

24

THE CHEMISTRY OF ORGANIC COMPOUNDS

24.1 | General Characteristics of Organic Molecules



We are all familiar with how chemical substances can influence our health and behavior. Aspirin, also known as acetylsalicylic acid, relieves aches and pains. The caffeine that is in coffee and tea and the ethanol that is in wine and beer are well-known molecules that, at proper doses, give us pleasure. Spices contain a host of molecules such as capsaicin (in chili peppers) and vanillin (in the vanilla bean). Other plant-derived compounds include quinine, for treating malaria, and taxol, for treating many cancers. All of these compounds are based on carbon.

WHAT'S AHEAD

- 24.1 ► General Characteristics of Organic Molecules
- 24.2 ► An Introduction to Hydrocarbons
- 24.3 ► Structures of Alkanes
- 24.4 ► Alkane Nomenclature
- 24.5 ► Cycloalkanes
- 24.6 ► Organic Functional Groups
- 24.7 ► Reactions of Alkanes

Over 20 million carbon-containing compounds are known, and approximately 90% of the new compounds synthesized each year contain carbon. The study of compounds of carbon constitutes a branch of chemistry called organic chemistry.

The term organic chemistry arose from the eighteenth-century belief that organic compounds could only be formed by living systems. This idea was disproved in 1828 when the German chemist Friedrich Wöhler synthesized urea (H_2NCONH_2), an organic substance found in the urine of mammals, by heating the inorganic substance ammonium cyanate (NH_4OCN).

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

- Appreciate the general structure of organic molecules

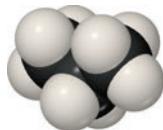
What is it about carbon that leads to the tremendous diversity of its compounds and allows them to play such a diverse role in biology and industry? Let's consider some general features of organic molecules and, as we do so, review principles we learned in earlier chapters.

The Structure of Organic Molecules

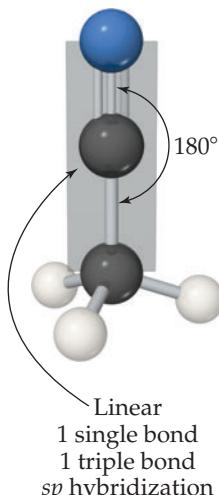
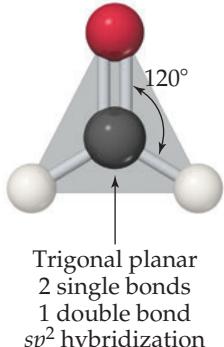
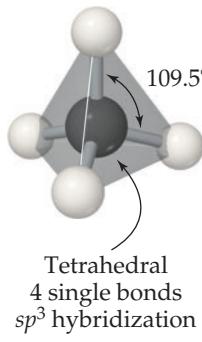
Because carbon has four valence electrons ($[\text{He}]2s^22p^2$), it forms four bonds in virtually all its compounds. When all four bonds are single bonds, the electron pairs are disposed in a tetrahedral arrangement. In the hybridization model, the carbon 2s and 2p orbitals are then sp^3 hybridized.

Although it is only a model, this approach has been used widely to describe qualitatively both structure and reactivity of organic compounds. When there is one double bond, the arrangement is trigonal planar (and modelled as sp^2 hybridization). With a triple bond, it is linear (and modelled as sp hybridization). Examples are shown in **Figure 24.1**.

Almost every organic molecule contains C—H bonds. Because the valence shell of H can hold only two electrons, hydrogen forms only one covalent bond. As a result, hydrogen atoms are always located on the surface of organic molecules whereas the C—C bonds form the backbone, or skeleton, of the molecule, as in the propane molecule:

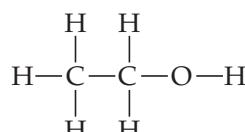


▼ Figure 24.1 Carbon geometries. The three common geometries around carbon are tetrahedral as in methane (CH_4), trigonal planar as in formaldehyde (CH_2O) and linear as in acetonitrile (CH_3CN). Notice that in all cases each carbon atom forms four bonds.



The Stabilities of Organic Molecules

Carbon forms strong bonds with a variety of elements, especially H, O, N and the halogens. Carbon also has an exceptional ability to bond to itself, forming a variety of molecules made up of chains or rings of carbon atoms. Most reactions with low or moderate activation energy begin when a region of high electron density on one molecule encounters a region of low electron density on another molecule. The regions of high electron density may be due to the presence of a multiple bond or to the more electronegative atom in a polar bond. Because of their strength and lack of polarity, both C—C single bonds and C—H bonds are relatively unreactive and form a stable base for the organic molecule. To understand the implications of these facts better, consider ethanol:



The differences in the electronegativity values of C (2.5) and O (3.5) and of O and H (2.1) indicate that the C—O and O—H bonds are quite polar while the C—H bond is only slightly polar and the C—C bond is non-polar. Thus many reactions of ethanol involve the C—O and O—H bonds while the hydrocarbon portion of the molecule remains intact. A group of atoms such as the C—O—H group, which determines how an organic molecule reacts (in other words, how the molecule *functions*), is called a **functional group**. As we progress through the chapter we will see that the functional group is the center of reactivity in an organic molecule.

Self-Assessment Exercise

- 24.1** Consider the following average bond enthalpies: C—C (348 kJ/mol), N—N (163 kJ/mol), O—O (146 kJ/mol), S—S (266 kJ/mol). Which element is most likely to form stable compounds containing chains of atoms of that element?

- (a) Carbon
(b) Nitrogen
(c) Oxy

Exercises

- 24.2** List five elements that are commonly found in organic compounds. Which ones are more electronegative than carbon?
- 24.3** Organic compounds containing C—O and C—Cl bonds are more reactive than simple alkane hydrocarbons.

Considering the comparative values of C—H, C—C, C—O and C—Cl bond energies (Table 8.4), why is this so?

24.1 (a)

Answers to Self-Assessment Exercise



24.2 | An Introduction to Hydrocarbons



One of the most important issues of our time is global warming. The sun heats the surface of the Earth during daytime and energy is radiated back into space at night. Nitrogen and oxygen, which make up 99% of our atmosphere, are transparent to infrared radiation and allow this heat loss to occur. However, other gases, most notably water vapor, methane, and carbon dioxide, absorb infrared radiation, trapping the heat in the atmosphere. These are called greenhouse gases. Since the industrial revolution, there has been a 50% increase in the amount of carbon dioxide released into the atmosphere with a consequent warming of the planet. As our standard of living rises, our demand for energy increases. In 2018, fossil fuels (coal, oil, and gas) accounted for 80% of the world's energy production. Mitigation strategies include switching to renewable energy sources, increasing energy efficiency in power production, transportation and manufacturing, and capturing greenhouse gases from the atmosphere. We all have a role to play in reducing our 'carbon footprint' and understanding some of the chemistry behind many of our modern materials can inform our choices. Organic chemistry plays a major part in this and we examine the basics of it over the next nine chapters.

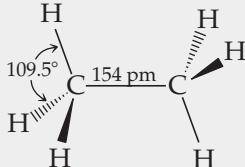
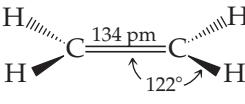
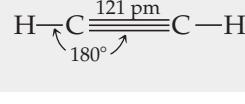
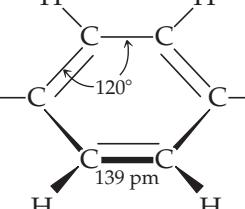
By the end of this section, you should be able to:

- Understand the general composition of the simplest of organic molecules, the hydrocarbons.
- Appreciate the link between molecular weight and a physical property such as melting point.

Because carbon compounds are so numerous, it is convenient to organize them into families that have structural similarities. Compounds that contain *only* carbon and hydrogen are called **hydrocarbons**. The key structural feature of hydrocarbons (and of most organic substances) is the presence of stable carbon–carbon bonds. Carbon is the only element capable of forming stable, extended chains of atoms bonded through single, double or triple bonds.

Hydrocarbons can be divided into four types, depending on the kinds of carbon–carbon bonds in the molecules. **Table 24.1** shows an example of each type.

TABLE 24.1 The four hydrocarbon types

Type	Classification			Example
Alkane	Saturated	Ethane	CH_3CH_3	 
Alkene	Unsaturated	Ethene	$\text{CH}_2=\text{CH}_2$	 
Alkyne	Unsaturated	Ethyne	$\text{CH}\equiv\text{CH}$	 
Aromatic	Unsaturated	Benzene	C_6H_6	 

These hydrocarbons are either *aliphatic* (from the Greek work *aleiphar*, meaning oil; these include alkanes, alkenes, and alkynes) or *aromatic*, and are classified as either saturated or unsaturated. In this chapter, we will explore aliphatic hydrocarbons that are **saturated** (that is, all carbons are bound to four other atoms and there are no double or triple bonds). Such hydrocarbons are called **alkanes**. We will look at the other classes of hydrocarbons in subsequent chapters.

Alkanes

The three simplest alkanes, which contain one, two and three carbon atoms, are methane (CH_4), ethane (C_2H_6) and propane (C_3H_8), respectively. These are illustrated in **Table 24.2**.

The names of the first 10 *straight-chain* alkanes are given in **Table 24.3**. You will notice that each aliphatic alkane has a name that ends in *-ane*. This suffix is true of all alkanes as it denotes this class of organic compounds. Alkanes longer than those described in Table 24.3 can be made by adding further CH_2 groups to the skeleton of the molecule.

TABLE 24.2 The simplest alkanes

Common name	Structural formula	Condensed structural formula	Ball-and-stick model	Space-filling representation
Methane	<pre> H H—C—H H </pre>	CH_4		
Ethane	<pre> H H H—C—C—H H H </pre>	CH_3CH_3		
Propane	<pre> H H H H—C—C—C—H H H </pre>	$\text{CH}_3\text{CH}_2\text{CH}_3$		

TABLE 24.3 First 10 members of the straight-chain alkane series

Name	Molecular formula	Condensed structural formula	Boiling point (°C)
Methane	CH_4	CH_4	-161
Ethane	C_2H_6	CH_3CH_3	-89
Propane	C_3H_8	$\text{CH}_3\text{CH}_2\text{CH}_3$	-44
Butane	C_4H_{10}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	-0.5
Pentane	C_5H_{12}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	36
Hexane	C_6H_{14}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	68
Heptane	C_7H_{16}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	98
Octane	C_8H_{18}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	125
Nonane	C_9H_{20}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	151
Decane	$\text{C}_{10}\text{H}_{22}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	174

Notice the trend within the molecular formulas in the second column of Table 24.3. For n carbon atoms ($n = 1, 2, 3 \dots$) there are $(2n + 2)$ hydrogen atoms, so alkanes have the general formula:



[24.1]

The condensed structural formula reveals the way in which atoms are bonded to one another but does not require us to draw in all the bonds. It is one of the most useful ways of representing organic molecules.

Applications and Physical Properties of Alkanes

Alkanes are very important in our society, whether they are gaseous, liquid or solid. Many of their common applications, illustrated in **Figure 24.2**, will be familiar to you. Methane, a colorless and odorless gas, is the major component of natural gas and is used for home heating and in gas stoves and water heaters. Propane is the major component of the bottled gas used for home heating and cooking in areas where natural gas is not available. Butane is used in disposable lighters and in fuel canisters for gas camping stoves and lanterns. Alkanes with 5–12 carbon atoms per molecule (C_5 — C_{12}) are found in petrol. This difference in application between different groups of alkanes is a result of their physical properties, such as boiling point (bp) and melting point (mp), which determine whether the alkane is a solid, liquid or gas at room temperature.

Homologous Series

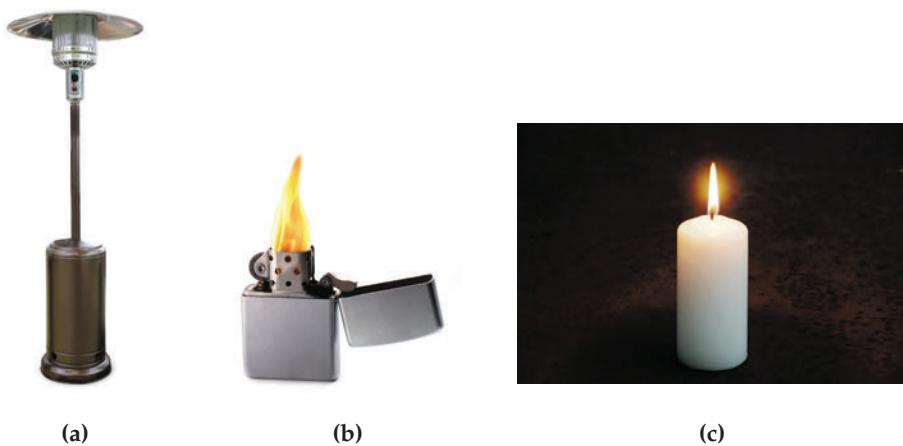
An n -alkane, sometimes called a “normal-alkane” is an alkane in which all of the carbon atoms are linked in one continuous chain. A series of compounds, like the n -alkanes, that differ only by the number of methine ($-CH_2-$) units is called a **homologous series**. Compounds in such a series possess similar chemical properties and show a gradation in physical properties as a result of increase in molecular size and mass (Table 24.3). The individual members of this series are called *homologues*. For example, pentane, decane, and octane are homologues. Physical properties in a homologous series, such as melting and boiling points or density, tend to increase smoothly with an increasing number of carbon atoms.

The difference in melting points and boiling points of hydrocarbons, including alkanes, result from *dispersion forces*. The larger the alkane molecules are, the more extensive these dispersion forces become. Hence, hydrocarbons tend to become less volatile with increasing molar mass. As a result, hydrocarbons of very low molecular weight, such as C_2H_6 (bp = $-89^\circ C$), are gases at room temperature; those of moderate molecular weight, such as C_6H_{14} (bp = $68^\circ C$), are liquids; and those of high molecular weight, such as $C_{22}H_{46}$ (mp = $44^\circ C$), are solids.

Hydrocarbon molecules such as alkanes are relatively nonpolar because carbon and hydrogen do not differ greatly in their electronegativities. Thus, alkanes dissolve readily in nonpolar solvents but are almost completely insoluble in water.

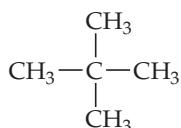
► Figure 24.2 Applications of alkanes.

Alkanes are very important in our modern society, whether gaseous, liquid or solid.
 (a) Methane is used as a source of heat.
 (b) Butane is commonly used in lighter fluid.
 (c) Candles are traditionally made from waxes, which are long-chain alkanes.

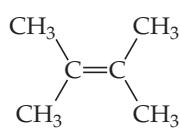


Self-Assessment Exercises

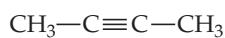
- 24.4** Which of the following structures represents a saturated aliphatic hydrocarbon?



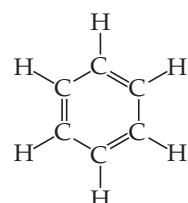
(a)



(b)

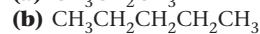


(c)



(d)

- 24.5** Which condensed structural formula represents the substance with the highest melting point?



Exercises

- 24.6** What can we tell about a compound when we know the empirical formula? What additional information is conveyed by the molecular formula? By the structural formula? Explain in each case using CH_2 as an empirical formula.
- 24.7** (a) What is a hydrocarbon? (b) Are all alkanes hydrocarbons? (c) Write the structural formula for propane (C_3H_8). (d) Butane is an alkane containing four carbon atoms in a line. Write a structural formula for this compound and determine its molecular and empirical formulas.

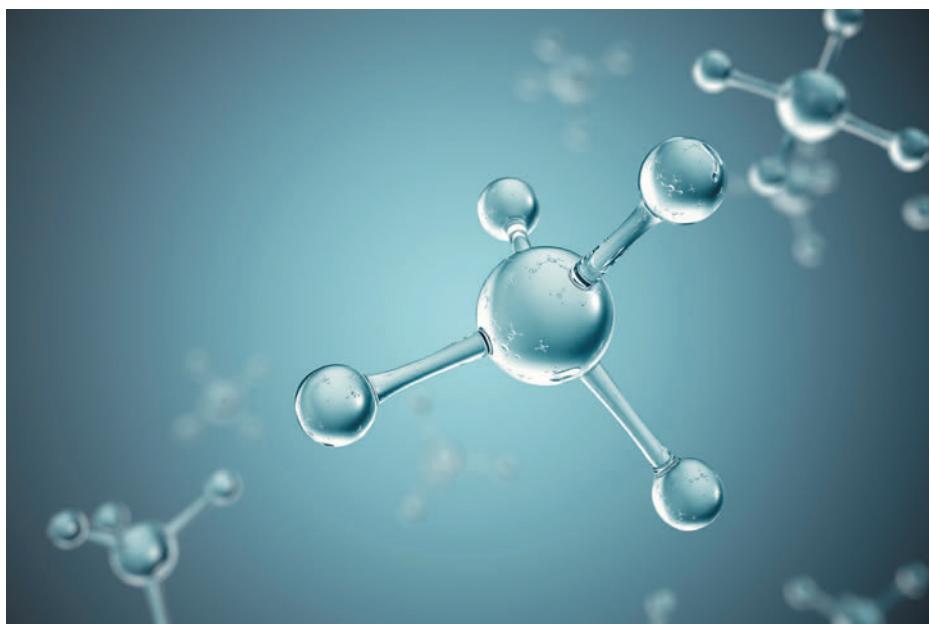
- 24.8** (a) What ending is used for the names of alkanes? (b) *Undecane* is an alkane with all its 11 carbon atoms in one chain. It is used as an attractant to cockroaches. Write a structural formula for this compound and determine its molecular and empirical formulas.

- 24.9** Rank the following in order of the strength of the London dispersion forces between two or more molecules of the same compound: $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$ (hexane); $\text{CH}_3\text{CH}_2\text{OH}$ (ethanol); $\text{CH}_3(\text{CH}_2)_{13}\text{CH}_2\text{COOH}$ (palmitic acid).

24.4 (a) 24.5 (c)

Answers to Self-Assessment Exercises

24.3 | Structures of Alkanes



So much of understanding in chemistry is based on a blend of the macroscopic, the microscopic, and the symbolic. This is particularly true as we investigate the structure of alkanes. For example, we may seek to explain trends in the boiling points of alkanes. Our starting point is the macroscopic—our observation of the temperature of a boiling liquid. This depends on the microscopic—the type, number, and arrangement of atoms that constitute the alkane; and is aided by the symbolic—how we represent the atoms and the bonding between them.

CHEMISTRY AND LIFE Petroleum Products

Petroleum, also called crude oil, is a complex mixture of organic compounds, mainly hydrocarbons, with smaller quantities of other organic compounds containing nitrogen, oxygen or sulfur. The usual first step in the refining of petroleum is to separate it on the basis of boiling point as shown in **Table 24.4**. Because petrol is the most commercially important of these separated mixtures, called *fractions*, various processes are used to maximize its yield.

Petrol is a blend of volatile hydrocarbons containing alkanes. In a car engine a mixture of air and petrol vapor is compressed by a piston and then ignited by a spark plug. The burning of petrol vapor should create a strong, smooth expansion of gas, forcing the piston outward and imparting force along the drive shaft of the engine. If the petrol vapor burns too rapidly, the piston receives a single hard slam rather than a strong, smooth push. The result is a “knocking” or “pinging” sound and a reduction in the efficiency with which energy produced by the combustion is converted to work.

The octane number of a petrol blend (**Figure 24.3**) is a measure of its resistance to knocking. Petrols with a high octane number burn

more smoothly and are thus more effective fuels. The octane number of unleaded petrol is obtained by comparing its knocking characteristics with those of 2,2,4-trimethylpentane (also known as isoctane) and heptane. 2,2,4-Trimethylpentane is assigned an octane number of 100, and heptane is assigned zero. Petrol with the same knocking characteristics as a mixture of 90% isoctane and 10% heptane has an octane rating of 90.

The petrol obtained directly from fractionation of petroleum contains mainly straight-chain hydrocarbons and has an octane number of around 50. It is therefore subjected to processes such as *cracking*, which convert the straight-chain alkanes into more desirable branched-chain and aromatic hydrocarbons (**Figure 24.4**). Cracking is also used to convert some of the less volatile kerosene and fuel-oil fractions into compounds with lower molecular weights that are suitable for use as motor fuel. The octane rating of petrol is also increased by adding aromatic compounds such as toluene ($C_6H_5CH_3$) and oxygenated hydrocarbons such as ethanol (CH_3CH_2OH).



▲ Figure 24.3 Octane rating. The octane rating of petrol measures its resistance to knocking when burned in an engine. The octane rating of this petroleum product is 89, as shown on the face of the pump.



▲ Figure 24.4 Fractional distillation. Petroleum is separated into fractions by distillation and subjected to catalytic cracking in a refinery.

TABLE 24.4 Hydrocarbon fractions from petroleum

Fraction	Carbon-chain lengths	Boiling-point range (°C)	Uses
Gas	C_1 to C_5	-160 to 30	Gaseous fuel, production of H_2
Petrol	C_5 to C_{12}	30 to 200	Motor fuel
Kerosene, fuel oil	C_{12} to C_{18}	180 to 400	Diesel fuel, furnace fuel, cracking
Lubricants	C_{16} and up	350 and up	Lubricants
Paraffins	C_{20} and up	Low melting solids	Candles
Asphalt	C_{36} and up	Gummy residues	Surfacing roads

By the end of this section, you should be able to

- Identify conformational isomers and recognize they are associated with different relative energies.
- Understand that alkanes with four or more carbon atoms give rise to constitutional isomers.

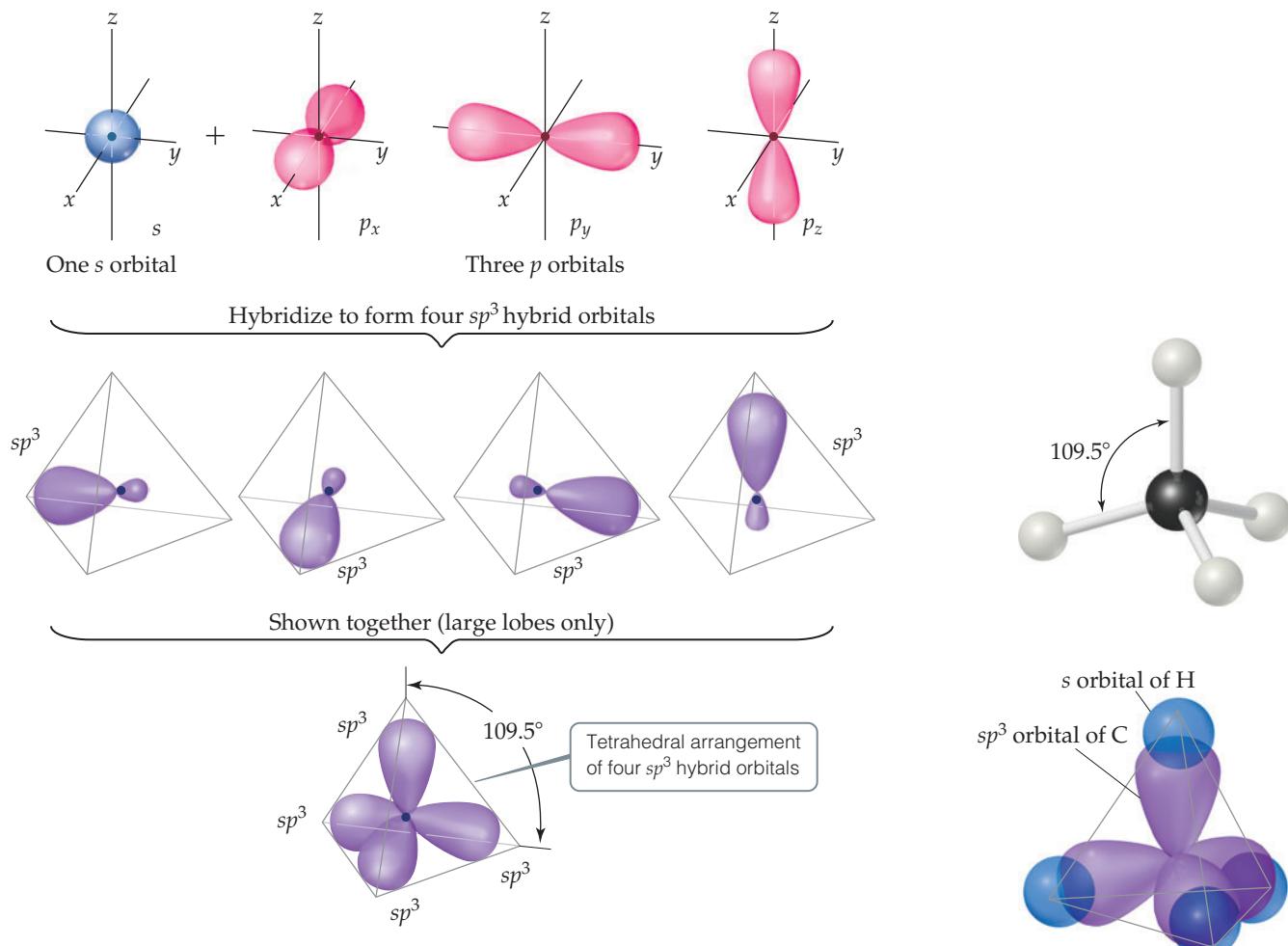
Recall that earlier in the text we described hybridization as the process of mixing atomic orbitals in a mathematical operation. The newly formed orbitals, called *hybrid orbitals*, are based on the atomic orbitals that constitute them (Figure 24.5). Hybridization and valence-bond theory are used predominantly by organic chemists to describe the bonding outcomes for carbon. In essence, the hybrid orbitals are defined by the geometry of the bonds formed by carbon that influence the overall shape and structure of the molecule. Any carbon bearing four single bonds must be tetrahedral and, hence, sp^3 hybridized.

The tetrahedral geometry leads to bond angles of 109.5° , which is the largest possible separation for the four one-electron sp^3 hybrid orbitals in free space. By way of example, the three-dimensional structure of methane can be represented as shown in Figure 24.6.

A covalent bond that is formed by the end-to-end interaction of two one-electron orbitals (either atomic, hybridized or a mixture of both), as described in Figure 24.6, is called a sigma (σ) bond.

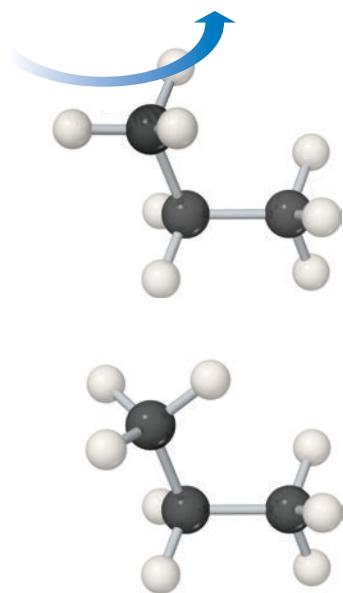
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How many atomic orbitals contribute to form the four sp^3 hybrid orbitals?



▲ **Figure 24.5** Formation of sp^3 hybrid orbitals. One *s* orbital and three *p* orbitals can hybridize to form four equivalent sp^3 hybrid orbitals. The large lobes of the hybrid orbitals point towards the corners of a tetrahedron.

▲ **Figure 24.6** Bonds about carbon in methane. This tetrahedral molecular geometry is found around all carbons in alkanes.



▲ **Figure 24.7** Rotation about a C–C bond occurs easily and rapidly in all alkanes.

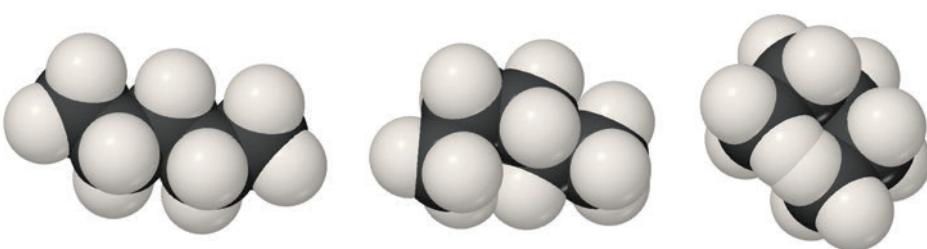
Alkane Shape and Conformations

Although organic molecules are drawn in a static way, remember that they are always dynamic. One of the properties of alkanes is their ability to change shape continuously (**Figure 24.7**). The three-dimensional arrangement of atoms in a molecule that results from rotation about a single bond is known as a **conformation**. When different conformations of a molecule are compared, they are said to be **isomers** of the same structure. Isomers are two or more compounds with the same molecular formula but different three-dimensional structure. **Figure 24.8** illustrates some of the **conformational isomers** (or *conformers*) of pentane. The **Newman projection** shown in **Figure 24.9** is a useful way of viewing a molecule and for gaining an idea of its energy relative to other possible conformers. Newman projections are derived by imagining you are looking along the carbon–carbon bond being rotated and comparing the positions of the three groups attached to the front carbon atom with those attached to the back carbon atom.

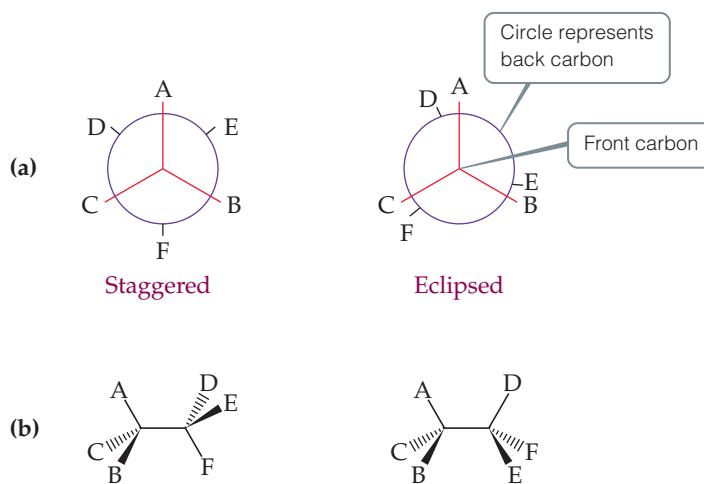
The number of conformational isomers within alkanes containing two or more carbon atoms is infinite because of free rotation about any of the carbon–carbon bonds. Each conformer, however, has a certain amount of energy associated with it. In this regard, there are two conformational isomers that are readily identifiable and usually represent the low and high energy forms. They are called **staggered** and **eclipsed**, and they define the energetic limits of all conformations. Often, a **Newman projection** is used to represent conformers. Here, the two bonded carbon atoms about which rotation will occur are imagined superimposed on one another with the front carbon atom represented as a point and the back carbon atom represented as a circle from which the other bonds associated with these carbon atoms radiate (**Figures 24.9** and **24.10**). Staggered conformations represent the lowest energy conformation, whereas eclipsed conformations are higher in energy. The difference in energy between the two states is due to added *non-bonded interaction* strain in the eclipsed conformation. This strain is derived from both **steric** (van der Waals interactions) and **torsional** effects, which are a resistance to twisting of the bonds. The magnitude depends on how close neighboring groups become and on the size of the two neighboring groups. For example, hydrogen atoms on adjacent carbons, as in ethane, have minimal but still measurable strain (approximately 12.1 kJ/mol separates the low and high energy conformers).

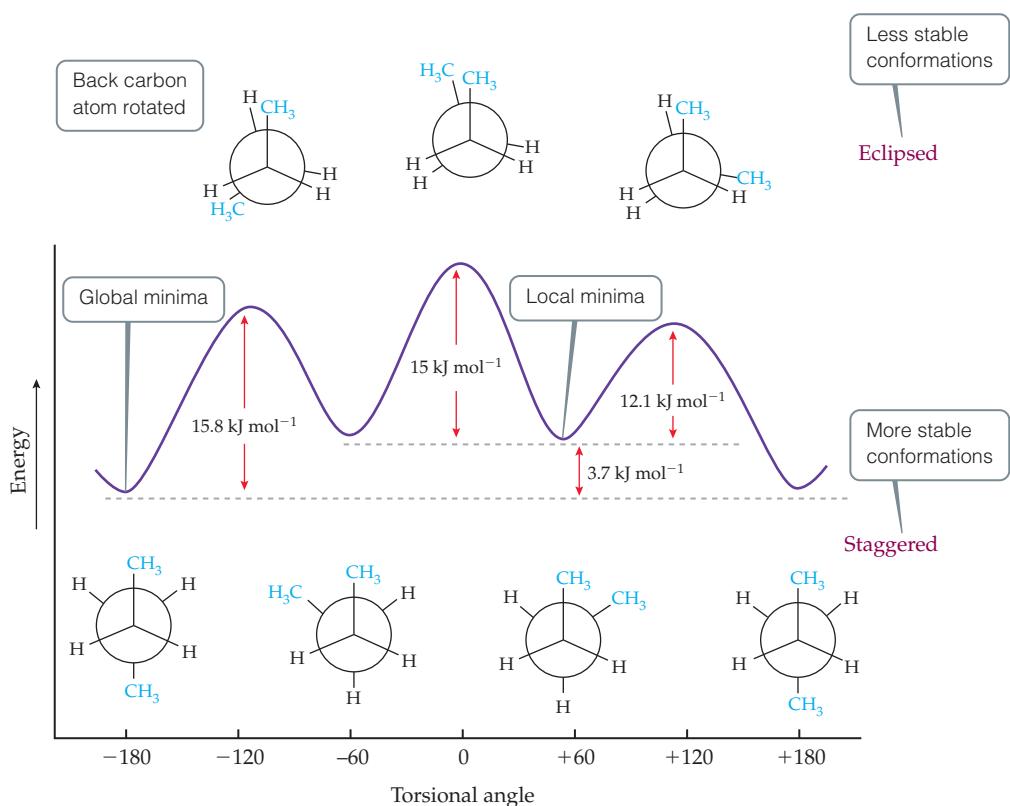
► **Figure 24.8** Conformers of pentane.

Rotation about carbon–carbon single bonds can result in noticeable changes in molecular shape.



► **Figure 24.9 (a)** **Newman projection.** In the staggered representation the groups attached to the adjacent carbon atoms are arranged as far apart as possible. The eclipsed conformation causes the groups on the adjacent carbon atoms to align one behind the other. By convention, the groups are drawn slightly offset so all may be seen. **(b)** **Sawhorse representation.** Here the molecule is represented from the side with the bond being rotated viewed as horizontal.





◀ Figure 24.10 Relative energy differences between staggered and eclipsed conformations of butane. Newman projections are used to illustrate the different conformers upon rotation about the C2—C3 bond.

With larger groups, such as bromo, iodo or methyl groups, the strain, and hence, energy difference, is larger. The vast majority of bonds in acyclic aliphatic alkanes are found in a staggered conformation. The eclipsed conformation represents the activation barrier between two staggered conformations.

Let's now investigate the strain effects for rotation about C2—C3 in butane (Figure 24.10). We will consider the staggered conformation of butane with the lowest energy as a useful starting point. This would be the case where the two methyl (CH_3) groups that terminate the butane chain are as far apart as possible. Make sure at this point that you can identify that this is a Newman projection for butane. Rotation about C2—C3 by 60° yields the first eclipsed conformer. Non-bonding interactions between the methyl groups and hydrogen atoms on the adjacent carbon atom in this eclipsed form strain the molecule making it a slightly less stable arrangement of atoms (by 15.8 kJ/mol) and giving a higher-energy conformer. A further rotation of 60° relieves the strain somewhat but, in doing so, the two methyl groups are able to interact weakly making it less stable by 3.7 kJ/mol than the staggered conformation we started with, so that a *local* energy minimum is reached. Rotation of the C2—C3 bond by another 60° causes the two methyl groups to interact strongly, forming the conformer with the highest relative energy (15.8 kJ/mol above our starting point). Note that, although the hydrogen atoms also contribute to the overall energy, it is the methyl interactions that dominate in this case. Any further rotation from this point mirrors the structures that have already been discussed. Finally, the methyl groups are again opposed, resulting once more in the orientation that yields the minimum energy conformation (sometimes referred to as the *global* minimum).

Constitutional/Structural Isomers

The alkanes listed in Table 24.3 are *straight-chain aliphatic hydrocarbons* because all the carbon atoms are joined in a continuous chain. Alkanes consisting of four or more carbon atoms can also have branched chains and are called *branched-chain alkanes*. Table 24.5 shows space-filling models, full structural formulas and condensed structural formulas for all the possible structures of alkanes containing four or five carbon atoms. Note that the molecular formula for a branched alkane is the same as for a straight-chain alkane with the same number of carbon atoms.

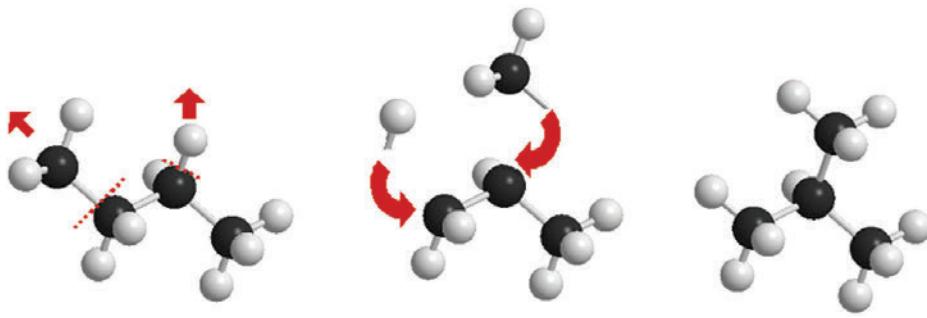
TABLE 24.5 Isomers of C₄H₁₀ and C₅H₁₂

Systematic name (common name)	Structural formula	Condensed structural formula	Space-filling model	Melting point (°C)	Boiling point (°C)
Butane (n-butane)	<pre> H H H H H—C—C—C—C—H H H H H—C—H H </pre>	CH ₃ CH ₂ CH ₂ CH ₃		-138 °C	-0.5 °C
2-Methylpropane (isobutane)	<pre> H H H H—C—C—C—H H CH₃ H—C—H H </pre>	CH ₃ —CH—CH ₃		-159 °C	-12 °C
Pentane (n-pentane)	<pre> H H H H H H—C—C—C—C—C—H H H H H—C—H H </pre>	CH ₃ CH ₂ CH ₂ CH ₂ CH ₃		-130 °C	+36 °C
2-Methylbutane (isopentane)	<pre> H H—C—H H H H H—C—C—C—H H H H—C—H H </pre>	CH ₃ —CH ₂ —CH ₂ —CH ₃		-160 °C	+28 °C
2,2-Dimethylpropane (neopentane)	<pre> H H—C—H H H H—C—C—H H H H—C—H H </pre>	CH ₃ —C(CH ₃) ₃		-16 °C	+9 °C

As we saw in Chapter 23, compounds with the same molecular formula but with different bonding arrangements (and hence different structures) are called **structural** or **constitutional isomers**.

This is easily envisaged if you think of alkanes as a series of building blocks made up of C, CH, CH₂ and CH₃ groups. **Figure 24.11** demonstrates the principle. Converting one constitutional isomer into another requires the breaking and making of bonds (unlike conformational isomers). Consequently, constitutional isomers are not easily interconverted at room temperature and may be separated from one another.

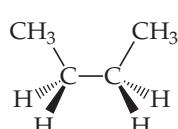
Constitutional isomers of a given alkane differ slightly from one another in physical properties. Note the melting and boiling points of the constitutional isomers of butane and pentane given in Table 24.5. These melting and boiling points are a measure of the energy needed to overcome weak and favourable interactions that give rise to the solid or liquid properties, respectively. The variation in melting and boiling points for a set of constitutional isomers is a result of the subtleties of molecular interactions. The number of possible constitutional isomers increases rapidly with the number of carbon atoms in the alkane. There are 18 possible constitutional isomers with the molecular formula C₈H₁₈, for example, and 75 possible isomers with the molecular formula C₁₀H₂₂.



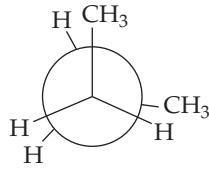
◀ Figure 24.11 Constitutional isomers of butane. If we were to remove a terminal (end) carbon unit in butane and attach it to the middle remaining carbon, a structure different from the initial straight chain of butane would be obtained. The connectivity changes, but the molecular formula is exactly the same. There are still four carbons within the molecule and, if we were to complete the structure again, there would still be 10 hydrogens to include. The two structures differ not only in their shape but also in their physical and chemical properties.

Self-Assessment Exercises

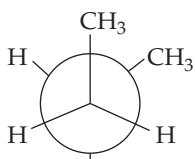
- 24.10** Which structure represents the lowest energy conformation of butane, C_4H_{10} ?



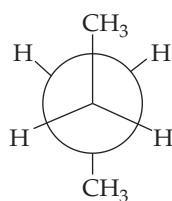
(a)



(b)

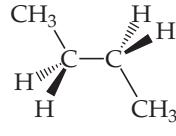


(c)

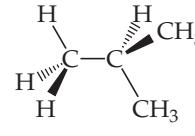


(d)

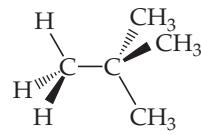
- 24.11** What is the relationship between the following pairs of structures?



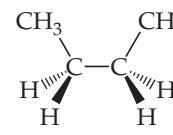
(A)



(B)



(C)



(D)

(a) Structures **A** and **B** are constitutional isomers.

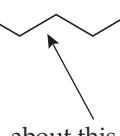
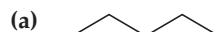
(b) Structures **A** and **C** are conformational isomers.

(c) Structures **A** and **D** are constitutional isomers.

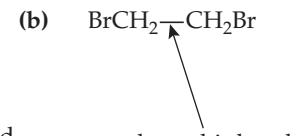
Exercises

- 24.12** Draw representations of the following orbitals: s , p_x , p_y , p_z . How do they relate to an sp^3 hybrid orbital?
- 24.13** How many constitutional isomers are possible for hexane (C_6H_{14})? Draw them.
- 24.14** Distinguish between constitutional and conformational isomers using butane as an example.
- 24.15** Draw Newman projections for the most stable and least stable conformers of propane.

- 24.16** Using Newman projections, draw the most stable staggered form of the following compounds:



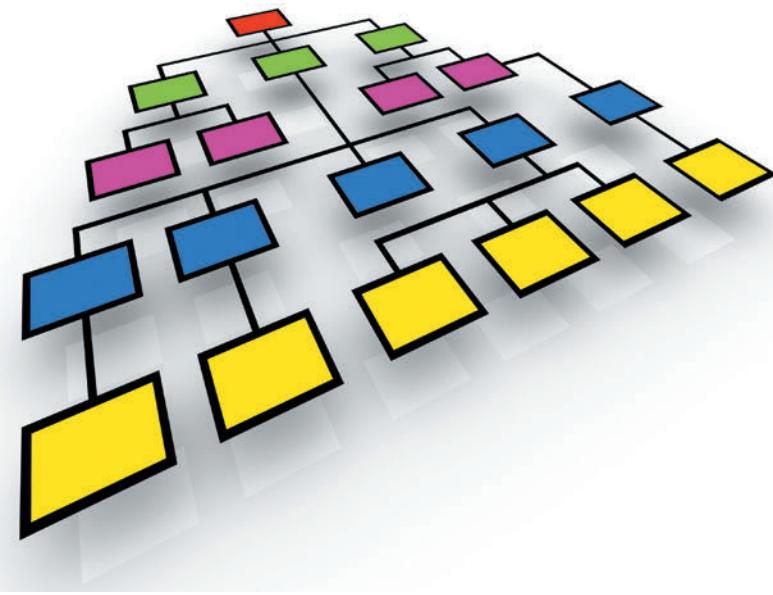
about this bond



about this bond

24.10 (d) 24.11 (a)

24.4 | Alkane Nomenclature



We can imagine a hierarchy of information which gives increasing detail about a substance—the empirical formula being the most basic bit of information all the way up to a name that uniquely describes a compound.

The need for a common “language” to name molecules was recognized early in the history of organic chemistry. In 1892, the International Union of Chemistry met in Geneva, Switzerland, to formulate a set of rules for systematically naming organic substances. Since that time, the task of updating the rules for naming all compounds has fallen to the International Union of Pure and Applied Chemistry (IUPAC). Chemists everywhere, regardless of their nationality or political affiliation, subscribe to a common system for naming compounds. This naming process, called **nomenclature**, provides a systematic way to define unambiguously which atoms are bonded to one another within a molecule and to be able to communicate the structure of a compound in writing.

By the end of this section, you should be able to use systematic nomenclature to:

- Convert between the name and structure of a simple alkane.

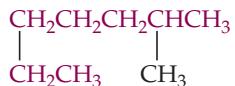
Constitutional isomerism complicates how we might describe organic molecules since a description based solely on molecular formulas is not nearly enough. Apart from ethane and propane, a number of different structures can be obtained from the same molecular formula. All of this means that we need a systematic means of naming organic compounds.

The IUPAC names for the isomers of butane and pentane are given in Table 24.5. These names, as well as those of other organic compounds, have three parts to them:

Prefix – Parent – Suffix

The following steps summarize the procedures used to arrive at the names of alkanes, all of which end with the suffix *-ane*. The prefix relates to the number, type and position of substituents (for example, the prefix 2,3-dibromo would indicate the compound contains two bromine atoms attached at positions 2 and 3). The parent name indicates the number of carbon atoms within the longest chain (for example, *eth* = two carbons, *pent* = five carbons). We use a similar approach to writing the names of other organic compounds and we develop a further understanding of organic nomenclature in Chapters 25–31.

In order to understand the steps to derive an appropriate nomenclature, let’s examine how we would name the following compound:

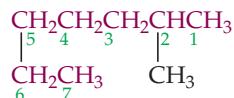


1. Find the longest continuous chain of carbon atoms and use the name of this chain (Table 24.3) as the base name of the compound.

Because this compound's longest chain is made up of seven C atoms (colored), it is named a substituted heptane (see Table 24.3). Groups attached to the main chain are called *substituents* because they are in substitution of a hydrogen atom on the main chain.

2. Number the carbon atoms in the longest chain, beginning with the end of the chain that is nearest to a substituent.

In our example, we number the C atoms from the right because that places the CH₃ substituent on the second C atom of the chain; if we number from the lower left, the CH₃ would be on the sixth C atom. The chain is numbered from the end that gives the lowest combined number for all substituent positions.



3. Name and give the location of each substituent group.

A substituent group that is formed by removing a hydrogen atom from an alkane is called an **alkyl group**. We have already been informally introduced to this nomenclature. Alkyl groups are named by replacing the *-ane* ending of the alkane name with *-yl*. **Table 24.6** lists the three simplest alkyl groups.

The name of our example is 2-methylheptane. Note the hyphen after the number. Note also that there is *no* space, comma or hyphen between methyl and heptane. The name should also allow you to draw the structure using these same three simple steps.

4. Where two or more substituents are present, list them in alphabetical order, ignoring multiplying prefixes.

Where there are two or more of the same substituent, the number of substituents of that type is indicated by a prefix: *di-* (two), *tri-* (three), *tetra-* (four), *penta-* (five)

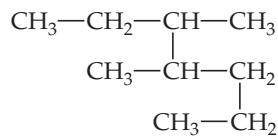
TABLE 24.6 Naming simple alkyl substituents

Substituent	Substituent name
CH ₃	methyl
CH ₃ CH ₂	ethyl
CH ₃ CH ₂ CH ₂	propyl

Sample Exercise 24.1

Naming alkanes

Give the systematic name for the following alkane

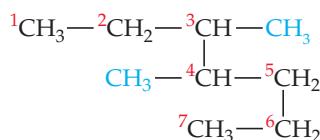


SOLUTION

Analyze We are given the condensed structural formula of an alkane and asked to give its name.

Plan Because the hydrocarbon is an alkane, its name ends in *-ane*. The name of the parent hydrocarbon is based on the longest continuous chain of carbon atoms. Branches are alkyl groups, named after the number of C atoms in the branch and located by counting C atoms along the longest continuous chain.

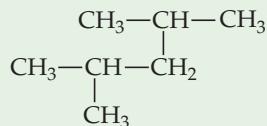
Solve The longest continuous chain of C atoms extends from the upper left CH₃ group to the lower left CH₃ group and is seven C atoms long:



The parent compound is thus heptane. There are two methyl groups branching off the main chain. Hence this compound is a dimethylheptane. To specify the location of the two methyl groups, we must number the C atoms from the end that gives the lower two numbers to the carbons bearing side chains. This means that we should start numbering at the upper left carbon. There is a methyl group on C3 and one on C4. The compound is thus 3,4-dimethylheptane.

► Practice Exercise

Name the following alkane:



**Sample Exercise 24.2****Writing condensed structural formulas**

Write the condensed structural formula for 3-ethyl-2-methylpentane.

SOLUTION

Analyze We are asked to draw the molecular structure of an organic compound from its systematic name.

Plan First we need to determine the classification of the organic compound, then work backwards from the parent compound, adding in functionality and side groups.

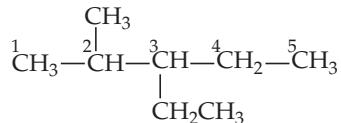
Solve Because the compound's name ends in *-ane*, it is an alkane, meaning that all the carbon–carbon bonds are single bonds. The parent hydrocarbon is pentane, indicating five C atoms (Table 24.3). There are two alkyl groups specified, an ethyl group (two carbon atoms, C_2H_5) and a methyl group (one carbon atom, CH_3). Counting from left to right along the five-carbon chain, the ethyl group will be attached to the third C atom and the methyl group will be attached to the second C atom.

We begin by writing a string of five C atoms attached to each other by single bonds. These represent the backbone of the parent pentane chain:

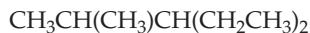


We next place a methyl group on the second C and an ethyl group on the third C atom of the chain. Hydrogens are then added

to all the other C atoms to make the four bonds to each saturated carbon, giving the following condensed structure:



The formula can be written even more concisely in the following style:

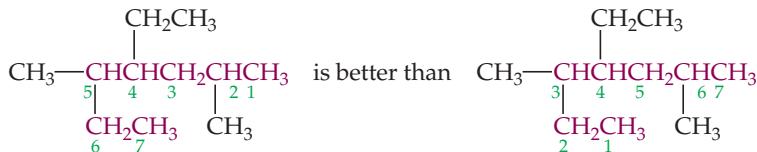


In this formula the branching alkyl groups are indicated in parentheses.

► Practice Exercise

Write the condensed structural formula for 2,3-dimethylhexane.

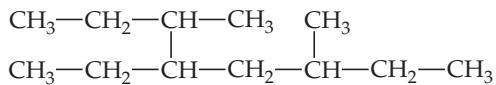
and so on. The position of each substituent is separated by a comma (for example, 2,3-dibromopentane). In the case where substituents are different, each prefix is separated from the next by a hyphen. Substituents are also listed alphabetically (ethyl, methyl, propyl and so on). Notice how the following example is named (and numbered):



for numbering because 4-ethyl-2,5-dimethylheptane gives a lower numbering than 4-ethyl-3,6-dimethylheptane does.

Self-Assessment Exercise

24.17 What is the systematic name of the following structure?



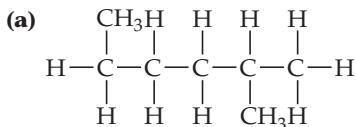
- (a) 3-butyl-5-methylheptane
- (b) 3-methyl-5-butylheptane
- (c) 4-ethyl-3,6-dimethyloctane
- (d) 5-ethyl-3,6-dimethyloctane

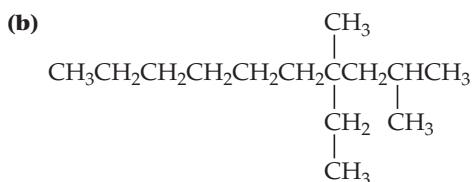
Exercises

24.18 What is the chemical formula of the propyl group?

24.19 Draw all possible isomers of C_5H_{12} . Systematically name each compound.

24.20 Draw the structural formula or give the IUPAC name, as appropriate, for the following:





- (c) 3-methylhexane
 (d) 4-ethyl-2,2-dimethyloctane
 (e) methylcyclohexane

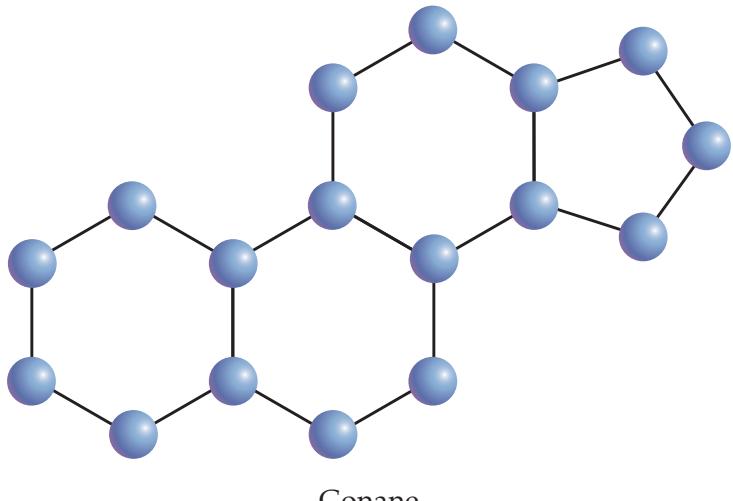
24.21 What do ethane, ethanol, and ethylene have in common with respect to their nomenclature? What can you infer about the number of carbon atoms in each compound?

24.17 (c)

Answers to Self-Assessment Exercise



24.5 | Cycloalkanes



We saw in Section 24.3 that we don't need many carbon atoms before it is possible to arrange them in a number of different ways, called constitutional isomers. Another way to arrange a chain of carbon atoms is in a ring, called a cyclic compound. For a given number of carbon atoms, the formula of the chain form and the ring form differ in the number of hydrogen atoms present, so the two forms are not classed as isomers but are distinct compounds, albeit closely related ones. The structure of gonane, with four rings fused together, is the core structure on which steroids are built, which are essential for many regulation and growth processes in living cells. By the end of this section, you should be able to

- Interpret a line drawing of a cyclic structure
- Recognize the difference between the two major conformations of cyclohexane

Hydrocarbons can form not only straight and branched chains but also rings, or cycles. Alkanes with this latter form of structure are called **cycloalkanes**. Cycloalkanes are formed by the loss of two C—H bonds and the formation of a C—C bond from the equivalent aliphatic alkane structure. As such, the general molecular formula for a cycloalkane differs from that of an alkane by two hydrogen atoms.



[24.2]

Table 24.7 illustrates a few simple cycloalkanes. Cycloalkanes containing from three to more than 30 carbon atoms are known. The most common forms contain five- (cyclopentane) and six- (cyclohexane) membered rings. Hydrocarbon rings containing fewer than five carbon atoms are strained because the C—C—C bond angle in these

TABLE 24.7 Cycloalkanes

Cycloalkane	Structural formula	Ball-and-stick representation	Line drawing
Cyclopropane			
Cyclobutane			
Cyclopentane			
Cyclohexane			

smaller rings must be much less than the 109.5° angle expected for an sp^3 hybridized atom. The amount of *ring strain* increases as the ring size gets smaller than that for cyclohexane. In cyclopropane, which has the shape of an equilateral triangle, the angle is only 60° ; as a result, this molecule is much more reactive than propane, its straight-chain analogue.

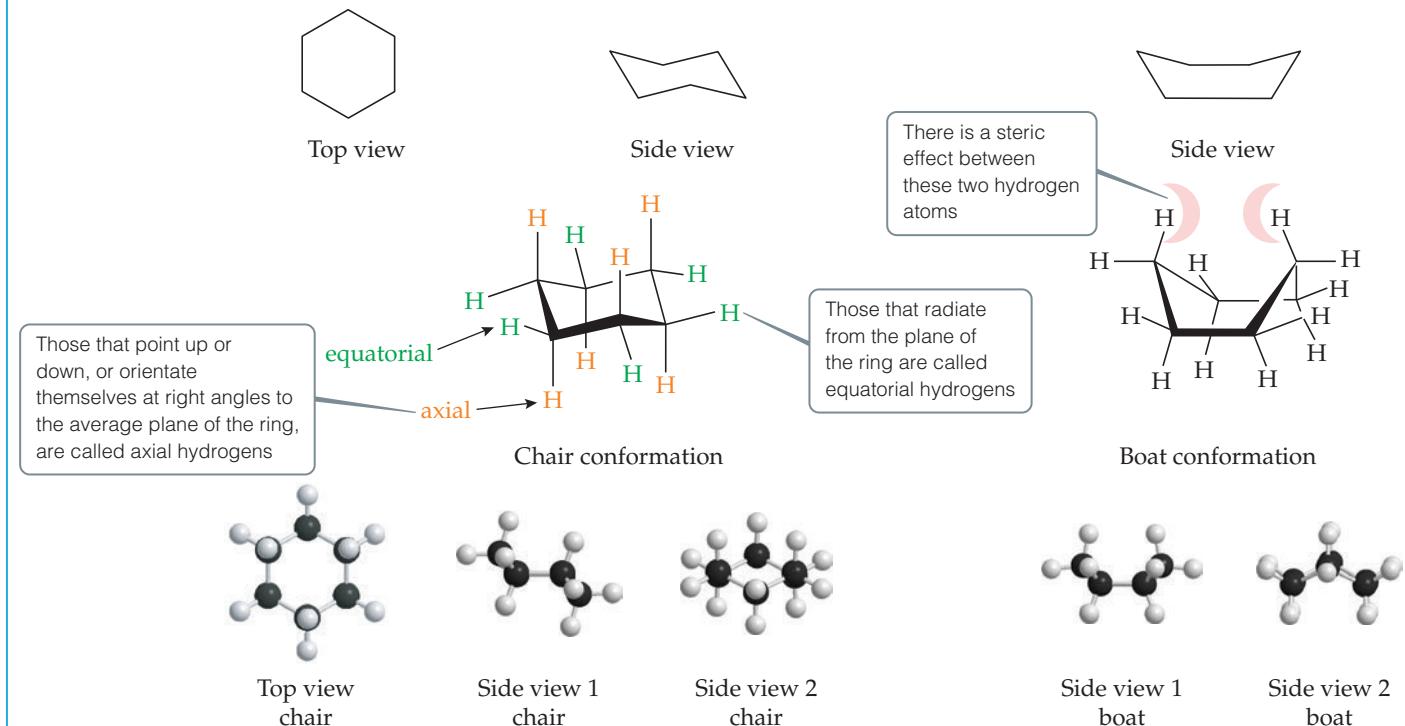
Apart from model and structural formula representations, Table 24.7 also demonstrates how cycloalkane structures can be drawn as simple polygons in which each corner of the polygon represents a CH_2 group and each side represents a C—C single bond. The hydrogen atoms are still present in this *line drawing* representation—we just don't include them in the drawing. When using this representation for cycloalkanes, however, remember that you are drawing a three-dimensional structure in two dimensions and that, as a consequence, geometric subtleties are lost. In fact, cycloalkane rings with four or more carbons are not planar.

To illustrate this point, consider the structure of cyclohexane as shown in [Figure 24.12](#). Looking at the structure from the top certainly gives the same hexagonal shape as represented by a line drawing. However, the view from any side tells a different and more complicated story. Two major conformations for cyclohexane are known, and they both allow bond angles of about 109.5° to be realized. The **chair conformation** is the more stable of the two types of conformers. It is called a chair structure because of its resemblance to a chair. In this case, the hydrogen atoms adopt one of two orientations. Those that point up or down, or orientate themselves at right angles to the average plane of the ring, are called **axial hydrogens**; those that radiate from the plane of the ring are called **equatorial hydrogens**. Substituents at these positions are also described in the same way. Note that


Go Figure

In which conformation of cyclohexane are neighboring hydrogens staggered and in which are they eclipsed?

Two major conformations for cyclohexane are known, and they both allow bond angles of about 109.5° to be realized



▲ Figure 24.12 Conformations of cyclohexane.

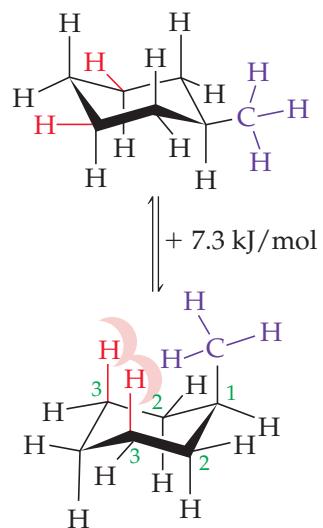
all bonds on adjacent carbons in cyclohexane are staggered, implying that in any given hemisphere the hydrogens alternate between axial and equatorial.

The less stable of the two forms (by about 30 kJ/mol) is described as the **boat conformation**. Its relative instability is caused by the non-bonding interactions generated by the close proximity of the two hydrogen atoms on C1 and C4 that overhang the ring system in this conformation (Figure 24.12), and by the eclipsing of hydrogens along the C2–C3 and C5–C6 bonds.

Now let's consider the effect of placing a single substituent on a cyclohexane ring. The substituent has two possible orientations, axial or equatorial. The two conformers do interconvert but the equatorial conformation is preferred because the methyl group experiences destabilising **1,3-diaxial interactions** with the other two axial hydrogens on that face (Figure 24.13) if it is axial. These types of interactions are minimized in the equatorial conformation as the methyl group and, more importantly, the hydrogen atoms on that methyl group point away from the ring system.

We do not need to number the position of the substituent for a cycloalkane with only one substituent, nor do we need to define the conformation as either *ax* (for axial) or *eq* (for equatorial). For example, both structures in Figure 24.13 are called methylcyclohexane, as this name is suitable enough to avoid ambiguity.

The concept of geometrical isomerism was introduced in Section 23.4 for coordination compounds. We will investigate the concept of *geometrical isomerism* in cycloalkanes in Chapter 25. Geometrical isomers occur in cycloalkanes when two or more substituents are found around the ring in axial, equatorial or both positions. Geometrical isomers differ in their physical properties and spatial orientation.



▲ Figure 24.13 1,3-Diaxial repulsion.
Substituents placed in an axial conformation interact strongly with the two axial hydrogens (red), destabilising this conformer relative to the equivalent equatorial conformer.

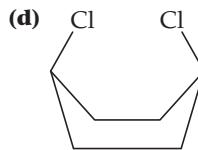
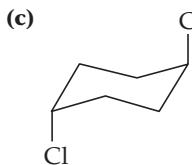
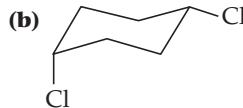
Self-Assessment Exercises

24.22 What is the molecular formula of the following structure?



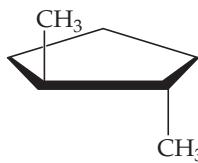
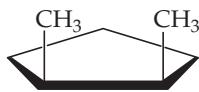
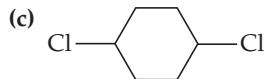
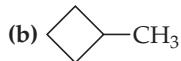
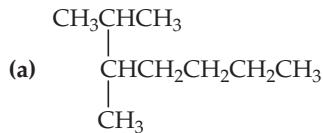
- (a) C₆H₁₄ (b) C₇H₁₄ (c) C₇H₁₆ (d) C₈H₁₆

24.23 Which structure represents the most stable conformer of 1,4-dichlorocyclohexane?



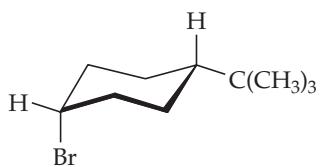
Exercises

24.24 Name the following compounds systematically:



24.25 (a) Draw line drawings for cyclopentane and cyclobutane. (b) Which of the two cycloalkanes has the higher ring strain? Why?

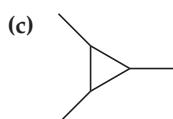
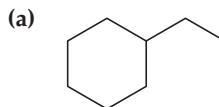
24.26 (a) 1-Bromo-4-*tert*-butylcyclohexane exists almost entirely in the conformation shown. Explain why based on the relative size of the two groups. (b) Label the Br and C(CH₃)₃ groups as axial or equatorial.



24.27 Of these two disubstituted cyclic compounds, indicate which would experience the fewest non-bonding interactions, and hence would be lower in energy.

24.28 (a) Draw the structure of cyclohexane in the chair conformation including hydrogen atoms. Highlight those hydrogens that are axial and those that are equatorial. (b) Draw a 1,2-disubstituted cyclohexane in the chair conformation with your choice of alkyl substituents in axial positions. Now flip the structure to the other chair conformation. What do you notice about the position of the two substituents? Are both substituents axial, or equatorial, or is there one of each? Is this general? Explain. (c) Systematically name the structure you drew in part (b).

24.29 (a) Provide the molecular formula and systematic name for the following structures. (b) Draw the structure of a constitutional isomer for each. (c) Why is it unnecessary to name the two conformers of methylcyclohexane as two distinct molecules?

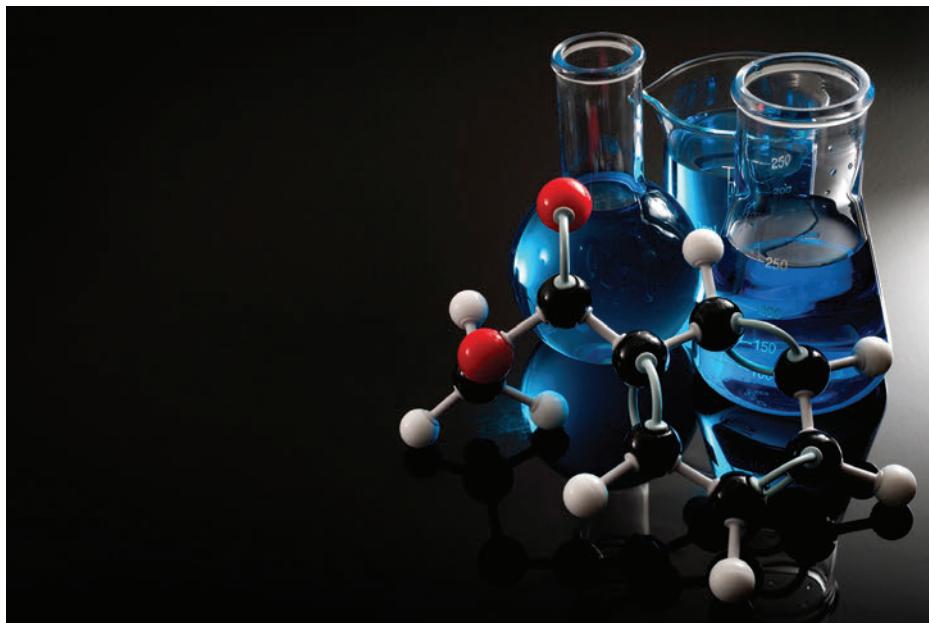


24.22 (b) 24.23 (a)

Answers to Self-Assessment Exercises



24.6 | Organic Functional Groups



The wealth of variety in organic chemistry results from the combination of a vast number of ways that carbon chains and rings may be constructed, punctuated by a selection of functional groups. These form the reactive part of the molecule and are given special attention, rather like an ace in a card game. By the end of this section, you should

- Be able to identify the common functional groups present in organic molecules.

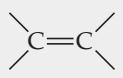
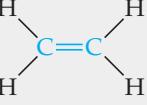
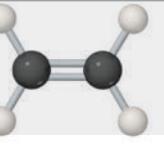
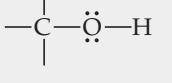
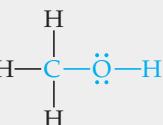
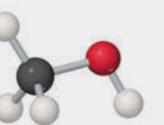
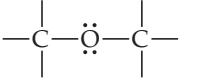
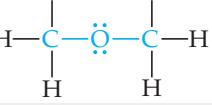
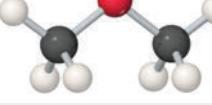
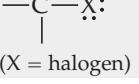
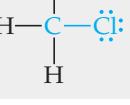
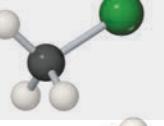
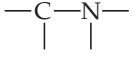
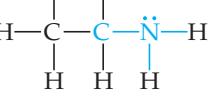
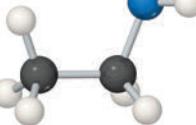
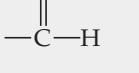
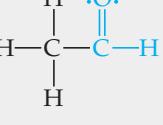
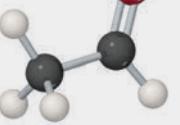
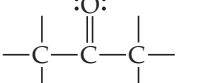
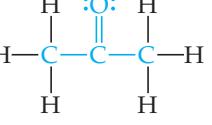
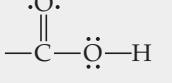
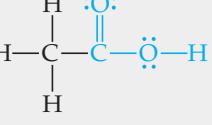
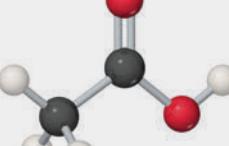
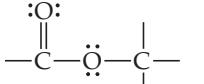
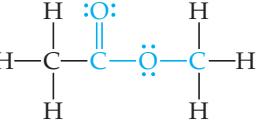
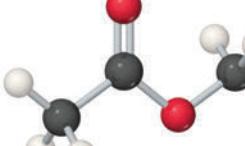
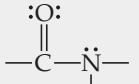
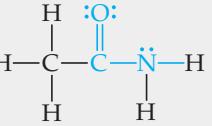
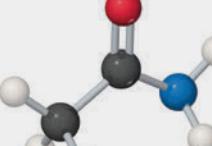
The reactivity of organic compounds can be attributed to particular atoms or groups of atoms within the molecule. A site of reactivity in an organic molecule is called a **functional group** because it characteristically controls how the molecule behaves, or functions under a given set of conditions. Functional groups define both the reactivity and class descriptions of organic molecules. As we will see in, the presence of carbon–carbon double or triple bonds in a hydrocarbon will markedly increase that compound’s reactivity. Furthermore, these two functional groups undergo similar yet characteristic reactions. The same is true of other functional groups. Each distinct kind of functional group often undergoes the same kinds of reactions, regardless of the size and complexity of the molecule. Thus the chemistry of an organic compound is largely determined by the functional groups it contains.

Table 24.8 lists the most common functional groups and gives examples of each. Notice that, in addition to carbon–carbon double bonds or carbon–carbon triple bonds, there are also many functional groups that contain elements other than just C and H. In fact, many of the functional groups found within organic molecules contain other non-metals such as O and N. In later chapters we examine the structure and chemical properties of important functional groups containing oxygen, that is, alcohols and ethers (Chapter 27), aldehydes and ketones (Chapter 28), carboxylic acids and esters (Chapter 29) and those containing nitrogen, such as amines and amides (Chapter 31).

Alkane groups constitute the less reactive portions of any compound and so are typically abbreviated to the symbol “R”. In describing the general features of organic compounds, chemists often use the designation R to represent any structural group: methyl, ethyl, propyl and so on ([Figure 24.14](#)); or, in fact, to represent a collective of atoms that do not participate in the reaction of interest. Alkanes, for example, which contain no functional group, are represented as R—H. **Alcohols**, which contain —OH, the alcohol functional group, are represented as R—OH. If two or more different structural groups are present in a molecule, we designate them R, R', R" and so forth.

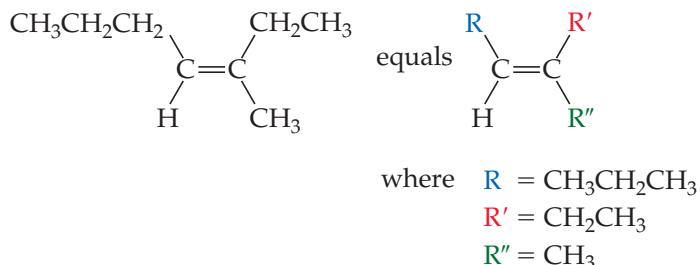
In organic chemistry, a **heteroatom** is defined as an atom other than hydrogen or carbon. Of the different types of heteroatoms associated with a hydrocarbon skeleton,

TABLE 24.8 Common functional groups

Functional group	Compound type	Suffix or prefix	Structural formula	Example Ball-and-stick model	Systematic name (Common name)
	Alkene	-ene			Ethene (Ethylene)
	Alkyne	-yne			Ethyne (Acetylene)
	Alcohol	-ol			Methanol (Methyl alcohol)
	Ether	ether			Dimethyl ether
	Haloalkane (X = halogen)	halo-			Chloromethane (Methyl chloride)
	Amine	-amine			Ethylamine
	Aldehyde	-al			Ethanal (Acetaldehyde)
	Ketone	-one			Propanone (Acetone)
	Carboxylic acid	-oic acid			Ethanoic acid (Acetic acid)
	Ester	-oate			Methyl ethanoate (Methyl acetate)
	Amide	-amide			Ethanamide (Acetamide)

$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ equals $\text{R}-\text{OH}$ when $\text{R}=\text{CH}_3\text{CH}_2\text{CH}_2$

CH_3OH equals $\text{R}'-\text{OH}$ when $\text{R}'=\text{CH}_3$



◀ Figure 24.14 The generalizations of organic chemistry.

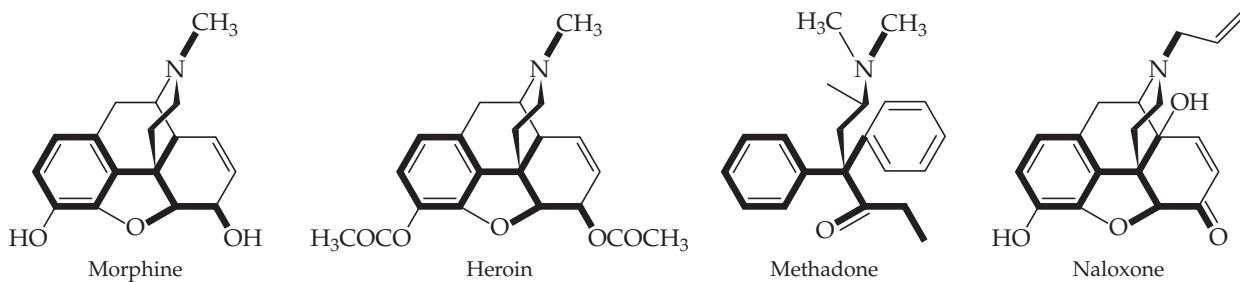
oxygen is the most prevalent. For oxygen to be added to a hydrocarbon, oxidation must occur. Because our atmosphere contains approximately 21% oxygen, oxidation reactions are always happening, and not only in the process of rusting. Carbon dioxide, water and most free radicals contain oxygen. Simple molecules containing oxygen, such as alcohols, are easily transformed into alkenes, haloalkanes, ethers, aldehydes and ketones and carboxylic acids and their derivatives. For the rest of this chapter we will investigate some of the common reactions used to functionalize alkanes.

CHEMISTRY AND LIFE Structure–Activity Relationships

Medicinal chemistry research to find the best molecule to elicit a particular response in the body often involves “structure–activity” relationships. This requires synthesizing a range of similar molecules and testing them to see if a small structural difference makes them more or less active in a particular cell culture. Sometimes, molecules that at first sight look different, may adopt a similar shape when twisted into a particular conformation. The advent of sophisticated 3-D modeling of structures has helped identify similarities between molecules.

Each of the following molecules has a similar structural element highlighted in bold. Morphine is extracted from the opium poppy and is used in the management of extreme pain. It works by acting on the central nervous system, blocking pain but allowing most nerve activity to continue. One side effect of its use is drowsiness. Indeed, the

name morphine is derived from Morpheus, the Greek god of dreams. The conversion of the alcohol functional groups into ester groups generates the compound heroin. This compound has been used as a recreational drug as it gives the user a feeling of euphoria. However, it is also devastatingly addictive and users quickly become physically dependent on it. Methadone is prescribed as a way of regulating, and ultimately reducing, heroin addiction. It is an *agonist*, which means that it binds to the opioid receptors in the brain and causes a response similar to that of heroin but one that is easier to control. In the case of a heroin overdose, an *antagonist*, naloxone, is used. This molecule binds strongly to the opioid receptors, displacing heroin, but does not cause any opioid response, so reversing the effect of the heroin. It is likely to precipitate withdrawal symptoms such as chills, sweating, stiffness, cramps, and anxiety.



Self-Assessment Exercise

24.30 Identify the functional groups in morphine

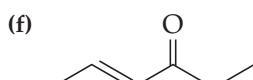
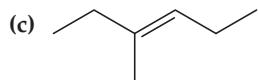
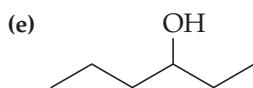
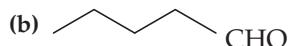
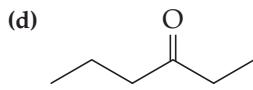
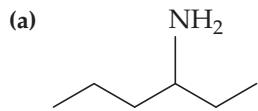
- (a) alkene, amide, ether, ketone
- (b) alcohol, alkyne, amine, ketone

(c) aldehyde, alkene, amide, ether

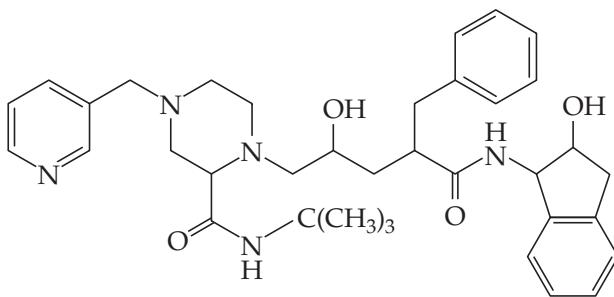
(d) alcohol, alkene, amine, ether

Exercises

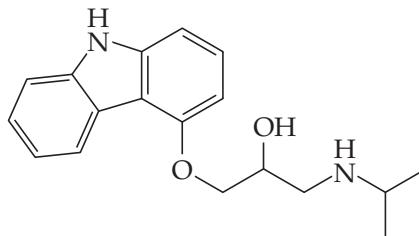
24.31 Circle the functional groups in each of the following compounds:



24.32 Indinavir is a HIV protease inhibitor. Identify the following functional groups and the number of each present in the structure of Indinavir: (a) alcohol; (b) amide; (c) amine.



24.33 Carazolol is an antihypertensive drug. Identify the following functional groups and the number of each present in the structure Carazolol: (a) alcohol; (b) ether; (c) amine.



24.30 (d)

Answers to Self-Assessment Exercise

24.7 | Reactions of Alkanes



The starting point for many of the manufactured materials that surround us is a combination of crude oil and natural gas that feeds the petrochemical industry. Here, it is transformed into a myriad of products that ultimately end up as polymers, plastics, synthetic fibres, solvents, glues, pharmaceuticals, paints, and fertilizers to name just a few items. In 2020, the industry was estimated to be worth USD 476 billion. While the processes used

in the industry may be rather different to those in the research laboratory, in both cases, the basic type of reactions are the same and involve the dozen functional groups that are the foundation of organic chemistry. By the end of this section, you should

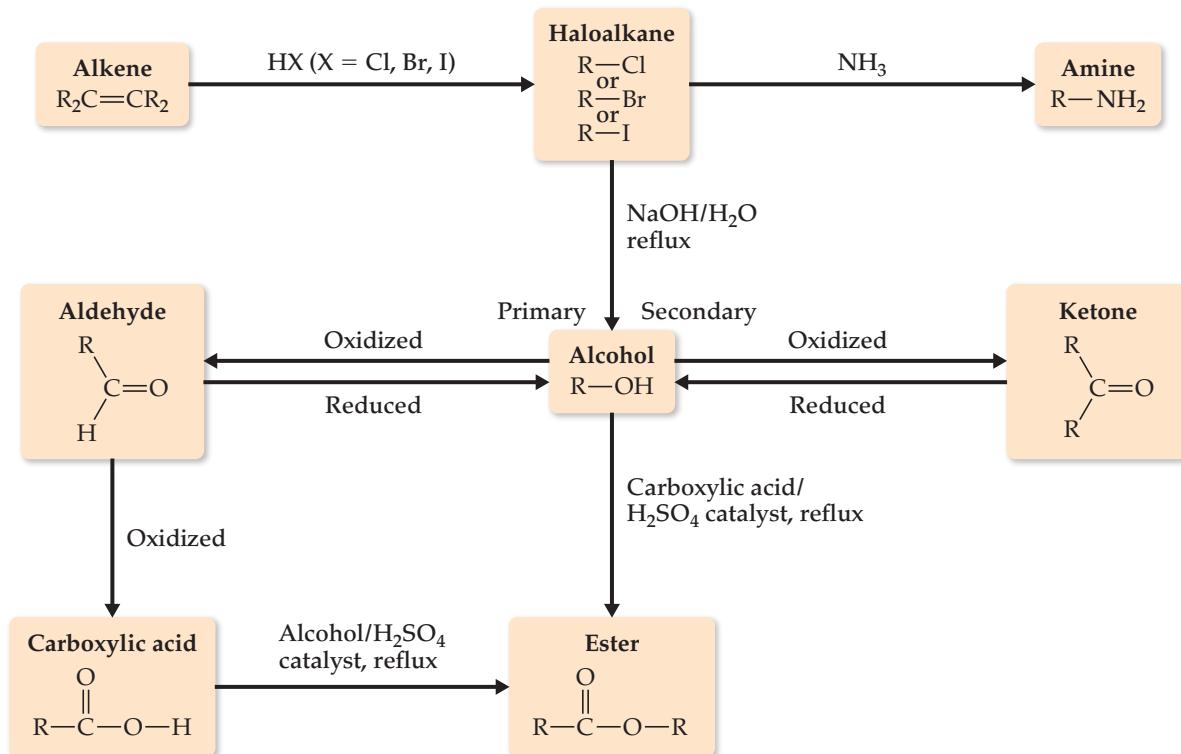
- Be able to identify primary, secondary, and tertiary carbon and hydrogen atoms
- Understand the mechanism of a free-radical polymerization reaction

Alkanes contain only C—C and C—H bonds and as a result are relatively unreactive. At room temperature, for example, alkanes do not react with any common acids, bases or strong oxidizing agents, and they are not even attacked by boiling nitric acid. Their low chemical reactivity is due primarily to the strength and lack of polarity of both C—C and C—H single bonds. The whole basis of organic chemistry—that is, converting one functional group into another by making or breaking bonds, leading to the formation of new compounds (Figure 24.15)—would fall apart if C—H and C—C bonds reacted under mild conditions. Essentially, organic molecules are composed of an inert hydrocarbon framework punctuated by functional groups, which are the reactive parts of the molecule. Functional groups not only define the reactivity but also the classes of organic molecules.

The following chapters show that hydrocarbons can be modified to impart greater reactivity by introducing unsaturation into the carbon–carbon framework and by attaching other reactive functional groups to the hydrocarbon backbone.

Combustion

Alkanes are not completely inert, however. Their relative high stability means that either harsh reaction conditions or the use of highly reactive reagents is needed to initiate a chemical reaction. One of the most commercially important reactions of alkanes is their **combustion** reaction in air, which is the basis of their use as fuels. The complete combustion of an alkane in the presence of oxygen *always* generates carbon dioxide and water

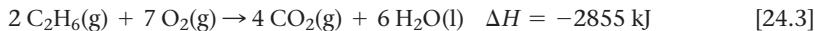


▲ **Figure 24.15 Functional group interconversion.** Functional groups are atoms or groups of atoms within a molecule that show a characteristic set of chemical properties. Some of the more common functional groups and their interconversion are shown. The functional group is the center of reactivity in an organic molecule. R = general representation for the rest of the molecule. Note that the basic hydrocarbon framework is unchanged in these reactions.



▲ **Figure 24.16 Combustion.** Ignition of a mixture of oxygen with flammable gases such as hydrogen or methane can have explosive consequences.

as the products of the reaction. For example, the balanced equation for the complete combustion of ethane is:



The reaction of any organic molecule with oxygen is another example of an **oxidation** reaction. We investigate these types of reactions in the context of organic chemistry in greater detail in Chapter 28.

We know from calorimetric measurements that the reaction of a simple alkane such as methane (CH_4) with oxygen is highly exothermic (Section 14.4). Indeed, the combustion of methane (which is the major component of natural gas) keeps many of our homes warm during the winter months. Although the reactions of alkanes with oxygen are exothermic, most alkanes are stable indefinitely at room temperature in the presence of air because the activation energy required for combustion is large. This activation barrier is usually overcome by heat generated from a flame or spark, typically with explosive consequences (Figure 24.16).

Classification of C and H

An important skill to develop in organic chemistry is the ability to recognize which functional group within a molecule will react under a given set of conditions. This ability allows the organic chemist to synthesize very complex molecules. Sometimes, however, there is a choice of positions within a molecule at which reaction is likely to occur. This is as valid with simple organic molecules, like alkanes, as it is for highly complex molecular structures. Before going on to discuss one of the few important reactions of the alkanes,

Sample Exercise 24.3

Oxidation of alkanes

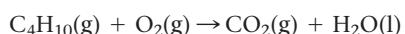
Write the equation for the complete combustion of 2-methylpropane.

SOLUTION

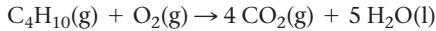
Analyze We are asked to react an alkane with oxygen under conditions that give the complete combustion products, namely CO_2 and H_2O .

Plan Write the molecular formula for 2-methylpropane and the reagent molecular oxygen on the reactants side of the equation and carbon dioxide and water on the products side. Then balance the equation for carbon, then hydrogen and finally oxygen.

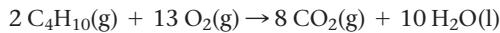
Solve The molecular formula for 2-methylpropane follows the general formula for alkanes. 2-methylpropane has four carbons so its molecular formula is C_4H_{10} . So, the unbalanced equation is



Balancing for carbon and hydrogen yields



Now, balancing for oxygen using the total of oxygen present on the product side yields the balanced equation



► Practice Exercise

Write the equation for the complete combustion of 2,3-dimethylbutane.

we need to have a way of distinguishing between the different kinds of carbons that appear. These classifications are important whenever we are trying to recognize which functional group or part of a molecule will react.

The classification used to distinguish between types of hydrogens and carbons and the appropriate symbolism is:

Primary (1°) carbon: a carbon atom bonded to one other carbon atom

1° H: a hydrogen bonded to a 1° carbon

Secondary (2°) carbon: a carbon atom bonded to two other carbon atoms

2° H: a hydrogen atom bonded to a 2° carbon

Tertiary (3°) carbon: a carbon bonded to three other carbon atoms

3° H: a hydrogen atom bonded to a 3° carbon

Quaternary (4°) carbon: a carbon bonded to four other carbon atoms

Figure 24.17 illustrates this classification by identifying the different carbon atoms of 2,2,3-trimethylpentane. This method of classification is useful, as we see in the following chapters, for determining the reactivity of a range of different functional groups.

Free-Radical Reactions and Electron Movement

The majority of alkane reactions occur through the formation of **free radicals**, either by the scission of a C—C bond or by hydrogen abstraction. Free radicals gain their reactivity from having an unpaired electron. Both C—C bond scission and hydrogen abstraction are examples of a **homolytic bond cleavage** because one electron contained with the two-electron σ -bond is transferred to each atom, yielding two free radicals.

At this point, we will use one form of free-radical chemistry to emphasize the point that a single covalent bond contains two electrons and that reactions occur by making and breaking such bonds.

The most common of all the free-radical reactions of alkanes is **halogenation**. This term simply means the incorporation of halogen (that is, F, Cl, Br, I), although chlorine and bromine atoms are the easiest and hence the most common to incorporate. This type of free-radical halogenation is generally called a **substitution reaction** because the reaction proceeds by abstracting a hydrogen atom and replacing or *substituting* it with a halogen. The chlorination of methane, for example, to yield the mono-, di-, tri- and tetra-chlorinated products (and HCl) occurs only in the presence of light (photolysis), with radiation in the range 200–500 nm most common. The reaction produces all permutations of substitution, as shown in Equation 24.5. The ratio of the four products formed is dictated by the amount of chlorine gas present, the photolysis time and the wavelength of light.



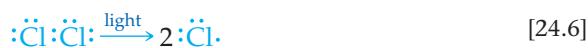
Electron movement in organic chemistry is a useful way of rationalising the conversion of starting materials to products. We call this the *mechanism* of a reaction. Remember that there are two electrons in any single covalent bond and how these electrons move gives rise to either a carbocation, carbanion or free radical, which are less stable (and hence more reactive) than the covalent bond from which they are formed. In Chapter 26, we will investigate a shorthand way of illustrating electron movement that simplifies the fundamental approach we are about to take to explain the free-radical halogenation of methane.

Here, we will begin our study of mechanisms and the three steps to a radical chain reaction:

1. **Initiation**
2. **Propagation**
3. **Termination**

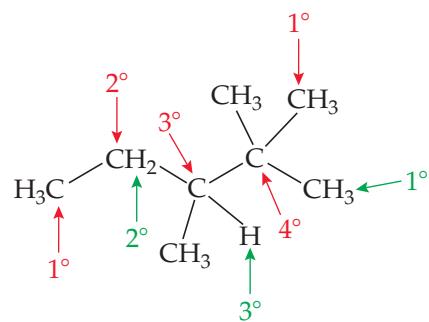
using Equation 24.5 as an example. We will employ Lewis structures to demonstrate the electron movement.

1. **Initiation step:** This step produces the first radicals. In this example, the absorption of light by Cl_2 causes the homolytic cleavage of the Cl—Cl bond, leading to the formation of two chlorine radicals:



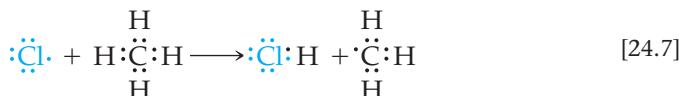
The generation of chlorine or bromine radicals can also be initiated by heat.

2. **Propagation steps:** As these newly formed radicals collide with other molecules (which are not radicals), they generate or *propagate* new radicals. In the example, a newly formed chlorine radical (chlorine atom) can remove a hydrogen atom from a methane molecule. This step produces a stable product molecule, HCl, and an unstable methyl radical that is highly reactive because its carbon has only seven valence electrons.



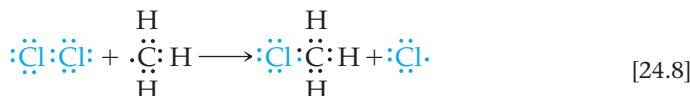
▲ **Figure 24.17** Classification of carbon and hydrogen atom types. The classification of a selected set of hydrogen (green) and carbon (red) atoms is shown for 2,2,3-trimethylpentane.

Step 1



When a molecule of Cl_2 encounters the methyl radical, one chlorine atom is transferred to the carbon to form a stable molecule of chloromethane. The second chlorine atom, now formed, can react with a new molecule of methane as in step 1.

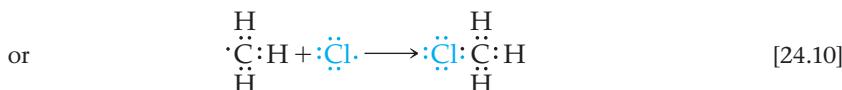
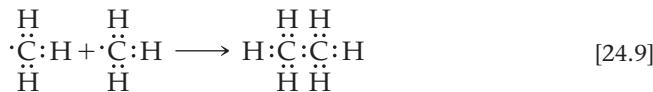
Step 2



The reaction of the methyl radical with chlorine (step 2) yields another chlorine radical which can propagate causing the *chain reaction*. Since each step produces a molecule of product and a newly formed radical, one radical gives rise to many product molecules. This means that only a small number of radicals need be generated during the initiation to allow the chain reaction to proceed.

Once the amount of CH_3Cl begins to build up in the mixture, it too can have a hydrogen atom abstracted by a chlorine radical, leading to the formation of CH_2Cl_2 . Chloroform (CHCl_3) and CCl_4 are formed by the same process.

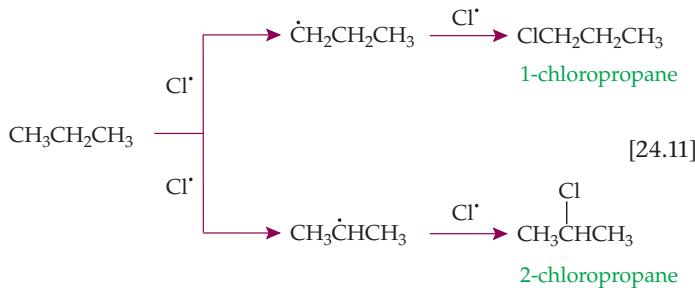
- 3. Termination steps:** These occur when two radicals combine to form an unreactive product. For example:



Termination steps such as those displayed in Equation 24.9 complicate the reaction by extending the carbon chain. Products such as those in Equations 24.9 and 24.10, which also contain C—H bonds, are also prone to further radical generation and

A CLOSER LOOK Reactivity by Carbon Classification

When propane is mono-halogenated two products are likely since both primary and secondary hydrogens exist (Equation 24.11).



The direction of the reaction—that is, via abstraction of the primary or secondary hydrogen atom—depends on two factors: the C—H bond dissociation energy and the relative stability of the two radical intermediates formed (Section 8.8). The two factors are interrelated. There is a trend that suggests the more stable the radical, the lower the energy needed to cause C—H bond homolysis. There is approximately 15 kJ/mol difference in C—H bond dissociation energies between primary C—H bonds and secondary C—H bonds, with the latter being easier to cleave. However, the size of the energy

difference between homolysis of a primary and secondary C—H bond cannot fully account for the approximate 1:1 product ratio.

There is also a valence bond argument that supports the bond dissociation energy arguments. Alkyl free radicals have a potentially filled *p* orbital and are stabilized by **electron-donating groups** such as alkyl groups. As a consequence, the order of alkyl radical stability is:

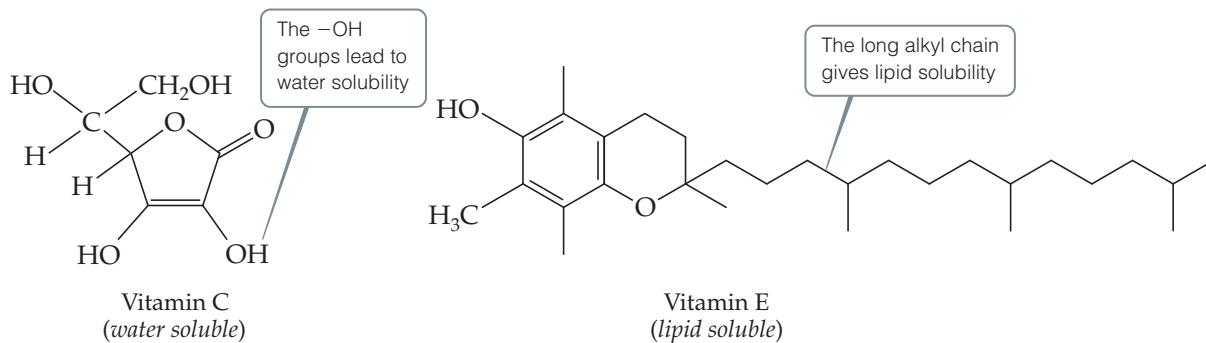


At this point, it appears there is little difference between the two pathways leading to the monochlorinated products if the product ratio is 1:1. Actually, there is a significant difference as it is statistically *three times* more likely to abstract a primary hydrogen (there are six of these in propane) as it is to abstract a secondary hydrogen (there are two of these in propane). So, in fact, there is a large discrimination for the formation of 2-chloropropane. Typically, the ratio of selectivity for monochlorination is of the order $1^\circ : 2^\circ : 3^\circ = 1 : 4 : 5$.

Bromine also reacts with alkanes via a free-radical mechanism and bromination is a more selective process. The ratio of **regioselectivity** for bromination is of the order $1^\circ : 2^\circ : 3^\circ = 1 : 100 : 1500$.

substitution steps. The generation of a single radical can lead to the formation of many product molecules before the chain is terminated.

Free-radical chain reactions are also found in biological systems, in which harmful radicals such as ·OH attack functional and structural molecules within cells, leading to dysfunction or cell death. Natural **antioxidants** such as vitamin C (ascorbic acid) and vitamin E (α -tocopherol) react readily with free radicals, terminating their propagation.



Sample Integrative Exercise

Putting concepts together

Combustion analysis of a hydrocarbon determined it contained 82.8% carbon and 17.2% hydrogen by mass. **(a)** What is the empirical formula of this compound? **(b)** Explain why your empirical formula cannot also be the molecular formula of this hydrocarbon. **(c)** If the molar mass of the compound is 58.1 g/mol, draw the structural formula of all possible constitutional isomers and give their names. **(d)** Does an equilibrium exist between the constitutional isomers at room temperature?

SOLUTION

Analyze In this problem we determine the formula of a compound and examine the relationship between its isomers.

Plan First determine the empirical formula of the compound then examine the bonding arrangement of the atoms involved to see if the empirical formula and molecular formula could be the same. Next determine the molecular formula and name all possible structures with this formula. Finally consider whether the constitutional isomers may be easily interconverted at room temperature.

Solve

(a) A 100 g sample of the hydrocarbon will contain 82.8 g of carbon and 17.2 g of hydrogen. This represents

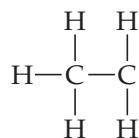
$$\frac{82.8 \text{ g}}{12.01 \text{ g/mol}} = 6.89 \text{ mol carbon}$$

$$\frac{17.2 \text{ g}}{1.008 \text{ g/mol}} = 17.1 \text{ mol hydrogen}$$

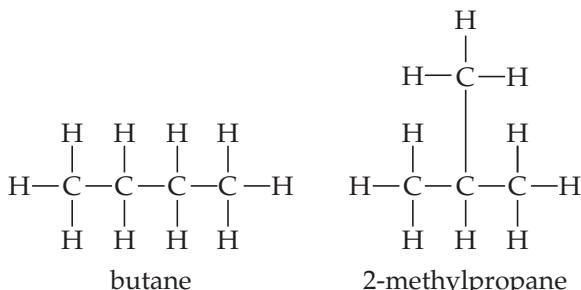
The mole ratio of C: H is $6.89 : 17.1 = 1 : 2.48$ or $2 : 5$

The empirical formula of the hydrocarbon is therefore C_2H_5 .

(b) In a stable bonding arrangement hydrogen forms one bond and carbon forms four bonds. The odd number of hydrogen atoms mean that it is not possible to construct a compound in which all atoms have a stable bonding arrangement; one carbon has just three bonds.



(c) An empirical formula of C_2H_5 would have a molar mass of 29.06 g/mol; the actual molar mass is double this and so the molecular formula is C_4H_{10} . The structural isomers with this formula are:



(d) To convert one constitutional isomer to another involves the breaking of chemical bonds. This requires quite a lot of energy and does not spontaneously occur at room temperature. So no equilibrium exists between the two isomers at room temperature.

Self-Assessment Exercises

24.34 How many primary, secondary and tertiary hydrogens are there in 2-methylbutane?

- (a) $3 \times 1^\circ\text{H}$; $2 \times 2^\circ\text{H}$; $1 \times 3^\circ\text{H}$
- (b) $9 \times 1^\circ\text{H}$; $2 \times 2^\circ\text{H}$; $1 \times 3^\circ\text{H}$
- (c) $1 \times 1^\circ\text{H}$; $2 \times 2^\circ\text{H}$; $9 \times 3^\circ\text{H}$

24.35 Name, in order of occurrence, the three steps in a radical polymerization.

- (a) Initiation, propagation, termination
- (b) Initiation, termination, propagation
- (c) Propagation, initiation, termination
- (d) Termination, propagation, initiation

Exercises

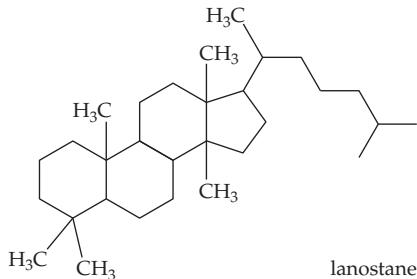
24.36 (a) Write a balanced equation for the complete combustion of propane. (b) Use table 8.3 and your answer to part (a) to estimate ΔH for this reaction.

24.37 An unknown aliphatic alkane, A, yields 4.800 g CO_2 and 2.475 g H_2O when fully combusted. Suggest a plausible molecular formula for A that is less than or equal to C_6H_{14} .

24.38 Propose structures for compounds with formulas less than C_6H_{14} containing:

- (a) two tertiary carbons
- (b) three primary carbons
- (c) a quaternary carbon
- (d) only two methyl groups.

24.39 The structure of lanostane, a biogenic precursor of steroids, is shown here. Classify each carbon atom as primary, secondary, tertiary, or quaternary.



24.40 Draw Lewis structures for the following radicals:

- (a) methyl radical
- (b) chlorine atom
- (c) isopropyl radical.

24.41 (a) What ratio of cyclohexane to chlorine would you suggest in order to achieve a monochlorination? (b) The free-radical chlorination of cyclohexane is much cleaner and occurs in far greater yield than that of hexane under the same conditions. Account for this difference.

24.34 (b) 24.35 (a)

Answers to Self-Assessment Exercises

Chapter Summary and Key Terms

INTRODUCTION AND SECTION 24.1 Organic chemistry is the study of compounds that contain carbon. We have encountered many aspects of organic chemistry in earlier chapters. Carbon forms four bonds in its stable compounds.

SECTION 24.2 The simplest class of organic molecules consists of hydrocarbons, which contain only carbon and hydrogen. Alkanes are hydrocarbons that contain only single bonds. Alkanes have names that end in *-ane*, such as methane and ethane. Alkanes are aliphatic, forming straight-chain, branched-chain and cyclic arrangements.

Alkanes are used primarily as fuels. Their properties, such as melting and boiling point, change in a regular fashion as the length of the chain increases. These properties are known as a homologous series.

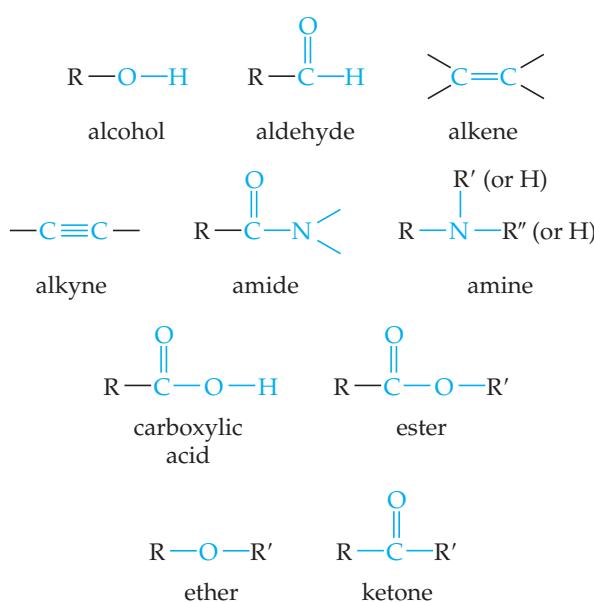
SECTION 24.3 Hybridization is used as a model to rationalize the bonding geometry of a saturated carbon atom (109.5°). The rotation about C—C single bonds gives rise to different conformations, ranging from staggered to eclipsed forms. The staggered forms dominate due to the added steric interactions involved in the eclipsed forms of a molecule. We can use Newman projections to describe the different conformers

easily. Structural or constitutional isomers have the same molecular formula but a different connectivity of atoms.

SECTION 24.4 The nomenclature used for hydrocarbons is based on the longest continuous chain of carbon atoms in the structure and contains a prefix, parent and suffix. The locations of alkyl groups, which branch off the chain, are specified by numbering along the carbon chain.

SECTION 24.5 Alkanes with ring structures are called cycloalkanes. Five- and six-membered rings are most common. Cyclohexane has two conformations, chair and boat forms. The chair form is more stable as it reduces unfavourable steric interactions and has two types of hydrogen positions, axial and equatorial. When a substituent is added to the ring, it typically adopts an equatorial position to minimize 1,3-diaxial interactions.

SECTION 24.6 The chemistry of organic compounds is dominated by the nature of their functional groups. The functional groups we have considered are:



R, R' and R'' represent hydrocarbon groups—for example, methyl (CH_3) or ethyl (CH_2CH_3). **Alcohols**, which contain —OH, the alcohol functional group, are represented as $\text{R}-\text{OH}$. Organic molecules need the reactivity imparted by **heteroatoms** in order to demonstrate their usefulness. Of the types of heteroatoms available, oxygen plays a major role.

SECTION 24.7 Alkanes and cycloalkanes are relatively unreactive. They do, however, undergo **combustion** in air (**oxidation**), and their main use is as sources of heat energy (exothermic reaction). Recognition of carbon and hydrogen atoms as primary, secondary or tertiary is important for determining the product distribution in organic reactions. **Free-radical** reactions are typically initiated by heat or light which leads to **homolytic bond cleavage** of halogens, leading to **halogenation**. The three phases of a free-radical reaction are **initiation**, **propagation** and **termination**. The preference of substitution is $3^\circ \text{H} > 2^\circ \text{H} > 1^\circ \text{H}$ and is assisted by the presence of **electron-donating groups** around the carbon-centered radical. The preference for one product over its isomer is called **regioselectivity**. **Antioxidants** such as vitamins E and C eliminate free-radicals within the human body.

Key Skills

- Draw alkane structures based on their names and name alkanes based on their structures. (Sections 24.2 and 24.3)
- Understand trends in the alkane homologous series. (Section 24.2)
- Be able to describe the concept of sp^3 hybridization and σ -bonds. (Section 24.3)
- Be able to name systematically alkanes from structures and draw structures from systematic names. (Section 24.4)
- Be able to draw cycloalkanes containing 3–8 carbon atoms. (Section 24.5)

- Understand the difference between equatorial and axial positions in cyclohexane. (Section 24.5)
- Know the structure of the functional groups: alkene, alkyne, alcohol, ether, aldehyde, ketone, carboxylic acid, amine, amide. (Section 24.6)
- Be able to identify primary, secondary and tertiary carbon atoms. (Section 24.6)
- Be able to demonstrate the making and breaking of σ -bonds in a free-radical reaction. (Section 24.7)

Key Equations

- General formula for alkanes
- General formula for cycloalkanes

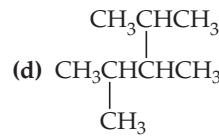
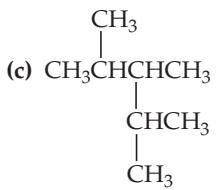
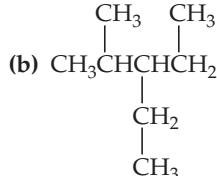
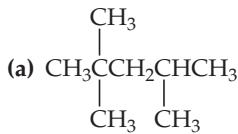
$$\text{C}_n\text{H}_{2n+2} \quad [24.1]$$

$$\text{C}_n\text{H}_{2n} \quad [24.2]$$

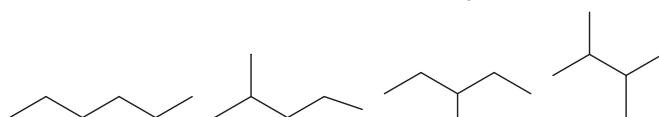
Exercises

Visualizing concepts

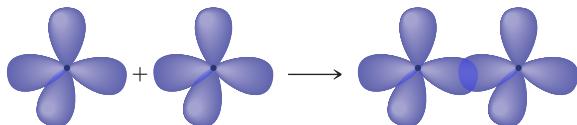
- 24.42** All the structures that follow have the same molecular formula, C_8H_{18} . Which structures are of the same molecule? [Section 24.2]



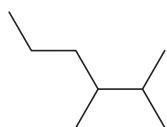
- 24.43** Which constitutional isomer is missing? [Section 24.3]



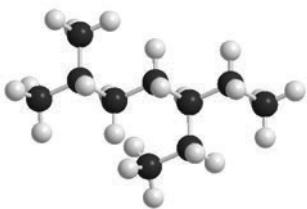
24.44 Define the following bond. [Section 24.3]



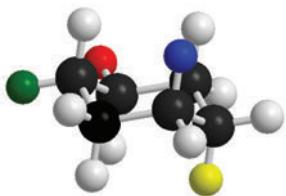
24.45 The structure of an alkane is drawn here as a line drawing representation. Is 2-propyl-3-methylbutane a suitable systematic name for this compound? Provide a better name using the guidelines in Section 24.4.



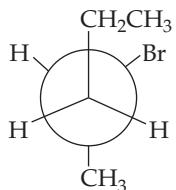
24.46 Draw the structural formula for the following molecular model. [Section 24.3]



24.47 A selection of hydrogen atoms on the chair conformation of cyclohexane are colored red, green, blue and yellow. Identify the position of each colored ball (that is, axial or equatorial). What happens to these positions if an interconversion occurs to produce the other possible chair conformation. [Section 24.5]



24.48 Convert the following Newman projection into a standard structural formula. [Section 24.3]



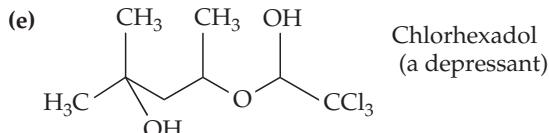
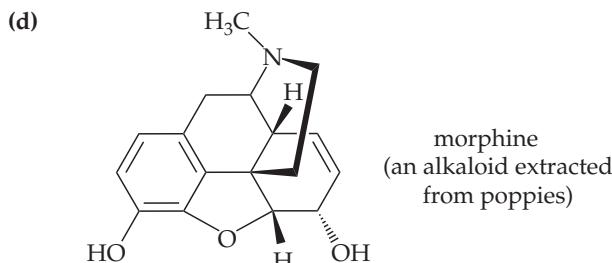
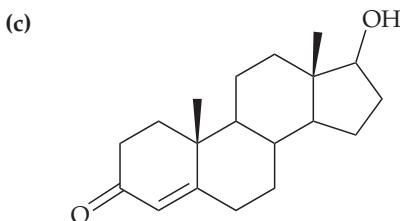
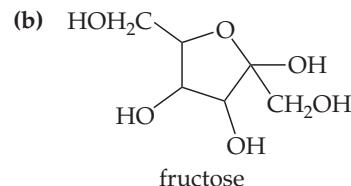
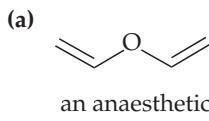
24.49 **(a)** Write the propagation steps leading to the formation of dichloromethane from chloromethane.



(b) Explain why free-radical halogenations usually give rise to mixtures of products. **(c)** Comment on the stoichiometry of chloromethane and chlorine needed to form carbon tetrachloride as the major product. [Section 24.7]



24.50 Identify each of the functional groups in the following molecules. [Section 24.6]



General Characteristics of Organic Molecules (Section 24.1)

24.51 Are carbon monoxide or ammonia considered organic molecules? Why or why not?

24.52 Urea has been identified as an organic molecule. What features make it so?

24.53 **(a)** What are the approximate bond angles about carbon in an alkane? **(b)** What are the characteristic hybrid orbitals employed by carbon in an alkane?

An Introduction to Hydrocarbons (Section 24.2)

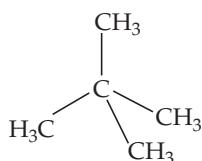
24.54 Give the molecular formula of a hydrocarbon containing six carbon atoms that is **(a)** an alkane, **(b)** aromatic.

24.55 What structural features help us identify a compound as **(a)** an alkane, **(b)** a cycloalkane, **(c)** a saturated hydrocarbon?

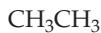
24.56 Rank the following compounds in order of increasing boiling points and explain your choice of order.



heptane

2,2-dimethylpropane
(neopentane)

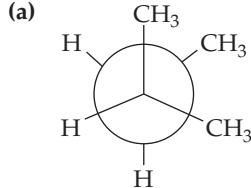
2,4-dimethylpentane



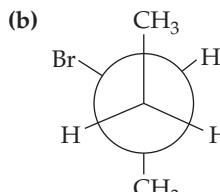
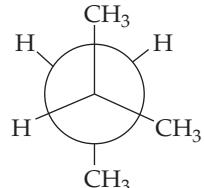
ethane

Structure of Alkanes (Section 24.3)

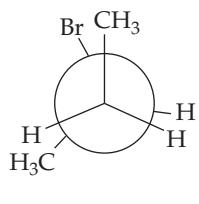
- 24.57** Draw a valence-bond description for ethane. Include the hybridization for each carbon atom.
- 24.58** Which conformer in each pair of Newman projections is lower in energy?



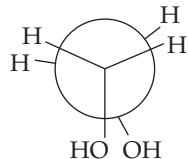
and



and

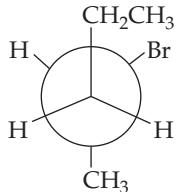


- 24.59** Ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) prefers to exist almost entirely in the following eclipsed form in the vapor phase. Give an explanation for this.

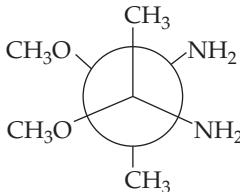


- 24.60** Convert the following Newman projections into their standard structural formula.

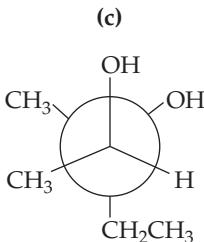
(a)



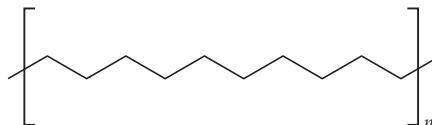
(b)



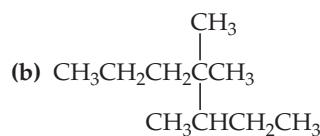
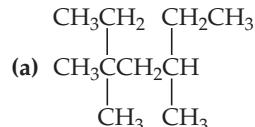
(c)



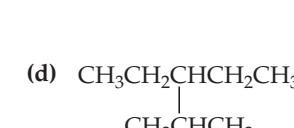
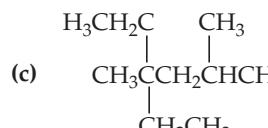
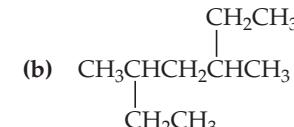
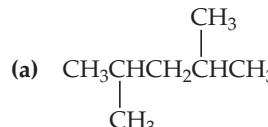
- 24.61** Polyethylene is a polymer used in many plastic applications, such as food wrap and soft-drink bottles. A general structure for polyethylene is shown here. Would such a polymer be more soluble in an organic solvent such as hexane or in water? Why?

**Alkane Nomenclature (Section 24.4)**

- 24.62** Draw the structural formula or give the systematic name, as appropriate, for the following:



- 24.63** Give IUPAC names for the following alkanes:



- 24.64** Draw 3-ethyl-2,3-dimethylbutane. What would be the correct systematic name for this compound?

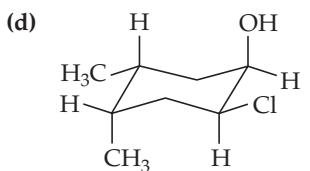
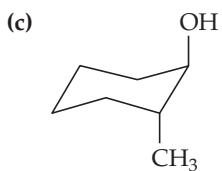
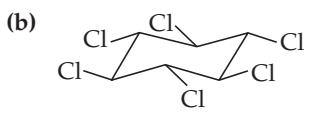
- 24.65** Butane and 2-methylpropane are both non-polar molecules and have the same molecular formula, yet butane has the higher boiling point (-0.5°C compared with -11.7°C). Explain.

Cycloalkanes (Section 24.5)

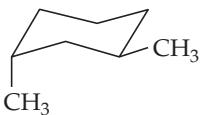
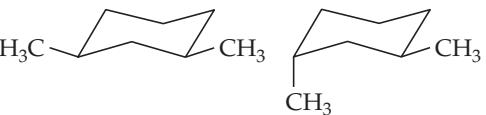
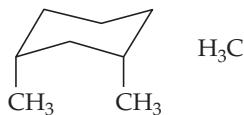
- 24.66** The molar heat of combustion of gaseous cyclopropane is $-2089 \text{ kJ mol}^{-1}$; that for gaseous cyclopentane is $-3317 \text{ kJ mol}^{-1}$. Calculate the heat of combustion per CH_2 group in the two cases, and account for the difference.

- 24.67** Draw both possible cyclic structural isomers of C_4H_8 . Systematically name each compound.

24.68 Label each CH_3 , OH or Cl group in the following compounds as axial or equatorial.

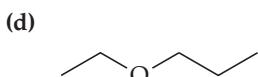
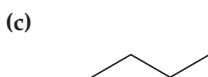
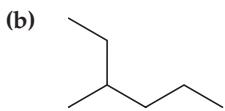
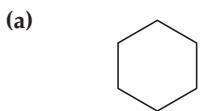


24.69 Place the following dimethylcycloalkanes in order of relative stability.

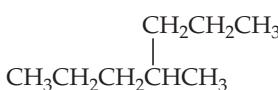
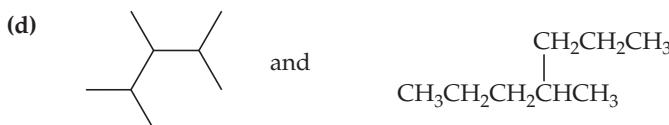
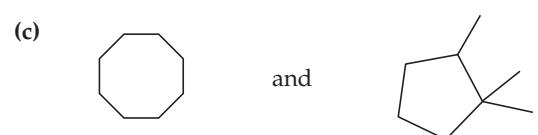
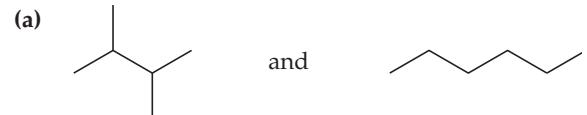


24.70 Why is geometric isomerism possible for cycloalkanes but not for alkanes?

24.71 Draw a cyclic, straight-chain or branched-chain constitutional isomer for each of the following:



24.72 Which of the following pairs are constitutional isomers?

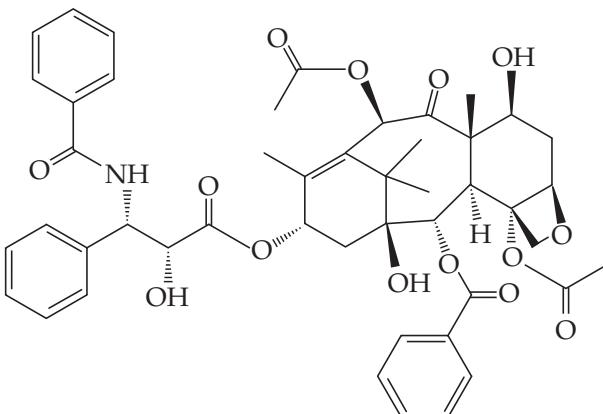


Functional Groups (Section 24.6)

24.73 (a) What is a functional group? (b) Why are functional groups important?

24.74 List three functional groups that are important in biology (there are more than three).

24.75 Taxol is a clinically important anticancer compound isolated from the bark of *Taxus*, the Pacific yew tree. Identify the following functional groups and the number of each present in the structure of Taxol: (a) alcohol; (b) ether; (c) amine; (d) amide; (e) carboxylic ester; (f) alkene; (g) ketone.



Reactions of Alkanes (Section 24.7)

24.76 (a) What is the difference between a substitution reaction and an oxidation reaction? (b) Using condensed structural formulas, write the balanced equation for the free-radical substitution reaction of 2,2,4-trimethylpentane with Br₂ in the presence of light. Explain, using this reaction as an example, what is meant by a regioselective reaction. (c) Write a balanced chemical equation for the complete combustion of 2,2-dimethylpropane.

24.77 When cyclopropane is treated with HI, 1-iodopropane is formed. A similar type of reaction does not occur with cyclopentane or cyclohexane. What physical aspect of cyclopropane might account for its reactivity?

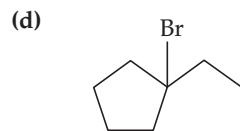
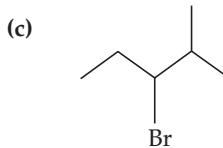
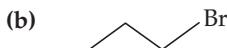
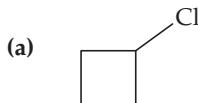
24.78 (a) How much oxygen is required for the complete combustion of 70 g of cyclohexane? (b) How much carbon dioxide is produced in this reaction?

24.79 (a) Write the propagation steps leading to the formation of dichloromethane, CH₂Cl₂, from methane. (b) Describe how termination of this chain reaction is possible.

24.80 Rank each radical in order of its relative stability.



- 24.81** Which of the following alkyl halides can be prepared in good yield by radical halogenation?



- 24.82** Draw all monobromo derivatives of 3-methylhexane. Which one of these configurational isomers would be produced in highest yield by the reaction of bromine with 3-methylhexane?

Additional Exercises

- 24.83** Draw the condensed structural formulas for two different molecules with the formula C_3H_4O .

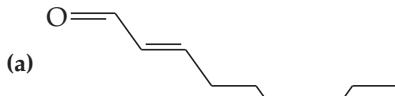
- 24.84** How many structural isomers are there for a five-member straight carbon chain with one double bond? For a six-member straight carbon chain with two double bonds?

- 24.85** Draw the condensed structural formulas for the *cis* and *trans* isomers of 2-pentene. Can cyclopentene exhibit *cis-trans* isomerism? Explain.

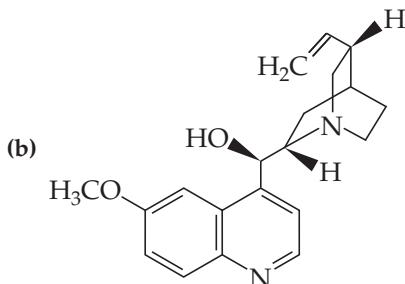
- 24.86** If a molecule is an “ene one”, what functional groups must it have?

- 24.87** Write the structural formulas for as many alcohols as you can think of that have empirical formula C_3H_6O .

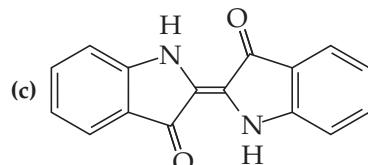
- 24.88** Identify each of the functional groups in these molecules:



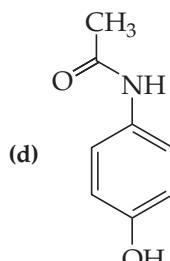
(Responsible for the odor of cucumbers)



(Quinine—an antimalarial drug)



(Indigo—a blue dye)

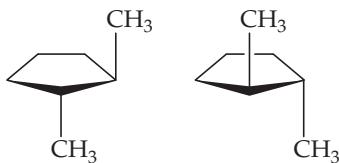


(Acetaminophen—aka Paracetamol)

- 24.89** Write a condensed structural formula for each of the following: (a) an acid with the formula $C_4H_8O_2$, (b) a cyclic ketone with the formula C_5H_8O , (c) a dihydroxy compound with the formula $C_3H_8O_2$, (d) a cyclic ester with the formula $C_5H_8O_2$.

Integrative Exercises

- 24.90** (a) What type of isomeric relationship exists between pentane and 2-methylbutane? (b) What is the relationship between the two shown here? (c) Name this compound. (d) Identify the most likely point(s) for bromination in each molecule.



- 24.91** (a) Draw a relative energy profile similar to that shown in Figure 24.16 to illustrate the stability of the different conformers produced by rotation about one C—C single bond in propane. (b) What is the product of the complete combustion of propane? (c) How much energy is released upon the complete combustion of 44 dm^3 of propane? (d) Propane is converted into 2-bromopropane by a first-order process. The rate constant is $5.4 \times 102\text{ h}^{-1}$. If the initial concentration of propane is 0.150 M , what will its concentration be after 24.0 h ?

24.92 An unknown substance is found to contain only carbon and hydrogen. It is a liquid that boils at 49 °C at 1 bar pressure. Upon analysis it is found to contain 85.7% carbon and 14.3% hydrogen by mass. At 100 °C and 735 torr, the vapor of this unknown has a density of 2.21 g dm^{-3} . When it is dissolved in hexane solution and bromine water is added, no reaction occurs. What is the identity of the unknown compound?

24.93 Methane is a greenhouse gas that is present at a concentration of 1.8 ppm and has a half-life in the atmosphere of approximately 10 years. **(a)** What is the partial pressure of methane assuming the total pressure is 102 kPa? **(b)** If no new methane was added to the atmosphere, how long would it take for the concentration to drop to a pre-industrial level of 0.5 ppm assuming first-order kinetics?

Design an Experiment

The precise mixture of alkanes contained in a crude oil sample depends on the origin of the oil. A small amount of oil has washed up on the shore close to a major shipping lane and, as a member of the local environmental protection agency, you want to determine the origin of the oil and, hence, the tanker it came from.

How would you collect samples of the oil to ensure they were representative of the spill? What physical property of alkanes enables you to separate them? How would you quantify the amount of the different alkanes present? How might you identify the alkanes present?