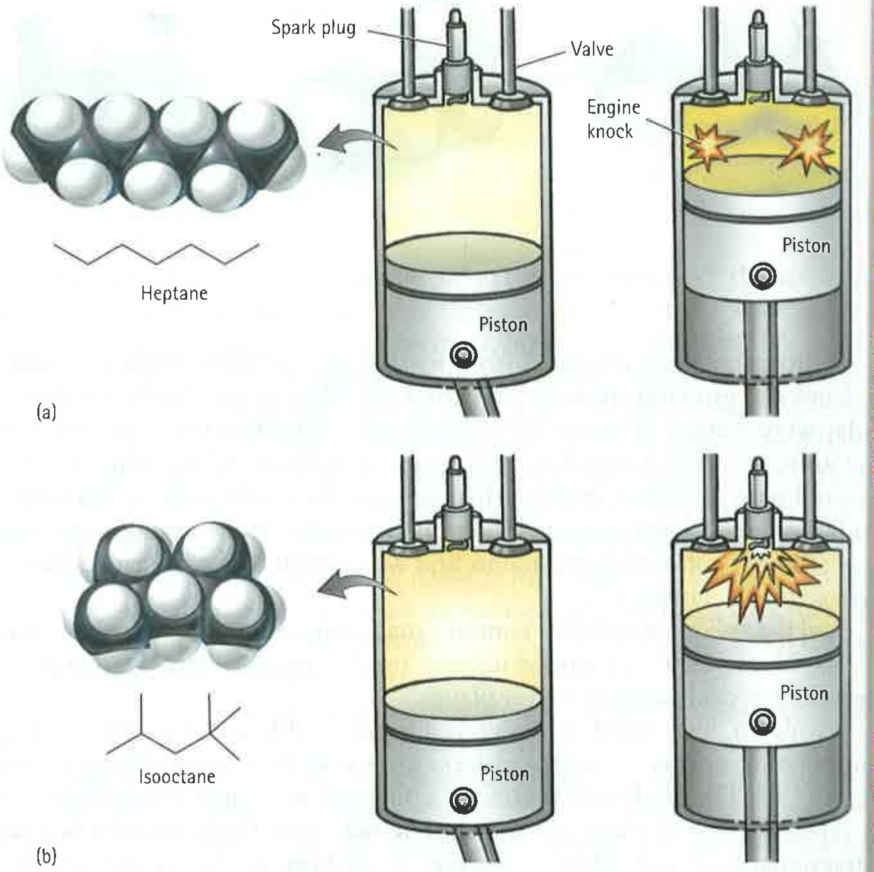


FIGURE 19.4
(a) A hydrocarbon, such as heptane, can be ignited from the heat generated as gasoline is compressed by the piston—before the spark plug fires. This upsets the timing of the engine cycle, giving rise to a knocking sound. (b) Branched hydrocarbons, such as isooctane, burn less readily and are ignited not by compression alone but only when the spark plug fires.

FIGURE 19.5
Octane ratings are posted on gasoline pumps. Interestingly, the engines of modern cars are designed to run best on 87 octane grade fuel. With higher octane fuels, not only do you lose performance, but you lose money as well.

The gasoline obtained from the fractional distillation of petroleum consist of a wide variety of hydrocarbons having similar boiling points. Some of thes components burn more efficiently than others in a car engine. The straight chain hydrocarbons, such as heptane, burn too quickly, causing what is calle *engine knock,* as illustrated in Figure 19.4. Gasoline hydrocarbons that have mor branching, such as isooctane, burn slowly and result in the engine running mor smoothly. These two compounds, heptane and isooctane, are used as standard in assigning *octane ratings* to gasoline. An octane rating of 100 is arbitrarily assigned to isooctane, and heptane is assigned an octane rating of 0. The anti knock performance of a particular gasoline is compared with that of variou mixtures of isooctane and heptane, and an octane rating is assigned. Figure 19. shows the octane information that appears on a typical gasoline pump.

CHECKPOINT

Which structural isomer shown in Figure 19.1 should have the highest octane rating?

Was this your answer?

The structural isomer with the greatest amount of branching in the carbon framework probably has the highest octane rating, making neopentane the clear winner. For your information, the ratings are as follows:

Compound	Octane Rating
Pentane	61.7
Isopentane	92.3
Neopentane	116

19.2 Unsaturated Hydrocarbons

EXPLAIN THIS With four unpaired valence electrons, how can carbon bond to only three adjacent atoms?

Recall from Section 15.1 that carbon has four unpaired valence electrons. As shown in Figure 19.6, each of these electrons is available for pairing with an electron from another atom, such as hydrogen, to form a covalent bond. In all the hydrocarbons discussed so far, including the methane shown in Figure 19.6, each carbon atom is bonded to four neighboring atoms by four single covalent bonds. Such hydrocarbons are known as **saturated hydrocarbons.** The term *saturated* means that each carbon has as many atoms bonded to it as possible. We now explore cases in which one or more carbon atoms in a hydrocarbon are bonded to fewer than four neighboring atoms. This occurs when at least one of the bonds between a carbon and a neighboring atom is a multiple bond. (See Section 15.5 for a review of multiple bonds.)

A hydrocarbon containing a multiple bond—either double or triple—is known as an **unsaturated hydrocarbon.** Because of the multiple bond, two of the carbons are bonded to fewer than four other atoms. These carbons are thus said to be *unsaturated.*

Figure 19.7 compares the saturated hydrocarbon butane with the unsaturated hydrocarbon 2-butene. The number of atoms that are bonded to each of the two middle carbons of butane is four, whereas each of the two middle carbons of 2-butene is bonded to only three other atoms—a hydrogen and two carbons.

A generic word for a saturated hydrocarbon is *alkane.* All of the molecules discussed in Section 19.1 are examples of **alkanes.** This is indicated by the suffix *-ane,* as in *butane.* Unsaturated hydrocarbons containing one or more double bonds are called **alkenes.** This is indicated by the suffix *-ene,* as in *butene.*

An important aspect of the double bond of alkenes is that it cannot rotate more than a few degrees. By analogy, connect two gumdrops with a single toothpick, and you'll be able to hold one gumdrop while rotating the other. Connect the two gumdrops with two toothpicks, however, and this rotational motion doesn't work because the two toothpicks can twist only so far. The

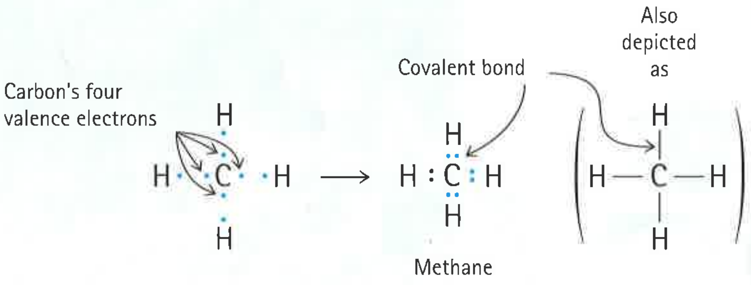


FIGURE 19.6
Carbon has four valence electrons. Each electron pairs with an electron from a hydrogen atom in the four covalent bonds of methane.

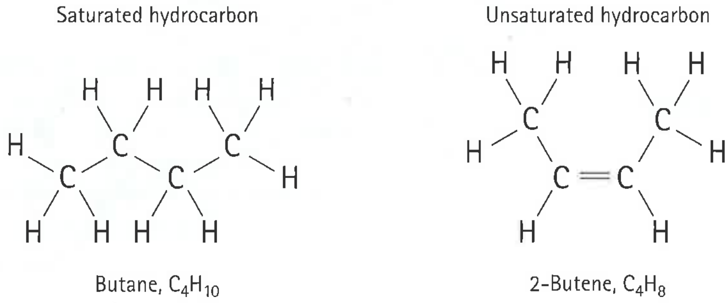
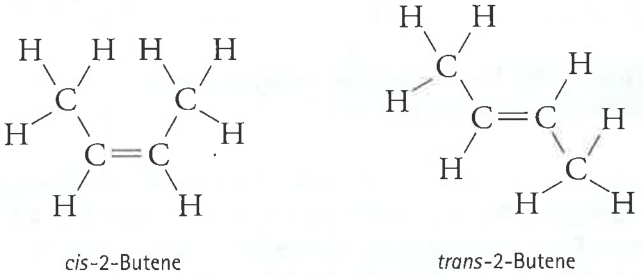


FIGURE 19.7
The carbons of the hydrocarbon butane are *saturated,* each being bonded to four other atoms. Because of the double bond, two of the carbons of the unsaturated hydrocarbon 2-butene are bonded to only three other atoms, which makes the molecule an unsaturated hydrocarbon.


cis-2-Butene

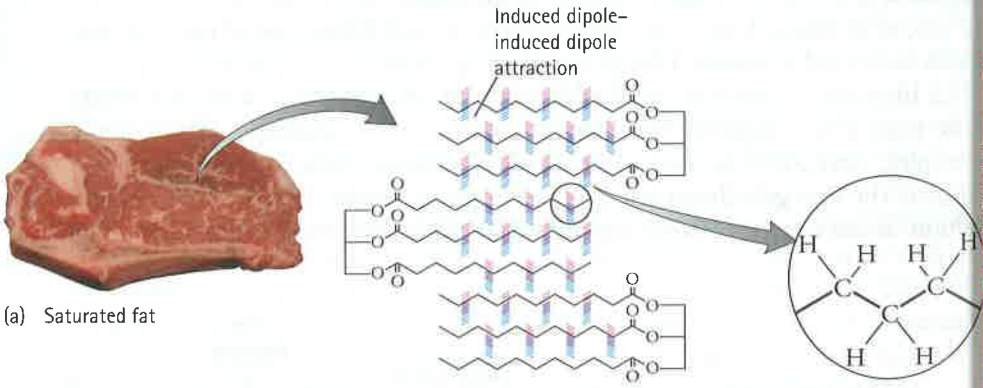
trans-2-Butene

FIGURE 19.8
The *cis*-isomer has the bulk of carbon atoms on the same site of the length of the double bond. The *trans*-isomer has these carbons on opposite sides. As a mnemonic, think "*cis*-same-side."

significance of this for alkenes is what we call *cis/trans isomerism.* We use th prefix *cis-* to indicate a structure in which the bulk of the carbons are on th same side of the length of the double bond, as shown in Figure 19.8. We us the prefix *trans-* to indicate a structure in which the bulk of the carbons are o opposite sides of the length of the double bond.

The fats in our diet have long carbon chains, as shown in Figure 19.9. Th chains within saturated fats tend to be straight, so they pack well together (lik wooden matches in a box). Hence saturated fats, such as lard, are solid at room temperature. The carbon chains of unsaturated fats have double bonds in the *c* orientation, which gives the molecules a bent shape, so they don't pack well together. Unsaturated fats, such as vegetable oils, are liquid at room temperatures

An important unsaturated hydrocarbon is benzene, C_6H_6, which may b drawn as three double bonds contained within a flat hexagonal ring, as shown i Figure 19.10a. Unlike the double-bond electrons in most other unsaturated hydrocarbons, the electrons of the double bonds in benzene are not fixed between



(a) Saturated fat

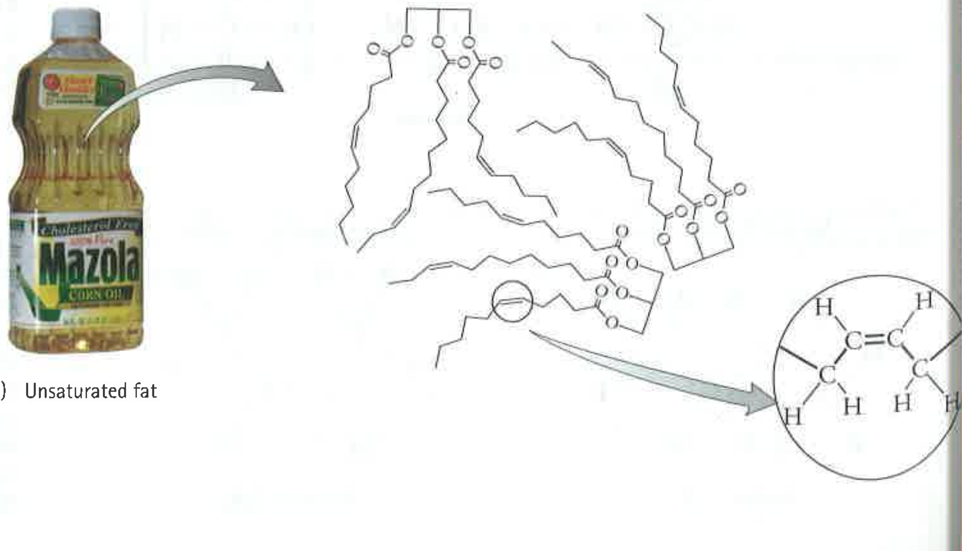

(b) Unsaturated fat

FIGURE 19.9
(a) Saturated fats are typically solid at room temperature because of molecular attractions between the carbon chains.
(b) Unsaturated fats are typically liquid at room temperature because molecular attractions are inhibited by the kinked nature of the carbon chains.

any two carbon atoms. Instead, these electrons can move freely around the ring. This is commonly represented by drawing a circle within the ring, as shown in Figure 19.10b, rather than by individual double bonds.

Many organic compounds contain one or more benzene rings in their structure. Because many of these compounds are fragrant, any organic molecule that contains a benzene ring is classified as an **aromatic compound** (even if it is not particularly fragrant). Figure 19.11 shows three examples. Toluene, a common solvent used as a paint thinner, is toxic and gives airplane glue its distinctive odor. Some aromatic compounds, such as naphthalene, contain two or more benzene rings fused together. At one time, mothballs were made of naphthalene. Most mothballs sold today, however, are made of the less toxic 1,4-dichlorobenzene.

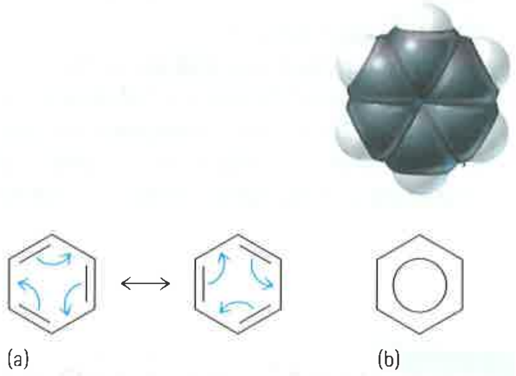


FIGURE 19.10
(a) The double bonds of benzene, C_6H_6, can migrate around the ring. (b) For this reason, they are often represented by a circle within the ring.

An example of an unsaturated hydrocarbon containing a triple bond is acetylene, C_2H_2. A confined flame of acetylene burning in oxygen is hot enough to melt iron, which makes acetylene a choice fuel for welding (Figure 19.12).

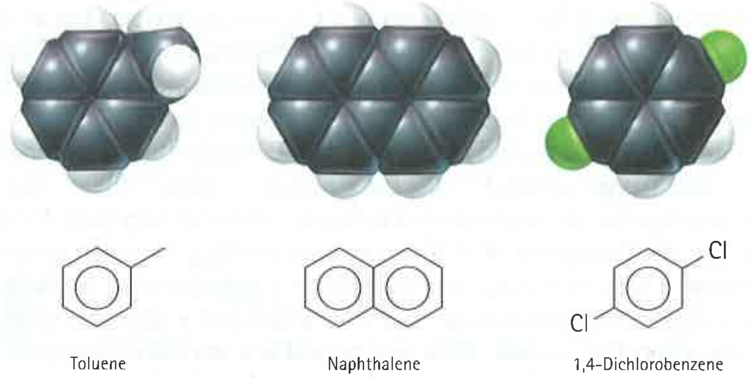


FIGURE 19.11
The structures for three odoriferous organic compounds that contain one or more benzene rings: toluene, naphthalene, and 1,4-dichlorobenzene.

FIGURE 19.12
The unsaturated hydrocarbon acetylene, C_2H_2, when burned in this torch, produces a flame that is hot enough to melt iron.

CHECKPOINT

Prolonged exposure to benzene increases the risk of developing certain cancers. The structure of aspirin contains a benzene ring. Does this indicate that prolonged exposure to aspirin increases a person's risk of developing cancer?

Was this your answer?
No. Although benzene and aspirin both contain a benzene ring, these two molecules have different overall structures and quite different chemical properties. Each carbon-containing organic compound has its own set of unique physical, chemical, and biological properties. Although benzene may cause cancer, aspirin works as a remedy for headaches.

19.3 Functional Groups

EXPLAIN THIS Why are there so many different organic compounds?

Carbon atoms can bond to one another and to hydrogen atoms in many ways, which results in an incredibly large number of hydrocarbons. But carbon atoms can bond to atoms of other elements as well, further increasing the number of possible organic molecules. In organic chemistry, any atom other than carbon or hydrogen in an organic molecule is called a **heteroatom,** where *hetero-* indicates that the atom is different from either carbon or hydrogen.

MasteringPhysics®
TUTORIAL:
Functional Groups

A hydrocarbon structure can serve as a framework for the attachment of various heteroatoms. This is analogous to a Christmas tree serving as the scaffolding on which ornaments are hung. Just as the ornaments give character to the tree, so do heteroatoms give character to an organic molecule. Heteroatoms have profound effects on the properties of an organic molecule.

Consider ethane, C_2H_6, and ethanol, C_2H_6O, which differ from each other by only a single oxygen atom. Ethane has a boiling point of $-88°C$, making it a gas at room temperature, and it does not dissolve in water very well. Ethanol, by contrast, has a boiling point of $+78°C$, making it a liquid at room temperature. It is infinitely soluble in water, and it is the active ingredient of alcoholic beverages. Consider further ethylamine, C_2H_7N, which has a nitrogen atom on the same two-carbon framework. This compound is a corrosive, pungent, highly toxic gas—very different from either ethane or ethanol.

The chemistry of hydrocarbons is surely interesting, but start adding heteroatoms to these organic molecules, and the chemistry becomes extraordinarily interesting. The organic chemicals of living organisms, for example, all contain heteroatoms.

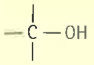
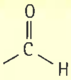
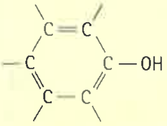
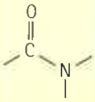
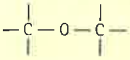
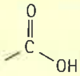
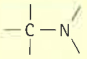
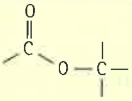
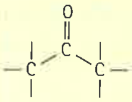
Organic molecules are classified according to the functional groups they contain. A **functional group** is defined as a combination of atoms that behave as a unit. Most functional groups are distinguished by the heteroatoms they contain; some common groups are listed in Table 19.1.

The remainder of this chapter introduces the classes of organic molecules shown in Table 19.1. The role heteroatoms play in determining the properties of each class is the underlying theme. As you study this material, focus on understanding the chemical and physical properties of the various classes of compounds; doing so will give you a greater appreciation of the remarkable diversity of organic molecules and their many applications.

CHECKPOINT
What is the significance of heteroatoms in an organic molecule?

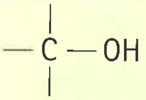
Was this your answer?
Heteroatoms largely determine an organic molecule's "personality."

TABLE 19.1 FUNCTIONAL GROUPS IN ORGANIC MOLECULES

General Structure	Class	General Structure	Class
 Hydroxyl group	Alcohols	 Aldehyde group	Aldehydes
 Phenolic group	Phenols	 Amide group	Amides
 Ether group	Ethers	 Carboxyl group	Carboxylic acids
 Amine group	Amines	 Ester group	Esters
 Ketone group	Ketones		

19.4 Alcohols, Phenols, and Ethers

EXPLAIN THIS What do alcohols, phenols, and ethers have in common?

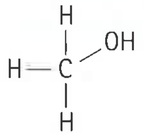
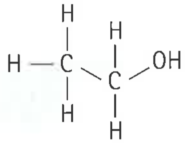
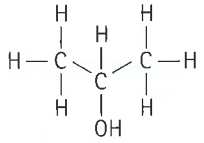

Hydroxyl group

Alcohols are organic molecules in which a *hydroxyl group* is bonded to a saturated carbon. The hydroxyl group consists of an oxygen bonded to a hydrogen. Because of the polarity of the oxygen–hydrogen bond, low-mass alcohols are often soluble in water, which is itself very polar. Three common alcohols and their melting and boiling points are listed in Table 19.2.

Worldwide, about 100 million metric tons of methanol, CH_3OH, are produced annually. Most of it is used for making formaldehyde and acetic acid, important starting materials in the production of plastics. In addition, methanol is used as a solvent, an octane booster, and an anti-icing agent in gasoline. Sometimes called *wood alcohol* because it can be obtained from wood, methanol should never be ingested because, in the body, it is metabolized to formaldehyde and formic acid. Formaldehyde is harmful to the eyes, can lead to blindness, and was once used to preserve dead biological specimens. Formic acid, the active ingredient in an ant bite, can lower the pH of the blood to dangerous levels. Ingesting only about 15 mL (about 3 Tbsp) of methanol may lead to blindness, and about 30 mL can cause death.

Ethanol, C_2H_5OH, on the other hand, is the "alcohol" of alcoholic beverages, and it is one of the oldest chemicals manufactured by humans. Ethanol

TABLE 19.2 SIMPLE ALCOHOLS

Structure	Scientific Name	Common Name	Melting Point (°C)	Boiling Point (°C)
	Methanol	Methyl alcohol	−97	65
	Ethanol	Ethyl alcohol	−115	78
	2-Propanol	Isopropyl alcohol	−126	97

is prepared by feeding the sugars of various plants to certain yeasts, which produce ethanol through a biological process known as *fermentation*. Ethanol is also widely used as an industrial solvent. For many years, ethanol intended for this purpose was made by fermentation, but today industrial-grade ethanol is more cheaply manufactured from petroleum by-products, such as ethene, as Figure 19.13 illustrates.

The liquid produced by fermentation has an ethanol concentration no greater than about 12% because at this concentration the yeast cells begin to die. This is why most wines have an alcohol content of about 12%—they are produced solely by fermentation. To attain the higher ethanol concentrations found in "hard" alcoholic beverages such as gin and vodka, the fermented liquid must be distilled. In the United States, the ethanol content of distilled alcoholic beverages is measured as *proof*, which is twice the percentage of ethanol. An 86-proof whiskey, for example, is 43% ethanol by volume. The term *proof* evolved from a crude method once employed to test alcohol content. Gunpowder was wetted with a beverage of suspect alcohol content. If the beverage was primarily water, the powder did not ignite. If the beverage contained a significant amount of ethanol, the powder burned, thus providing "proof" of the beverage's worth.

A third well-known alcohol is isopropyl alcohol, also called 2-propanol. This is the rubbing alcohol you buy at the drugstore. Although 2-propanol has a relatively high boiling point, it evaporates readily, leading to a pronounced cooling effect when it is applied to skin—an effect once used to reduce fevers. (Isopropyl alcohol is very toxic if ingested. See the activities at the end of this chapter to understand why. In place of isopropyl alcohol, washcloths wetted with cold water

fyi

- Just as the body metabolizes methanol into formaldehyde, HCOH, it metabolizes ethanol into acetaldehyde, CH_3COH. Acetaldehyde won't cause you to go blind, but it does have some painful side effects, which people who drink too much experience as part of their "hangover."

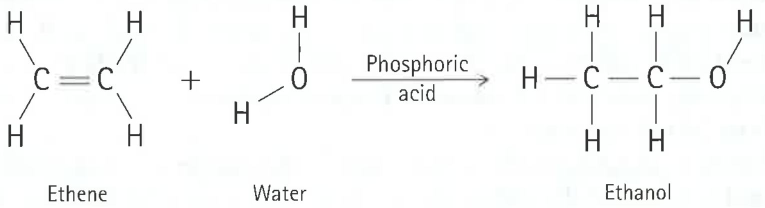


FIGURE 19.13
Ethanol can be synthesized from the unsaturated hydrocarbon ethene, with phosphoric acid as a catalyst.

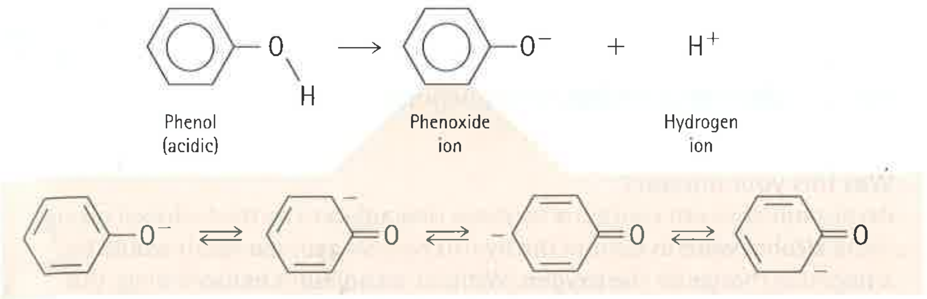


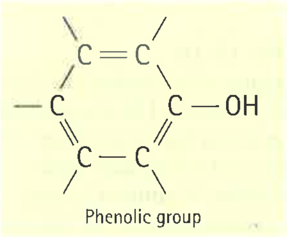
FIGURE 19.14
The negative charge of the phenoxide ion can migrate to select positions on the benzene ring. This mobility helps accommodate the negative charge, which is why the phenolic group readily donates a hydrogen ion.

are nearly as effective in reducing fever, and they are far safer.) You are probably most familiar with the use of isopropyl alcohol as a topical disinfectant.

Phenols contain a phenolic group, which consists of a hydroxyl group attached to a benzene ring. Because of the presence of the benzene ring, the hydrogen of the hydroxyl group is readily lost in an acid–base reaction, which makes the phenolic group mildly acidic.

The reason for this acidity is illustrated in Figure 19.14. How readily an acid donates a hydrogen ion is a function of how well the acid can accommodate the resulting negative charge it gains after donating the hydrogen ion. After phenol donates the hydrogen ion, it becomes a negatively charged phenoxide ion. The negative charge of the phenoxide ion, however, is not restricted to the oxygen atom. Recall that the electrons of the benzene ring can migrate around the ring. In a similar manner, the electrons responsible for the negative charge of the phenoxide ion can migrate around the ring, as shown in Figure 19.14. Just as several people can easily hold a hot potato by quickly passing it around, the phenoxide ion can easily hold the negative charge because the charge gets passed around. Because the negative charge of the ion is so nicely accommodated, the phenolic group is more acidic than it would be otherwise.

The simplest phenol, shown in Figure 19.15, is called phenol. In 1867, Joseph Lister (1827–1912) discovered the antiseptic value of phenol, which, when applied to surgical instruments and incisions, greatly increased surgery survival rates. Phenol was the first purposefully used antibacterial solution, or *antiseptic*. Phenol damages healthy tissue, however, and so a number of milder phenols have since been introduced. The phenol 4-hexylresorcinol, for example, is commonly used in throat lozenges and mouthwashes. This compound has even greater antiseptic properties than phenol, and yet it does not damage tissue. Listerine brand mouthwash (named after Joseph Lister) contains the antiseptic phenols thymol and methyl salicylate.



We're classifying organic molecules based on the functional groups they contain. As you will see shortly, however, organic molecules may contain more than one type of functional group. A single organic molecule, therefore, might be classified as both a phenol and an ether.

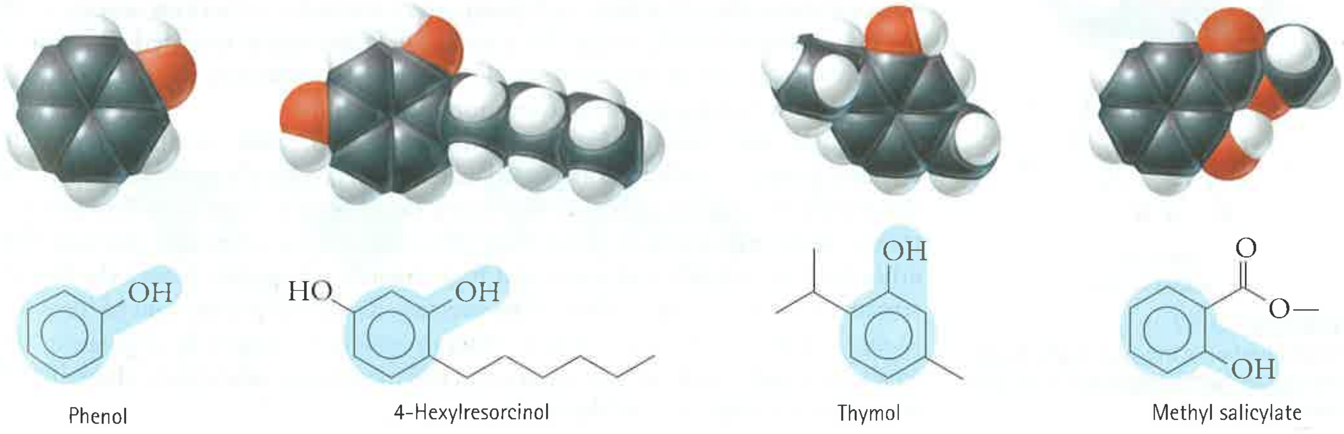


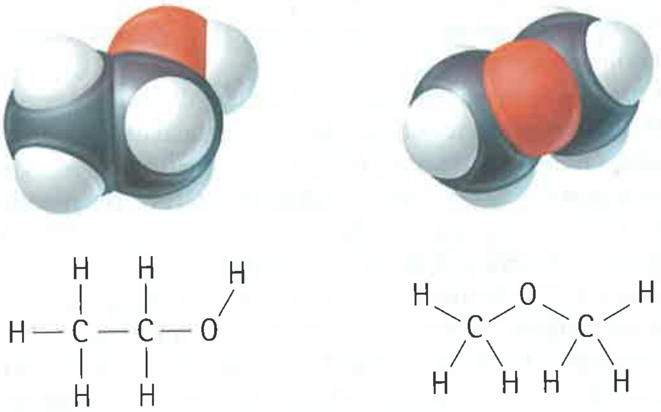
FIGURE 19.15
Every phenol contains a phenolic group (highlighted in blue).

CHECKPOINT

Why are alcohols less acidic than phenols?

Was this your answer?

An alcohol does not contain a benzene ring adjacent to the hydroxyl group. If the alcohol were to donate the hydroxyl hydrogen, the result would be a negative charge on the oxygen. Without an adjacent benzene ring, this negative charge has nowhere to go. As a result, an alcohol behaves only as a very weak acid, much the way water does.

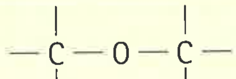


Ethanol: High solubility in water, boiling point 78°C

Dimethyl ether: Low solubility in water, boiling point −25°C

FIGURE 19.16

The oxygen in an alcohol, such as ethanol, is bonded to one carbon atom and one hydrogen atom. The oxygen in an ether, such as dimethyl ether, is bonded to two carbon atoms. Because of this difference, alcohols and ethers of similar molecular mass have vastly different physical properties.



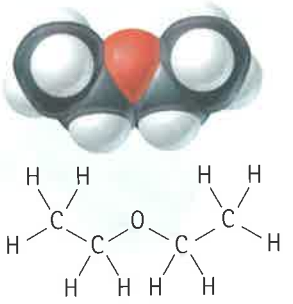
$-\underset{|}{\overset{|}{C}}-O-\underset{|}{\overset{|}{C}}-$

Ether group

Ethers are organic compounds structurally related to alcohols. The oxyge atom in an ether group, however, is bonded not to a carbon and a hydrogen bu rather to two carbons. As we see in Figure 19.16, ethanol and dimethyl ethe have the same chemical formula, C_2H_6O, but their physical properties are vast different. Whereas ethanol is a liquid at room temperature (boiling point 78°C and mixes quite well with water, dimethyl ether is a gas at room temperatu (boiling point −25°C) and is much less soluble in water.

Ethers are not very soluble in water because without the hydroxyl group th are unable to form strong hydrogen bonds with water (Section 15.8). Furthe more, without the polar hydroxyl group, the molecular attractions among eth molecules are relatively weak. As a result, little energy is required to separa ether molecules from one another. This is why low-formula-mass ethers ha relatively low boiling points and evaporate so readily.

Diethyl ether, shown in Figure 19.17, was one of the first anesthetics. The a esthetic properties of this compound were discovered in the early 1800s, and i use revolutionized the practice of surgery. Because of its high volatility at roo temperature, inhaled diethyl ether rapidly enters the bloodstream. Because th ether has low solubility in water and high volatility, it quickly leaves the bloo stream. Because of these physical properties, a surgical patient can be broug in and out of anesthesia (a state of unconsciousness) simply by regulating t gases breathed. Modern gaseous anesthetics have fewer side effects than diet ether, but they operate on the same principle.



Diethyl ether, boiling point 35°C

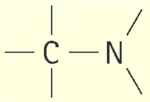
FIGURE 19.17

Diethyl ether is the systematic name for the "ether" historically used as an anesthetic.

19.5 Amines and Alkaloids

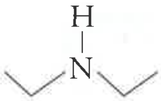
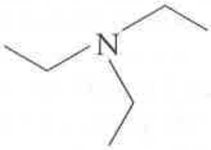
EXPLAIN THIS Why are rainforests of great interest to pharmaceutical companies?

Amines are organic compounds that contain the amine group—a nitrogen atom bonded to one, two, or three saturated carbons. Amines are typically less soluble in water than are alcohols because the nitrogen–hydrogen bond is not quite as polar as the oxygen–hydrogen bond. The lower polarity of amines also means their boiling points are typically somewhat lower than those of alcohols of similar formula mass. Table 19.3 lists three simple amines.



Amine group

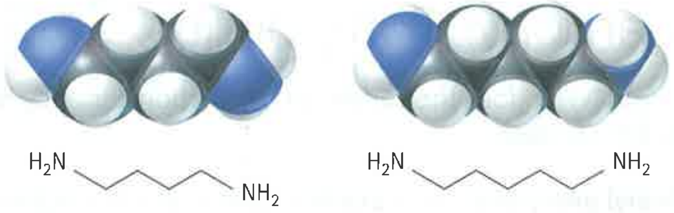
TABLE 19.3 THREE SIMPLE AMINES

Structure	Melting Name	Boiling Point (°C)	Point (°C)
	Ethylamine	−18	17
	Diethylamine	−50	55
	Triethylamine	−7	89

One of the most notable physical properties of many low-formula-mass amines is their offensive odor. Figure 19.18 shows two appropriately named amines, putrescine and cadaverine, which are partly responsible for the odor of decaying flesh.

Amines are typically alkaline because the nitrogen atom readily accepts a hydrogen ion from water, as Figure 19.19 (next page) illustrates.

A group of naturally occurring complex molecules that are alkaline because they contain nitrogen atoms are often called *alkaloids*. Because many alkaloids have medicinal value, there is great interest in isolating these compounds from



Putrescine
(1,4-butanediamine)

Cadaverine
(1,5-pentanediamine)

FIGURE 19.18
Low-formula-mass amines such as these tend to have offensive odors.

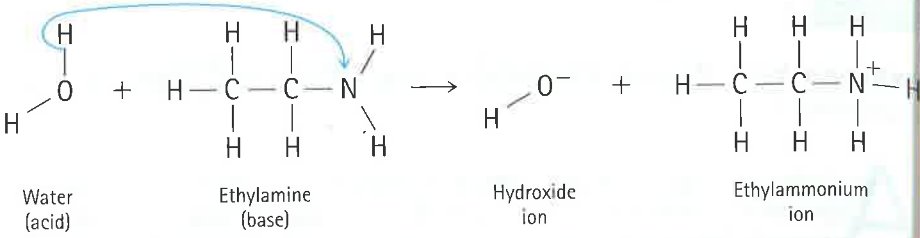


FIGURE 19.19
Ethylamine acts as a base and accepts a hydrogen ion from water to become the ethylammonium ion. This reaction generates a hydroxide ion, which increases the pH of the solution.

plants or marine organisms that contain them. As shown in Figure 19.20, a alkaloid reacts with an acid to form a salt that is usually quite soluble in water This is in contrast to the non-ionized form of the alkaloid, known as a *free bas* which is typically insoluble in water.

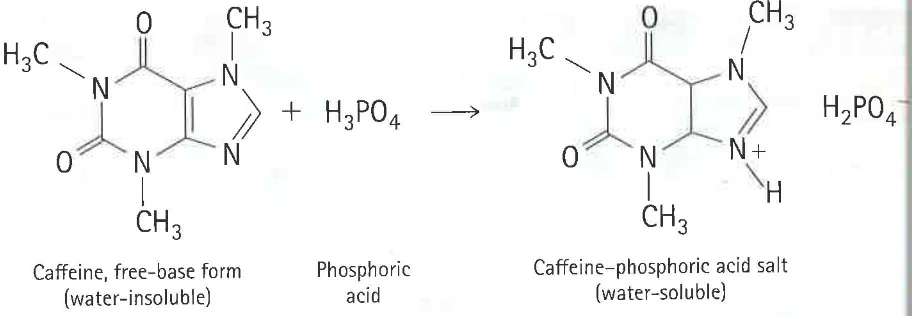


FIGURE 19.20
All alkaloids are bases that react with acids to form salts. An example is the alkaloid caffeine, shown here reacting with phosphoric acid.

Most pharmaceuticals that can be administered orally contain nitrogen heteroatoms in the water-soluble salt form.

Most alkaloids exist in nature not in their free-base form but rather as th salts of naturally occurring acids known as *tannins,* a group of phenol-base organic acids that have complex structures. The alkaloid salts of these acids ar usually much more soluble in hot water than in cold water. The caffeine in cof fee and tea exists in the form of the tannin salt, which is why coffee and tea ar more effectively brewed in hot water. As Figure 19.21 relates, tannins are als responsible for the stains caused by these beverages.

CHECKPOINT

Why do most caffeinated soft drinks also contain phosphoric acid?

Was this your answer?

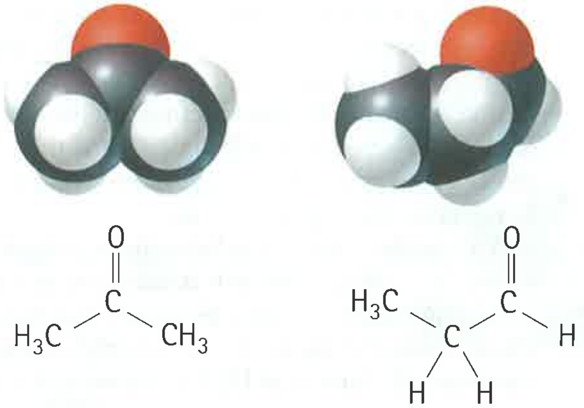
Phosphoric acid, as shown in Figure 19.20, reacts with caffeine to form the caffeine–phosphoric acid salt, which is much more soluble in cold water than the naturally occurring tannin salt.

FIGURE 19.21
Tannins are responsible for the brown stains in coffee mugs or on a coffee drinker's teeth. Because tannins are acidic, they can be readily removed with an alkaline cleanser. Use a little laundry bleach on the mug, and brush your teeth with baking soda.

19.6 Carbonyl Compounds

EXPLAIN THIS Why does the carbon of the carbonyl usually have a slightly positive charge?

A **carbonyl group** consists of a carbon atom double-bonded to an oxyg atom. It occurs in the organic compounds known as ketones, aldehyd amides, carboxylic acids, and esters.



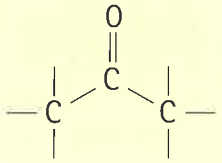
Acetone
(a)

Propionaldehyde
(b)

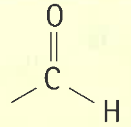
FIGURE 19.22
(a) When the carbon of a carbonyl group is bonded to two carbon atoms, the result is a ketone. An example is acetone. (b) When the carbon of a carbonyl group is bonded to at least one hydrogen atom, the result is an aldehyde. An example is propionaldehyde.

A **ketone** is a carbonyl-containing organic molecule in which the carbonyl carbon is bonded to two carbon atoms. A familiar example of a ketone is *acetone,* which is often used in fingernail-polish remover and is shown in Figure 19.22a. In an **aldehyde,** the carbonyl carbon is bonded either to one carbon atom and one hydrogen atom, as in Figure 19.22b, or, in the special case of formaldehyde, to two hydrogen atoms.

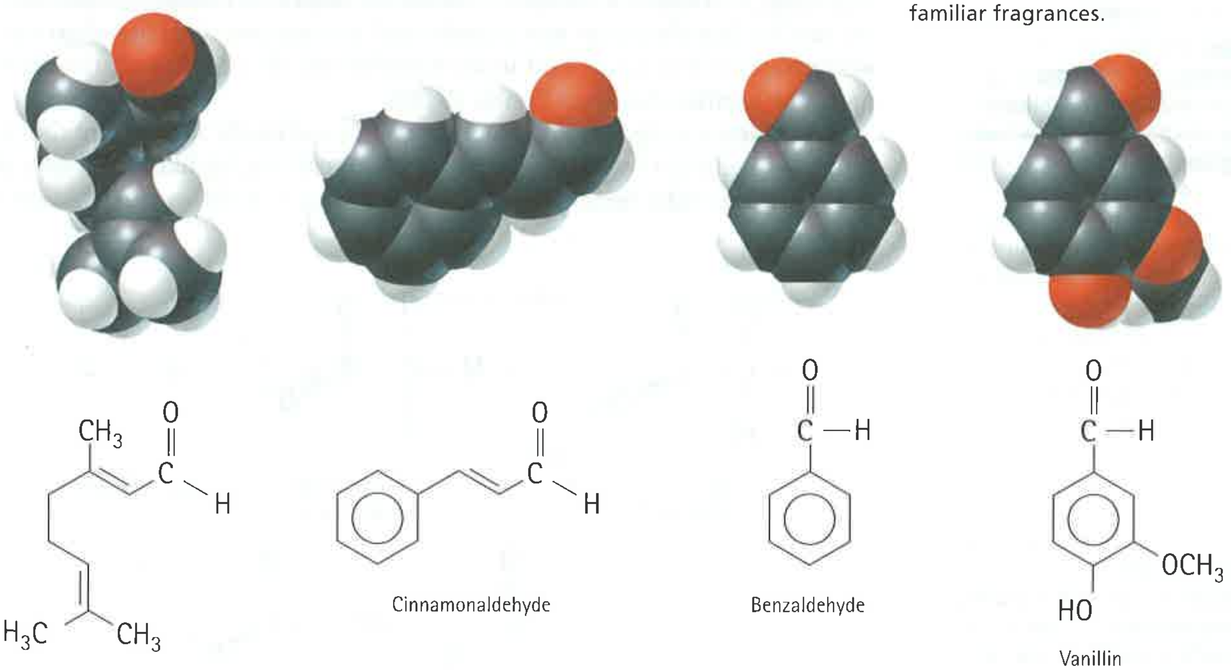
Many aldehydes are particularly fragrant. A number of flowers, for example, owe their pleasant odor to the presence of simple aldehydes. The smells of lemons, cinnamon, and almonds are due to the aldehydes citral, cinnamaldehyde, and benzaldehyde, respectively. The structures of these three aldehydes are shown in Figure 19.23. Another aldehyde, vanillin, which was introduced at the beginning of this chapter, is the key flavoring molecule derived from seed pods of the vanilla orchid. You may have noticed that vanilla seed pods and vanilla extract are fairly expensive. Imitation vanilla flavoring is less expensive because it is merely a solution of the compound vanillin, which is economically synthesized from waste chemicals from the wood-pulp industry. Imitation



Ketone group



Aldehyde group



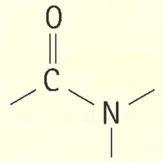
Citral

Cinnamonaldehyde

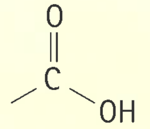
Benzaldehyde

Vanillin

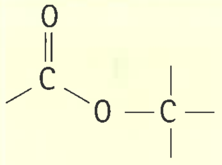
FIGURE 19.23
Aldehydes are responsible for many familiar fragrances.



Amide group



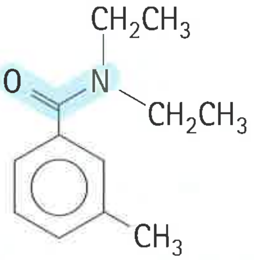
Carboxyl group



Ester group

vanilla does not taste the same as natural vanilla extract, however, because, in addition to vanillin, many other flavorful molecules contribute to the complex taste of natural vanilla. Many books manufactured in the days before "acid-free" paper smell of vanilla because of the vanillin formed and released as the paper ages, a process that is accelerated by the acids the paper contains.

An **amide** is a carbonyl-containing organic molecule in which the carbonyl carbon is bonded to a nitrogen atom. The active ingredient of most mosquito repellents is an amide whose chemical name is *N,N*-diethyl-*m*-toluamide but is commercially known as DEET, shown in Figure 19.24. This compound is actually not an insecticide. Rather, it causes certain insects, especially mosquitoes, to lose their sense of direction, which effectively protects DEET wearers from being bitten.



N,N-Diethyl-*m*-toluamide
(DEET)

FIGURE 19.24
N,N-diethyl-*m*-toluamide is an example of an amide. Amides contain the amide group, shown highlighted in blue.

A **carboxylic acid** is a carbonyl-containing organic molecule in which the carbonyl carbon is bonded to a hydroxyl group. As its name implies, this functional group can donate hydrogen ions. Organic molecules that contain it are therefore acidic. An example is acetic acid, $C_2H_4O_2$, which, after water, is the main ingredient of vinegar. You may recall that this organic compound was used as an example of a weak acid back in Chapter 18.

As with phenols, the acidity of a carboxylic acid results in part from the ability of the functional group to accommodate the negative charge of the ion that forms after the hydrogen ion has been donated. As shown in Figure 19.25, a carboxylic acid transforms to a carboxylate ion as it loses the hydrogen ion. The negative charge of the carboxylate ion can then pass back and forth between the two oxygens. This spreading out helps accommodate the negative charge.

An interesting example of an organic compound that contains both a carboxylic acid and a phenol is salicylic acid, found in the bark of willow trees and illustrated in Figure 19.26a. At one time brewed for its antipyretic (fever-reducing) effect, salicylic acid is an important analgesic (painkiller), but it causes nausea and stomach upset because of its relatively high acidity, a result of the presence of two acidic functional groups. In 1899, Friedrich Bayer and Company, in Germany, introduced a chemically modified version of this compound in which the acidic phenolic group was transformed into an ester functional group. The result was the less acidic and more tolerable acetylsalicylic acid, the chemical name for aspirin, shown in Figure 19.26b.

An **ester** is an organic molecule similar to a carboxylic acid except that in the ester, the hydroxyl hydrogen is replaced by a carbon. Unlike carboxylic acids, esters are not acidic because they lack the hydrogen of the hydroxyl group. Like

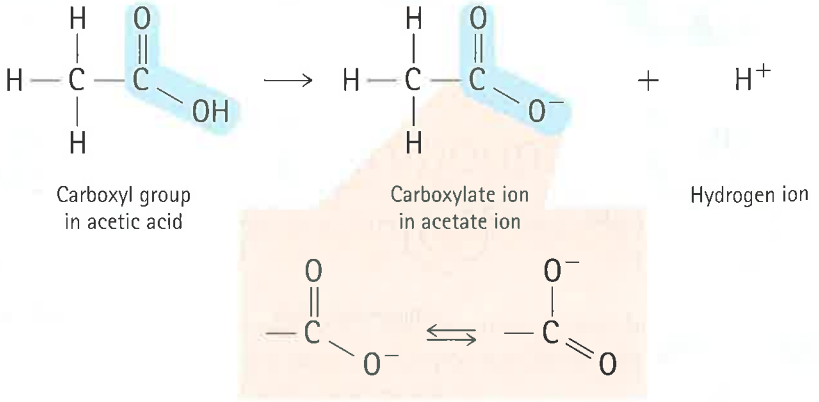


FIGURE 19.25
The negative charge of the carboxylate ion can pass back and forth between the two oxygen atoms of the carboxyl group.

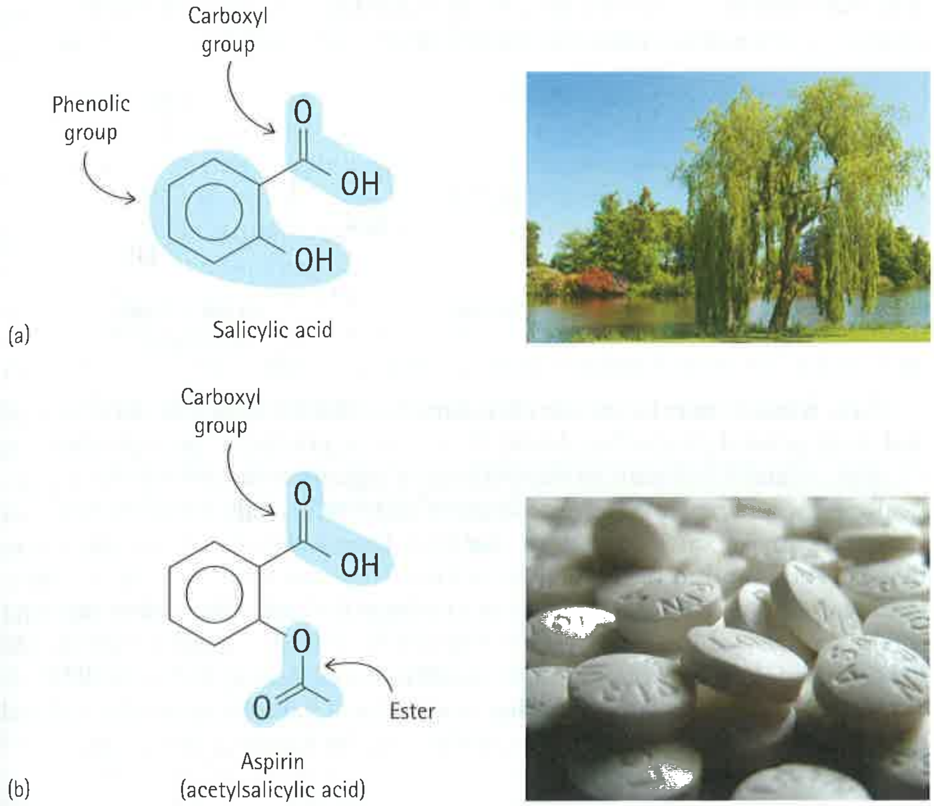
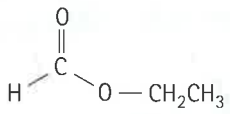
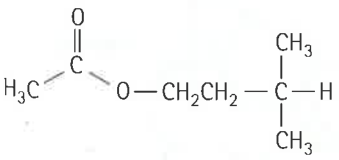
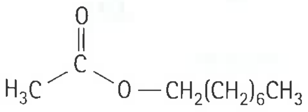
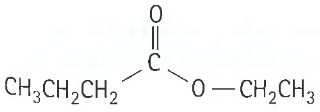


FIGURE 19.26
(a) Salicylic acid, which is found in the bark of willow trees, is an example of a molecule that contains both a carboxyl group and a phenolic group. (b) Aspirin, acetylsalicylic acid, is less acidic than salicylic acid because it no longer contains the acidic phenolic group, which has been converted to an ester.

aldehydes, many simple esters have notable fragrances and are often used as flavorings. Some familiar ones are listed in Table 19.4.

Esters are fairly easy to synthesize by dissolving a carboxylic acid in an alcohol and then bringing the mixture to a boil in the presence of a strong acid, such as sulfuric acid, H_2SO_4. The synthesis of methyl salicylate from salicylic

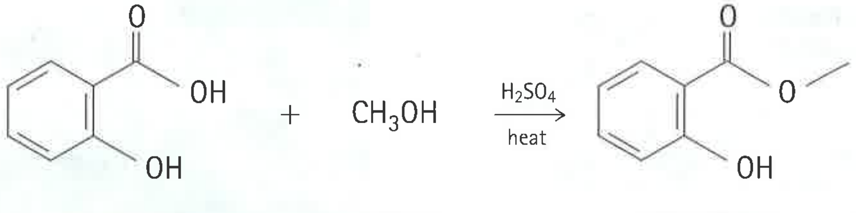
TABLE 19.4 SOME ESTERS AND THEIR FLAVORS AND ODORS

Structure	Name	Flavor/Odor
	Ethyl formate	Rum
	Isopentyl acetate	Banana
	Octyl acetate	Orange
	Ethyl butyrate	Pineapple

fyi

- In the 1800s most salicylic acid used by people was produced not from willow bark but from coal tar. Tar residues within the salicylic acid had a nasty taste. This, combined with salicylic acid's stomach irritation, led many to view the salicylic acid cure as worse than the disease. Felix Hoffman, a chemist working at Bayer, added the acetyl group to the phenol group of salicylic acid in 1897. According to Bayer, Hoffman was inspired by his father, who had been complaining about salicylic acid's side effects. To market the new drug, Bayer invented the name *aspirin,* in which "a" is for acetyl; "spir" is for the spirea flower, another natural source of salicylic acid; and "in" is used as a common suffix for medications. After World War I, Bayer, a German company, lost the rights to use the name *aspirin*. Bayer didn't regain these rights until 1994 for a steep price of $1 billion.

acid and methanol is one example. Methyl salicylate is responsible for the smell of wintergreen and is a common ingredient of hard candies.



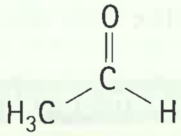
salicylic acid methanol methyl salicylate (wintergreen)

There is much more to organic chemistry than just learning functional groups and their general properties. Many, if not most, practicing organic chemists dedicate much of their time to the synthesis of organic molecules that have practical applications, such as for agriculture or pharmaceuticals. Often these target molecules are organic compounds that have been isolated from nature, where they can be found in only small quantities. To create large amounts of these chemicals, the organic chemist devises a pathway through which the compound can be synthesized in the laboratory from readily available smaller compounds. Once synthesized, the compound produced in the laboratory is chemically identical to that found in nature. In other words, it will have the same physical and chemical properties and will also have the same biological effects, if any.

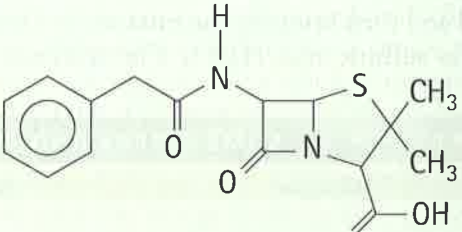
We eat organic chemicals daily. In fact, organic chemicals are the only things we eat, except for some important minerals, such as the ions of sodium and calcium.

CHECKPOINT

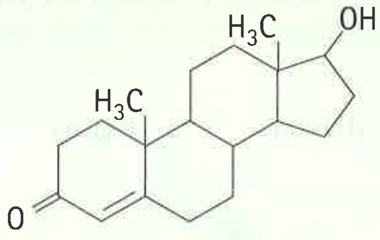
Identify all the functional groups in these four molecules (ignore the sulfur group in penicillin G).



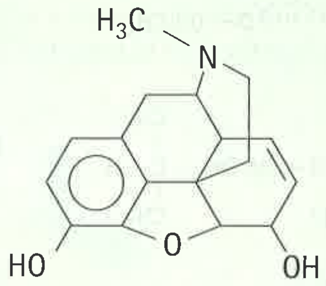
Acetaldehyde



Penicillin G



Testosterone



Morphine

Were these your answers?

Acetaldehyde: aldehyde. Penicillin G: amide (two amide groups) and carboxylic acid. Testosterone: alcohol and ketone. Morphine: alcohol, phenol, ether, and amine.

19.7 Polymers

EXPLAIN THIS Why are plastics generally so inexpensive?

Polymers are exceedingly long molecules that consist of repeating molecular units called **monomers,** as Figure 19.27 illustrates. Monomers have relatively simple structures consisting of anywhere from 4 to 100 atoms per molecule. When monomers are chained together, they can form polymers consisting of hundreds of thousands of atoms per molecule. These large molecules are still too small to be seen with the unaided eye. They are, however, giants in the submicroscopic world—if a typical polymer molecule were as thick as a kite string, it would be 1 km long.

MasteringPhysics®
TUTORIAL: Polymers
TUTORIAL: Polymers from Monomers

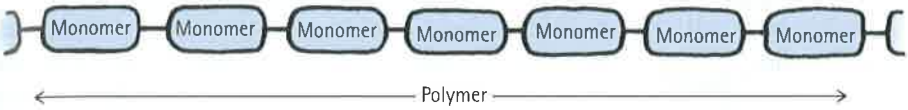


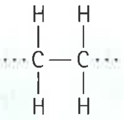
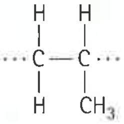
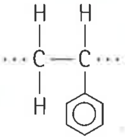
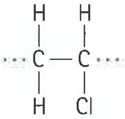
FIGURE 19.27
A polymer is a long molecule consisting of many smaller monomer molecules linked together.

Many of the molecules that constitute living organisms are polymers, including DNA, proteins, the cellulose of plants, and the complex carbohydrates of starchy foods. For now, we focus on the human-made polymers, also known as synthetic polymers, that make up the class of materials that are commonly known as plastics.

We will begin by exploring the two major types of synthetic polymers used today—*addition polymers* and *condensation polymers.*

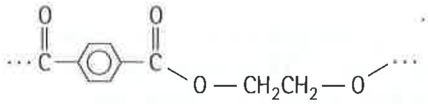
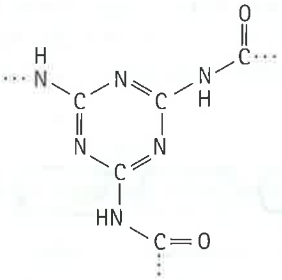
As shown in Table 19.5, addition and condensation polymers have a wide variety of uses. Solely the product of human design, these polymers pervade modern living. In the United States, for example, synthetic polymers have surpassed steel as the most widely used material.

TABLE 19.5 ADDITION AND CONDENSATION POLYMERS

Polymers	Repeating Unit	Common Uses	Recycling Code
Addition			
Polyethylene (PE)	 $\cdots\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\cdots$	Plastic bags, bottles	2 HDPE 4 LDPE
Polypropylene (PP)	 $\cdots\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}\cdots$	Indoor–outdoor carpets	5 PP
Polystyrene (PS)		Plastic utensils, insulation	6 PS
Polyvinyl chloride (PVC)	 $\cdots\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}\cdots$	Shower curtains, tubing	3 V

(continued)

TABLE 19.5 CONTINUED

Polymers	Repeating Unit	Common Uses	Recycling Code
Condensation			
Polyethylene terephthalate		Clothing, plastic bottles	1 PET
Melamine–formaldehyde resin (Melmac, Formica)		Dishes, countertops	Not recycled

Addition Polymers

Addition polymers form simply by the joining of monomer units. For this to happen, each monomer must contain at least one double bond. As shown in Figure 19.28, polymerization occurs when two of the electrons from each double bond split away from each other to form new covalent bonds with neighboring monomer molecules. During this process, no atoms are lost, so the total mass of the polymer is equal to the sum of the masses of all the monomers.

Worldwide, about 80 million metric tons of polyethylene are produced annually. The monomer from which it is synthesized, ethylene, is an unsaturated hydrocarbon produced in large quantities from petroleum.

Two principal forms of polyethylene are produced by using different catalysts and reaction conditions. High-density polyethylene (HDPE), shown schematically in Figure 19.29a, consists of long strands of straight-chain molecules packed closely together. The tight alignment of neighboring strands makes

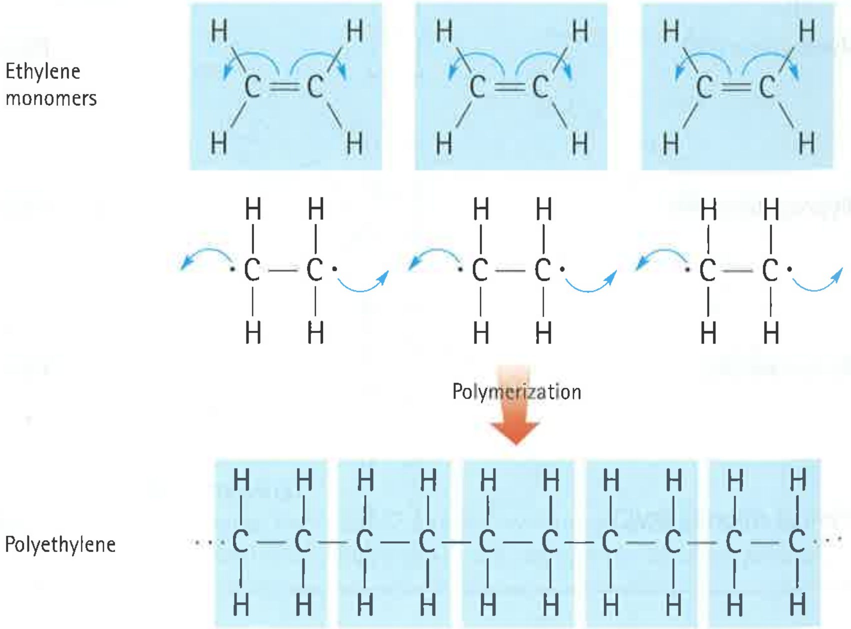


FIGURE 19.28
The addition polymer polyethylene is formed as electrons from the double bonds of ethylene monomer molecules split away and become unpaired valence electrons. Each unpaired electron then joins with an unpaired electron of a neighboring carbon atom to form a new covalent bond that links two monomer units.

HDPE a relatively rigid, tough plastic useful for such things as bottles and milk jugs. Low-density polyethylene (LDPE), shown in Figure 19.29b, is made of strands of highly branched chains, an architecture that prevents the strands from packing closely together. This makes LDPE more bendable than HDPE and gives it a lower melting point. HDPE holds its shape in boiling water; LDPE deforms. LDPE is most useful for such items as plastic bags, photographic film, and electrical-wire insulation.

Other addition polymers are created by using different monomers. The only requirement is that the monomer must contain a double bond. The monomer propylene, for example, yields polypropylene, as shown in Figure 19.30. Polypropylene is a tough plastic material useful for pipes, hard-shell suitcases, and appliance parts. Fibers of polypropylene are used for upholstery, indoor–outdoor carpets, and even thermal underwear.

Figure 19.31 shows that using styrene as the monomer yields polystyrene. Transparent plastic cups are made of polystyrene, as are thousands of other household items. Blowing gas into liquid polystyrene generates Styrofoam, which is widely used for coffee cups, packing material, and insulation.

The addition polymer polytetrafluoroethylene, shown in Figure 19.33 (next page), is what you know as Teflon. In contrast to the chlorine-containing Saran, fluorine-containing Teflon has a nonstick surface because the fluorine atoms tend not to experience any molecular attractions. In addition, because carbon–fluorine bonds are unusually strong, Teflon can be heated to high temperatures before decomposing. These properties make Teflon an ideal coating for cooking surf-aces. It is also relatively inert, which is why many corrosive chemicals are shipped or stored in Teflon containers.

(a) Molecular strands of HDPE

(b) Molecular strands of LDPE

FIGURE 19.29
(a) The polyethylene strands of HDPE can pack closely together, much like strands of uncooked spaghetti.
(b) The polyethylene strands of LDPE are branched, which prevents the strands from packing well.

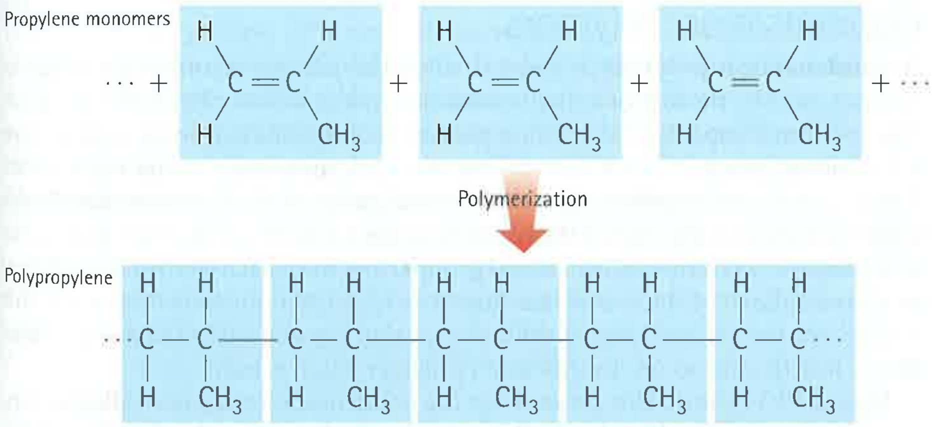


FIGURE 19.30
Propylene monomers polymerize to form polypropylene.

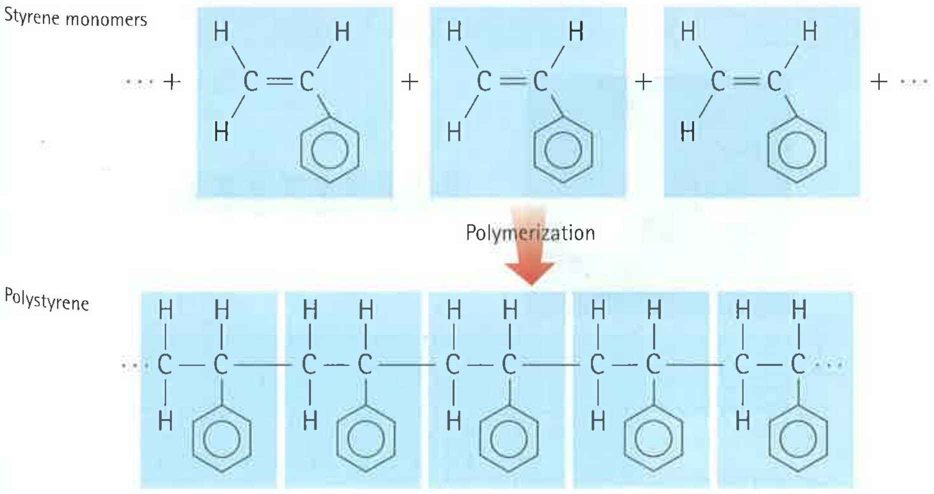
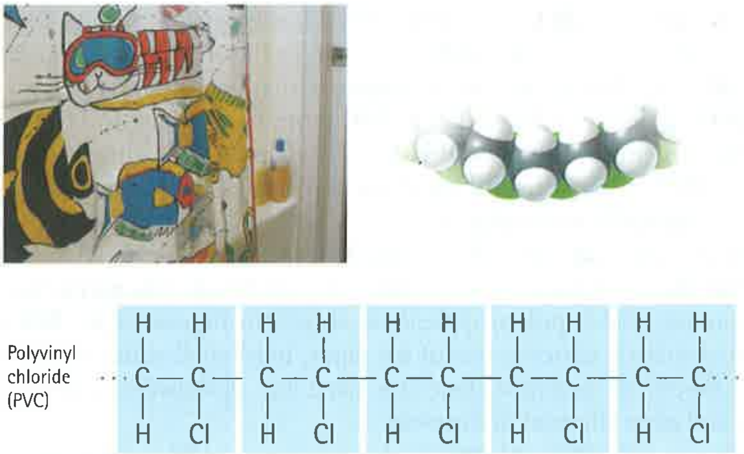


FIGURE 19.31
Styrene monomers polymerize to form polystyrene.

FIGURE 19.32
Another important addition polymer is polyvinyl chloride (PVC), which is used to fabricate many household items.



fyi

- So if nothing sticks to Teflon, how is Teflon made to adhere to a pan as a coating? That's a trade secret, but rumor has it that there are microscopic pits in the metal pan that help the Teflon adhere physically. Of course, we all know that the Teflon is fairly easy to scrape out of the pan, which is why manufacturers recommend that you stir-fry with a wooden utensil.

CHECKPOINT

What do all monomers that are used to make addition polymers have in common?

Was this your answer?
A double covalent bond between two carbon atoms

Condensation Polymers

A **condensation polymer** is formed when the joining of monomer units is accompanied by the loss of a small molecule, such as water or hydrochloric acid. Any monomer capable of becoming part of a condensation polymer must have a functional group on each end. When two such monomers come together to form a condensation polymer, one functional group of the first monomer links with one functional group of the other monomer. The result is a two-monomer unit that has two terminal functional groups, one from each of the two original monomers. Each of these terminal functional groups in the two-monomer unit is now free to link with one of the functional groups of a third monomer, and then a fourth, and so on. In this way a polymer chain is built.

Figure 19.34 shows this process for the condensation polymer called nylon, which was created in 1937 by DuPont chemist Wallace Carothers (1896–1937).

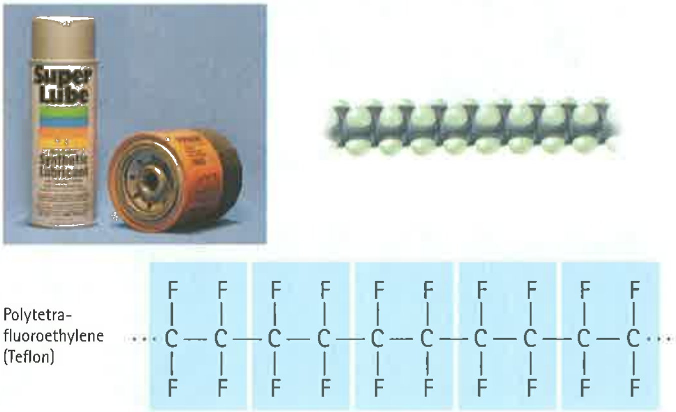


FIGURE 19.33
The fluorine atoms in polytetrafluoroethylene tend not to experience molecular attractions, which is why this addition polymer is used as a nonstick coating and lubricant.

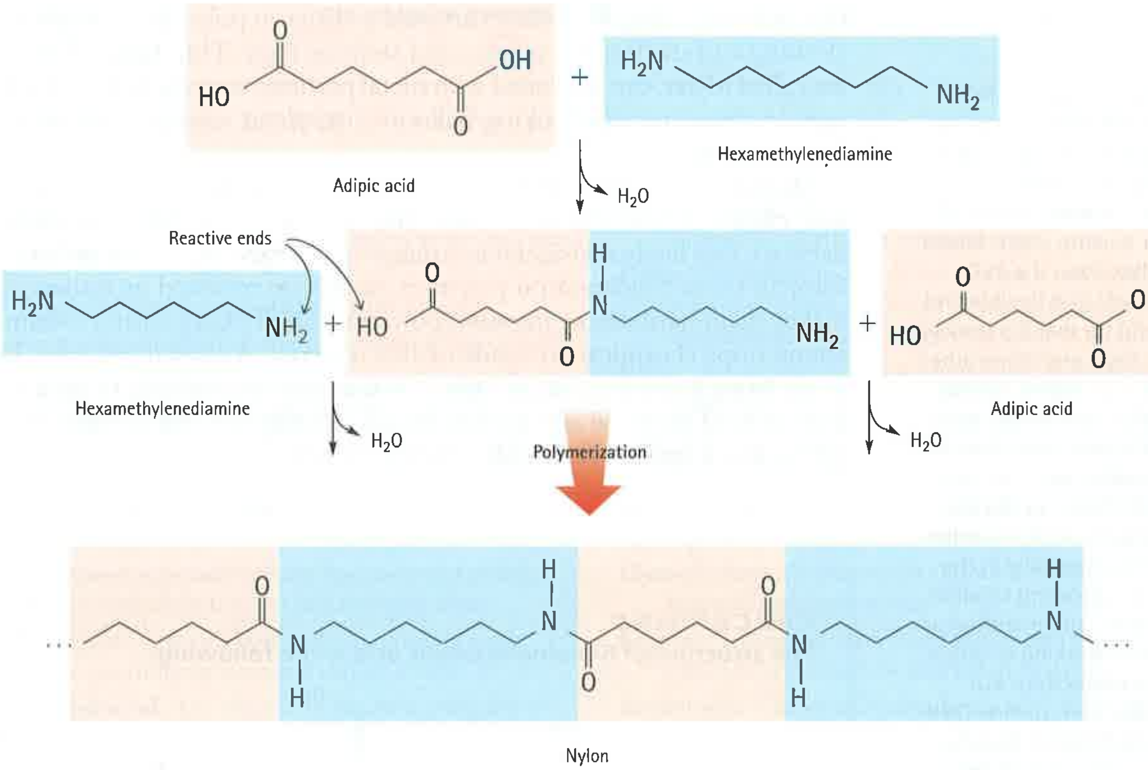
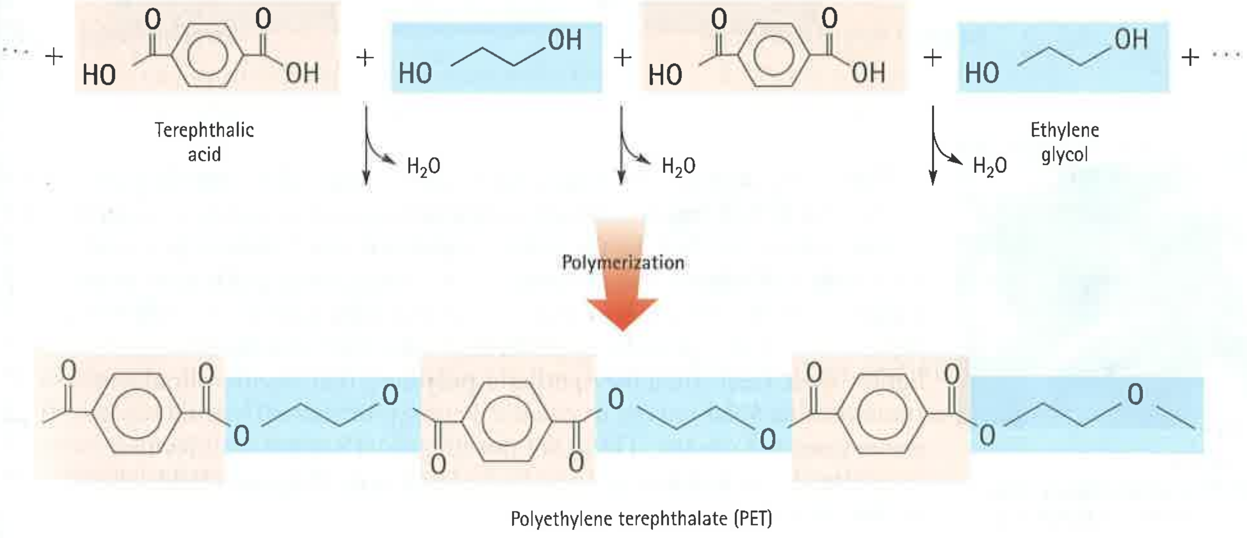


FIGURE 19.34
Adipic acid and hexamethylenediamine polymerize to form the condensation copolymer nylon.

This polymer is composed of two different monomers, which classifies it as a *copolymer.* One monomer is adipic acid, which contains two reactive end groups, both carboxyl groups. The second monomer is hexamethylenediamine, in which two amine groups are the reactive end groups. One end of an adipic acid molecule and one end of a hexamethylenediamine molecule can be made to react with each other, splitting off a water molecule in the process. After two monomers have joined, reactive ends still remain for further reactions, which leads to a growing polymer chain. Aside from its use in hosiery, nylon also finds important uses in the manufacture of ropes, parachutes, clothing, and carpets.

Another widely used condensation polymer is polyethylene terephthalate (PET), which is formed from the copolymerization of ethylene glycol and terephthalic acid, as shown in Figure 19.35. Plastic soda bottles are made from

FIGURE 19.35
Terephthalic acid and ethylene glycol polymerize to form the condensation copolymer polyethylene terephthalate.



fyi

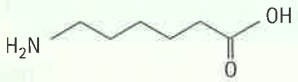
- **Rigid** polymers such as PVC can be made soft by incorporating small molecules called plasticizers. Pure PVC, for example, is a tough material great for making pipes. Mixed with a plasticizer, the PVC becomes soft and flexible and thus useful for making shower curtains, toys, and many other products now found in most households. One of the more commonly used plasticizers is the phthalates, some of which have been shown to disrupt the development of reproductive organs, especially in the fetus and in growing children. Governments and manufacturers are now working to phase out these plasticizers. But some phthalates, such as DINP, have been shown to be safe. For social and political simplicity, should all phthalates be banned or just the ones shown to be harmful? This question has yet to be resolved.

this polymer. Also, PET fibers are sold as Dacron polyester, a product used in clothing and stuffing for pillows and sleeping bags. Thin films of PET, which are called Mylar, can be coated with metal particles to make magnetic recording tape or those metallic-looking balloons for sale at most grocery store checkout counters.

Monomers that contain three reactive functional groups can also form polymer chains. These chains become interlocked in a rigid three-dimensional network that lends considerable strength and durability to the polymer. Once formed, these condensation polymers cannot be remelted or reshaped, which makes them hard-set, or *thermoset,* polymers. Hard plastic dishes (Melmac) and countertops (Formica) are made of this material. A similar polymer, Bakelite, made from formaldehyde and phenols that contain multiple oxygen atoms, is used to bind plywood and particle board. Bakelite was synthesized in the early 1900s, and it was the first widely used polymer.

CHECKPOINT

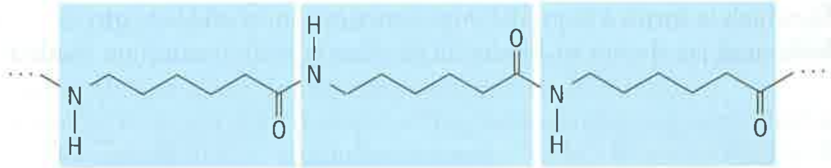
The structure of 6-aminohexanoic acid is the following:



Is this compound a suitable monomer for forming a condensation polymer? If so, what is the structure of the polymer formed, and what small molecule is split off during the condensation?

Were these your answers?

Yes, because the molecule has two reactive ends. You know both ends are reactive because they are the ends shown in Figure 19.34. The only difference here is that both types of reactive ends are on the same molecule. Monomers of 6-aminohexanoic acid combine by splitting off water molecules to form the polymer known as nylon-6:



The synthetic-polymers industry has grown remarkably over the past century. Today, it is a challenge to find any consumer item that does *not* contain a plastic of one sort or another. In the future, watch for new kinds of polymers with a wide range of remarkable properties. One interesting application is shown in Figure 19.36. We already have polymers that conduct electricity, others that emit light, others that replace body parts, and still others that are stronger but much lighter than steel. Imagine synthetic polymers that mimic photosynthesis by transforming solar energy to chemical energy, or that efficiently separate fresh water from the oceans. These are not dreams. They are realities that chemists have already been demonstrating in the laboratory. Polymers hold a clear promise for the future.

FIGURE 19.36
Flexible and flat video displays can now be fabricated from polymers.

For assigned homework and other learning materials, go to MasteringPhysics®. MP

SUMMARY OF TERMS (KNOWLEDGE)

Addition polymer A polymer formed by the joining together of monomer units with no atoms being lost as the polymer forms.

Alkane A generic term for a saturated hydrocarbon.

Alkene An unsaturated hydrocarbon containing one or more double bonds.

Alcohol An organic molecule that contains a hydroxyl group bonded to a saturated carbon.

Aldehyde An organic molecule containing a carbonyl group, the carbon of which is bonded either to one carbon atom and one hydrogen atom or to two hydrogen atoms.

Amide An organic molecule containing a carbonyl group, the carbon of which is bonded to a nitrogen atom.

Amine An organic molecule containing a nitrogen atom bonded to one or more saturated carbon atoms.

Aromatic compound Any organic molecule containing a benzene ring.

Carbonyl group A carbon atom double-bonded to an oxygen atom; found in ketones, aldehydes, amides, carboxylic acids, and esters.

Carboxylic acid An organic molecule containing a carbonyl group, the carbon of which is bonded to a hydroxyl group.

Condensation polymer A polymer formed by the joining together of monomer units accompanied by the loss of small molecules, such as water.

Configuration A description of how the atoms within a molecule are connected. For example, two structural isomers consist of the same number and same kinds of atoms, but in different configurations.

Conformation One of a wide range of possible spatial orientations of a particular configuration.

Ester An organic molecule containing a carbonyl group, the carbon of which is bonded to one carbon atom and one oxygen atom bonded to another carbon atom.

Ether An organic molecule containing an oxygen atom bonded to two carbon atoms.

Functional group A specific combination of atoms that behaves as a unit in an organic molecule.

Heteroatom Any atom other than carbon or hydrogen in an organic molecule.

Hydrocarbon A chemical compound containing only carbon and hydrogen atoms.

Ketone An organic molecule containing a carbonyl group, the carbon of which is bonded to two carbon atoms.

Monomers The small molecular units from which a polymer is formed.

Organic chemistry The study of carbon-containing compounds.

Phenol An organic molecule in which a hydroxyl group is bonded to a benzene ring.

Polymer A long organic molecule made of many repeating units.

Saturated hydrocarbon A hydrocarbon containing no multiple covalent bonds, with each carbon atom bonded to four other atoms.

Structural isomers Molecules that have the same molecular formula but different chemical structures.

Unsaturated hydrocarbon A hydrocarbon containing at least one multiple covalent bond.

READING CHECK QUESTIONS (COMPREHENSION)

19.1 Hydrocarbons

1. How do two structural isomers differ from each other?
2. How are two structural isomers similar to each other?
3. What physical property of hydrocarbons is used in fractional distillation?
4. What types of hydrocarbons are more abundant in higher-octane gasoline?

19.2 Unsaturated Hydrocarbons

5. To how many atoms is a saturated carbon atom bonded?
6. What is the difference between a saturated hydrocarbon and an unsaturated hydrocarbon?
7. How many multiple bonds must a hydrocarbon have in order to be classified as unsaturated?
8. What kind of ring do aromatic compounds contain?

19.3 Functional Groups

9. What is a heteroatom?
10. Why do heteroatoms make such a difference in the physical and chemical properties of an organic molecule?

19.4 Alcohols, Phenols, and Ethers

11. Why are low-formula-mass alcohols soluble in water?
12. What distinguishes an alcohol from a phenol?
13. What distinguishes an alcohol from an ether?

19.5 Amines and Alkaloids

14. Which heteroatom is characteristic of an amine?
15. Do amines tend to be acidic, neutral, or basic?
16. Are alkaloids found in nature?
17. What are some examples of alkaloids?

19.6 Carbonyl Compounds

18. Which elements make up the carbonyl group?
19. How are ketones and aldehydes related to each other? How are they different from each other?
20. How are amides and carboxylic acids related to each other? How are they different from each other?
21. From what naturally occurring compound is aspirin prepared?

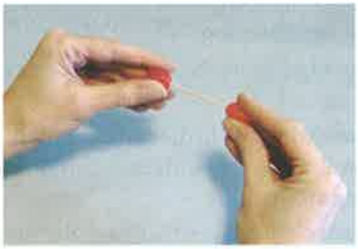
19.7 Polymers

22. What happens to the double bond of a monomer participating in the formation of an addition polymer?
23. What is released in the formation of a condensation polymer?
24. Why is plastic wrap made of polyvinylidene chloride stickier than plastic wrap made of polyethylene?
25. What is a copolymer?

ACTIVITIES (HANDS-ON APPLICATION)

26. Two carbon atoms connected by a single bond can rotate relative to each other. This ability to rotate can give rise to numerous conformations (spatial orientations) of an organic molecule. Is it also possible for two carbon atoms connected by a double bond to rotate relative to each other?

Hold two toothpicks side by side and attach one jellybean to each end such that each jellybean has both toothpicks poked into it. Hold one jellybean while rotating the other. What kind of rotations are possible? Relate what you observe to the carbon–carbon double bond. Which structure of Figure 19.7 do you suppose has more possible conformations: butane or 2-butene? What do you suppose is generally true about the ability of atoms connected by a carbon–carbon triple bond to twist relative to each other?



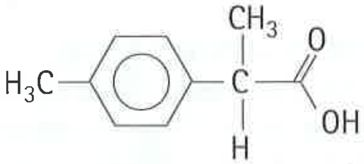
27. A property of polymers is their glass transition temperature, T_g, which is the approximate temperature below which the polymer is hard and rigid, but above which the polymer is soft and flexible. The T_g of polyethylene is a chilly −125°C, which is why polyethylene food wrap is flexible at ambient temperatures. Consider the two polymers polyethylene terephthalate (PETE) and polystyrene (PS). Which do you suppose has the higher T_g? Dip some plastics of these two polymers in boiling water to find out. A common polymer used to make chewing gum is polyvinyl acetate, with a T_g of about 28°C, which is below body temperature but above room temperature. That's why most chewing gums are hard until they soften up in your warm mouth. Drink ice water while chewing gum and note how it quickly hardens.

28. Isopropyl alcohol, also known as rubbing alcohol, is very toxic if ingested. This is because it acts to destroy the digestive proteins and other important biomolecules in your stomach. Do this activity to see firsthand the destructive action of isopropyl alcohol on proteins. Crack open an egg and place the egg white and the yolk into two separate bowls. Pour a capful of isopropyl alcohol into the egg white and observe what happens. In the second bowl, stir the yolk with a fork. Add another capful of isopropyl alcohol to the stirred yolk and observe what happens. The same sort of destruction would occur to your own stomach proteins, as well as various tissues, upon ingesting the isopropyl alcohol. Not good! Our skin, however, is more impervious to the destructive powers of isopropyl alcohol, which therefore serves as a good topical antiseptic.

THINK AND RANK (ANALYSIS)

29. Rank the following molecules in order of the phase they form at room temperature: solid, liquid, gas.

(a)



(b) $CH_3CH_2CH_2CH_3$

(c) $CH_3CH_2CH_2CH_2 — OH$

30. Rank the following hydrocarbons in order of increasing number of hydrogen atoms:

Cyclobutane
(a)

Butane
(b)

2-Butene
(c)

31. Rank the following hydrocarbons in order of increasing number of hydrogen atoms:

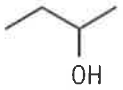
(a)

(b)

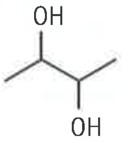
(c)

32. Rank the following organic molecules in order of increasing solubility in water:


(a)

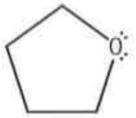


(b)

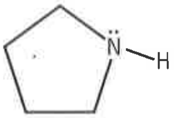


(c)

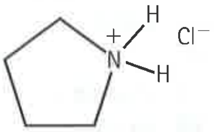
33. Rank the following organic molecules in order of increasing solubility in water:



(a)



(b)



(c)

EXERCISES (SYNTHESIS)

19.1 Hydrocarbons

34. What property of carbon allows for the formation of so many different organic molecules?

35. Why does the melting point of hydrocarbons increase as the number of carbon atoms per molecule increases?

36. Draw all the structural isomers for hydrocarbons having the molecular formula C_6H_{14}.

37. How many structural isomers are shown here?

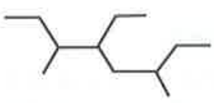
38. According to Figure 19.3, which has the higher boiling point: gasoline or kerosene?

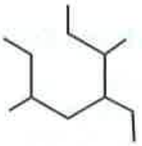
39. The temperatures in a fractionating tower at an oil refinery are important, but so are the pressures. Where might the pressure in a fractionating tower be greatest: at the bottom or at the top? Defend your answer.

40. There are five atoms in the methane molecule, CH_4. One of these five atoms is a carbon atom, which means the molecule is $1/5 \times 100 = 20\%$ carbon. What is the percent carbon in ethane, C_2H_6? propane, C_3H_8? In butane, C_4H_{10}?

41. Do heavier hydrocarbons tend to produce more or less carbon dioxide upon combustion than do lighter hydrocarbons? Why?

42. What do these two structures have in common?

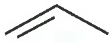

(a)


(b)

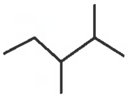
19.2 Unsaturated Hydrocarbons

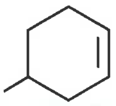
43. What do the compounds cyclopropane and propene have in common?

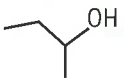

Cyclopropane


Propene

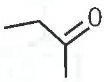
44. What are the chemical formulas for the following structures?


(a)


(b)

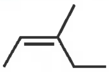


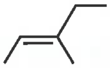
(c)

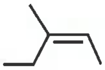


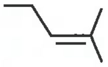
(d)

45. Remember that carbon–carbon single bonds can rotate, whereas carbon–carbon double bonds cannot rotate. How many different structures are shown below?





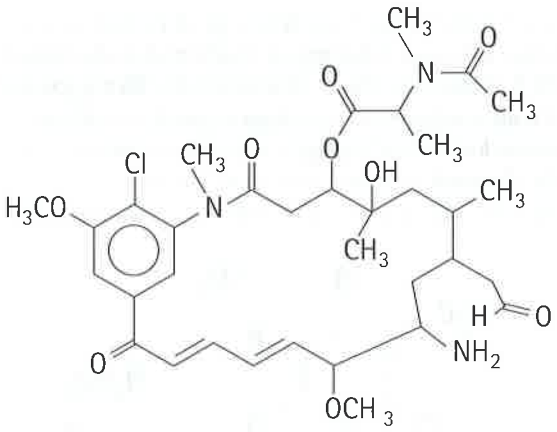




46. Which of the structures shown in the previous question are either the *cis*- or the *trans*-isomers of 3-methyl-2-pentene? Circle them.

19.3 Functional Groups

47. Identify the following functional groups in this organic molecule: amide, ester, ketone, ether, alcohol, aldehyde, amine.



48. What must be added to a double bond to transform it into an alcohol? Would this be an example of oxidation or reduction? (See Figure 18.20)

49. What do phenols and carboxylic acids have in common?

50. What is the difference between a ketone and an aldehyde?

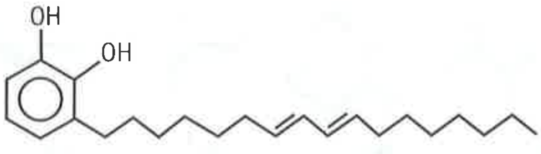
51. An ether is to an alcohol as an ester is to
   - (a) a phenol.
   - (b) a carboxylic acid.
   - (c) an amide.
   - (d) an ether.

19.4 Alcohols, Phenols, and Ethers

52. Why do ethers typically have lower boiling points than alcohols?

53. What is the percent volume of water in 80-proof vodka?

54. One of the skin-irritating components of poison oak is tetrahydrourushiol:



The long, nonpolar hydrocarbon tail embeds itself in a person's oily skin, where the molecule initiates an allergic response. Scratching the itch spreads tetrahydrourushiol molecules over a greater surface area, causing the zone of irritation to grow. Is this compound an alcohol or a phenol? Defend your answer.

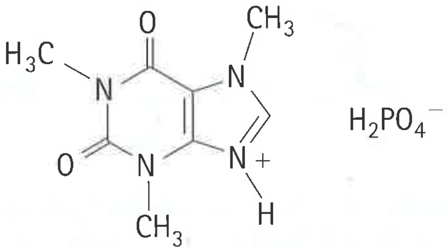
55. Cetyl alcohol, $C_{16}H_{34}O$, is a common ingredient of soaps and shampoos. It was once commonly obtained from whale oil, which is where it gets its name (*cetyl* is derived from the word *cetacean*, which is used to refer to members of the family of mammals that includes whales, dolphins, and porpoises). Review the discussion of soaps, in Section 16.5 and then draw the likely chemical structure for this alcohol.

19.5 Amines and Alkaloids

56. A common inactive ingredient in products such as sunscreen lotions and shampoo is triethylamine, also known as TEA. What is the chemical structure for this compound?

57. A common inactive ingredient in products such as sunscreen lotions and shampoo is triethanolamine. What is the chemical structure for this tri-alcohol?

58. The phosphoric acid salt of caffeine has the structure

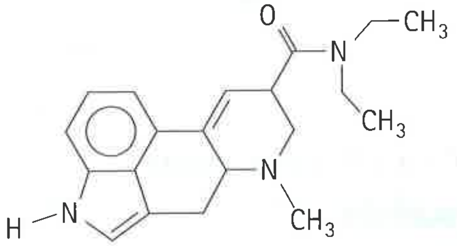


Caffeine–phosphoric acid salt

This molecule behaves as an acid in that it can donate a hydrogen ion, created from the hydrogen atom bonded to the positively charged nitrogen atom. What are all the products formed when 1 mole of this salt reacts with 1 mole of sodium hydroxide, NaOH, a strong base?

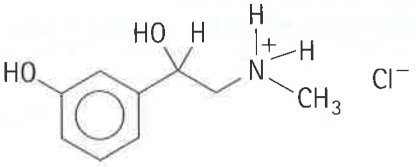
59. Draw all the structural isomers for amines having the molecular formula C_3H_9N.

60. In water, does the following molecule act as an acid, a base, neither, or both?



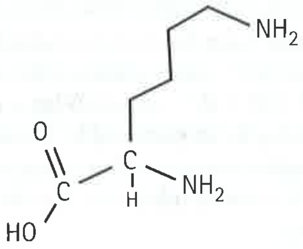
Lysergic acid diethylamide

61. If you saw the label phenylephrine · HCl on a decongestant, would you worry that consuming it would expose you to the strong acid hydrochloric acid? Explain.



Phenylephrine–hydrochloric acid salt

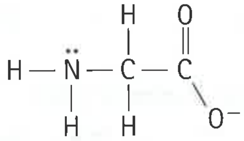
62. The amino acid lysine is shown below. What functional group must be removed in order to produce cadaverine, as shown in Figure 19.18?

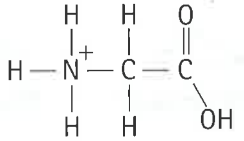


Lysine

19.6 Carbonyl Compounds

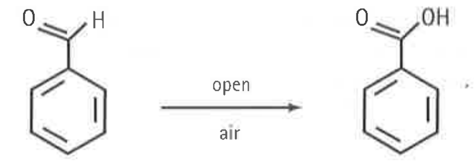
63. An amino acid is an organic molecule that contains both an amine group and a carboxyl group. At an acidic pH, which structure is most likely? Explain your answer.

(a)


(b)


64. Suggest an explanation why aspirin has a sour taste.

65. Benzaldehyde is a fragrant oil. If stored in an uncapped bottle, this compound will slowly transform into benzoic acid along the surface. Is this an oxidation or a reduction?

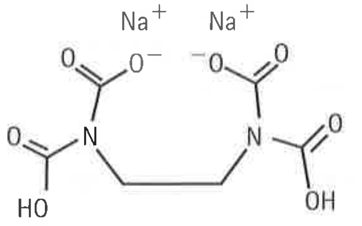


Benzaldehyde

Benzoic acid

66. What products are formed upon the reaction of benzoic acid with sodium hydroxide, NaOH? One of these products is a common food preservative. Can you name it?

67. The disodium salt of ethylenediaminetetraacetic acid, also known as EDTA, has a great affinity for lead ions, Pb^{2+}. Why? Can you think of any useful applications of this chemistry?



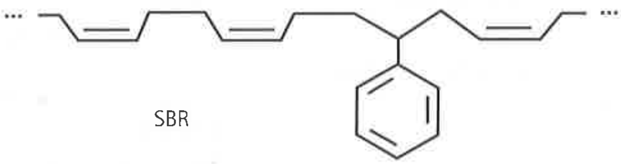
EDTA

19.7 Polymers

68. Would you expect polypropylene to be more dense or less dense than low-density polyethylene? Why?

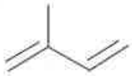
69. Hydrocarbons release a lot of energy when ignited. Where does this energy come from?

70. The polymer styrene–butadiene rubber (SBR), shown below, is used for making tires as well as bubble gum. Is it an addition polymer or a condensation polymer?

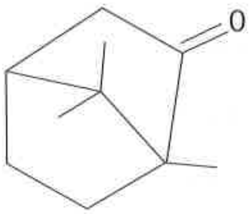


SBR

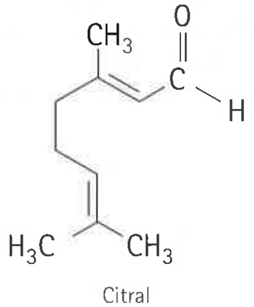
71. Citral and camphor are both 10-carbon odoriferous natural products made from the joining of two isoprene units plus the addition of a carbonyl functional group. Shown below are their chemical structures. Find and circle the two isoprene units in each of these molecules.



Isoprene
(2-methyl-1,3-butadiene)

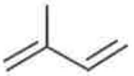


Camphor

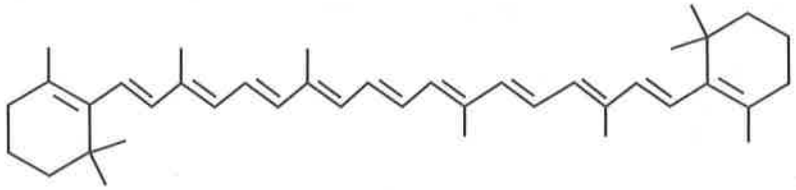


Citral

72. Many of the natural product molecules synthesized by photosynthetic plants are formed by the joining together of isoprene monomers via an addition polymerization. A good example is the nutrient beta-carotene. How many isoprene units are needed to make one beta-carotene molecule? Find and circle these units within the beta-carotene structure shown below.



Isoprene
(2-methyl-1,3-butadiene)



beta-Carotene

DISCUSSION QUESTIONS (EVALUATION)

73. The solvent diethyl ether can be mixed with water but only by shaking the two liquids together. After the shaking is stopped, the liquids separate into two layers, much like oil and vinegar. The free-base form of the alkaloid caffeine is readily soluble in diethyl ether but not in water. Suggest what might happen to the caffeine of a caffeinated beverage if the beverage was first made alkaline with sodium hydroxide and then shaken with some diethyl ether.
74. Alkaloid salts are not very soluble in the organic solvent diethyl ether. What might happen to the free-base form of caffeine dissolved in diethyl ether if gaseous hydrogen chloride, HCl, were bubbled into the solution?
75. Go online and look up the total synthesis of the anti-cancer drug Taxol. With this major accomplishment in mind, discuss the relative merits of specializing in a single area versus becoming an expert in many different areas. When in life do we have the opportunity of simultaneously narrowing our focus while expanding our horizons?

READINESS ASSURANCE TEST (RAT)

If you have a good handle on this chapter, then you should be able to score at least 7 out of 10 on this RAT. If you score less than 7, you need to study further before moving on.

Choose the BEST answer to the question or the BEST way to complete the statement.

1. Why does the melting point of hydrocarbons increase as the number of carbon atoms per molecule increases?
   (a) An increase in the number of carbon atoms per molecule also means an increase in the density of the hydrocarbon.
   (b) The induced dipole–induced dipole molecular attractions are stronger.
   (c) Larger hydrocarbon chains tend to be branched.
   (d) The molecular mass also increases.
2. How many structural isomers are there for hydrocarbons that have the molecular formula C_4H_{10}?
   (a) None
   (b) One
   (c) Two
   (d) Three
3. Which contains more hydrogen atoms: a five-carbon saturated hydrocarbon molecule or a five-carbon unsaturated hydrocarbon molecule?
   (a) The unsaturated hydrocarbon has more hydrogen atoms.
   (b) The saturated hydrocarbon has more hydrogen atoms.
   (c) They both have the same number of hydrogen atoms.
   (d) It depends on whether the unsaturation is due to a double bond or a triple bond.
4. Heteroatoms make a difference in the physical and chemical properties of an organic molecule because
   (a) they add extra mass to the hydrocarbon structure.
   (b) each heteroatom has its own characteristic chemistry.
   (c) they can enhance the polarity of the organic molecule.
   (d) all of the above
5. Why might a high-formula-mass alcohol be insoluble in water?
   (a) A high-formula-mass alcohol is too attracted to itself to be soluble in water.
   (b) The bulk of a high-formula-mass alcohol likely consists of nonpolar hydrocarbons.
   (c) Such an alcohol is likely in a solid phase.
   (d) In order for two substances to be soluble in each other, their molecules need to be of comparable mass.
6. Alkaloid salts are not very soluble in the organic solvent diethyl ether. What might happen to the free-base form of caffeine (an alkaloid) dissolved in diethyl ether if gaseous hydrogen chloride, HCl, were bubbled into the solution?
   (a) A second layer of water would form.
   (b) Nothing; the HCl gas would merely bubble out of solution.
   (c) The diethyl ether–insoluble caffeine salt would form as a white preciptitate.
   (d) The acid–base reaction would release heat, which would cause the diethyl ether to start evaporating.
7. Explain why caprylic acid, $CH_3(CH_2)_6COOH$, dissolves in a 5% aqueous solution of sodium hydroxide but caprylaldehyde, $CH_3(CH_2)_6CHO$, does not.
   (a) With two oxygens, the caprylic acid is about twice as polar as the caprylaldehyde.
   (b) The caprylaldehyde is a gas at room temperature.
   (c) The caprylaldehyde behaves as a reducing agent, which neutralizes the sodium hydroxide.
   (d) The caprylic acid reacts to form the water-soluble salt.
8. How many oxygen atoms are bonded to the carbon of the carbonyl of an ester functional group?
   (a) None
   (b) One
   (c) Two
   (d) Three