Alkanes

Alkanes are composed of only carbon atoms and hydrogen atoms and contain only *single bonds*. Compounds that contain only carbon and hydrogen are called **hydrocarbons**. Thus, an alkane is a hydrocarbon that has only single bonds.

Alkanes in which the carbons form a continuous chain with no branches are called **straight-chain alkanes**. The names of the four smallest straight-chain alkanes have historical roots, but the others are based on Greek numbers. It is important that you learn the names of at least the first 10 straight-chain alkanes in Table 3.1.

Table 3.1 Nomenclature and Physical Properties of Straight-Chain Alkanes						
Number of carbons	Molecular formula	Name	Condensed structure	Boiling point (°C)	Melting point (°C)	Density ^a (g/mL)
1	CH ₄	methane	CH ₄	-167.7	-182.5	
2	C_2H_6	ethane	CH ₃ CH ₃	-88.6	-183.3	
3	C_3H_8	propane	CH ₃ CH ₂ CH ₃	-42.1	-187.7	
4	C_4H_{10}	butane	CH ₃ CH ₂ CH ₂ CH ₃	-0.5	-138.3	
5	C_5H_{12}	pentane	$CH_3(CH_2)_3CH_3$	36.1	-129.8	0.5572
6	C_6H_{14}	hexane	$CH_3(CH_2)_4CH_3$	68.7	-95.3	0.6603
7	C_7H_{16}	heptane	$CH_3(CH_2)_5CH_3$	98.4	-90.6	0.6837
8	C_8H_{18}	octane	$CH_3(CH_2)_6CH_3$	125.7	-56.8	0.7026
9	C_9H_{20}	nonane	$CH_3(CH_2)_7CH_3$	150.8	-53.5	0.7177
10	$C_{10}H_{22}$	decane	$CH_3(CH_2)_8CH_3$	174.0	-29.7	0.7299
11	$C_{11}H_{24}$	undecane	$CH_3(CH_2)_9CH_3$	195.8	-25.6	0.7402
12	$C_{12}H_{26}$	dodecane	$CH_3(CH_2)_{10}CH_3$	216.3	- 9.6	0.7487
13	$C_{13}H_{28}$	tridecane	$CH_3(CH_2)_{11}CH_3$	235.4	-5.5	0.7546
:	:	:	:	:	:	:
20	$C_{20}H_{42}$	eicosane	$CH_3(CH_2)_{18}CH_3$	343.0	36.8	0.7886
21	$C_{21}H_{44}$	heneicosane	$CH_3(CH_2)_{19}CH_3$	356.5	40.5	0.7917
:	:	:	:	:	:	:
30	$C_{30}H_{62}$	triacontane	$CH_3(CH_2)_{28}CH_3$	449.7	65.8	0.8097

^aDensity is temperature-dependent. The densities given are those determined at 20 °C ($d^{20^{\circ}}$).

The family of alkanes shown in the table is an example of a homologous series. A **homologous** series (*homos* is Greek for "the same as") is a family of compounds in which each member differs from the one before it in the series by one **methylene** (CH₂) **group.** The members of a homologous series are called **homologues.**

The relative numbers of carbons and hydrogens in the alkanes in Table 3.1 show that the general molecular formula for an alkane is C_nH_{2n+2} , where n is any positive integer. So if an alkane has one carbon, it must have four hydrogens; if it has two carbons, it must have six hydrogens; and so on.

Methane, Ethane, and Propane

We saw that carbon forms four covalent bonds and hydrogen forms only one covalent bond (Section 1.4). This means that there is only one possible structure for an alkane with molecular formula CH_4 (methane) and only one possible structure for an alkane with molecular formula C_2H_6 (ethane). We examined the structures of these compounds in Section 1.7. There is also only one possible structure for an alkane with molecular formula C_3H_8 (propane).

name	molecular formula	Kekulé structure	condensed structure	ball-and-stick model
methane	$\mathrm{CH_4}$	H H-C-H H	CH ₄	
ethane	C_2H_6	H H H-C-C-H H H	CH₃CH₃	3 8
propane	$\mathrm{C_{3}H_{8}}$	H H H H-C-C-C-H H H H	CH ₃ CH ₂ CH ₃	
butane	C_4H_{10}	H H H H H-C-C-C-C-H 	CH ₃ CH ₂ CH ₂ CH ₃	3-6

Butane

There are, however, two possible structures for an alkane with molecular formula C_4H_{10} —a straight-chain alkane called butane and a branched alkane called isobutane. Both of these structures fulfill the requirement that each carbon forms four bonds and each hydrogen forms one bond.



Compounds such as butane and isobutane that have the same molecular formula but differ in the way the atoms are connected are called **constitutional isomers**—their molecules have different constitutions. In fact, isobutane got its name because it is an *iso*mer of butane. The structural unit consisting of *a carbon bonded to a hydrogen and two CH*₃ *groups*, which occurs in isobutane, has come to be called "iso." Thus, the name *isobutane* tells you that the compound is a four-carbon alkane with an iso structural unit.

Pentane

There are three alkanes with molecular formula C_5H_{12} . You have already learned how to name two of them. Pentane is the straight-chain alkane. Isopentane, as its name indicates, has an iso structural unit and five carbons. We cannot name the other branched-chain alkane without defining a name for a new structural unit. (For now, ignore the names written in blue.)

Hexane

There are five constitutional isomers with molecular formula C_6H_{14} . Again, we are able to name only two of them, unless we define new structural units.

$$\begin{array}{c} \text{common name:} \\ \text{systematic name:} \\ \text{systematic name:} \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{hexane} \\ \text{hexane} \\ \text{hexane} \\ \text{hexane} \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{CH}_3 \\ \text{isohexane} \\ \text{2-methylpentane} \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH} - \text{CHCH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH} - \text{CHCH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH} - \text{CHCH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{CH}_3\text{CH}_3 \\ \text{CH}_3 \\$$

Heptane

There are nine alkanes with molecular formula C_7H_{16} . We can name only two of them (heptane and isoheptane).

$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\\ \text{common name:}\\ \text{systematic name:} & \begin{array}{c} \text{heptane}\\ \text{heptane} \\ \text{heptane} \end{array} \\ \begin{array}{c} \text{isoheptane}\\ \text{2-methylhexane} \end{array}$$

Systematic/IUPAC Nomenclature

The number of constitutional isomers increases rapidly as the number of carbons in an alkane increases. For example, there are 75 alkanes with molecular formula $C_{10}H_{22}$ and 4347 alkanes with molecular formula $C_{15}H_{32}$. To avoid having to memorize the names of thousands of structural units, chemists have devised rules for creating systematic names that describe the compound's structure. That way, only the rules must be learned. Because the name describes the structure, these rules make it possible to deduce the structure of a compound from its name.

This method of nomenclature is called **systematic nomenclature**. It is also called **IUPAC nomenclature** because it was designed by a commission of the International Union of Pure and Applied Chemistry (abbreviated IUPAC and pronounced "eye-you-pack") in 1892.

The IUPAC rules have been continually revised by the commission since then. A name such as *isobutane*—a nonsystematic name—is called a **common name**. When both names are shown in this book, common names are shown in red and systematic (IUPAC) names in blue. Before we can understand how a systematic name for an alkane is constructed, we must learn how to name alkyl groups.

PROBLEM 1 ♠

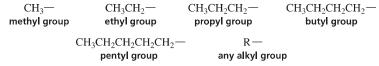
- a. How many hydrogens does an alkane with 17 carbons have?
- b. How many carbons does an alkane with 74 hydrogens have?

PROBLEM 2

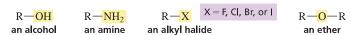
Draw the structures of octane and isooctane.

ALKYL GROUPS

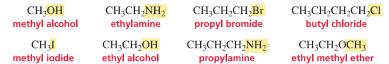
Removing a hydrogen from an alkane results in an alkyl group (or an alkyl substituent). Alkyl groups are named by replacing the "ane" ending of the alkane with "yl." The letter "R" is used to indicate any alkyl group.



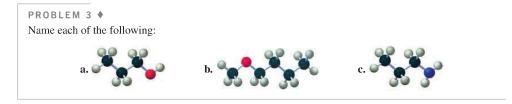
If a hydrogen in an alkane is replaced by an OH, the compound becomes an alcohol; if it is replaced by an NH₂, the compound becomes an **amine**; if it is replaced by a halogen, the compound becomes an alkyl halide; and if it is replaced by an OR, the compound becomes an ether.



The alkyl group name followed by the name of the class of the compound (alcohol, amine, and so on) yields the common name of the compound. The two alkyl groups in ethers are listed in alphabetical order. The following examples show how alkyl group names are used to build common names:



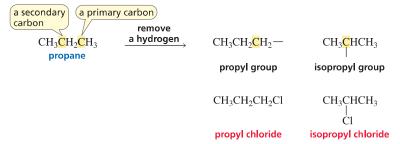
Notice that for most compounds, there is a space between the name of the alkyl group and the name of the class of compound. For amines, however, the entire name is written as one word.



Three-Carbon Alkyl Groups

There are two alkyl groups—the propyl group and the isopropyl group—that contain three carbons.

- A propyl group is obtained when a hydrogen is removed from a primary carbon of propane. A **primary carbon** is a carbon bonded to only one other carbon.
- An isopropyl group is obtained when a hydrogen is removed from the secondary carbon of propane. A **secondary carbon** is a carbon bonded to two other carbons.



Notice that an isopropyl group, as its name indicates, has three carbon atoms arranged as an iso structural unit—that is, a carbon bonded to a hydrogen and to two CH₃ groups.





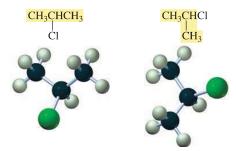
methyl chloride



methylamine

Molecular structures can be drawn in different ways. For example, isopropyl chloride is drawn below in two ways. Both representations depict the same compound. Although the two-dimensional representations may appear at first to be different (the methyl groups are placed at opposite ends in one structure and at right angles in the other), the structures are identical because carbon is tetrahedral. The four groups bonded to the central carbon—a hydrogen, a chlorine, and two methyl groups—point to the corners of a tetrahedron. If you rotate the three-dimensional model on the right 90° in a clockwise direction, you should be able to see that the two models are the same.

two ways to draw isopropyl chloride

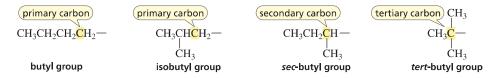


NOTE TO THE STUDENT

 Build models of the two representations of isopropyl chloride to see that they represent the same compound.

Four-Carbon Alkyl Groups

There are four alkyl groups that contain four carbons. Two of them, the butyl and isobutyl groups, have a hydrogen removed from a primary carbon. A *sec*-butyl group has a hydrogen removed from a secondary carbon (*sec*-, sometimes abbreviated *s*-, stands for secondary), and a *tert*-butyl group has a hydrogen removed from a tertiary carbon (*tert*-, often abbreviated *t*-, stands for tertiary). A **tertiary carbon** is bonded to three other carbons. Notice that the isobutyl group is the only one with an iso structural unit.



A primary carbon is bonded to one carbon, a secondary carbon is bonded to two carbons, and a tertiary carbon is bonded to three carbons.

The names of straight-chain alkyl groups often have the prefix "n" (for "normal") to emphasize that the carbons are in an unbranched chain.

Like the carbons, the hydrogens in a molecule are also referred to as primary, secondary, and tertiary. **Primary hydrogens** are attached to a primary carbon, **secondary hydrogens** are attached to a secondary carbon, and **tertiary hydrogens** are attached to a tertiary carbon.

Primary hydrogens are attached to a primary carbon, secondary hydrogens to a secondary carbon, and tertiary hydrogens to a tertiary carbon.

A chemical name must specify one compound only. The prefix "sec," therefore, can be used only for sec-butyl compounds. The name "sec-pentyl" cannot be used because pentane has two different secondary carbons. Thus, removing a hydrogen from a secondary carbon of pentane

produces one of two different alkyl groups, depending on which hydrogen is removed. As a result, *sec*-pentyl chloride would specify two different alkyl chlorides, so it is *not* a correct name.

A name must specify one compound only.

The prefix "tert" can be used for both tert-butyl and tert-pentyl compounds because each of these substituent names describes only one alkyl group. The name "tert-hexyl" cannot be used because it describes two different alkyl groups.

Notice in the following structures that whenever the prefix "iso" is used, the iso structural unit is at one end of the molecule and the group replacing a hydrogen is at the other end:

Notice that an iso group has a methyl group on the next-to-the-last carbon in the chain. Also notice that all isoalkyl compounds have the substituent (OH, Cl, NH₂, and so on) on a primary carbon, except for isopropyl, which has the substituent on a secondary carbon. Thus, the isopropyl group could have been called a *sec*-propyl group. Either name would have been appropriate because the group has an iso structural unit and a hydrogen has been removed from a secondary carbon. Chemists decided to call it isopropyl, however, which means that "sec" is used only for sec-butyl.

Alkyl group names are used so frequently that you need to learn them. Some of the most common alkyl group names are compiled in Table 3.2.

Table 3.2	Names of Some Common Alkyl Groups						
methyl	СН3—	isobutyl	CH ₃ CHCH ₂ —	pentyl	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ —		
ethyl	CH ₃ CH ₂ —		CH_3	isopentyl	CH ₃ CHCH ₂ CH ₂ —		
propyl	CH ₃ CH ₂ CH ₂ —	sec-butyl	CH ₃ CH ₂ CH—		CH_3		
isopropyl	СН3СН—		CH ₃				
	CH ₃		CH_3	hexyl	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ —		
butyl	CH ₃ CH ₂ CH ₂ CH ₂ —	tert-butyl	CH ₃ C—	isohexyl	CH ₃ CHCH ₂ CH ₂ CH ₂ —		
			CH ₃		$ m CH_3$		

PROBLEM 4 ♦

Draw the structure of a compound with molecular formula C₅H₁₂ that has

a. one tertiary carbon.

b. no secondary carbons.

PROBLEM 5 ♦

Draw the structures and name the four constitutional isomers with molecular formula C₄H₉Br.

PROBLEM 6 ♦

Which of the following statements can be used to prove that carbon is tetrahedral?

- a. CH₃Br does not have constitutional isomers.
- **b.** CBr₄ does not have a dipole moment.
- c. CH₂Br₂ does not have constitutional isomers.

PROBLEM 7 ♦

Draw the structure for each of the following:

- **a.** isopropyl alcohol
- **c.** *sec*-butyl iodide
- e. tert-butylamine

- **b.** isopentyl fluoride
- **d.** tert-pentyl alcohol
- **f.** *n*-octyl bromide

PROBLEM 8 ♦

Name the following compounds:

a. CH₃OCH₂CH₃

CH₃CH₂CHNH

e. CH₃CHCH₂Br

| Сн.

b. CH₃OCH₂CH₂CH₃

d. CH₃CH₂CH₂CH₂OH

f. CH₃CH₂CHCl

3.2 THE NOMENCLATURE OF ALKANES

The systematic name of an alkane is obtained using the following rules:

1. Determine the number of carbons in the longest continuous carbon chain. The longest continuous chain is not always in a straight line; sometimes you must "turn a corner" to obtain the longest continuous chain. This chain is called the **parent hydrocarbon**. The name that indicates the number of carbons in the parent hydrocarbon becomes the alkane's "last name." For example, a parent hydrocarbon with eight carbons is called *octane*.

LEARN THE STRATEGY

First determine the number of carbons in the longest continuous chain.

2. The name of any alkyl substituent that is attached to the parent hydrocarbon is placed in front of the name of the parent hydrocarbon, together with a number to designate the carbon to which the alkyl substituent is attached. The carbons in the parent chain are numbered in the direction that gives the substituent as low a number as possible. The substituent's name and the name of the parent hydrocarbon are joined into one word, preceded by a hyphen that connects the substituent's number with its name.

Number the chain in the direction that gives the substituent as low a number as possible.

Numbers are used only for systematic names, never for common names.

Substituents are listed in alphabetical order.

A number and a word are separated by a hyphen; numbers are separated by a comma.

"di," "tri," "tetra," "sec," and "tert" are ignored in alphabetizing substituents.

Only systematic names have numbers; common names never contain numbers.

$$\begin{array}{c} CH_3 \\ CH_3CHCH_2CH_2CH_3 \\ \\ \text{common name:} \\ \text{systematic name:} \\ \\ \text{systematic name:} \\ \end{array}$$

3. If more than one substituent is attached to the parent hydrocarbon, the chain is numbered in the direction that produces a name containing the lowest of the possible numbers. The substituents are listed in alphabetical order, with each substituent preceded by the appropriate number. In the following example, the correct name contains a 3 as its lowest number, whereas the incorrect name contains a 4 as its lowest number:

If two or more substituents are the same, the prefixes "di," "tri," and "tetra" are used to indicate how many identical substituents the compound has. The numbers indicating the locations of the identical substituents are listed together, separated by commas. There are no spaces on either side of a comma. There must be as many numbers in a name as there are substituents. The prefixes "di," "tri," "tetra," "sec," and "tert" are ignored in alphabetizing substituents.

4. When numbering in either direction leads to the same lowest number for one of the substituents, the chain is numbered in the direction that gives the lowest possible number to one of the remaining substituents.

5. If the same substituent numbers are obtained in both directions, the first group listed receives the lower number.

Only if the same set of numbers is obtained in both directions does the first group listed get the lower number.

6. Systematic names for branched substituents are obtained by numbering the alkyl substituent starting at the carbon attached to the parent hydrocarbon. This means that the carbon attached to the parent hydrocarbon is always the number-1 carbon of the substituent. In a compound such as 4-(1-methylethyl)octane, the substituent name is in parentheses; the number inside the parentheses indicates a position on the substituent, whereas the number outside the parentheses indicates a position on the parent hydrocarbon. (If a prefix such as "di" is part of a branch name, it *is* included in the alphabetization.)

If the substituent has a common name, the common name can be used instead of the parenthetical name.

If the substituent does not have a common name, the parenthetical name must be used.

$$\begin{array}{cccc} CH_2CH_2CH_3 & CH_3 & CH_3 \\ CH_3CH_2CH_2CH_2CH_2CH_2CH_3 & CH_3CHCH_2CHCH_2CH_2CH_3 \\ CH_3CH_2CH_2CH_2CH_3 & CH_3CHCHCH_2CHCH_2CH_2CH_3 \\ CH_3CH_2CH_2CH_3 & CH_3CH_2CH_2CH_2CH_3 \\ CH_3 & CH_2CH_2CH_2CH_2CH_3 \\ \end{array}$$

7. If a compound has two or more chains of the same length, the parent hydrocarbon is the chain with the greatest number of substituents.

In the case of two hydrocarbon chains with the same number of carbons, choose the one with the most substituents.

These rules allow you to name thousands of alkanes, and eventually you will learn the additional rules necessary to name many other kinds of compounds. The rules are important for looking up a compound in the scientific literature, because it usually is listed by its systematic name. Nevertheless, you must also learn common names because they are so entrenched in chemists' vocabularies that they are widely used in scientific conversation and are often found in the literature.

Look at the systematic names (the ones written in blue) for the isomeric hexanes and isomeric heptanes shown on p. 91 to make sure you understand how they are constructed.

USETHE STRATEGY

```
PROBLEM 9 ♦
What is each compound's systematic name?
                        CH_3
                                      CH_3
                                                                                                            f. CH<sub>3</sub>C — CHCH<sub>2</sub>CH<sub>3</sub> CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
a. CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>CCH<sub>3</sub>
                                       ĊНа
                                                                                                             g. CH<sub>3</sub>CH<sub>2</sub>C(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
b. CH_3CH_2C(CH_3)_3
c. CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
                                                                                                             h. CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
                        CH3CHCH2CH3
                                                                                                                                                       CH(CH<sub>3</sub>)<sub>2</sub>
               CH_3
                                       CH<sub>3</sub>
                                                                                                             i. CH3CHCH2CH2CHCH3
d. CH3CHCH2CH2CCH3
                                                                                                                            CH<sub>2</sub>CH<sub>3</sub>
e. CH<sub>3</sub>CH<sub>2</sub>C(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>CH(CH<sub>3</sub>)CH(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>
```

How Is the Octane Number of Gasoline Determined?

The gasoline engines used in most cars operate by creating a series of carefully timed, controlled explosions. Fuel is mixed with air in the engine cyclinders, compressed, and then ignited by a spark. If the fuel ignites too easily, the heat of compression can initiate combustion before the spark plug fires. The result is a pinging or knocking sound and a loss of power.

Higher-quality fuels are less likely to knock. The quality of a fuel is indicated by its octane number. Straight-chain hydrocarbons have low octane numbers and make poor fuels. Heptane, for example, with an arbitrarily assigned octane number of 0, causes engines to knock badly. Branched-chain alkanes have more hydrogens bonded to primary carbons. These are the bonds that require the most energy to break and, therefore, make combustion more difficult to initiate, thereby reducing knocking. For example, 2,2,4-trimethylpentane does not cause knocking and has arbitrarily been assigned an octane number of 100.





The octane number of a gasoline is determined by comparing its knocking with the knocking of mixtures of heptane and 2,2,4-trimethylpentane. The octane number given to the gasoline corresponds to the percent of 2,2,4-trimethylpentane in the matching mixture. Thus, a gasoline with an octane rating of 91 has the same "knocking" property as a mixture of 91% 2,2,4-trimethylpentane and 9% heptane. The term *octane number* originated from the fact that 2,2,4-trimethylpentane contains eight carbons. Because slightly different methods are used to determine the octane number, gasoline in Canada and the United States has an octane number that is 4 to 5 points less than the same gasoline in Europe and Australia.

PROBLEM 10 SOLVED

LEARN THE STRATEGY

USE THE STRATEGY

Draw the structure for 2,2-dimethyl-4-propyloctane.

SOLUTION The name of the parent hydrocarbon is *octane*, so the longest continuous chain has eight carbons. Now draw the parent hydrocarbon and number it.

$$\overset{1}{C} \overset{2}{-C} \overset{3}{-C} \overset{4}{-C} \overset{5}{-C} \overset{6}{-C} \overset{7}{-C} \overset{8}{-C}$$

Put the substituents (two methyl groups and a propyl group) on the appropriate carbons.

Add the appropriate number of hydrogens so that each carbon is bonded to four atoms.

$$\begin{array}{cccc} CH_3 & CH_2CH_2CH_3 \\ -CH_3 - C-CH_2 - CH-CH_2-CH_2-CH_2-CH_3 \\ -CH_3 \end{array}$$

PROBLEM 11 ♦

Draw the structure for each of the following:

- a. 2,2-dimethyl-4-isopropyloctane
- **b.** 2,3-dimethylhexane
- c. 4,4-diethyldecane

- **d.** 2,4,5-trimethyl-4-(1-methylethyl)heptane
- e. 2,5-dimethyl-4-(2-methylpropyl)octane
- **f.** 4-(1,1-dimethylethyl)octane

PROBLEM 12 SOLVED

- a. Draw the 18 isomeric octanes.
- **b.** Give each isomer its systematic name.
- c. How many isomers have common names?
- d. Which isomers contain an isopropyl group?
- e. Which isomers contain a sec-butyl group?
- **f.** Which isomers contain a *tert*-butyl group?

SOLUTION TO 12 a. Start with the isomer with an eight-carbon continuous chain. Then draw isomers with a seven-carbon continuous chain plus one methyl group. Next, draw isomers with a six-carbon continuous chain plus two methyl groups or one ethyl group. Then draw isomers with a five-carbon continuous chain plus three methyl groups or one methyl group and one ethyl group. Finally, draw a four-carbon continuous chain with four methyl groups. (Your answers to Problem 12 b. will tell you whether you have drawn duplicate structures, because if two structures have the same systematic name, they represent the same compound.)

PROBLEM 13

Give each substituent on the nine-carbon chain a common name and a parenthetical name.

PROBLEM 14 ♦

Draw the structure and give the systematic name for a compound with molecular formula C_5H_{12} that has

- a. only primary and secondary hydrogens.
- c. one tertiary hydrogen.

b. only primary hydrogens.

d. two secondary hydrogens.

3.3 THE NOMENCLATURE OF CYCLOALKANES

Cycloalkanes are alkanes with their carbon atoms arranged in a ring. Cycloalkanes are named by adding the prefix "cyclo" to the alkane name that signifies the number of carbons in the ring.









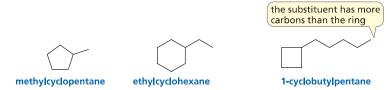
Cycloalkanes are generally written as skeletal structures. Because of the ring, a cycloalkane has two fewer hydrogens than an acyclic (noncyclic) alkane with the same number of carbons. This means that the general molecular formula for a cycloalkane is C_nH_{2n} .

The rules for naming cycloalkanes resemble the rules for naming acyclic (noncyclic) alkanes:

1. In a cycloalkane with an attached alkyl substituent, the ring is the parent hydrocarbon unless the substituent has more carbons than the ring. In that case, the substituent is the parent hydrocarbon and the ring is named as a substituent. There is no need to number the position of a single substituent on a ring.

LEARN THE STRATEGY

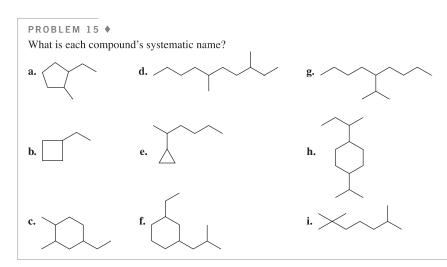
If there is only one substituent on a ring, do not give that substituent a number.



2. If the ring has two different substituents, they are listed in *alphabetical order* and the number-1 position is given to the substituent listed first.

3. If there are more than two substituents on the ring, they are listed in alphabetical order, and the substituent given the number-1 position is the one that results in a second substituent getting as low a number as possible. If two substituents have the same low numbers, the ring is numbered—either clockwise or counterclockwise—in the direction that gives the third substituent the lowest possible number.

USETHE STRATEGY



PROBLEM-SOLVING STRATEGY

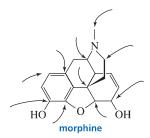
Interpreting a Skeletal Structure

How many hydrogens are attached to each of the indicated carbons in cholesterol?

None of the carbons in the compound has a charge, so each needs to be bonded to four atoms. Thus, if the carbon has only one bond showing, it must be attached to three hydrogens that are not shown; if the carbon has two bonds showing, it must be attached to two hydrogens that are not shown; and so on. Check each of the answers (shown in red) to see that this is so.

PROBLEM 16

How many hydrogens are attached to each of the indicated carbons in morphine?



PROBLEM 17 ♦

Convert the following condensed structures into skeletal structures:

- a. CH₃CH₂CH₂CH₂CH₂CH₂OH
- **b.** $CH_3CH_2CH_2CH_2CH_3$

c. CH₃CH₂CHCH₂CHCH₂CH₃

- d. CH₃CH₂CH₂CH₂OCH₃
- e. CH₃CH₂NHCH₂CH₂CH₃
 - CH₂
- f. CH₃CHCH₂CH₂CHCH₃

PROBLEM 18

Convert the structures in Problem 9 into skeletal structures.

PROBLEM 19

Draw a condensed and a skeletal structure for each of the following:

a. 3,4-diethyl-2-methylheptane

b. 2,2,5-trimethylhexane

LEARN THE STRATEGY

USETHE STRATEGY

Condensed structures show atoms but show few, if any, bonds, whereas skeletal structures show bonds but show few, if any, atoms.

3.4 THE NOMENCLATURE OF ALKYL HALIDES

An **alkyl halide** is a compound in which a hydrogen of an alkane has been replaced by a halogen. Alkyl halides are classified as primary, secondary, or tertiary, depending on the carbon to which the halogen is attached (Section 3.1).