

CHEMISTRY

Chapter 20 ORGANIC CHEMISTRY

PowerPoint Image Slideshow



FIGURE 20.1



All organic compounds contain carbon and most are formed by living things, although they are also formed by geological and artificial processes. (credit left: modification of work by Jon Sullivan; credit left middle: modification of work by Deb Tremper; credit right middle: modification of work by “annszyp”/Wikimedia Commons; credit right: modification of work by George Shuklin)

CH. 20 OUTLINE



1. Hydrocarbons
2. Alcohols and Ethers
3. Aldehydes, Ketones, Carboxylic Acids, and Esters
4. Amines and Amides

INTRODUCTION



- All living things on earth are formed mostly of carbon compounds. The prevalence of carbon compounds in living things has led to the epithet “carbon-based” life.
- The truth is we know of no other kind of life. Early chemists regarded substances isolated from *organisms* (plants and animals) as a different type of matter that could not be synthesized artificially, and these substances were thus known as *organic compounds*.

INTRODUCTION

- The widespread belief called vitalism held that organic compounds were formed by a vital force present only in living organisms.
- The German chemist Friedrich Wohler was one of the early chemists to refute this aspect of vitalism, when, in 1828, he reported the synthesis of urea, a component of many body fluids, from nonliving materials.
- Since then, it has been recognized that organic molecules obey the same natural laws as inorganic substances, and the category of organic compounds has evolved to include both natural and synthetic compounds that contain carbon.

INTRODUCTION

- Some carbon-containing compounds are *not* classified as organic, for example, carbonates and cyanides, and simple oxides, such as CO and CO₂.
- Although a single, precise definition has yet to be identified by the chemistry community, most agree that a defining trait of organic molecules is the presence of carbon as the principal element, bonded to hydrogen and other carbon atoms.

INTRODUCTION



- Today, organic compounds are key components of plastics, soaps, perfumes, sweeteners, fabrics, pharmaceuticals, and many other substances that we use every day.
- The value to us of organic compounds ensures that organic chemistry is an important discipline within the general field of chemistry.

INTRODUCTION



In this chapter, we discuss why the element carbon gives rise to a vast number and variety of compounds, how those compounds are classified, and the role of organic compounds in representative biological and industrial settings.

20.1 Hydrocarbons

By the end of this section, you will be able to:

- Explain the importance of hydrocarbons and the reason for their diversity
- Name saturated and unsaturated hydrocarbons, and molecules derived from them
- Describe the reactions characteristic of saturated and unsaturated hydrocarbons
- Identify structural and geometric isomers of hydrocarbons

20.1 Hydrocarbons

- The simplest **organic compounds** contain only the elements carbon and hydrogen, and are called hydrocarbons.
- Even though they are composed of only two types of atoms, there is a wide variety of hydrocarbons because they may consist of varying lengths of chains, branched chains, and rings of carbon atoms, or combinations of these structures.
- In addition, hydrocarbons may differ in the types of carbon-carbon bonds present in their molecules. Many hydrocarbons are found in plants, animals, and their fossils; other hydrocarbons have been prepared in the laboratory..

20.1 Hydrocarbons

- We use hydrocarbons every day, mainly as fuels, such as natural gas, acetylene, propane, butane, and the principal components of gasoline, diesel fuel, and heating oil.
- The familiar plastics polyethylene, polypropylene, and polystyrene are also hydrocarbons.
- We can distinguish several types of hydrocarbons by differences in the bonding between carbon atoms.
- This leads to differences in geometries and in the hybridization of the carbon orbitals

ALKANES



Alkanes, or **saturated hydrocarbons**, contain only single covalent bonds between carbon atoms. Each of the carbon atoms in an alkane has sp^3 hybrid orbitals and is bonded to four other atoms, each of which is either carbon or hydrogen.

The Lewis structures and models of methane, ethane, and pentane.

Carbon chains are usually drawn as straight lines in Lewis structures, but one has to remember that Lewis structures are not intended to indicate the geometry of molecules.

ALKANES



Notice that the carbon atoms in the structural models (the ball-and-stick and space-filling models) of the pentane molecule do not lie in a straight line.

Because of the sp^3 hybridization, the bond angles in carbon chains are close to 109.5° , giving such chains in an alkane a zigzag shape.

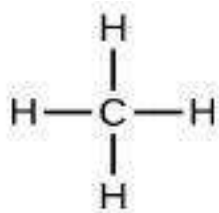
ALKANES



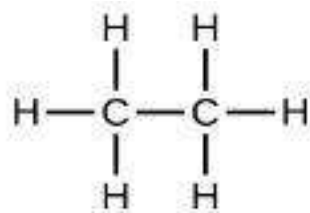
- The structures of alkanes and other organic molecules may also be represented in a less detailed manner by condensed structural formulas (or simply, *condensed formulas*).
- Instead of the usual format for chemical formulas in which each element symbol appears just once, a condensed formula is written to suggest the bonding in the molecule.

- These formulas have the appearance of a Lewis structure from which most or all of the bond symbols have been removed.
- Condensed structural formulas for ethane and pentane, and several additional examples are provided in the exercises at the end of this chapter.

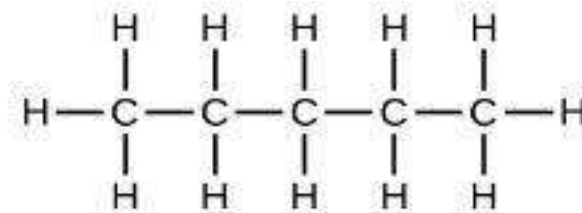
FIGURE 20.2



methane
CH₄



ethane
CH₃CH₃ or C₂H₆



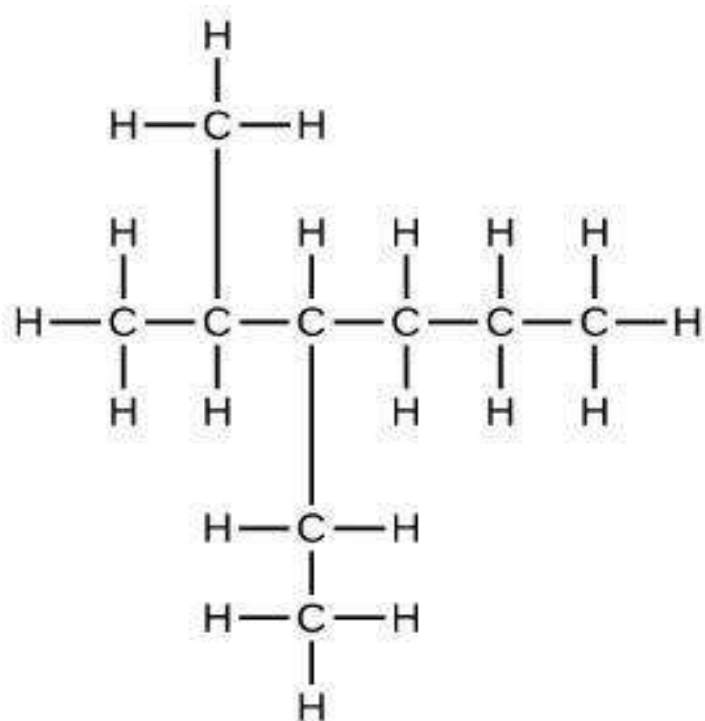
pentane
CH₃CH₂CH₂CH₂CH₃ or C₅H₁₂

Pictured are the Lewis structures, ball-and-stick models, and space-filling models for molecules of methane, ethane, and pentane.

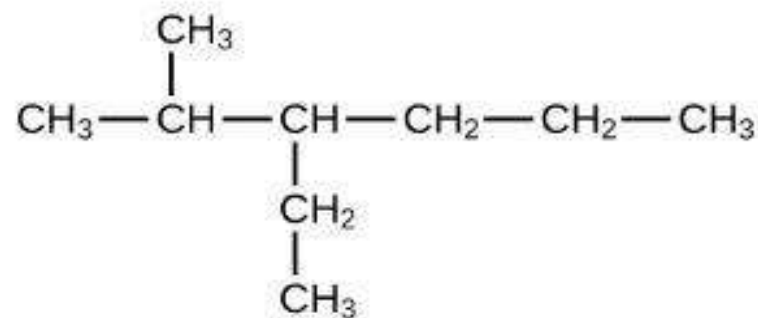
ALKANES

- A common method used by organic chemists to simplify the drawings of larger molecules is to use a **skeletal structure** (also called a line-angle structure).
- In this type of structure, carbon atoms are not symbolized with a C, but represented by each end of a line or bend in a line.
- Hydrogen atoms are not drawn if they are attached to a carbon.
- Other atoms besides carbon and hydrogen are represented by their elemental symbols.

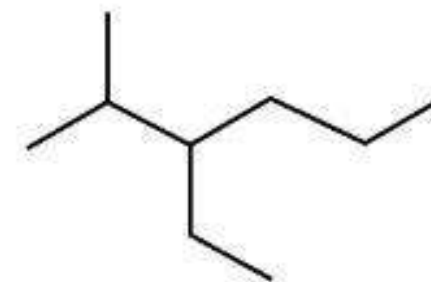
FIGURE 20.3



Expanded formula



Condensed formula

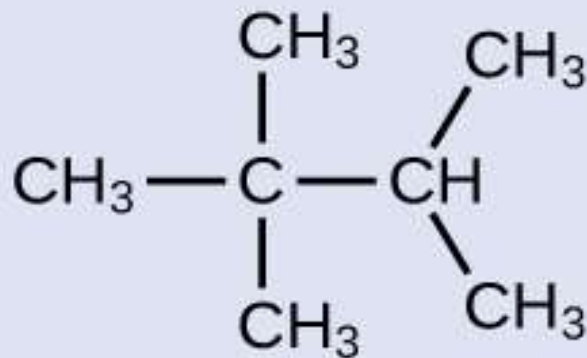


Skeletal structure

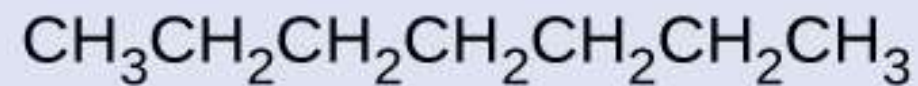
The same structure can be represented three different ways: an expanded formula, a condensed formula, and a skeletal structure.

EXAMPLE 20.1.1

Draw the skeletal structures for these two molecules:



(a)



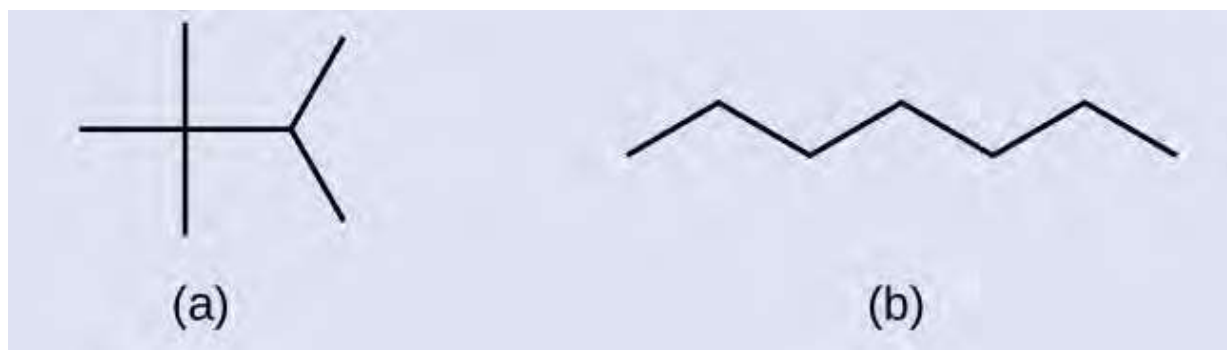
(b)

EXAMPLE 20.1.1

Solution

Each carbon atom is converted into the end of a line or the place where lines intersect.

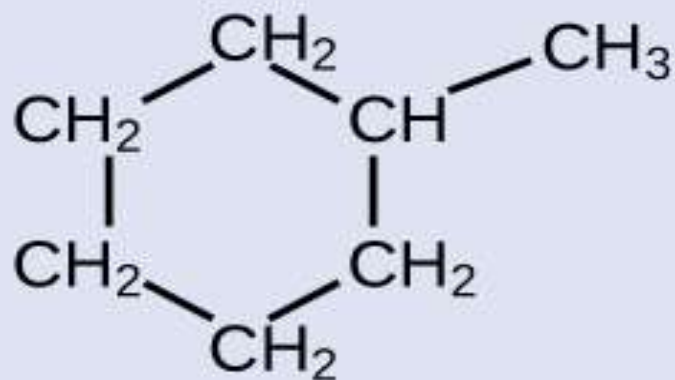
All hydrogen atoms attached to the carbon atoms are left out of the structure (although we still need to recognize they are there):



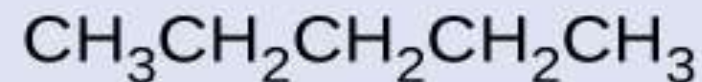
EXAMPLE 20.1.3

Check Your Learning

Draw the skeletal structures for these two molecules:



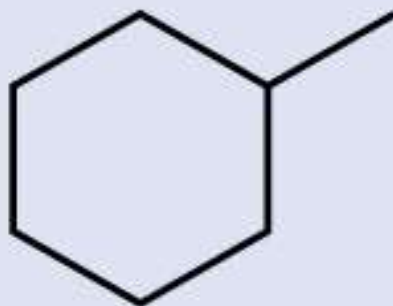
(a)



(b)

EXAMPLE 20.1.4

Answer:



(a)

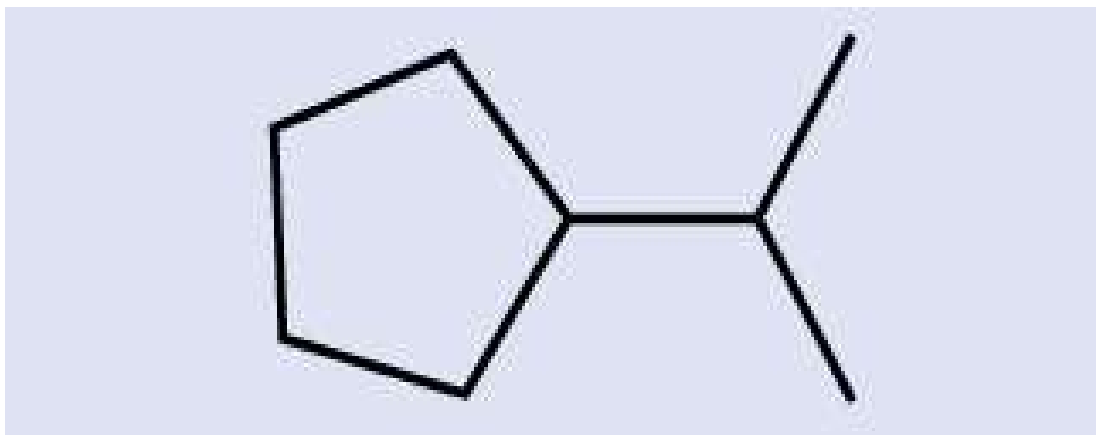


(b)

EXAMPLE 20.2.1

Interpreting Skeletal Structures

Identify the chemical formula of the molecule represented here:



Example 20.2.1

INTERPRETING SKELETAL STRUCTURES

Solution

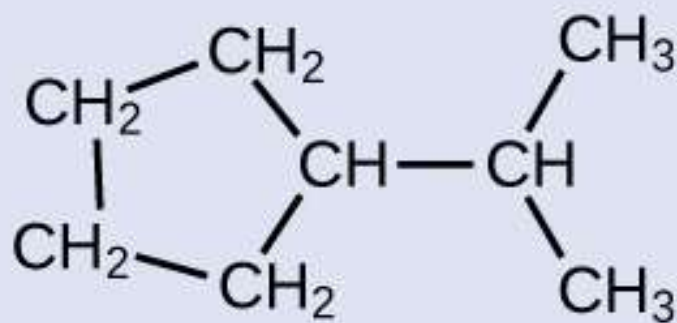
There are eight places where lines intersect or end, meaning that there are eight carbon atoms in the molecule.

Since we know that carbon atoms tend to make four bonds, each carbon atom will have the number of hydrogen atoms that are required for four bonds.

This compound contains 16 hydrogen atoms for a molecular formula of C_8H_{16} .

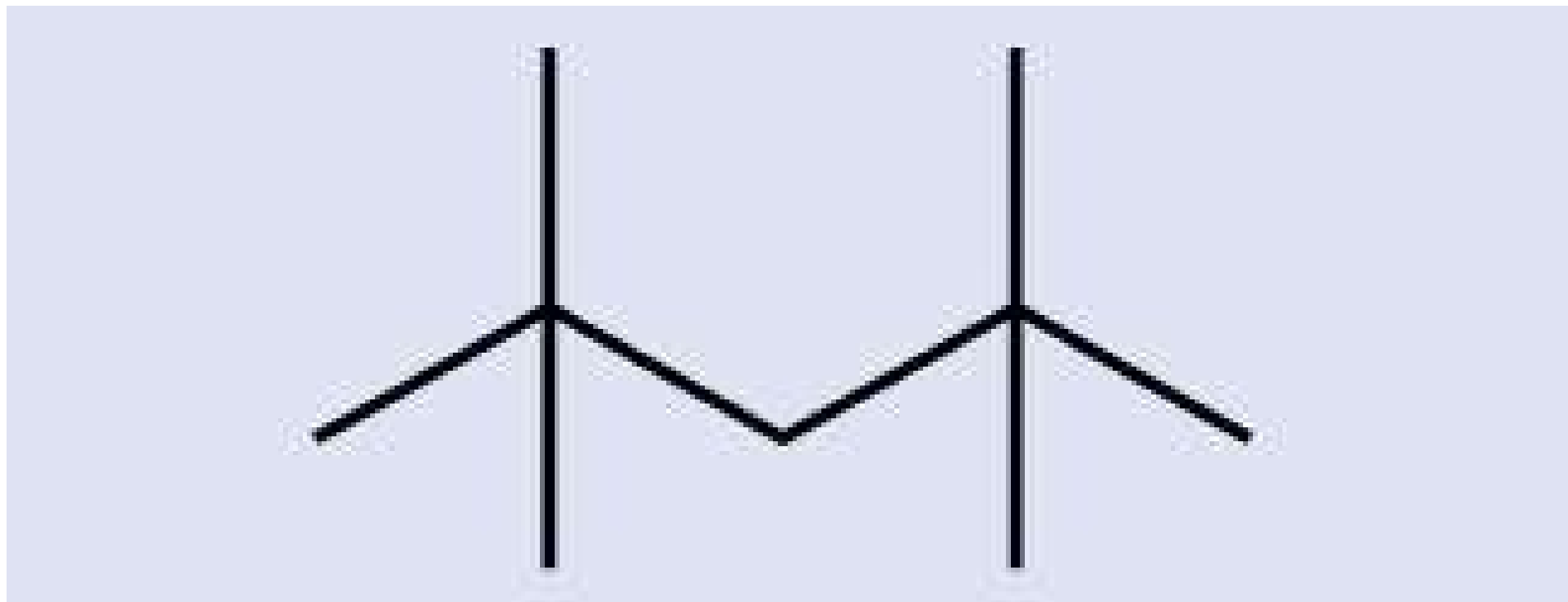
EXAMPLE 20.2.2

Location of the hydrogen atoms:



EXAMPLE 20.2.3

Identify the chemical formula of the molecule represented here:



Answer: C₉H₂₀

ALKANES

All alkanes are composed of carbon and hydrogen atoms, and have similar bonds, structures, and formulas; noncyclic alkanes all have a formula of C_nH_{2n+2} .

The number of carbon atoms present in an alkane has no limit.

Greater numbers of atoms in the molecules will lead to stronger intermolecular attractions (dispersion forces) and correspondingly different physical properties of the molecules.

Properties such as melting point and boiling point (**Table 20.1**) usually change smoothly and predictably as the number of carbon and hydrogen atoms in the molecules change.

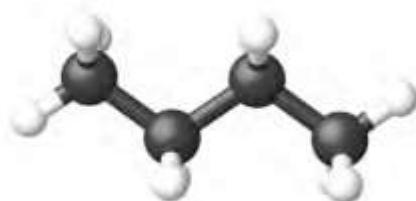
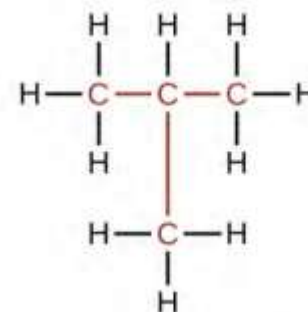
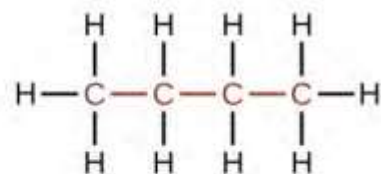
Table 20.1

Properties of Some Alkanes^[3]

Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Phase at STP ^[4]	Number of Structural Isomers
methane	CH ₄	-182.5	-161.5	gas	1
ethane	C ₂ H ₆	-183.3	-88.6	gas	1
propane	C ₃ H ₈	-187.7	-42.1	gas	1
butane	C ₄ H ₁₀	-138.3	-0.5	gas	2
pentane	C ₅ H ₁₂	-129.7	36.1	liquid	3
hexane	C ₆ H ₁₄	-95.3	68.7	liquid	5
heptane	C ₇ H ₁₆	-90.6	98.4	liquid	9
octane	C ₈ H ₁₈	-56.8	125.7	liquid	18
nonane	C ₉ H ₂₀	-53.6	150.8	liquid	35
decane	C ₁₀ H ₂₂	-29.7	174.0	liquid	75
tetradecane	C ₁₄ H ₃₀	5.9	253.5	solid	1858
octadecane	C ₁₈ H ₃₈	28.2	316.1	solid	60,523

Alkanes

Hydrocarbons with the same formula, including alkanes, can have different structures. For example, two alkanes have the formula C_4H_{10} : They are called *n*-butane and 2-methylpropane (or isobutane), and have the following Lewis structures:



n-butane



2-methylpropane

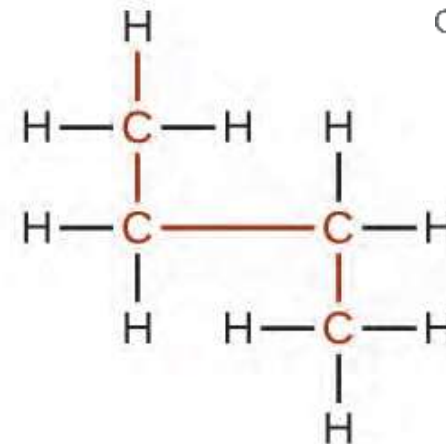
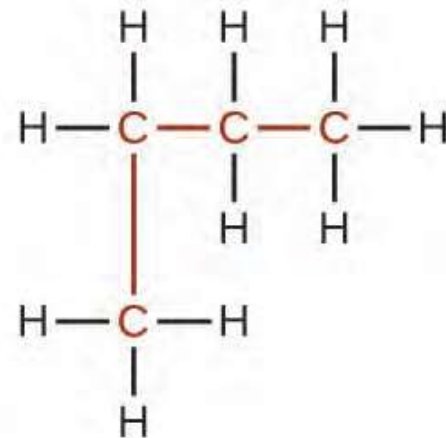
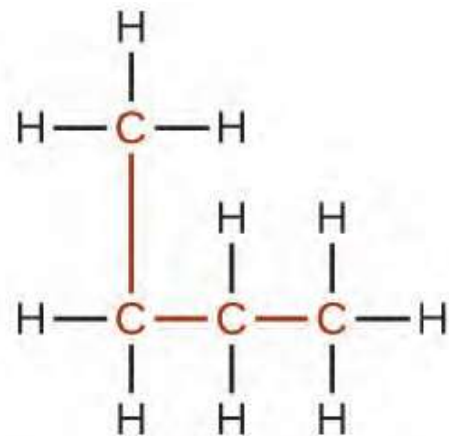
- The compounds *n*-butane and 2-methylpropane are structural isomers (the term constitutional isomers is also commonly used).
- Constitutional isomers have the same molecular formula but different spatial arrangements of the atoms in their molecules.
- The *n*-butane molecule contains an *unbranched chain*, meaning that no carbon atom is
 - bonded to more than two other carbon atoms. We use the term *normal*, or the prefix *n*, to refer to a chain of carbon atoms without branching.
- The compound 2-methylpropane has a branched chain (the carbon atom in the center of the Lewis structure is bonded to three other carbon atoms)

FIGURE 20.4

Identifying isomers from Lewis structures is not as easy as it looks. Lewis structures that look different may actually represent the same isomers.

For example, the three structures in all represent the same molecule, *n* butane, and hence are not different isomers. They are identical because each contains an unbranched chain of four carbon atoms.

FIGURE 20.4



These three representations of the structure of n-butane are not isomers because they all contain the same arrangement of atoms and bonds.

THE BASICS OF ORGANIC NOMENCLATURE: NAMING ALKANES

The International Union of Pure and Applied Chemistry (IUPAC) has devised a system of nomenclature that begins with the names of the alkanes and can be adjusted from there to account for more complicated structures.

The nomenclature for alkanes is based on two rules:

1. To name an alkane, first identify the longest chain of carbon atoms in its structure. A two-carbon chain is called ethane; a three-carbon chain, propane; and a four-carbon chain, butane.
2. Longer chains are named as follows: pentane (five-carbon chain), hexane (6), heptane (7), octane (8), nonane (9), and decane (10).

THE BASICS OF ORGANIC NOMENCLATURE:

NAMING ALKANES

2. Add prefixes to the name of the longest chain to indicate the positions and names of **substituents**.

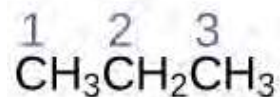
Substituents are branches or functional groups that replace hydrogen atoms on a chain.

The position of a substituent or branch is identified by the number of the carbon atom it is bonded to in the chain.

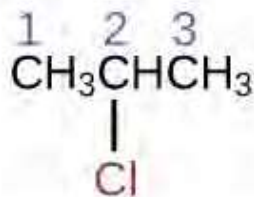
We number the carbon atoms in the chain by counting from the end of the chain nearest the substituents.

Multiple substituents are named individually and placed in alphabetical order at the front of the name.

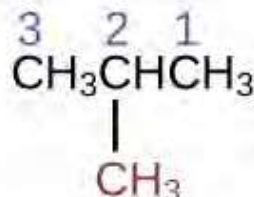
The Basics of Organic Nomenclature: Naming Alkanes



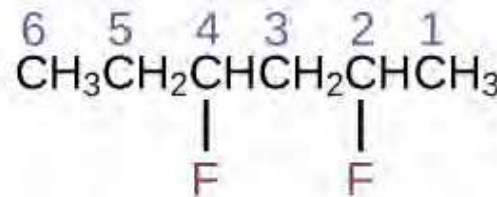
propane



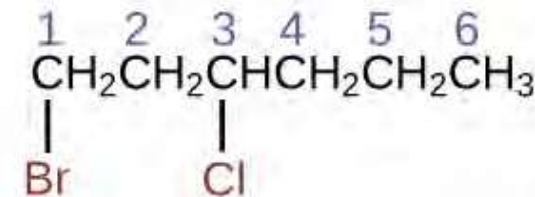
2-chloropropane



2-methylpropane



2,4-difluorohexane



1-bromo-3-chlorohexane

When more than one substituent is present, either on the same carbon atom or on different carbon atoms, the substituents are listed alphabetically. Because the carbon atom numbering begins at the end closest to a substituent, the longest chain of carbon atoms is numbered in such a way as to produce the lowest number for the substituents.

THE BASICS OF ORGANIC NOMENCLATURE: NAMING ALKANES

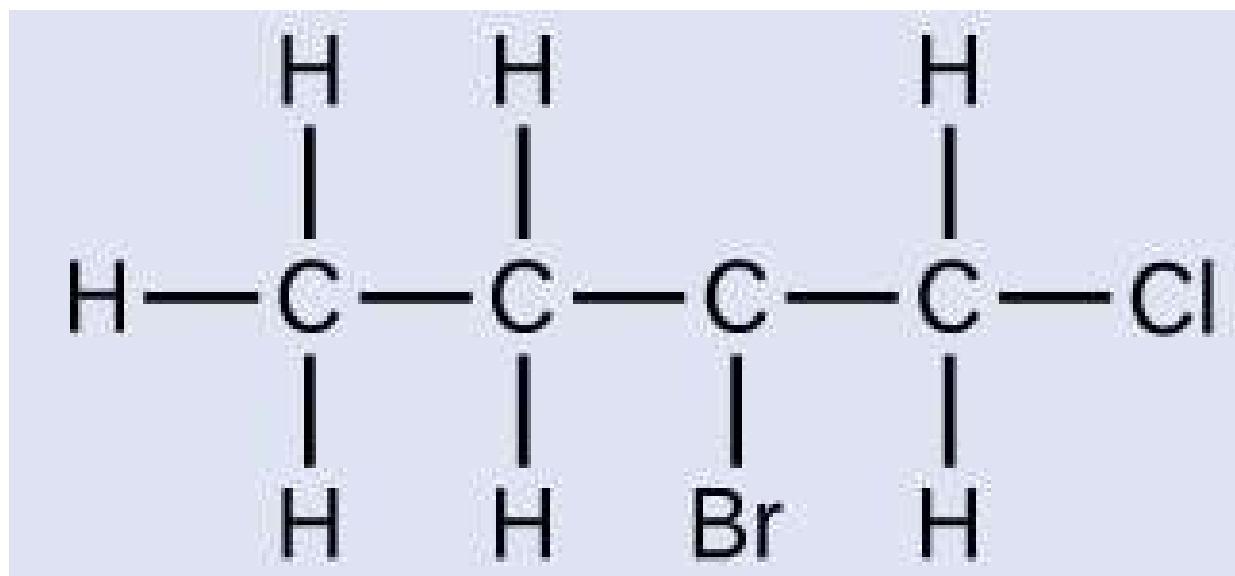
The ending *-o* replaces *-ide* at the end of the name of an electronegative substituent (in ionic compounds, the negatively charged ion ends with *-ide* like chloride; in organic compounds, such atoms are treated as substituents and the *-o* ending is used).

The number of substituents of the same type is indicated by the prefixes *di-* (two), *tri-* (three), *tetra-* (four), and so on (for example, *difluoro-* indicates two fluoride substituents).

EXAMPLE 20.3.1

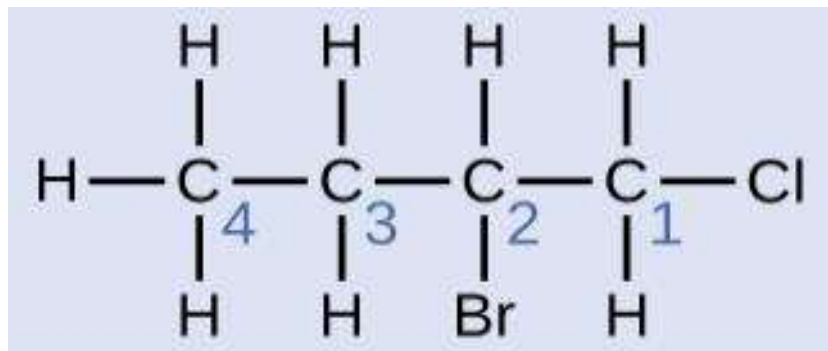
Naming Halogen-substituted Alkanes

Name the molecule whose structure is shown here:



EXAMPLE 20.3.2

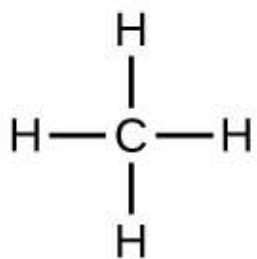
Solution



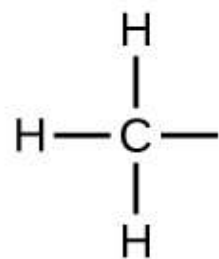
- The four-carbon chain is numbered from the end with the chlorine atom. This puts the substituents on positions 1 and 2 (numbering from the other end would put the substituents on positions 3 and 4).
- Four carbon atoms means that the base name of this compound will be butane.
- The bromine at position 2 will be described by adding 2-bromo-; this will come at the beginning of the name, since bromo- comes before chloro- alphabetically.
- The chlorine at position 1 will be described by adding 1-chloro-, resulting in the
- name of the molecule being 2-bromo-1-chlorobutane.

EXAMPLE 20.3.3

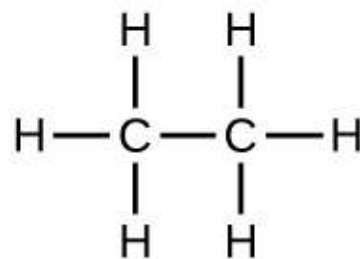
We call a substituent that contains one less hydrogen than the corresponding alkane an alkyl group. The name of an **alkyl group** is obtained by dropping the suffix *-ane* of the alkane name and adding *-yl*:



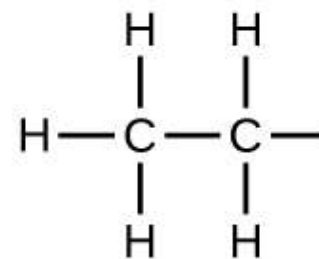
methane



methyl group



ethane



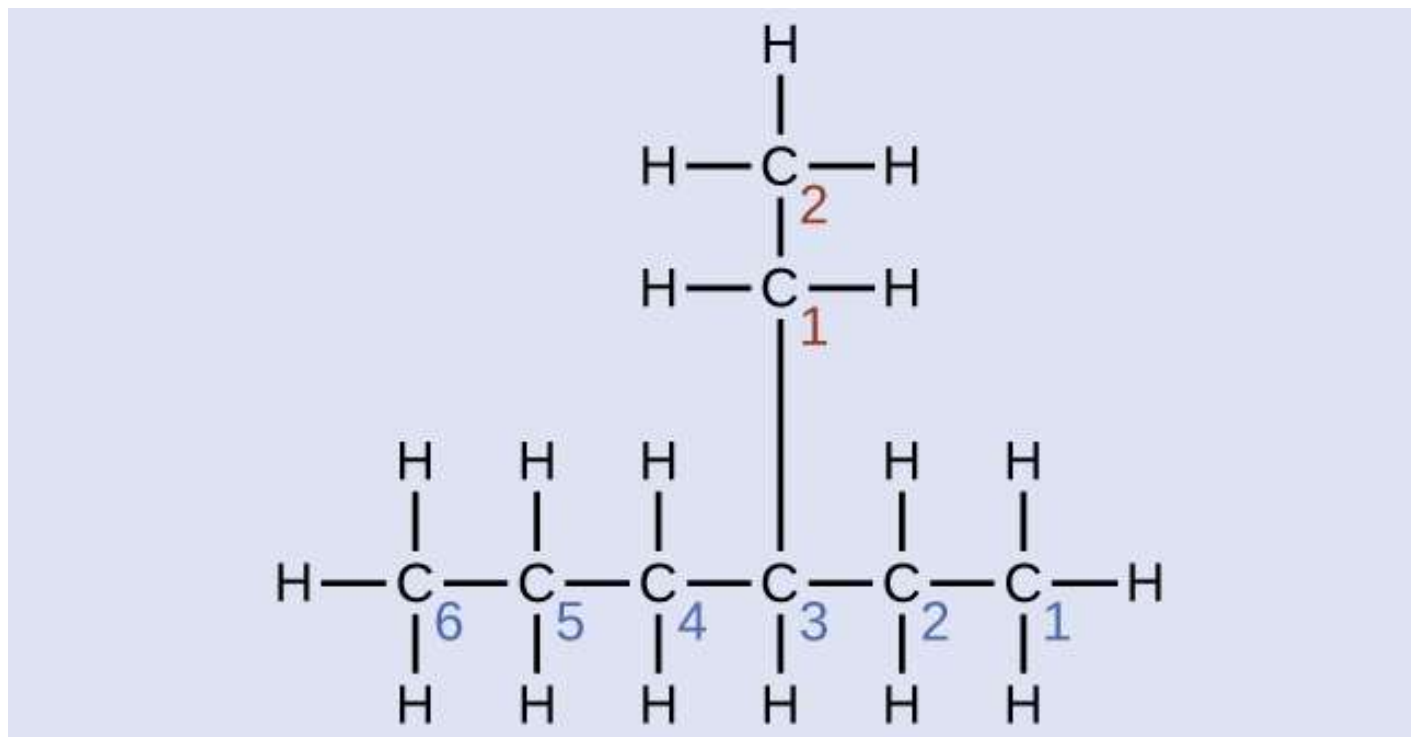
ethyl group

The open bonds in the methyl and ethyl groups indicate that these alkyl groups are bonded to another atom.

EXAMPLE 20.4.1

Naming Substituted Alkanes

Name the molecule whose structure is shown here:



EXAMPLE 20.4.1

Solution

The longest carbon chain runs horizontally across the page and contains six carbon atoms (this makes the base of the name hexane, but we will also need to incorporate the name of the branch).

In this case, we want to number from right to left (as shown by the red numbers) so the branch is connected to carbon 3 (imagine the numbers from left to right—this would put the branch on carbon 4, violating our rules).

The branch attached to position 3 of our chain contains two carbon atoms (numbered in blue)—so we take our name for two carbons *eth-* and attach *-yl* at the end to signify we are describing a branch.

Putting all the pieces together, this molecule is 3-ethylhexane.

THE BASICS OF ORGANIC NOMENCLATURE: NAMING ALKANES

Some hydrocarbons can form more than one type of alkyl group when the hydrogen atoms that would be removed have different “environments” in the molecule.

This diversity of possible alkyl groups can be identified in the following way: The four hydrogen atoms in a methane molecule are equivalent; they all have the same environment.

THE BASICS OF ORGANIC NOMENCLATURE: NAMING ALKANES

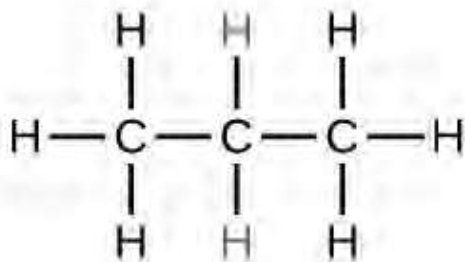
They are equivalent because each is bonded to a carbon atom (the same carbon atom) that is bonded to three hydrogen atoms. (It may be easier to see the equivalency in the ball and stick models.

Removal of any one of the four hydrogen atoms from methane forms a methyl group. Likewise, the six hydrogen atoms in ethane are equivalent and removing any one of these hydrogen atoms produces an ethyl group.

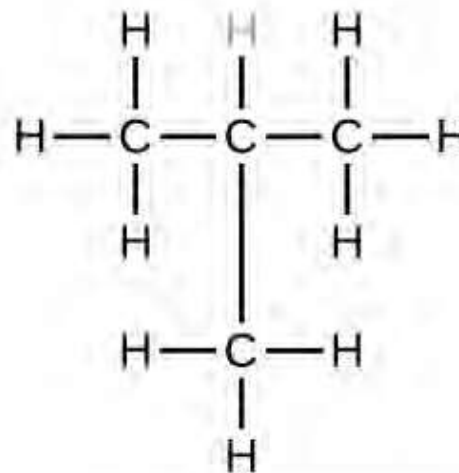
THE BASICS OF ORGANIC NOMENCLATURE: NAMING ALKANES

Each of the six hydrogen atoms is bonded to a carbon atom that is bonded to two other hydrogen atoms and a carbon atom.

However, in both propane and 2-methylpropane, there are hydrogen atoms in two different environments, distinguished by the adjacent atoms or groups of atoms:



propane



2-methylpropane

THE BASICS OF ORGANIC NOMENCLATURE:

NAMING ALKANES

Each of the six equivalent hydrogen atoms of the first type in propane and each of the nine equivalent hydrogen atoms of that type in 2-methylpropane (all shown in black) are bonded to a carbon atom that is bonded to only one other carbon atom. The two purple hydrogen atoms in propane are of a second type.

They differ from the six hydrogen atoms of the first type in that they are bonded to a carbon atom bonded to two other carbon atoms.

The green hydrogen atom in 2-methylpropane differs from the other nine hydrogen atoms in that molecule and from the purple hydrogen atoms in propane.

THE BASICS OF ORGANIC NOMENCLATURE: NAMING *ALKANES*

The green hydrogen atom in 2-methylpropane is bonded to a carbon atom bonded to three other carbon atoms.

Two different alkyl groups can be formed from each of these molecules, depending on which hydrogen atom is removed.

Figure 20.5

Alkyl Group	Structure
methyl	$\text{CH}_3\text{—}$
ethyl	$\text{CH}_3\text{CH}_2\text{—}$
<i>n</i> -propyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{—}$
isopropyl	$\begin{array}{c} \\ \text{CH}_3\text{CHCH}_3 \end{array}$
<i>n</i> -butyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$
sec-butyl	$\begin{array}{c} \\ \text{CH}_3\text{CH}_2\text{CHCH}_3 \end{array}$
isobutyl	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{—} \\ \\ \text{CH}_3 \end{array}$
<i>tert</i> -butyl	$\begin{array}{c} \\ \text{CH}_3\text{CCH}_3 \\ \\ \text{CH}_3 \end{array}$

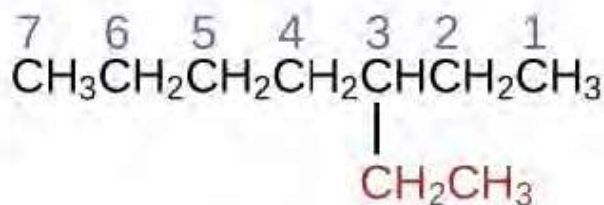
This listing gives the names and formulas for various alkyl groups formed by the removal of hydrogen atoms from different locations.

THE BASICS OF ORGANIC NOMENCLATURE:

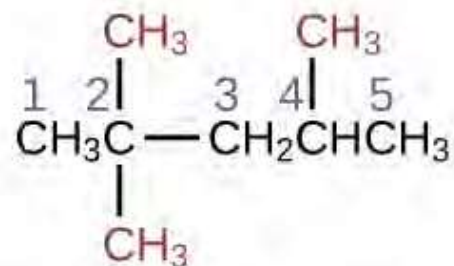
NAMING *ALKANES*

Note that alkyl groups do not exist as stable independent entities. They are always a part of some larger molecule.

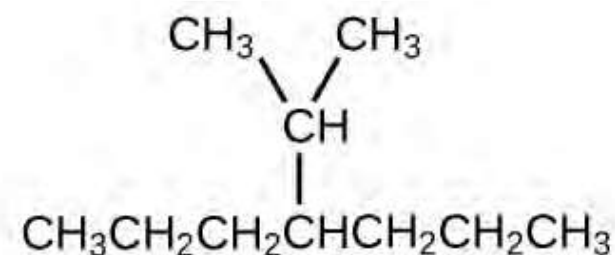
The location of an alkyl group on a hydrocarbon chain is indicated in the same way as any other substituent:



3-ethylheptane



2,2,4-trimethylpentane

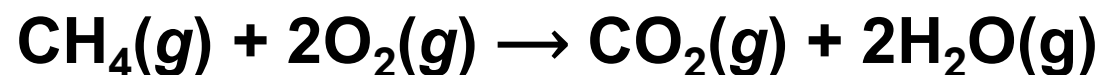


4-isopropylheptane

The Basics of Organic Nomenclature:

Naming *Alkanes*

Alkanes are relatively stable molecules, but heat or light will activate reactions that involve the breaking of C–H or C–C single bonds. Combustion is one such reaction:



Alkanes burn in the presence of oxygen, a highly exothermic oxidation-reduction reaction that produces carbondioxide and water. As a consequence, alkanes are excellent fuels.

For example, methane, CH_4 , is the principal component of natural gas. Butane, C_4H_{10} , used in camping stoves and lighters is an alkane.

THE BASICS OF ORGANIC NOMENCLATURE:

NAMING *ALKANES*

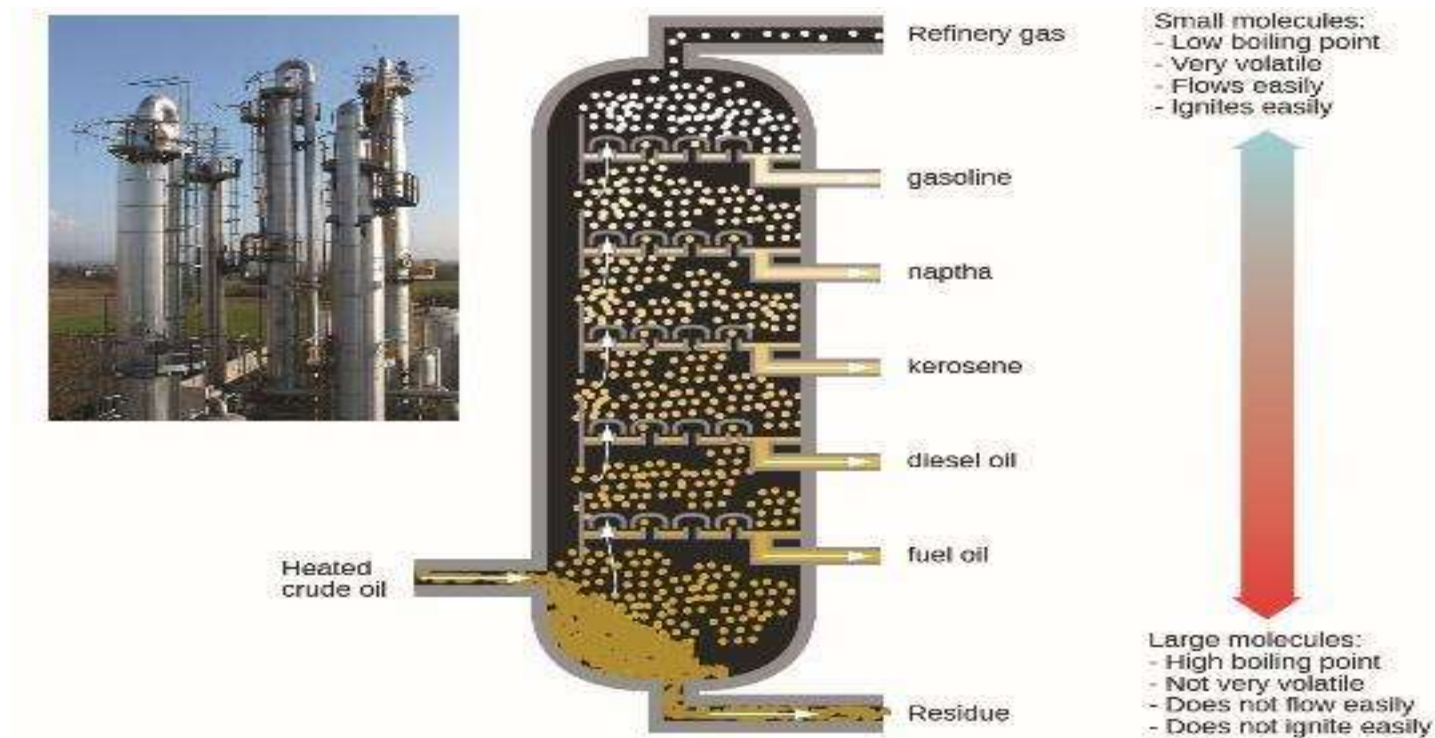
Gasoline is a liquid mixture of continuous- and branched-chain alkanes, each containing from five to nine carbon atoms, plus various additives to improve its performance as a fuel.

Kerosene, diesel oil, and fuel oil are primarily mixtures of alkanes with higher molecular masses.

The main source of these liquid alkane fuels is crude oil, a complex mixture that is separated by fractional distillation.

Fractional distillation takes advantage of differences in the boiling points of the components of the mixture (see **Figure 20.6**). You may recall that boiling point is a function of intermolecular interactions, which was discussed in the chapter on solutions and colloids.

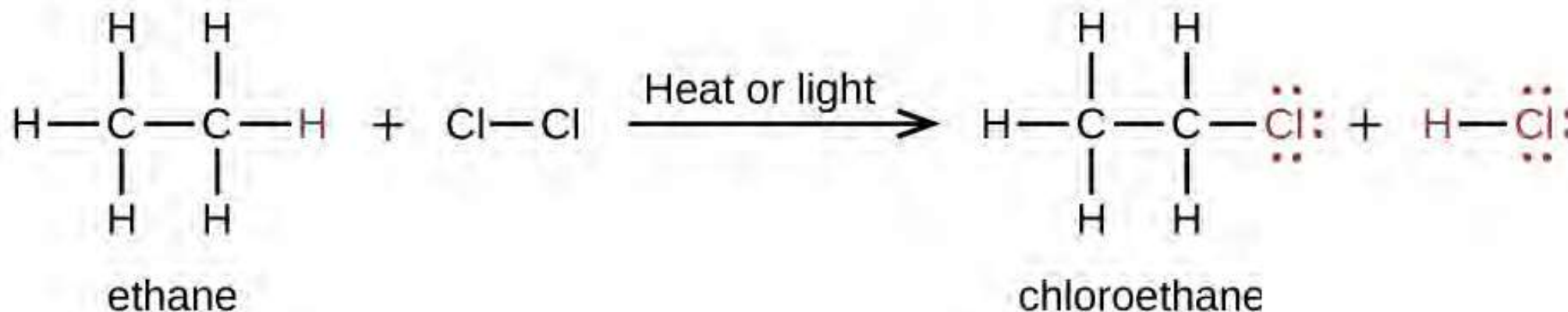
FIGURE 20.6



In a column for the fractional distillation of crude oil, oil heated to about 425 °C in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off. (credit left: modification of work by Luigi Chiesa)

The Basics of Organic Nomenclature: Naming Alkanes

In a **substitution reaction**, another typical reaction of alkanes, one or more of the alkane's hydrogen atoms is replaced with a different atom or group of atoms. No carbon-carbon bonds are broken in these reactions, and the hybridization of the carbon atoms does not change. For example, the reaction between ethane and molecular chlorine depicted here is a substitution reaction:



THE BASICS OF ORGANIC NOMENCLATURE: NAMING *ALKANES*

The C–Cl portion of the chloroethane molecule is an example of a **functional group**, the part or moiety of a molecule that imparts a specific chemical reactivity. The types of functional groups present in an organic molecule are major determinants of its chemical properties and are used as a means of classifying organic compounds.

ALKENES

- Organic compounds that contain one or more double or triple bonds between carbon atoms are described as unsaturated.
- You have likely heard of unsaturated fats. These are complex organic molecules with long chains of carbon atoms, which contain at least one double bond between carbon atoms.
- Unsaturated hydrocarbon molecules that contain one or more double bonds are called **alkenes**.

ALKENES

- Carbon atoms linked by a double bond are bound together by two bonds, one σ bond and one π bond.
- Double and triple bonds give rise to a different geometry around the carbon atom that participates in them, leading to important differences in molecular shape and properties.
- The differing geometries are responsible for the different properties of unsaturated versus saturated fats.

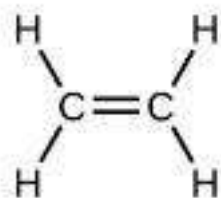
ALKENES

Ethene, C_2H_4 , is the simplest alkene.

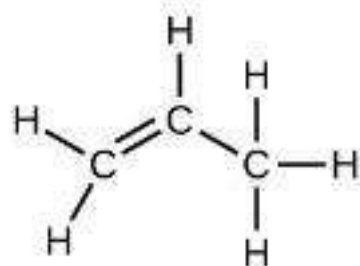
Each carbon atom in ethene, commonly called ethylene, has a trigonal planar structure. The second member of the series is propene (propylene) the butene isomers follow in the series.

Four carbon atoms in the chain of butene allows for the formation of isomers based on the position of the double bond, as well as a new form of isomerism.

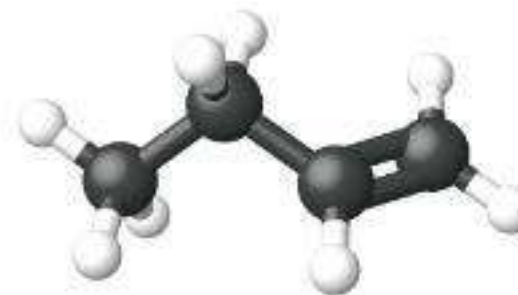
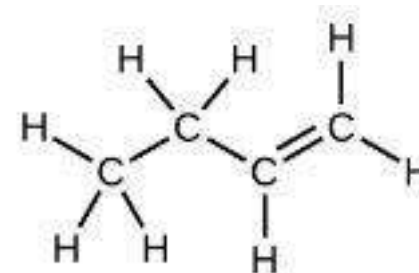
FIGURE 20.7



ethene



propene



1-butene

Expanded structures, ball-and-stick structures, and space-filling models for the alkenes ethene, propene, and 1-butene are shown.

ALKENES

Ethylene (the common industrial name for ethene) is a basic raw material in the production of polyethylene and other important compounds.

Over 135 million tons of ethylene were produced worldwide in 2010 for use in the polymer, petrochemical, and plastic industries.

Ethylene is produced industrially in a process called cracking, in which the long hydrocarbon chains in a petroleum mixture are broken into smaller molecules.

Recycling Plastics

Polymers (from Greek words *poly* meaning “many” and *mer* meaning “parts”) are large molecules made up of repeating units, referred to as monomers.

Polymers can be natural (starch is a polymer of sugar residues and proteins are polymers of amino acids) or synthetic [like polyethylene, polyvinyl chloride (PVC), and polystyrene].

Recycling Plastics

The variety of structures of polymers translates into a broad range of properties and uses that make them integral parts of our everyday lives.

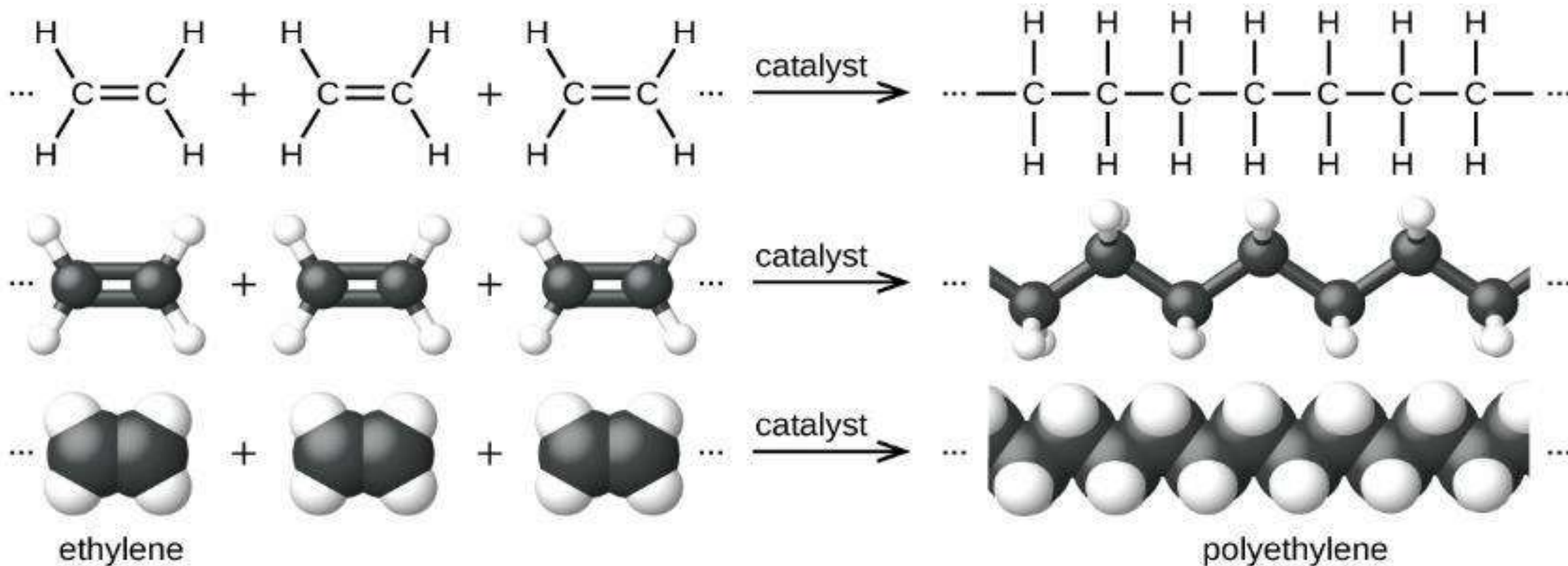
Adding functional groups to the structure of a polymer can result in significantly different properties (see the discussion about Kevlar later in this chapter).

RECYCLING PLASTICS

The monomer ethylene (C_2H_4) is a gas at room temperature, but when polymerized, using a transition metal catalyst, it is transformed into a solid material made up of long chains of $\text{—CH}_2\text{—}$ units called polyethylene.

Polyethylene is a commodity plastic used primarily for packaging (bags and films).

FIGURE 20.8



The reaction for the polymerization of ethylene to polyethylene is shown.

RECYCLING PLASTICS

- Polyethylene is a member of one subset of synthetic polymers classified as plastics.
- Plastics are synthetic organic solids that can be molded; they are typically organic polymers with high molecular masses.
- Most of the monomers that go into common plastics (ethylene, propylene, vinyl chloride, styrene, and ethylene terephthalate) are derived from petrochemicals and are not very biodegradable, making them candidate materials for recycling.
- Recycling plastics helps minimize the need for using more of the petrochemical supplies and also minimizes the environmental damage caused by throwing away these nonbiodegradable materials.








RECYCLING PLASTICS

- Plastic recycling is the process of recovering waste, scrap, or used plastics, and reprocessing the material into useful products. For example, polyethylene terephthalate (soft drink bottles) can be melted down and used for plastic furniture, in carpets, or for other applications.
- Other plastics, like polyethylene (bags) and polypropylene (cups, plastic food containers), can be recycled or reprocessed to be used again.

RECYCLING PLASTICS

- Many areas of the country have recycling programs that focus on one or more of the commodity plastics that have been assigned a recycling code.
- These operations have been in effect since the 1970s and have made the production of some plastics among the most efficient industrial operations today.

FIGURE 20.9

	polyethylene terephthalate (PETE)	Soda bottles and oven-ready food trays
	high-density polyethylene (HDPE)	Bottles for milk and dishwashing liquids
	polyvinyl chloride (PVC)	Food trays, plastic wrap, bottles for mineral water and shampoo
	low density polyethylene (LDPE)	Shopping bags and garbage bags
	polypropylene (PP)	Margarine tubs, microwaveable food trays
	polystyrene (PS)	Yogurt tubs, foam meat trays, egg cartons, vending cups, plastic cutlery, packaging for electronics and toys
	any other plastics (OTHER)	Plastics that do not fall into any of the above categories One example is melamine resin (plastic plates, plastic cups)

Each type of recyclable plastic is imprinted with a code for easy identification.

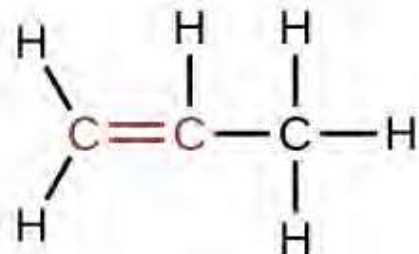
Alkenes

The name of an alkene is derived from the name of the alkane with the same number of carbon atoms. The presence of the double bond is signified by replacing the suffix *-ane* with the suffix *-ene*.

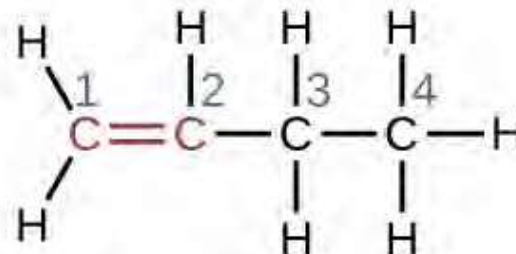
The location of the double bond is identified by naming the smaller of the numbers of the carbon atoms participating in the double bond:



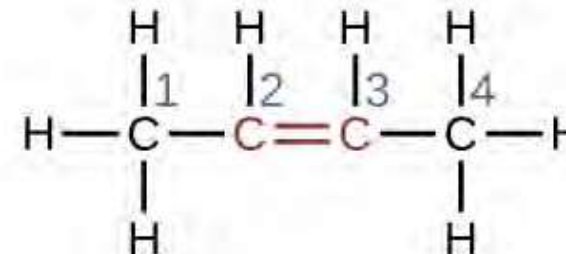
ethene
(ethylene)



propene
(propylene)



1-butene



2-butene

ISOMERS OF ALKENES

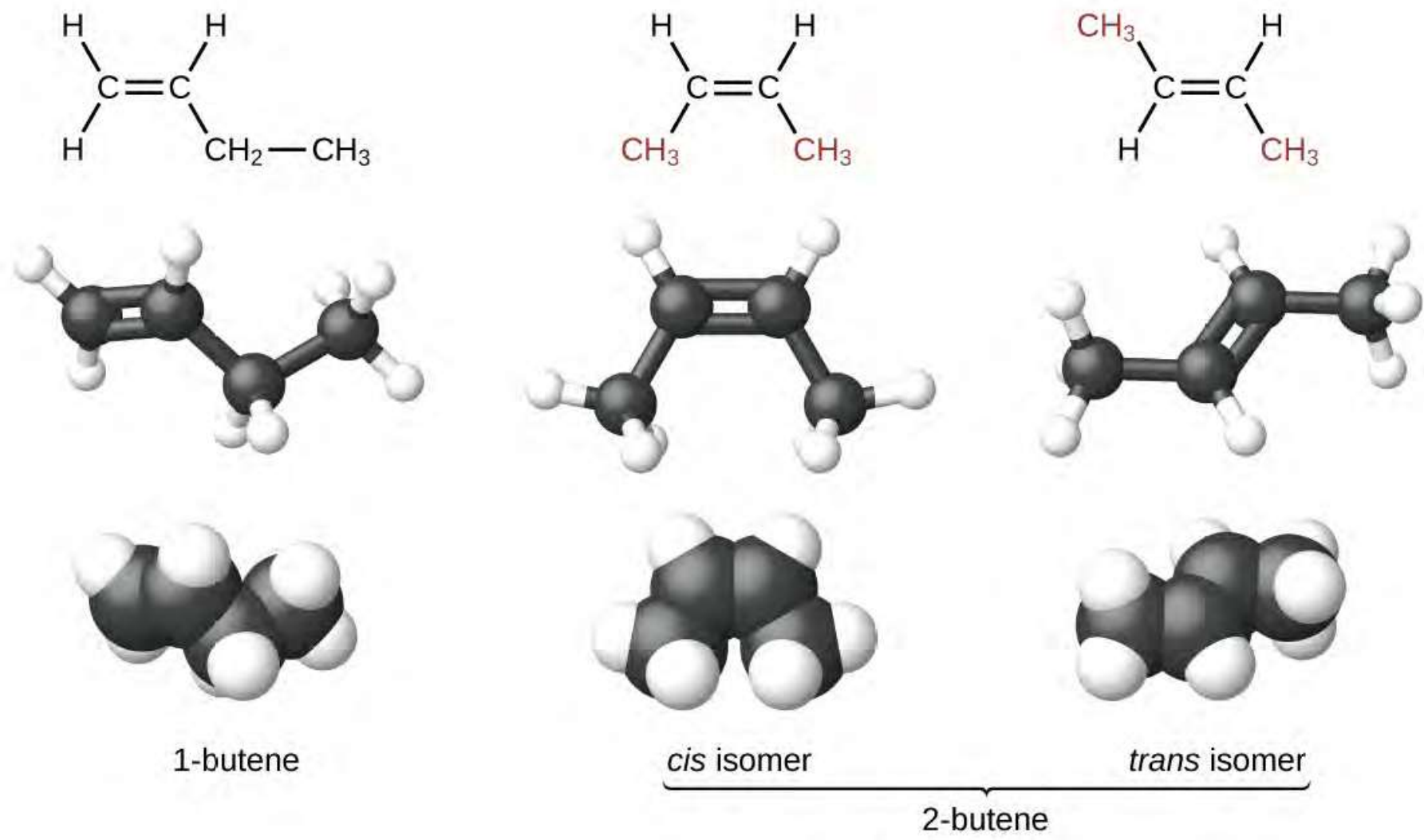
Molecules of 1-butene and 2-butene are structural isomers; the arrangement of the atoms in these two molecules differs.

As an example of arrangement differences, the first carbon atom in 1-butene is bonded to two hydrogen atoms; the first carbon atom in 2-butene is bonded to three hydrogen atoms.

The compound 2-butene and some other alkenes also form a second type of isomer called a geometric isomer.

In a set of geometric isomers, the same types of atoms are attached to each other in the same order, but the geometries of the two molecules differ. Geometric isomers of alkenes differ in the orientation of the groups on either side of a C = C bond.

FIGURE 20.10



These molecular models show the structural and geometric isomers of butene.

Isomers of Alkenes

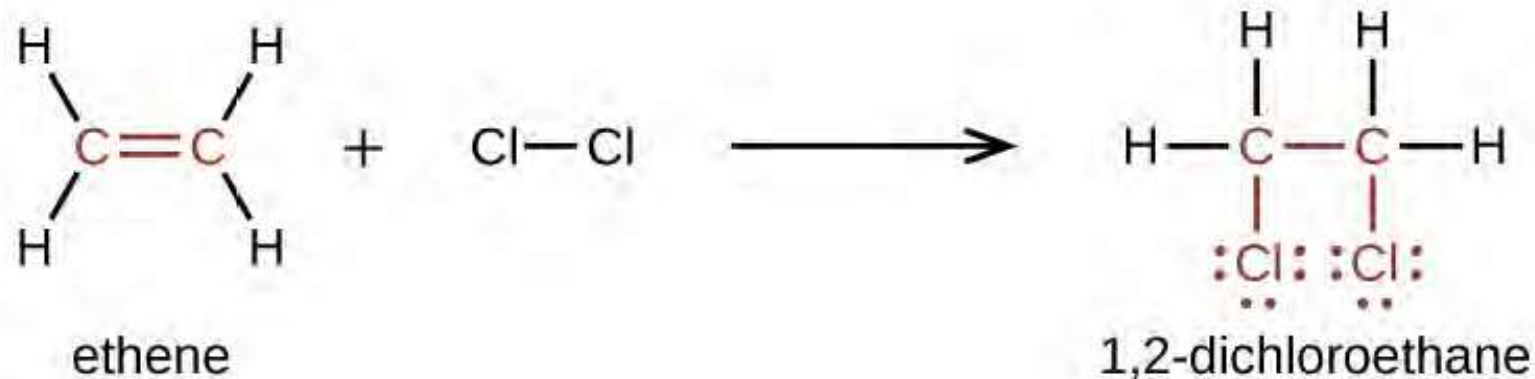
Alkenes are much more reactive than alkanes because the $C = C$ moiety is a reactive functional group.

A π bond, being a weaker bond, is disrupted much more easily than a σ bond.

Thus, alkenes undergo a characteristic reaction in which the π bond is broken and replaced by two σ bonds. This reaction is called an addition reaction.

The hybridization of the carbon atoms in the double bond in an alkene changes from sp^2 to sp^3 during an addition reaction.

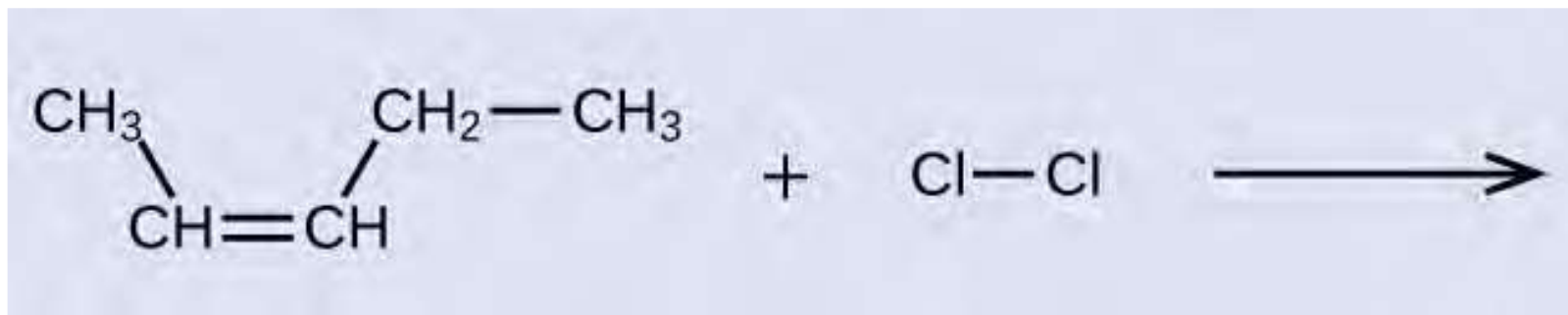
For example, halogens add to the double bond in an alkene instead of replacing hydrogen, as occurs in an alkane:



EXAMPLE 20.5.1

Alkene Reactivity and Naming

Provide the IUPAC names for the reactant and product of the halogenation reaction shown here:



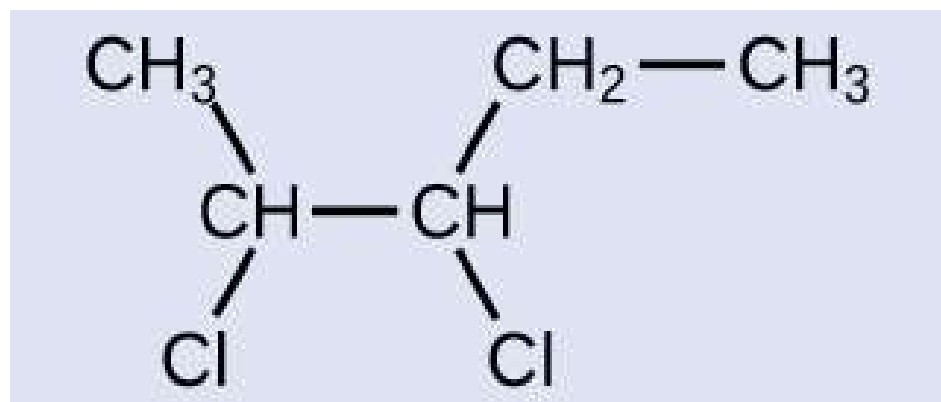
Solution

The reactant is a five-carbon chain that contains a carbon-carbon double bond, so the base name will be pentene. We begin counting at the end of the chain closest to the double bond—in this case, from the left—the double bond spans carbons 2 and 3, so the name becomes 2-pentene.

Since there are two carbon-containing groups attached to the two carbon atoms in the double bond—and they are on the same side of the double bond—this molecule is the *cis*-isomer, making the name of the starting alkene *cis*-2-pentene.

EXAMPLE 20.5.2

The product of the halogenation reaction will have two chlorine atoms attached to the carbon atoms that were a part of the carbon-carbon double bond:



This molecule is now a substituted alkane and will be named as such. The base of the name will be pentane.

We will count from the end that numbers the carbon atoms where the chlorine atoms are attached as 2 and 3, making the name of the product 2,3-dichloropentane.

Alkynes

- Hydrocarbon molecules with one or more triple bonds are called **alkynes**; they make up another series of unsaturated hydrocarbons. Two carbon atoms joined by a triple bond are bound together by one σ bond and two π bonds.
- The *sp* hybridized carbons involved in the triple bond have bond angles of 180° , giving these types of bonds a linear, rod-like shape.
- The simplest member of the alkyne series is ethyne, C_2H_2 , commonly called acetylene.
- The Lewis structure for ethyne, a linear molecule, is:



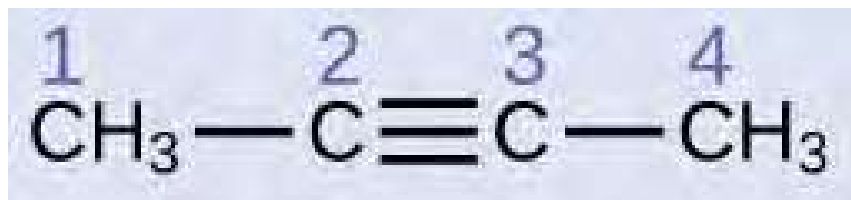
ethyne (acetylene)

The IUPAC nomenclature for alkynes is similar to that for alkenes except that the suffix *-yne* is used to indicate a triple bond in the chain. For example, $CH_3CH_2C \equiv CH$ is called 1-butyne.

EXAMPLE 20.6.1

Structure of Alkynes

Describe the geometry and hybridization of the carbon atoms in the following molecule:

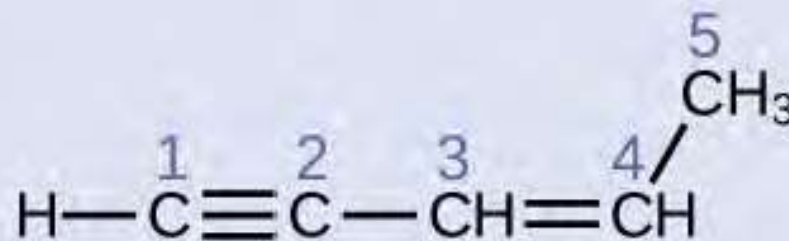


Solution

Carbon atoms 1 and 4 have four single bonds and are thus tetrahedral with sp^3 hybridization. Carbon atoms 2 and 3 are involved in the triple bond, so they have linear geometries and would be classified as sp hybrids.

EXAMPLE 20.6.2

Identify the hybridization and bond angles at the carbon atoms in the molecule shown:

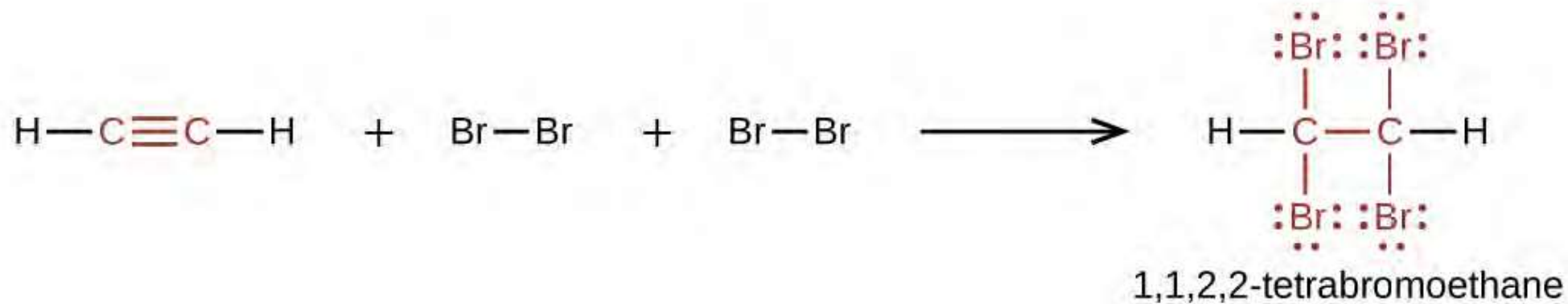


Answer: carbon 1: sp , 180° ; carbon 2: sp , 180° ; carbon 3: sp^2 , 120° ; carbon 4: sp^2 , 120° ; carbon 5: sp^3 , 109.5°

Alkynes

Chemically, the alkynes are similar to the alkenes. Since the $\text{C} \equiv \text{C}$ functional group has two π bonds, alkynes typically react even more readily, and react with twice as much reagent in addition reactions.

The reaction of acetylene with bromine is a typical example:



Acetylene and the other alkynes also burn readily. An acetylene torch takes advantage of the high heat of combustion for acetylene.

Aromatic Hydrocarbons

Benzene, C_6H_6 , is the simplest member of a large family of hydrocarbons, called **aromatic hydrocarbons**.

These compounds contain ring structures and exhibit bonding that must be described using the resonance hybrid concept of valence bond theory or the delocalization concept of molecular orbital theory.

(To review these concepts, refer to the earlier chapters on chemical bonding). The resonance structures for benzene, C_6H_6 , are:

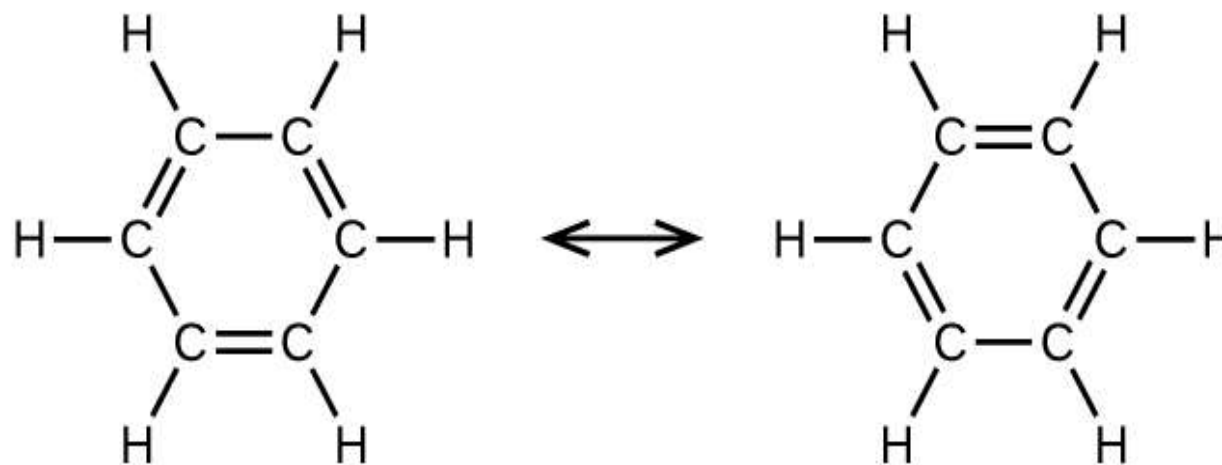


FIGURE 20.11

Valence bond theory describes the benzene molecule and other planar aromatic hydrocarbon molecules as hexagonal rings of sp^2 -hybridized carbon atoms with the unhybridized p orbital of each carbon atom perpendicular to the plane of the ring.

Three valence electrons in the sp^2 hybrid orbitals of each carbon atom and the valence electron of each hydrogen atom form the framework of σ bonds in the benzene molecule.

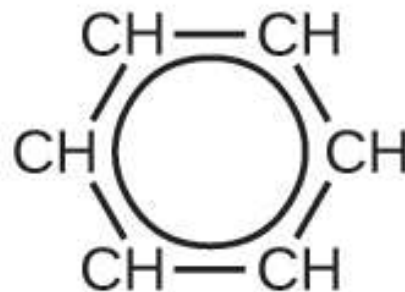
The fourth valence electron of each carbon atom is shared with an adjacent carbon atom in their unhybridized p orbitals to yield the π bonds.

AROMATIC HYDROCARBONS

Benzene does not, however, exhibit the characteristics typical of an alkene.

Each of the six bonds between its carbon atoms is equivalent and exhibits properties that are intermediate between those of a C–C single bond and a C = C double bond.

To represent this unique bonding, structural formulas for benzene and its derivatives are typically drawn with single bonds between the carbon atoms and a circle within the ring



This condensed formula shows the unique bonding structure of benzene.

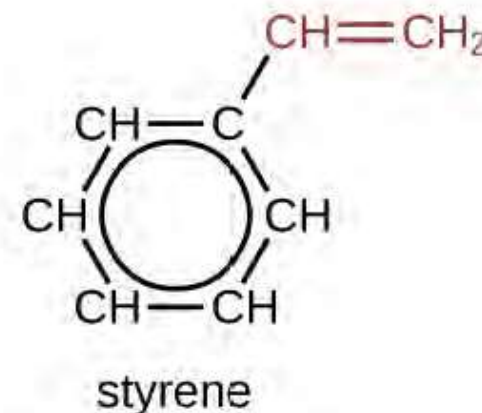
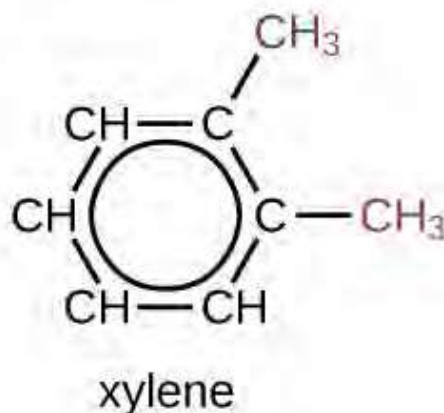
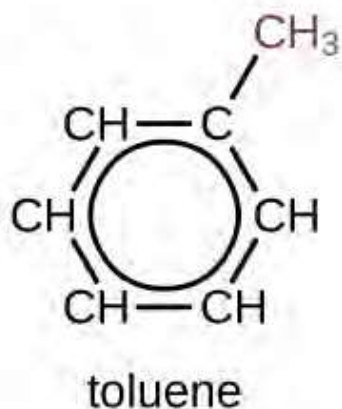
Aromatic Hydrocarbons

There are many derivatives of benzene.

The hydrogen atoms can be replaced by many different substituents.

Aromatic compounds more readily undergo substitution reactions than addition reactions; replacement of one of the hydrogen atoms with another substituent will leave the delocalized double bonds intact.

The following are typical examples of substituted benzene derivatives:



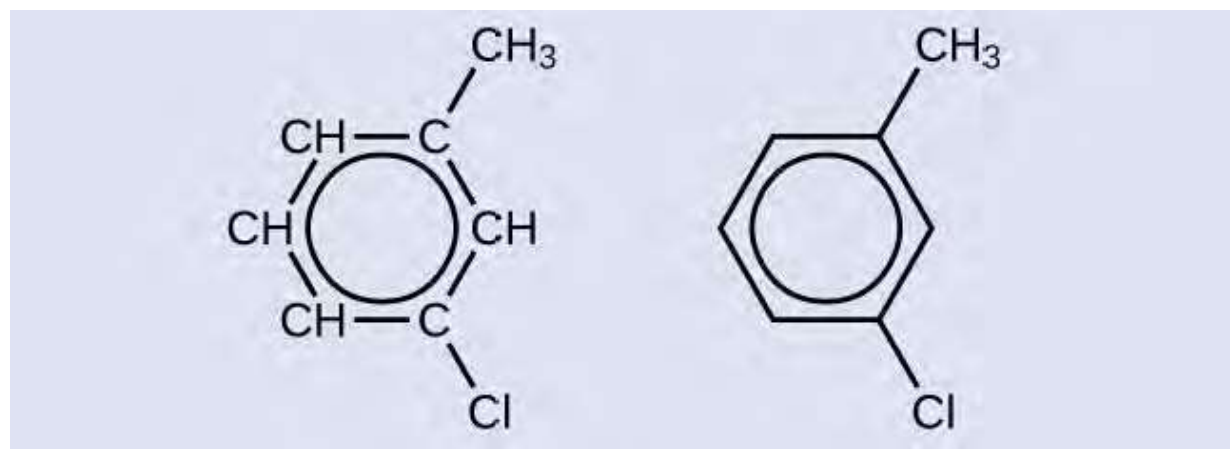
Toluene and xylene are important solvents and raw materials in the chemical industry. Styrene is used to produce the polymer polystyrene.

EXAMPLE 20.7.1

Structure of Aromatic Hydrocarbons

One possible isomer created by a substitution reaction that replaces a hydrogen atom attached to the aromatic ring of toluene with a chlorine atom is shown here.

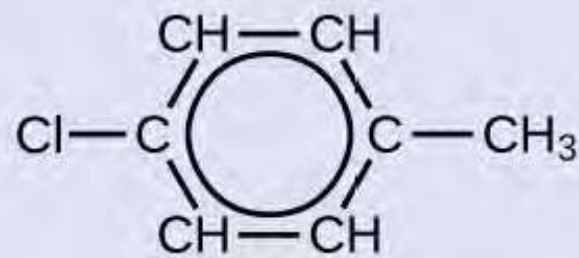
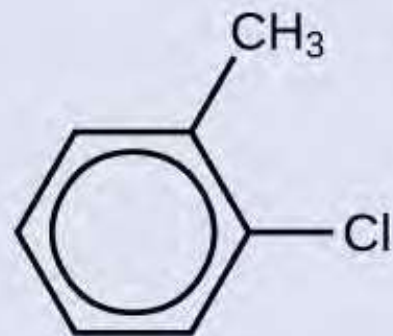
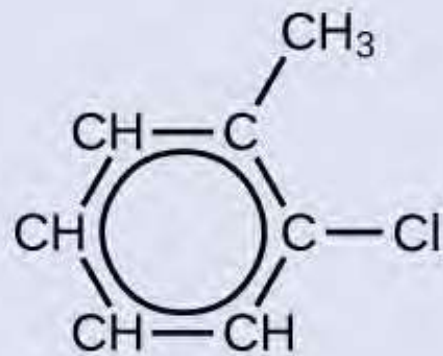
Draw two other possible isomers in which the chlorine atom replaces a different hydrogen atom attached to the aromatic ring:



EXAMPLE 20.7.2

Solution

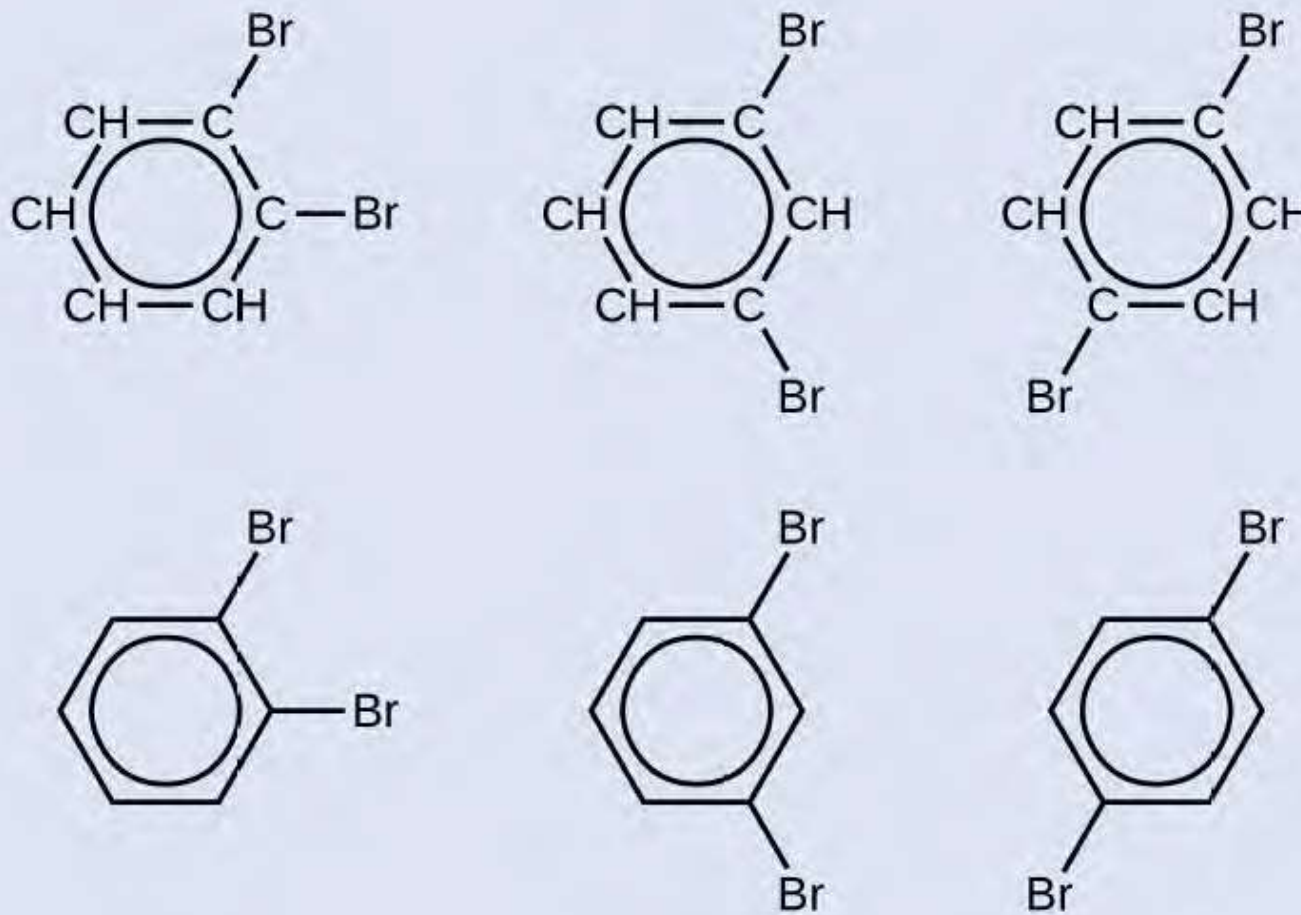
Since the six-carbon ring with alternating double bonds is necessary for the molecule to be classified as aromatic, appropriate isomers can be produced only by changing the positions of the chloro-substituent relative to the methyl-substituent:



EXAMPLE 20.7.3

Draw three isomers of a six-membered aromatic ring compound substituted with two bromines.

Answer:



20.2 Alcohols and Ethers

By the end of this section, you will be able to:

- Describe the structure and properties of alcohols
- Describe the structure and properties of ethers
- Name and draw structures for alcohols and ethers

In this section, we will learn about alcohols and ethers.

ALCOHOLS

Incorporation of an oxygen atom into carbon- and hydrogen-containing molecules leads to new functional groups and new families of compounds.

When the oxygen atom is attached by single bonds, the molecule is either an alcohol or ether.

Alcohols are derivatives of hydrocarbons in which an -OH group has replaced a hydrogen atom. Although all alcohols have one or more hydroxyl (-OH) functional groups, they do not behave like bases such as NaOH and KOH .

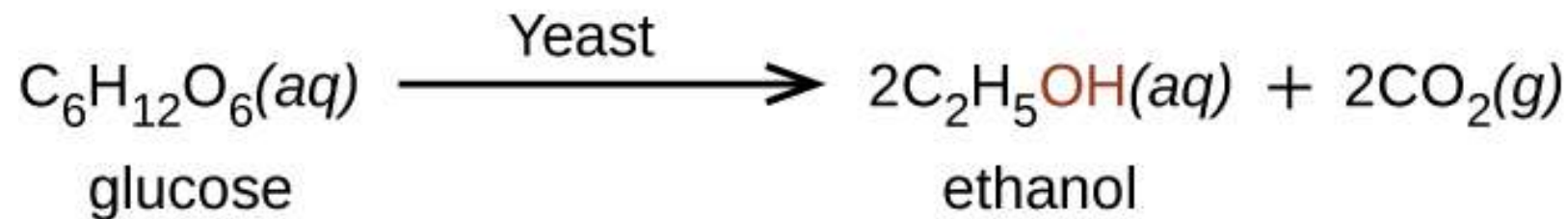
NaOH and KOH are ionic compounds that contain OH^- ions. Alcohols are covalent molecules; the -OH group in an alcohol molecule is attached to a carbon atom by a covalent bond.

ALCOHOLS

Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, also called ethyl alcohol, is a particularly important alcohol for human use.

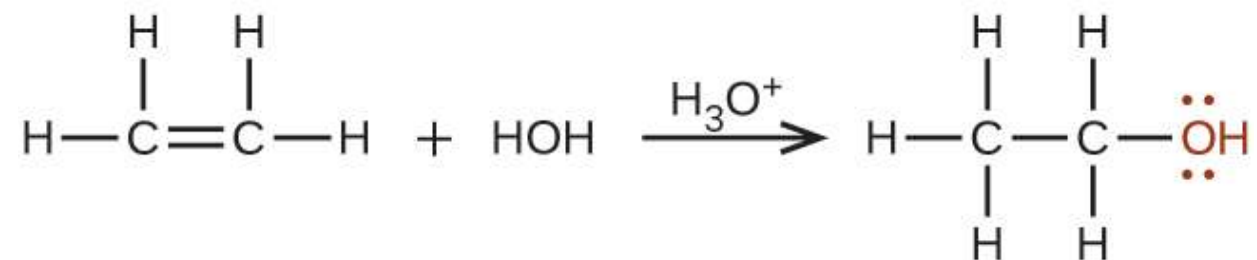
Ethanol is the alcohol produced by some species of yeast that is found in wine, beer, and distilled drinks.

It has long been prepared by humans harnessing the metabolic efforts of yeasts in fermenting various sugars:



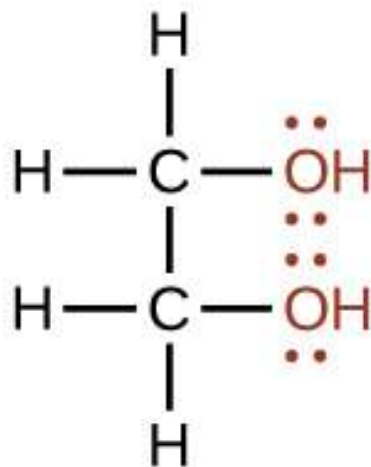
Alcohols

Large quantities of ethanol are synthesized from the addition reaction of water with ethylene using an acid as a catalyst:

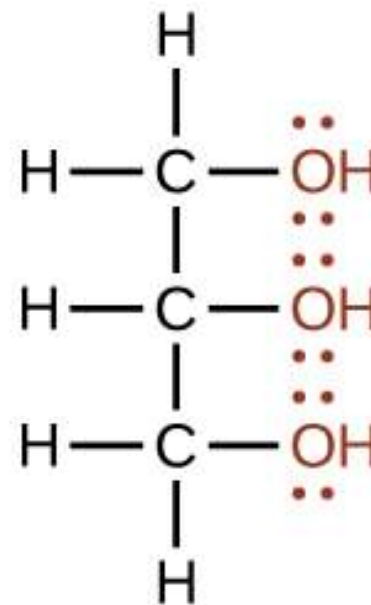


Alcohols containing two or more hydroxyl groups can be made. Examples include 1,2-ethanediol (ethylene glycol, used in antifreeze) and 1,2,3-propanetriol (glycerine, used as a solvent for cosmetics and medicines):

ALCOHOLS



1,2-ethanediol



1,2,3-propanetriol

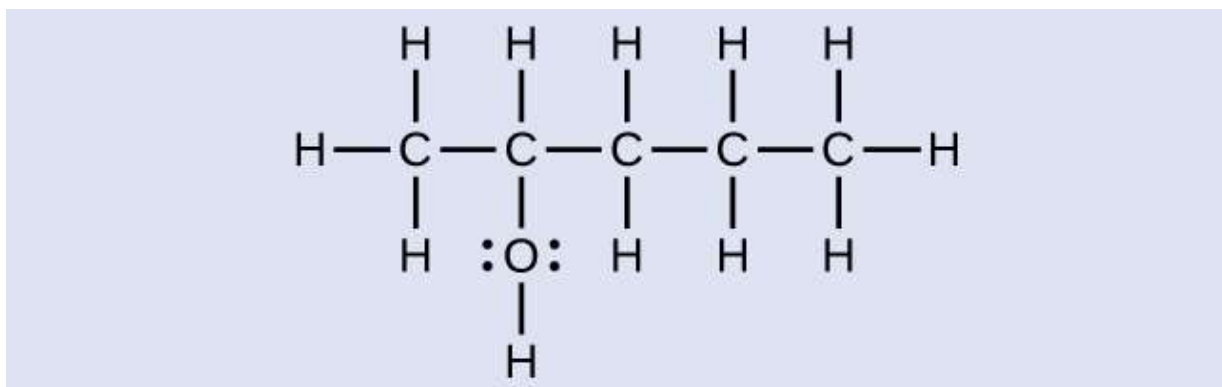
Naming Alcohols

The name of an alcohol comes from the hydrocarbon from which it was derived. The final -e in the name of the hydrocarbon is replaced by -ol, and the carbon atom to which the -OH group is bonded is indicated by a number placed before the name.

EXAMPLE 20.8.1

Naming Alcohols

Consider the following example. How should it be named?



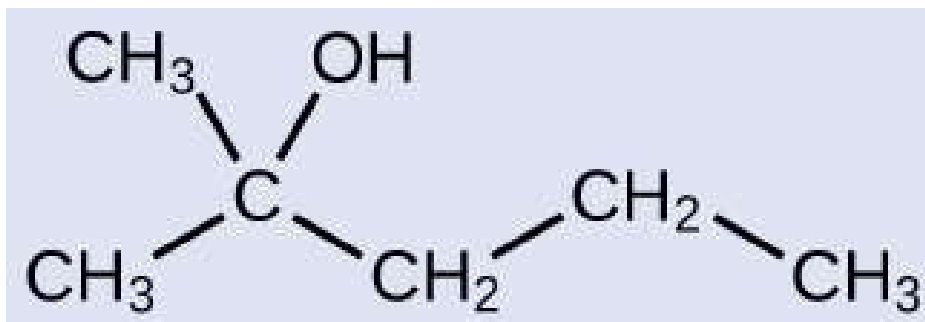
Solution

The carbon chain contains five carbon atoms. If the hydroxyl group was not present, we would have named this molecule pentane.

To address the fact that the hydroxyl group is present, we change the ending of the name to *-ol*. In this case, since the -OH is attached to carbon 2 in the chain, we would name this molecule 2-pentanol.

EXAMPLE 20.8.2

Name the following molecule:



Answer: 2-methyl-2-pentanol

Ethers

Ethers are compounds that contain the functional group —O— . Ethers do not have a designated suffix like the other types of molecules we have named so far.

In the IUPAC system, the oxygen atom and the smaller carbon branch are named as an alkoxy substituent and the remainder of the molecule as the base chain, as in alkanes.

As shown in the following compound, the red symbols represent the smaller alkyl group and the oxygen atom, which would be named “methoxy.”

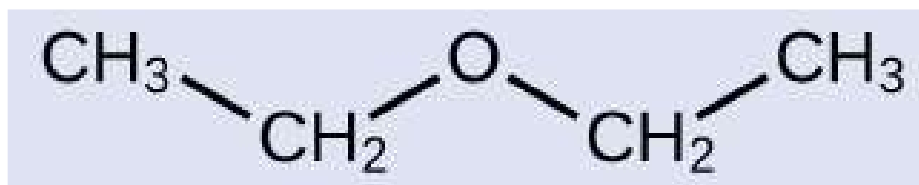
The larger carbon branch would be ethane, making the molecule methoxyethane.

Many ethers are referred to with common names instead of the IUPAC system names.

EXAMPLE 20.9.1

Naming Ethers

Provide the IUPAC and common name for the ether shown here:



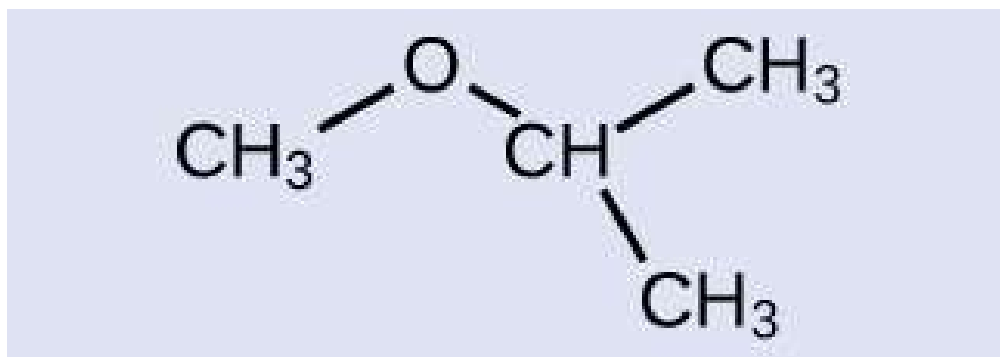
Solution

IUPAC: The molecule is made up of an ethoxy group attached to an ethane chain, so the IUPAC name would be ethoxyethane.

Common: The groups attached to the oxygen atom are both ethyl groups, so the common name would be diethyl ether.

EXAMPLE 20.9.2

Provide the IUPAC and common name for the ether shown:

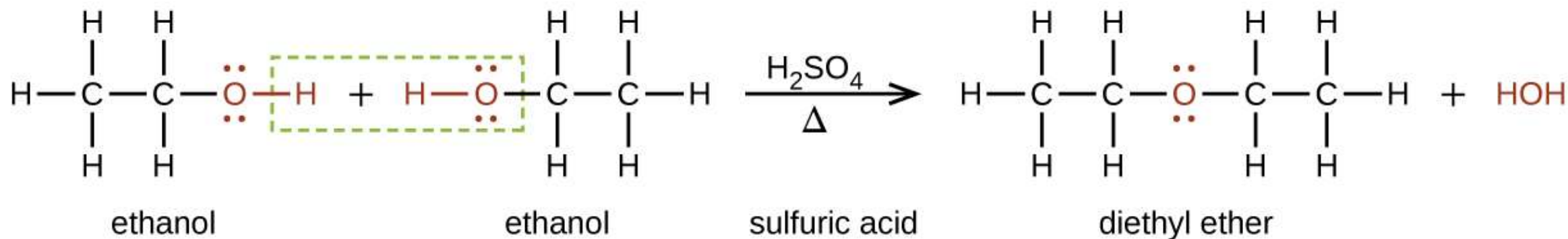


Answer: IUPAC: 2-methoxypropane; common: isopropylmethyl ether

Ethers

Ethers can be obtained from alcohols by the elimination of a molecule of water from two molecules of the alcohol.

For example, when ethanol is treated with a limited amount of sulfuric acid and heated to 140 °C, diethyl ether and water are formed:



In the general formula for ethers, $R-O-R$, the hydrocarbon groups (R) may be the same or different.

Diethyl ether, the most widely used compound of this class, is a colorless, volatile liquid that is highly flammable.

It was first used in 1846 as an anesthetic, but better anesthetics have now largely taken its place.

Diethyl ether and other ethers are presently used primarily as solvents for gums, fats, waxes, and resins.

Tertiary-butyl methyl ether, $C_4H_9OCH_3$ (abbreviated MTBE—italicized portions of names are not counted when ranking the groups alphabetically—so butyl comes before methyl in the common name), is used as an additive for gasoline.

MTBE belongs to a group of chemicals known as oxygenates due to their capacity to increase the oxygen content of gasoline.

Carbohydrates and Diabetes

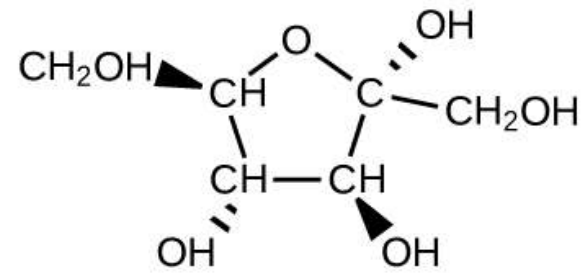
- Carbohydrates are large biomolecules made up of carbon, hydrogen, and oxygen.
- The dietary forms of carbohydrates are foods rich in these types of molecules, like pastas, bread, and candy.
- The name “carbohydrate” comes from the formula of the molecules, which can be described by the general formula $C_m(H_2O)_n$, which shows that they are in a sense “carbon and water” or “hydrates of carbon.” In many cases, m and n have the same value, but they can be different.
- The smaller carbohydrates are generally referred to as “sugars,” the biochemical term for this group of molecules is “saccharide” from the Greek word for sugar.

Depending on the number of sugar units joined together, they may be classified as monosaccharides (one sugar unit), disaccharides (two sugar units), oligosaccharides (a few sugars), or polysaccharides (the polymeric version of sugars—polymers were described in the feature box earlier in this chapter on recycling plastics).

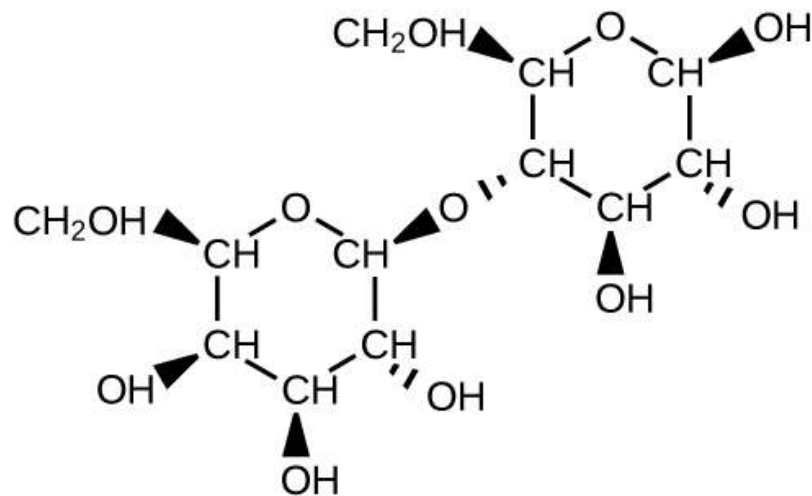
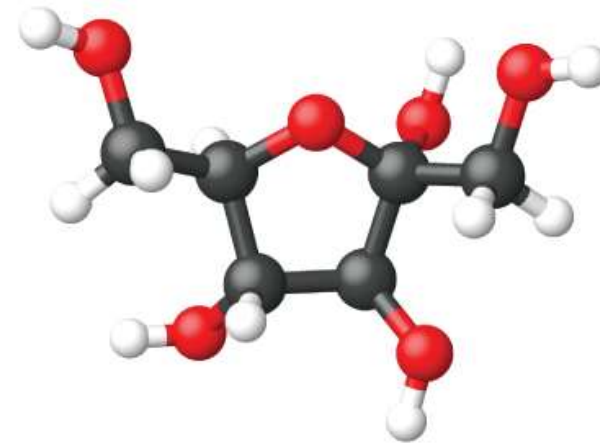
The scientific names of sugars can be recognized by the suffix -ose at the end of the name (for instance, fruit sugar is a monosaccharide called “fructose” and milk sugar is a disaccharide called lactose composed of two monosaccharides, glucose and galactose, connected together).

Sugars contain some of the functional groups we have discussed: Note the alcohol groups present in the structures and how monosaccharide units are linked to form a disaccharide by formation of an ether.

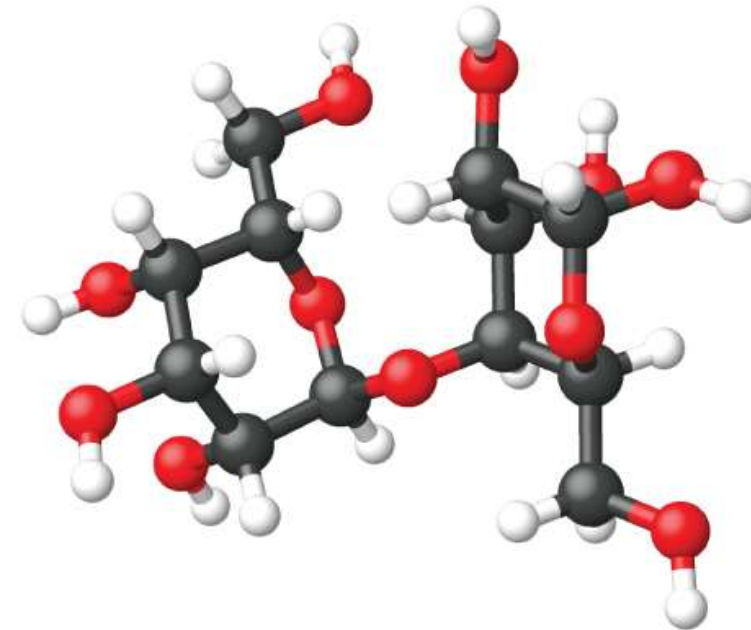
Figure 20.12



fructose



lactose



The illustrations show the molecular structures of fructose, a five-carbon monosaccharide, and of lactose, a disaccharide composed of two isomeric, six-carbon sugars.

CHEMISTRY IN EVERYDAY LIFE

Organisms use carbohydrates for a variety of functions.

Carbohydrates can store energy, such as the polysaccharides glycogen in animals or starch in plants.

They also provide structural support, such as the polysaccharide cellulose in plants and the modified polysaccharide chitin in fungi and animals.

The sugars ribose and deoxyribose are components of the backbones of RNA and DNA, respectively.

Other sugars play key roles in the function of the immune system, in cell-cell recognition, and in many other biological roles.

CHEMISTRY IN EVERYDAY LIFE

- Diabetes is a group of metabolic diseases in which a person has a high sugar concentration in their blood.
- Diabetes may be caused by insufficient insulin production by the pancreas or by the body's cells not responding properly to the insulin that is produced.
- In a healthy person, insulin is produced when it is needed and functions to transport glucose from the blood into the cells where it can be used for energy.
- The long-term complications of diabetes can include loss of eyesight, heart disease, and kidney failure.
- In 2013, it was estimated that approximately 3.3% of the world's population (~380 million people) suffered from diabetes, resulting in over a million deaths annually.
- Prevention involves eating a healthy diet, getting plenty of exercise, and maintaining a normal body weight.
- Treatment involves all of these lifestyle practices and may require injections of insulin.

FIGURE 20.13



Diabetes is a disease characterized by high concentrations of glucose in the blood. Treating diabetes involves making lifestyle changes, monitoring blood-sugar levels, and sometimes insulin injections. (credit: “Blausen Medical Communications”/Wikimedia Commons)

20.3 ALDEHYDES, KETONES, CARBOXYLIC ACIDS, AND ESTERS

By the end of this section, you will be able to:

- Describe the structure and properties of aldehydes, ketones, carboxylic acids and esters

20.3 ALDEHYDES, KETONES, CARBOXYLIC ACIDS, AND ESTERS

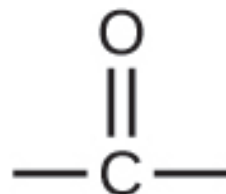
Another class of organic molecules contains a carbon atom connected to an oxygen atom by a double bond, commonly called a carbonyl group.

The trigonal planar carbon in the carbonyl group can attach to two other substituents leading to several subfamilies (aldehydes, ketones, carboxylic acids and esters) described in this section.

Aldehydes and Ketones

Both **aldehydes** and **ketones** contain a **carbonyl group**, a functional group with a carbon-oxygen double bond.

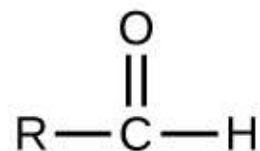
The names for aldehyde and ketone compounds are derived using similar nomenclature rules as for alkanes and alcohols, and include the class-identifying suffixes *-al* and *-one*, respectively:



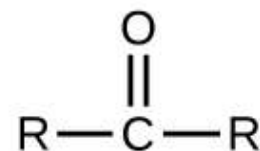
ALDEHYDES AND KETONES

In an aldehyde, the carbonyl group is bonded to at least one hydrogen atom.

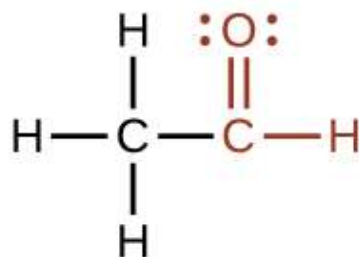
In a ketone, the carbonyl group is bonded to two carbon atoms:



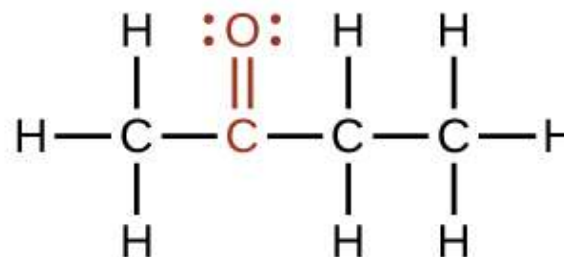
Functional group
of an aldehyde



Functional group
of a ketone



CH_3CHO
An aldehyde
ethanal (acetaldehyde)



$\text{CH}_3\text{COCH}_2\text{CH}_3$
A ketone
butanone

ALDEHYDES AND KETONES

As text, an aldehyde group is represented as —CHO ; a ketone is represented as —C(O)— or —CO— .

In both aldehydes and ketones, the geometry around the carbon atom in the carbonyl group is trigonal planar; the carbon atom exhibits sp^2 hybridization.

Two of the sp^2 orbitals on the carbon atom in the carbonyl group are used to form σ bonds to the other carbon or hydrogen atoms in a molecule.

The remaining sp^2 hybrid orbital forms a σ bond to the oxygen atom.

The unhybridized p orbital on the carbon atom in the carbonyl group overlaps a p orbital on the oxygen atom to form the π bond in the double bond.

ALDEHYDES AND KETONES

Like the C = O bond in carbon dioxide, the C = O bond of a carbonyl group is polar (recall that oxygen is significantly more electronegative than carbon, and the shared electrons are pulled toward the oxygen atom and away from the carbon atom).

Many of the reactions of aldehydes and ketones start with the reaction between a Lewis base and the carbon atom at the positive end of the polar C = O bond to yield an unstable intermediate that subsequently undergoes one or more structural rearrangements to form the final product

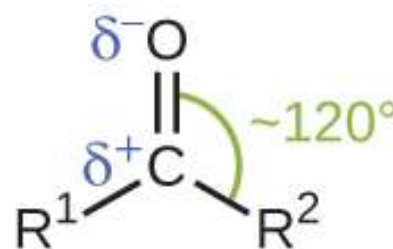


Figure 20.14 The carbonyl group is polar, and the geometry of the bonds around the central carbon is trigonal planar.

ALDEHYDES AND KETONES

The importance of molecular structure in the reactivity of organic compounds is illustrated by the reactions that produce aldehydes and ketones.

We can prepare a carbonyl group by oxidation of an alcohol—for organic molecules, oxidation of a carbon atom is said to occur when a carbon-hydrogen bond is replaced by a carbon-oxygen bond.

The reverse reaction—replacing a carbon-oxygen bond by a carbon-hydrogen bond—is a reduction of that carbon atom.

ALDEHYDES AND KETONES

Recall that oxygen is generally assigned a -2 oxidation number unless it is elemental or attached to a fluorine.

Hydrogen is generally assigned an oxidation number of $+1$ unless it is attached to a metal.

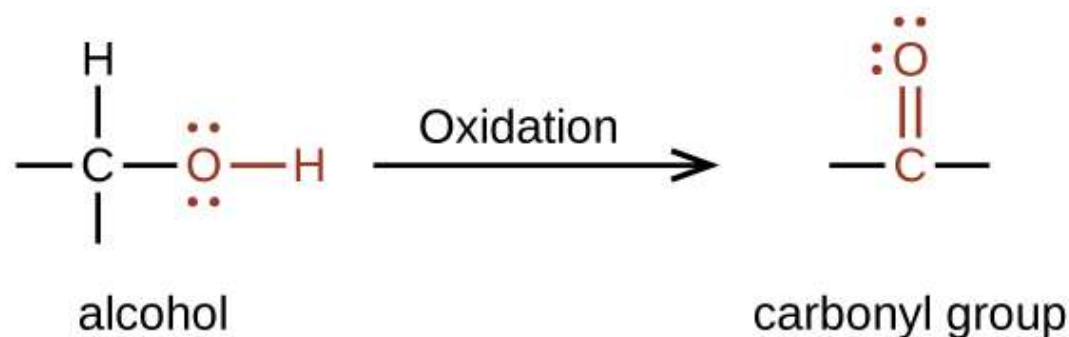
Since carbon does not have a specific rule, its oxidation number is determined algebraically by factoring the atoms it is attached to and the overall charge of the molecule or ion.

ALDEHYDES AND KETONES

In general, a carbon atom attached to an oxygen atom will have a more positive oxidation number and a carbon atom attached to a hydrogen atom will have a more negative oxidation number.

This should fit nicely with your understanding of the polarity of C–O and C–H bonds.

The other reagents and possible products of these reactions are beyond the scope of this chapter, so we will focus only on the changes to the carbon atoms:

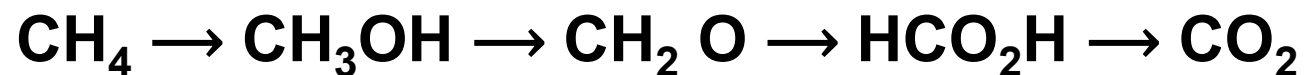


EXAMPLE 20.10.1

Oxidation and Reduction in Organic Chemistry

Methane represents the completely reduced form of an organic molecule that contains one carbon atom.

Sequentially replacing each of the carbon-hydrogen bonds with a carbon-oxygen bond would lead to an alcohol, then an aldehyde, then a carboxylic acid (discussed later), and, finally, carbon dioxide:



What are the oxidation numbers for the carbon atoms in the molecules shown here?

OXIDATION AND REDUCTION IN ORGANIC CHEMISTRY

Solution

For CH_4 , the carbon atom carries a -4 oxidation number (the hydrogen atoms are assigned oxidation numbers of $+1$ and the carbon atom balances, that by having an oxidation number of -4).

For the alcohol (in this case, methanol), the carbon atom has an oxidation number of -2 (the oxygen atom is assigned -2 , the four hydrogen atoms each are assigned $+1$, and the carbon atom balances the sum by having an oxidation number of -2 ; note that compared to the carbon atom in CH_4 , this carbon atom has lost two electrons so it was oxidized);

OXIDATION AND REDUCTION IN ORGANIC CHEMISTRY

for the aldehyde, the carbon atom's oxidation number is 0 (−2 for the oxygen atom and +1 for each hydrogen atom already balances to 0, so the oxidation number for the carbon atom is 0);

for the carboxylic acid, the carbon atom's oxidation number is +2 (two oxygen atoms each at −2 and two hydrogen atoms at +1); and for carbon dioxide, the carbon atom's oxidation number is +4 (here, the carbon atom needs to balance the −4 sum from the two oxygen atoms).

ALDEHYDES AND KETONES

Aldehydes are commonly prepared by the oxidation of alcohols whose –OH functional group is located on the carbon atom at the end of the chain of carbon atoms in the alcohol:



Alcohols that have their –OH groups in the middle of the chain are necessary to synthesize a ketone, which requires the carbonyl group to be bonded to two other carbon atoms:



ALDEHYDES AND KETONES

An alcohol with its -OH group bonded to a carbon atom that is bonded to no or one other carbon atom will form an aldehyde.

An alcohol with its -OH group attached to two other carbon atoms will form a ketone.

If three carbons are attached to the carbon bonded to the -OH , the molecule will not have a C-H bond to be replaced, so it will not be susceptible to oxidation.

Formaldehyde, an aldehyde with the formula HCHO , is a colorless gas with a pungent and irritating odor.

It is sold in an aqueous solution called formalin, which contains about 37% formaldehyde by weight.

ALDEHYDES AND KETONES

Formaldehyde causes coagulation of proteins, so it kills bacteria (and any other living organism) and stops many of the biological processes that cause tissue to decay.

Thus, formaldehyde is used for preserving tissue specimens and embalming bodies.

It is also used to sterilize soil or other materials. Formaldehyde is used in the manufacture of Bakelite, a hard plastic having high chemical and electrical resistance.

ALDEHYDES AND KETONES

- Dimethyl ketone, CH_3COCH_3 , commonly called acetone, is the simplest ketone. It is made commercially by fermenting corn or molasses, or by oxidation of 2-propanol.
- Acetone is a colorless liquid.
- Among its many uses are as a solvent for lacquer (including fingernail polish), cellulose acetate, cellulose nitrate, acetylene, plastics, and varnishes; as a paint and varnish remover; and as a solvent in the manufacture of pharmaceuticals and chemicals.

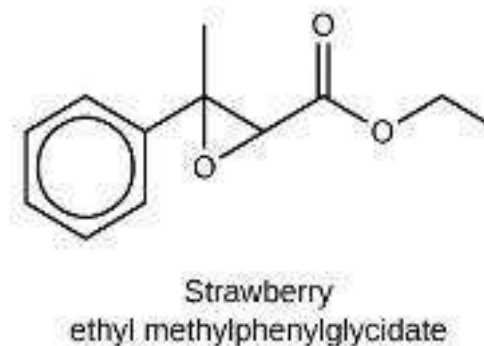
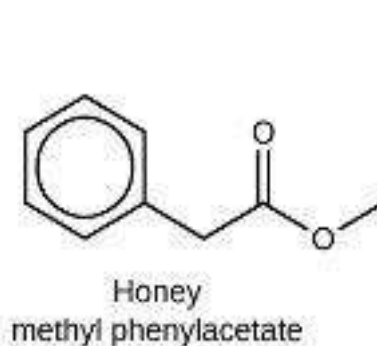
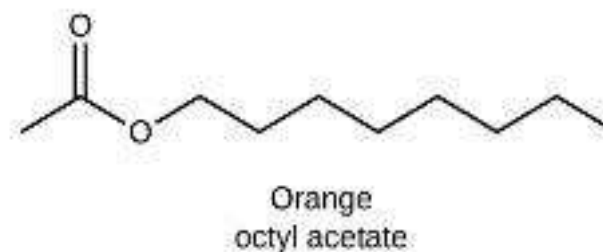
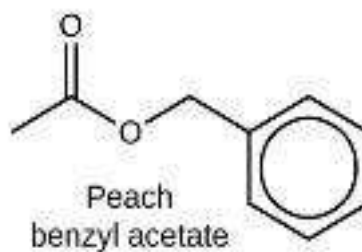
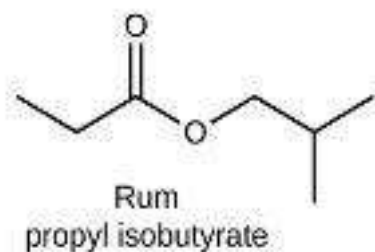
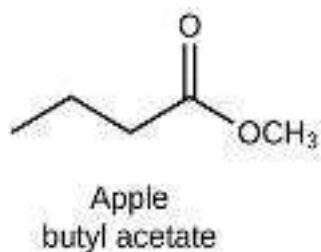
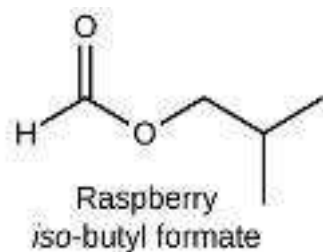
CARBOXYLIC ACIDS AND ESTERS

The odor of vinegar is caused by the presence of acetic acid, a carboxylic acid, in the vinegar.

The odor of ripe bananas and many other fruits is due to the presence of esters, compounds that can be prepared by the reaction of a carboxylic acid with an alcohol.

Because esters do not have hydrogen bonds between molecules, they have lower vapor pressures than the alcohols and carboxylic acids from which they are derived

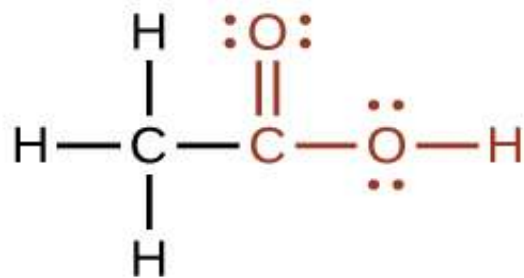
FIGURE 20.15



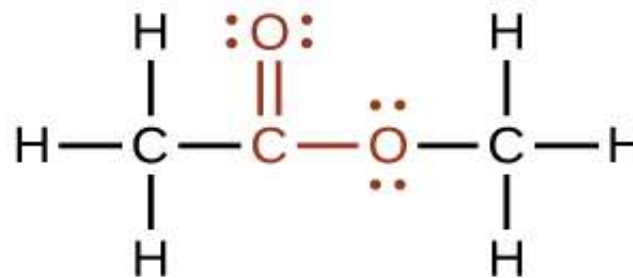
Esters are responsible for the odors associated with various plants and their fruits.

Carboxylic Acids and Esters

Both **carboxylic acids** and **esters** contain a carbonyl group with a second oxygen atom bonded to the carbon atom in the carbonyl group by a single bond. In a carboxylic acid, the second oxygen atom also bonds to a hydrogen atom. In an ester, the second oxygen atom bonds to another carbon atom. The names for carboxylic acids and esters include prefixes that denote the lengths of the carbon chains in the molecules and are derived following nomenclature rules similar to those for inorganic acids and salts (see these examples):



ethanoic acid
(acetic acid)

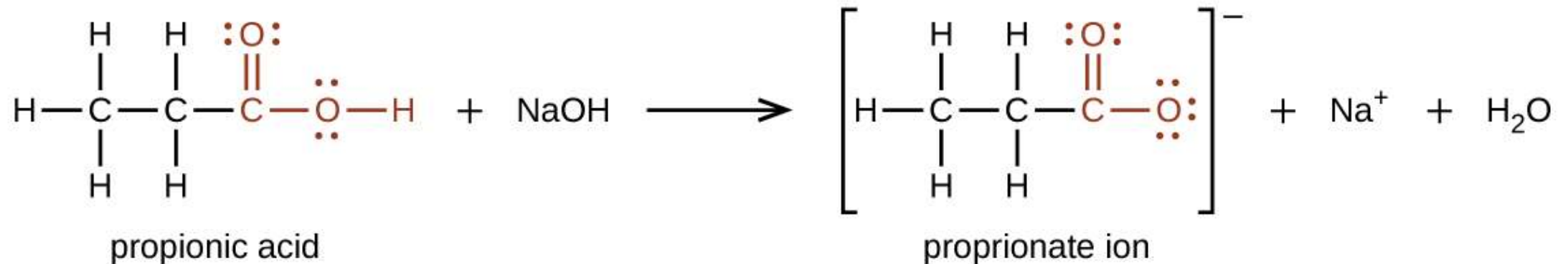


methyl ethanoate
(methyl acetate)

Carboxylic Acids and Esters

The functional groups for an acid and for an ester are shown in red in these formulas.

The hydrogen atom in the functional group of a carboxylic acid will react with a base to form an ionic salt:



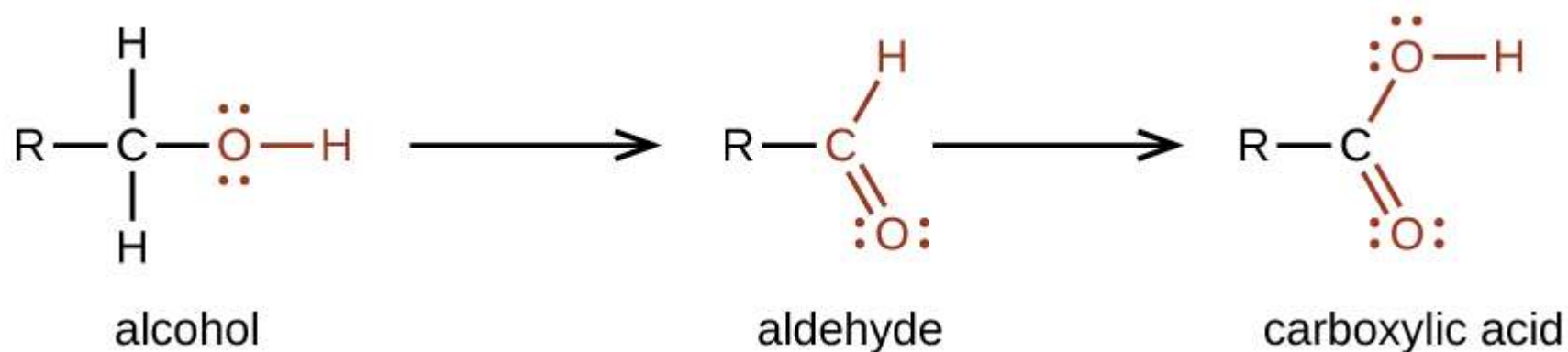
Carboxylic acids are weak acids (see the chapter on acids and bases), meaning they are not 100% ionized in water.

Generally only about 1% of the molecules of a carboxylic acid dissolved in water are ionized at any given time.

The remaining molecules are undissociated in solution.

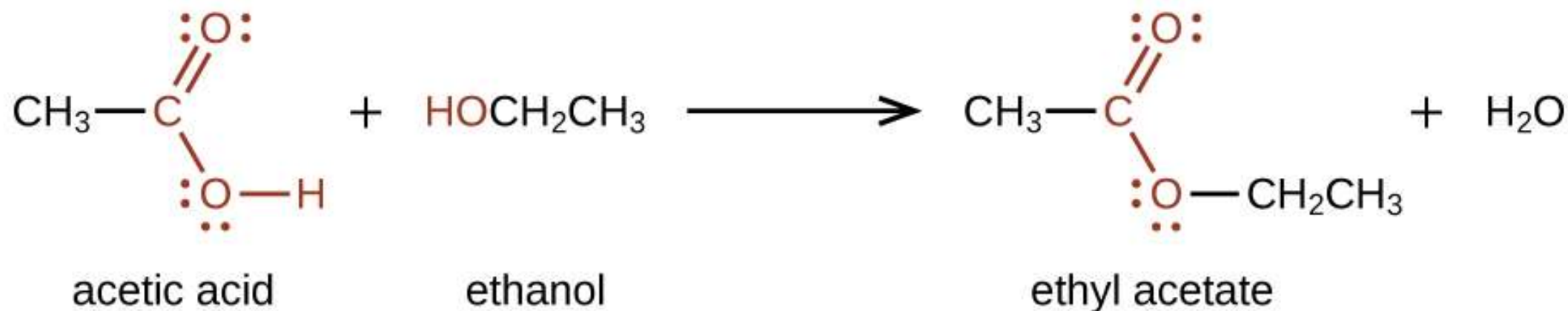
CARBOXYLIC ACIDS AND ESTERS

We prepare carboxylic acids by the oxidation of aldehydes or alcohols whose –OH functional group is located on the carbon atom at the end of the chain of carbon atoms in the alcohol:



CARBOXYLIC ACIDS AND ESTERS

Esters are produced by the reaction of acids with alcohols. For example, the ester ethyl acetate, $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$, is formed when acetic acid reacts with ethanol:



CARBOXYLIC ACIDS AND ESTERS

The simplest carboxylic acid is formic acid, HCO_2H , known since 1670.

Its name comes from the Latin word *formicus*, which means “ant”; it was first isolated by the distillation of red ants.

It is partially responsible for the pain and irritation of ant and wasp stings, and is responsible for a characteristic odor of ants that can be sometimes detected in their nests.

CARBOXYLIC ACIDS AND ESTERS

- Acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, constitutes 3–6% vinegar.
- Cider vinegar is produced by allowing apple juice to ferment without oxygen present.
- Yeast cells present in the juice carry out the fermentation reactions.
- The fermentation reactions change the sugar present in the juice to ethanol, then to acetic acid.
- Pure acetic acid has a penetrating odor and produces painful burns.
- It is an excellent solvent for many organic and some inorganic compounds, and it is essential in the production of cellulose acetate, a component of many synthetic fibers such as rayon.

CARBOXYLIC ACIDS AND ESTERS

- The distinctive and attractive odors and flavors of many flowers, perfumes, and ripe fruits are due to the presence of one or more esters .
- Among the most important of the natural esters are fats (such as lard, tallow, and butter) and oils (such as linseed, cottonseed, and olive oils), which are esters of the trihydroxyl alcohol glycerine, $\text{C}_3\text{H}_5(\text{OH})_3$, with large carboxylic acids, such as palmitic acid, $\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$, stearic acid, $\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$, and oleic acid, $\text{CH}_3(\text{CH}_2)_7 \text{CH} = \text{CH}(\text{CH}_2)_7 \text{CO}_2 \text{H}$.
- Oleic acid is an unsaturated acid; it contains a $\text{C} = \text{C}$ double bond.
- Palmitic and stearic acids are saturated acids that contain no double or triple bonds.

FIGURE 20.16



Over 350 different volatile molecules (many members of the ester family) have been identified in strawberries. (credit: Rebecca Siegel)

20.4 AMINES AND AMIDES

By the end of this section, you will be able to:

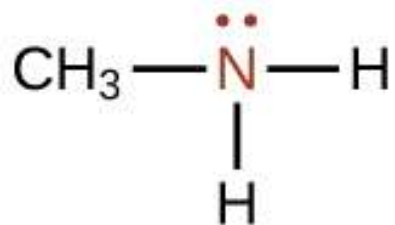
- Describe the structure and properties of an amine
- Describe the structure and properties of an amide

20.4 Amines and Amides

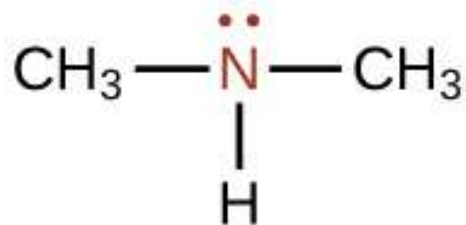
Amines are molecules that contain carbon-nitrogen bonds.

The nitrogen atom in an amine has a lone pair of electrons and three bonds to other atoms, either carbon or hydrogen.

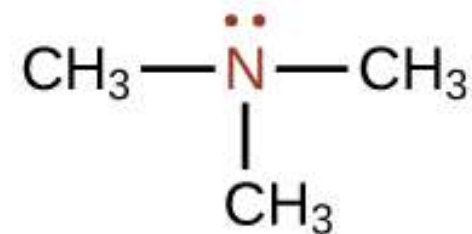
Various nomenclatures are used to derive names for amines, but all involve the class-identifying suffix *-ine* as illustrated here for a few simple examples:



methyl amine



dimethyl amine



trimethyl amine

20.4 AMINES AND AMIDES

In some amines, the nitrogen atom replaces a carbon atom in an aromatic hydrocarbon. Pyridine is one such heterocyclic amine.

A heterocyclic compound contains atoms of two or more different elements in its ring structure.

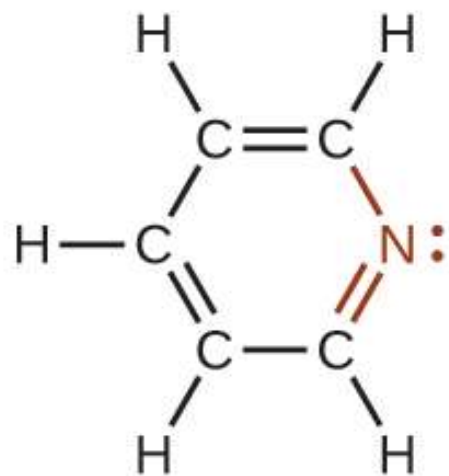


Figure 20.17 The illustration shows one of the resonance structures of pyridine.

HOW SCIENCES INTERCONNECT

DNA in Forensics and Paternity

The genetic material for all living things is a polymer of four different molecules, which are themselves a combination of three subunits.

The genetic information, the code for developing an organism, is contained in the specific sequence of the four molecules, similar to the way the letters of the alphabet can be sequenced to form words that convey information.

The information in a DNA sequence is used to form two other types of polymers, one of which are proteins.

The proteins interact to form a specific type of organism with individual characteristics.

DNA IN FORENSICS AND PATERNITY

A genetic molecule is called DNA, which stands for deoxyribonucleic acid.

The four molecules that make up DNA are called nucleotides.

Each nucleotide consists of a single- or double-ringed molecule containing nitrogen, carbon, oxygen, and hydrogen called a nitrogenous base.

Each base is bonded to a five-carbon sugar called deoxyribose.

The sugar is in turn bonded to a phosphate group ($-\text{PO}_4^{3-}$). When new DNA is made, a polymerization reaction occurs that binds the phosphate group of one nucleotide to the sugar group of a second nucleotide.

DNA IN FORENSICS AND PATERNITY

The nitrogenous bases of each nucleotide stick out from this sugar-phosphate backbone.

DNA is actually formed from two such polymers coiled around each other and held together by hydrogen bonds between the nitrogenous bases.

Thus, the two backbones are on the outside of the coiled pair of strands, and the bases are on the inside.

The shape of the two strands wound around each other is called a double helix.

DNA IN FORENSICS AND PATERNITY

It probably makes sense that the sequence of nucleotides in the DNA of a cat differs from those of a dog.

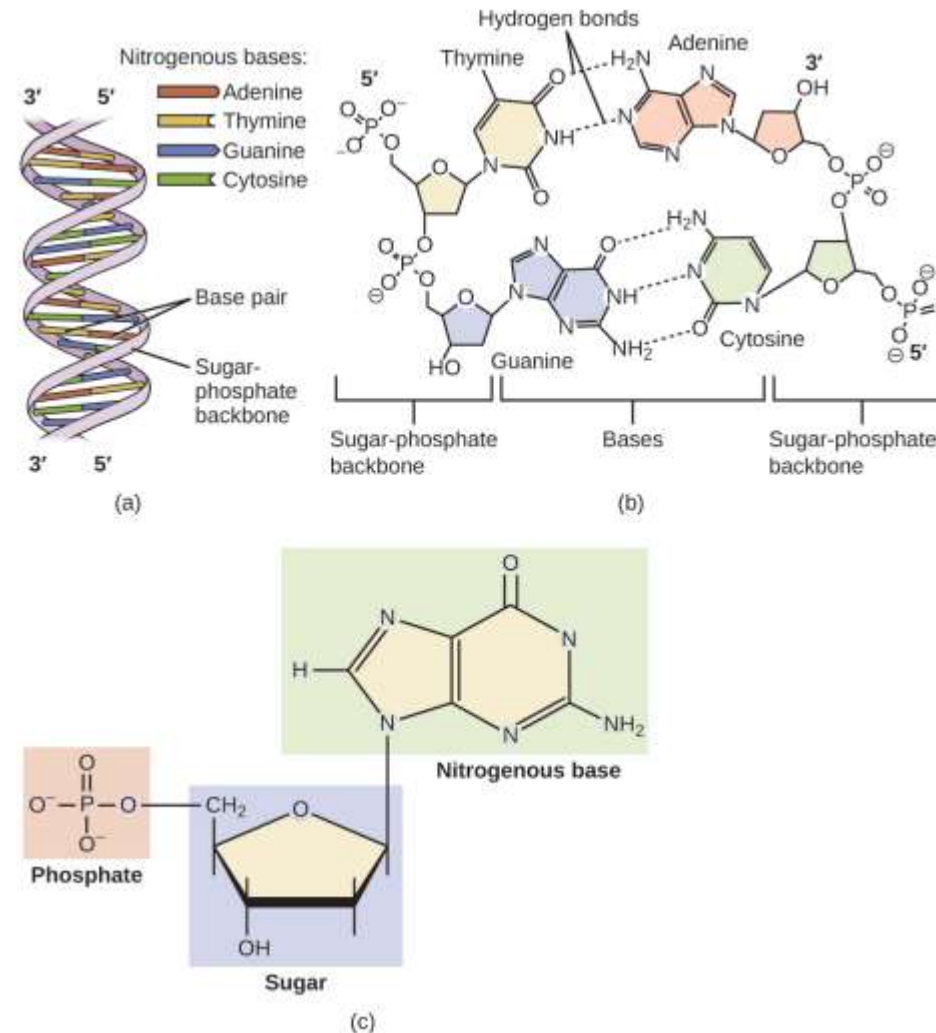
But it is also true that the sequences of the DNA in the cells of two individual pugs differ.

Likewise, the sequences of DNA in you and a sibling differ (unless your sibling is an identical twin), as do those between you and an unrelated individual.

However, the DNA sequences of two related individuals are more similar than the sequences of two unrelated individuals, and these similarities in sequence can be observed in various ways.

This is the principle behind DNA fingerprinting, which is a method used to determine whether two DNA samples came from related (or the same) individuals or unrelated individuals.

FIGURE 20.18



DNA is an organic molecule and the genetic material for all living organisms. (a) DNA is a double helix consisting of two single DNA strands hydrogen bonded together at each nitrogenous base. (b) This detail shows the hydrogen bonding (dotted lines) between nitrogenous bases on each DNA strand and the way in which each nucleotide is joined to the next, forming a backbone of sugars and phosphate groups along each strand. (c) This detail shows the structure of one of the four nucleotides that makes up the DNA polymer. Each nucleotide consists of a nitrogenous base (a double-ring molecule, in this case), a five-carbon sugar (deoxyribose), and a phosphate group.

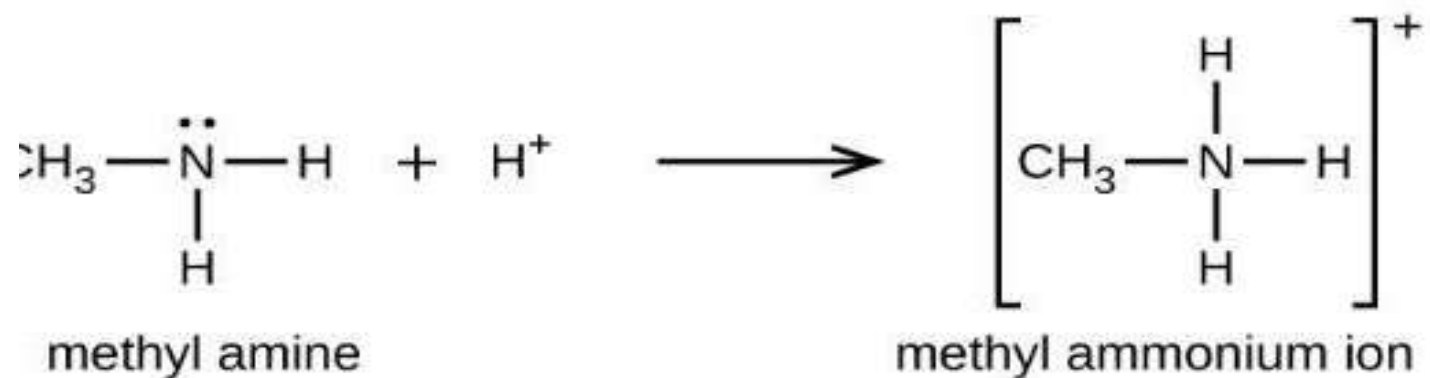
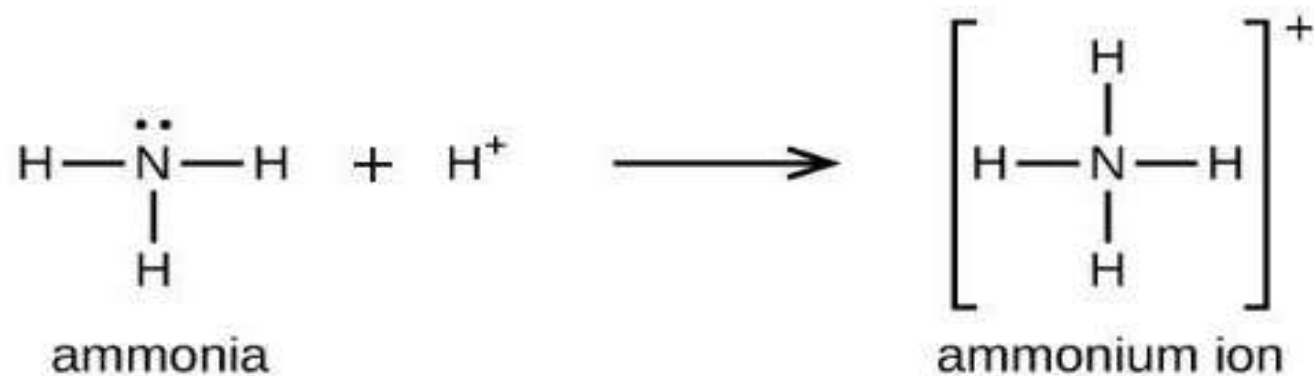
DNA IN FORENSICS AND PATERNITY

Using similarities in sequences, technicians can determine whether a man is the father of a child (the identity of the mother is rarely in doubt, except in the case of an adopted child and a potential birth mother).

Likewise, forensic geneticists can determine whether a crime scene sample of human tissue, such as blood or skin cells, contains **DNA** that matches exactly the **DNA** of a suspect.

DNA in Forensics and Paternity

Like ammonia, amines are weak bases due to the lone pair of electrons on their nitrogen atoms:



DNA IN FORENSICS AND PATERNITY

- The basicity of an amine's nitrogen atom plays an important role in much of the compound's chemistry.
- Amine functional groups are found in a wide variety of compounds, including natural and synthetic dyes, polymers, vitamins, and medications such as penicillin and codeine.
- They are also found in many molecules essential to life, such as amino acids, hormones, neurotransmitters, and DNA.

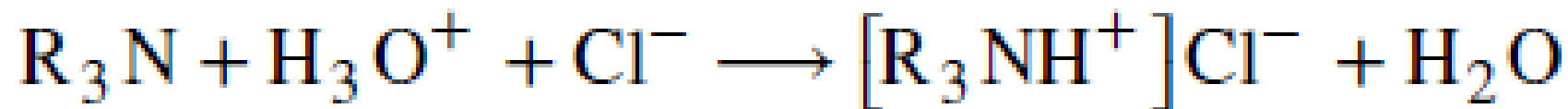
Addictive Alkaloids

Since ancient times, plants have been used for medicinal purposes.

One class of substances, called *alkaloids*, found in many of these plants has been isolated and found to contain cyclic molecules with an amine functional group.

These amines are bases.

They can react with H_3O^+ in a dilute acid to form an ammonium salt, and this property is used to extract them from the plant:



ADDICTIVE ALKALOIDS

The name alkaloid means “like an alkali.” Thus, an alkaloid reacts with acid.

The free compound can be recovered after extraction by reaction with a base:

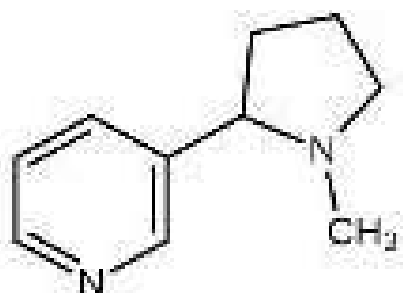


ADDICTIVE ALKALOIDS

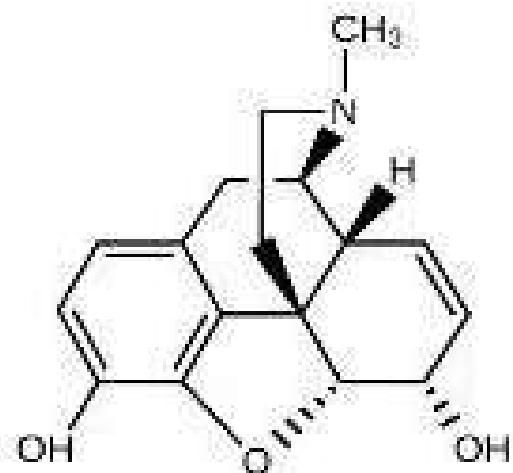
The structures of many naturally occurring alkaloids have profound physiological and psychotropic effects in humans.

Examples of these drugs include nicotine, morphine, codeine, and heroin.

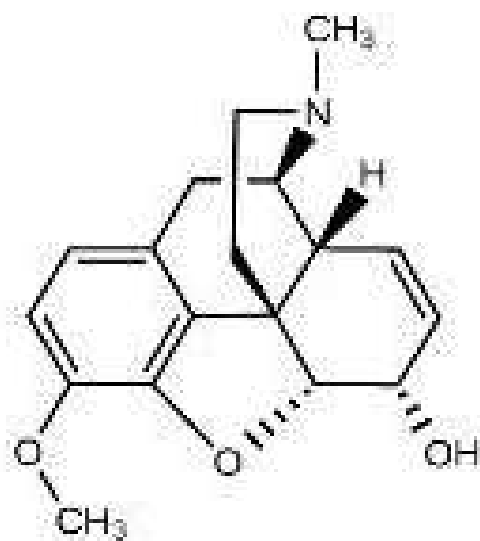
The plant produces these substances, collectively called secondary plant compounds, as chemical defenses against the numerous pests that attempt to feed on the plant:



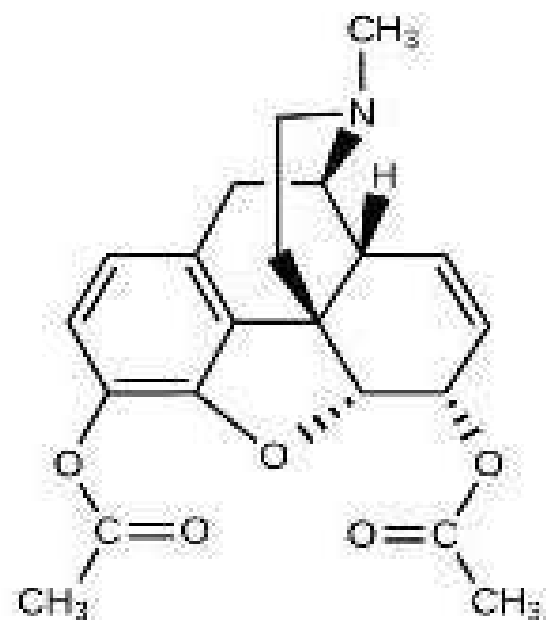
nicotine



morphine



codeine



heroin

ADDICTIVE ALKALOIDS

In these diagrams, as is common in representing structures of large organic compounds, carbon atoms in the rings and the hydrogen atoms bonded to them have been omitted for clarity.

The solid wedges indicate bonds that extend out of the page.

The dashed wedges indicate bonds that extend into the page.

Notice that small changes to a part of the molecule change the properties of morphine, codeine, and heroin.

ADDICTIVE ALKALOIDS

Morphine, a strong narcotic used to relieve pain, contains two hydroxyl functional groups, located at the bottom of the molecule in this structural formula.

Changing one of these hydroxyl groups to a methyl ether group forms codeine, a less potent drug used as a local anesthetic.

If both hydroxyl groups are converted to esters of acetic acid, the powerfully addictive drug heroin results.

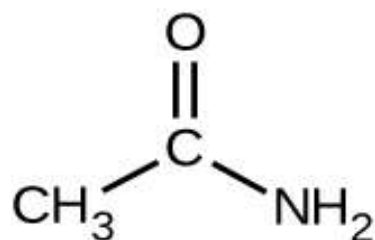
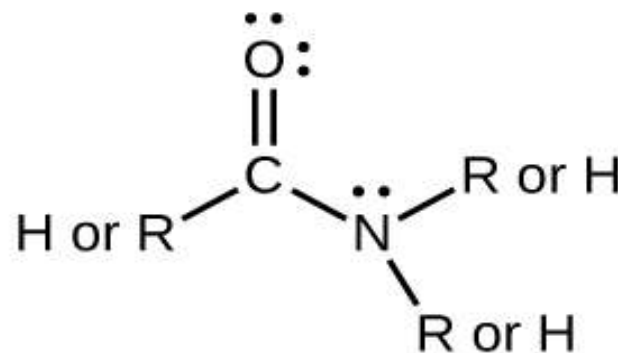
FIGURE 20.19



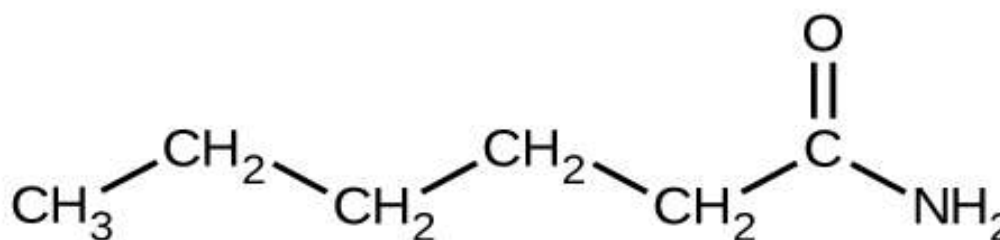
Poppies can be used in the production of opium, a plant latex that contains morphine from which other opiates, such as heroin, can be synthesized. (credit: Karen Roe)

Amides

Amides are molecules that contain nitrogen atoms connected to the carbon atom of a carbonyl group. Like amines, various nomenclature rules may be used to name amides, but all include use of the class-specific suffix *-amide*:



acetamide

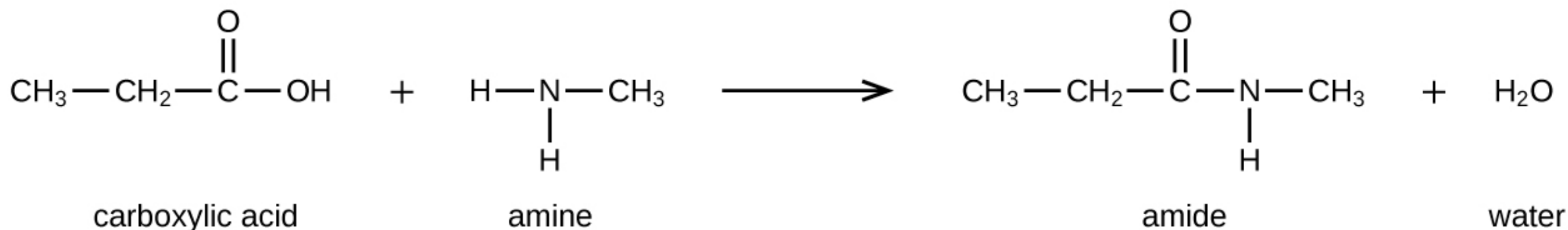


hexanamide

Amides

Amides can be produced when carboxylic acids react with amines or ammonia in a process called amidation.

A water molecule is eliminated from the reaction, and the amide is formed from the remaining pieces of the carboxylic acid and the amine (note the similarity to formation of an ester from a carboxylic acid and an alcohol discussed in the



The reaction between amines and carboxylic acids to form amides is biologically important.

It is through this reaction that amino acids (molecules containing both amine and carboxylic acid substituents) link together in a polymer to form proteins.

Proteins and Enzymes

Proteins are large biological molecules made up of long chains of smaller molecules called amino acids.

Organisms rely on proteins for a variety of functions—proteins transport molecules across cell membranes, replicate DNA, and catalyze metabolic reactions, to name only a few of their functions.

PROTEINS AND ENZYMES

The properties of proteins are functions of the combination of amino acids that compose them and can vary greatly.

Interactions between amino acid sequences in the chains of proteins result in the folding of the chain into specific, three dimensional structures that determine the protein's activity.

PROTEINS AND ENZYMES

Amino acids are organic molecules that contain an amine functional group (-NH_2), a carboxylic acid functional group (-COOH), and a side chain (that is specific to each individual amino acid).

Most living things build proteins from the same 20 different amino acids.

Amino acids connect by the formation of a peptide bond, which is a covalent bond formed between two amino acids when the carboxylic acid group of one amino acid reacts with the amine group of the other amino acid.

PROTEINS AND ENZYMES

The formation of the bond results in the production of a molecule of water (in general, reactions that result in the production of water when two other molecules combine are referred to as condensation reactions).

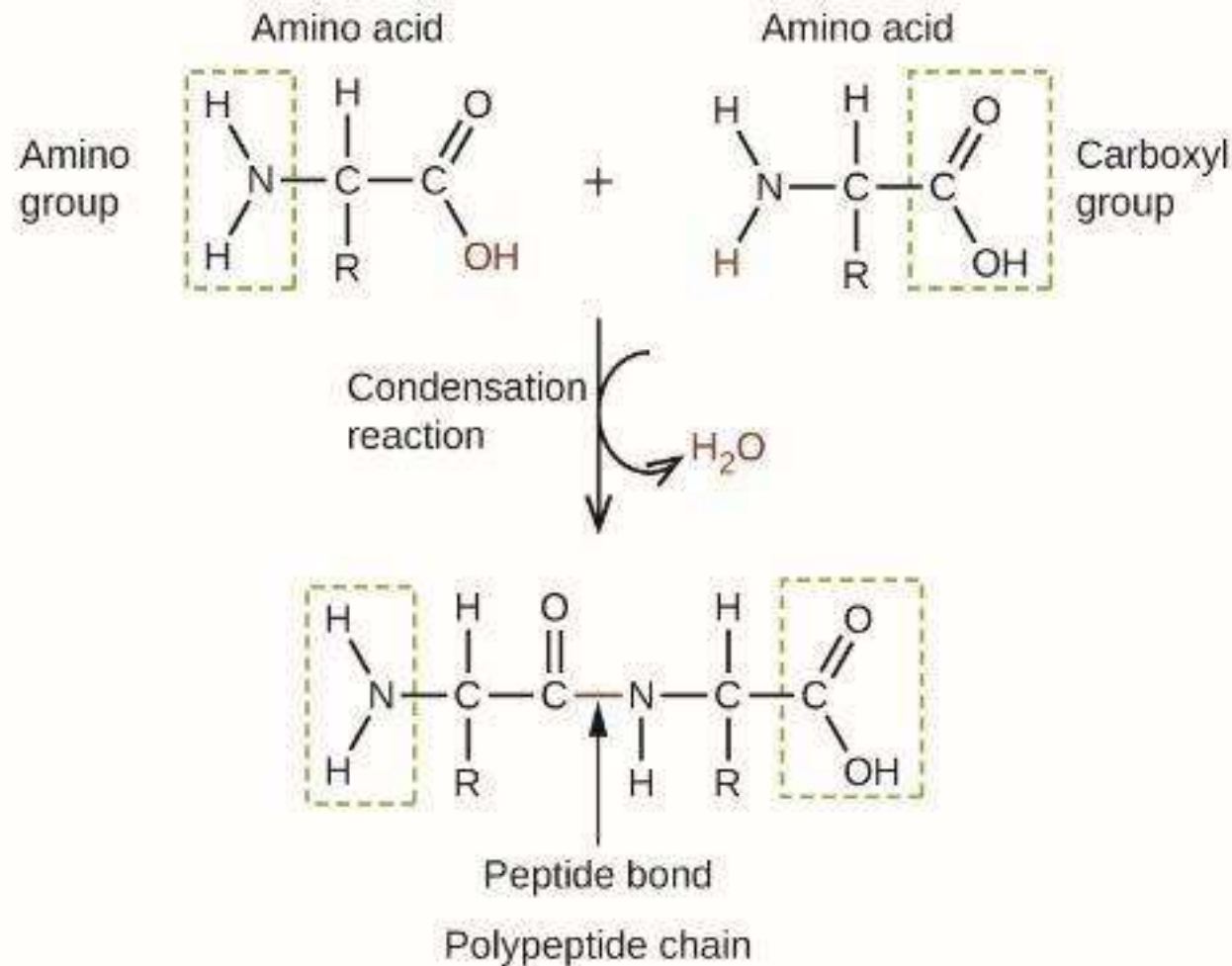
The resulting bond—between the carbonyl group carbon atom and the amine nitrogen atom is called a peptide link or peptide bond.

PROTEINS AND ENZYMES

Since each of the original amino acids has an unreacted group (one has an unreacted amine and the other an unreacted carboxylic acid), more peptide bonds can form to other amino acids, extending the structure.

A chain of connected amino acids is called a polypeptide. Proteins contain at least one long polypeptide chain.

FIGURE 20.20



This condensation reaction forms a dipeptide from two amino acids and leads to the formation of water.

PROTEINS AND ENZYMES

- Enzymes are large biological molecules, mostly composed of proteins, which are responsible for the thousands of metabolic processes that occur in living organisms.
- Enzymes are highly specific catalysts; they speed up the rates of certain reactions.
- Enzymes function by lowering the activation energy of the reaction they are catalyzing, which can dramatically increase the rate of the reaction.

PROTEINS AND ENZYMES

- Most reactions catalyzed by enzymes have rates that are millions of times faster than the non catalyzed version.
- Like all catalysts, enzymes are not consumed during the reactions that they catalyze.
- Enzymes do differ from other catalysts in how specific they are for their substrates (the molecules that an enzyme will convert into a different product).
- Each enzyme is only capable of speeding up one or a few very specific reactions or types of reactions.

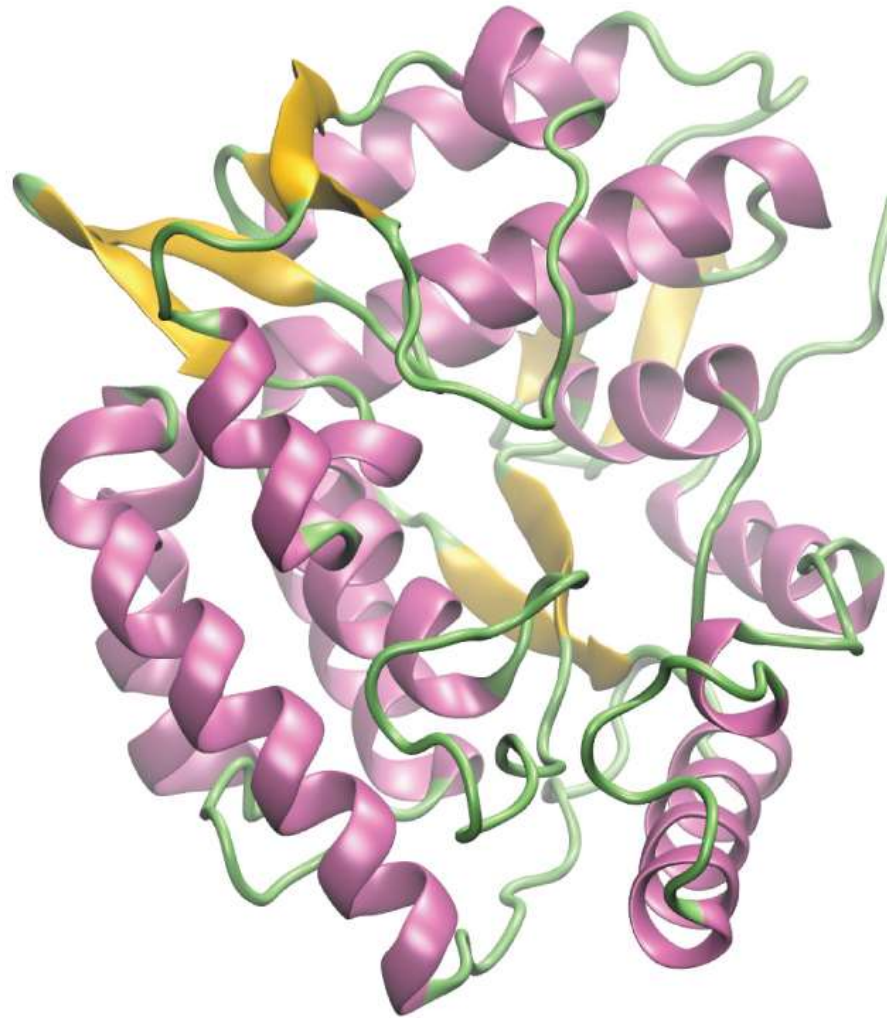
PROTEINS AND ENZYMES

Since the function of enzymes is so specific, the lack or malfunctioning of an enzyme can lead to serious health consequences.

One disease that is the result of an enzyme malfunction is phenylketonuria. In this disease, the enzyme that catalyzes the first step in the degradation of the amino acid phenylalanine is not functional.

Untreated, this can lead to an accumulation of phenylalanine, which can lead to intellectual disabilities.

FIGURE 20.21



A computer rendering shows the three-dimensional structure of the enzyme phenylalanine hydroxylase. In the disease phenylketonuria, a defect in the shape of phenylalanine hydroxylase causes it to lose its function in breaking down phenylalanine.

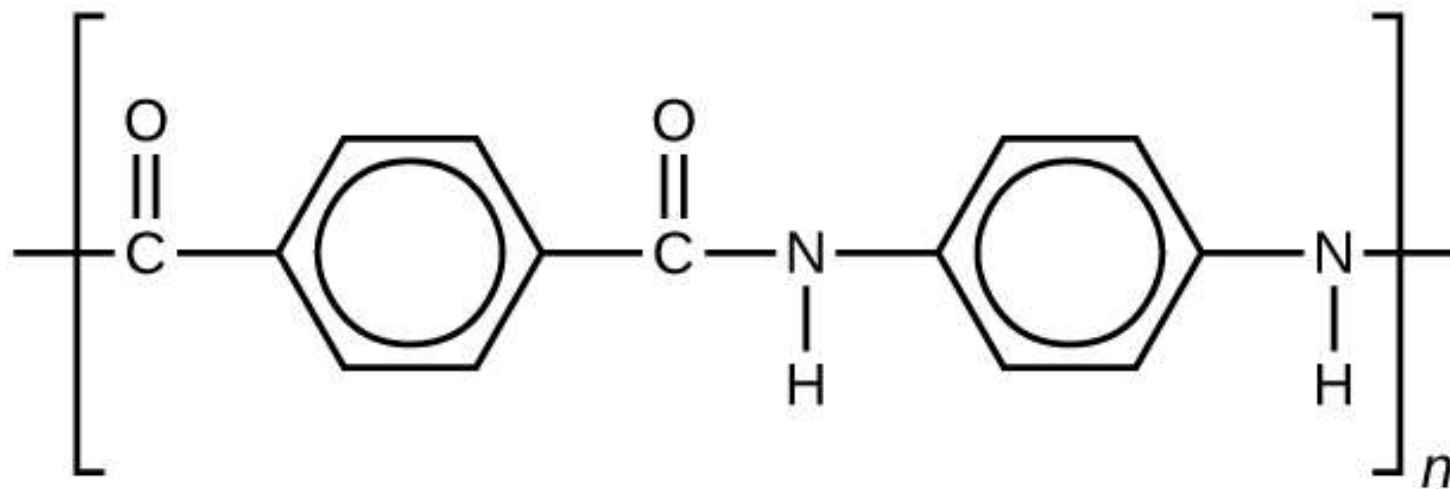
Kevlar

Kevlar is a synthetic polymer made from two monomers 1,4-phenylene-diamine and terephthaloyl chloride (Kevlar is a registered trademark of DuPont).

Kevlar's first commercial use was as a replacement for steel in racing tires. Kevlar is typically spun into ropes or fibers.

The material has a high tensile strength-to-weight ratio (it is about 5 times stronger than an equal weight of steel), making it useful for many applications from bicycle tires to sails to body armor.

FIGURE 20.22



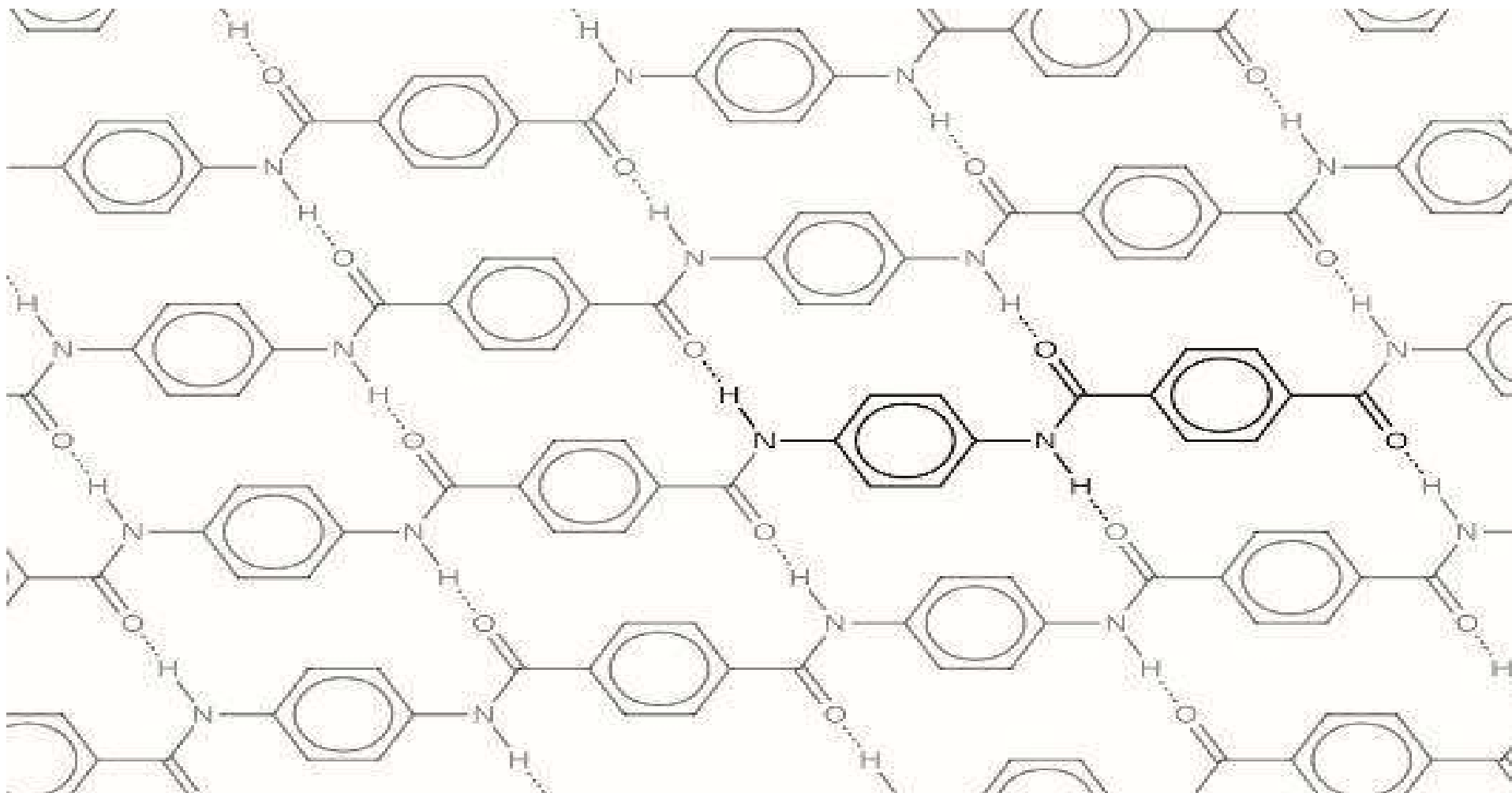
This illustration shows the formula for polymeric Kevlar.

The material owes much of its strength to hydrogen bonds between polymer chains (refer back to the chapter on intermolecular interactions).

These bonds form between the carbonyl group oxygen atom (which has a partial negative charge due to oxygen's electronegativity) on one monomer and the partially positively charged hydrogen atom in the N–H bond of an adjacent monomer in the polymer structure.

There is additional strength derived from the interaction between the unhybridized p orbitals in the sixmembered rings, called aromatic stacking.

FIGURE 20.23



The diagram shows the polymer structure of Kevlar, with hydrogen bonds between polymer chains represented by dotted lines.

Kevlar may be best known as a component of body armor, combat helmets, and face masks.

Since the 1980s, the US military has used Kevlar as a component of the PASGT (personal armor system for ground troops) helmet and vest. Kevlar is also used to protect armored fighting vehicles and aircraft carriers.

Civilian applications include protective gear for emergency service personnel such as body armor for police officers and heat-resistant clothing for fire fighters.

Kevlar based clothing is considerably lighter and thinner than equivalent gear made from other materials

FIGURE 20.24



(a)













(b)



(c)

(a) These soldiers are sorting through pieces of a Kevlar helmet that helped absorb a grenade blast. Kevlar is also used to make (b) canoes and (c) marine mooring lines. (credit a: modification of work by “Cla68”/Wikimedia Commons; credit b: modification of work by “OakleyOriginals”/Flickr; credit c: modification of work by Casey H. Kyhl)

Compound Name	Structure of Compound and Functional Group (red)	Example	
		Formula	Name
alkene	$\text{C}=\text{C}$	C_2H_4 	ethene
alkyne	$\text{C}\equiv\text{C}$	C_2H_2 	ethyne
alcohol	$\text{R}-\ddot{\text{O}}-\text{H}$	$\text{CH}_3\text{CH}_2\text{OH}$ 	ethanol
ether	$\text{R}-\ddot{\text{O}}-\text{R}'$	$(\text{C}_2\text{H}_5)_2\text{O}$ 	diethyl ether
aldehyde	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$	CH_3CHO 	ethanal
ketone	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\text{R}' \end{array}$	$\text{CH}_3\text{COCH}_2\text{CH}_3$ 	methyl ethyl ketone
carboxylic acid	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\ddot{\text{O}}-\text{H} \end{array}$	CH_3COOH 	acetic acid
ester	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\ddot{\text{O}}-\text{R}' \end{array}$	$\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$ 	ethyl acetate
amine	$\begin{array}{c} \text{:N:} \\ \\ \text{R}-\text{N}-\text{H} \\ \\ \text{H} \end{array} \quad \begin{array}{c} \text{:N:} \\ \\ \text{R}-\text{N}-\text{H} \\ \\ \text{R}' \end{array} \quad \begin{array}{c} \text{:N:} \\ \\ \text{R}-\text{N}-\text{R}' \\ \\ \text{R}' \end{array}$	$\text{C}_2\text{H}_5\text{NH}_2$ 	ethylamine
amide	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\ddot{\text{N}}-\text{R}' \\ \\ \text{H} \end{array}$	CH_3CONH_2 	acetamide