Manahan, Stanley E. "ORGANIC CHEMISTRY"
Environmental Chemistry
Boca Raton: CRC Press LLC, 2000

29 ORGANIC CHEMISTRY

29.1. ORGANIC CHEMISTRY

Most carbon-containing compounds are **organic chemicals** and are addressed by the subject of **organic chemistry**. Organic chemistry is a vast, diverse discipline because of the enormous number of organic compounds that exist as a consequence of the versatile bonding capabilities of carbon. Such diversity is due to the ability of carbon atoms to bond to each other through single (2 shared electrons) bonds, double (4 shared electrons) bonds, and triple (6 shared electrons) bonds in a limitless variety of straight chains, branched chains, and rings.

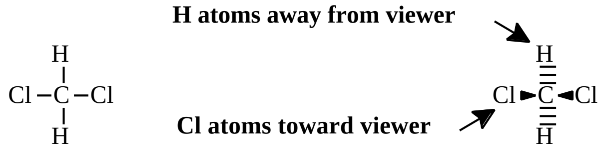
Among organic chemicals are included the majority of important industrial compounds, synthetic polymers, agricultural chemicals, biological materials, and most substances that are of concern because of their toxicities and other hazards. Pollution of the water, air, and soil environments by organic chemicals is an area of significant concern.

Chemically, most organic compounds can be divided among hydrocarbons, oxygen-containing compounds, nitrogen-containing compounds, sulfur-containing compounds, organohalides, phosphorus-containing compounds, or combinations of these kinds of compounds. Each of these classes of organic compounds is discussed briefly here.

All organic compounds, of course, contain carbon. Virtually all also contain hydrogen and have at least one C–H bond. The simplest organic compounds, and those easiest to understand, are those that contain only hydrogen and carbon. These compounds are called **hydrocarbons** and are addressed first among the organic compounds discussed in this chapter. Hydrocarbons are used here to illustrate some of the most fundamental points of organic chemistry, including organic formulas, structures, and names.

Molecular Geometry in Organic Chemistry

The three-dimensional shape of a molecule, that is, its molecular geometry, is particularly important in organic chemistry. This is because its molecular geometry determines in part the properties of an organic molecule, particularly its interactions with biological systems and how it is metabolized by organisms. Shapes of molecules are represented in drawings by lines of normal, uniform thickness for bonds in the plane of the paper; broken lines for bonds extending away from the viewer; and heavy lines for bonds extending toward the viewer. These conventions are shown by the example of dichloromethane, CH_2Cl_2, an important organochloride solvent and extractant illustrated in Figure 29.1.



Structural formula of dichloromethane in two dimensions

Representation of the three-dimensional structure of dichloromethane

Figure 29.1. Structural formulas of dichloromethane, CH_2Cl_2; the formula on the right provides a three-dimensional representation.

29.2. HYDROCARBONS

As noted above, hydrocarbon compounds contain only carbon and hydrogen. The major types of hydrocarbons are alkanes, alkenes, alkynes, and aryl compounds. Examples of each are shown in Figure 29.2.

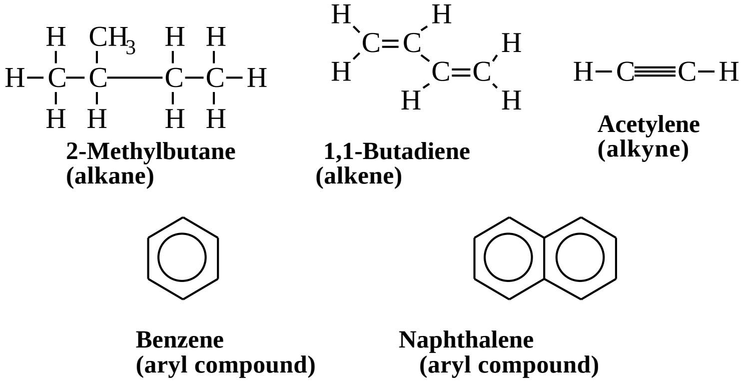
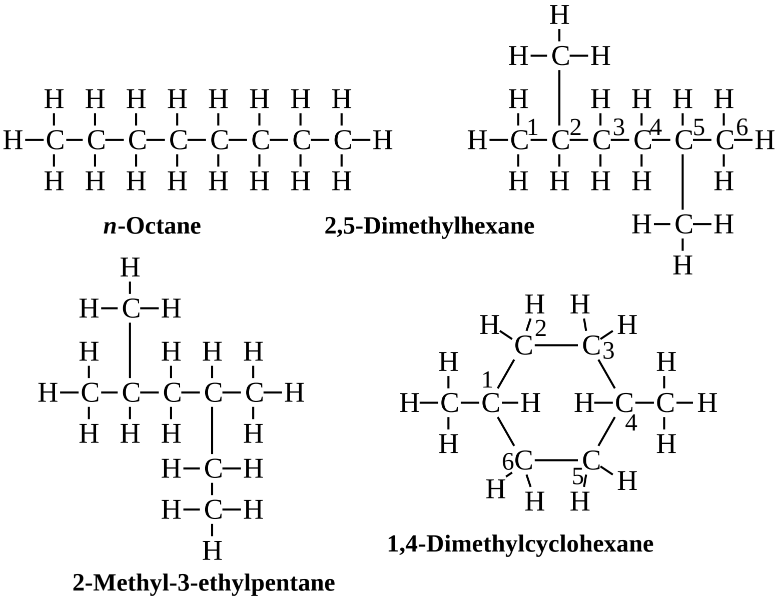


Figure 29.2. Examples of major types of hydrocarbons.

Alkanes

Alkanes, also called **paraffins** or **aliphatic hydrocarbons**, are hydrocarbons in which the C atoms are joined by single covalent bonds (sigma bonds) consisting of two shared electrons (see Section 28.3). Some examples of alkanes are shown in Figure 29.2. As with other organic compounds, the carbon atoms in alkanes may form straight chains, branched chains, or rings. These three kinds of alkanes are, respectively, **straight-chain alkanes**, **branched-chain alkanes**, and **cycloalkanes**. As shown in Figure 29.2, a typical branched chain alkane is 2-methylbutane, a volatile, highly flammable liquid. It is a component of gasoline, which may explain why it is commonly found as an air pollutant in urban air. The general molecular formula for straight- and branched-chain alkanes is C_nH_{2n+2}, and that of cyclic alkanes is C_nH_{2n}. The four hydrocarbon molecules in Figure 29.3 contain 8 carbon atoms each. In one of the molecules, all of the carbon atoms are in a straight chain and in two they are in branched chains, whereas in a fourth, 6 of the carbon atoms are in a ring.



***n*-Octane** **2,5-Dimethylhexane**

2-Methyl-3-ethylpentane **1,4-Dimethylcyclohexane**

Figure 29.3. Structural formulas of four hydrocarbons, each containing 8 carbon atoms, that illustrate the structural diversity possible with organic compounds. Numbers used to denote locations of atoms for purposes of naming are shown on two of the compounds.

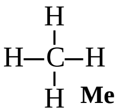
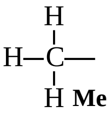
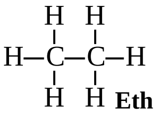
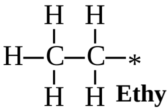
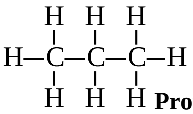
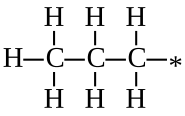
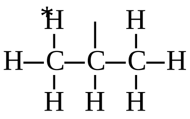
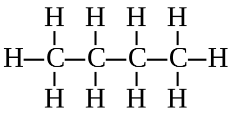
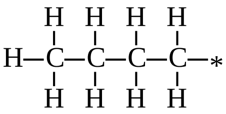
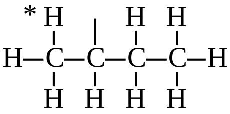
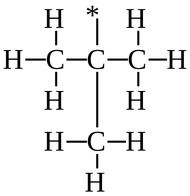
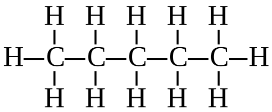
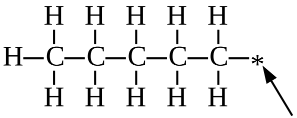
Formulas of Alkanes

Formulas of organic compounds present information at several different levels of sophistication. **Molecular formulas**, such as that of octane (C_8H_{18}), give the number of each kind of atom in a molecule of a compound. As shown in Figure 29.3, however, the molecular formula of C_8H_{18} may apply to several alkanes, each one of which has unique chemical, physical, and toxicological properties. These different compounds are designated by **structural formulas** showing the order in which the atoms in a molecule are arranged. Compounds that have the same molecular but different structural formulas are called **structural isomers**. Of the compounds shown in Figure 29.3, *n*-octane, 2,5-dimethylhexane, and 2-methyl-3-ethylpentane are structural isomers, all having the formula C_8H_{18}, whereas 1,4-dimethylcyclohexane is not a structural isomer of the other three compounds because its molecular formula is C_8H_{16}.

Alkanes and Alkyl Groups

Most organic compounds can be derived from alkanes. In addition, many important parts of organic molecules contain one or more alkane groups minus a hydrogen atom bonded as substituents onto the basic organic molecule. As a consequence of these factors, the names of many organic compounds are based upon alkanes, and it is useful to know the names of some of the more common alkanes and substituent groups derived from them as shown in Table 29.1.

Table 29.1. Some Alkanes and Substituent Groups Derived from Them.

Alkane	Substituent groups derived from alkane	
 **Methane**	 **Methyl group**	
 **Ethane**	 **Ethyl group**	
 **Propane**	 ***n*-Propyl group**	 **Isopropyl group**
 ***n*-Butane**	 ***n*-Butyl group**	 ***sec*-Butyl group**
	 ***tert*-Butyl group**	
 ***n*-Pentane**	 ***n*-Pentyl group**	**Asterisk denotes point attachment to molecule**

Names of Alkanes and Organic Nomenclature

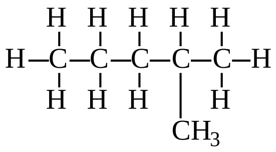
Systematic names, from which the structures of organic molecules can be deduced, have been assigned to all known organic compounds. The more common organic compounds, including many toxic and hazardous organic sustances, likewise have **common names** that have no structural implications. Although it is not possible to cover organic nomenclature in any detail in this chapter, the basic approach to nomenclature (naming) is presented in the chapter along with some pertinent examples. The simplest approach is to begin with names of alkane hydrocarbons.

Consider the alkanes shown in Figure 29.3. The fact that *n*-octane has no side chains is denoted by "*n*", that it has 8 carbon atoms is denoted by "oct," and that it is an alkane is indicated by "ane." The names of compounds with branched chains or atoms other than H or C attached make use of numbers that stand for positions on the longest continuous chain of carbon atoms in the molecule. This convention is illustrated by the second compound in Figure 29.3. It gets the hexane part of the name from the fact that it is an alkane with 6 carbon atoms in its longest continuous chain ("hex" stands for 6). However, it has a methyl group (CH_3) attached on the second carbon atom of the chain and another on the fifth. Hence the full systematic name of the compound is 2,5-dimethylhexane, where "di" indicates two methyl groups. In the case of 2-methyl-3-ethylpentane, the longest continuous chain of carbon atoms contains 5 carbon atoms, denoted by *pent*ane, a methyl group is attached to the second carbon atom, and an ethyl group, C_2H_5, on the third carbon atom The last compound shown in the figure has 6 carbon atoms in a ring, indicated by the prefix "cyclo," so it is a cyclo*hex*ane compound. Furthermore, the carbon in the ring to which one of the methyl groups is attached is designated by "1" and another methyl group is attached to the fourth carbon atom around the ring. Therefore, the full name of the compound is 1,4-dimethylcyclohexane.

Summary of Organic Nomenclature as Applied to Alkanes

Naming relatively simple alkanes is a straightforward process. The basic rules to be followed are the following:

1. The name of the compound is based upon the longest continuous chain of carbon atoms. (The structural formula may be drawn such that this chain is not immediately obvious.)
2. The carbon atoms in the longest continous chain are numbered sequentially from one end. The end of the chain from which the numbering is started is chosen to give the lower numbers for substituent groups in the final name. For example, the compound,

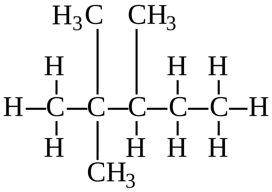


$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & | & & H & & \\ & & & & & & & & CH_3 & & & & \end{array}$$

could be named 4-methylpentane (numbering the 5-carbon chain from the left), but should be named 2-methylpentane (numbering the 5-carbon chain from the right).

3. All groups attached to the longest continuous chain are designated by the number of the carbon atoms to which they are attached and by the name of the substituent group (“2-methyl” in the example cited in Step 2, above).

4. A prefix is used to denote multiple substitutions by the same kind of group. This is illustrated by 2,2,3-trimethylpentane



in which the prefix *tri* is used to show that *three* methyl groups are attached to the pentane chain.

5. The complete name is assigned such that it denotes the longest continuous chain of carbon atoms and the name and location on this chain of each substituent group.

Reactions of Alkanes

Alkanes contain only C-C and C-H bonds, both of which are relatively strong. For that reason they have little tendency to undergo many kinds of reactions common to some other organic chemicals, such as acid-base reactions or low-temperature oxidation-reduction reactions. However, at elevated temperatures alkanes readily undergo oxidation, more specifically combustion, with molecular oxygen in air as shown by the following reaction of propane:

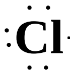
$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O + \text{heat} \qquad (29.7.1)$$

Common alkanes are highly flammable and the more volatile lower molecular mass alkanes form explosive mixtures with air. Furthermore, combustion of alkanes in an oxygen-deficient atmosphere or in an automobile engine produces significant quantities of carbon monoxide, CO, the toxic properties of which are discussed in Chapter 23.

In addition to combustion, alkanes undergo **substitution reactions** in which one or more H atoms on an alkane are replaced by atoms of another element. The most common such reaction is the replacement of H by chlorine, to yield **organochlorine** compounds. For example, methane reacts with chlorine to give chloromethane. This reaction begins with the dissociation of molecular chlorine, usually initiated by ultraviolet electromagnetic radiation:

$$Cl_2 + \text{UV energy} \rightarrow Cl\cdot + Cl\cdot \qquad (29.7.2)$$

The Cl· product is a **free radical** species in which the chlorine atom has only 7 outer shell electrons as shown by the Lewis symbol,



instead of the favored octet of 8 outer-shell electrons. In gaining the octet required for chemical stability, the chlorine atom is very reactive. It abstracts a hydrogen from methane,

$$Cl\cdot + CH_4 \rightarrow HCl + CH_3\cdot \tag{29.7.3}$$

to yield HCl gas and another reactive species with an unpaired electron, $CH_3\cdot$, called methyl radical. The methyl radical attacks molecular chlorine,

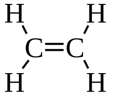
$$CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot \tag{29.7.4}$$

to give the chloromethane (CH_3Cl) product and regenerate Cl·, which can attack additional methane as shown in Reaction 29.7.3. The reactive Cl· and $CH_3\cdot$ species continue to cycle through the two preceding reactions.

The reaction sequence shown above illustrates three important aspects of chemistry that are shown to be very important in the discussion of atmospheric chemistry in Chapters 9-14. The first of these is that a reaction may be initiated by a **photochemical process** in which a photon of “light” (electromagnetic radiation) energy produces a reactive species, in this case the Cl· atom. The second point illustrated is the high chemical reactivity of **free radical species** with unpaired electrons and incomplete octets of valence electrons. The third point illustrated is that of **chain reactions**, which can multiply manyfold the effects of a single reaction-initiating event, such as the photochemical dissociation of Cl_2.

Alkenes and Alkynes

Alkenes or **olefins** are hydrocarbons that have double bonds consisting of 4 shared electrons. The simplest and most widely manufactured alkene is ethylene,



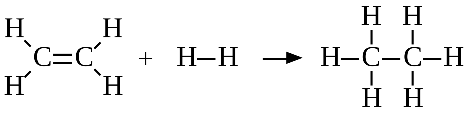
Ethylene (ethene)

used for the production of polyethylene polymer. Another example of an important alkene is 1,3-butadiene (Figure 29.3), widely used in the manufacture of polymers, particularly synthetic rubber. The lighter alkenes, including ethylene and 1,3-butadiene, are highly flammable. Like other gaseous hydrocarbons, they form explosive mixtures with air.

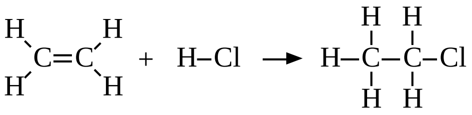
Acetylene (Figure 29.3) is an **alkyne**, a class of hydrocarbons characterized by carbon-carbon triple bonds consisting of 6 shared electrons. Acetylene is a highly flammable gas that forms dangerously explosive mixtures with air. It is used in large quantities as a chemical raw material. Acetylene is the fuel in oxyacetylene torches used for cutting steel and for various kinds of welding applications.

Addition Reactions

The double and triple bonds in alkenes and alkynes have “extra” electrons capable of forming additional bonds. So the carbon atoms attached to these bonds can add atoms without losing any atoms already bonded to them, and the multiple bonds are said to be **unsaturated**. Therefore, alkenes and alkynes both undergo **addition reactions** in which pairs of atoms are added across unsaturated bonds as shown in the reaction of ethylene with hydrogen to give ethane:


(29.7.5)

This is an example of a **hydrogenation reaction**, a very common reaction in organic synthesis, food processing (manufacture of hydrogenated oils), and petroleum refining. Another example of an addition reaction is that of HCl gas with acetylene to give vinyl chloride:


(29.7.6)

This kind of reaction, which is not possible with alkanes, adds to the chemical and metabolic versatility of compounds containing unsaturated bonds and is a factor contributing to their generally higher toxicities. It makes unsaturated compounds much more chemically reactive, more hazardous to handle in industrial processes, and more active in atmospheric chemical processes such as smog formation (see Chapter 13).

Alkenes and *Cis-trans* Isomerism

As shown by the two simple compounds in Figure 29.4, the two carbon atoms connected by a double bond in alkenes cannot rotate relative to each other. For this reason, another kind of isomerism, known as ***cis-trans*** isomerism, is possible for alkenes. *Cis-trans* isomers have different parts of the molecule oriented differently in space, although these parts occur in the same order. Both alkenes illustrated in Fig-

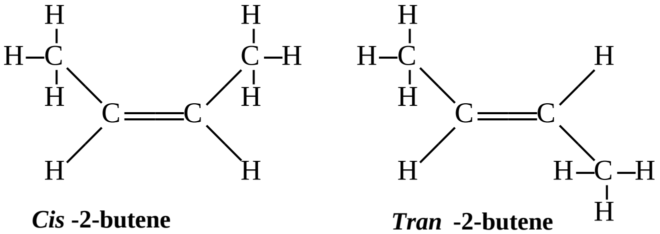

***Cis* -2-butene** ***Tran* -2-butene**

Figure 29.4. *Cis* and *trans* isomers of the alkene, 2-butene.

ure 29.4 have a molecular formula of C_4H_8. In the case of *cis*-2-butene, the two CH_3 (methyl) groups attached to the C=C carbon atoms are on the same side of the double bond, whereas in *trans*-2-butene they are on opposite sides.

Condensed Structural Formulas

To save space, structural formulas are conveniently abbreviated as **condensed structural formulas** such as $CH_3CH(CH_3)CH(C_2H_5)CH_2CH_3$ for 2-methyl-3-ethylpentane, where the CH_3 (methyl) and C_2H_5 (ethyl) groups are placed in parentheses to show that they are branches attached to the longest continuous chain of carbon atoms, which contains 5 carbon atoms. It is understood that each of the methyl and ethyl groups is attached to the carbon immediately preceding it in the condensed structural formula (methyl attached to the second carbon atom, ethyl to the third).

As illustrated by the examples in Figure 29.5, the structural formulas of organic molecules may be represented in a very compact form by lines and by figures such as hexagons. The ends and intersections of straight line segments in these formulas

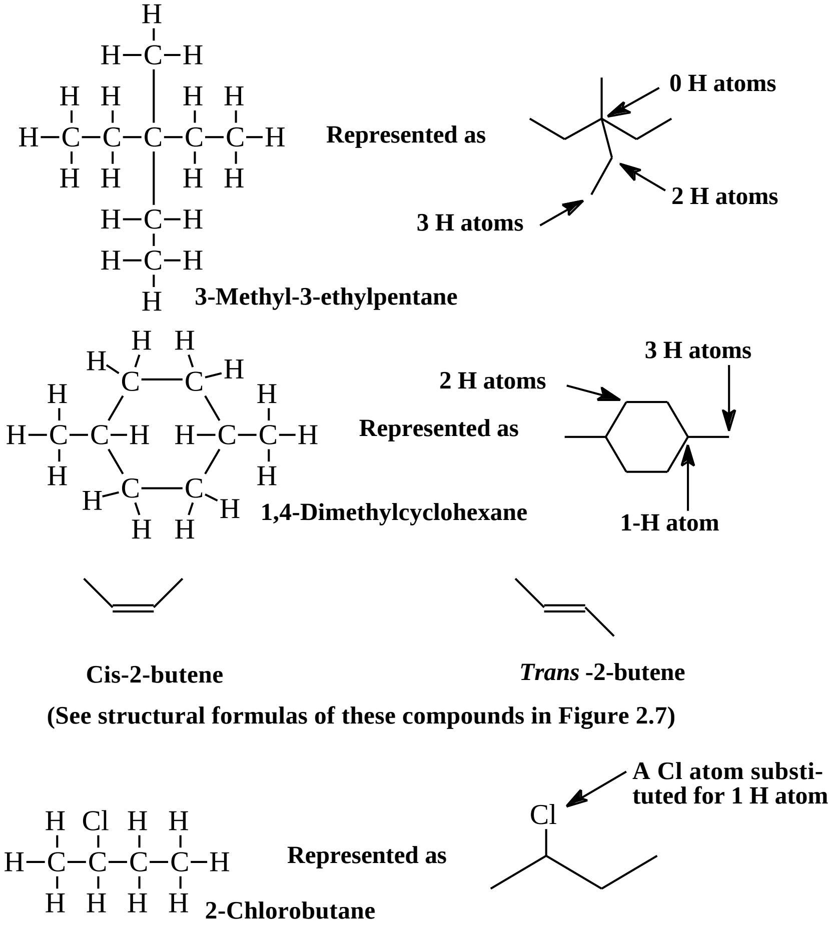


Figure 29.5. Representation of structural formulas with lines. A carbon atom is understood to be at each corner and at the end of each line. The numbers of hydrogen atoms attached to carbons at several specific locations are shown with arrows.

indicate the locations of carbon atoms. Carbon atoms at the terminal ends of lines are understood to have three H atoms attached, C atoms at the intersections of two lines are understood to have *two* H atoms attached to each, *one* H atom is attached to a carbon represented by the intersection of three lines, and *no* hydrogen atoms are bonded to C atoms where four lines intersect. Other atoms or groups of atoms, such as the Cl atom or OH group, that are substituted for H atoms are shown by their symbols attached to a C atom with a line.

Aryl Hydrocarbons

Benzene (Figure 29.6) is the simplest of a large class of **aryl** or **aromatic** hydrocarbons. Many important aryl compounds have substituent groups containing atoms of elements other than hydrogen and carbon and are called **aryl compounds** or **aromatic compounds**. Most aromatic compounds discussed in this book contain 6-carbon-atom benzene rings as shown for benzene, C_6H_6, in Figure 29.13. Aromatic compounds have ring structures and are held together in part by particularly stable bonds that contain delocalized clouds of so-called π (pi, pronounced “pie”) electrons. In an oversimplified sense, the structure of benzene can be visualized as resonating between the two equivalent structures shown on the left in Figure 29.6 by the shifting of electrons in chemical bonds to form a hybrid structure. This structure can be shown more simply and accurately by a hexagon with a circle in it.

Aryl compounds have special characteristics of **aromaticity**, which include a low hydrogen:carbon atomic ratio; C–C bonds that are quite strong and of intermediate length between such bonds in alkanes and those in alkenes; tendency to undergo substitution reactions rather than the addition reactions characteristic of alkenes; and delocalization of π electrons over several carbon atoms. The last phenomenon adds substantial stability to aromatic compounds and is known as **resonance stabilization**.

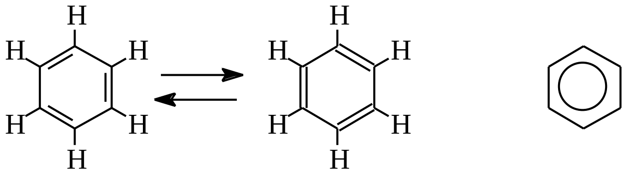


Figure 29.6. Representation of the aromatic benzene molecule with two resonance structures (left) and, more accurately, as a hexagon with a circle in it (right). Unless shown by symbols of other atoms, it is understood that a C atom is at each corner and that one H atom is bonded to each C atom.

First isolated from hydrocarbon liquids produced in the coking of coal (heating in absence of air to produce a carbonaceous residue used in steelmaking), benzene, toluene, and other low-molecular-mass aryl compounds have found widespread use as solvents, in chemical synthesis, and as a fuel. Many toxic substances, environmental pollutants, and hazardous waste compounds, such as benzene, toluene, naphthalene, and chlorinated phenols, are aryl compounds (see Figure 29.7). As shown in Figure 29.7, some arenes, such as naphthalene and the polycyclic aromatic compound, benzo(a)pyrene, contain fused rings.

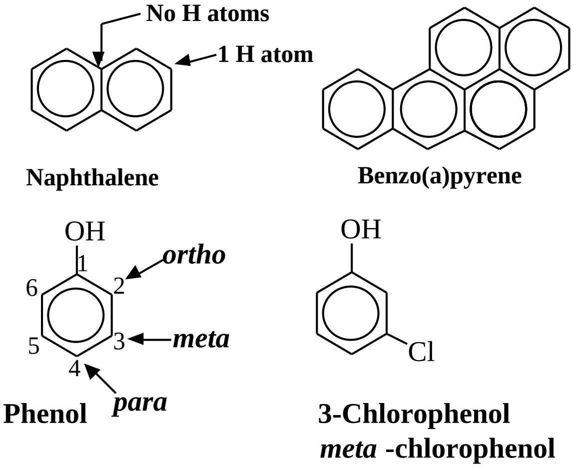


Figure 29.7. Aromatic compounds containing fused rings (top) and showing the numbering of carbon atoms for purposes of nomenclature.

Benzene and Naphthalene

Benzene is a volatile, colorless, highly flammable liquid that is consumed as a raw material for the manufacture of phenolic and polyester resins, polystyrene plastics, alkylbenzene surfactants, chlorobenzenes, insecticides, and dyes. It is hazardous both for its ignitability and toxicity (exposure to benzene causes blood abnormalities that may develop into leukemia). Naphthalene is the simplest member of a large number of polycyclic (multicyclic) aromatic hydrocarbons having two or more fused rings. It is a volatile white crystalline solid with a characteristic odor and has been used to make mothballs. The most important of the many chemical derivatives made from naphthalene is phthalic anhydride, from which phthalate ester plasticizers are synthesized.

Polycyclic Aromatic Hydrocarbons

Benzo(a)pyrene (Figure 29.7) is the most studied of the polycyclic aromatic hydrocarbons (PAHs), which are characterized by condensed ring systems (“chicken wire” structures). These compounds are formed by the incomplete combustion of other hydrocarbons, a process that consumes hydrogen in preference to carbon. The carbon residue is left in the thermodynamically favored condensed aromatic ring system of the PAH compounds.

Because there are so many partial combustion and pyrolysis processes that favor production of PAHs, these compounds are encountered abundantly in the atmosphere, soil, and elsewhere in the environment from sources that include engine exhausts, wood stove smoke, cigarette smoke, and char-broiled food. Coal tars and petroleum residues such as road and roofing asphalt have high levels of PAHs. Some PAH compounds, including benzo(a)pyrene, are of toxicological concern because they are precursors to cancer-causing metabolites.

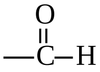
29.3. ORGANIC FUNCTIONAL GROUPS AND CLASSES OF ORGANIC COMPOUNDS

The discussion of organic chemistry so far in this chapter has emphasized hydrocarbon compounds, those that contain only hydrogen and carbon. It has been shown that hydrocarbons may exist as alkanes, alkenes, and arenes, depending upon the kinds of bonds between carbon atoms. The presence of elements other than hydrogen and carbon in organic molecules greatly increases the diversity of their chemical behavior. **Functional groups** consist of specific bonding configurations of atoms in organic molecules. Most functional groups contain at least one element other than carbon or hydrogen, although two carbon atoms joined by a double bond (alkenes) or triple bond (alkynes) are likewise considered to be functional groups. Table 29.2 shows some of the major functional groups that determine the nature of organic compounds.

Organooxygen Compounds

The most common types of compounds with oxygen-containing functional groups are epoxides, alcohols, phenols, ethers, aldehydes, ketones, and carboxylic acids. The functional groups characteristic of these compounds are illustrated by the examples of oxygen-containing compounds shown in Figure 29.8.

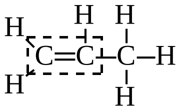
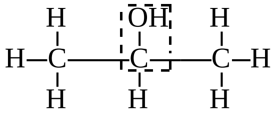
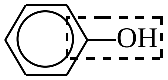
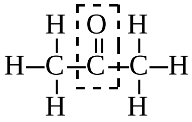
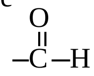
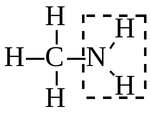
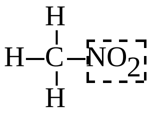
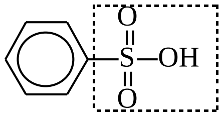
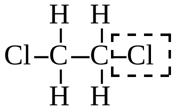
Ethylene oxide is a moderately to highly toxic, sweet-smelling, colorless, flammable, explosive gas used as a chemical intermediate, sterilant, and fumigant. It is a mutagen and a carcinogen to experimental animals. It is classified as hazardous for both its toxicity and ignitability. **Methanol** is a clear, volatile, flammable liquid alcohol used for chemical synthesis, as a solvent, and as a fuel. It is used as a gasoline additive to reduce emissions of carbon monoxide and other air pollutants. Ingestion of methanol can be fatal, and blindness can result from sublethal doses. **Phenol** is a dangerously toxic aryl alcohol widely used for chemical synthesis and polymer manufacture. **Methyltertiarybutyl ether**, MTBE, is an ether that has become the octane booster of choice to replace tetraethyllead in gasoline. **Acrolein** is an alkenic aldehyde and a volatile, flammable, highly reactive chemical. It forms explosive peroxides upon prolonged contact with O_2. An extreme lachrimator and strong irritant, acrolein is quite toxic by all routes of exposure. **Acetone** is the lightest of the ketones. Like all ketones, acetone has a carbonyl (C=O) group that is bonded to *two* carbon atoms (that is, it is somewhere in the middle of a carbon atom chain). Acetone is a good solvent and is chemically less reactive than the aldehydes which all have the functional group,



$$-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

in which binding of the C=O to H makes the molecule significantly more reactive. **Propionic acid** is a typical organic carboxylic acid. The $-CO_2H$ group of carboxylic acids may be viewed as the most oxidized functional group (other than peroxides) on an oxygenated organic compound, and carboxylic acids may be synthesized by oxidizing alcohols or aldehydes that have an -OH group or C=O group on an end carbon atom.

Table 29.2. Examples of Some Important Functional Groups

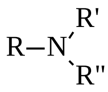
Type of functional group	Example compound	Structural formula of group[1]
Alkene (olefin)	Propene (propylene)	
Alkyne	Acetylene	$H{-}C{\equiv}C{-}H$
Alcohol (-OH attached to alkyl group)	2-Propanol	
Phenol (-OH attached to aryl group)	Phenol	
Ketone	Acetone	
(When  $-\overset{\overset{O}{\parallel}}{C}-H$ group is on end carbon, compound is an aldehyde)		
Amine	Methylamine	
Nitro compounds	Nitromethane	
Sulfonic acids	Benzenesulfonic acid	
Organohalides	1,1–Dichloro-ethane	

[1] Functional group outlined by dashed line

Organonitrogen Compounds

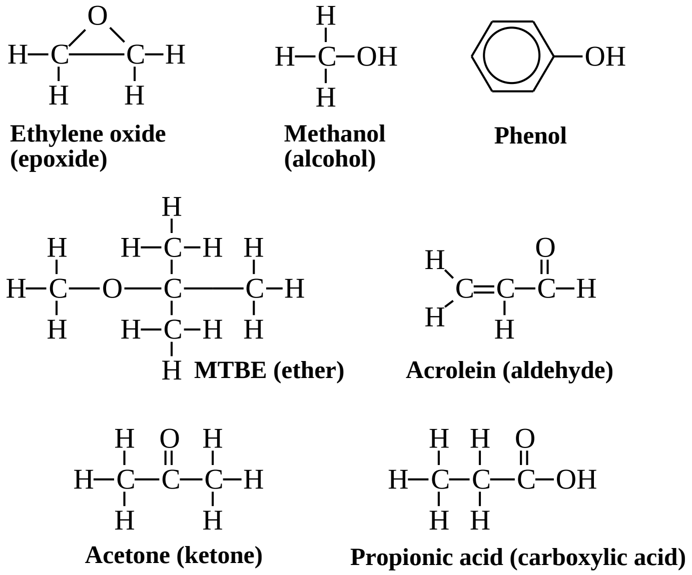
Figure 29.9 shows examples of three classes of the many kinds of compounds that contain N (amines, nitrosamines, and nitro compounds). Nitrogen occurs in many functional groups in organic compounds, some of which contain nitrogen in ring structures, or along with oxygen.

Methylamine is a colorless, highly flammable gas with a strong odor. It is a severe irritant affecting eyes, skin, and mucous membranes. Methylamine is the simplest of the **amine** compounds, which have the general formula,



$$\mathrm{R{-}N}\begin{matrix}\mathrm{R'}\\ \mathrm{R''}\end{matrix}$$

where the R’s are hydrogen or hydrocarbon groups, at least one of which is the latter.



Ethylene oxide (epoxide)

Methanol (alcohol)

Phenol

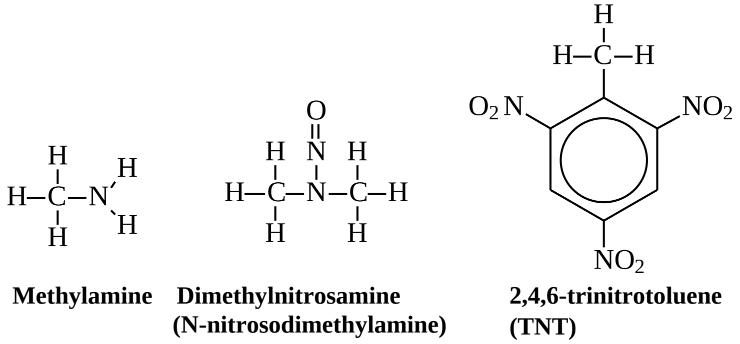
MTBE (ether)

Acrolein (aldehyde)

Acetone (ketone)

Propionic acid (carboxylic acid)

Figure 29.8. Examples of oxygen-containing organic compounds that may be significant as wastes, toxic substances, or environmental pollutants.



Methylamine

Dimethylnitrosamine (N-nitrosodimethylamine)

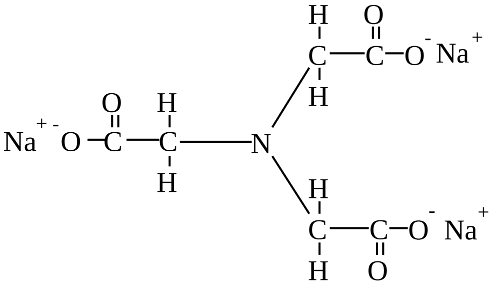
2,4,6-trinitrotoluene (TNT)

Figure 29.9. Examples of organonitrogen that may be significant as wastes, toxic substances, or environmental pollutants.

Dimethylnitrosamine is an N-nitroso compound, all of which are characterized by the N-N=O functional group. It was once widely used as an industrial solvent, but caused liver damage and jaundice in exposed workers. Subsequently, numerous other N-nitroso compounds, many produced as by-products of industrial operations and food and alcoholic beverage processing, were found to be carcinogenic.

Solid **2,4,6-trinitrotoluene** (TNT) has been widely used as a military explosive. TNT is moderately to very toxic and has caused toxic hepatitis or aplastic anemia in exposed individuals, a few of whom have died from its toxic effects. It belongs to the general class of nitro compounds characterized by the presence of $-NO_2$ groups bonded to a hydrocarbon structure.

Some organonitrogen compounds are chelating agents that bind strongly to metal ions and play a role in the solubilization and transport of heavy metal wastes. Prominent among these are salts of the aminocarboxylic acids which, in the acid form, have $-CH_2CO_2H$ groups bonded to nitrogen atoms. An important example of such a compound is the monohydrate of trisodium nitrilotriacetate (NTA):



This compound can be used as a substitute for detergent phosphates to bind to calcium ion and make the detergent solution basic. NTA is used in metal plating formulations. It is highly water soluble and quickly eliminated with urine when ingested. It has a low acute toxicity and no chronic effects have been shown for plausible doses. However, concern does exist over its interaction with heavy metals in waste treatment processes and in the environment.

Organohalide Compounds

Organohalides (Figure 29.10) exhibit a wide range of physical and chemical properties. These compounds consist of halogen-substituted hydrocarbon molecules, each of which contains at least one atom of F, Cl, Br, or I. They may be saturated (**alkyl halides**), unsaturated (**alkenyl halides**), or aromatic (**aryl halides**). The most widely manufactured organohalide compounds are chlorinated hydrocarbons, many of which are regarded as environmental pollutants or as hazardous wastes.

Alkyl Halides

Substitution of halogen atoms for one or more hydrogen atoms on alkanes gives **alkyl halides**, example structural formulas of which are given in Figure 29.10. Most of the commercially important alkyl halides are derivatives of alkanes of low molecular mass. A brief discussion of the uses of the compounds listed in Figure 29.10 is given here to provide an idea of the versatility of the alkyl halides.

Dichloromethane is a volatile liquid with excellent solvent properties for nonpolar organic solutes. It has been used as a solvent for the decaffeination of coffee, in paint strippers, as a blowing agent in urethane polymer manufacture, and to depress vapor pressure in aerosol formulations. Once commonly sold as a solvent and stain remover, highly toxic **carbon tetrachloride** is now largely restricted to uses

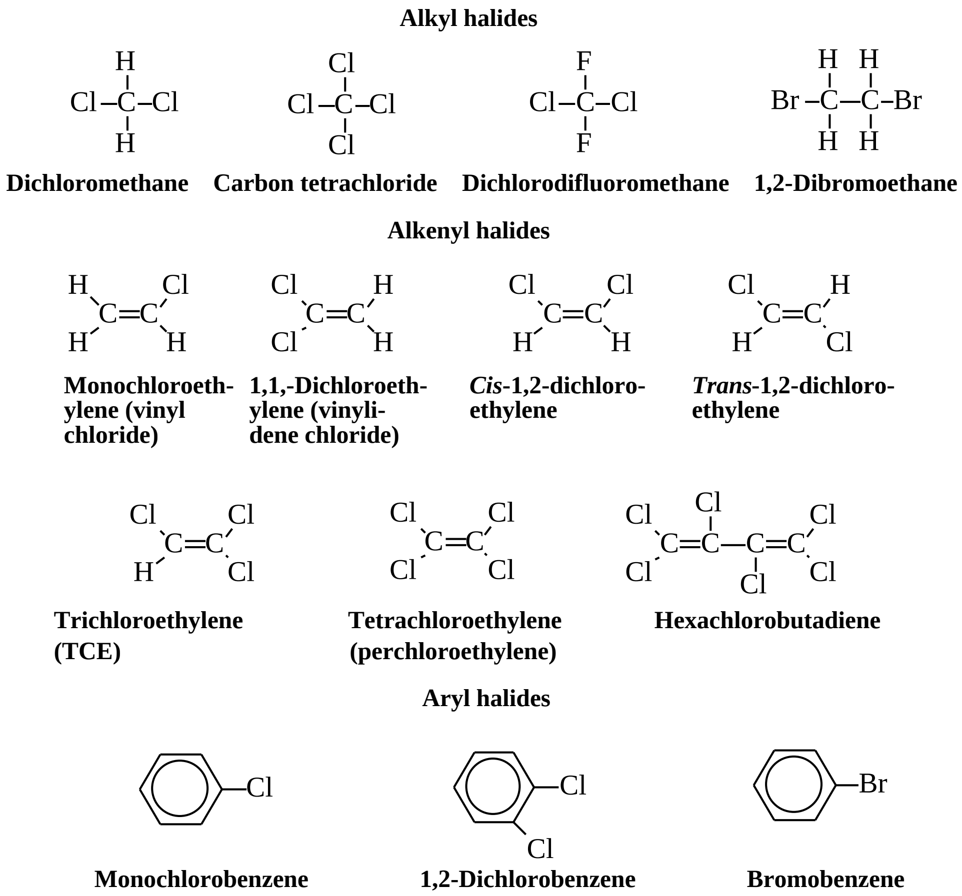


Figure 29.10. Some example organohalide compounds.

as a chemical intermediate under controlled conditions, primarily to manufacture chlorofluorocarbon refrigerant fluid compounds, which are also discussed in this section. Insecticidal **1,2-dibromoethane** has been consumed in large quantities as a lead scavenger in leaded gasoline and to fumigate soil, grain, and fruit (Fumigation with this compound has been discontinued because of toxicological concerns). An effective solvent for resins, gums, and waxes, it serves as a chemical intermediate in the syntheses of some pharmaceutical compounds and dyes.

Alkenyl Halides

Viewed as hydrocarbon-substituted derivatives of alkenes, the **alkenyl** or **olefinic organohalides** contain at least one halogen atom and at least one carbon-carbon double bond. The most significant of these are the lighter chlorinated compounds, such as those illustrated in Figure 29.17.

Vinyl chloride is consumed in large quantities as a raw material to manufacture pipe, hose, wrapping, and other products fabricated from polyvinylchloride plastic. This highly flammable, volatile, sweet-smelling gas is a known human carcinogen.

As shown in Figure 29.10, there are three possible dichloroethylene compounds, all clear, colorless liquids. Vinylidene chloride forms a copolymer with vinyl chloride used in some kinds of coating materials. The geometrically isomeric 1,2-dichloroethylenes are used as organic synthesis intermediates and as solvents. **Trichloroethylene** is a clear, colorless, nonflammable, volatile liquid. It is an excellent degreasing and drycleaning solvent and has been used as a household solvent and for food extraction (for example, in decaffeination of coffee). Colorless, nonflammable liquid **tetrachloroethylene** has properties and uses similar to those of trichloroethylene. **Hexachlorobutadiene**, a colorless liquid with an odor somewhat like that of turpentine, is used as a solvent for higher hydrocarbons and elastomers, as a hydraulic fluid, in transformers, and for heat transfer.

Aryl Halides

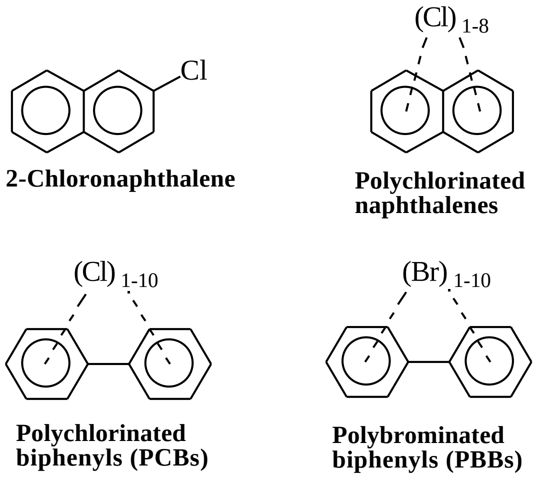
Aryl halide derivatives of benzene and toluene have many uses in chemical synthesis, as pesticides and raw materials for pesticides manufacture, as solvents, and a diverse variety of other applications. These widespread uses over many decades have resulted in substantial human exposure and environmental contamination. Three example aryl halides are shown in Figure 29.17. Monochlorobenzene is a flammable liquid boiling at 132˚C. It is used as a solvent, heat transfer fluid, and synthetic reagent. Used as a solvent, 1,2-dichlorobenzene is employed for degreasing hides and wool. It also serves as a synthetic reagent for dye manufacture. Bromobenzene is a liquid boiling at 156˚C that is used as a solvent, motor oil additive, and intermediate for organic synthesis.

Halogenated Naphthalene and Biphenyl

Two major classes of halogenated aryl compounds containing two benzene rings are made by the chlorination of naphthalene and biphenyl and have been sold as mixtures with varying degrees of chlorine content. Examples of chlorinated naphthalenes, and polychlorinated biphenyls (PCBs discussed later), are shown in Figure 29.11. The less highly chlorinated of these compounds are liquids, and those with higher chlorine contents are solids. Because of their physical and chemical stabilities and other desirable qualities, these compounds have had many uses, including heat transfer fluids, hydraulic fluids, and dielectrics. Polybrominated biphenyls (PBBs) have served as flame retardants. However, because chlorinated naphthalenes, PCBs, and PBBs are environmentally extremely persistent, their uses have been severely curtailed.

Chlorofluorocarbons, Halons, and Hydrogen-Containing Chlorofluorocarbons

Chlorofluorocarbons (**CFC**s) are volatile 1**-** and 2-carbon compounds that contain Cl and F bonded to carbon. These extremely stable and nontoxic compounds are discussed in some detail in Section 12.7. They were once widely used in the fabrication of flexible and rigid foams, and as fluids for refrigeration and air conditi-



2-Chloronaphthalene

Polychlorinated naphthalenes

Polychlorinated biphenyls (PCBs)

Polybrominated biphenyls (PBBs)

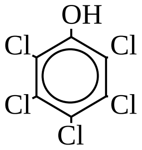
Figure 29.11. Halogenated naphthalenes and biphenyls.

tioning, but have now been essentially phased out because of their potential to cause harm to the stratospheric ozone layer. The most widely manufactured of these compounds in the past were CCl_3F (CFC-11), CCl_2F_2 (CFC-12), $C_2Cl_3F_3$ (CFC-113), $C_2Cl_2F_4$ (CFC-114), and C_2ClF_5 (CFC-115). **Halons** are related compounds that contain bromine and are used in fire extinguisher systems. The most commonly produced commercial halons were $CBrClF_2$ (Halon-1211), $CBrF_3$ (Halon-1301), and $C_2Br_2F_4$ (Halon-2402), where the sequence of numbers denotes the number of carbon, fluorine, chlorine, and bromine atoms, respectively, per molecule. Halons have also been implicated as ozone-destroying gases in the stratosphere and are being phased out, although finding suitable replacements has been difficult.

Hydrohalocarbons are hydrogen-containing chlorofluorocarbons (HCFCs) and hydrogen-containing fluorocarbons (HFCs) that are now produced as substitutes for chlorofluorocarbons. These compounds include CH_2FCF_3 (HFC-134a, a substitute for CFC-12 in automobile air conditioners and refrigeration equipment), $CHCl_2CF_3$ (HCFC-123, substitute for CFC-11 in plastic foam-blowing), CH_3CCl_2F (HCFC-141b, substitute for CFC-11 in plastic foam-blowing), and $CHClF_2$ (HCFC-22, air conditioners and manufacture of plastic foam food containers). Because each molecule of these compounds has at least one H-C bond, which is much more readily broken than C-Cl or C-F bonds, the HCFCs do not persist in the atmosphere and pose essentially no threat to the stratospheric ozone layer.

Chlorinated Phenols

The chlorinated phenols, particularly **pentachlorophenol** and the trichlorophenol isomers, are significant hazardous wastes. These compounds are biocides that are used to treat wood to prevent rot by fungi and to prevent termite infestation. They are toxic, causing liver malfunction and dermatitis. However, contaminant polychlorinated dibenzodioxins (“dioxin”) may be responsible for some of the observed effects. Pentachlorophenol and other aryl halides and aryl hydrocarbons used as wood preservatives are encountered at many hazardous waste sites in wastewaters and sludges.



Pentachlorophenol

Organosulfur Compounds

The chemistry of sulfur is similar to but perhaps more diverse than that of oxygen. Whereas, with the exception of peroxides, most chemically combined organic oxygen is in the -2 oxidation state, sulfur occurs in the -2, +4, and +6 oxidation states. Many organosulfur compounds are noted for their foul, “rotten egg” or garlic odors. A number of example organosulfur compounds are shown in Figure 29.12.

Thiols and Thioethers

Substitution of alkyl or aryl hydrocarbon groups such as phenyl and methyl for H on hydrogen sulfide, H_2S, leads to a number of different organosulfur **thiols** (mercaptans, R–SH) and **sulfides**, also called thioethers (R–S–R). Structural formulas of examples of these compounds are shown in Figure 29.12.

Methanethiol and other lighter alkyl thiols are fairly common air pollutants that have “ultragarlic” odors; both 1- and 2-butanethiol are associated with skunk odor. Gaseous methanethiol is used as an odorant leak-detecting additive for natural gas, propane, and butane; it is also employed as an intermediate in pesticide synthesis. A toxic, irritating volatile liquid with a strong garlic odor, 2-propene-1-thiol (allyl mercaptan) is a typical alkenyl mercaptan. Benzenethiol (phenyl mercaptan) is the simplest of the aryl thiols. It is a toxic liquid with a severely “repulsive” odor.

Alkyl sulfides or thioethers contain the C-S-C functional group. The lightest of these compounds is dimethyl sulfide, a volatile liquid (bp 38˚C) that is moderately toxic by ingestion. It was mentioned in Chapter 11, Section 11.4, as a major source of gaseous sulfur entering the atmosphere over the oceans due to its production by marine organisms. Cyclic sulfides contain the C-S-C group in a ring structure. The most common of these compounds is thiophene, a heat-stable liquid (bp 84˚C) with a solvent action much like that of benzene, that is used to make pharmaceuticals, dyes, and resins. Its saturated analog is tetrahydrothiophene, or thiophane.

Nitrogen-Containing Organosulfur Compounds

Many important organosulfur compounds also contain nitrogen. One such compound is **thiourea**, the sulfur analog of urea. Its structural formula is shown in Figure 29.12. Thiourea and **phenylthiourea** have been used as rodenticides. Commonly called ANTU, **1-naphthylthiourea** is an excellent rodenticide that is virtually tasteless and has a very high rodent:human toxicity ratio.

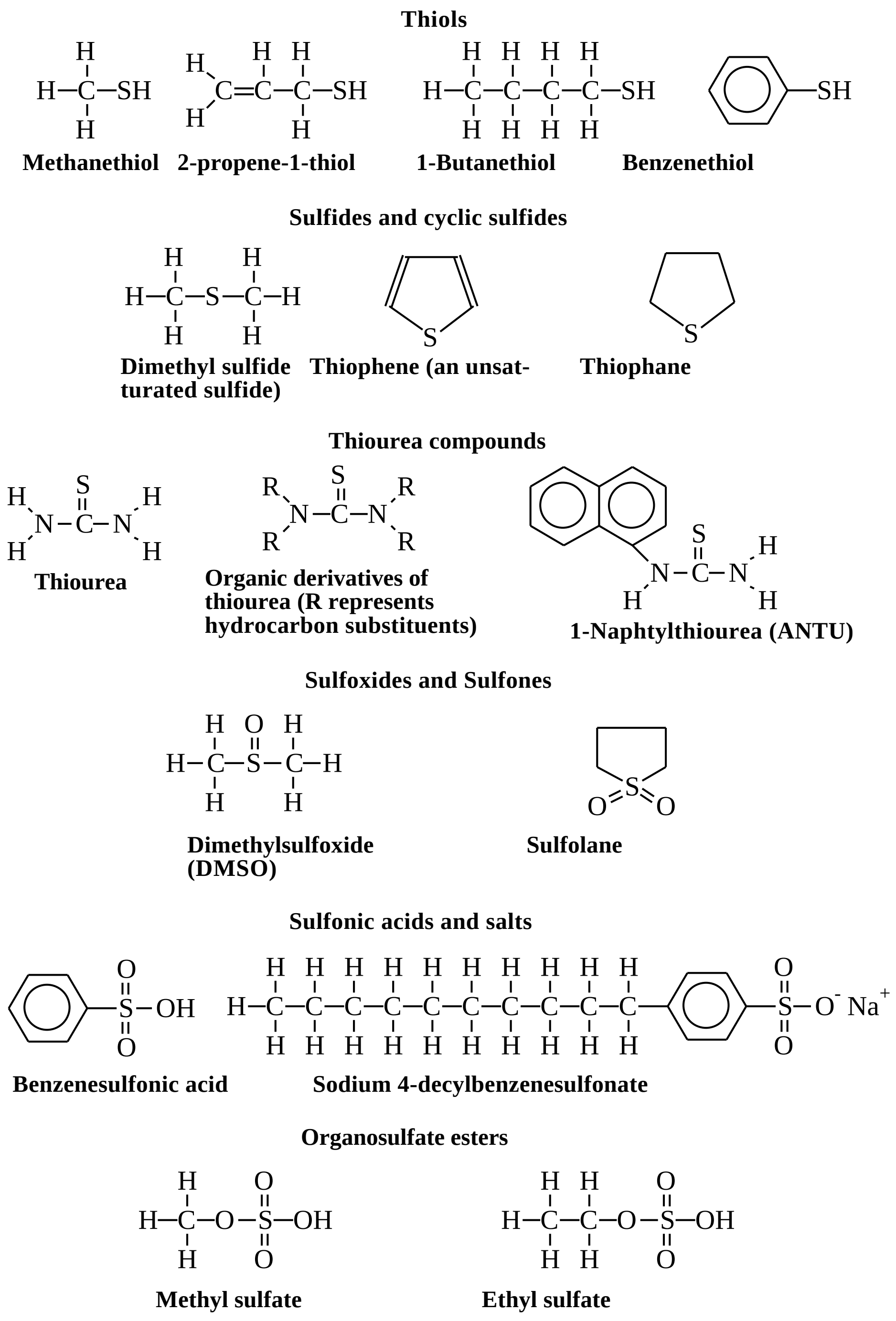


Figure 29.12. Examples of organosulfur compounds.

Sulfoxides and Sulfones

Sulfoxides and **sulfones** (Figure 29.12) contain both sulfur and oxygen. **Dimethylsulfoxide** (DMSO) is a liquid with numerous uses and some very interesting properties. It is used to remove paint and varnish, as a hydraulic fluid, mixed with water as an antifreeze solution, and in pharmaceutical applications as an anti-inflammatory and bacteriostatic agent. A polar aprotic (no ionizable H) solvent with a relatively high dielectric constant, **sulfolane** dissolves both organic and inorganic solutes. It is the most widely produced sulfone because of its use in an industrial process called BTX processing in which it selectively extracts benzene, toluene, and xylene from aliphatic hydrocarbons; as the solvent in the Sulfinol process by which thiols and acidic compounds are removed from natural gas; as a solvent for polymerization reactions; and as a polymer plasticizer.

Sulfonic Acids, Salts, and Esters

Sulfonic acids and sulfonate salts contain the $–SO_3H$ and $–SO_3^-$ groups, respectively, attached to a hydrocarbon moiety. The structural formula of benzenesulfonic acids and of sodium 1-(*p*-sulfophenyl)decane, a biodegradable detergent surfactant, are shown in Figure 29.19. The common sulfonic acids are water-soluble strong acids that lose virtually all ionizable H^+ in aqueous solution. They are used commercially to hydrolyze fat and oil esters to fatty acids and glycerol.

Organic Esters of Sulfuric Acid

Replacement of 1 H on sulfuric acid, H_2SO_4, with a hydrocarbon group yields an acid ester, and replacement of both yields an ester. Examples of these esters are shown in Figure 29.10. Sulfuric acid esters are used as alkylating agents, which act to attach alkyl groups (such as methyl) to organic molecules in the manufacture of agricultural chemicals, dyes, and drugs. **Methylsulfuric acid** and **ethylsulfuric acid** are oily, water-soluble liquids that are strong irritants to skin, eyes, and mucous tissue.

Organophosphorus Compounds

Alkyl and Aryl Phosphines

The first two examples in Figure 29.11, illustrate that the structural formulas of alkyl and aryl phosphine compounds may be derived by substituting organic groups for the H atoms in phosphine (PH_3), the hydride of phosphorus discussed as a toxic inorganic compound in Chapter 23, Section 23.3. **Methylphosphine** is a colorless, reactive gas. Crystalline, solid **triphenylphosphine** has a low reactivity and moderate toxicity when inhaled or ingested.

As shown by the reaction,

$$4C_3H_9P + 26O_2 \rightarrow 12O_2 + 18H_2O + P_4O_{10} \qquad (29.8.4)$$

combustion of aryl and alkyl phosphines produces P_4O_{10}, a corrosive, irritant, toxic substance that reacts with moisture in the air to produce droplets of corrosive orthophosphoric acid, H_3PO_4.

Organophosphate Esters

The structural formulas of three esters of orthophosphoric acid (H_3PO_4) and an ester of pyrophosphoric acid ($H_4P_2O_6$) are shown in Figure 29.13. Although **trimethylphosphate** is considered to be only moderately toxic, **tri-*o*-cresylphosphate**, **TOCP,** has a notorious record of poisonings. **Tetraethylpyrophosphate**, **TEPP**, was developed in Germany during World War II as a substitute for insecticidal nicotine. Although it is a very effective insecticide, its use in that application was of very short duration because it kills almost everything else, too.

Phosphorothionate Esters

Parathion, shown in Figure 29.13, is an example of **phosphorothionate** esters. These compounds are used as insecticidal acetylcholinesterase inhibitors. They contain the P=S (thiono) group, which increases their insect:mammal toxicity ratios. Since the first organophosphate insecticides were developed in Germany during the 1930s and 1940s, many insecticidal organophosphate compounds have been synthesized. One of the earliest and most successful of these is **parathion**, *O*,*O*-diethyl-*O*-*p*-nitrophenylphosphorothionate (banned from use in the U.S. in 1991 because of its acute toxicity to humans). From a long-term environmental standpoint, organophosphate insecticides are superior to the organohalide insecticides that they largely displaced because the organophosphates readily undergo biodegradation and do not bioaccumulate.

29.4. SYNTHETIC POLYMERS

A large fraction of the chemical industry worldwide is devoted to polymer manufacture, which is very important in the area of hazardous wastes, as a source of environmental pollutants, and in the manufacture of materials used to alleviate environmental and waste problems. Synthetic **polymers** are produced when small molecules called **monomers** bond together to form a much smaller number of very large molecules. Many natural products are polymers; for example, cellulose produced by trees and other plants and found in wood, paper, and many other materials, is a polymer of the sugar glucose. Synthetic polymers form the basis of many industries, such as rubber, plastics, and textiles manufacture.

An important example of a polymer is that of polyvinylchloride, shown in Figure 29.14. This polymer is synthesized in large quantities for the manufacture of water and sewer pipe, water-repellant liners, and other plastic materials. Other major polymers include polyethylene (plastic bags, milk cartons), polypropylene, (impact-resistant plastics, indoor-outdoor carpeting), polyacrylonitrile (Orlon, carpets), polystyrene (foam insulation), and polytetrafluoroethylene (Teflon coatings, bearings); the monomers from which these substances are made are shown in Figure 29.15.

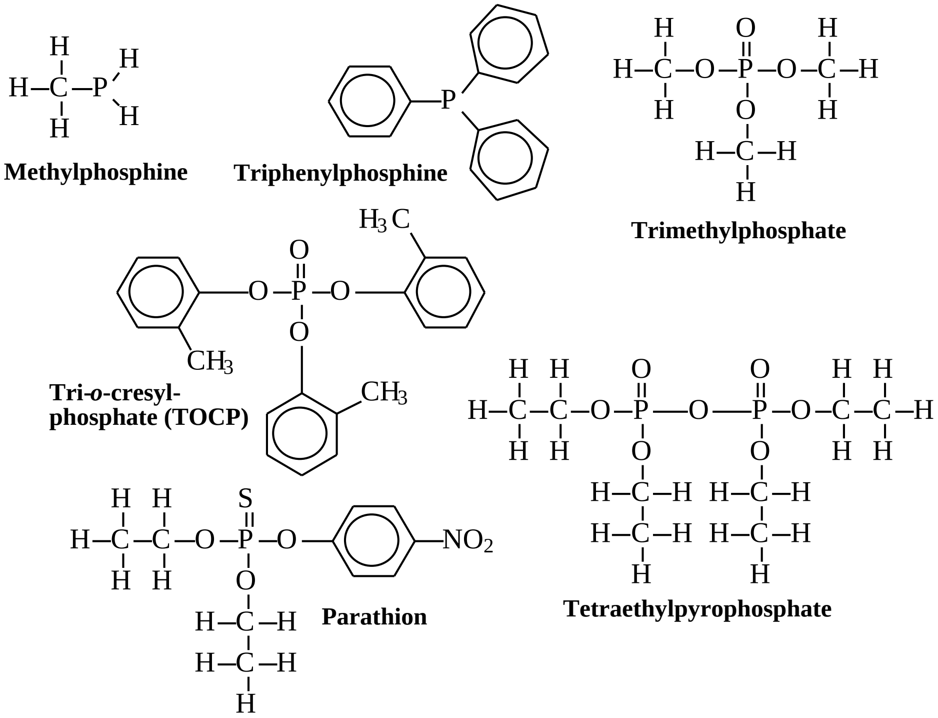


Figure 29.13. Some representative organophosphorus compounds.

Many of the hazards from the polymer industry arise from the monomers used as raw materials. Many monomers are reactive and flammable, with a tendency to form explosive vapor mixtures with air. All have a certain degree of toxicity; vinyl chloride is a known human carcinogen. The combustion of many polymers may result in the evolution of toxic gases, such as hydrogen cyanide (HCN) from polyacrylonitrile, or hydrogen chloride (HCl) from polyvinylchloride. Another hazard presented by plastics results from the presence of **plasticizers** added to provide essential properties such as flexibility. The most widely used plasticizers are phthalates, which are environmentally persistent, resistant to treatment processes, and prone to undergo bioaccumulation.

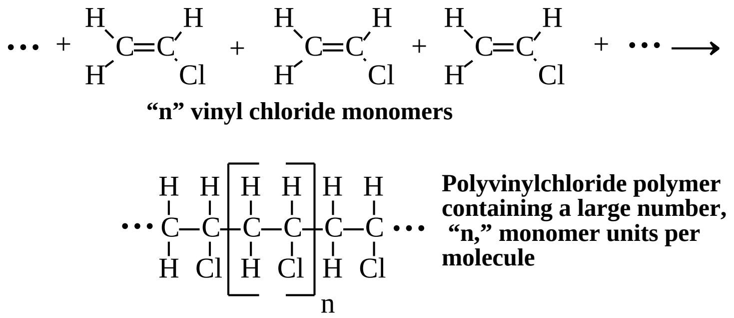


Figure 29.14. Polyvinylchloride polymer.

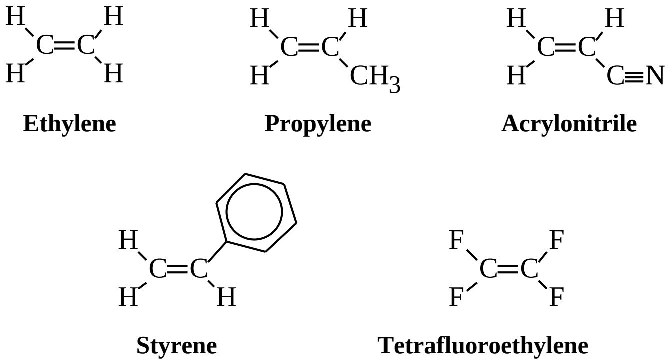


Figure 29.15. Monomers from which commonly used polymers are synthesized.

Polymers have a number of applications in waste treatment and disposal. Waste disposal landfill liners are made from synthetic polymers, as are the fiber filters which remove particulate pollutants from flue gas in baghouses. Membranes used for ultrafiltration and reverse osmosis treatment of water are composed of very thin sheets of synthetic polymers. Organic solutes can be removed from water by sorption onto hydrophobic (water-repelling) organophilic beads of Amberlite XAD resin. Heavy metal pollutants are removed from wastewater by cation exchange resins made of polymers with anionic functional groups. Typically, these resins exchange harmless sodium ion, Na^+, on the solid resin for toxic heavy metal ions in water. Figure 29.16 shows a segment of the polymeric structure of a cation exchange resin in the sodium form. In the treatment of heavy-metal-containing waste solutions, these resins can exchange toxic heavy metal ions in solution, such as Cd^{2+}, for nontoxic Na^+ ions. Ion exchange resins are used in nuclear reactors to remove traces of metals, some of which may be radioactive, from the water used in the reactor for heat exchange. Ion exchange resins have also been developed in which the ion-exchanging functional group is an iminiodiacetate $\{-N(CH_2CO_2^-)_2\}$ group that has a particularly strong affinity for heavy metals.

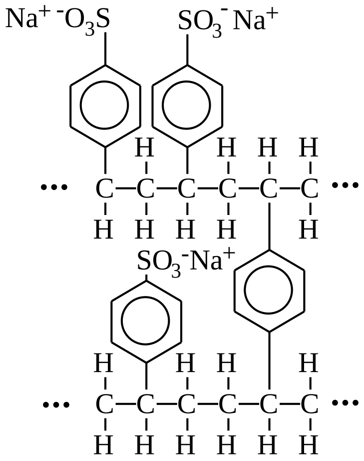


Figure 29.16. Polymeric cation exchanger in the sodium form.

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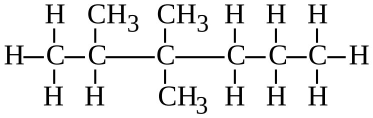
QUESTIONS AND PROBLEMS

1. Explain the bonding properties of carbon that makes organic chemistry so diverse.
2. Distinguish among alkanes, alkenes, alkynes, and aryl compounds. To which general class of organic compounds do all belong?
3. In what sense are alkanes saturated? Why are alkenes more reactive than alkanes?
4. Name the compound below:



$$\begin{array}{ccccccccccccccc} & & \mathrm{H} & & \mathrm{CH_3} & & \mathrm{CH_3} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & | & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{CH_3} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

5. What is indicated by “*n*” in a hydrocarbon name?
6. Discuss the chemical reactivity of alkanes. Why are they chemically reactive or unreactive?
7. Discuss the chemical reactivity of alkenes. Why are they chemically reactive or unreactive?
8. What are the characteristics of aromaticity? What are the chemical reactivity characteristics of aromatic compounds?
9. Describe chain reactions, discussing what is meant by free radicals and photochemical processes.
10. Define, with examples, what is meant by isomerism.
11. Describe how the two forms of 1,2-dichloroethylene can be used to illustrate *cis-trans* isomerism.
12. Give the structural formula corresponding to the condensed structural formula of $CH_3CH(C_2H_5)CH(C_2H_5)CH_2CH_3$.
13. Discuss how organic functional groups are used to define classes of organic compounds.
14. Give the functional groups corresponding to (a) alcohols, (b) aldehydes, (c) carboxylic acids, (d) ketones, (e) amines, (f) thiol compounds, and (g) nitro compounds.
15. Give an example compound of each of the following: epoxides, alcohols, phenols, ethers, aldehydes, ketones, and carboxylic acids.
16. Which functional group is characteristic of N-nitroso compounds, and why are these compounds toxicologically significant?
17. Give an example of each of the following: Alkyl halides, alkenyl halides, aryl halides.
18. Give an example compound of a chlorinated naphthalene and of a PCB.

19. What explains the tremendous chemical stability of CFCs? What kinds of compounds are replacing CFCs? Why?
20. How does a thio differ from a thioether?
21. How do sulfoxides differ from sulfones?
22. Which inorganic compound is regarded as the parent compound of alkyl and aryl phosphines? Give an example of each of these.
23. What are organophosphate esters and what is their toxicological significance?
24. Define what is meant by a polymer and give an example of one.