

# 12

## Introduction to Organic Chemistry: Alkanes

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### CONCEPTS TO REVIEW

- A. Covalent Bonds  
[Sections 4.1 and 4.2]
- B. Multiple Covalent Bonds  
[Section 4.3]
- C. Drawing Lewis Structures  
[Section 4.7]
- D. VSEPR and Molecular Shapes  
[Section 4.8]
- E. Polar Covalent Bonds  
[Section 4.9]
- F. Polar Molecules  
[Section 4.10]



▲ As a mother attends to her daughter's scrape, organic chemistry aids in the healing process, in the form of the antibiotic cream she is using.

Think back to the days when you first learned to ride a bike; at some time you undoubtedly fell off and scraped an elbow or knee. Your mom or dad came to the rescue, picking you up, dusting you off, and putting some antibacterial ointment and a bandage on your scrape. Or think of the times you went camping or to the beach and your lips got so chapped that the lip balm you had so fortuitously brought with you felt like it saved your life. Both of these instances are examples of organic chemistry at work. Organic chemistry

impacts your life on a daily basis and is the foundation upon which biochemistry, the chemistry of life, is built. In Chapters 12–17 of this book, we will discuss organic chemistry, then later, in Chapters 18–29, the biochemistry that is built upon it. We will look at how organic molecules form, the reactions they undergo, and how those molecules, with their unique shapes, structures, and chemistries, affect our bodies and those of other living organisms.

The term *organic chemistry* was first introduced to describe the study of compounds derived from living organisms, whereas *inorganic chemistry* was used to refer to the study of compounds obtained from minerals. Scientists long believed that organic compounds could only be obtained from a living source; this concept, known as *vitalism*, hindered the study of these types of molecules because vitalist chemists believed that organic materials could not be synthesized from inorganic components. In 1828, Friedrich Wöhler prepared an organic compound, urea, from an inorganic salt, ammonium cyanate, disproving the theory of vitalism and truly pioneering the field of organic chemistry. Since compounds from living sources contain carbon as their primary component, organic chemistry is now defined as the study of carbon-based compounds.

Carbon is special because it can readily form strong bonds with both other carbon atoms and atoms of other elements (primarily hydrogen, oxygen, nitrogen, and halogens) to produce long chains and rings of organic compounds. Only carbon is able to form such a diverse and immense array of compounds; chemists have discovered or prepared more than 18 million organic compounds (versus less than 2 million inorganic compounds), the simplest class of which are called the hydrocarbons, or *alkanes*, compounds composed of only carbon and hydrogen connected by single bonds.

So, how does any of this relate to a scraped knee or chapped lips? While hydrocarbons themselves are important from an industrial and energy standpoint (being responsible for waxes, lubricants, and fuels, so-called *petrochemicals*), their biological and medical significance is sometimes lost at first glance. One of the hydrocarbon products obtained from petroleum is *petrolatum* (petroleum jelly; commonly known as Vaseline). This product is the footing upon which many medically useful ointments are based. Neosporin, a common antibiotic cream, is composed of a mixture of three different antibiotics in a petrolatum-based matrix. Lip balms (such as ChapStick or Carmex) also heavily rely on the presence of petroleum jelly for their healing properties, which, because of their *hydrophobic* nature, seal moisture in allowing the chapped skin to heal quickly. In fact, petroleum jelly alone, with no additives, is believed to be just as effective as either antibiotic ointments or lip balms in promoting the healing of wounded or dry skin. We will learn more about petrochemicals and petroleum jelly in the Chemistry in Action on page 428. As you can see, hydrocarbons play such a fundamental role in our everyday world it is appropriate that we begin our study of organic chemistry with alkanes.

## 12.1 The Nature of Organic Molecules

### Learning Objective:

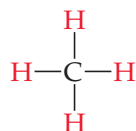
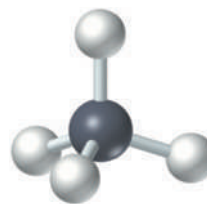
- Identify the general structural characteristics of organic molecules, in particular, the tetravalent nature of carbon and the different ways in which it can be expressed.

Let us begin our study of **organic chemistry**—the chemistry of carbon compounds—by reviewing what we have learned in earlier chapters about covalent bonds and molecular compounds and seeing how this applies to organic molecules in general (as you go through this section, take note of the three-dimensional shapes these molecules possess):

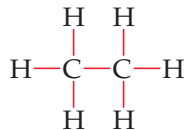
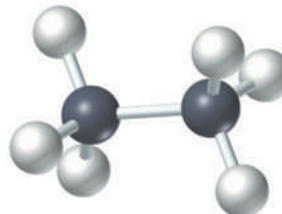
- **Carbon is tetravalent; it always forms four bonds** (Section 4.2). With the four valence electrons it already possesses, carbon has the ability to pick up four more from other atoms to fill out its octet. In the organic compound methane, for example, carbon is connected to four hydrogen atoms, with each hydrogen donating its valence electron to carbon to fill out its octet. Because it has groups attached to the carbon, methane is both tetrahedral (Section 4.8) and tetravalent.

**Organic chemistry** The study of carbon compounds.

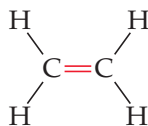
◀◀ **CONCEPTS TO REVIEW** Recall that a bond is formed when two electrons are shared between atoms.

Methane,  $\text{CH}_4$ 

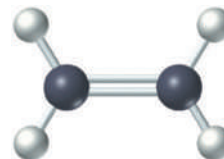
- **Organic molecules, which are primarily composed of nonmetals, have covalent bonds** (Section 4.2). In ethane, for example, the bonds result from the sharing of two electrons, either between two C atoms or a C and an H atom.

Ethane,  $\text{C}_2\text{H}_6$ 

- **Carbon forms multiple covalent bonds by sharing more than two electrons with a neighboring atom** (Section 4.3). In ethene, for example, the two carbon atoms share four electrons to form a double bond; in ethyne, the two carbons share six electrons to form a triple bond. Notice, however, that each carbon still possesses an octet: in ethene, four shared between the two carbons and two each shared with the hydrogens; in ethyne, six shared between the carbons and two with the hydrogen. The carbons in ethene and ethyne are not tetrahedral, but they are tetravalent.

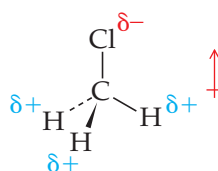


Ethene

Ethyne,  $\text{C}_2\text{H}_2$ 

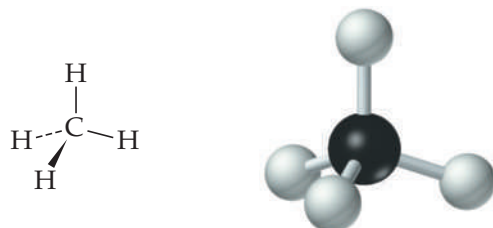
In general, we can make the following statements:

1. A carbon that has four groups attached will be tetrahedral (e.g., methane or ethane);
  2. A carbon that has three groups attached will be trigonal planar (e.g., ethene);
  3. A carbon that has two groups attached will be linear (e.g., ethyne).
- **When carbon bonds to a more electronegative element, polar covalent bonds result** (Section 4.9). C—H bonds are considered nonpolar, as are most C—C bonds; however, if you replace a hydrogen with an oxygen or a halogen, for example, a polar covalent bond results. In chloromethane, for example, the electronegative chlorine atom attracts electrons more strongly than carbon, resulting in polarization of the C—Cl bond so that carbon and hydrogens have a partial positive charge,  $\delta+$ , and chlorine has a partial negative charge,  $\delta-$ . It is useful to think of polar covalent bonds in this manner, as it will later help to explain their reactivity. In electrostatic potential maps (Section 4.9), the chlorine atom is therefore in the red region of the map and the carbon atom in the blue region.

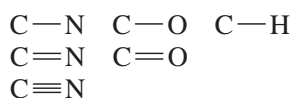
Chloromethane,  $\text{CH}_3\text{Cl}$ 

A group is any atom or collection of atoms attached to the carbon.

- **Organic molecules have specific three-dimensional shapes** (Section 4.8). For example, when carbon is bonded to four atoms, as in methane,  $\text{CH}_4$ , the bonds are oriented toward the four corners of a regular tetrahedron with carbon in the center. Such three-dimensionality is commonly shown using normal lines for bonds in the plane of the page, dashed lines for bonds receding behind the page, and wedged lines for bonds coming out of the page.



- In addition to carbon, most **organic molecules always contain hydrogen and often also contain nitrogen and oxygen** (Section 4.7). Nitrogen can form single, double, and triple bonds to carbon, whereas oxygen can form single and double bonds. Hydrogen can only form single bonds to carbon because hydrogen can only hold two electrons in its valence shell:



Covalent bonding makes organic compounds quite different from the inorganic compounds we have been concentrating on up to this point. For example, inorganic compounds such as  $\text{NaCl}$  have high melting points and high boiling points because they consist of a large network of oppositely charged ions held together by strong electrical attractions. By contrast, organic compounds consist of atoms joined by covalent bonds, forming individual molecules. Because the organic molecules are attracted to one another only by weak nonionic intermolecular forces, organic compounds generally have lower melting and boiling points than inorganic salts. As a result, many simple organic compounds are liquids or low melting solids at room temperature, and a few are gases.

Other important differences between organic and inorganic compounds include solubility and electrical conductivity. Whereas many inorganic compounds dissolve in water to yield solutions of ions that conduct electricity, most organic compounds are insoluble in water, and almost all of those that are soluble do not conduct electricity. Only small polar organic molecules, such as glucose and ethanol, or large molecules with many polar groups, such as some proteins, interact with water molecules through both dipole–dipole interactions and/or hydrogen bonding and, thus, dissolve in water. This lack of water solubility for organic compounds has important practical consequences, varying from the difficulty in removing greasy dirt and cleaning up environmental oil spills to drug delivery and ensuring that a drug reaches its target organ or tissue.

◀◀ Other unique properties of ionic compounds are discussed in Section 3.10

◀◀ Recall from Section 8.2 the various intermolecular forces: dipole–dipole forces, London dispersion forces, and hydrogen bonds.

◀◀ Section 9.9 explores how anions and cations in solution conduct electric current.

◀◀ Recall from Section 9.2 that a compound is only soluble when the intermolecular forces between solvent and solute are comparable in strength to the intermolecular forces of the pure solvent or solute.



▲ Oil spills can be a serious environmental problem because oil is insoluble in water.

**LOOKING AHEAD** ▶▶ The interior of a living cell is largely a water solution that contains many hundreds of different compounds. In Section 23.7, we will see how cells use membranes composed of water-insoluble organic molecules to enclose their watery interiors and to regulate the flow of substances across the cell boundary.

## 12.2 Families of Organic Molecules: Functional Groups

### Learning Objectives:

- Define functional group.
- Identify the functional groups in organic molecules.

More than 18 *million* organic compounds are described in scientific literature, each with unique chemical and physical properties, and many also having unique biological properties (both desired and undesired). How can we ever understand them all?

Chemists have learned through experience that organic compounds can be classified into families according to their structural features, and that the chemical behavior of family members is often predictable based on their specific grouping of atoms. As a result, the millions of compounds can be sorted into just a few general families of

organic compounds with simple chemical patterns.



**Functional group** An atom or group of atoms within a molecule that has a characteristic physical and chemical behavior.

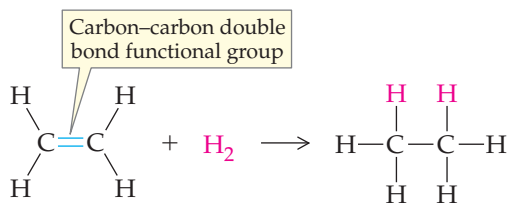
The structural features that allow us to classify organic compounds into distinct chemical families are called **functional groups**. A functional group is an atom or group of atoms that has a characteristic physical and chemical behavior. Each functional group is always part of a larger molecule, and a molecule may have more than one class of functional group present, as we shall soon see. An important property of functional groups is that a given functional group *tends to undergo the same types of reactions in every molecule that contains it*. Once a functional group undergoes a chemical reaction it quite often changes the chemical behavior of the entire molecule. For example, the carbon–carbon double bond is a common functional group. Ethene ( $\text{C}_2\text{H}_4$ ), the simplest compound with a carbon–carbon double bond, undergoes many chemical reactions similar to those of oleic acid ( $\text{C}_{18}\text{H}_{34}\text{O}_2$ ), a much larger and more complex compound that also contains a carbon double bond. Both, for example, react with hydrogen gas in the same manner, as shown in Figure 12.1. We will see in Chapter 13 that the double bond reacts with water and acid to produce alcohols; in doing so a molecule that is completely insoluble in water (such as ethene) is converted to one that shows a substantial increase in its water solubility (ethanol). These identical reactions with hydrogen are typical: *The chemistry of an organic molecule is primarily determined by the functional groups it contains, not by its size or complexity.*

► **Figure 12.1**

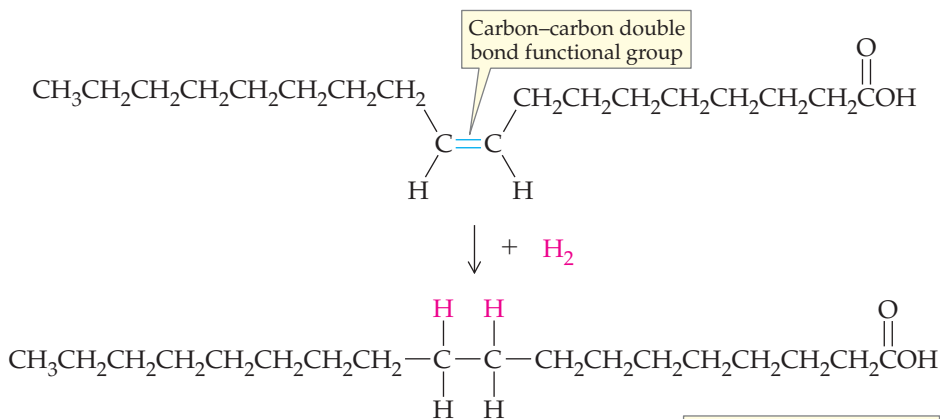
**The reactions of (a) ethene and (b) oleic acid with hydrogen; reaction of (c) ethene with water in the presence of acid.**

The carbon-carbon double-bond functional group adds 2 hydrogen atoms in both cases, regardless of the complexity of the rest of the molecule.

**(a) Reaction of ethene with hydrogen**



**(b) Reaction of oleic acid with hydrogen**



(c) Reaction of ethene with water

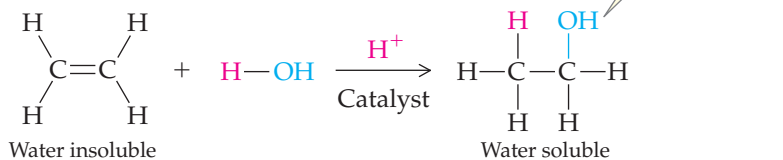


Table 12.1 lists some of the most important families of organic molecules and their distinctive functional groups. Compounds that contain a C=C double bond functional group, for instance, are in the *alkene* family, compounds that have an —OH group bound to a tetravalent carbon are in the *alcohol* family, and so on. To aid in identifying the organic functional groups you will encounter, we have included an Organic Functional Group Concept Map (Figure 12.5) at the end of this chapter; it should be used in

**Table 12.1** Some Important Families of Organic Molecules

Family Name	Functional Group Structure*	Simple Example	Line Structure	Name Suffix
Alkane (Chapter 12)	No readily reactive bonds. Contains only C—H and C—C single bonds	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> Propane		-ane
Alkene (Chapter 13)		H <sub>2</sub> C=CH <sub>2</sub> Ethene		-ene
Alkyne (Chapter 13)		H—C≡C—H Ethyne		-yne
Aromatic (Chapter 13)		Benzene		None
Alkyl halide (Chapters 12, 14)		CH <sub>3</sub> CH <sub>2</sub> Cl Chloroethane		None
Alcohol (Chapter 14)		CH <sub>3</sub> CH <sub>2</sub> OH Ethanol		-ol
Ether (Chapter 14)		CH <sub>3</sub> CH <sub>2</sub> —O—CH <sub>2</sub> CH <sub>3</sub> Diethyl ether		None
Amine (Chapter 16)		CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> Ethanamine		-amine
Aldehyde (Chapter 15)		CH <sub>3</sub> —C(=O)—H Ethanal		-al
Ketone (Chapter 15)		CH <sub>3</sub> —C(=O)—CH <sub>3</sub> Acetone		-one
Carboxylic acid (Chapter 17)		CH <sub>3</sub> —C(=O)—OH Acetic acid		-ic acid
Anhydride (Chapter 17)		CH <sub>3</sub> —C(=O)—O—C(=O)—CH <sub>3</sub> Acetic anhydride		None
Ester (Chapter 17)		CH <sub>3</sub> —C(=O)—O—CH <sub>3</sub> Methyl acetate		-ate
Amide (Chapter 17)		CH <sub>3</sub> —C(=O)—NH <sub>2</sub> Acetamide		-amide
Thiol (Chapter 14)		CH <sub>3</sub> CH <sub>2</sub> SH Ethanethiol		None
Disulfide (Chapter 14)		CH <sub>3</sub> SSCH <sub>3</sub> Dimethyl disulfide		None
Sulfide (Chapter 14)		CH <sub>3</sub> CH <sub>2</sub> SCH <sub>3</sub> Ethyl methyl sulfide		None

The bonds shown in RED refer to the functional group of interest and the atoms required.

conjunction with Table 12.1. Also at the end of each organic chemistry chapter you will find a summary of functional group reactions discussed in that chapter. You will find Table 12.1, Figure 12.5, and these Functional Group Summaries helpful as you proceed through the remainder of this text.

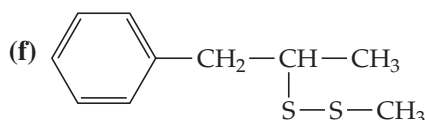
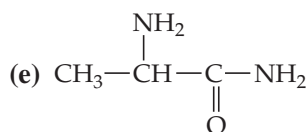
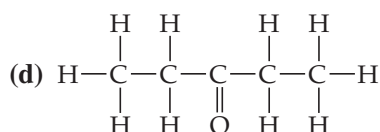
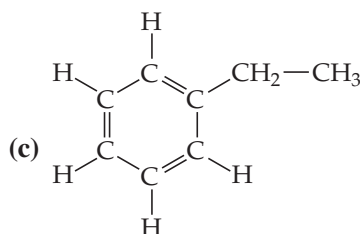
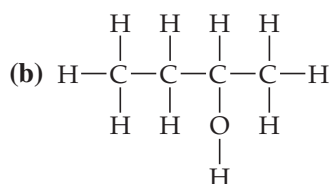
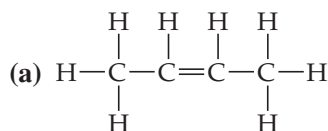
Much of the chemistry discussed in this and the next five chapters is the chemistry of the families listed in Table 12.1, so it is best to learn the names and become familiar with their structures now. Note that they fall into four groups:

**Hydrocarbon** An organic compound that contains only carbon and hydrogen.

- The first four families in Table 12.1 are **hydrocarbons**, organic compounds that contain only carbon and hydrogen. *Alkanes* have only single bonds and contain no functional groups. As we will see later in this chapter, the absence of functional groups makes alkanes relatively unreactive. *Alkenes* contain a carbon–carbon double-bond functional group; *alkynes* contain a carbon–carbon triple-bond functional group; and *aromatic* compounds contain a six-membered benzene ring of carbon atoms with three alternating double bonds.
- The next four families in Table 12.1 have functional groups that contain only single bonds and have a carbon atom bonded to an electronegative atom. *Alkyl halides* have a carbon–halogen bond; *alcohols* have a carbon–oxygen bond; *ethers* have two carbons bonded to the same oxygen; and *amines* have a carbon–nitrogen bond.
- The next six families in Table 12.1 have functional groups that contain a carbon–oxygen double bond: *aldehydes*, *ketones*, *carboxylic acids*, *anhydrides*, *esters*, and *amides*.
- The remaining three families in Table 12.1 have functional groups that contain sulfur: *thioalcohols* (known simply as *thiols*), *sulfides*, and *disulfides*. These three families play an important role in protein function (Chapter 18).
- Many of the organic molecules we will come across in later chapters (in particular the biochemistry chapters) will have more than one functional group present in the same molecule (see, e.g., for the amino acids Section 18.3). When this is the case, we will classify the molecule as chemically belonging to multiple functional group families; from a biological and medical standpoint these molecules are quite often classified according to their biologically relevant function (e.g., neurotransmitters (Sections 28.5 to 28.7) or nucleic acids (Section 26.2)).

### Worked Example 12.1 Molecular Structures: Identifying Functional Groups

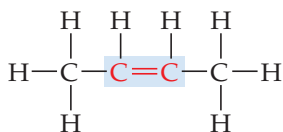
To which family of organic compounds do the following compounds belong? Explain.



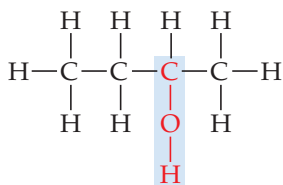
**ANALYSIS** Use the Organic Functional Group Concept Map (Figure 12.5, see end of chapter) and Table 12.1 to identify each functional group, and name the corresponding family to which the compound belongs. Begin by determining what elements are present and whether multiple bonds are present.

## SOLUTION

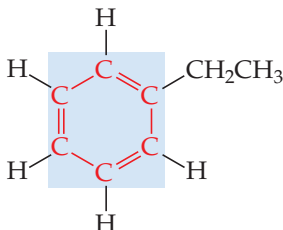
- (a) This compound contains only carbon and hydrogen atoms, so it is a *hydrocarbon*. There is only one carbon–carbon double bond, so it is an *alkene*.



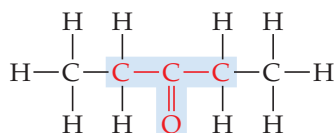
- (b) This compound contains an oxygen and has only single bonds. The presence of the O—H group bonded to tetravalent carbon identifies this compound as an *alcohol*.



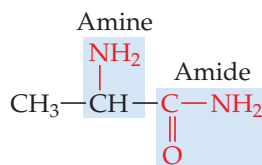
- (c) This compound also contains only carbon and hydrogen atoms, which identifies it as a *hydrocarbon*. It has three double bonds in a ring. The six-membered carbon ring with alternating double bonds also identifies this compound as an *aromatic* hydrocarbon compound.



- (d) This molecule contains an oxygen that is double bonded to a carbon (a *carbonyl group*, discussed in Chapter 16), and there is no singly bound oxygen or nitrogen also connected to the carbon. The carbon–oxygen double bond is connected to two other carbons (as opposed to a hydrogen) that identifies this compound as a *ketone*.

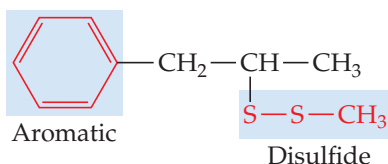


- (e) Here, we have an example of a molecule belonging to multiple functional group families. This molecule contains oxygen and nitrogen in addition to carbon and hydrogen, so it is not a hydrocarbon. The presence of the carbonyl group further classifies this molecule, but here we run into a problem: one —NH<sub>2</sub> is attached to the carbonyl but the other —NH<sub>2</sub> is not. This leads us to conclude that there are two functional groups present: an *amide* and an *amine*.



▶▶ We will see in Chapter 16 that while the NH<sub>2</sub> of an amine produces a basic molecule, the NH<sub>2</sub> of an amide does not, and that amides, despite having a nitrogen in them, are nonbasic (Chapter 17).

- (f) This molecule also contains two functional groups: a ring containing alternating carbon–carbon single and double bonds as well as an S—S group. From our concept map, we trace the double bond to indicate we have an aromatic hydrocarbon, while the sulfurs indicate the presence of a disulfide.





**Worked Example 12.2** Molecular Structures: Drawing Functional Groups

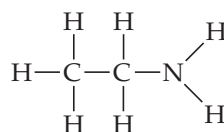
Given the family of organic compounds to which the compound belongs, propose structures for compounds having the following chemical formulas.

- (a) An amine having the formula  $C_2H_7N$   
 (b) An alkyne having the formula  $C_3H_4$   
 (c) An ether having the formula  $C_4H_{10}O$

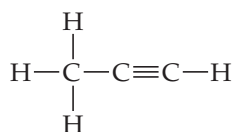
**ANALYSIS** Identify the functional group for each compound from Table 12.1. Once the atoms in this functional group are eliminated from the chemical formula, the remaining structure can be determined. (Remember that each carbon atom forms four bonds, nitrogen forms three bonds, oxygen forms two bonds, and hydrogen forms only one bond.)

**SOLUTION**

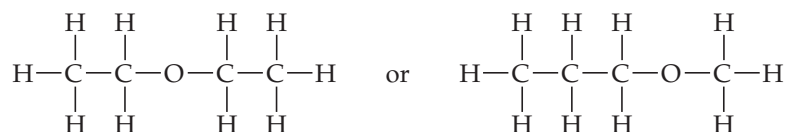
- (a) Amines have a  $C-NH_2$  group. Eliminating these atoms from the formula leaves 1 C atom and 5 H atoms. Since only the carbons are capable of forming more than one bond, the 2 C atoms must be bonded together. The remaining H atoms are then bonded to the carbons until each C has 4 bonds.



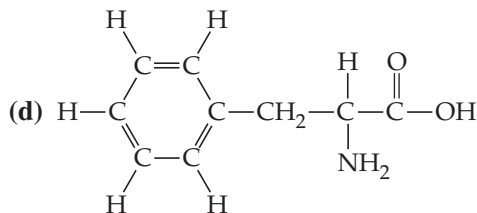
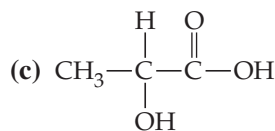
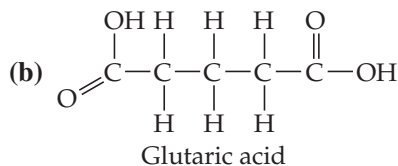
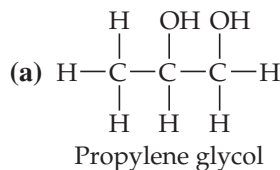
- (b) The alkynes contain a  $C\equiv C$  bond. This leaves 1 C atom and 4 H atoms. Attach this C to one of the carbons in the triple bond, and then distribute the H atoms until each carbon has a full complement of four bonds.



- (c) The ethers contain a  $C-O-C$  group. Eliminating these atoms leaves 2 C atoms and 10 H atoms. The C atoms can be distributed on either end of the ether group, and the H atoms are then distributed until each carbon atom has a full complement of four bonds.

**PROBLEM 12.1**

Locate and identify the functional groups in (a) propylene glycol, one of the major ingredients used in electronic cigarettes; (b) glutaric acid, produced in the body during the metabolism of lysine and tryptophan; (c) lactic acid, from sour milk; and (d) phenylalanine, an amino acid found in proteins.



## PROBLEM 12.2

Draw structures for molecules that fit the following descriptions:

- $\text{C}_3\text{H}_6\text{O}$  containing an aldehyde functional group
- $\text{C}_3\text{H}_6\text{O}$  containing a ketone functional group
- $\text{C}_3\text{H}_6\text{O}_2$  containing a carboxylic acid functional group

## HANDS-ON CHEMISTRY 12.1

To see how much organic chemistry impacts your daily life, let's take a look at some of the common products that you should have around your home and see what is "organic" in them. You will need to have an internet connection to fully carry out this activity.

- Let's begin by looking at a simple substance found in almost every pantry: vinegar. Vinegar is simply diluted acetic acid. Look up the structure of acetic acid and draw it. Circle the functional group in it. What other food products can you find that contain vinegar? You may want to look in your refrigerator as well as your pantry.
- Other common organic compounds found in a home are citric acid, folic acid, dextrose, and thiamine. Look up the structures of each of these and draw them, circling and

identifying as many functional groups present as you can. Do any of these four compounds go by a more recognizable name? If so, what? See if you can find at least one food item than contains one or more of these in it. Canned items such as soups are a good place to start. Some of them may be listed as their salt forms (like citrate, folate, thiamine mononitrate, etc). You may have to make a trip to the store to complete this. Provide at least one role the compound plays in the item in which it is present.

- In the chapter opener, the antibiotic ointment Neosporin was mentioned. What are the three antibiotics found in it? Look up the structures of each of these and draw them, circling and identifying as many functional groups present as you can.

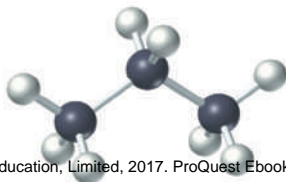
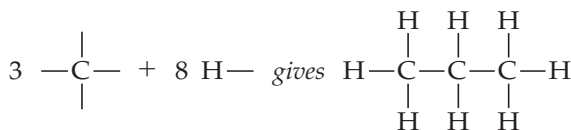
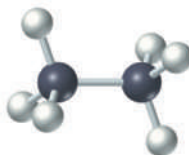
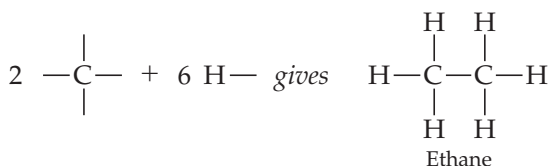
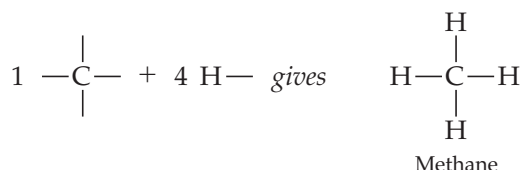
## 12.3 The Structure of Organic Molecules: Alkanes and Their Isomers

## Learning Objective:

- Recognize structural (constitutional) isomers and functional group isomers.

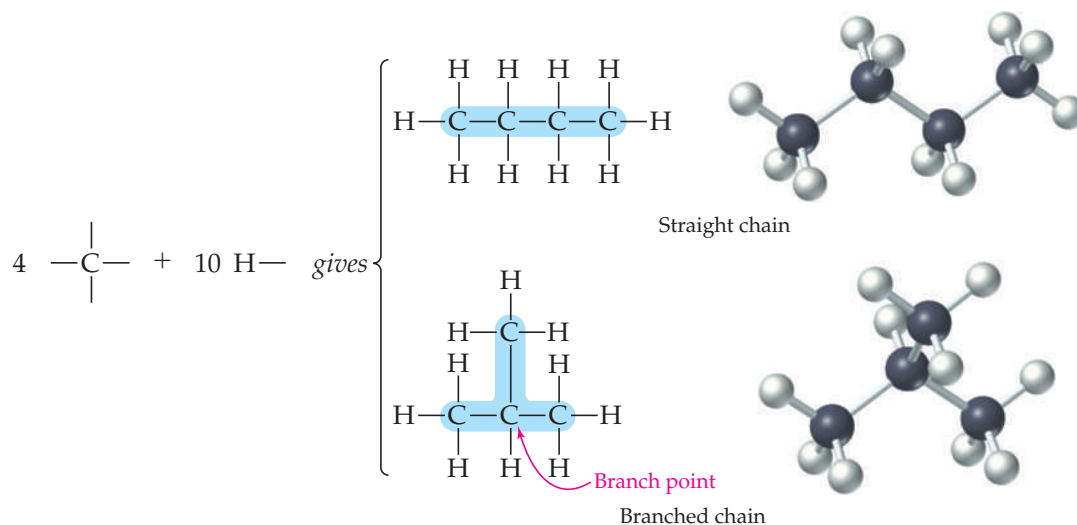
Hydrocarbons that contain only single bonds belong to the family of organic molecules called **alkanes**. Alkanes are most commonly found and used as fuels; the tank of gas found on a backyard barbecue is usually the hydrocarbon propane. Imagine how 1 carbon and 4 hydrogens can combine, and you will realize there is only one possibility: methane,  $\text{CH}_4$ . Now, imagine how 2 carbons and 6 hydrogens can combine—only ethane,  $\text{CH}_3\text{CH}_3$ , is possible. Likewise, with the combination of 3 carbons with 8 hydrogens—only propane,  $\text{CH}_3\text{CH}_2\text{CH}_3$ , is possible. The general rule for *all* hydrocarbons except methane is that each carbon *must* be bonded to at least one other carbon. The carbon atoms bond together to form the "backbone" of the compound, with the hydrogens on the periphery. The general formula for alkanes is  $\text{C}_n\text{H}_{2n+2}$ , where  $n$  is the number of carbons in the compound.

**Alkane** A hydrocarbon that has only single bonds.

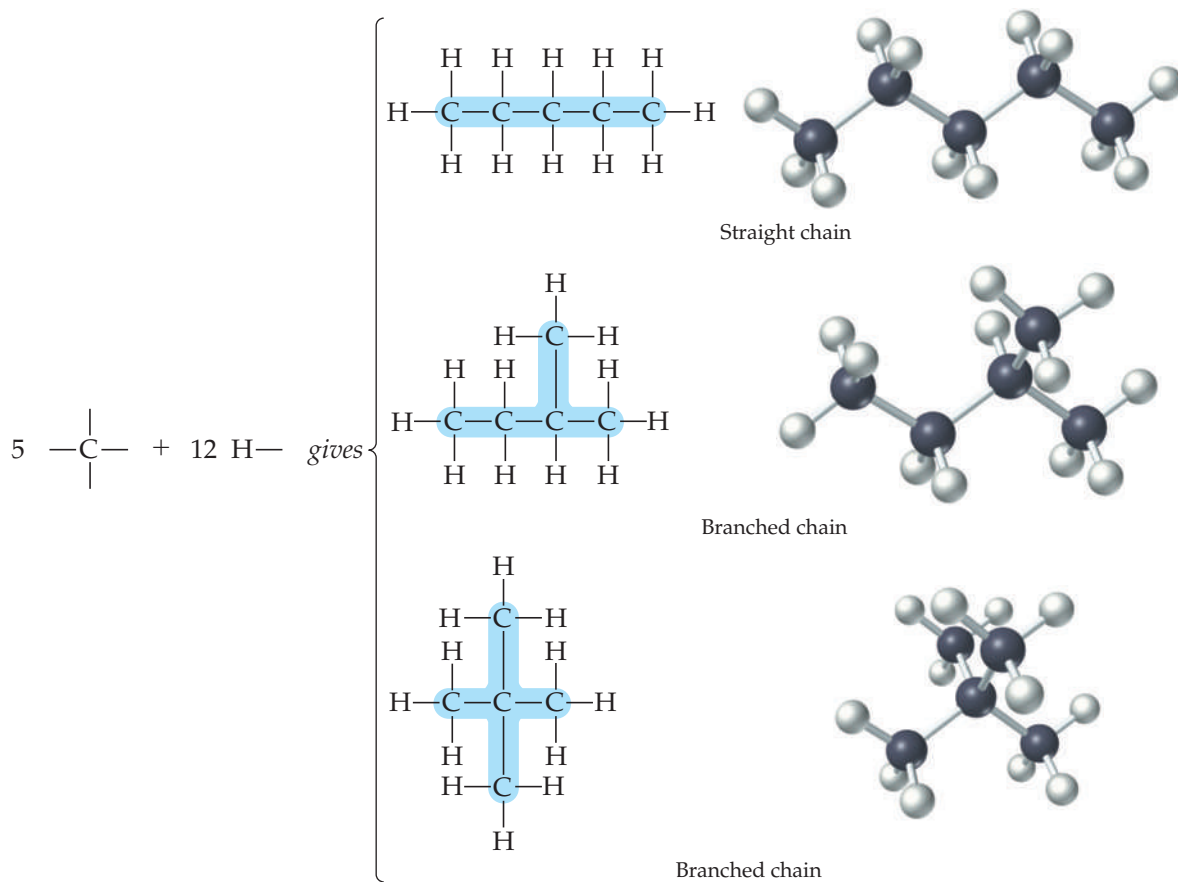


**Isomers** Compounds with the same molecular formula but different structures.

In alkanes, as the number of carbons becomes greater than three, the ability to form *isomers* arises. Compounds that have the same molecular formula but different structural formulas are called **isomers** of one another. For example, there are two ways in which molecules that have the formula  $C_4H_{10}$  can be formed. The 4 carbons can either be joined in a continuous row or have a branched arrangement:



The same is seen with the molecules that have the formula  $C_5H_{12}$ , for which three isomers are possible.



Compounds with all their carbons connected in a continuous chain are called **straight-chain alkanes**; those with a branching connection of carbons are called **branched-chain alkanes**. Note that in a straight-chain alkane, you can draw a line through all the carbon atoms without lifting your pencil from the paper. In a branched-chain alkane, however, you must either lift your pencil from the paper or retrace your steps to draw a line through all the carbons.

The two isomers of  $C_4H_{10}$  and the three isomers of  $C_5H_{12}$  shown above are **constitutional (or structural) isomers**—compounds with the same molecular formula but with different connections among their constituent atoms. Needless to say, the number of possible alkane isomers grows rapidly as the number of carbon atoms increases.

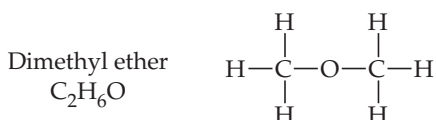
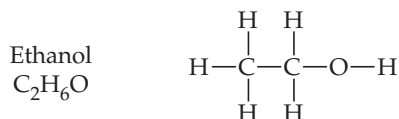
Constitutional isomers of a given molecular formula are chemically distinct from one another. They have different structures, physical properties (such as melting and boiling points), and potentially different physiological properties. When the molecular formula contains atoms other than carbon and hydrogen, the constitutional isomers obtained can also be **functional group isomers**: isomers that differ in both molecular connection and family classification. In these cases, the differences between isomers can be dramatic. For example, ethanol and dimethyl ether both have the formula  $C_2H_6O$ , but ethanol is a liquid with a boiling point of  $78.5^\circ\text{C}$  ( $351.5\text{ K}$ ) and dimethyl ether is a gas with a boiling point of  $23^\circ\text{C}$  ( $296\text{ K}$ ). While ethanol is a depressant of the central nervous system, dimethyl ether is a nontoxic compound with anesthetic properties at high concentrations. Clearly, molecular formulas by themselves are not very useful in organic chemistry; knowledge of structures is also necessary.

**Straight-chain alkane** An alkane that has all its carbons connected in a row.

**Branched-chain alkane** An alkane that has a branching connection of carbons.

**Constitutional isomers** Compounds with the same molecular formula but different connections among their atoms. Also known as structural isomers.

**Functional group isomer** Isomers having the same chemical formula but belonging to different chemical families due to differences in bonding; ethanol and dimethyl ether are examples of functional group isomers.



### Worked Example 12.3 Molecular Structures: Drawing Isomers

Draw all isomers that have the formula  $C_6H_{14}$ .

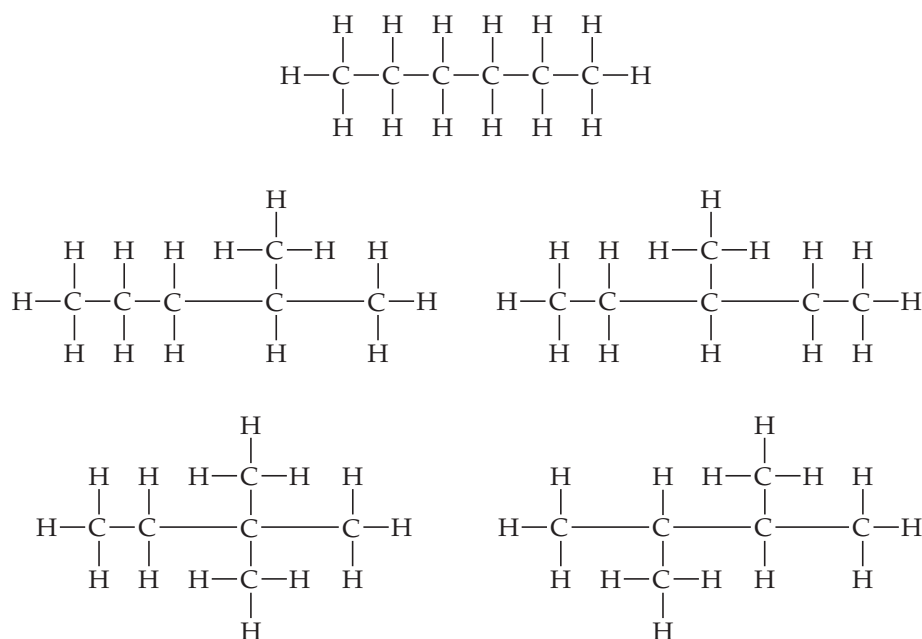
**ANALYSIS** Knowing that all the carbons must be bonded together to form the molecule, find all possible arrangements of the 6 carbon atoms. Begin with the isomer that has all 6 carbons in a straight chain, then draw the isomer that has 5 carbons in a straight chain, using the remaining carbon to form a branch, then repeat for the isomer having 4 carbons in a straight chain and 2 carbons in branches. Once each carbon backbone is drawn, arrange the hydrogens around the carbons to complete the structure. (Remember that each carbon can only have *four* bonds total.)

#### SOLUTION

The straight-chain isomer contains all 6 carbons bonded to form a chain with no branches. The branched isomers are drawn by starting with either a 5-carbon chain or a 4-carbon chain and by adding the extra carbons as branches in the middle of the chain. Hydrogens are added until each carbon has a full complement of four bonds.

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**PROBLEM 12.3**

Draw the straight-chain isomer with the formula (a)  $C_7H_{16}$  and (b)  $C_9H_{20}$ .

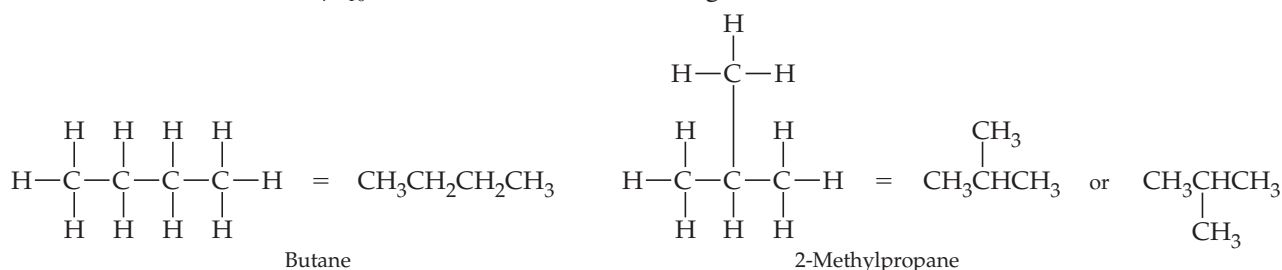
**PROBLEM 12.4**

There are two branched-chain isomers with the formula  $C_7H_{16}$ , where the longest chain in the molecule is six carbons long. Draw them.

**12.4 Drawing Organic Structures****Learning Objectives:**

- Draw structural, condensed, and line formulas for simple chemical compounds.
- Convert any given structural, condensed, or line formula into its corresponding alternative.

Drawing structural formulas that show every atom and every bond in a molecule is both time-consuming and awkward, even for relatively small molecules. Much easier is the use of **condensed structures**, which are simpler but still show the essential information about which functional groups are present and how atoms are connected. In condensed structures,  $C-C$  and  $C-H$  single bonds are not necessarily shown; rather, they are “understood.” If a carbon atom has three hydrogens bonded to it, we write  $CH_3$  (or  $H_3C$  if needed; this is only done in special cases); if the carbon has two hydrogens bonded to it, we write  $CH_2$ ; and so on. For example, the 4-carbon, straight-chain alkane called butane and its branched-chain isomer (2-methylpropane), both of which have the formula  $C_4H_{10}$  can be written as the following condensed structures:



Structural formula

Condensed formula

Structural formula

Condensed formula



Note in these condensed structures for butane and 2-methylpropane that the bonds between carbons are not usually shown—the  $\text{CH}_3$  and  $\text{CH}_2$  units are simply placed next to one another—but that the branch in the 2-methylpropane isomer *is* shown for clarity. It does not matter whether the branch is drawn above or below the main chain.

Occasionally, as a further simplification, not all the  $\text{CH}_2$  groups (called **methylene**s) are shown. Instead,  $\text{CH}_2$  is shown once in parentheses, with a subscript indicating the number of methylene units strung together. For example, the 6-carbon straight-chain alkane (hexane) can be written as:



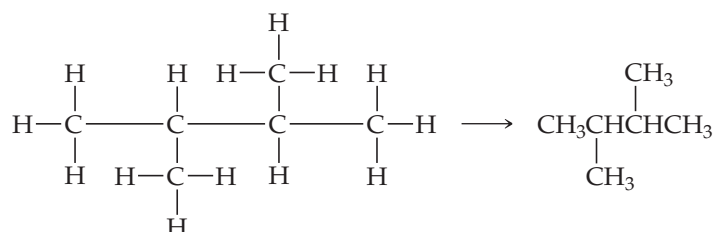
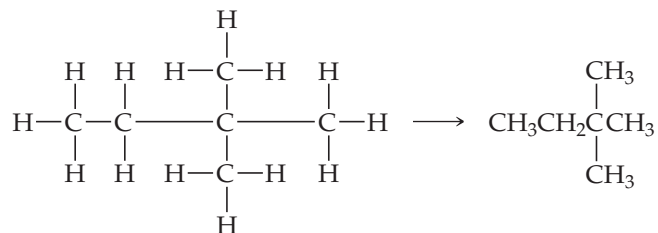
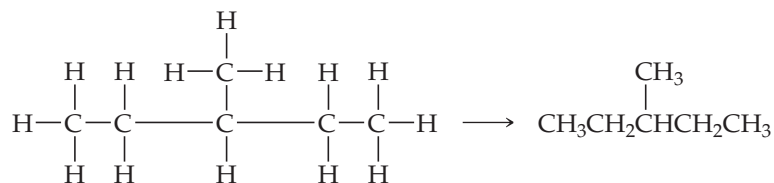
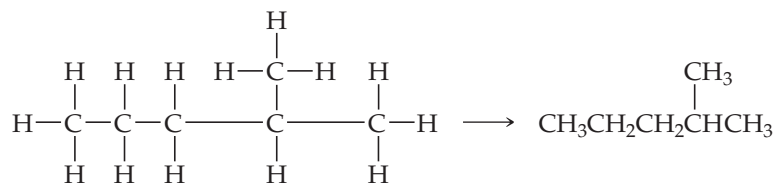
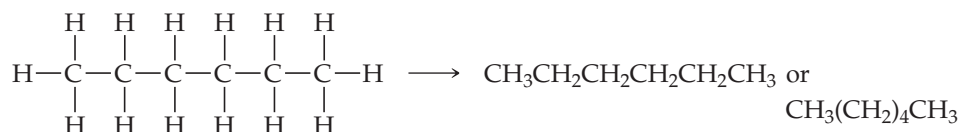
**Methylene** Another name for a  $\text{CH}_2$  unit.

### Worked Example 12.4 Molecular Structures: Writing Condensed Structures

Write condensed structures for the isomers from Worked Example 12.3.

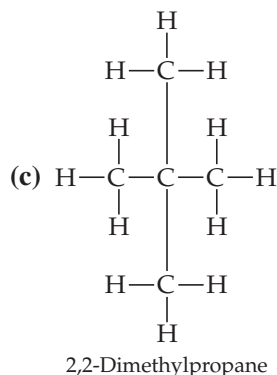
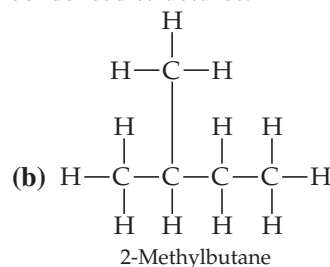
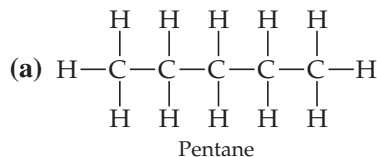
**ANALYSIS** Eliminate all horizontal bonds, substituting reduced formula components ( $\text{CH}_3$ ,  $\text{CH}_2$ , and so on) for each carbon in the compound. Show bonds in branched isomers for clarity.

#### SOLUTION



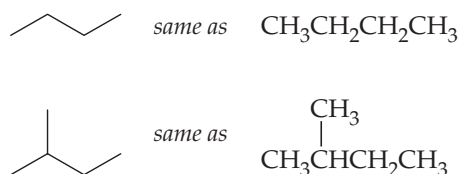
## PROBLEM 12.5

Draw the following three isomers of  $C_5H_{12}$  as condensed structures:



**Line structure** Also known as line-angle structure; a shorthand way of drawing structures in which carbon and hydrogen atoms are not explicitly shown. Instead, a carbon atom is understood to be wherever a line begins or ends and at every intersection of two lines, and hydrogens are understood to be wherever they are needed to have each carbon form four bonds.

Another way of representing organic molecules is to use **line (or line-angle) structures**, which are structures in which the symbols C and H do not appear. Instead, a chain of carbon atoms and their associated hydrogens are represented by a zigzag arrangement of short lines, with any branches off the main chain represented by additional lines. The line structure for butane and its branched-chain isomer 2-methylbutane, for instance, is

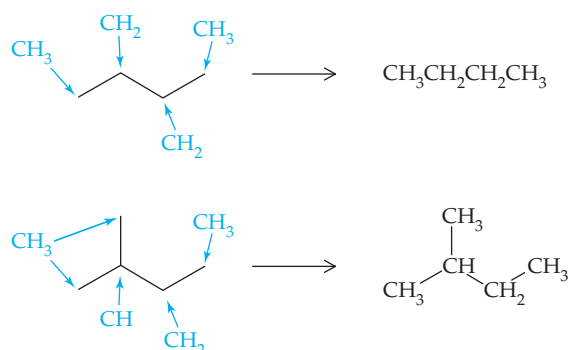


Line structures are a simple and quick way to represent organic molecules without showing all carbons and hydrogens present. Chemists, biologists, pharmacists, doctors, and nurses all use line structures to conveniently convey to one another very complex organic structures. Another advantage is that a line structure gives a more realistic depiction of the angles seen in a carbon chain.

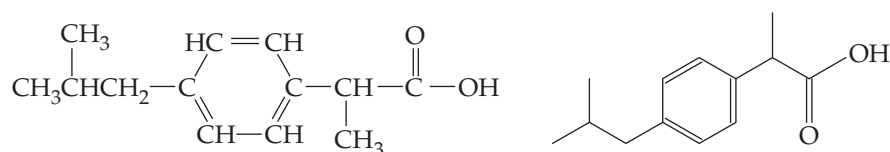
Drawing a molecule in this way is simple, provided one follows these guidelines:

1. Each carbon-carbon bond is represented by a line.
2. Anywhere a line ends or begins, as well as any vertex where two lines meet, represents a carbon atom.
3. Any atom other than another carbon or a hydrogen attached to a carbon must be shown.
4. Since a neutral carbon atom forms four bonds, all bonds not shown for any carbon are understood to be the number of carbon-hydrogen bonds needed to have

the carbon form four bonds. Only bonds between two carbons (or carbon and an element other than hydrogen) are shown.



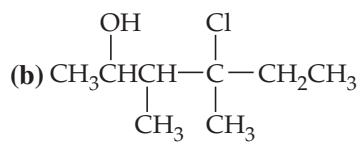
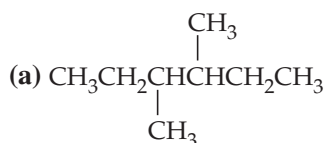
Converting line structures to structural formulas or to condensed structures is simply a matter of correctly interpreting each line ending and each intersection in a line structure. For example, the common pain reliever ibuprofen has the condensed and line structures



Finally, it is important to note that chemists and biochemists often use a mixture of structural formulas, condensed structures, and line structures to represent the molecules they study. As you progress through this textbook, you will see many complicated molecules represented in this way, so it is a good idea to get used to thinking interchangeably in all three formats.

### Worked Example 12.5 Molecular Structures: Converting Condensed Structures to Line Structures

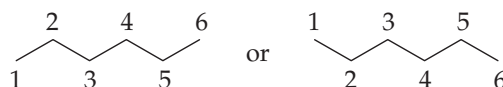
Convert the following condensed structures to line structures:



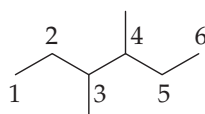
**ANALYSIS** Find the longest continuous chain of carbon atoms in the condensed structure. Begin the line structure by drawing a zigzag line in which the number of vertices plus line ends equals the number of carbon atoms in the chain. Show branches coming off the main chain by drawing vertical lines at the vertices as needed. Show all atoms that are not carbons or are not hydrogens attached to carbons.

#### SOLUTION

(a) Begin by drawing a zigzag line in which the total number of ends + vertices equals the number of carbons in the longest chain (here six, with the carbons numbered for clarity):



Looking at the condensed structure, you see  $\text{CH}_3$  groups on carbons 3 and 4; these two  $\text{CH}_3$  groups (methyl groups) are represented by lines coming off those carbons in the line structure:

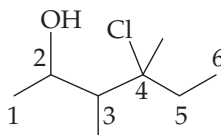


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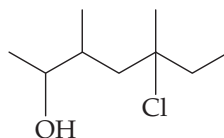
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This is the complete line structure. Notice that the hydrogens are not shown but understood. For example, carbon 4 has three bonds shown: one to carbon 3, one to carbon 5, and one to the branch  $\text{CH}_3$  group; the fourth bond this carbon must have is understood to be to a hydrogen.

- (b) Proceed as in (a), drawing a zigzag line for the longest chain of carbon atoms, which again contains 6 carbons. Next draw a line coming off each carbon bonded to a  $\text{CH}_3$  group (carbons 3 and 4). Both the OH and the Cl groups must be shown to give the final structure:

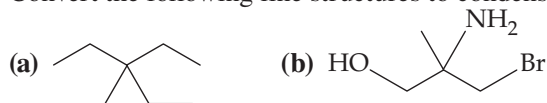


Note from this line structure that it does not matter in such a two-dimensional drawing what direction you show for a group that branches off the main chain, as long as it is attached to the correct carbon. This is true for condensed structures as well. Quite often, the direction that a group is shown coming off a main chain of carbon atoms is chosen simply for aesthetic reasons. The line structure can also be shown this way:



## Worked Example 12.6 Molecular Structures: Converting Line Structures to Condensed Structures

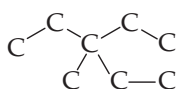
Convert the following line structures to condensed structures:



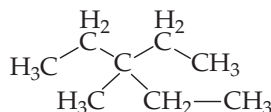
**ANALYSIS** Convert all vertices and line ends to carbons. Write in any noncarbon atoms and any hydrogens bonded to a noncarbon atom. Add hydrogens as needed so that each carbon has four groups attached. Remove lines connecting carbons except for branches.

### SOLUTION

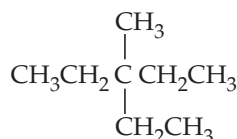
- (a) Anywhere a line ends and anywhere two lines meet, write a C:



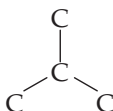
Because there are no atoms other than carbons and hydrogens in this molecule, the next step is to add hydrogens as needed to have four bonds for each carbon:



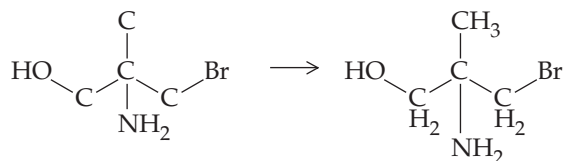
Finally, eliminate all lines except for branches to get the condensed structure:



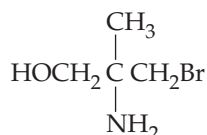
- (b) Begin the condensed structure with a drawing showing a carbon at each line end and at each intersection of two lines:



Next, write in all the noncarbon atoms and the hydrogen bonded to the oxygen. Then, add hydrogens so that each carbon forms four bonds:

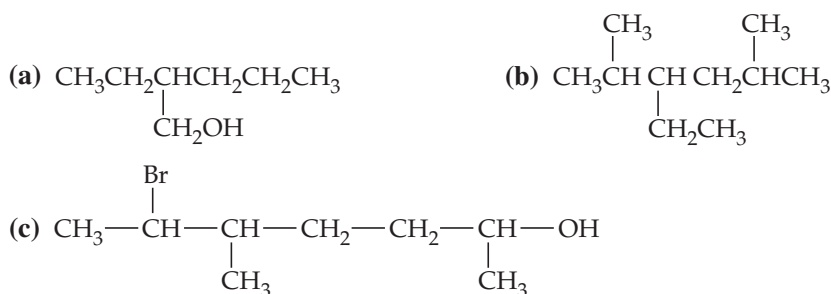


Eliminate all lines except for branches for the completed condensed structure:



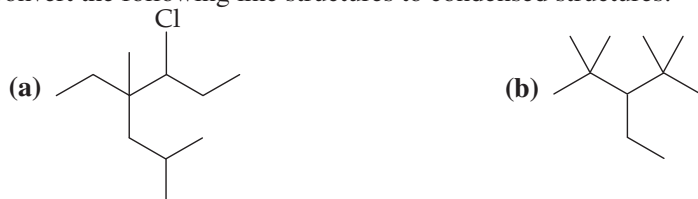
### PROBLEM 12.6

Convert the following condensed structures to line structures:



### PROBLEM 12.7

Convert the following line structures to condensed structures:



### PROBLEM 12.8

Draw both condensed and line structures for the chemicals listed in Problem 12.1.

## 12.5 The Shapes of Organic Molecules

### Learning Objective:

- Determine if two given structures are the different conformers of the same molecule, different structural isomers, or different molecules.

Every carbon atom in an alkane has its four bonds pointing toward the four corners of a tetrahedron, but chemists do not usually worry about three-dimensional shapes when writing condensed structures. Condensed structures do not imply any particular three-dimensional shape; they only indicate the connections between atoms without specifying geometry. Line structures do try to give some limited feeling for the shape of a molecule, but even here, the ability to show three-dimensional shape is limited unless dashed and wedged lines are used for the bonds (Sections 4.8 and 14.10).

Butane, for example, has no one single shape because *rotation* takes place around carbon–carbon single bonds. The two parts of a molecule joined by a carbon–carbon



**Conformation** The specific three-dimensional arrangement of atoms in a molecule achieved specifically through rotations around carbon–carbon single bonds.

**Conformer** Molecular structures having identical connections between atoms where the interconversion of C—C bond rotations results only in a different spatial arrangement of atoms.

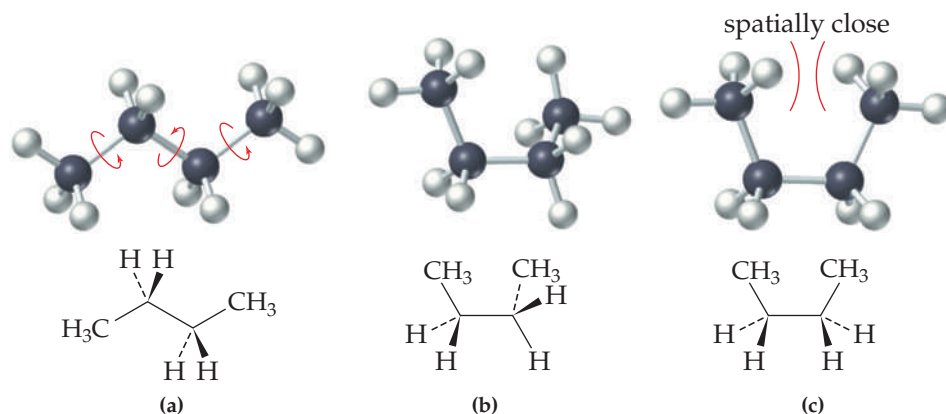
▶ In Section 14.10, we will see how the three dimensional structure of some organic molecules can lead to enantiomers (isomers that are nonsuperimposable mirror images of one another), an important property of many biologically active molecules.

► Figure 12.2

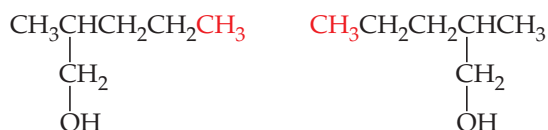
**Some conformations of butane (there are many others as well).**

The least crowded, extended conformation in (a) is the lowest-energy one, whereas the eclipsed conformation shown in (c), where the two CH<sub>3</sub> groups are spatially on top of one another, is the highest-energy one. In this drawing, those bonds shown with a wedge are coming out of the plane of the paper toward the reader, whereas those with a dash are going out of the plane, away from the reader.

single bond in a noncyclic structure (like butane) are free to spin around the bond, giving rise to an infinite number of possible three-dimensional geometries, or **conformations**. The various conformations of a molecule such as butane are called **conformers** of one another. Conformers differ from one another as a result of rotation around carbon–carbon single bonds. Although the conformers of a given molecule have different three-dimensional shapes (due to the bond angles in the molecule) and different energies (due to how groups are oriented with respect to one another), the conformers cannot be separated from one another. A given butane molecule might be in its fully extended conformation at one instant but in a more twisted conformation an instant later (Figure 12.2). An actual sample of butane contains a great many molecules that are constantly changing conformation. Some of these conformations have the groups staggered with respect to each other (Figure 12.2a and 12.2b), whereas some have all groups eclipsing one another (Figure 12.2c). Because molecules do have a three-dimensional shape and because atoms do occupy space, a more crowded conformer, where groups larger than H are near one another (Figure 12.2b), will have higher energy than the least crowded conformer, where the large groups are as far apart as possible (Figure 12.2a). Those conformers where groups on adjacent atoms are eclipsed will have the highest energy of all due to what is known as steric crowding. At any given instant, however, most of the molecules have the least crowded, lowest-energy extended conformation shown in Figure 12.2a. The same is true for all other alkanes: At any given instant, most molecules are in the least crowded conformation.



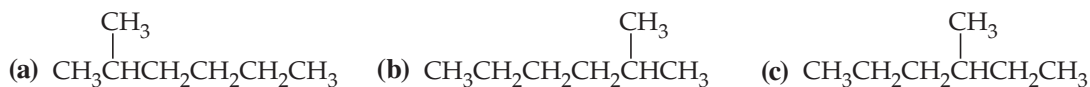
As long as any two structures have identical connections between atoms and are interconvertible either by “flipping” the molecule or by rotating C—C bonds, they are conformers of each other and represent the same compound, no matter how the structures are drawn. It is important to remember that no bonds are broken and reformed when interconverting conformers. Sometimes, you have to mentally rotate structures to see whether they are conformers or actually different molecules. To see that the following two structures represent conformers of the same compound rather than two isomers, picture one of them flipped right to left so that the red CH<sub>3</sub> groups are on the same side.



Another way to determine whether two structures are conformers is to name each one using the International Union of Pure and Applied Chemistry (IUPAC) nomenclature rules (Section 12.6). If two structures have the same name, they are conformers of the same compound.

**Worked Example 12.7** Molecular Structures: Identifying Conformers

The following structures all have the formula  $C_7H_{16}$ . Which of them represent the same molecule?



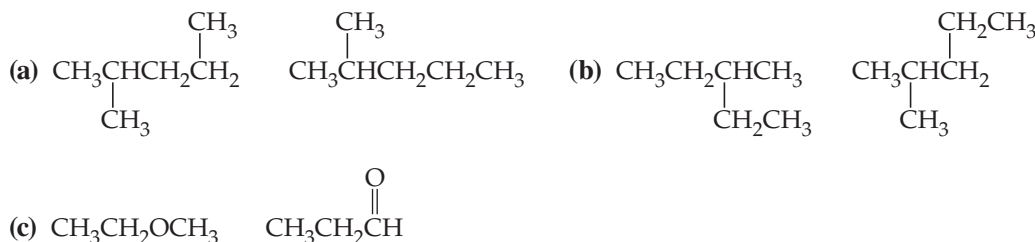
**ANALYSIS** Pay attention to the *connections* between atoms. Do not get confused by the apparent differences caused by writing a structure right to left versus left to right. Begin by identifying the longest chain of carbon atoms in the molecule.

**SOLUTION**

Molecule (a) has a straight chain of six carbons with a  $-\text{CH}_3$  branch on the second carbon from the end. Molecule (b) also has a straight chain of six carbons with a  $-\text{CH}_3$  branch on the second carbon from the end and is therefore identical to (a). That is, (a) and (b) are conformers of the same molecule. The only difference between (a) and (b) is that one is written “forward” and one is written “backward.” Molecule (c), by contrast, has a straight chain of 6 carbons with a  $-\text{CH}_3$  branch on the *third* carbon from the end and is, therefore, an isomer of (a) and (b).

**Worked Example 12.8** Molecular Structures: Identifying Conformers and Isomers

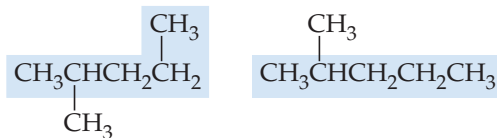
Are the following pairs of compounds the same (conformers), isomers, or unrelated?



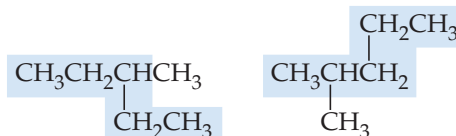
**ANALYSIS** First compare molecular formulas to see if the compounds are related, and then look at the structures to see if they are the same compound or isomers. Find the longest continuous carbon chain in each, and then compare the locations of the substituents connected to the longest chain.

**SOLUTION**

(a) Both compounds have the same molecular formula ( $C_6H_{14}$ ), so they are related. Since the  $-\text{CH}_3$  group is on the second carbon from the end of a 5-carbon chain in both cases, these structures represent the same compound and are conformers of each other.



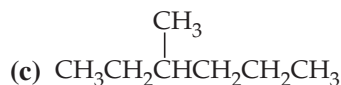
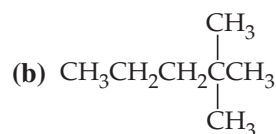
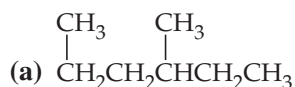
(b) Both compounds have the same molecular formula ( $C_6H_{14}$ ), and the longest chain in each is 5 carbon atoms. A comparison shows, however, that the  $-\text{CH}_3$  group is on the middle carbon atom in one structure and on the second carbon atom in the other. These compounds are isomers of each other.



(c) These compounds have different formulas ( $C_3H_8O$  and  $C_3H_6O$ ), so they are unrelated; they are neither conformers nor isomers of each other.

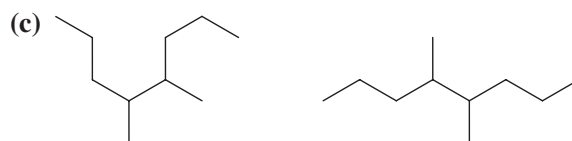
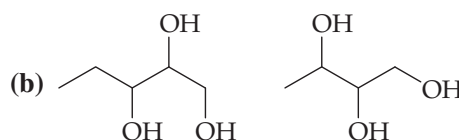
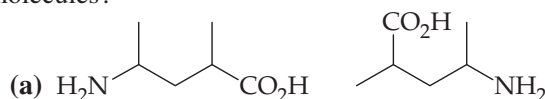
## PROBLEM 12.9

Which of the following structures represent the same molecule?



## PROBLEM 12.10

Are the pairs of compounds shown below the same molecule, isomers, or different molecules?



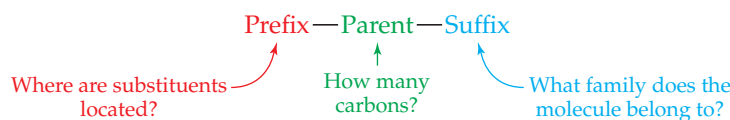
## 12.6 Naming Alkanes

## Learning Objective:

- Name an alkane given its structure and draw an alkane given its name.

When relatively few pure organic chemicals were known, new compounds were named at the whim of their discoverer. Thus, urea is a crystalline substance first isolated from urine, and the barbiturates were named by their discoverer in honor of his friend Barbara. As more and more compounds became known, however, the need for a systematic method of naming compounds became apparent.

The system of naming (*nomenclature*) now used is one devised by IUPAC (pronounced *eye-you-pack*). In the IUPAC system for simple organic compounds, a chemical name has three parts: *prefix*, *parent*, and *suffix*. The prefix specifies the location of functional groups and other **substituents** in the molecule; the parent tells how many carbon atoms are present in the longest continuous chain; and the suffix identifies what family the molecule belongs to.



Straight-chain alkanes are named by counting the number of carbon atoms and adding the family suffix *-ane*. With the exception of the first four compounds—*methane*, *ethane*, *propane*, and *butane*—whose parent names have historical origins, the alkanes are named from Greek numbers according to the number of carbons present (Table 12.2). Thus, *pentane* is the 5-carbon alkane, *hexane* is the 6-carbon alkane, and so on. Straight-chain alkanes have no substituents, so prefixes are not needed. The first 10 alkane names are so common that they should be memorized.

Substituents, such as  $-\text{CH}_3$  and  $-\text{CH}_2\text{CH}_3$ , that branch off the main chain are called **alkyl groups**. An alkyl group can be thought of as the part of an alkane that

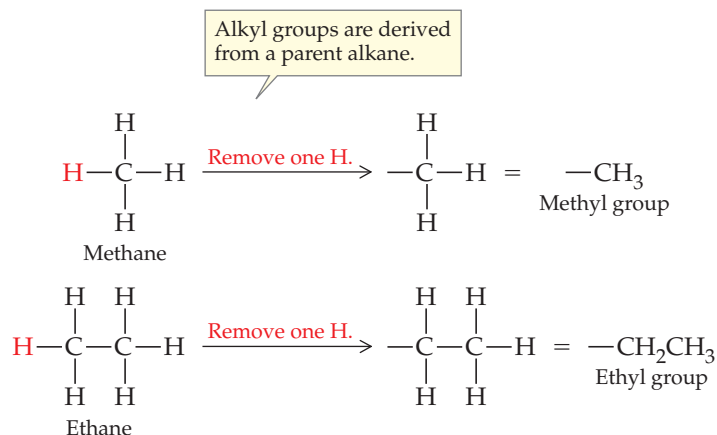
**Substituent** An atom or group of atoms attached to a parent compound.

**Alkyl group** The part of an alkane that remains when a hydrogen atom is removed.

**Table 12.2** Names of Straight-Chain Alkanes

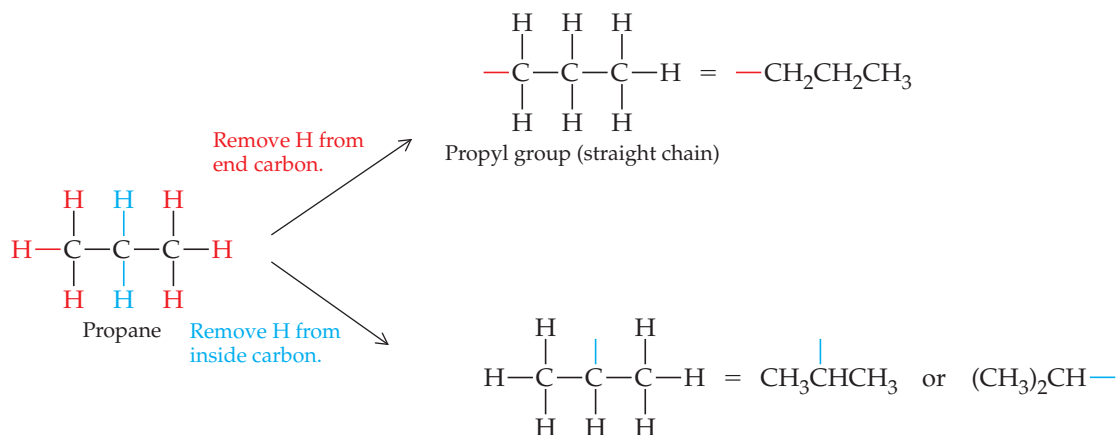
Number of Carbons	Structure	Name
1	CH <sub>4</sub>	Methane
2	CH <sub>3</sub> CH <sub>3</sub>	Ethane
3	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	Propane
4	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Butane
5	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Pentane
6	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Hexane
7	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Heptane
8	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Octane
9	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Nonane
10	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Decane

remains when one hydrogen atom is removed to create an available bonding site. For example, removal of a hydrogen from methane, CH<sub>4</sub>, gives the **methyl group**, —CH<sub>3</sub>, and removal of a hydrogen from ethane, CH<sub>3</sub>CH<sub>3</sub>, gives the **ethyl group**, —CH<sub>2</sub>CH<sub>3</sub>. Notice that these alkyl groups are named simply by replacing the *-ane* ending of the parent alkane with an *-yl* ending:



Both methane and ethane have only one “kind” of hydrogen. It does not matter which of the four methane hydrogens is removed, so there is only one possible methyl group. Similarly, it does not matter which of the six equivalent ethane hydrogens is removed, so only one ethyl group is possible.

The situation is more complex for larger alkanes, which contain more than one kind of hydrogen. Propane, for example, has two different kinds of hydrogens. Removal of any one of the 6 hydrogens attached to an end carbon yields a straight-chain alkyl group called **propyl**, whereas removal of either one of the two hydrogens attached to the central carbon yields a branched-chain alkyl group called **isopropyl**:



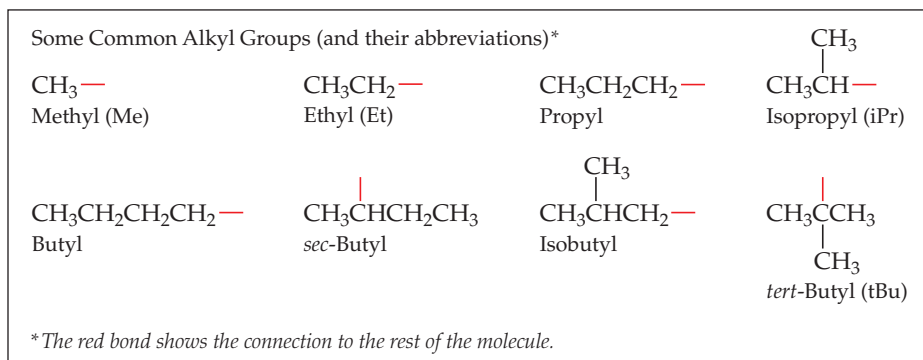
**Methyl group** The —CH<sub>3</sub> alkyl group.

**Ethyl group** The —CH<sub>2</sub>CH<sub>3</sub> alkyl group.

**Propyl group** The straight-chain alkyl group —CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>.

**Isopropyl group** The branched-chain alkyl group —CH(CH<sub>3</sub>)<sub>2</sub>.

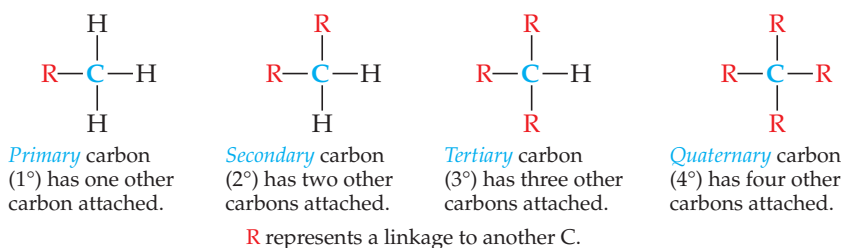
It is important to realize that alkyl groups are not compounds but rather are simply partial structures that help us name compounds. The names of some common alkyl groups are listed in Figure 12.3; you will want to commit them to memory.



▲ Figure 12.3

The most common alkyl groups found in organic molecules are shown here; the red bond shows the attachment the group has to the rest of the molecule.\*

There are four possible substitution patterns for carbons attached to four atoms and these are designated *primary*, *secondary*, *tertiary*, and *quaternary*. It is important to note that these designations strictly apply to carbons having only single bonds. Notice that four butyl (4-carbon) groups are listed in Figure 12.3: butyl, *sec*-butyl, isobutyl, and *tert*-butyl. The prefix *iso* stands for isomer, and was introduced to distinguish an alkyl group that was attached through a primary carbon, but was branched rather than an unbranched chain. The prefix *sec*- stands for *secondary* (since the attachment point of the alkyl group is via a secondary carbon), and the prefix *tert*- stands for *tertiary*, as the attachment point is a tertiary carbon. A **primary (1°) carbon atom** has one other carbon attached to it (typically indicated as an —R group in the molecular structure), a **secondary (2°) carbon atom** has two other carbons attached, a **tertiary (3°) carbon atom** has three other carbons attached, and a **quaternary (4°) carbon atom** has four other carbons attached:



Organic chemists use the abbreviation R to represent an unspecified group where the direct attachment to the atom under discussion is a carbon; it could be as simple as a CH<sub>3</sub>, or as complicated as you could ever imagine! It is used so chemists can focus on a particular group of interest (a functional group, or a specific carbon atom) without the clutter of the rest of the molecule, and allows for more general discussions of reactivity. It is common that when abbreviations are used, some qualifier be placed on them (e.g., R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>).

Table 12.3 contains a list of the most common abbreviations you will see in this text. We will keep the use of these to a minimum; you should only use them yourself if your instructor approves. The use of abbreviations can greatly simplify discussions of reactions; for example, the generalized formula for an alcohol might refer to an

**Primary (1°) carbon atom** A carbon atom with one other carbon attached to it.

**Secondary (2°) carbon atom** A carbon atom with two other carbons attached to it.

**Tertiary (3°) carbon atom** A carbon atom with three other carbons attached to it.

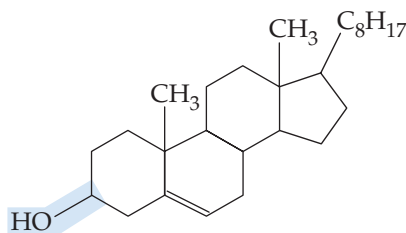
**Quaternary (4°) carbon atom** A carbon atom with four other carbons attached to it.



**Table 12.3** Common Abbreviations in Organic Chemistry

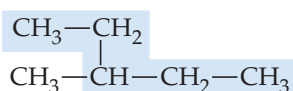
<b>R</b>	Residue or Rest of the molecule; used to represent the part of the organic molecule <i>not</i> under consideration for the current discussion. Does not contain functional groups that can also react under the conditions being examined. Usually means a carbon group but can generally be anything.
<b>R', R'', R'''</b>	Prime notation; used when different R groups are needed. Read as “R-prime”, “R-double prime”, etc.
<b>X</b>	A polar group; usually reserved to represent a halogen. Almost always used to represent a “leaving group”: An atom or group that can leave in either its anionic or neutral form.
<b>Y or Z</b>	Also a polar group; used when different polar groups are present. Usually used to indicate a group attached via an O or S atom. Infrequently used.
<b>M</b>	A metal or metal ion; used primarily when the exact identity of the metal is not crucial to the discussion. Typically a Na or K.
<b>Ar</b>	An aromatic group (“Aryl”); a more specific <b>R</b> group. Typically used when its presence imparts special properties on the C to which it is attached. The most common is a phenyl group (Chapter 13).
<b>Ph</b>	A phenyl group ( $-\text{C}_6\text{H}_5$ ; Chapter 13); a benzene ring with a single group attached.

alcohol as simple as  $\text{CH}_3\text{OH}$  or  $\text{CH}_3\text{CH}_2\text{OH}$  or one as complicated as cholesterol, shown here:



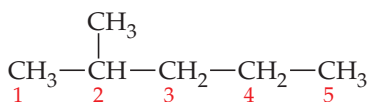
Branched-chain alkanes can be named by following four steps:

**STEP 1: Name the main chain.** Find the longest continuous chain of carbons, and name the chain according to the number of carbon atoms it contains. The longest chain may not be immediately obvious because it is not always written on one line; you may have to “turn corners” to find it.



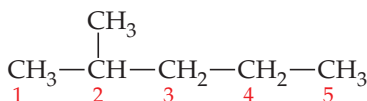
Name as a substituted pentane, not as a substituted butane, because the *longest* chain has five carbons.

**STEP 2: Number the carbon atoms in the main chain,** beginning at the end nearer the first branch point.



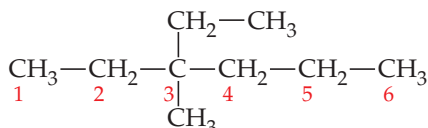
The first (and only) branch occurs at C2 if we start numbering from the left, but would occur at C4 if we started from the right by mistake.

**STEP 3: Identify the branching substituents, and number each** according to its point of attachment to the main chain.



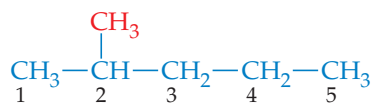
The main chain is a pentane. There is one methyl ( $-\text{CH}_3$ ) substituent group connected to C2 of the chain.

If there are two substituents on the same carbon, assign the same number to both. There must always be as many numbers in the name as there are substituents.

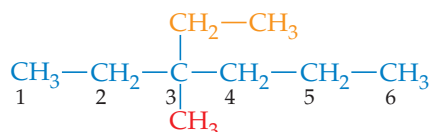


The main chain is a hexane. There are two substituents, a methyl ( $-\text{CH}_3$ ) and an ethyl ( $-\text{CH}_2\text{CH}_3$ ), both connected to C3 of the chain.

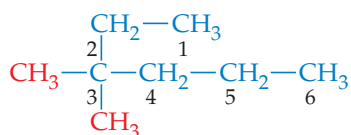
**STEP 4:** Write the name as a single word, using hyphens to separate the numbers from the different prefixes and commas to separate numbers, if necessary. If two or more different substituent groups are present, cite them in alphabetical order. If two or more identical substituents are present, use one of the prefixes *di-*, *tri-*, *tetra-*, and so forth, but do not use these prefixes for alphabetizing purposes.



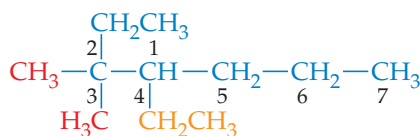
**2-Methylpentane** (a 5-carbon main chain with a 2-methyl substituent)



**3-Ethyl-3-methylhexane** (a 6-carbon main chain with 3-ethyl and 3-methyl substituents cited alphabetically)



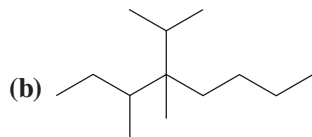
**3,3-Dimethylhexane** (a 6-carbon main chain with two 3-methyl substituents)



**4-Ethyl-3,3-dimethylheptane** (a 7-carbon main chain with two 3-methyl substituents and one 4-ethyl substituent, cited alphabetically based on the group, not the prefix (di)).

### Worked Example 12.9 Naming Organic Compounds: Alkanes

What is the IUPAC name of the following alkanes?

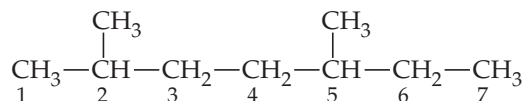


**ANALYSIS** Follow the four steps outlined in the text.

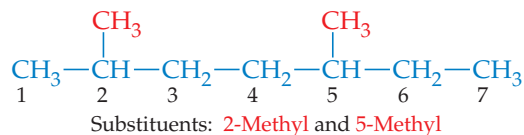
#### SOLUTION

(a) **STEP 1:** The longest continuous chain of carbon atoms is seven, so the main chain is a *heptane*.

**STEP 2:** Number the main chain beginning at the end nearer the first branch.



**STEP 3:** Identify and number the substituents (a 2-methyl and a 5-methyl in this case):

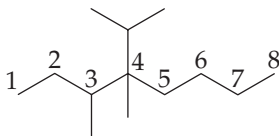


**STEP 4:** Write the name as one word, using the prefix *di-* because there are two methyl groups. Separate the two numbers by a comma, and use a hyphen between the numbers and the word.

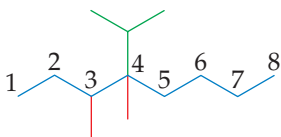
Name: 2, 5-Dimethylheptane

(b) **STEP 1:** The longest continuous chain of carbon atoms is eight, so the main chain is an *octane*.

**STEP 2:** Number the main chain beginning at the end nearer the first branch.



**STEP 3:** Identify and number the substituents.



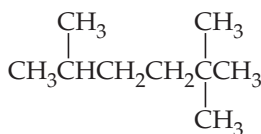
3-Methyl, 4-Methyl, 4-Isopropyl

**STEP 4:** Write the name as one word, again using the prefix *di-* because there are two methyl groups.

Name: 3, 4-Dimethyl-4-isopropyloctane

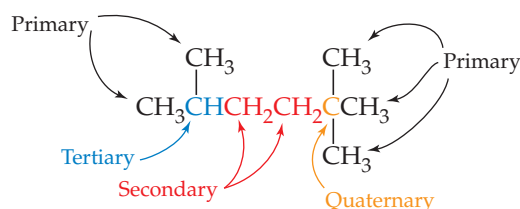
### Worked Example 12.10 Molecular Structure: Identifying 1°, 2°, 3°, and 4° Carbons

Identify each carbon atom in the following molecule as primary, secondary, tertiary, or quaternary.



**ANALYSIS** Look at each carbon atom in the molecule, count the number of other carbon atoms attached, and make the assignment accordingly: primary (1 carbon attached), secondary (2 carbons attached), tertiary (3 carbons attached), and quaternary (4 carbons attached).

#### SOLUTION



Note: Hydrogens, when attached to a carbon, are given the same primary, secondary, or tertiary designation as the C to which they are attached (and this is why they have been given the same color as their carbons in the figure above).

▶▶ We will see the primary, secondary, and tertiary classification used again when we study alcohols and alkyl halides in Chapter 14, as well as when we study amines in Chapter 16. For alcohols and alkyl halides, the classification will be identical to that used for hydrogens; this will change slightly when we discuss amines.

### Worked Example 12.11 Molecular Structures: Drawing Condensed Structures from Names

Draw condensed and line structures corresponding to the following IUPAC names:

- (a) 2,3-Dimethylpentane
- (b) 3-Ethylheptane
- (c) 4-*tert*-Butylheptane

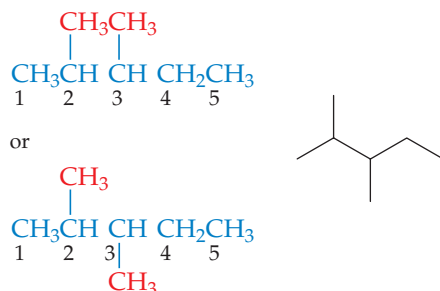
**ANALYSIS** Starting with the parent chain, add the named alkyl substituent groups to the appropriately numbered carbon atoms.

—continued on next page

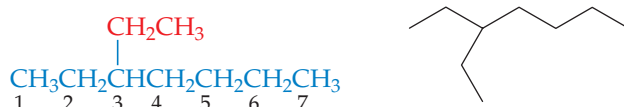
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**SOLUTION**

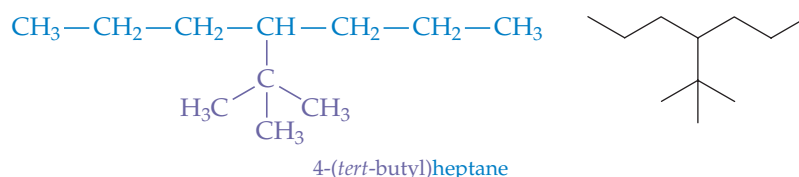
- (a) The parent chain has 5 carbons (*pentane*), with two methyl groups ( $-\text{CH}_3$ ) attached to the second and third carbon in the chain.



- (b) The parent chain has 7 carbons (*heptane*), with one ethyl group ( $-\text{CH}_2\text{CH}_3$ ) attached to the third carbon in the chain.



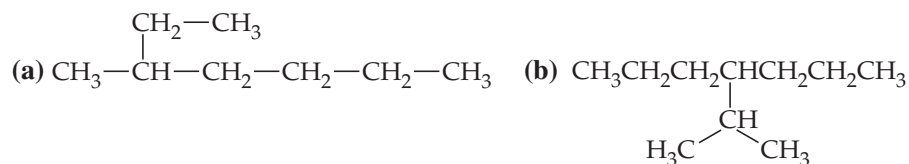
- (c) Again, the parent chain has 7 carbons (*heptane*), with one *tert*-butyl group ( $-\text{C}(\text{CH}_3)_3$ ) attached to the fourth carbon in the chain.

**PROBLEM 12.11**

Identify each carbon in the molecule shown in Worked Example 12.9b as primary, secondary, tertiary, or quaternary.

**PROBLEM 12.12**

What are the IUPAC names of the following alkanes?

**PROBLEM 12.13**

Draw both condensed and line structures corresponding to the following IUPAC names and label each carbon as primary, secondary, tertiary, or quaternary.

- (a) 3-Methylhexane      (b) 3,4-Dimethyloctane      (c) 2,2,4-Trimethylpentane

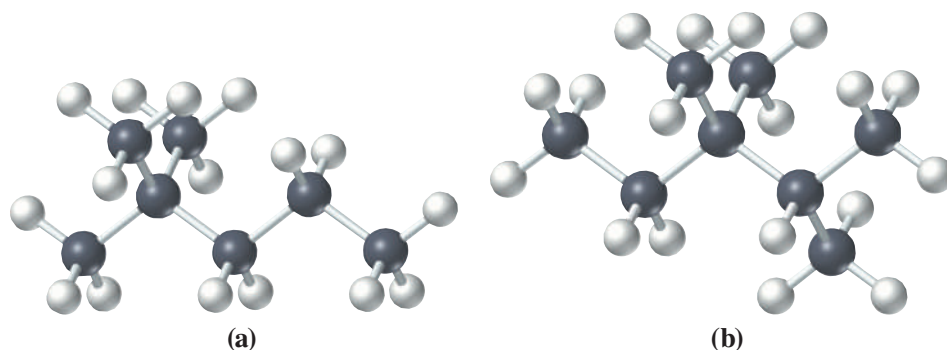
**PROBLEM 12.14**

Draw and name alkanes that meet the following descriptions:

- (a) A 5-carbon alkane with a tertiary carbon atom  
 (b) A 7-carbon alkane that has both a tertiary and a quaternary carbon atom

### KEY CONCEPT PROBLEM 12.15

What are the IUPAC names of the following alkanes?



## CHEMISTRY IN ACTION

### How Important Can a Methyl Group Really Be?

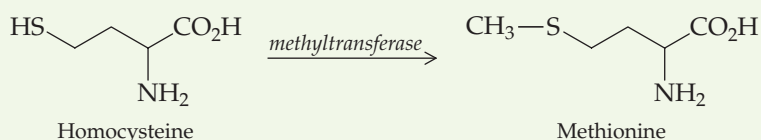
How does a living organism make a molecule as complex and beautiful as DNA (Chapter 26) or the neurotransmitters (Chapter 28) from simple starting points? Most complicated biomolecules are synthesized via an anabolic pathway (a biochemical pathway that creates molecules). Anabolic pathways will take a relatively simple starting material (usually obtained from food digestion) and convert it into the desired end product via a series of biochemical steps. Sometimes, however, this is not enough and what is known as a post synthetic modification must be carried out at the cellular level. Universally, one of the most important of these is methylation, the addition of a lowly  $\text{—CH}_3$  group to a nitrogen (N-methylation), an oxygen (O-methylation), or a sulfur (S-methylation). Addition of a simple methyl group can greatly change the function of molecules. Biological systems typically need assistance to carry out these molecular conversions, which is accomplished through the use of a class of enzyme known as methyltransferases (Section 19.3), many of which rely on the B vitamins as cofactors (Section 19.2). This highly controlled process is found in every cell in the body and is key to a number of processes, including the regulation of healing, cell energy, and expression of DNA. In fact, the efficiency of the process of biological methylation reduces with time and can cause a number of age-related disorders, including cardiovascular disease and even cancer. Consider homocysteine, a naturally occurring, nonprotein amino acid that is typically found in blood plasma when body chemistry is out of balance. Biologically, it forms from the amino acid methionine (Chapter 18) by loss of the methyl group from sulfur.

Homocysteine is a pro-oxidant and as such is poisonous to cells (cytotoxic). A pro-oxidant is a chemical that interferes with the way cells use or get rid of oxygen and other oxidizing species. One consequence of this is the buildup of the reactive oxygen species (radicals) that cause oxidative damage to the cell (as



▲ Blood analysis is an invaluable aid in the diagnosis of disease. For example, abnormal levels of homocysteine can indicate an increased risk of atherosclerosis.

as a note, the over-the-counter pain medication paracetamol [Tylenol] can also act as a pro-oxidant; overdoses of paracetamol can fatally damage the liver, where it is metabolized). High levels of homocysteine result in a number of disorders, including DNA strand breakage and an increase in the risk of heart disease. Normally, homocysteine has low circulating levels due to its rapid re-methylation to methionine. Deficiencies in the B vitamins B-12, B-6, and folic acid, the cofactors necessary for the methyltransferases to work, typically lead to high levels of homocysteine. The simple addition of a  $\text{—CH}_3$  methyl group to the sulfur of homocysteine can neutralize its cytotoxic behavior.



**CIA Problem 12.1** What is an anabolic pathway?

**CIA Problem 12.2** What does “cytotoxic” mean?

**CIA Problem 12.3** What cofactors are necessary for methyltransferases to work?



## 12.7 Properties of Alkanes

## Learning Objective:

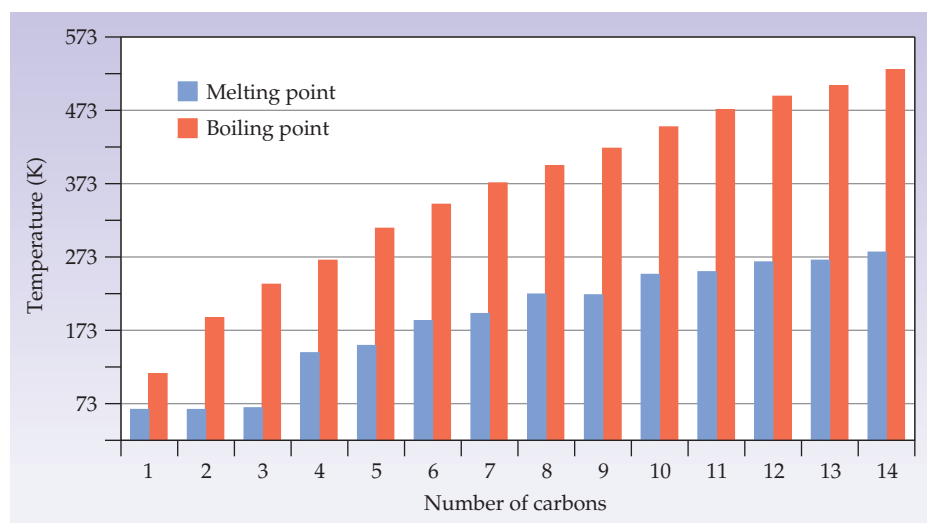
- Identify the physical properties of alkanes.

There are three major intermolecular forces that need to be considered when discussing the properties of organic molecules: dipole–dipole forces (attractions between the  $\delta^+$  and  $\delta^-$  ends of adjacent polar molecules; Section 8.2), hydrogen bonding (seen in molecules that contain N—H and O—H groups; Section 8.2), and London dispersion forces (due to instantaneous polarizations of a molecule's electron cloud, these are the only intermolecular forces available to nonpolar molecules; Section 8.2). Intermolecular forces are what cause molecules to aggregate or “stick” to one another; hydrogen bonds are the strongest, dipole–dipole forces follow in strength, and London dispersion forces are the weakest. Alkanes contain only nonpolar C—C and C—H bonds, so the only intermolecular forces influencing them are weak London dispersion forces. London dispersion forces increase both as molecules get bigger (due to an increase in the number of electrons within the molecule) and as their surface area increases. The effect of these forces is shown in the regularity with which the melting and boiling points of straight-chain alkanes increase with molecular size (Figure 12.4). The first four alkanes—methane, ethane, propane, and butane—are gases at room temperature and pressure. Alkanes with 5–15 carbon atoms are liquids; those with 16 or more carbon atoms are generally low-melting, waxy solids. Similar results are seen for branched alkanes; however, due to the ability of these to have more compact, spherical shapes, their melting and boiling points can be quite different from their straight-chain counterparts.

Review the effects of London dispersion forces on molecules in Section 8.2.

► **Figure 12.4**

The boiling and melting points for the straight-chain alkanes increase with molecular size.



Since they do not possess significant dipole moments, alkanes are nonpolar and as such are insoluble in polar solvents such as water but soluble in nonpolar organic solvents, such as pentane, hexane, and other alkanes (“like dissolves like”). Because of this aversion to water, alkanes are said to be hydrophobic (“water hating”). Because alkanes are generally less dense than water, they float on its surface. Low-molecular-mass alkanes are volatile and must be handled with care because their vapors are flammable. Mixtures of alkane vapors and air can explode when ignited by a single spark.

The physiological effects of alkanes are limited. Methane, ethane, and propane gases are nontoxic, but the danger of inhaling them lies in potential suffocation due to lack of oxygen. Breathing the vapor of larger alkanes in large concentrations can

Recall from Section 9.2 the rule of thumb when predicting solubility: “like dissolves like.”

induce loss of consciousness. There is also a danger in breathing droplets of liquid alkanes because they dissolve nonpolar substances in lung tissue and cause pneumonia-like symptoms.

Mineral oil, petroleum jelly, and paraffin wax are mixtures of higher alkanes. All are harmless to body tissue and are used in numerous food and medical applications. Mineral oil passes through the body unchanged and is sometimes used as a laxative. Petroleum jelly (sold as Vaseline) softens, lubricates, and protects the skin. Paraffin wax is used in candle making, on surfboards, and in home canning. See the Chemistry in Action on page 428 for more surprising uses of alkanes.

### Properties of Alkanes:

- Odorless or mild odor; colorless; tasteless; nontoxic
- Nonpolar; insoluble in water but soluble in nonpolar organic solvents; less dense than water
- Flammable; otherwise not very reactive

## 12.8 Reactions of Alkanes

### Learning Objectives:

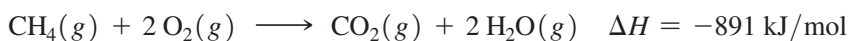
- Determine the basic reactions of alkanes.
- Draw the isomeric products formed during the halogenation of simple alkanes.

Alkanes do not react with acids, bases, or most other common laboratory *reagents* (a substance that causes a reaction to occur). Their only major reactions are with oxygen (combustion) and with halogens (halogenation). Both of these reaction types have complicated mechanisms and occur through the intermediacy of free radicals (see “Halogenation” later in the chapter).

▶▶ Another important radical reaction is found in the formation of the polymers that make up such things as plastics; this is a radical reaction seen primarily with organic molecules that contain double bonds (Section 13.7).

### Combustion

Most of you probably get to school every day using some sort of transportation that uses gasoline, which is a mixture of alkanes, or use a mixture of alkanes when cooking on your gas stove or grilling on your backyard gas barbecue. To power a vehicle or use a gas grill, that mixture of alkanes must be converted into energy. The reaction of an alkane with oxygen is called **combustion**, an oxidation reaction that commonly takes place in a controlled manner in an engine or furnace. Carbon dioxide and water are always the products of complete combustion of any hydrocarbon, and a large amount of heat is released ( $\Delta H$  is a negative number). Some examples were given in Table 7.1.



When hydrocarbon combustion is incomplete because of faulty engine or furnace performance, carbon monoxide and carbon-containing soot are among the products. Carbon monoxide is a highly toxic and dangerous substance, especially so because it has no odor and can easily go undetected (see the Chemistry in Action “CO and NO: Pollutants or Miracle Molecules?” in Chapter 4). Breathing air that contains as little as 2% CO for only one hour can cause respiratory and nervous system damage or death. The supply of oxygen to the brain is cut off by carbon monoxide because it binds strongly to blood hemoglobin at the site where oxygen is normally bound. By contrast with CO, CO<sub>2</sub> is nontoxic and causes no harm, except by suffocation when present in high concentration.

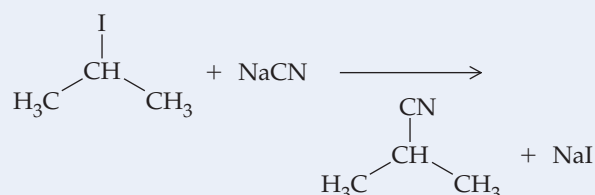
**Combustion** A chemical reaction that produces a flame, usually because of burning with oxygen.

◀◀ Combustion reactions are exothermic, as we learned in Section 7.3.

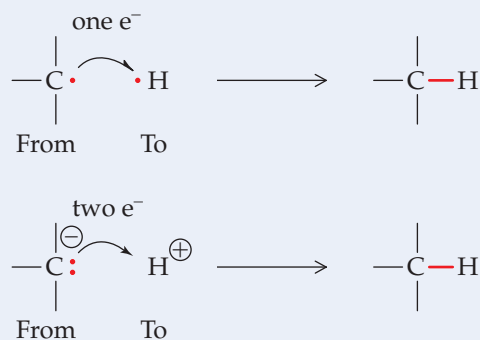
## MASTERING REACTIONS

## Organic Chemistry and the Curved Arrow Formalism

Starting with this chapter and continuing on through the remainder of this text, you will be exploring the world of organic chemistry and its close relative, biochemistry. Both of these areas of chemistry are much more “visual” than those you have been studying; organic chemists, for example, look at how and why reactions occur by examining the flow of electrons. For example, consider the following reaction of 2-iodopropane with sodium cyanide:

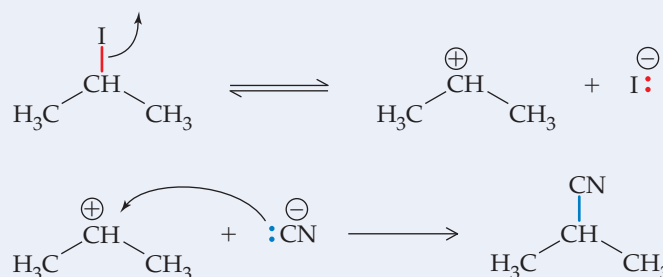


This seemingly simple process (known as a *substitution reaction*, discussed in Chapter 13) is not adequately described by the equation. To help to understand what may really be going on, organic chemists use what is loosely described as “electron pushing” and have adopted what is known as *curved arrow formalism* to represent it. The movement of electrons is depicted using curved arrows, where the number of electrons corresponds to the head of the arrow. Single-headed arrows represent movement of one electron, whereas a double-headed arrow indicates the movement of two.

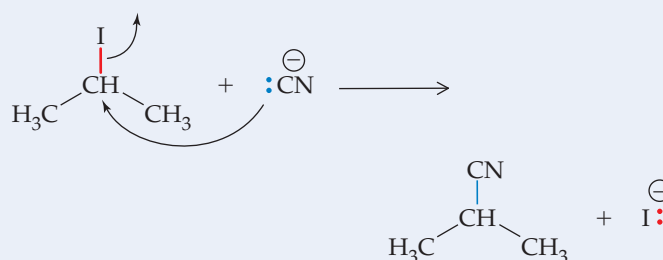


The convention is to show the movement *from* an area of high electron density (the start of the arrow) *to* one of lower electron density (the head of the arrow). Using curved arrow formalism, we can examine the reaction of 2-iodopropane with sodium cyanide in more detail. There are two distinct paths by which this reaction can occur.

Path 1

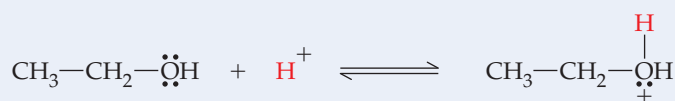


Path 2



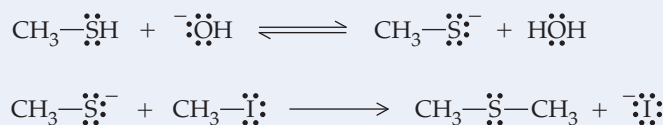
Notice that while both pathways lead ultimately to the same product, the curved arrow formalism shows us that they have significantly different ways of occurring. Although it is not important right now to understand which of the two paths is actually operative (it turns out to be a function of solvent, concentrations, catalysts, temperature, and other conditions), it is important that you get used to thinking of reactions as an “electron flow” of sorts. Throughout the next several chapters, you will see more of these “Mastering Reactions” boxes; they are intended to give you a little more insight into the otherwise seemingly random reactions that organic molecules undergo.

**MR Problem 12.1** When ethanol is treated with acid, the initially formed intermediate is known as an oxonium ion.



Using the curved arrow formalism, show how this process most likely occurs.

**MR Problem 12.2** Consider the following two-step process:



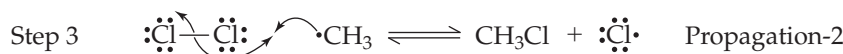
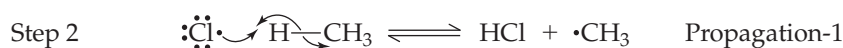
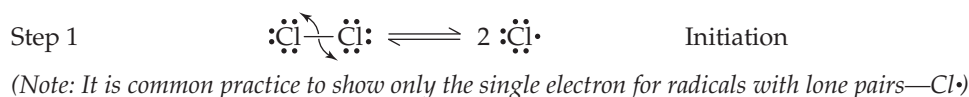
Using the curved arrow formalism, show how each step of this process is most likely to occur.

## PROBLEM 12.16

Write a balanced equation for the complete combustion of methane with oxygen (see Worked Example 5.3 for guidance).

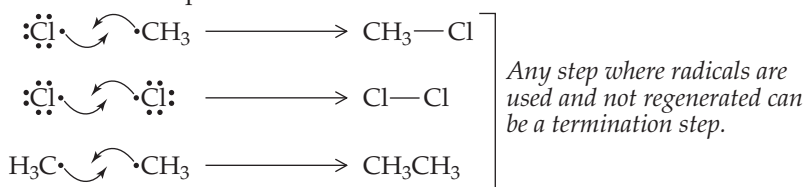
## Halogenation

The second notable reaction of alkanes is *halogenation*, the replacement of an alkane hydrogen by a chlorine or bromine in a process initiated by heat or light. This process is known as “free radical halogenation” and occurs in a step-wise manner (a “free radical”, or a “radical”, is a molecule or atom containing a single, unpaired electron; since a radical does not have an octet of electrons around all of its atoms, it is highly reactive). Following is the reaction of methane with chlorine gas; the process is identical for bromine.



The reaction starts by the formation of chlorine radicals ( $\text{Cl}\cdot$ ); this occurs because the  $\text{Cl--Cl}$  bond is extremely weak and therefore reactive, in this case being easily broken upon exposure to sunlight or heat. Radicals contain seven electrons (one short of the desired octet) and are extremely reactive, so much so they can remove a hydrogen from a carbon (Step 2). The newly formed carbon radical (here,  $\text{H}_3\text{C}\cdot$ ) reacts with another  $\text{Cl}_2$  to give chloromethane and regenerate the chlorine radical (Step 3), which is then free to react with another  $\text{C--H}$  bond (Step 2). Step 1 is called the initiation step, as a radical is initially formed where none were before. Steps 2 and 3 are called propagation steps, since one radical is used and another generated; this is known as a chain reaction, as the chlorine radical generated in Step 3 reenters the reaction to cause Step 2 to occur again. This process will occur over and over until either (i) the reaction is intentionally stopped, (ii) all  $\text{C--H}$  bonds have been replaced by  $\text{Cl}$ , or (iii) a termination step occurs (a step in which two radicals combine, thus eliminating radicals from the reaction).

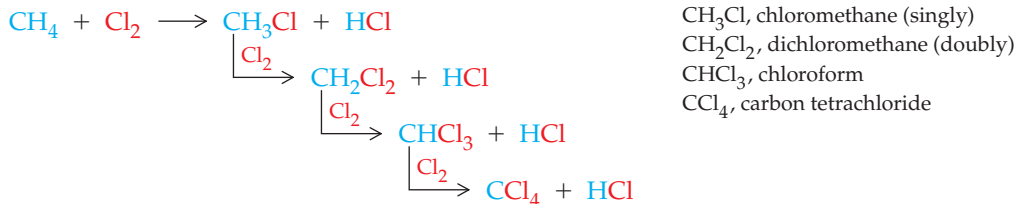
## Termination Steps



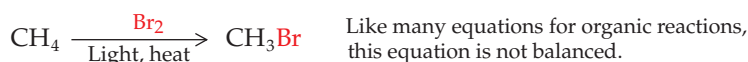
Halogenation is important because it is used to prepare both a number of molecules that are key industrial solvents (such as dichloromethane, chloroform, and carbon tetrachloride) as well as others (such as bromoethane) that are used for the preparation of other larger organic molecules. As shown above, only one H at a time is replaced; however, if allowed to react for a long enough time, all Hs will be replaced with halogens. Complete chlorination of methane, for example, yields carbon tetrachloride:



Although the above equation for the reaction of methane with chlorine is balanced, it does not fully represent what actually happens. In fact, this reaction, like many organic reactions, yields a mixture of products.



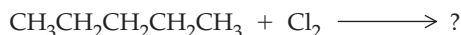
When we write the equation for an organic reaction, our attention is usually focused on converting a particular reactant into a desired product; any minor by-products and inorganic compounds (such as the HCl formed in the chlorination of methane) are often of little interest and are ignored. Thus, it is not always necessary to balance the equation for an organic reaction as long as the reactant, the major product, and any necessary reagents and conditions are shown. A chemist who plans to convert methane into bromomethane might therefore, write the equation as



In using this convention, it is customary to put reactants and reagents above the arrow and conditions, solvents, and catalysts below the arrow.

### Worked Example 12.12 Drawing Isomers of Singly Chlorinated or Brominated Alkanes

(a) Draw all singly chlorinated isomers obtained upon the reaction of pentane with Cl<sub>2</sub>.



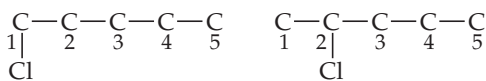
**ANALYSIS** First, identify the parent alkane and then add chlorine systematically to each carbon to create new structures. Compare structures to determine whether they are unique or identical to others you have drawn.

#### SOLUTION

**STEP 1:** Begin by drawing the structure of the alkane starting material. Remove all hydrogens to get a skeletal structure; number the carbons.

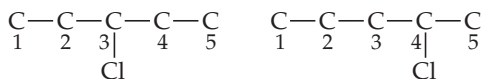


**STEP 2:** One at a time, place a Cl on each carbon that is connected to three or less carbon atoms and draw that skeletal structure.



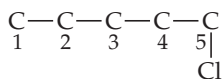
A

B



C

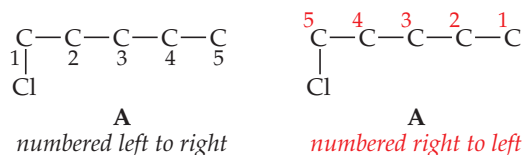
D



E

In this example, there are only carbons attached to one or two other carbons.

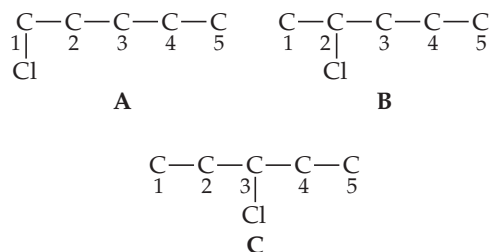
**STEP 3:** Now compare the structures you drew in Step 2, eliminating all that are the same. The simplest way to do this is to designate each structure you drew as a “C#” isomer. Be sure to check numbering in both directions.



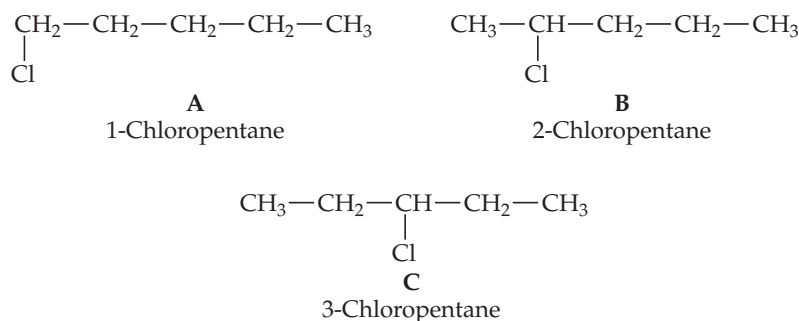
Structure A is the C1 isomer if numbered from left to right or the C5 isomer if numbered from right to left. Doing this for all structures obtained, we get the following correlations:

Structure **A** = C1 or C5      Structure **B** = C2 or C4      Structure **C** = C3 in either direction  
 Structure **D** = C4 or C2      Structure **E** = C5 or C1

Based on this, structures A and E are the same, as are B and D. Structure C is unique. Keep all unique structures, as well as one of each identical pair (here, we will keep A and B, since they have the lowest index numbers). From this, we get:

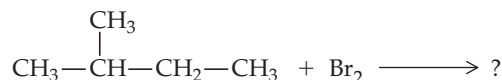


**STEP 4:** Finish by putting in hydrogens so that each C has four bonded atoms.



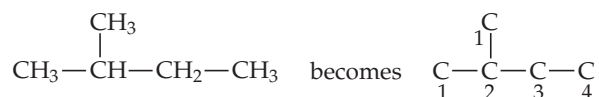
Note: One trick to use if you are not sure if two compounds are the same or different is to name them. Identical compounds will have the same name; if the compounds have different names, they are different compounds.

(b) Repeat for monobromination of the branched alkane 2-methylbutane.



## SOLUTION

**STEP 1:** Draw and number the skeletal structure:



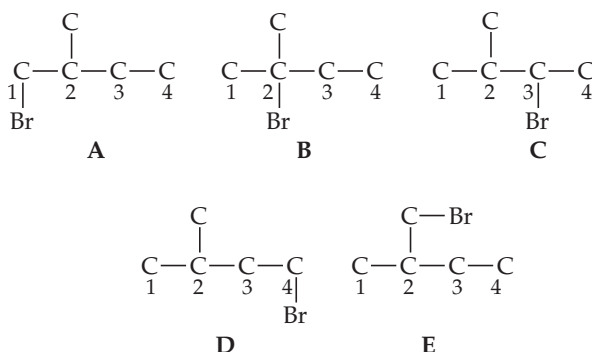
With branched isomers, you need only number in the direction that gives the branch point the lowest number possible. Number in both directions only if you get the same number for the branch point either way.

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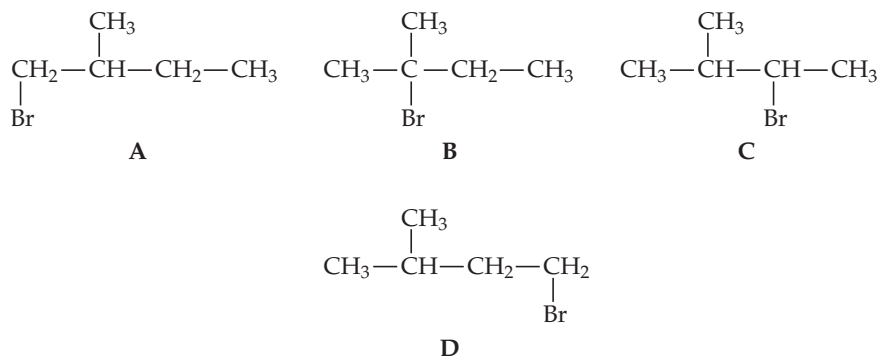
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**STEP 2:** The possible monobromo isomers are as follows:



**STEP 3:** Here, only A and E are identical; all others are unique.

**STEP 4:** The isomers are, therefore:



Note: This method can be used to draw isomers of almost any combination of carbons and functional groups (such as —OH, —NH<sub>2</sub>, etc.)

### PROBLEM 12.17

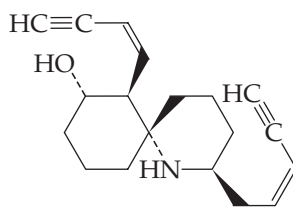
Write the structures of all singly chlorinated products that form when 2,4-dimethylpentane is reacted with Cl<sub>2</sub>.

## 12.9 Cycloalkanes

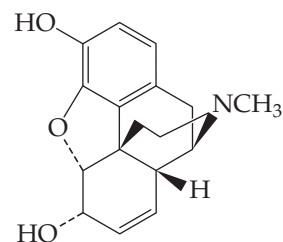
### Learning Objective:

- Identify a cycloalkane from its structure.

The organic compounds described thus far have all been open-chain, or *acyclic*, alkanes. **Cycloalkanes**, which contain rings of carbon atoms, are also well known and are widespread throughout nature, with many of them having unique biological properties:

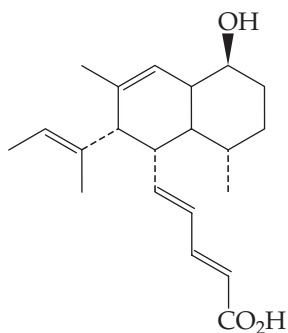


Histrionicotoxin 283A  
Toxin isolated from poison dart frog



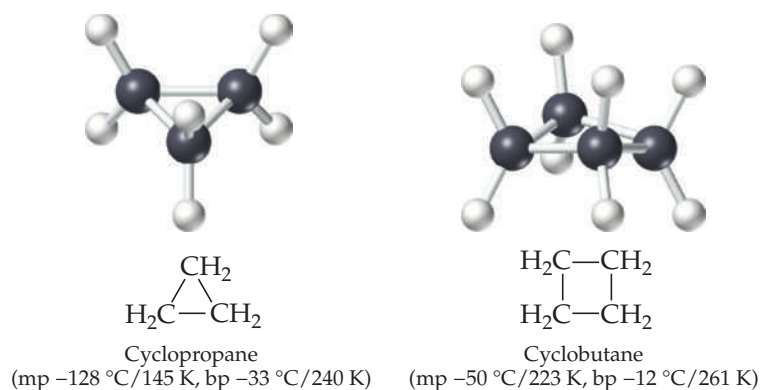
Morphine  
Pain killer

**Cycloalkane** An alkane that contains a ring of carbon atoms.



Phomopsidin  
Inhibitor of microtubule assembly;  
isolated from a marine-derived fungi

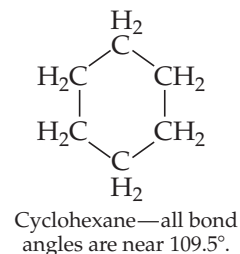
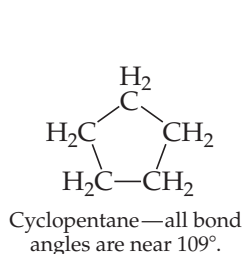
To form a closed ring requires an additional C—C bond and the loss of 2 H atoms. Compounds of all ring sizes from 3 through 30 and beyond have been prepared in the laboratory. The two simplest cycloalkanes—cyclopropane and cyclobutane—contain 3 and 4 carbon atoms, respectively.



Note that if we flatten the rings in cyclopropane and cyclobutane, the C—C—C bond angles are  $60^{\circ}$  and  $90^{\circ}$ , respectively—values that are considerably compressed from the normal tetrahedral value of  $109.5^{\circ}$ . As a result, these compounds are less stable and more reactive than other cycloalkanes. The five-membered (cyclopentane) ring has nearly ideal bond angles, and so does the six-membered (cyclohexane) ring. Both cyclopentane and cyclohexane accomplish this nearly ideal state by adopting a puckered, nonplanar shape, further discussion of which, while important, is beyond the scope of this textbook. Both cyclopentane and cyclohexane rings are therefore stable, and many naturally occurring and biochemically active molecules, such as the steroids (Chapter 28), contain such rings. These rings, and the shape they impart on the molecules that contain them, are an important component of what is known as structure–activity relationships in rational drug design.

Cyclic and acyclic alkanes are similar in many of their properties. Cyclopropane and cyclobutane are gases at room temperature (like propane and butane), whereas larger cycloalkanes, like larger alkanes, are liquids or solids. Like alkanes, cycloalkanes are nonpolar, insoluble in water, and flammable. Because of their cyclic structures, however, cycloalkane molecules are more rigid and less flexible than their open-chain counterparts. Rotation is not possible around the carbon–carbon bonds in cycloalkanes without breaking open the ring. This property is known as **restricted rotation** and can lead to isomer formation (see Group Problem 12.76).

**Restricted Rotation** The limited ability of a molecule to rotate around a given bond.



## 12.10 Drawing and Naming Cycloalkanes

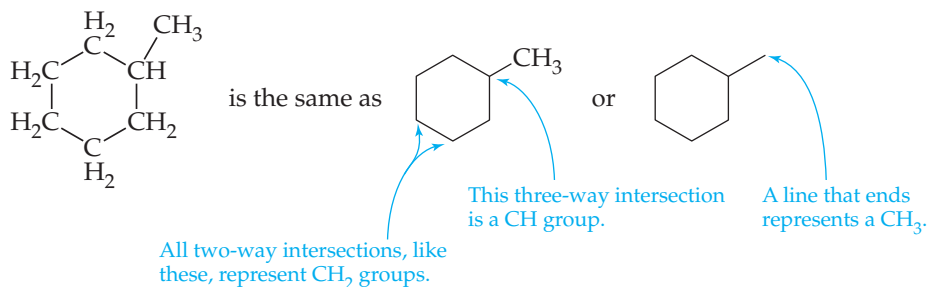
### Learning Objective:

- Name a cycloalkane given its structure and draw a cycloalkane given its name.

Even condensed structures become awkward when we work with large molecules that contain rings. Thus, line structures are used almost exclusively in drawing cycloalkanes, with *polygons* used for the cyclic parts of the molecules. A triangle represents cyclopropane, a square represents cyclobutane, a pentagon represents cyclopentane, and so on, where, just like alkanes, a carbon is found at every point two or more lines meet, or wherever a line ends.

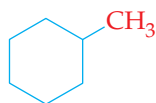


Methylcyclohexane, for example, looks like this in a line structure.



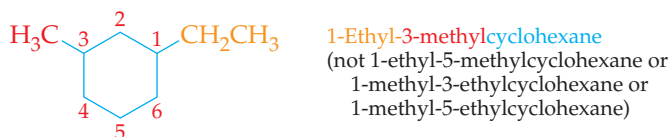
Cycloalkanes are named by a straightforward extension of the rules for naming open-chain alkanes. In most cases, only two steps are needed.

**STEP 1:** Use the cycloalkane name as the parent. That is, compounds are named as alkyl-substituted cycloalkanes rather than as cycloalkyl-substituted alkanes. If there is only one substituent on the ring, it is not even necessary to assign a number because all ring positions are identical.



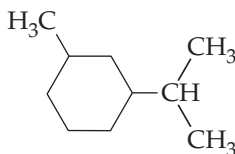
Parent compound: Cyclohexane  
Name: Methylcyclohexane  
(not cyclohexylmethane)

**STEP 2: Identify and number the substituents.** Start numbering at the group that has alphabetical priority, and proceed around the ring in the direction that gives the second substituent the lowest possible number.



### Worked Example 12.13 Naming Organic Compounds: Cycloalkanes

What is the IUPAC name of the following cycloalkane?

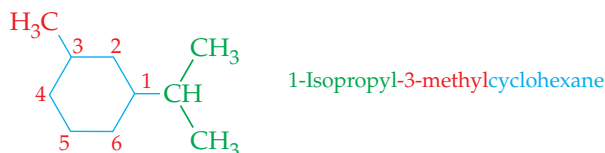


**ANALYSIS** First, identify the parent cycloalkane and then add the positions and identity of any substituents.

#### SOLUTION

**STEP 1:** The parent cycloalkane contains six carbons (*hexane*), hence, *cyclohexane*.

**STEP 2:** There are two substituents; a methyl ( $\text{—CH}_3$ ) and an isopropyl ( $\text{—CH}(\text{CH}_3)_2$ ). Alphabetically, the isopropyl group is given priority (number 1); the methyl group is then found on the third carbon in the ring.



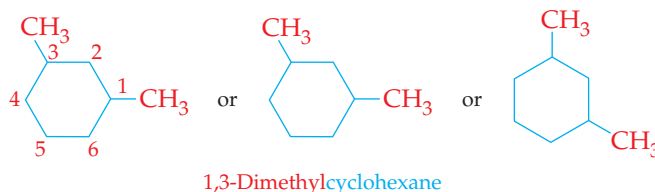
### Worked Example 12.14 Molecular Structures: Drawing Line Structures for Cycloalkanes

Draw a line structure for 1,3-dimethylcyclohexane.

**ANALYSIS** This structure consists of a 6-carbon ring (*cyclohexane*) with two methyl groups (*dimethyl*) attached at positions 1 and 3. Draw a hexagon to represent a cyclohexane ring, and attach a  $\text{—CH}_3$  group at an arbitrary position that becomes the first carbon in the chain, designated as C1. Then count around the ring to the third carbon (C3), and attach another  $\text{—CH}_3$  group.

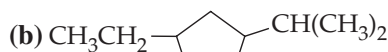
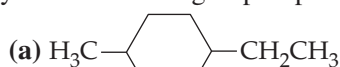
#### SOLUTION

Note that the C3 methyl group could have been written as  $\text{H}_3\text{C—}$  to emphasize that attachment to the ring is through the carbon. This is a common practice for methyl groups that are attached on the left side of a cycloalkane ring. Note also that as long as the methyl groups are 1, 3 to one another, it does not matter how we orient the ring.



### PROBLEM 12.18

What are the IUPAC names of the following cycloalkanes? Remember to assign priority to the attached groups alphabetically.



## PROBLEM 12.19

Draw line structures that represent the following IUPAC names:

- (a) 1,1-Diethylcyclohexane                      (b) 1,3,5-Trimethylcycloheptane

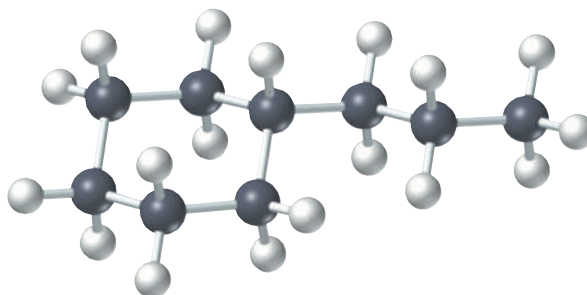
## PROBLEM 12.20

What is wrong with the following names? It will be helpful to draw the structures as named before making your decision.

- (a) 1,4,5-Trimethylcyclohexane                      (b) Cyclohexylcyclopentane  
(c) 1-Ethyl-2-methyl-3-ethylcyclopentane

## KEY CONCEPT PROBLEM 12.21

Redraw the following cycloalkane in both condensed and line formula format. What is its IUPAC name?



## CHEMISTRY IN ACTION

## Surprising Uses of Petroleum

Petroleum, arising from the decay of ancient plants and animals, is found deep below the earth's crust; it is a mixture of hydrocarbons of varying sizes. Petroleum's worth as both a portable, energy-dense fuel and as the starting point of many industrial chemicals makes it one of the world's most important commodities. About 90% of vehicular fuel needs worldwide are met by oil. In addition, 40% of total energy consumption in the United States is petroleum-based. In an effort to create a "greener" environment and more sustainable energy, a great fervor has developed to find alternative energy sources, but a question arises: Can we completely eliminate the need for petroleum from our lives, even if we could find an alternative energy for transportation purposes?

*Petrochemicals*, which we first mentioned in the chapter opener, are chemical products derived specifically from petroleum and generally refer to those products that are not used for fuels. When crude oil is refined and cracked (the process during which complex organic molecules found in oil are converted into simpler molecules by breaking carbon-carbon bonds), a number of fractions having different boiling ranges are obtained. The primary petrochemicals obtained can be broken down into three categories:

1. Alkenes (or olefins; Chapter 13): Primarily ethene, propene, and butadiene. Ethene and propene are important sources of industrial chemicals and plastics products.
2. Aromatics (Chapter 13): Most important among these are benzene, toluene, and the xylenes. These raw materials are used for making a variety of compounds, from dyes



▲ Petroleum jelly, originally an unwanted by-product of drilling, has found many uses in today's average household.

and synthetic detergents, to plastics and synthetic fibers, to pharmaceutical starting materials.

3. Synthesis gas: A mixture of carbon monoxide and hydrogen used to make methanol (which is used as both a solvent and starting point for other products).

What specific types of products are made from these petrochemicals? Let's look at a few:

Lubricants such as light machine oils, motor oils, and greases are products used to keep almost all mechanical devices running smoothly and to prevent them from seizing up under high-use conditions. Wax is another raw petroleum product. Paraffin waxes are used to make candles and polishes as well as food packaging such as milk cartons. The shine you see on the fruit in your local supermarket is also a result of the use of wax.

Most of the rubber soles found on today's shoes are derived from butadiene. Natural rubber becomes sticky when hot and stiff when cold, but man-made rubber stays much more flexible. Car tires are also made from synthetic rubber, which makes them much safer to drive on. Today, the demand for synthetic rubber is four-times greater than for natural rubber.

One very interesting petroleum-derived material was once considered a nuisance by-product of oil drilling. "Black rod wax" is a paraffin-like substance that forms on oil-drilling rigs, causing the drills to malfunction. Workers had to scrape the thick, viscous material off to keep the drills running. However, they found that when applied to cuts and burns it would cause these injuries to heal faster. A young chemist named Robert Chesebrough, after purifying the material, obtained a light-colored gel he named vaseline, or petroleum jelly. Chesebrough demonstrated his miracle product by burning his skin, then spreading the healing ointment on his injuries. Its use in promoting the healing of minor cuts, abrasions, and dry skin and lips soon followed, as we saw in the opening

of this chapter. While the use of Vaseline® for burns has fallen out of favor (due to its ability to seal in heat as well as moisture), it is still important as a base for a number of antibacterial ointments. Today, we know that the primary effect that petroleum jelly has on the healing process is that of sealing wounds from moisture loss, allowing the skin to heal from the bottom up more effectively.

As you can see, petroleum has many uses that are key in our everyday lives. Although lessening its use as a fuel for transportation can help to conserve what reserves we have, its complete elimination from our lives is, at this point in time, nearly impossible.

**CIA Problem 12.4** (a) Why is the demand for synthetic rubber greater than that of natural rubber? (b) Butadiene is used in the manufacture of synthetic rubber. Why is this more desirable than natural rubber?

**CIA Problem 12.5** (a) What common produce items might you see paraffin waxes being used on? (b) What consumer products are manufactured with ethene and propene?

## SUMMARY REVISITING THE CHAPTER LEARNING OBJECTIVES

- **Identify the general structural characteristics of organic molecules, in particular, the tetravalent nature of carbon and the different ways in which it can be expressed.** Compounds made up primarily of carbon and hydrogen atoms are classified as organic. Each carbon atom in an organic molecule is tetravalent, meaning it can form a total of four bonds. Many organic compounds contain carbon atoms that are joined in chains by a combination of single ( $C-C$ ), double ( $C=C$ ), or triple ( $C\equiv C$ ) bonds. We focused here primarily on *alkanes and cycloalkanes*, hydrocarbon compounds that contain only single bonds between all C atoms [see Problems 27, 29, 30, 68, 70, and 74].
- **Define functional group.** Organic compounds can be classified into various families according to the functional groups they contain (Table 12.1). A *functional group* is a part of a larger molecule and is composed of a group of atoms that has characteristic structure and chemical reactivity [see Problem 28].
- **Identify the functional groups in organic molecules.** Being able to identify the functional group family to which an organic molecule belongs is important, as a given functional group undergoes nearly the same chemical reactions in every molecule where it occurs [see Problems 23, 31–35, 64, and 71].
- **Recognize structural (constitutional) isomers and functional group isomers.** Structural or constitutional isomers are compounds that have the same formula but different structural connections of atoms. When atoms other than carbon and hydrogen are present, the ability to have *functional group isomers* arises; these are molecules that, due to the differences in their connections, have not only different structures but also belong to different families of organic molecules [see Problems 26, 36–47, 58, 73, and 76].
- **Draw structural, condensed, and line formulas for simple chemical compounds.** Organic compounds can be represented by *structural formulas* in which all atoms and bonds are shown, by *condensed structures* in which not all bonds are drawn, or by *line structures* in which the carbon skeleton is represented by lines and the locations of C and H atoms are understood [see Problems 22, 23, 73, and 75].
- **Convert any given structural, condensed, or line formula into its corresponding alternative.** Chemists and biochemists often use a mixture of structural, condensed, and line formula to represent the complicated molecules they study. Since organic molecules are often drawn using any one of these methods, being able to think

interchangeably in all three formats is important in the study of organic and biological molecules [see Problems 49, 52, and 53].

- **Determine if two given structures are the different conformers of the same molecule, different structural isomers, or different molecules.** Structural isomers have the same chemical formula but different connections of atoms; different molecules have different chemical formulas; and conformers have the same chemical formula and connections of atoms with different spatial arrangements of those atoms. Free rotation around  $C-C$  single bonds allows a given organic compound the ability to adopt a number of different spatial arrangements. These are called *conformations* or *conformers*. Different conformations of a molecule have different energies depending on whether large groups of atoms are close to one another or not [see Problems 46, 47, 49, 72, and 76].
- **Name an alkane given its structure and draw an alkane given its name.** A *straight-chain alkane* has all its carbons connected in a row, and a *branched-chain alkane* has a branching connection of atoms somewhere along its chain. Straight-chain alkanes are named by adding the family ending *-ane* to a parent; this tells how many carbon atoms are present. Branched-chain alkanes are named by using the longest continuous chain of carbon atoms for the parent and then identifying the *alkyl groups* present as branches off the main chain. The positions of the substituent groups on the main chain are identified by numbering the carbons in the chain so that the substituents have the lowest index numbers [see Problems 24, 25, and 50–53].
- **Identify the physical properties of alkanes.** Alkanes are generally nonpolar, insoluble in water (hydrophobic), and unreactive. They possess low melting and/or boiling points due to their weak intermolecular forces. Alkanes are generally nontoxic and therefore have limited physiological effects [see Problems 68 and 78].
- **Determine the basic reactions of alkanes.** Alkanes possess low reactivity; their principal chemical reactions are *combustion*, a reaction with oxygen that gives carbon dioxide and water, and *halogenation*, a reaction in which hydrogen atoms are replaced by chlorine or bromine [see Problems 60 and 71].
- **Draw the isomeric products formed during the halogenation of simple alkanes.** Drawing the isomeric products obtained on halogenation of an alkane can be accomplished by systematically and methodically replacing hydrogens one carbon at a time and then comparing each structure obtained with one another to determine if the



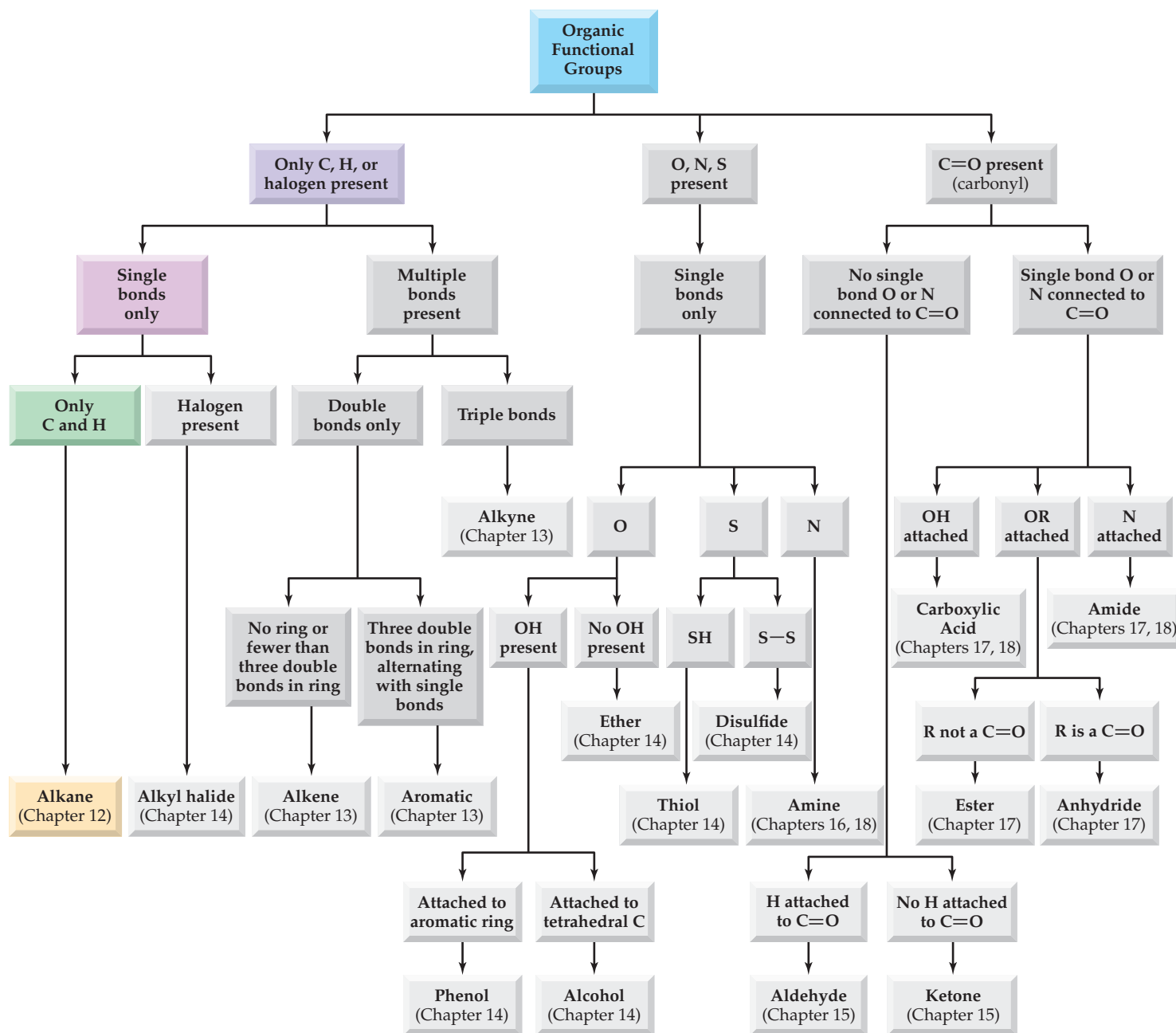
molecules are the same or different structurally. One way to tell if the compounds are the same or different is to name them; identical compounds have the same name. This procedure for drawing isomeric products can be used to draw isomers of almost any combination of carbons and functional groups [see Problems 62, 63, and 69].

• **Identify a cycloalkane from its structure.** Hydrocarbons that have only single bonds arranged in a ring of carbon atoms are called *cycloalkanes*. Due to their cyclic nature, they have what is known as restricted rotation, meaning they cannot adopt as wide a range of conformations as the corresponding alkanes can. Cycloalkanes

possess almost identical physical and chemical properties as alkanes [see Problems 25 and 54–56].

• **Name a cycloalkane given its structure and draw a cycloalkane given its name.** Cycloalkanes are named by adding *cyclo-* as a prefix to the name of the alkane corresponding to the number of carbons in the ring. Cycloalkanes-containing groups attached to the main ring are named the same way as branches in an alkane are. The positions of the substituent groups on the ring are identified by numbering the carbons in the chain so that the substituents have the lowest possible set of position numbers [see Problems 25, 41, 53, and 59].

## CONCEPT MAP: INTRODUCTION TO ORGANIC CHEMISTRY FAMILIES



▲ **Figure 12.5 Functional Group Concept Map.** Learning to classify organic molecules by the families they belong to is a crucial skill you need to develop, since the chemistry that both organic and biological molecules undergo is directly related to their functional groups. This concept map will aid you in this classification. First introduced in Section 12.2, it will be a key reference as you proceed through the rest of the chapters in this book. As we discuss each family in later chapters, sections of it will be reproduced and expanded to help also tie in the chemistry that those functional groups undergo. Functional groups will be drawn out until they are discussed as each functional group is discussed, it will become colorized.

## KEY WORDS

Alkane, p. 399

Alkyl group, p. 410

Branched-chain alkane,  
p. 401

Combustion, p. 419

Condensed structure,  
p. 402

Conformation, p. 408

Conformer, p. 408

Constitutional isomers,  
p. 401

Cycloalkane, p. 424

Ethyl group, p. 411

Functional group, p. 394

Functional group isomer,  
p. 401

Hydrocarbon, p. 396

Isomers, p. 400

Isopropyl group, p. 411

Line structure, p. 404

Methyl group, p. 411

Methylene group, p. 403

Organic chemistry,  
p. 391Primary (1°) carbon atom,  
p. 412

Propyl group, p. 411

Quaternary (4°) carbon  
atom, p. 412

Restricted rotation, p. 425

Secondary (2°) carbon atom,  
p. 412

Straight-chain alkane, p. 401

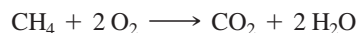
Substituent, p. 410

Tertiary (3°) carbon atom,  
p. 412

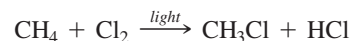
## SUMMARY OF KEY REACTIONS

Beginning with this chapter, and continuing through Chapter 17, you will find a “Summary of Key Reactions” section located right before the end of chapter problems. In this section, we will summarize all the key reactions discussed in that chapter, along with references to those previously discussed as needed. It is intended as an aid in your study of organic and biochemistry and will be a useful reference guide.

1. Combustion of an alkane with oxygen to yield carbon dioxide and water (Section 12.8):

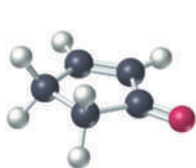


2. Halogenation of an alkane to yield an alkyl halide (Section 12.8):

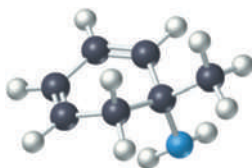


## KEY UNDERSTANDING KEY CONCEPTS

12.22 Convert the following models into line drawings (black = C; white = H; red = O; blue = N):

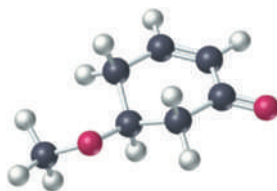


(a)

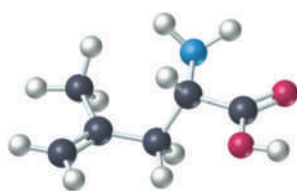


(b)

12.23 Convert the following models into line drawings and identify the functional groups in each:

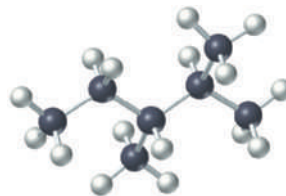


(a)

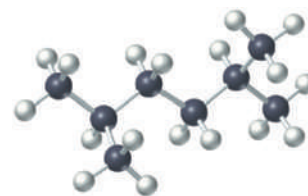


(b)

12.24 Give the IUPAC names for the following alkanes:

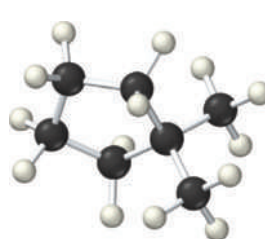


(a)

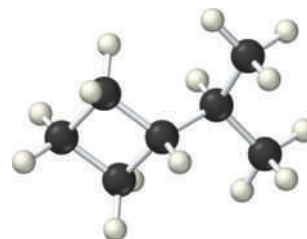


(b)

12.25 Give the IUPAC names for the following cycloalkanes:

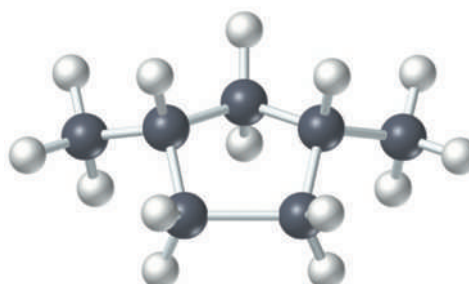
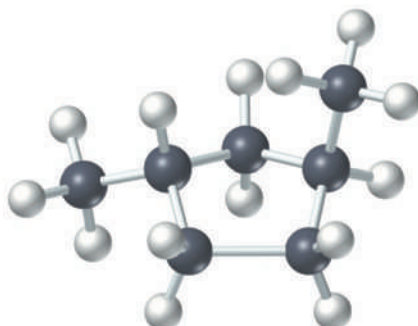


(a)



(b)

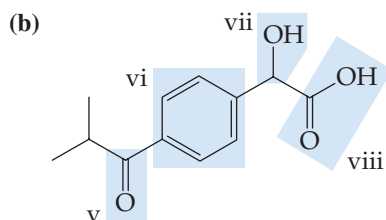
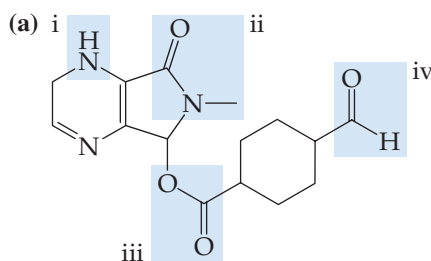
12.26 The following two compounds are isomers, even though both can be named 1,3-dimethylcyclopentane. What is the difference between them?



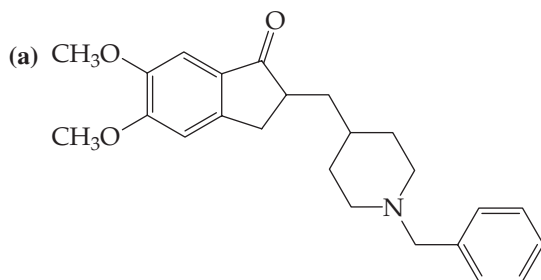
## ADDITIONAL PROBLEMS

## ORGANIC MOLECULES AND FUNCTIONAL GROUPS (SECTIONS 12.1, 12.2)

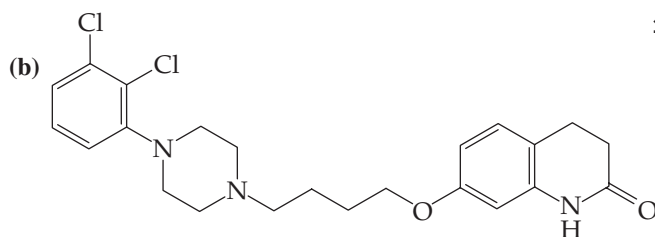
- 12.27** What characteristics of carbon make possible the existence of so many different organic compounds?
- 12.28** What are functional groups, and why are they important?
- 12.29** Why are most organic compounds nonconducting and insoluble in water?
- 12.30** What is meant by the term *polar covalent bond*? Give an example of such a bond.
- 12.31** For each of the following, give an example of a member compound containing 5 carbons total:
- (a) Alcohol (b) Amine  
(c) Carboxylic acid (d) Ether
- 12.32** Identify the highlighted functional groups in the following molecules:



- 12.33** Identify the functional groups in the following molecules:



Donepezil  
(used in Alzheimer's treatment)



Aripiprazole  
(Abilify)

- 12.34** Propose structures for molecules that fit the following descriptions:
- (a) An aldehyde with the formula  $C_5H_{10}O$   
(b) An ester with the formula  $C_6H_{12}O_2$   
(c) A compound with the formula  $C_3H_7NOS$  that is both an amide and a thiol
- 12.35** Propose structures for molecules that fit the following descriptions:
- (a) An amide with the formula  $C_4H_9NO$   
(b) An aldehyde that has a ring of carbons,  $C_6H_{10}O$   
(c) An aromatic compound that is also an ether,  $C_8H_{10}O$

## ALKANES AND ISOMERS (SECTIONS 12.3, 12.4, 12.9)

- 12.36** What requirement must be met for two compounds to be isomers?
- 12.37** If one compound has the formula  $C_5H_{10}$  and another has the formula  $C_4H_{10}$ , are the two compounds isomers? Explain.
- 12.38** (a) What is the difference between a secondary carbon and a tertiary carbon? (b) What about the difference between a primary carbon and a quaternary carbon? (c) How many secondary carbons does the structure shown in Additional Problem 12.33b have? Redraw the structure and highlight them all. (Ignore all double-bonded carbons.)
- 12.39** Why is it not possible for a compound to have a *quintary* carbon (five groups attached to C)?
- 12.40** Give examples of compounds that meet the following descriptions:
- (a) A six carbon alkane with 2 tertiary carbons  
(b) Three different cyclohexanes with having two methyl groups attached.
- 12.41** Give an example of a compound that meets the following descriptions:
- (a) A 5-carbon alkane with only primary and quaternary carbons  
(b) A cycloalkane with three substituents
- 12.42** (a) There are two isomers with the formula  $C_4H_{10}$ . Draw both the condensed and line structure for each isomer.  
(b) Using the structures you drew in (a) as a starting point, draw both the condensed and line structures for the four isomeric chlorides having the chemical formula  $C_4H_9Cl$ .
- 12.43** Write condensed structures for the following molecular formulas. More than one isomer will be required for each.
- (a) Isomers of  $C_8H_{18}$  that contain three methyl groups and a longest chain of 5 carbons  
(b) Cyclohexanes with a chemical formula of  $C_8H_{16}$   
(c)  $C_2H_4O$   
(d) Ketones and aldehydes with  $C_4H_8O$   
(e) Write the line structures for (b) and (d).

**12.44** How many straight-chain isomers can you write that fit the following descriptions? See Worked Example 12.12 for guidance.

- (a) Alcohols ( $\text{—OH}$ ) with a longest chain of 6 carbons  
 (b) Amines ( $\text{—NH}_2$ ) with a longest chain of 7 carbons

**12.45** How many isomers can you write that fit the following descriptions? See Worked Example 12.12 for guidance.

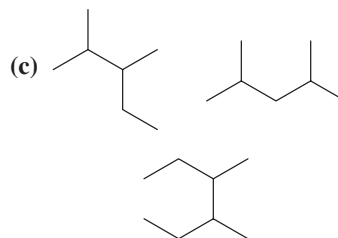
- (a) Monobromides formed from 2-methylpentane  
 (b) Monochlorides formed from 3-methylpentane  
 (c) Alcohols ( $\text{—OH}$ ) formed from 2-methylhexane

**12.46** Which of the following pairs of structures are identical, which are isomers, and which are unrelated?

- (a)  $\text{CH}_3\text{CH}_2\text{CH}_3$  and  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2\text{CH}_3 \end{array}$   
 (b)  $\begin{array}{c} \text{CH}_3-\text{N}-\text{CH}_3 \\ | \\ \text{H} \end{array}$  and  $\begin{array}{c} \text{CH}_3\text{CH}_2-\text{N}-\text{H} \\ | \\ \text{H} \end{array}$   
 (c)  $\text{CH}_3\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3$  and  $\begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{CH}_2\text{CH}_2-\text{C}-\text{CH}_3 \end{array}$   
 (d)  $\begin{array}{c} \text{O} \\ || \\ \text{CH}_3-\text{C}-\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2 \end{array}$  and  $\begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{CH}_2-\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$   
 (e)  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2-\text{O}-\text{H}$  and  $\begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{CH}_2\text{CH}-\text{C}-\text{H} \\ | \\ \text{CH}_3 \end{array}$

**12.47** Which structures in each group represent the same compound and which represent isomers?

- (a)  $\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ | & | & | & | \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ | & | & | & | \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$   $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H} \end{array}$   $\begin{array}{c} \text{H} & \text{H} & \text{H} \\ | & | & | \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ | & | & | \\ \text{H} & \text{H} & \text{H} \end{array}$   $\begin{array}{c} \text{H} & \text{H} & \text{H} \\ | & | & | \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ | & | & | \\ \text{H} & \text{H} & \text{H} \end{array}$   
 (b)  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CHCHCH}_3 \\ | \\ \text{Br} \end{array}$   $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CHCHCH}_3 \\ | \\ \text{Br} \end{array}$   $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2\text{CHCH}_2\text{CH}_3 \\ | \\ \text{Br} \end{array}$

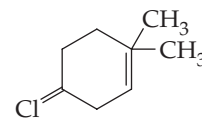


- (d) See if you can find some caraway seeds and some mint leaves. Crush each separately and compare their smells. Now look up the structures primarily responsible for the smell of each and carefully compare them. How are they related? These are what are known as *stereoisomers*; this advanced topic is one that will be discussed in Chapter 14.

**12.48** What is wrong with the following structures?

- (a)  $\text{CH}_3=\text{CHCH}_2\text{CH}_2\text{OH}$  (b)  $\text{CH}_3\text{CH}_2\text{CH}=\text{C}=\text{CH}_3$   
 (c)  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_3 \end{array}$

**12.49** There are two things wrong with the following structure. What are they?



### ALKANE NOMENCLATURE (SECTIONS 12.6, 12.10)

**12.50** What are the IUPAC names of the following alkanes?

- (a)  $\begin{array}{c} \text{CH}_2\text{CH}_3 \\ | \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCHCH}_2\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$   
 (b)  $\begin{array}{c} \text{CH}_3\text{CHCH}_3 \\ | \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CHCH}_3 \\ | \\ \text{CH}_2\text{CH}_3 \end{array}$   
 (c)  $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{CHCH}_3 \\ | \\ \text{CH}_3 \end{array}$   
 (d)  $\begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CCH}_3 \\ | \\ \text{CH}_3\text{CHCH}_3 \end{array}$   
 (e)  $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{CH}_3\text{CCH}_2\text{CCH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$  (f)  $\begin{array}{c} \text{CH}_3\text{CH}_2 \quad \text{CH}_3 \\ | \quad | \\ \text{CH}_3\text{CH}_2\text{CCH}_2\text{CH} \\ | \quad | \\ \text{CH}_3\text{CH}_2 \quad \text{CH}_3 \end{array}$   
 (g)  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3(\text{CH}_2)_7\text{C}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$

**12.51** Give IUPAC names for the five isomers with the formula  $C_6H_{14}$ .

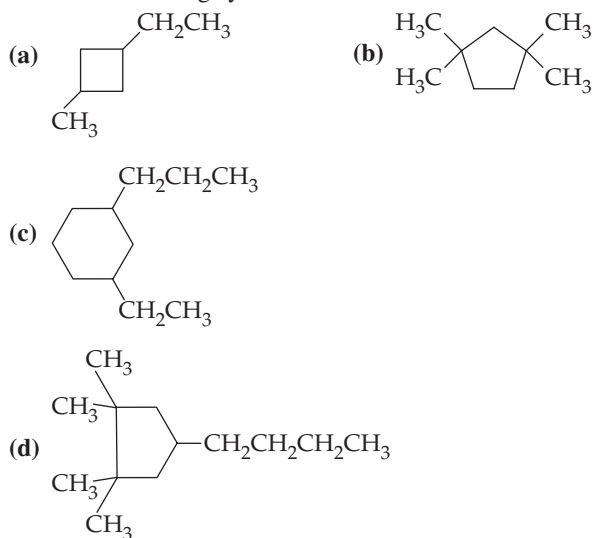
**12.52** Write condensed structures for the following compounds:

- (a) 4-*tert*-Butyl-2-methylheptane
- (b) 2,4-Dimethylpentane
- (c) 4,4-Diethyl-3-methyloctane
- (d) 3-Ethyl-1-isopropyl-5-methylcycloheptane
- (e) 1,1,3-Trimethylcyclopentane

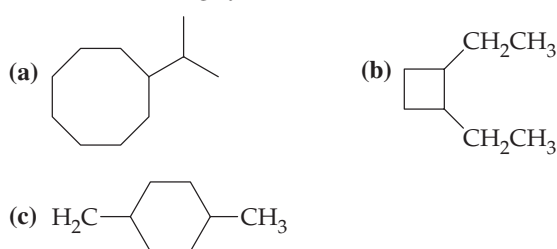
**12.53** Draw line structures for the following cycloalkanes:

- (a) 1,1-Dimethylcyclopropane
- (b) 1,3-Dimethylcyclopentane
- (c) Ethylcyclohexane
- (d) Cycloheptane
- (e) 1-Methyl-3-propylcyclohexane
- (f) 1-Ethyl-4-isopropylcyclooctane

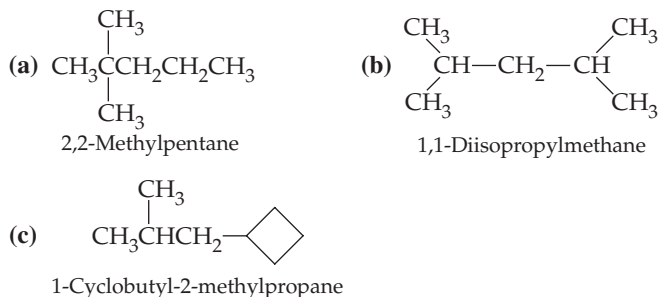
**12.54** Name the following cycloalkanes:



**12.55** Name the following cycloalkanes:



**12.56** The following names are incorrect. Tell what is wrong with each, and provide the correct names.



**12.57** The following names are incorrect. Write the structural formula that agrees with the apparent name, and then write the correct name of the compound.

- (a) 2-Ethylbutane
- (b) 2-Isopropyl-2-methylpentane
- (c) 5-Ethyl-1,1-methylcyclopentane
- (d) 3-Ethyl-3,5,5-trimethylhexane
- (e) 1,2-Dimethyl-4-ethylcyclohexane
- (f) 2,4-Diethylpentane
- (g) 5,5,6,6-Methyl-7,7-ethyldecane

**12.58** Draw structures and give IUPAC names for the nine isomers of  $C_7H_{16}$ .

**12.59** Draw the structural formulas and name all cyclic isomers with the formula  $C_5H_{10}$ .

### REACTIONS OF ALKANES (SECTION 12.8)

**12.60** Propane, commonly known as liquid petroleum (LP) gas, burns in air to yield  $CO_2$  and  $H_2O$ . Write a balanced equation for the reaction.

**12.61** Write a balanced equation for the combustion of isooctane,  $C_8H_{18}$ , a component of gasoline.

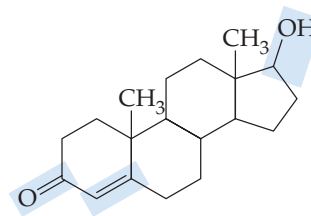
**12.62** Write the formulas of the four singly chlorinated isomers formed when 2-methylbutane reacts with  $Cl_2$  in the presence of light.

**12.63** Write the formulas of the three doubly brominated isomers formed when 2-methylpropane reacts with  $Br_2$  in the presence of light.

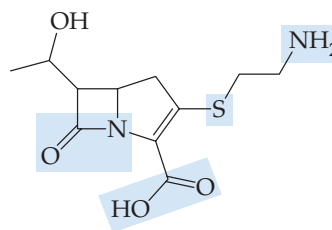
### CONCEPTUAL PROBLEMS

**12.64** Identify the indicated functional groups in the following molecules:

(a) Testosterone, a male sex hormone

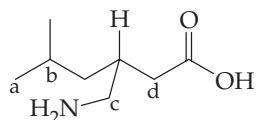


(b) Thienamycin, an antibiotic



(c) Look up the structure of lisdexamfetamine (Vyvanse), a drug used in the treatment of attention deficit hyperactivity disorder (ADHD). Redraw it and identify all the functional groups present. What is known about its therapeutic properties?

- 12.65** The line structure for pregabalin (Lyrica) is shown as follows:



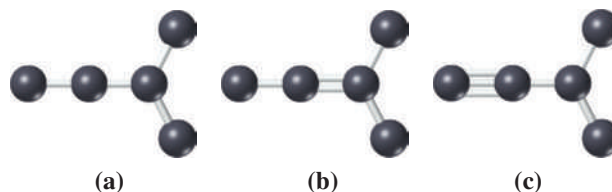
Identify carbons a–d as primary, secondary, tertiary, or quaternary.

- 12.66** Consider the compound shown in Problem 12.65; how many tertiary carbons does it have?
- 12.67** If someone reported the preparation of a compound with the formula  $C_3H_9$ , most chemists would be skeptical. Why?
- 12.68** Most lipsticks are about 70% castor oil and wax. Why is lipstick more easily removed with petroleum jelly than with water?
- 12.69** When pentane is exposed to  $Br_2$  in the presence of light, a halogenation reaction occurs. Write the formulas of:
- All possible products containing only one bromine
  - All possible products containing two bromines that are *not* on the same carbon
- 12.70** Which do you think has a higher boiling point, pentane or neopentane (2,2-dimethylpropane)? Why?
- 12.71** Propose structures for the following:
- A carboxylic acid,  $C_4H_8O_2$
  - An iodo-substituted alkene,  $C_5H_9I$
  - A cyclopentane having a chemical formula  $C_7H_{14}$
  - An alkene containing only two methyl groups and a chemical formula  $C_4H_8$

- 12.73** In Problem 12.4, you drew the two branched-chain isomers with the formula  $C_7H_{16}$ , where the longest chain in the molecule is 6 carbons long. Now see how many other isomers with this chemical formula you can draw.

- 12.74** Since its discovery, petroleum jelly has been shown to be a household product with many practical uses. Search the internet and see if you can come up with 10 different uses for this “wonder” product.

- 12.75** How many hydrogen atoms are needed to complete the hydrocarbon formulas for the following carbon backbones?



- 12.76** Refer to the structures shown in Problem 12.26. Using a model kit or the “gum drops and toothpicks” method presented in Hands-On Chemistry 4.1, build models of both structures (a) and (b). These two isomers demonstrate how restricted rotation comes into play for organic molecules (Section 12.9). Can you convert (a) into (b) without breaking any bonds?

## GROUP PROBLEMS

- 12.72** Which of the following structures represent the same molecule?

