ORGANIC CHEMISTRY I

Organic Compounds: Alkanes and Their Stereochemistry

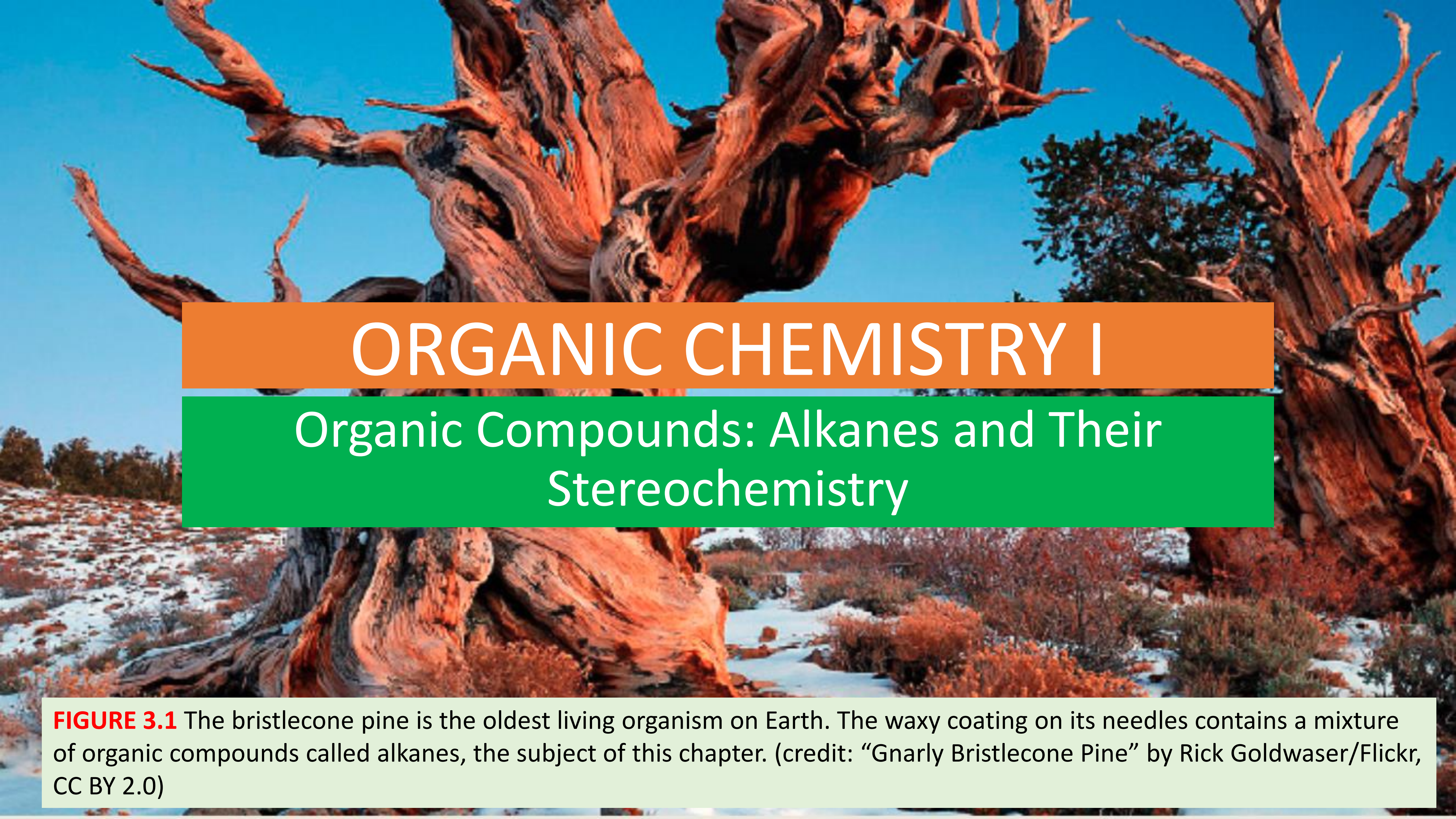


FIGURE 3.1 The bristlecone pine is the oldest living organism on Earth. The waxy coating on its needles contains a mixture of organic compounds called alkanes, the subject of this chapter. (credit: “Gnarly Bristlecone Pine” by Rick Goldwaser/Flickr, CC BY 2.0)

Topic Discussion

Why This Chapter?
3.1 Functional Groups
3.2 Alkanes and Alkane Isomers
3.3 Alkyl Groups
3.4 Naming Alkanes
3.5 Properties of Alkanes
3.6 Conformations of Ethane
3.7 Conformations of Other Alkanes
Chemistry Matters—Gasoline

Why This Chapter?

- The group of organic compounds called alkanes are simple and relatively unreactive, but they nevertheless provide a useful vehicle for introducing some important general ideas.

- In this chapter, we'll use alkanes to introduce the basic approach to naming organic compounds and to take an initial look at some of the three-dimensional aspects of molecules, a topic of particular importance in understanding biological organic chemistry.

3.1 Functional Groups

The structural features that make it possible to classify compounds into families are called functional groups. A **functional group** is a group of atoms within a molecule that has a characteristic chemical behavior.

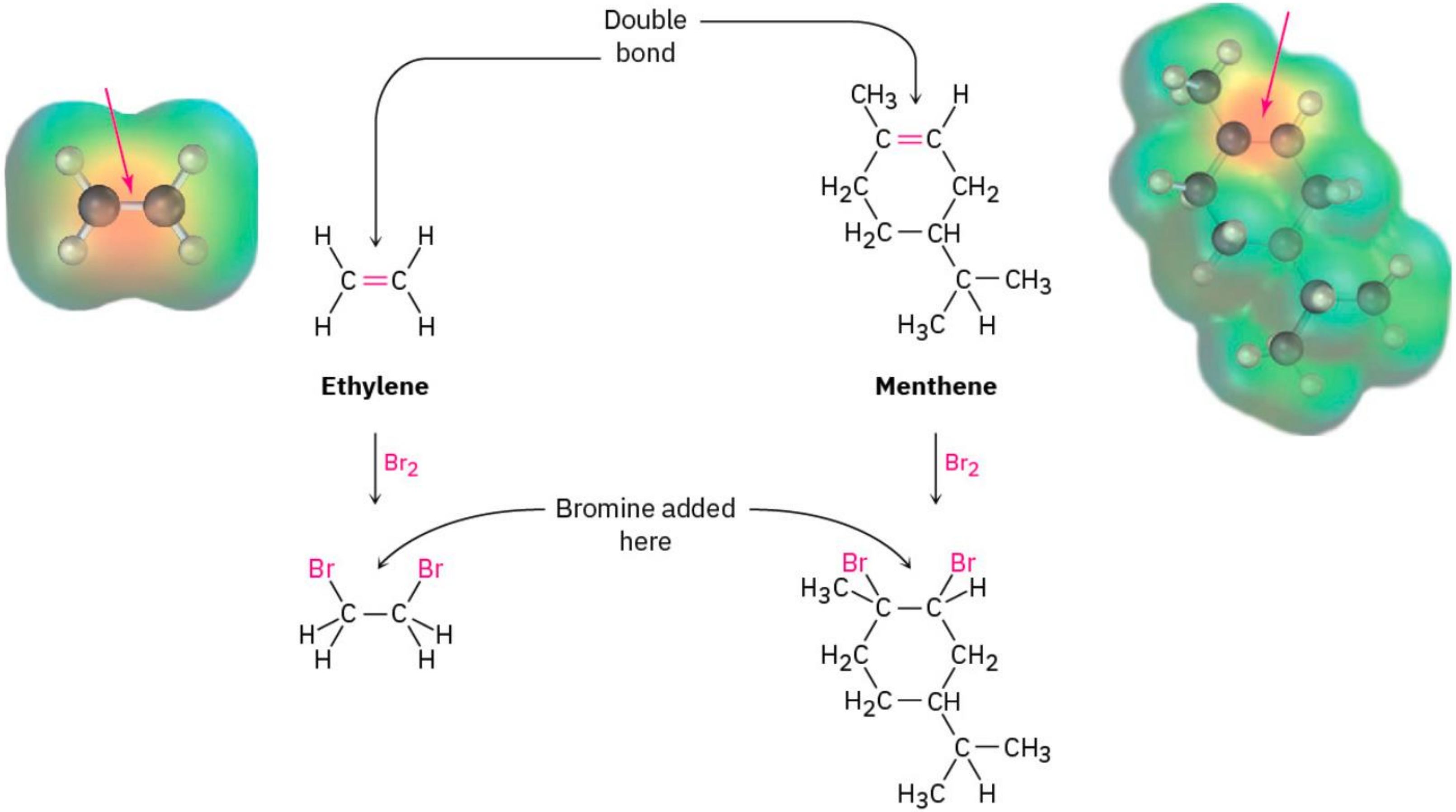
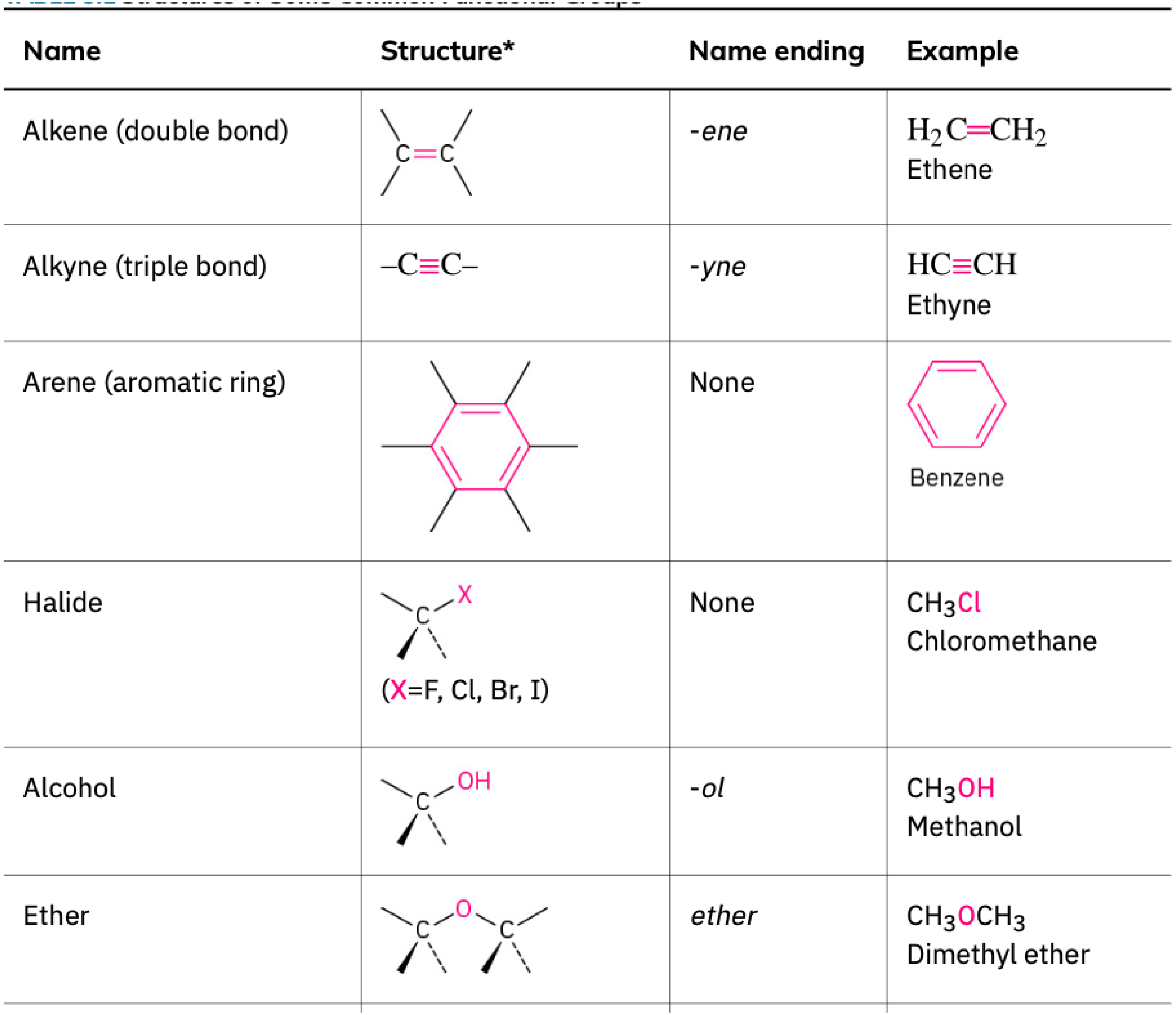


FIGURE 3.2
The reactions of ethylene and menthene with bromine. In both molecules, the carbon–carbon double-bond functional group has a similar polarity pattern, so both molecules react with Br_2 in the same way. The size and complexity of the molecules are not important.

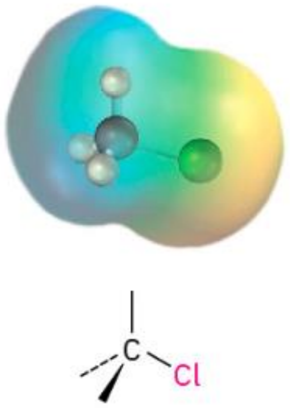
TABLE 3.1 Structures of Some Common Functional Groups



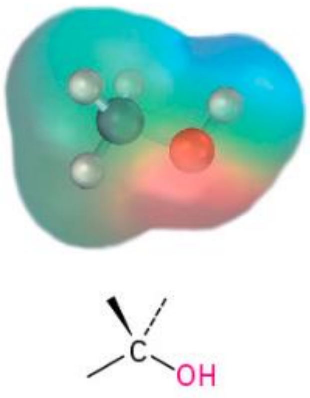
Name	Structure*	Name ending	Example
Alkene (double bond)	C=C	-*ene*	$H_2C{=}CH_2$ Ethene
Alkyne (triple bond)	$-C\equiv C-$	-*yne*	$HC\equiv CH$ Ethyne
Arene (aromatic ring)		None	Benzene
Halide	C X (X=F, Cl, Br, I)	None	CH_3Cl Chloromethane
Alcohol	C OH	-*ol*	CH_3OH Methanol
Ether	C O C	*ether*	CH_3OCH_3 Dimethyl ether

etc.

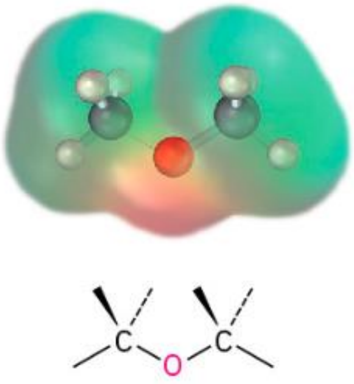
Functional Groups with Carbon Singly Bonded to an Electronegative Atom



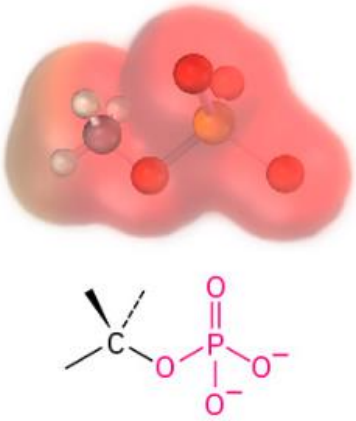
**Alkyl halide
(haloalkane)**



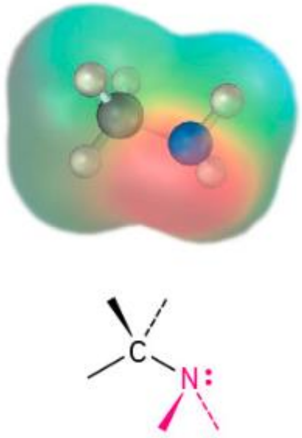
Alcohol



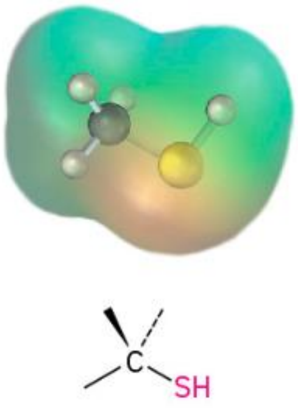
Ether



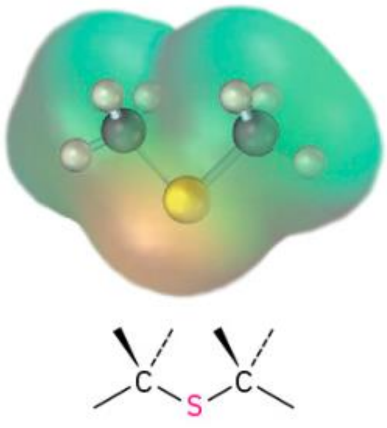
Phosphate



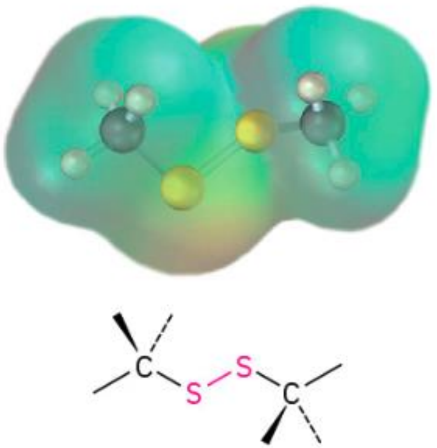
Amine



Thiol

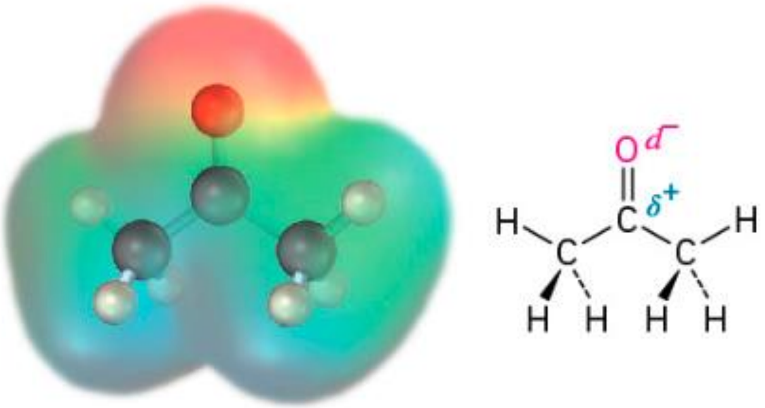


Sulfide

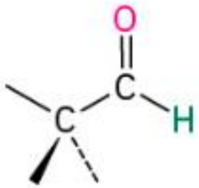


Disulfide

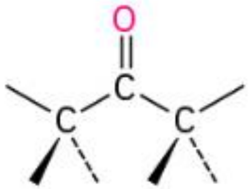
Functional Groups with a Carbon–Oxygen Double Bond (Carbonyl Groups)



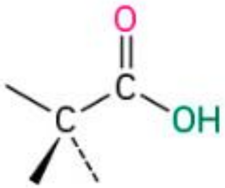
Acetone—a typical carbonyl compound



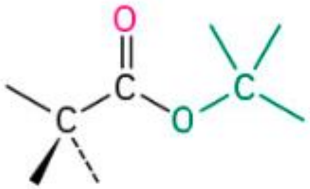
Aldehyde



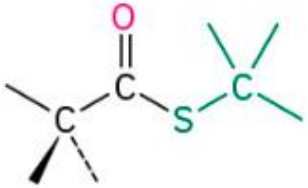
Ketone



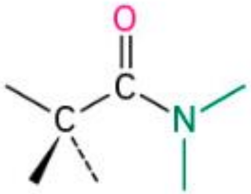
Carboxylic acid



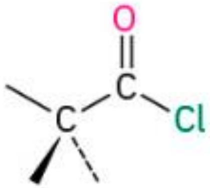
Ester



Thioester

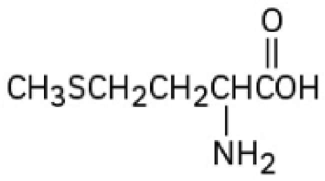


Amide

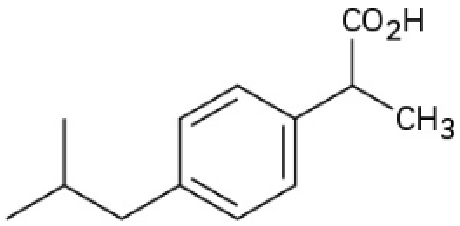


Acid chloride

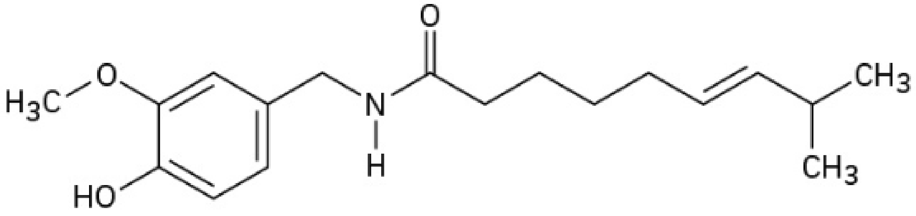
PROBLEM 3-1 Use Table 3.1 to identify the functional groups in each of the following molecules: (a) Methyonine, amino acids. (b) Ibuprofen, pain reliever



$CH_3SCH_2CH_2\underset{NH_2}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}OH$

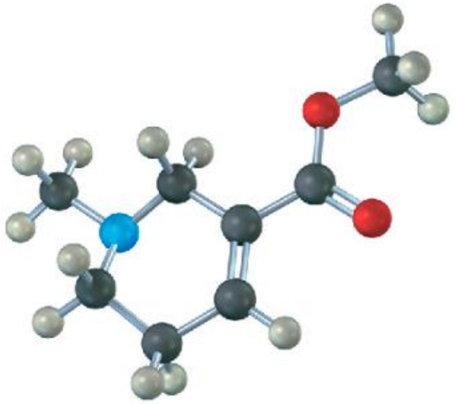


(c) Capsaicin, the pungent substance in chili peppers:

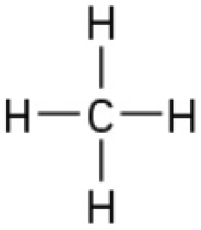


PROBLEM 3-2 Propose structures for simple molecules that contain the following functional groups: (a) Alcohol (b) Aromatic ring (c) Carboxylic acid (d) Amine (e) Both ketone and amine (f) Two double bonds

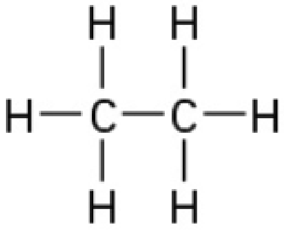
PROBLEM 3-3 Identify the functional groups in the following model of arecoline, aveterinary drug used to control worms in animals. Convert the drawing in to a line-bond structure and a molecular formula (red= O, blue = N, black = C, gray = H).



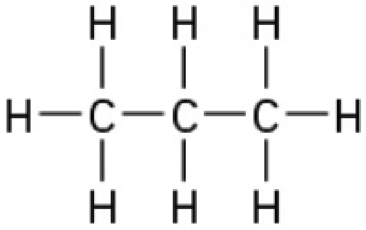
3.2 Alkanes and Alkane Isomers



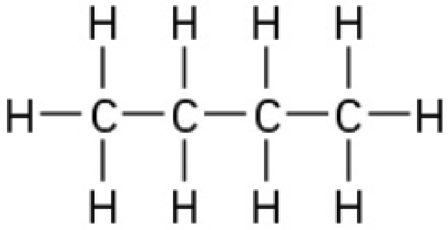
Methane



Ethane



Propane

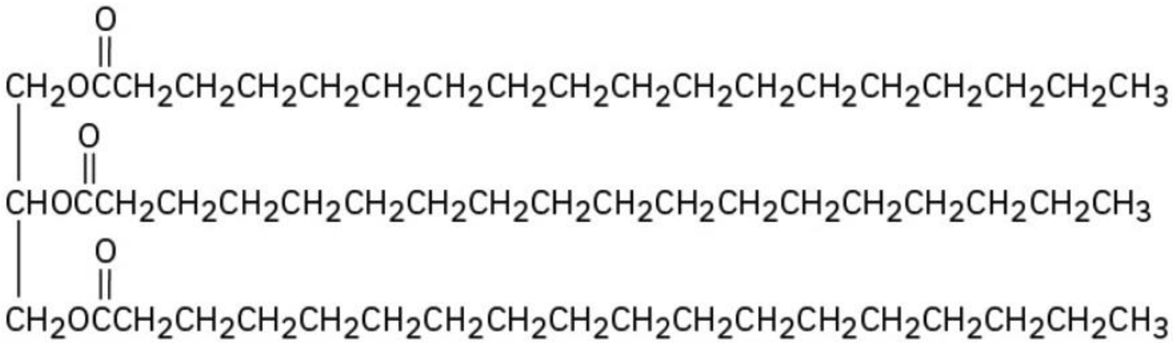


. . . and so on

Butane

Alkanes are often described as saturated hydrocarbons: **hydrocarbons** because they contain only carbon and hydrogen; **saturated** because they have only C–C and C–H single bonds and thus contain the maximum possible number of hydrogens per carbon. They have the general formula **C_nH_{2n+2}**, where **n** is an integer.

Alkanes are also occasionally called **aliphatic** compounds, a name derived from the Greek aleiphas, meaning “fat.” We’ll see in **Section 27.1** that many animal fats contain long carbon chains similar to alkanes.



A typical animal fat

Think about the ways that carbon and hydrogen might combine to make alkanes. With one carbon and four hydrogens, only one structure is possible: methane, CH_4. Similarly, there is only one combination of two carbons with six hydrogens (ethane, CH_3CH_3) and only one combination of three carbons with eight hydrogens (propane, $CH_3CH_2CH_3$).

CH_4

Methane, CH_4

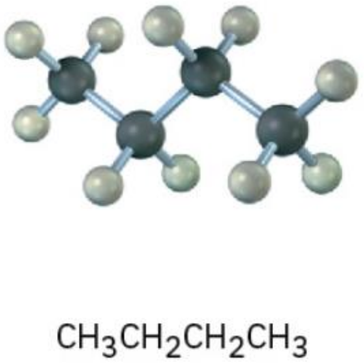
CH_3CH_3

Ethane, C_2H_6

$CH_3CH_2CH_3$

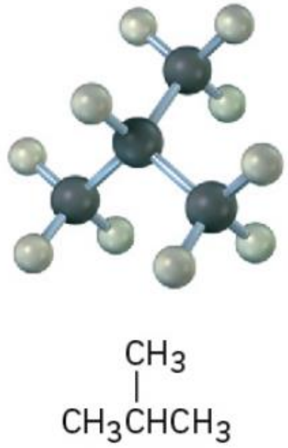
Propane, C_3H_8

When larger numbers of carbons and hydrogens combine, however, more than one structure is possible. For example, there are two substances with the formula C4H10: the four carbons can all be in a row (butane), or they can branch (isobutane). Similarly, there are three C_5H_{12} molecules, and so on for larger alkanes.



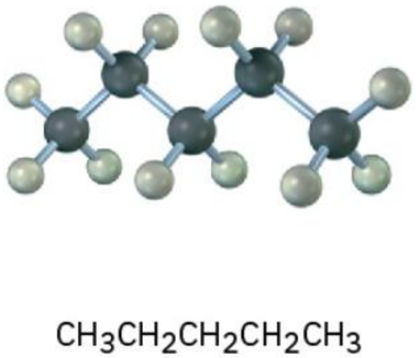
$CH_3CH_2CH_2CH_3$

Butane, C_4H_{10}



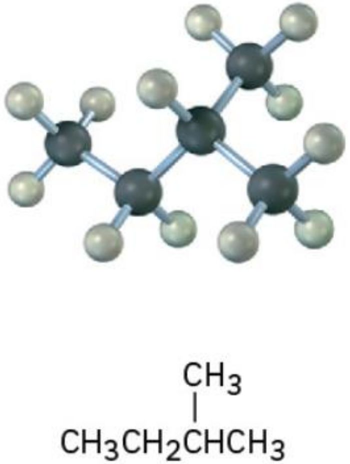
$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3$$

Isobutane, C_4H_{10}
(2-methylpropane)



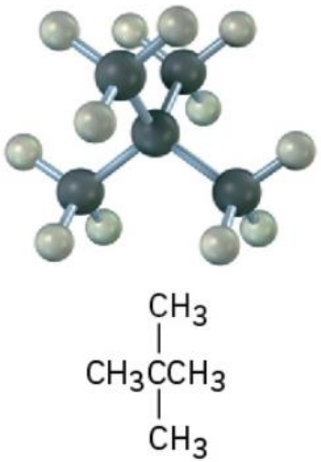
$CH_3CH_2CH_2CH_2CH_3$

Pentane, C_5H_{12}



$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3$$

2-Methylbutane, C_5H_{12}



$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_3$$

2,2-Dimethylpropane, C_5H_{12}

Compounds like butane and pentane, whose carbons are all connected in a row, are called **straight-chain alkanes**, or normal alkanes. Compounds like 2-methylpropane (isobutane), 2-methylbutane, and 2,2-dimethylpropane, whose carbon chains branch, are called **branched-chain alkanes**.

Compounds like the two C4H10 molecules and the three C5H12 molecules, which have the same formula but different structures, are called **Isomers**, from the Greek isos + meros, meaning “made of the same parts.” Isomers have the same numbers and kinds of atoms but differ in the way the atoms are arranged. Compounds like butane and isobutane, whose atoms are connected differently, are called **constitutional isomers**.

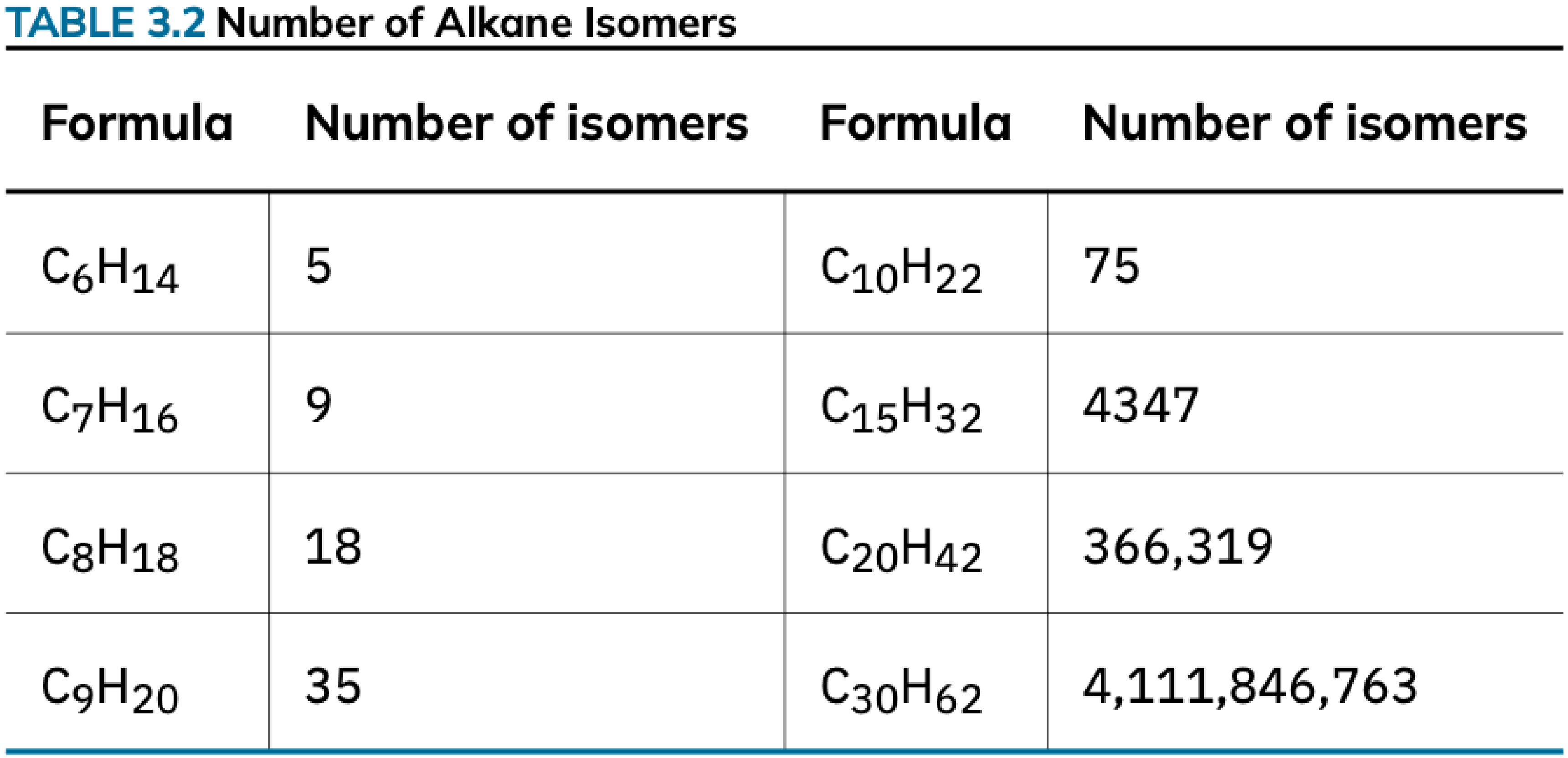
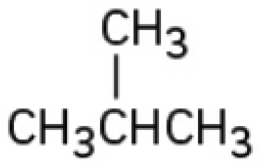


TABLE 3.2 **Number of Alkane Isomers**

Formula	Number of isomers	Formula	Number of isomers
C_6H_{14}	5	$C_{10}H_{22}$	75
C_7H_{16}	9	$C_{15}H_{32}$	4347
C_8H_{18}	18	$C_{20}H_{42}$	366,319
C_9H_{20}	35	$C_{30}H_{62}$	4,111,846,763

Different carbon skeletons
C_4H_{10}



$\mathrm{CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3}$

and

$CH_3CH_2CH_2CH_3$

2-Methylpropane (isobutane)

Butane

Different functional groups
C_2H_6O

CH_3CH_2OH

and

CH_3OCH_3

Ethanol

Dimethyl ether

Different position of functional groups
C_3H_9N

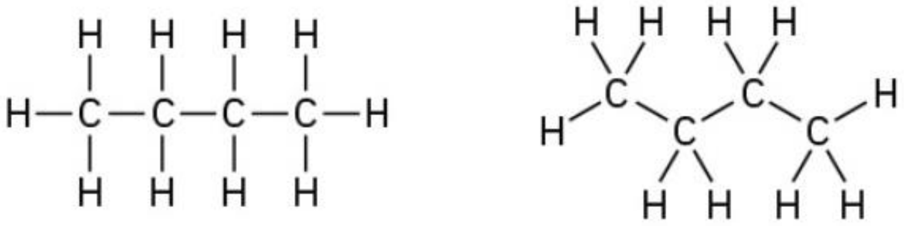
$\mathrm{CH_3\overset{\overset{\displaystyle NH_2}{|}}{C}HCH_3}$

and

$CH_3CH_2CH_2NH_2$

Isopropylamine

Propylamine



$CH_3{-}CH_2{-}CH_2{-}CH_3$ $CH_3CH_2CH_2CH_3$ $CH_3(CH_2)_2CH_3$

FIGURE 3.3 Some representations of butane, C_4H_{10}. The molecule is the same regardless of how it's drawn. These structures imply only that butane has a continuous chain of four carbon atoms; they do not imply any specific geometry.

Straight-chain alkanes are named according to the number of carbon atoms they contain, as shown in **TABLE 3.3**. With the exception of the first four compounds—methane, ethane, propane, and butane—whose names have historical roots, the alkanes are named based on Greek numbers. The suffix -ane is added to the end of each name to indicate that the molecule identified is an alkane. Thus, pentane is the five-carbon alkane, hexane is the six-carbon alkane, and so on.

TABLE 3.3 Names of Straight-Chain Alkanes

Number of carbons (n)	Name	Formula (C_nH_{2n+2})	Number of carbons (n)	Name	Formula (C_nH_{2n+2})
1	Methane	CH_4	9	Nonane	C_9H_{20}
2	Ethane	C_2H_6	10	Decane	$C_{10}H_{22}$
3	Propane	C_3H_8	11	Undecane	$C_{11}H_{24}$
4	Butane	C_4H_{10}	12	Dodecane	$C_{12}H_{26}$
5	Pentane	C_5H_{12}	13	Tridecane	$C_{13}H_{28}$
6	Hexane	C_6H_{14}	20	Icosane	$C_{20}H_{42}$
7	Heptane	C_7H_{16}	30	Triacontane	$C_{30}H_{62}$
8	Octane	C_8H_{18}			

WORKED EXAMPLE 3.1

Drawing the Structures of Isomers

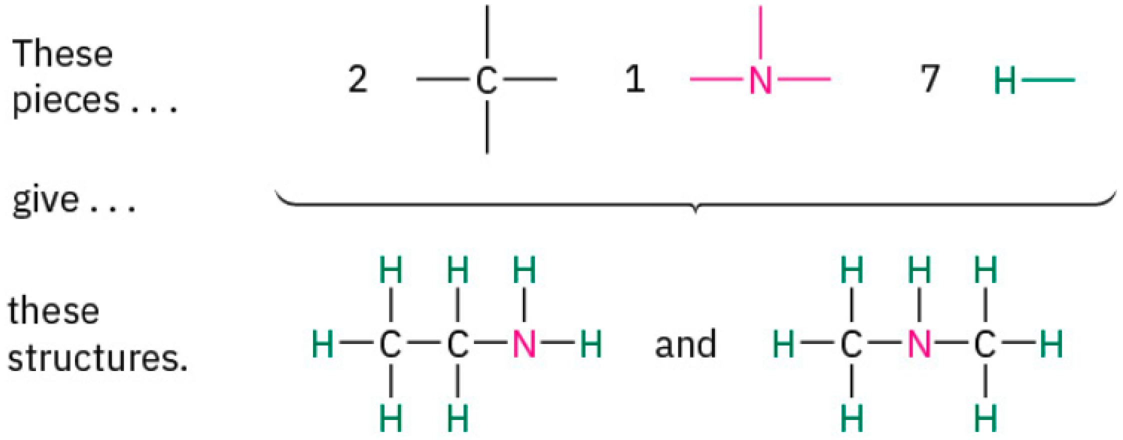
Propose structures for two isomers with the formula C_2H_7N.

Strategy

We know that carbon forms four bonds, nitrogen forms three, and hydrogen forms one. Write down the carbon atoms first, and then use trial and error plus intuition to put the pieces together.

Solution

There are two isomeric structures. One has the connection C–C–N, and the other has the connection C–N–C.



PROBLEM 3-4 Draw structures of the five isomers of C_6H_{14}.

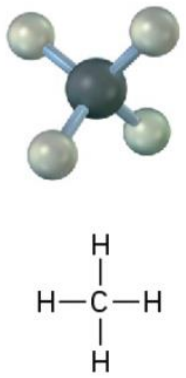
PROBLEM 3-5 Propose structures that meet the following descriptions:

(a) Two isomeric esters with the formula $C_5H_{10}O_2$:
(b) Two isomeric nitriles with the formula C_4H_7N
(c) Two isomeric disulfides with the formula $C_4H_{10}S_2$

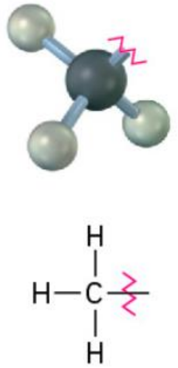
PROBLEM 3-6 How many isomers are there with the following descriptions?

(a) Alcohols with the formula C_3H_8O **(b)** Bromoalkanes with the formula C_4H_9Br
(c) Thioesters with the formula C_4H_8OS

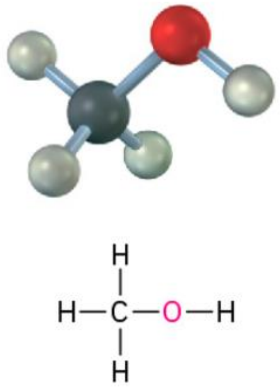
3.3 Alkyl Groups



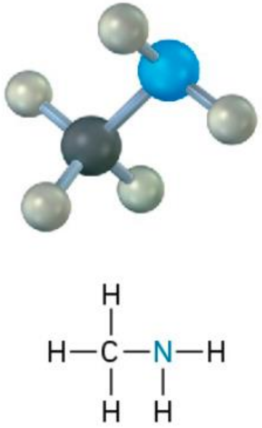
Methane



A methyl group



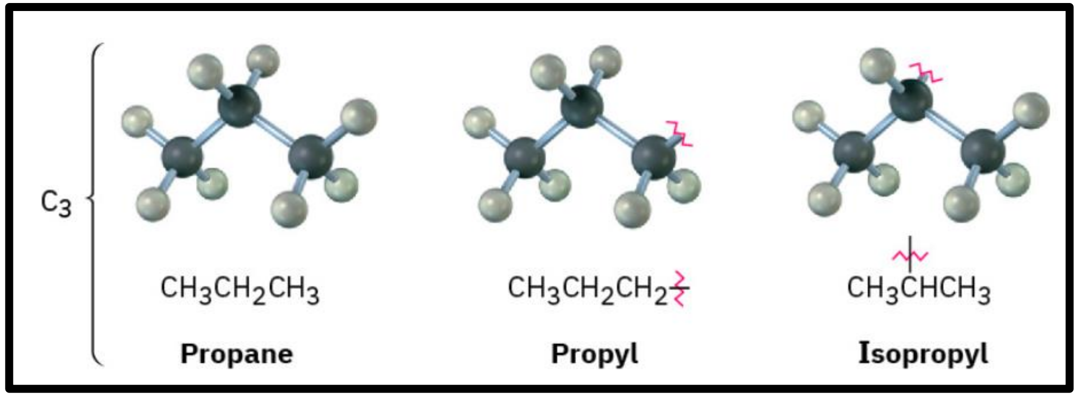
Methyl alcohol (methanol)



Methylamine

TABLE 3.4 Some Straight-Chain Alkyl Groups

Alkane	Name	Alkyl group	Name (abbreviation)
CH_4	Methane	$-CH_3$	Methyl (Me)
CH_3CH_3	Ethane	$-CH_2CH_3$	Ethyl (Et)
$CH_3CH_2CH_3$	Propane	$-CH_2CH_2CH_3$	Propyl (Pr)
$CH_3CH_2CH_2CH_3$	Butane	$-CH_2CH_2CH_2CH_3$	Butyl (Bu)
$CH_3CH_2CH_2CH_2CH_3$	Pentane	$-CH_2CH_2CH_2CH_2CH_3$	Pentyl, or amyl



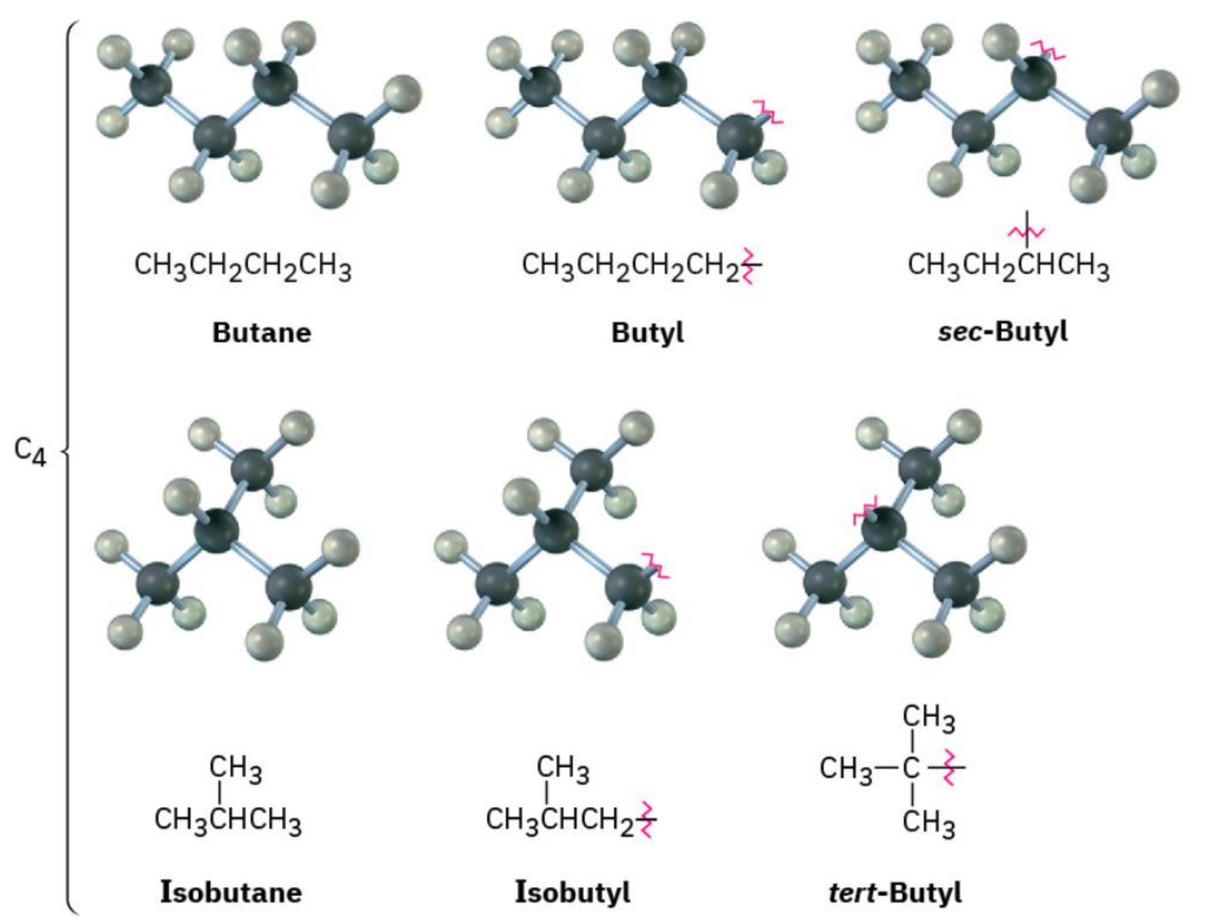
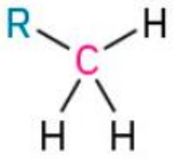


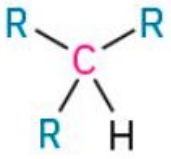
FIGURE 3.4 Alkyl groups generated from straight-chain alkanes.

One further comment about naming alkyl groups: the prefixes sec- (for secondary) and tert- (for tertiary) used for the C4 alkyl groups in **FIGURE 3.4** refer to the number of other carbon atoms attached to the branching carbon atom. There are four possibilities: primary (1°), secondary (2°), tertiary (3°), and quaternary (4°).

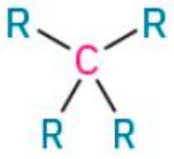


***Primary* carbon (1°) is bonded to one other carbon.**

***Secondary* carbon (2°) is bonded to two other carbons.**



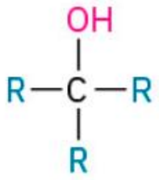
***Tertiary* carbon (3°) is bonded to three other carbons.**



***Quaternary* carbon (4°) is bonded to four other carbons.**

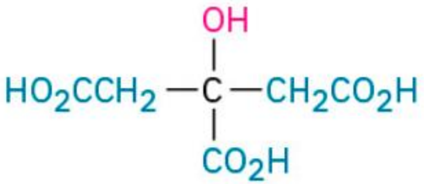
The symbol **R** is used here and throughout organic chemistry to represent a generalized organic group. The R group can be methyl, ethyl, propyl, or any of a multitude of others. You might think of **R** as representing the **R**est of the molecule, which isn’t specified.

The terms primary, secondary, tertiary, and quaternary are routinely used in organic chemistry, and their meanings need to become second nature.



$$\begin{array}{c} \mathrm{OH} \\ | \\ \mathrm{R-C-R} \\ | \\ \mathrm{R} \end{array}$$

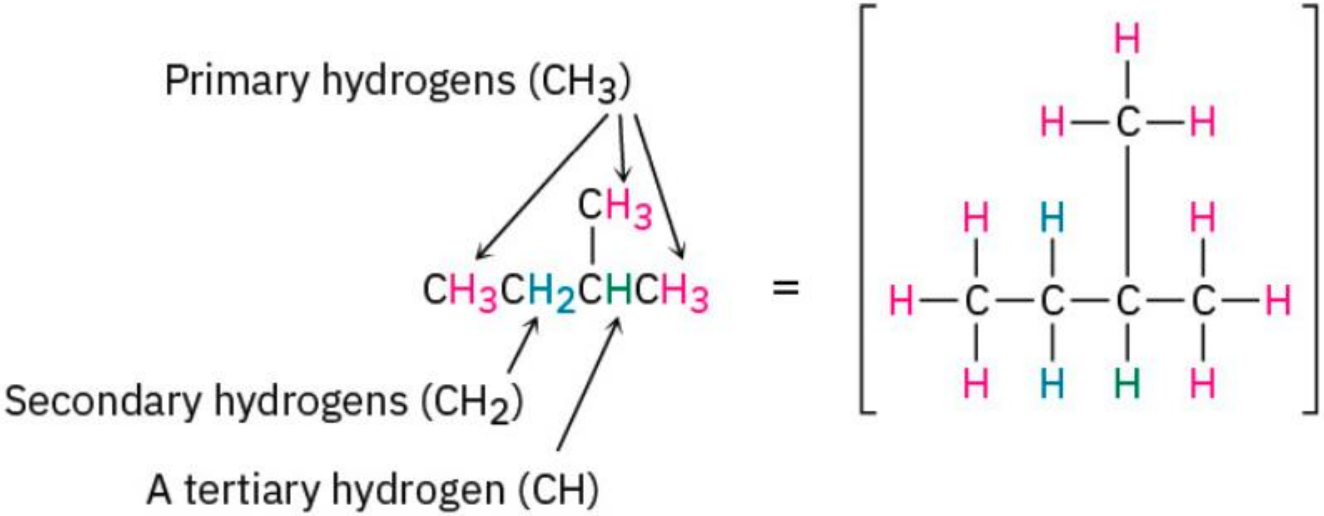
General class of tertiary alcohols, R_3COH



$$\begin{array}{c} \mathrm{OH} \\ | \\ \mathrm{HO_2CCH_2-C-CH_2CO_2H} \\ | \\ \mathrm{CO_2H} \end{array}$$

Citric acid—a specific tertiary alcohol

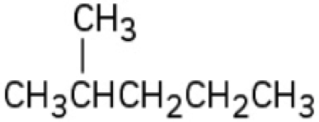
In addition to speaking of carbon atoms as being primary, secondary, or tertiary, we speak of hydrogens in the same way.



PROBLEM 3-7 Draw the eight 5-carbon alkyl groups (pentyl isomers).

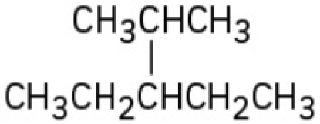
PROBLEM 3-8 Identify the carbon atoms in the following molecules as primary, secondary, tertiary, or quaternary:

(a)



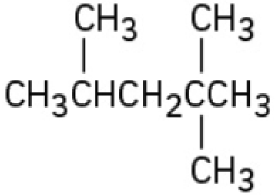
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_3$

(b)



$CH_3CH_2\overset{CH_3CHCH_3}{\overset{|}{C}}HCH_2CH_3$

(c)



$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_3$

PROBLEM 3-9 Identify the hydrogen atoms on the compounds shown in Problem 3-8 as primary, secondary, or tertiary.

PROBLEM 3-10 Draw structures of alkanes that meet the following descriptions:

(a) An alkane with two tertiary carbons **(b)** An alkane that contains an isopropyl group

(c) An alkane that has one quaternary and one secondary carbon

3.4 Naming Alkanes

A chemical name typically has four parts in the IUPAC system: parent, prefix, locant, and suffix. The **parent** name identifies the main part of the molecule and tells how many carbon atoms are in that part. **Prefixes** identify the various **substituent** groups attached to the parent. **Locants** give the positions of the attached substituents. And the **suffix** identifies the primary functional group attached to the parent.

Locant — Prefix — Parent — Suffix

Where are the substituents and functional groups?

What are the substituents?

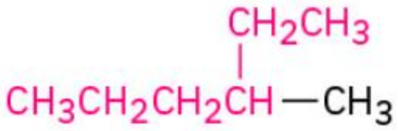
How many carbons?

What is the primary functional group?

STEP 1

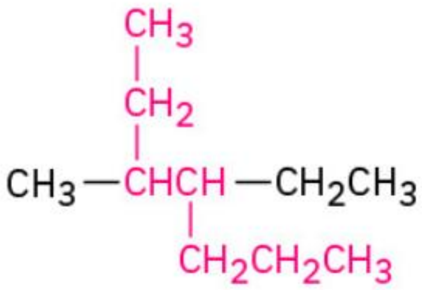
Identify the parent hydrocarbon.

(a) Find the longest continuous chain of carbon atoms in the molecule, and use the name of that chain as the parent name. The longest chain may not always be apparent from the manner of writing; you may have to “turn corners.”



$CH_3CH_2CH_2\overset{\overset{CH_2CH_3}{|}}{C}H-CH_3$

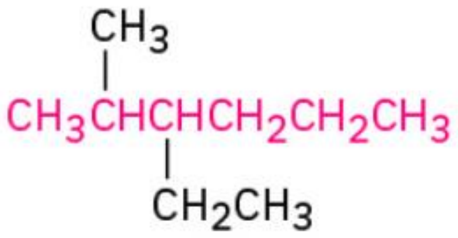
Named as a substituted hexane



$CH_3-\overset{\overset{\overset{CH_3}{|}}{CH_2}}{\overset{|}{C}}H\underset{\underset{CH_2CH_2CH_3}{|}}{C}H-CH_2CH_3$

Named as a substituted heptane

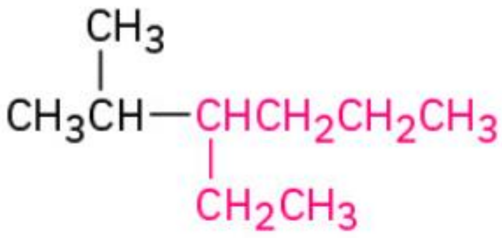
(b) If two different chains of equal length are present, choose the one with the larger number of branch points as the parent.



$CH_3\overset{\overset{CH_3}{|}}{C}H\underset{\underset{CH_2CH_3}{|}}{C}HCH_2CH_2CH_3$

Named as a hexane with *two* substituents

NOT



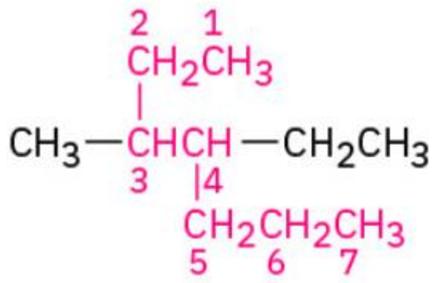
$CH_3\overset{\overset{CH_3}{|}}{C}H-\underset{\underset{CH_2CH_3}{|}}{C}HCH_2CH_2CH_3$

as a hexane with *one* substituent

STEP 2

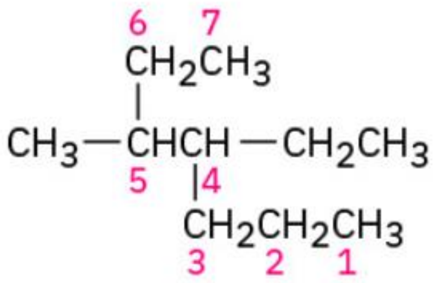
Number the atoms in the longest chain.

(a) Beginning at the end nearer the first branch point, number each carbon atom in the parent chain.



$$CH_3{-}\underset{3}{\overset{\overset{2\quad 1}{CH_2CH_3}}{\overset{|}{C}H}}\underset{\underset{\underset{5\quad 6\quad 7}{CH_2CH_2CH_3}}{|\,4}}{CH}{-}CH_2CH_3$$

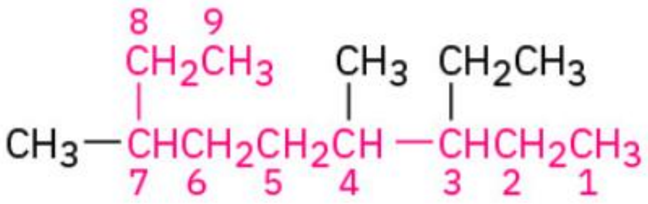
NOT



$$CH_3{-}\underset{5}{\overset{\overset{6\quad 7}{CH_2CH_3}}{\overset{|}{C}H}}\underset{\underset{\underset{3\quad 2\quad 1}{CH_2CH_2CH_3}}{|\,4}}{CH}{-}CH_2CH_3$$

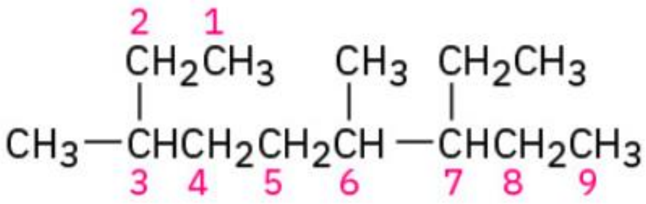
The first branch occurs at C3 in the proper system of numbering, not at C4.

(b) If there is branching an equal distance away from both ends of the parent chain, begin numbering at the end nearer the second branch point.



$$CH_3{-}\underset{7}{\overset{\overset{8\quad 9}{CH_2CH_3}}{\overset{|}{C}H}}\underset{6}{C}H_2\underset{5}{C}H_2\underset{4}{\overset{\overset{CH_3}{|}}{C}H}{-}\underset{3}{\overset{\overset{CH_2CH_3}{|}}{C}H}\underset{2}{C}H_2\underset{1}{C}H_3$$

NOT

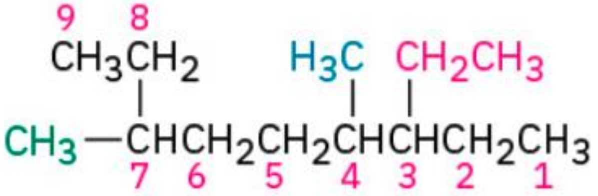


$$CH_3{-}\underset{3}{\overset{\overset{2\quad 1}{CH_2CH_3}}{\overset{|}{C}H}}\underset{4}{C}H_2\underset{5}{C}H_2\underset{6}{\overset{\overset{CH_3}{|}}{C}H}{-}\underset{7}{\overset{\overset{CH_2CH_3}{|}}{C}H}\underset{8}{C}H_2\underset{9}{C}H_3$$

STEP 3

Identify and number the substituents.

(a) Assign a number to each substituent to locate its point of attachment to the parent chain.

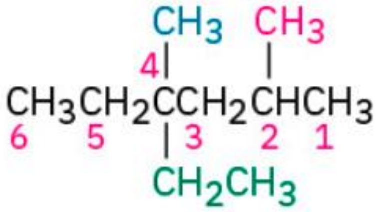


$$CH_3-\underset{7}{\overset{\overset{9\;\;8}{CH_3CH_2}}{C}}H\,\underset{6}{C}H_2\,\underset{5}{C}H_2\,\underset{4}{\overset{H_3C}{C}}H\,\underset{3}{\overset{CH_2CH_3}{C}}H\,\underset{2}{C}H_2\,\underset{1}{C}H_3$$

Named as a nonane

Substituents:		
	On C3, CH_2CH_3	(3-ethyl)
	On C4, CH_3	(4-methyl)
	On C7, CH_3	(7-methyl)

(b) If there are two substituents on the same carbon, give both the same number. There must be as many numbers in the name as there are substituents.



$$\underset{6}{C}H_3\,\underset{5}{C}H_2\,\overset{\overset{CH_3}{4|}}{\underset{\underset{CH_2CH_3}{|\,3}}{C}}\,CH_2\,\underset{2}{\overset{\overset{CH_3}{|}}{C}}H\,\underset{1}{C}H_3$$

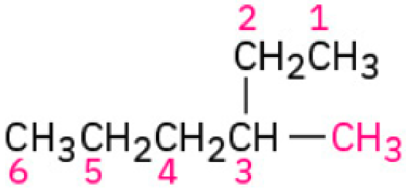
Named as a hexane

Substituents:		
	On C2, CH_3	(2-methyl)
	On C4, CH_3	(4-methyl)
	On C4, CH_2CH_3	(4-ethyl)

STEP 4

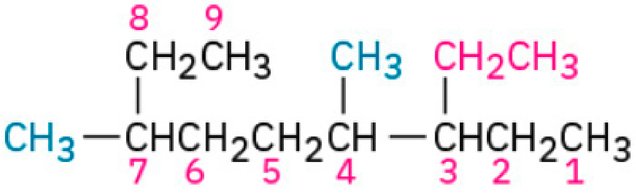
Write the name as a single word.

Use hyphens to separate the different prefixes, and use commas to separate numbers. If two or more different substituents are present, cite them in alphabetical order. If two or more identical substituents are present on the parent chain, use one of the multiplier prefixes *di*-, *tri*-, *tetra*-, and so forth, but don't use these prefixes for alphabetizing. Full names for some of the examples we have been using are as follows:



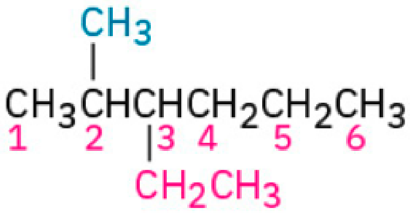
$CH_3CH_2CH_2\overset{CH_2CH_3}{C}H-CH_3$

3-Methylhexane



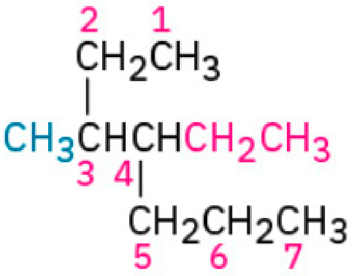
$CH_3-\overset{CH_2CH_3}{C}HCH_2CH_2\overset{CH_3}{C}H-\overset{CH_2CH_3}{C}HCH_2CH_3$

3-Ethyl-4,7-dimethylnonane



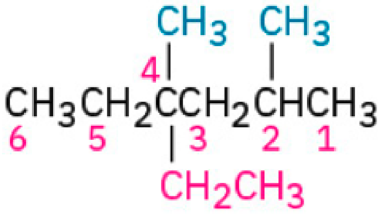
$CH_3\overset{CH_3}{C}H\underset{CH_2CH_3}{C}HCH_2CH_2CH_3$

3-Ethyl-2-methylhexane



$CH_3\overset{CH_2CH_3}{C}H\underset{CH_2CH_2CH_3}{C}HCH_2CH_3$

4-Ethyl-3-methylheptane



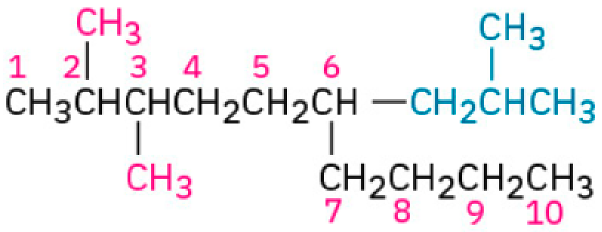
$CH_3CH_2\overset{CH_3}{\underset{CH_2CH_3}{C}}CH_2\overset{CH_3}{C}HCH_3$

4-Ethyl-2,4-dimethylhexane

STEP 5

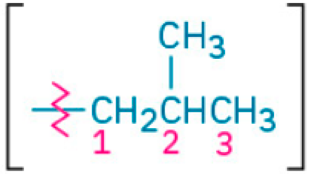
Name a branched substituent as though it were itself a compound.

In some particularly complex cases, a fifth step is necessary. It occasionally happens that a substituent on the main chain is itself branched. In the following case, for instance, the substituent at C6 is a three-carbon chain with a methyl group. To name the compound fully, the branched substituent must first be named.



$$CH_3\overset{CH_3}{\overset{|}{C}}H\underset{\underset{CH_3}{|}}{C}HCH_2CH_2\underset{\underset{CH_2CH_2CH_2CH_3}{|}}{C}H-CH_2\overset{CH_3}{\overset{|}{C}}HCH_3$$

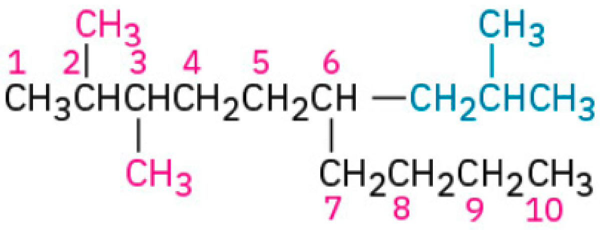
Named as a 2,3,6-trisubstituted decane



$$\left[-CH_2\overset{CH_3}{\overset{|}{C}}HCH_3\right]$$

A 2-methylpropyl substituent

Number the branched substituent beginning at the point of its attachment to the main chain, and identify it—in this case, a 2-methylpropyl group. The substituent is treated as a whole and is alphabetized according to the first letter of its complete name, including any numerical prefix. It is set off in parentheses when naming the entire molecule.



$$CH_3\overset{CH_3}{\overset{|}{C}}H\underset{\underset{CH_3}{|}}{C}HCH_2CH_2\underset{\underset{CH_2CH_2CH_2CH_3}{|}}{C}H-CH_2\overset{CH_3}{\overset{|}{C}}HCH_3$$

2,3-Dimethyl-6-(2-methylpropyl)decane

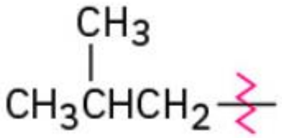
For historical reasons, some of the simpler branched-chain alkyl groups also have nonsystematic, common names, as noted earlier.

CH_3CHCH_3

Isopropyl (*i*-Pr)

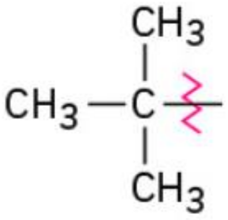
$CH_3CH_2CHCH_3$

***sec*-Butyl (*sec*-Bu)**



$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2-$

Isobutyl

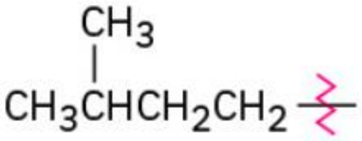


$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-$

***tert*-Butyl (*t*-butyl or *t*-Bu)**

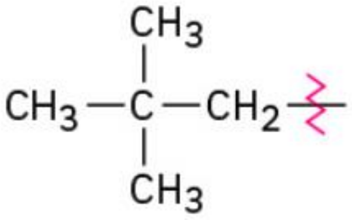
3-Carbon alkyl group

4-Carbon alkyl groups



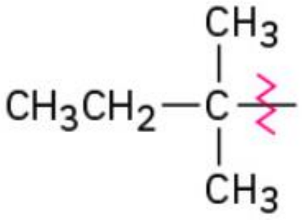
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2-$

Isopentyl, also called isoamyl (*i*-amyl)



$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-$

Neopentyl



$CH_3CH_2-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-$

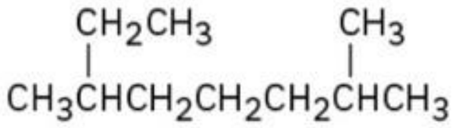
***tert*-Pentyl, also called *tert*-amyl (*t*-amyl)**

5-Carbon alkyl groups

WORKED EXAMPLE 3.2

Naming Alkanes

What is the IUPAC name for the following alkane?

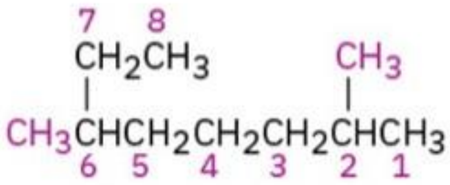


$$CH_3\overset{\overset{\displaystyle CH_2CH_3}{|}}{C}HCH_2CH_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3$$

Strategy

Find the longest continuous carbon chain in the molecule, and use that as the parent name. This molecule has a chain of eight carbons—octane—with two methyl substituents. (You have to turn corners to see it.) Numbering from the end nearer the first methyl substituent indicates that the methyls are at C2 and C6.

Solution



$$CH_3\overset{\overset{\displaystyle \overset{7}{C}H_2\overset{8}{C}H_3}{|}}{\underset{6}{C}}H\underset{5}{C}H_2\underset{4}{C}H_2\underset{3}{C}H_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{2}{C}}H\underset{1}{C}H_3$$

2,6-Dimethyloctane

WORKED EXAMPLE 3.3

Converting a Chemical Name into a Structure

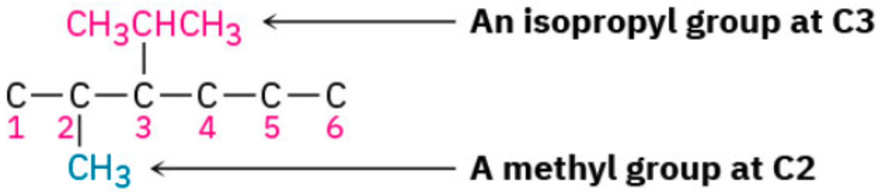
Draw the structure of 3-isopropyl-2-methylhexane.

Strategy

This is the reverse of **Worked Example 3.2** and uses a reverse strategy. Look at the parent name (hexane), and draw its carbon structure.

C–C–C–C–C–C **Hexane**

Next, find the substituents (3-isopropyl and 2-methyl), and place them on the proper carbons.



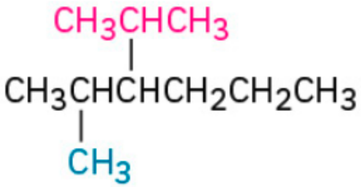
$$\mathrm{C{-}\underset{\displaystyle CH_3}{C}{-}\overset{\displaystyle CH_3CHCH_3}{C}{-}C{-}C{-}C}$$

An isopropyl group at C3

A methyl group at C2

Finally, add hydrogens to complete the structure.

Solution



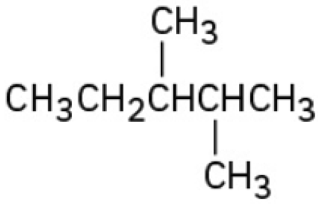
$$\mathrm{CH_3\underset{\displaystyle CH_3}{C}H\overset{\displaystyle CH_3CHCH_3}{C}HCH_2CH_2CH_3}$$

3-Isopropyl-2-methylhexane

PROBLEM 3-11 Give IUPAC names for the following compounds:

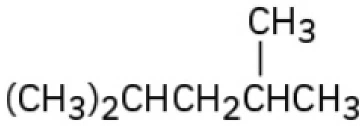
(a) The three isomers of C_5H_{12}

(b)



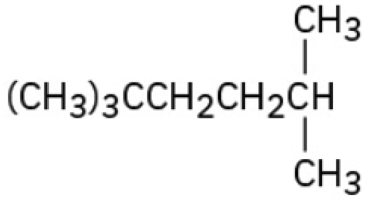
$CH_3CH_2\overset{CH_3}{\overset{|}{C}}H\underset{\underset{CH_3}{|}}{C}HCH_3$

(c)



$(CH_3)_2CHCH_2\overset{CH_3}{\overset{|}{C}}HCH_3$

(d)



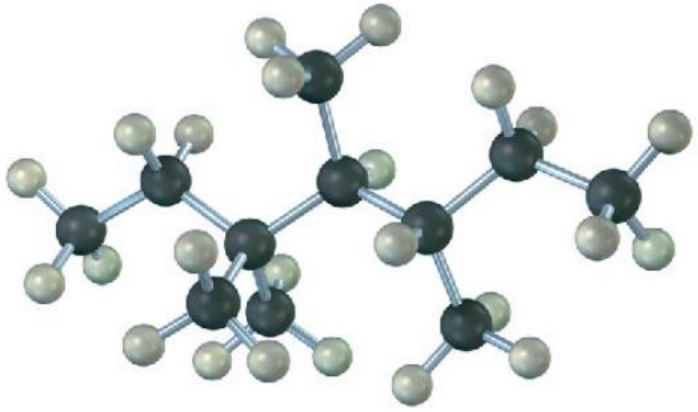
$(CH_3)_3CCH_2CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}H$

PROBLEM 3-12 Draw structures corresponding to the following IUPAC names:

(a) 3,4-Dimethylnonane **(b)** 3-Ethyl-4,4-dimethylheptane **(c)** 2,2-Dimethyl-4-propyloctane **(d)** 2,2,4-Trimethylpentane

PROBLEM 3-13 Name the eight 5-carbon alkyl groups you drew in Problem 3-7.

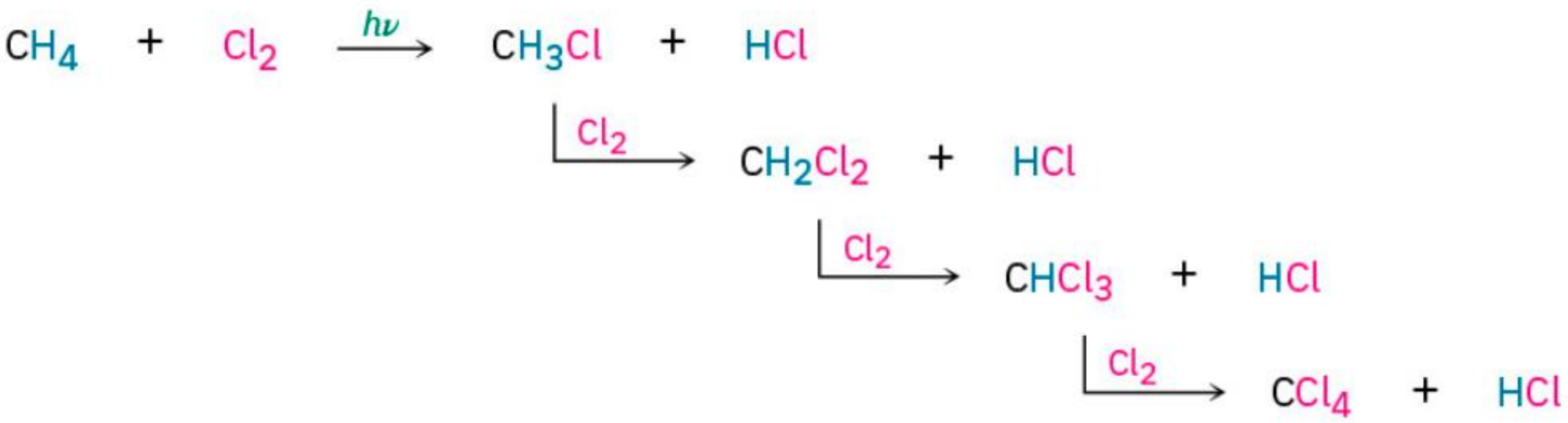
PROBLEM 3-14 Give the IUPAC name for the following hydrocarbon, and convert the drawing into a skeletal structure.



3.5 Properties of Alkanes

Alkanes are sometimes referred to as paraffins, a word derived from the Latin parum affinis, meaning “little affinity.” This term aptly describes their behavior, for alkanes show little chemical affinity for other substances and are chemically inert to most laboratory reagents. They are also relatively inert biologically and are not often involved in the chemistry of living organisms. Alkanes do, however, react with oxygen, halogens, and a few other substances under appropriate conditions.

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + 890\text{ kJ/mol (213 kcal/mol)}$$



$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$
$$CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 + HCl$$
$$CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 + HCl$$
$$CHCl_3 \xrightarrow{Cl_2} CCl_4 + HCl$$

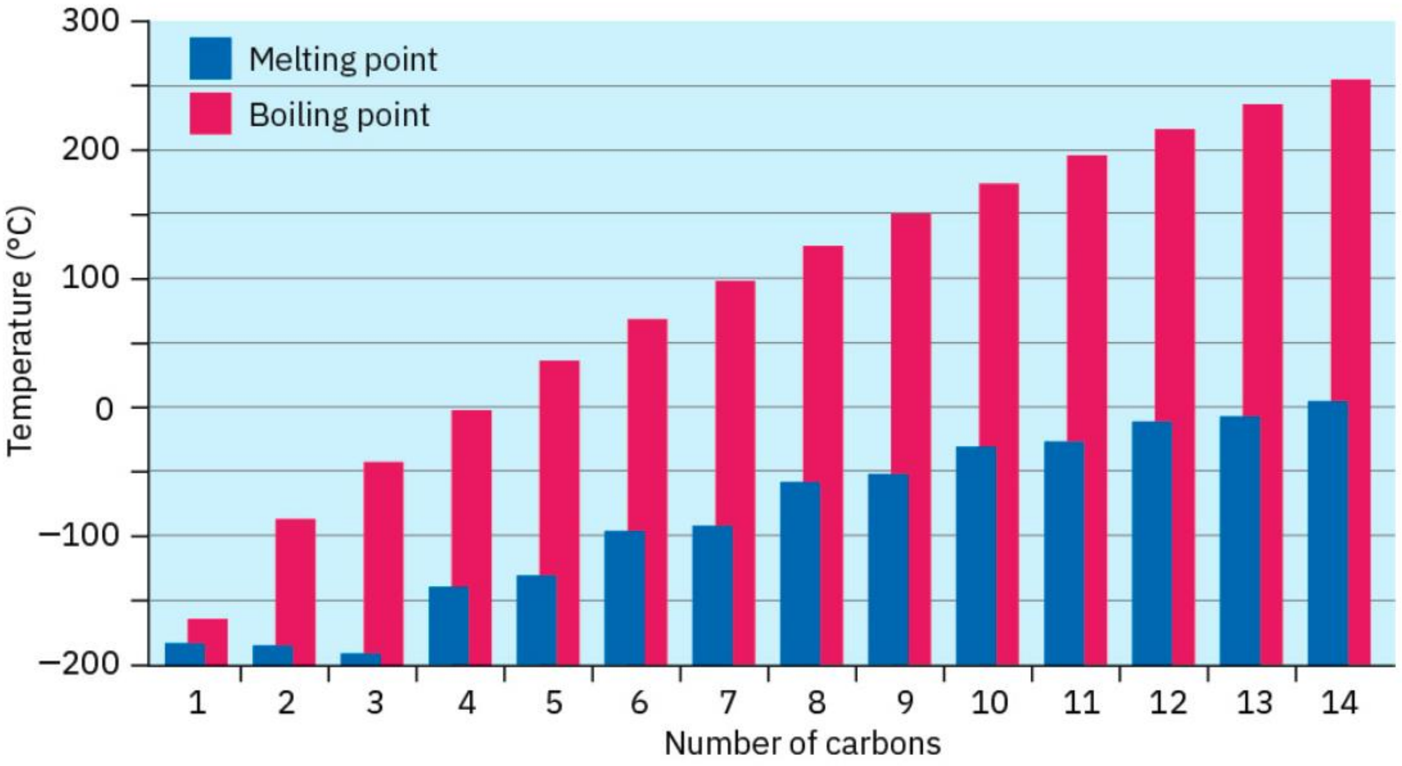


FIGURE 3.5 A plot of melting and boiling points versus number of carbon atoms for the C1–C14 straight-chain alkanes. There is a regular increase with molecular size.

Another effect seen in alkanes is that increased branching lowers an alkane's boiling point. Thus, pentane has no branches and boils at 36.1 °C, isopentane (2-methylbutane) has one branch and boils at 27.85 °C, and neopentane (2,2-dimethylpropane) has two branches and boils at 9.5 °C. Similarly, octane boils at 125.7 °C, whereas isooctane (2,2,4-trimethylpentane) boils at 99.3 °C. Branched-chain alkanes are lower-boiling because they are more nearly spherical than straight-chain alkanes, have smaller surface areas, and consequently have smaller dispersion forces.

3.6 Conformations of Ethane

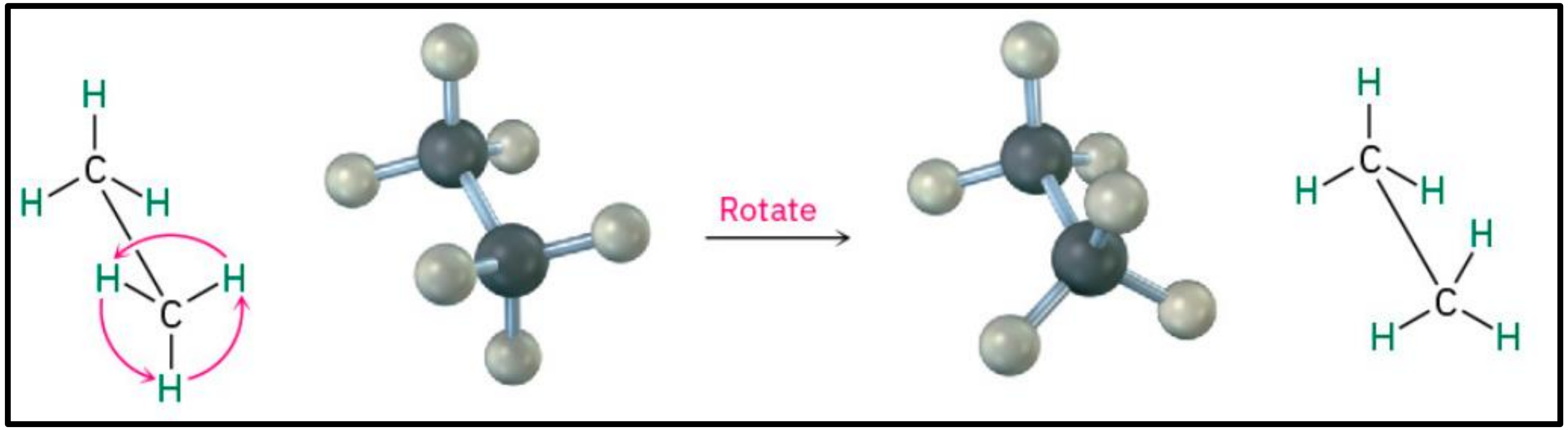


FIGURE 3.6 Rotation occurs around the carbon–carbon single bond in ethane because of σ bond cylindrical symmetry.

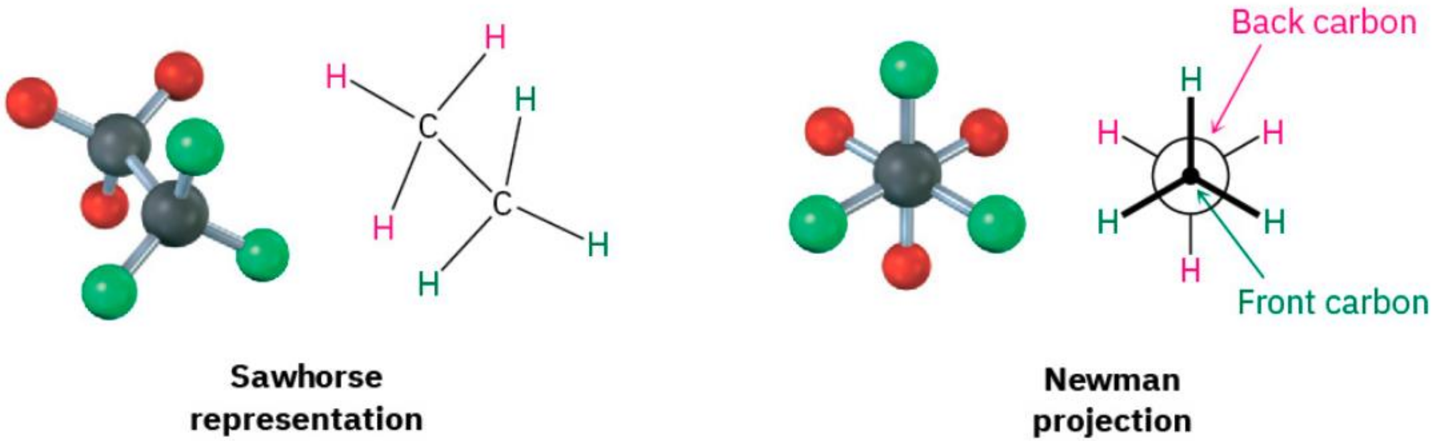
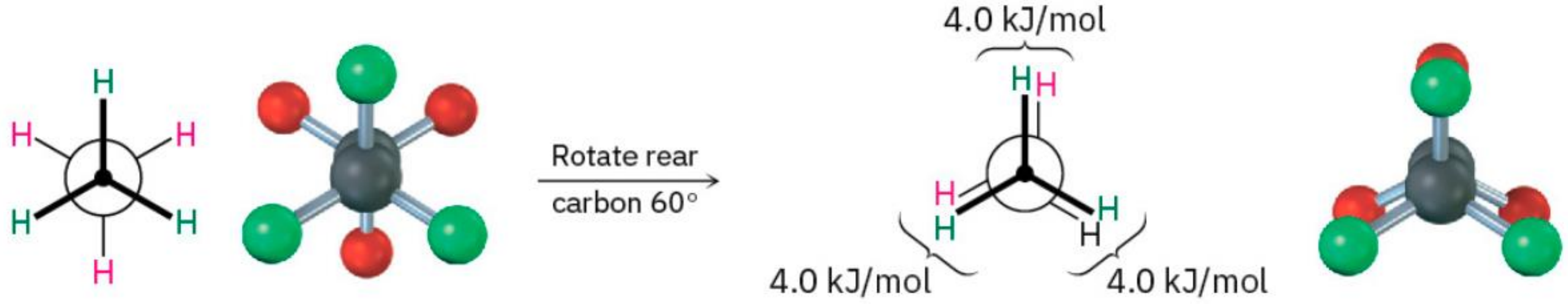


FIGURE 3.7 A sawhorse representation and a Newman projection of ethane. The sawhorse representation views the molecule from an oblique angle, while the Newman projection views the molecule end-on. Note that the molecular model of the Newman projection appears at first to have six atoms attached to a single carbon. Actually, the front carbon, with three attached green atoms, is directly in front of the rear carbon, with three attached red atoms.

The highest- energy, least stable conformation is the one in which the six C–H bonds are as close as possible—eclipsed in a Newman projection. At any given instant, about 99% of ethane molecules have an approximately **staggered conformation** and only about 1% are near the **eclipsed conformation**.



Ethane—staggered conformation

Ethane—eclipsed conformation

The extra 12 kJ/mol of energy present in the eclipsed conformation of ethane is called **torsional strain**. Its cause has been the subject of controversy, but the major factor is an interaction between C–H bonding orbitals on one carbon and antibonding orbitals on the adjacent carbon, which stabilizes the staggered conformation relative to the eclipsed one.

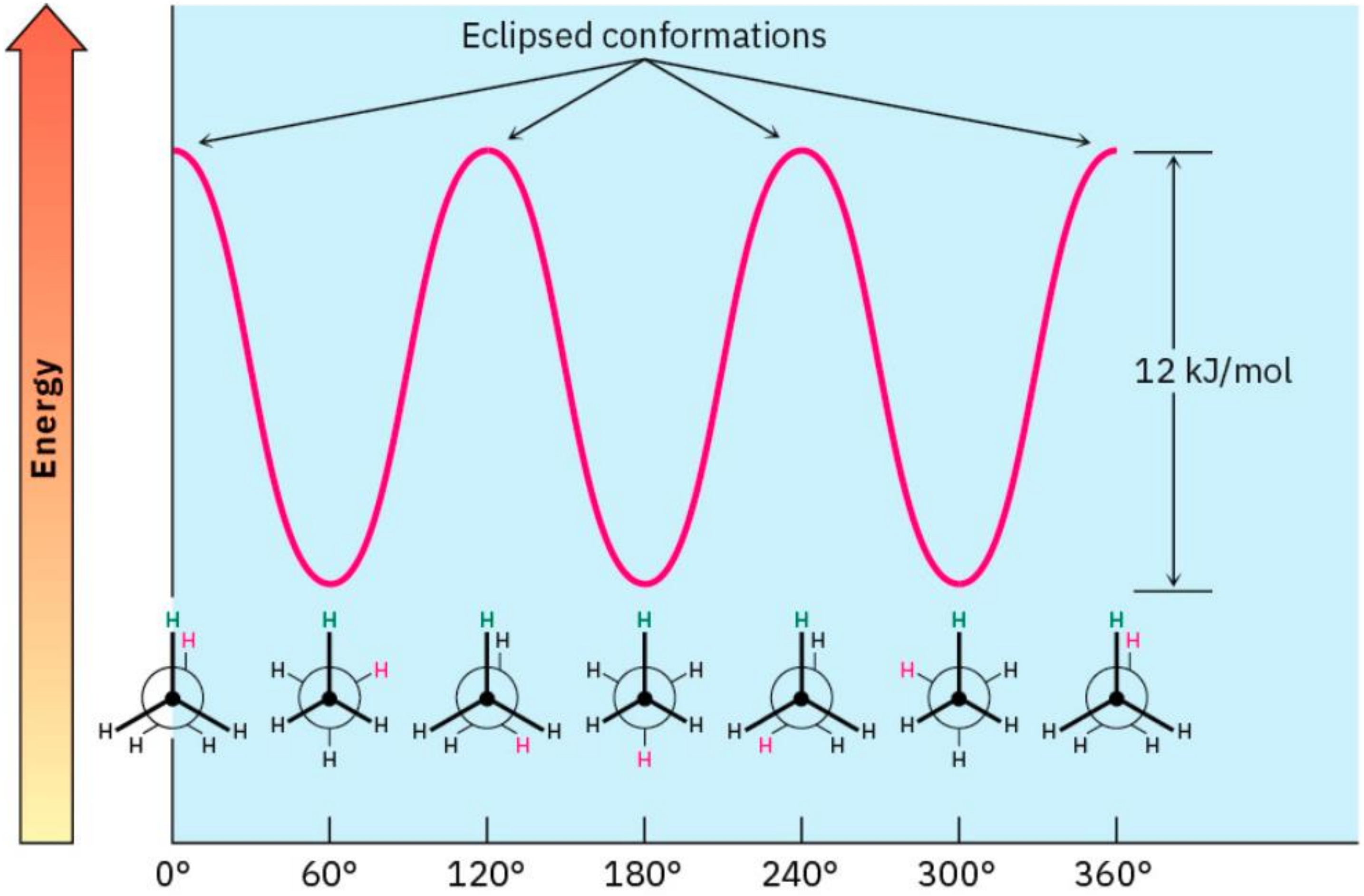


FIGURE 3.8 A graph of potential energy versus bond rotation in ethane. The staggered conformations are 12 kJ/mol lower in energy than the eclipsed conformations.

3.7 Conformations of Other Alkanes

The eclipsed conformation of propane has three interactions—two ethane-type hydrogen–hydrogen interactions and one additional hydrogen–methyl interaction. Since each eclipsing H ⟷ H interaction is the same as that in ethane and thus has an energy "cost" of 4.0 kJ/mol, we can assign a value of 14 – (2 × 4.0) = 6.0 kJ/mol (1.4 kcal/mol) to the eclipsing H ⟷ CH_3 interaction (**FIGURE 3.9**).

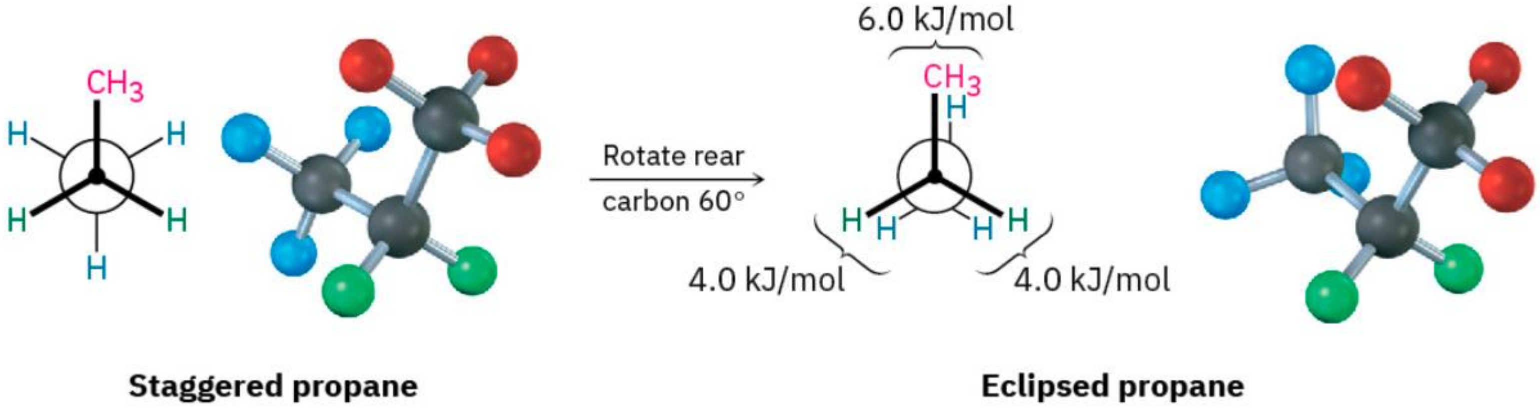
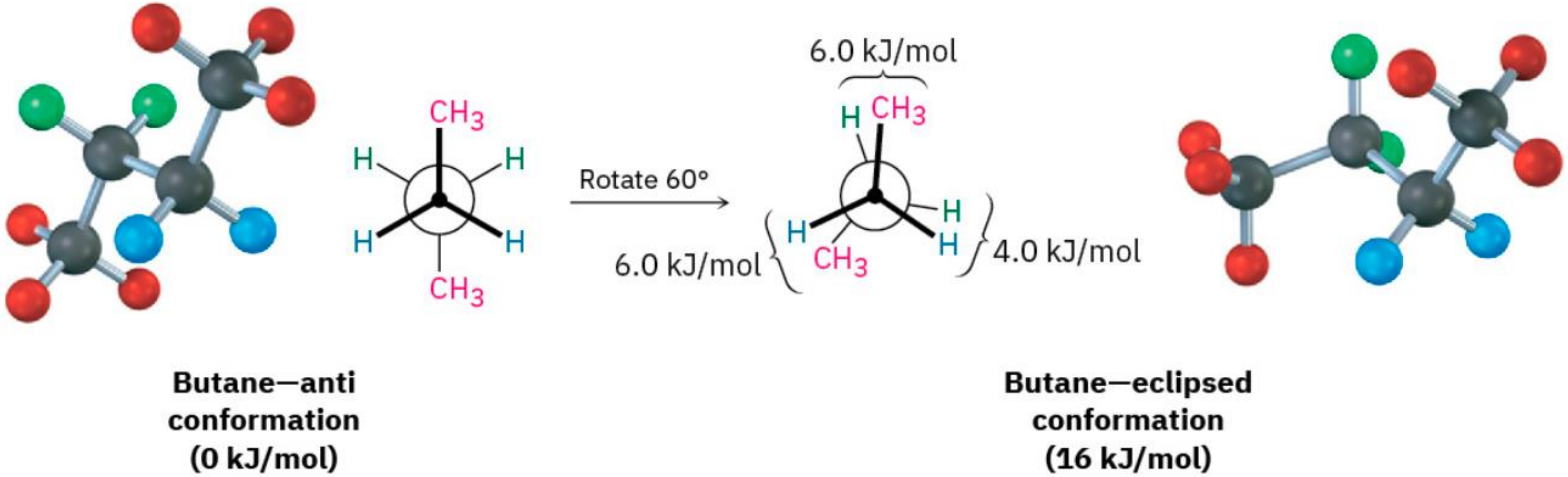
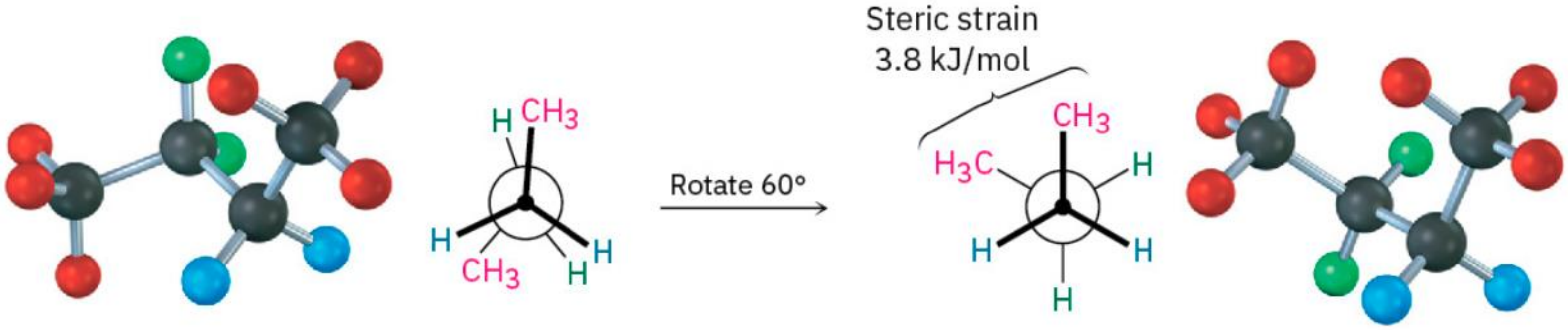


FIGURE 3.9 Newman projections of propane showing staggered and eclipsed conformations. The staggered conformer is lower in energy by 14 kJ/mol.

The conformational situation becomes more complex for larger alkanes because not all staggered conformations have the same energy and not all eclipsed conformations have the same energy.

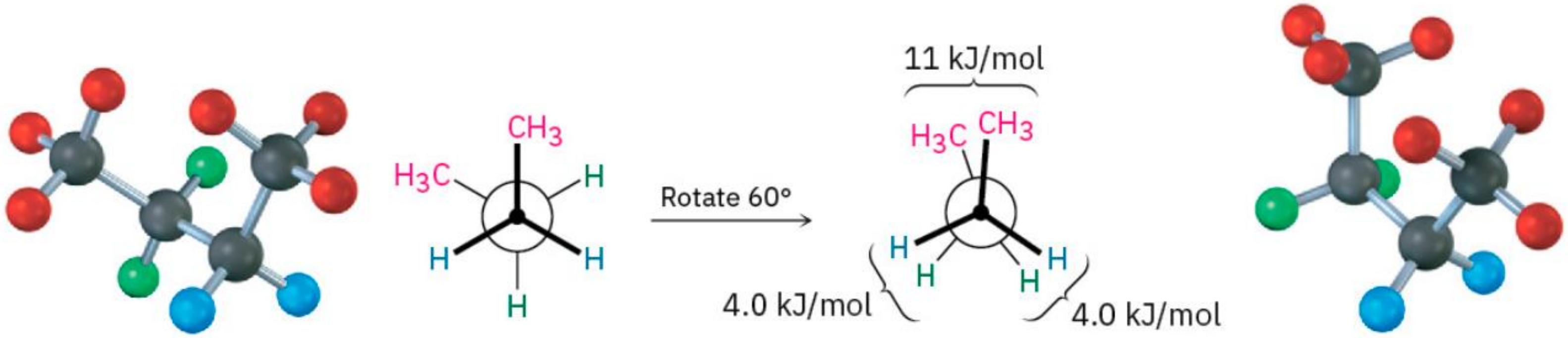
In butane, for instance, the lowest-energy arrangement, called the **anti conformation**, is the one in which the two methyl groups are as far apart as possible—180° away from each other. As rotation around the C2–C3 bond occurs, an eclipsed conformation is reached where there are two $CH_3 \leftrightarrow H$ interactions and one $H \leftrightarrow H$ interaction. Using the energy values derived previously from ethane and propane, this eclipsed conformation is more strained than the anti conformation by 2 × 6.0 kJ/mol + 4.0 kJ/mol (two $CH_3 \leftrightarrow H$ interactions plus one $H \leftrightarrow H$ interaction), for a total of 16 kJ/mol (3.8 kcal/mol).





Butane—eclipsed conformation (16 kJ/mol)

Butane—gauche conformation (3.8 kJ/mol)



Butane—gauche conformation (3.8 kJ/mol)

Butane—eclipsed conformation (19 kJ/mol)

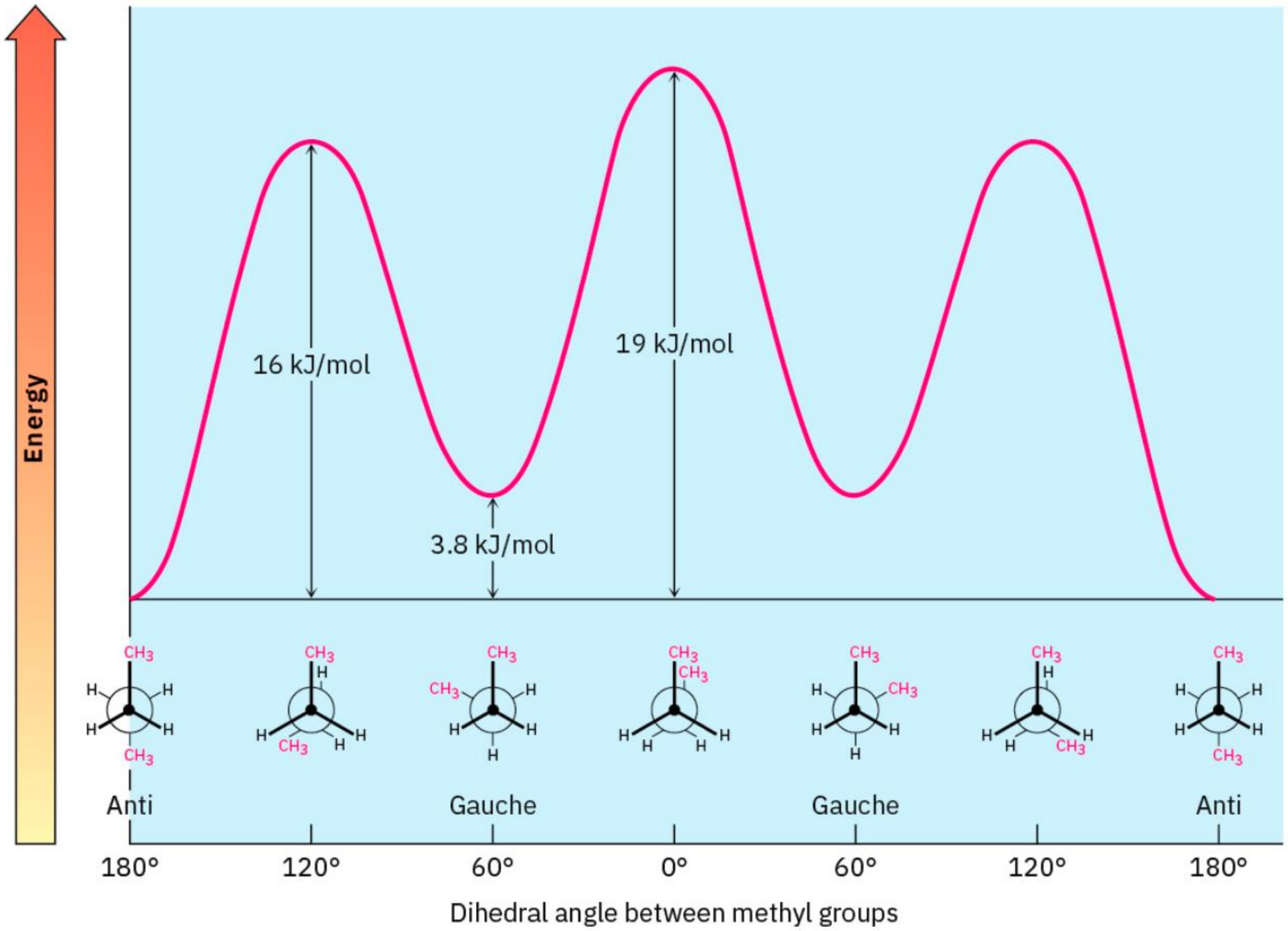
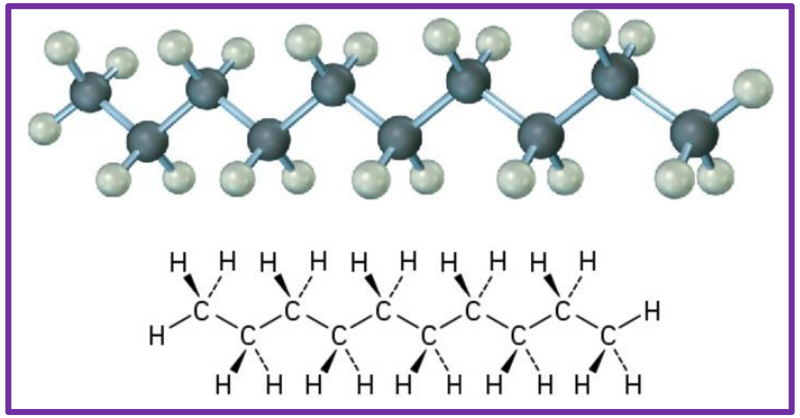


FIGURE 3.10 A plot of potential energy versus rotation for the C2−C3 bond in butane. The energy maximum occurs when the two methyl groups eclipse each other, and the energy minimum occurs when the two methyl groups are 180° apart (anti).

TABLE 3.5 **Energy Costs for Interactions in Alkane Conformers**

Interaction	Cause	Energy cost	
		(kJ/mol)	(kcal/mol)
H ⟷ H eclipsed	Torsional strain	4.0	1.0
H ⟷ CH_3 eclipsed	Mostly torsional strain	6.0	1.4
CH_3 ⟷ CH_3 eclipsed	Torsional and steric strain	11.0	2.6
CH_3 ⟷ CH_3 gauche	Steric strain	3.8	0.9

FIGURE 3.11 The most stable alkane conformation is the one in which all substituents are staggered and the carbon–carbon bonds are arranged anti, as shown in this model of decane.



WORKED EXAMPLE 3.4

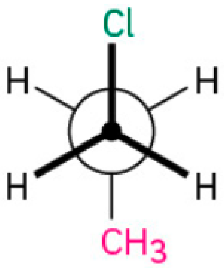
Newman Projections

Sight along the C1–C2 bond of 1-chloropropane, and draw Newman projections of the most stable and least stable conformations.

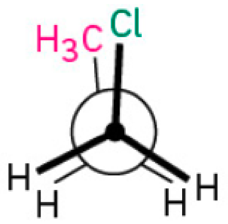
Strategy

The most stable conformation of a substituted alkane is generally a staggered one in which large groups have an anti relationship. The least stable conformation is generally an eclipsed one in which large groups are as close as possible.

Solution



Most stable (staggered)



Least stable (eclipsed)

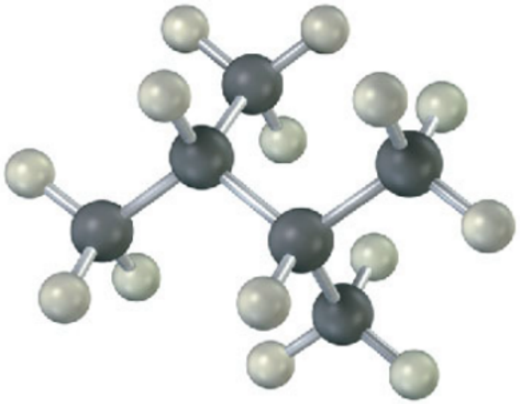
PROBLEM 3-15 Make a graph of potential energy versus angle of bond rotation for propane, and assign values to the energy maxima.

PROBLEM 3-16 Sight along the C2–C1 bond of 2-methylpropane (isobutane).

- **(a)** Draw a Newman projection of the most stable conformation.
- **(b)** Draw a Newman projection of the least stable conformation.
- **(c)** Make a graph of energy versus angle of rotation around the C2–C1 bond.
- **(d)** Assign relative values to the maxima and minima in your graph, given that an H ⟷ H eclipsing interaction costs 4.0 kJ/mol and an H ⟷ CH_3 eclipsing interaction costs 6.0 kJ/mol.

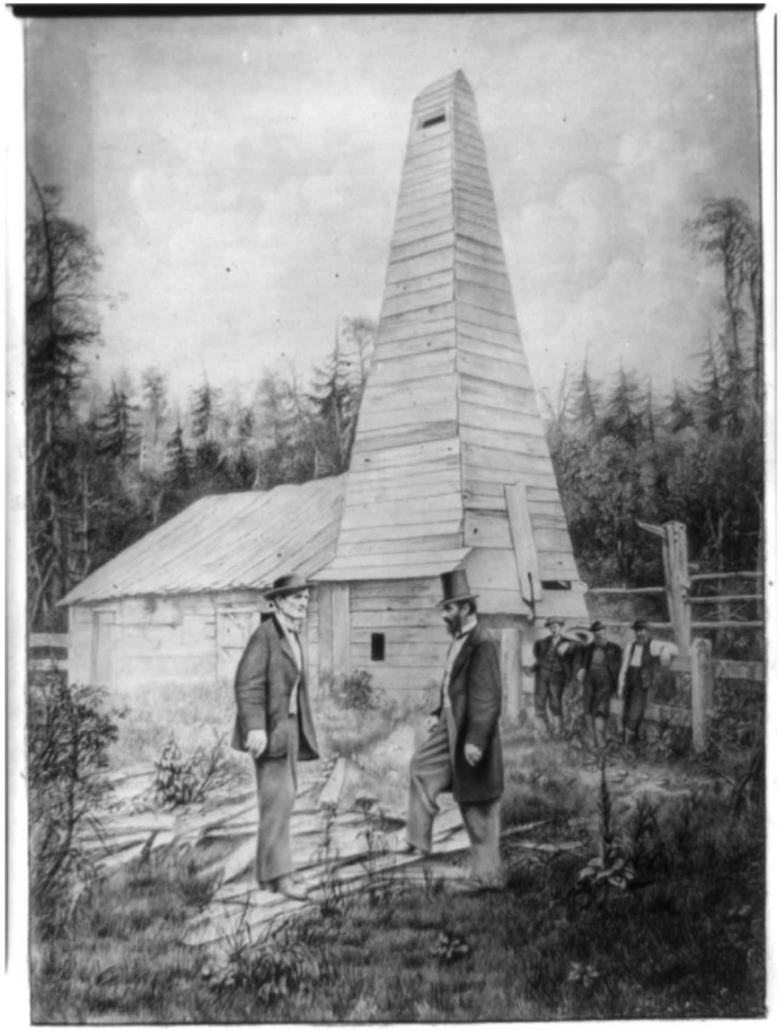
PROBLEM 3-17 Sight along the C2—C3 bond of 2,3-dimethylbutane, and draw a Newman projection of the most stable conformation.

PROBLEM 3-18 Draw a Newman projection along the C2–C3 bond of the following conformation of 2,3-dimethylbutane, and calculate a total strain energy:



CHEMISTRY MATTERS

Gasoline



By far, the major sources of alkanes are the world's natural gas and petroleum deposits. Laid down eons ago, these deposits are thought to be derived primarily from the decomposition of tiny single- celled marine organisms called foraminifera.

Petroleum refining begins by fractional distillation of crude oil into three principal cuts according to boiling point (bp): straight-run gasoline (bp 30–200 °C), kerosene (bp 175–300 °C), and heating oil, or diesel fuel (bp 275–400 °C). Further distillation under reduced pressure then yields lubricating oils and waxes and leaves a tarry residue of asphalt.

FIGURE 3.12 Gasoline is a finite resource. It won't be around forever. (credit: **"The first oil well" (https://www.loc.gov/item/ 2010649522/)** by Unknown/Library of Congress)