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THE WONDERFUL WORLD OF CARBON: ORGANIC CHEMISTRY AND BIOCHEMICALS

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Abstract :

Most of the molecules of chemical compounds studied so far have been clusters of only a few atoms. Therefore, molecules of water, H2O, exist as individual clusters of 2 H atoms bonded to 1 O atom and molecules of ammonia, NH3, each consist of an atom of N to which are bonded 3 H atoms. In cases where atoms of a particular element in chemical compounds have a tendency to bond with atoms of the same element, the number of possible compounds is increased tremendously. This is the case with carbon, C. Groups of carbon atoms can bond together to form straight chains, branched chains, and rings, leading to a virtually limitless number of chemical compounds. Such carbon-containing compounds are **organic chemicals**, the study of which is **organic chemistry**. Adding to the enormous diversity of organic chemistry is the fact that two carbon atoms may be connected by **single bonds** consisting of 2 shared electrons, **double bonds** composed of 4 shared electrons, and even **triple bonds** that contain 6 shared electrons.

Organic chemicals comprise most of the substances with which chemists are involved. Petroleum, which serves as the raw material for vast polymer, plastics, rubber, and other industries consists of hundreds of compounds composed of hydrogen and carbon called **hydrocarbons**. Among organic chemicals are included the majority of important industrial compounds, synthetic polymers, agricultural chemicals, and most substances that are of concern because of their toxicities and other hazards. The carbohydrates, proteins, lipids (fats and oils), and nucleic acids (DNA) that make up the biomass of living organisms are organic chemicals made by biological processes. The feedstock chemicals needed to manufacture a wide range of chemical products are mostly organic chemicals, and their acquisition and processing are of great concern in the practice of green chemistry. The largest fraction of organic chemicals acquired from petroleum and natural gas sources are burned to fuel vehicles, airplanes, home furnaces, and power plants. Prior to burning, these substances may be processed to give them desired properties. This is particularly true of the constituents of gasoline, the molecules of which are processed and modified to give gasoline desired properties of smooth burning (good antiknock properties) and low air pollution potential. Pollution of the water, air, and soil environments by organic chemicals is an area of significant concern. Much of the effort put into green chemistry has involved the safe manufacture, recycling, and disposal of organic compounds.

A number of organic compounds are made by very sophisticated techniques to possess precisely tailored properties. This is especially true of pharmaceuticals, which must be customized to deliver the desired effects with minimum undesirable side effects. A single organic compound that is effective against one of the major health problems — usually one out of hundreds or even thousands tested — has the potential for hundreds of millions of dollars per year in profits.

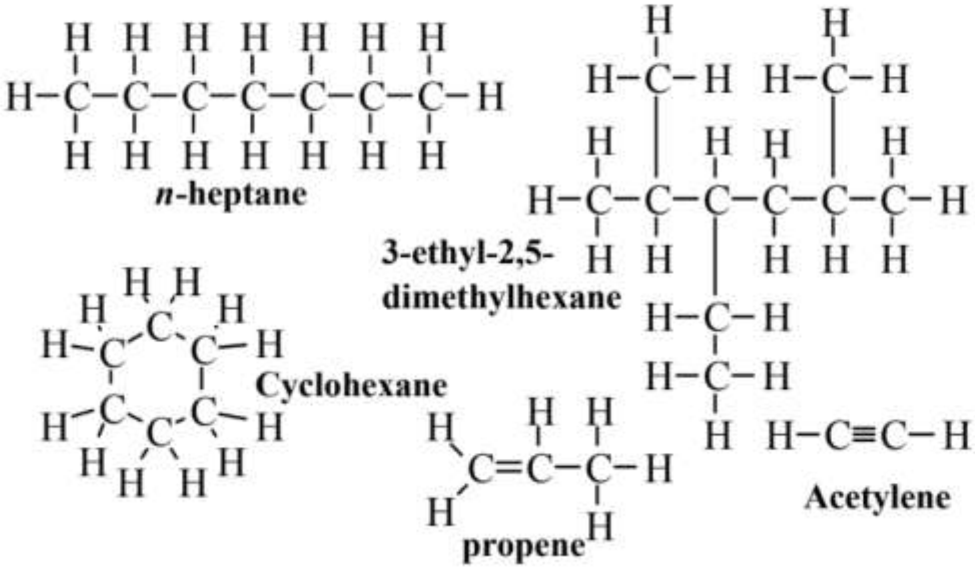
Organic chemicals differ widely in their toxicities. Some compounds are made and used because of their toxicities to undesirable organisms. These are the **pesticides**,

including, especially, **insecticides** used to kill unwanted insects and **herbicides** used to eradicate weeds that compete with desired crops. Green chemistry is very much involved with these kinds of applications. One of the more widely applied uses of genetically modified crops has been the development of crops that produce their own insecticides in the form of insecticidal proteins normally made by certain kinds of bacteria whose genes have been spliced into field crops. Another application of green chemistry through genetic engineering is the development of crops that resist the effects of specific organic molecules commonly used as herbicides. These herbicides may be applied directly to target crops, leaving them unscathed while competing weeds are killed.

It should be obvious from this brief discussion that organic chemistry is a vast, diverse, highly useful discipline based upon the unique bonding properties of the carbon atom. The remainder of this chapter discusses major aspects of organic chemistry. Many of the most interesting and important organic chemicals are made by biological processes. Indeed, until 1828, it was generally believed that only organisms could synthesize organic chemicals. In that year, Friedrich Wöhlers succeeded in making urea, an organic chemical that is found in urine, from ammonium cyanate, an inorganic material. Because of the important role of organisms in making organic chemicals, several of the most significant kinds of these chemicals made biologically are also discussed in this chapter. Additional details regarding the ways in which living organisms make and process chemicals are given in Chapters 9 and 13.

COMPOUNDS OF CARBON AND HYDROGEN: HYDROCARBONS

The tremendous variety and diversity of organic chemistry is due to the ability of carbon atoms to bond with each other in a variety of straight chains, branched chains, and rings and of adjacent carbon atoms to be joined by single, double, or triple bonds. This bonding ability can be illustrated with the simplest class of organic chemicals, the **hydrocarbons** consisting only of hydrogen and carbon. Figure 5.1 shows some hydrocarbons in various configurations.



Some typical hydrocarbons. These formulas illustrate the bonding diversity of carbon which gives rise to an enormous variety of hydrocarbons and other organic compounds.

Hydrocarbons are the major ingredients of petroleum and are pumped from the ground as crude oil or extracted as natural gas. They have two major uses. The first of these is combustion as a source of fuel. The most abundant hydrocarbon in natural gas, methane, CH_4, is burned in home furnaces, electrical power plants, and even in vehicle engines,

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat energy}$$

to provide energy. The second major use of hydrocarbons is as a raw material for making rubber, plastics, polymers, and many other kinds of materials. Given the value of hydrocarbons as a material, it is unfortunate that so much of hydrocarbon production is simply burned to provide energy, which could be generated by other means.

There are several major class of hydrocarbons, all consisting of only hydrogen and carbon. **Alkanes** have only single bonds between carbon atoms. Cyclohexane, *n*heptane, and 3-ethyl-2,5-dimethylhexane in Figure 5.1 are alkanes; the cyclohexane is a cyclic hydrocarbon. **Alkenes**, such as propene shown in Figure 5.1, have at least one double bond consisting of 4 shared electrons between two of the carbon atoms in the molecule. **Alkynes** have at least one triple bond between carbon atoms in the molecule as shown for acetylene in Figure 5.1. Acetylene is an important fuel for welding and cutting torches; otherwise, the alkynes are of relatively little importance and will not be addressed farther. A fourth class of hydrocarbon consists of **aromatic** compounds which have rings of carbon atoms with special bonding properties as discussed later in this chapter.

Alkanes :

The molecular formulas of non-cyclic alkanes are C_nH_{2n+2}. By counting the numbers of carbon and hydrogen atoms in the molecules of alkanes shown in Figure 5.1, it is seen that the molecular formula of *n*-heptane is C_7H_{16} and that of 3-ethyl-2,5-dimethylhexane is $C_{10}H_{22}$, both of which fit the general formula given above. The general formula of cyclic alkanes is C_nH_{2n}; that of cyclohexane, the most common cyclic alkane, is C_6H_{12}. These formulas are **molecular formulas**, which give the number of carbon and hydrogen atoms in each molecule, but do not tell anything about the structure of the molecule. The formulas given in Figure 5.1 are **structural formulas** which show how the molecule is assembled. The structure of *n*-heptane is that of a straight chain of carbon atoms; each carbon atom in the middle of the chain is bound to 2 H atoms and the 2 carbon atoms at the ends of the chain are each bound to 3 H atoms. The prefix *hep* in the name denotes 7 carbon atoms and the *n*- indicates that the compound consists of a single straight chain. This compound can be represented by a **condensed structural formula** as $CH_3(CH_2)_5CH_3$ representing 7 carbon atoms in a straight chain. In addition to methane mentioned previously, the lower alkanes include the following:

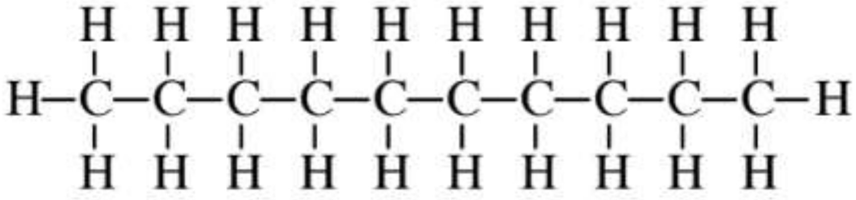
Ethane: CH_3CH_3 Propane: $CH_3CH_2CH_3$
Butane: $CH_3(CH_2)_2CH_3$ *n*-Pentane: $CH_3(CH_2)_3CH_3$

For alkanes with 5 or more carbon atoms, the prefix (*pen* for 5, *hex* for 6, *hept* for 7, *oc t* for 8, *non* for 9) shows the total number of carbon atoms in the compound and *n*- may be used to denote a straight-chain alkane. Condensed structural formulas may be used to represent branched chain alkanes as well. The condensed structural formula of 3-ethyl- 2,5-dimethylhexane is

$$CH_3CH_2(CH_3)CH_2(C_2H_3)CH_2CH_2(CH_3)CH_3$$

In this formula, the C atoms and their attached H atoms that are not in parentheses show carbons that are part of the main hydrocarbon chain. The (CH_3) after the second C in the chain shows a methyl group attached to it, the (C_2H_5) after the third carbon atom in the chain shows an ethyl group attached to it, and the (CH_3) after the fifth carbon atom in the chain shows a methyl group attached to it.

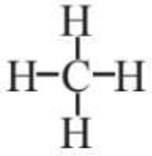
Compounds that have the same molecular formulas but different structural formulas are **structural isomers**. For example, the straight-chain alkane with the molecular formula $C_{10}H_{22}$ is *n*-decane,



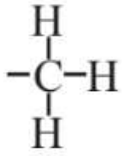
***n*-decane**

which is a structural isomer of 3-ethyl-2,5-dimethylhexane.

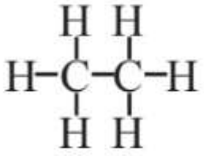
The names of organic compounds are commonly based upon the structure of the hydrocarbon from which they are derived using the longest continuous chain of carbon atoms in the compound as the basis for the name. For example, the longest continuous chain of carbon atoms in 3-ethyl-2,5-dimethylhexane shown in Figure 5.1 is 6 carbon atoms, so the name is based upon *hex*ane. The names of the chain branches are also based upon the alkanes from which they are derived. As shown below,



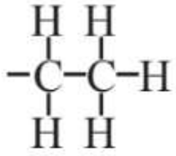
Methane (CH_4)



Methyl group (CH_3)



Ethane (C_2H_6)



Ethyl group (C_2H_5)

the two shortest-chain alkanes are methane with 1 carbon atom and ethane with 2 carbon atoms. Removal of 1 of the H atoms from methane gives the **methyl** group and removal of 1 of the H atoms from ethane gives the **ethyl** group. These terms are used in the name 3-ethyl-2,5-dimethylhexane to show groups attached to the basic hexane chain. The carbon atoms in this chain are numbered sequentially from left to right. An ethyl group is attached to the 3rd carbon atom, yielding the “3-ethyl” part of the name, and methyl groups are attached to the 2nd and 5th carbon atoms, which gives the “2,5-dimethyl” part of the name.

The names discussed above are **systematic names**, which are based upon the actual structural formulas of the molecules. In addition, there are **common names** of organic compounds that do not indicate the structural formulas. Naming organic compounds is a complex topic, and no attempt is made here to teach it to the reader. However, from the names of compounds given in this and later chapters, some appreciation of the rationale for organic compound names should be obtained.

Other than burning them for energy, the major kind of reaction with alkanes consists
of **substitution reactions** such as,

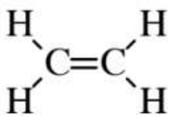
$$C_2H_6 + 2Cl_2 \rightarrow C_2H_4Cl_2 + 2HCl$$

in which one or more H atoms are displaced by another kind of atom. This is normally the first step in converting alkanes to compounds containing elements other than carbon or hydrogen for use in synthesizing a wide variety of organic compounds.

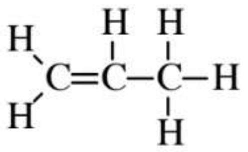
Alkenes :

Four common alkenes are shown in Figure 5.2. Alkenes have at least one C=C double bond per molecule and may have more. The first of the alkenes in Figure 5.2, ethylene, is a very widely produced hydrocarbon used to synthesize polyethylene plastic and other organic compounds. About 25 billion kilograms (kg) of ethylene are processed in the U.S.

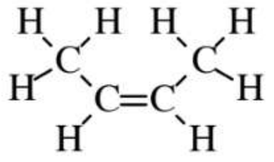
each year. About 14.5 billion kg of propylene are used in the U.S. each year to produce polypropylene plastic and other chemicals. The two 2-butene compounds illustrate an important aspect of alkenes, the possibility of ***cis-trans*** isomerism. Whereas carbon atoms and the groups substituted onto them joined by single bonds can freely rotate relative to each other as though they were joined by a single shaft, carbon atoms connected by a double bond behave as though they were attached by two parallel shafts and are not free to rotate. So, *cis*-2-butene in which the two end methyl (-CH_3) groups are on the same side of the molecule is a different compound from *trans*-2-butene in which they are on opposite sides. These two compounds are *cis-trans* isomers.



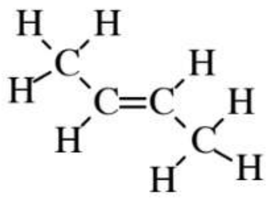
Ethylene



Propylene (propene)

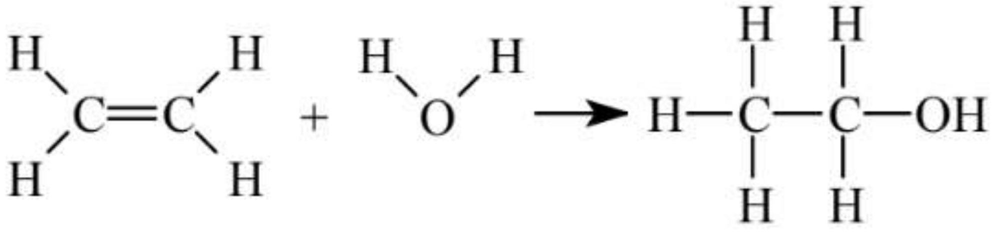


***Cis*-2-butene**



***Trans*-2-butene**

Alkenes are chemically much more active than alkanes. This is because the double bond is **unsaturated** and has electrons available to form additional bonds with other atoms. This leads to **addition reactions** in which a molecule is added across a double bond. For example, the addition of H_2O to ethylene,

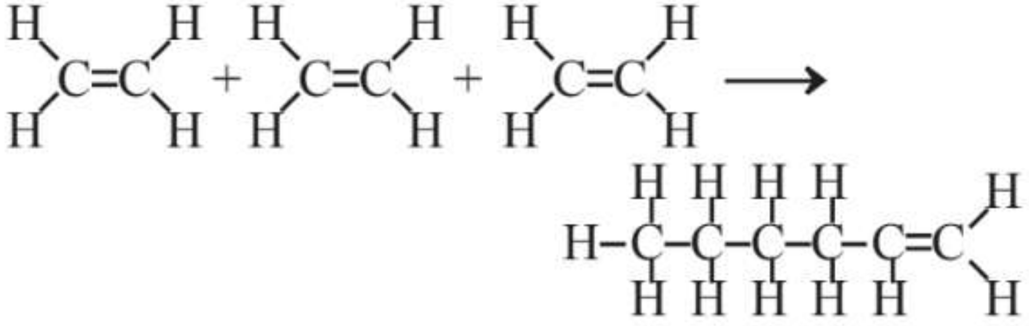


(6.2.3)

Ethylene **Water** **Ethanol**

yields ethanol, the same kind of alcohol that is in alcoholic beverages. In addition to adding immensely to the chemical versatility of alkenes, addition reactions make them quite reactive in the atmosphere during the formation of photochemical smog. The presence of double bonds also adds to the biochemical and toxicological activity of compounds in organisms.

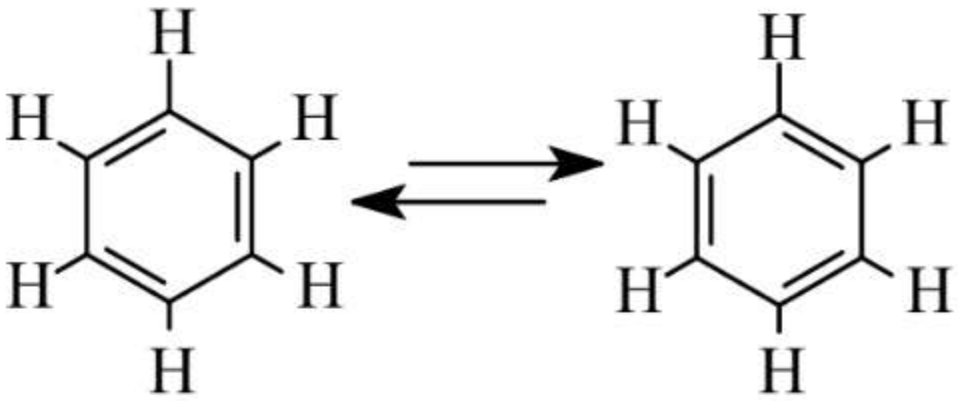
Because of their double bonds, alkenes can undergo **polymerization** reactions in which large numbers of individual molecules add to each other to produce large molecules called **polymers**. For example, 3 ethylene molecules can add together as follows:



a process that can continue, forming longer and longer chains and resulting in the formation of the very large molecules that constitute polyethylene.

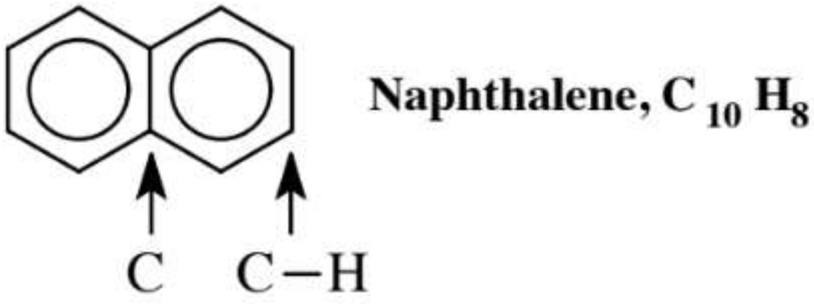
Aromatic Hydrocarbons :

A special class of hydrocarbons consists of rings of carbon atoms, almost always containing 6 C atoms, which can be viewed as having alternating single and double bonds as shown below:

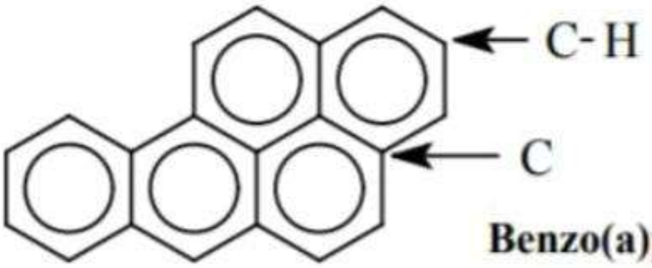


These structures show the simplest aromatic hydrocarbon, benzene, C6H6. Although the benzene molecule is represented with 3 double bonds, chemically it differs greatly from alkenes, for example undergoing substitution reactions rather than addition reactions. The properties of aromatic compounds are special properties called **aromaticity**. The two structures shown above are equivalent **resonance** structures, which can be viewed as having atoms that stay in the same places, but in which the bonds joining the atoms can shift positions with the movement of electrons composing the bonds. Since benzene has different chemical properties from those implied by either of the above structures, it is commonly represented as a hexagon with a circle in the middle:

Many aromatic hydrocarbons have two or more rings. The simplest of these is naphthalene,



a two-ringed compound in which two benzene rings share the carbon atoms at which they are joined; these two carbon atoms do not have any H attached, each of the other 8 C atoms in the compound has 1 H attached. Aromatic hydrocarbons with multiple rings, called **polycyclic aromatic hydrocarbons**, PAH, are common and are often produced as byproducts of combustion. One of the most studied of these is benzo(a)pyrene,



Benzo(a)pyrene, $C_{20}H_{12}$

found in tobacco smoke, diesel exhaust, and charbroiled meat. This compound is toxicologically significant because it is partially oxidized by enzymes in the body to produce a cancer-causing metabolite.

The presence of hydrocarbon groups and of elements other than carbon and hydrogen bonded to an aromatic hydrocarbon ring gives a variety of **aromatic compounds**. Three examples of common aromatic compounds are given below. Toluene is widely used for chemical synthesis and as a solvent. The practice of green chemistry now calls for substituting toluene for benzene wherever possible because benzene is suspected of causing leukemia, whereas the body is capable of metabolizing toluene to harmless metabolites (see Chapter 13). About 850 million kg of aniline are made in the U.S. each year as an intermediate in the synthesis of dyes and other organic chemicals. Phenol is a relatively toxic oxygen-containing aromatic compound which, despite its toxicity to humans, was the first antiseptic used in the 1800s

Toluene

Aniline

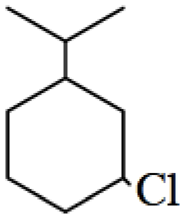
Phenol

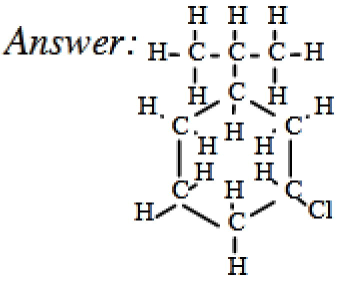
LINES SHOWING ORGANIC STRUCTURAL FORMULAS

The aromatic structures shown above use a hexagon with a circle in it to denote an aromatic benzene ring. Organic chemistry uses lines to show other kinds of structural formulas as well. The reader who may have occasion to look up organic formulas will probably run into this kind of notation, so it is important to be able to interpret these kinds of formulas. Some line formulas are shown in Figure 5.3.

In using lines to represent organic structural formulas, the corners where lines intersect and the ends of lines represent C atoms, and each line stands for a covalent bond (2 shared electrons). It is understood that each C atom at the end of a single line has 3 H atoms attached, each C atom at the intersection of 2 lines has 2 C atoms attached, each C at the intersection of 3 lines has 1 H attached, and the intersection of 4 lines denotes a C atom with no H atoms attached. Multiple lines represent multiple bonds as shown for the double bonds in 1,3-butadiene. Substituent groups are shown by their symbols (for individual atoms), or formulas of functional groups consisting of groups of atoms; it is understood that each such group substitutes for a hydrogen atom as shown in the formula of 2,3-dichlorobutane in Figure 5.2. The 6-carbon-atom aromatic ring is denoted by a hexagon with a circle in it.

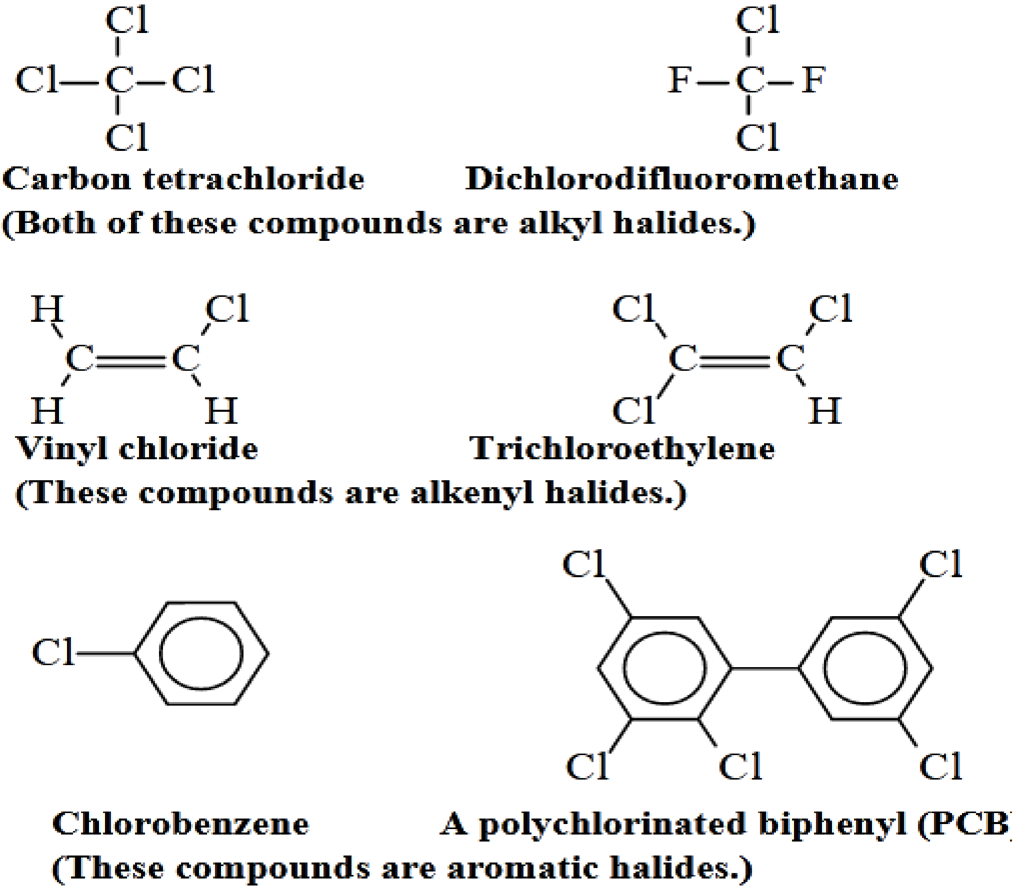
Exercise: What is the structural formula of the compound represente on the left, below?





Organohalide Compounds

Organohalides exemplified by those shown in Figure 5.5 are organic compounds that contain halogens — F, Cl, Br, or I — but usually chlorine, on alkane, alkene, or aromatic molecules. Organo halides have been widely produced and distributed for a variety of applications, including industrial solvents, chemical intermediates, coolant fluids, pesticides, and other applications. They are for the most part environmentally persistent and, because of their tendency to accumulate in adipose (fat) tissue, they tend to undergo bioaccumulation and biomagnification in organisms.



Carbon tetrachloride **Dichlorodifluoromethane**

(Both of these compounds are alkyl halides.)

Vinyl chloride **Trichloroethylene**

(These compounds are alkenyl halides.)

Chlorobenzene **A polychlorinated biphenyl (PCB**

(These compounds are aromatic halides.)

Figure 5.5. Examples of important organohalide compounds including alkyl halides based upon alkanes,alkenyl halides based upon alkenes, and aromatic halides.

Carbon tetrachloride is produced when all four H atoms on methane, CH_4, are substituted by Cl. This compound was once widely used and was even sold to the public as a solvent to remove stains and in fire extinguishers, where the heavy CCl_4 vapor smothers fires. It was subsequently found to be very toxic, causing severe liver damage, and its uses are severely restricted. **Dichlorodifluoromethane** is a prominent member of the **chlorofluorocarbon** class of compounds, popularly known as Freons. Developed as refrigerant fluids, these compounds are notably unreactive and nontoxic. However, as discussed in Chapter 8, they were found to be indestructible in the lower atmosphere, persisting to very high altitudes in the stratosphere where chlorine split from them by ultraviolet radiation destroys stratospheric ozone. So the manufacture of

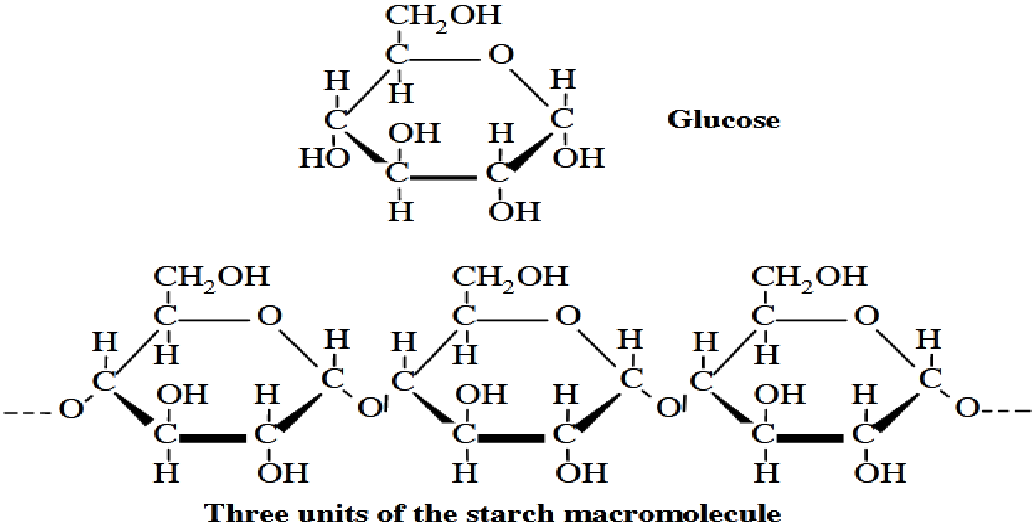
LIFE CHEMICALS

As noted at the beginning of this chapter, living organisms produce a variety of organic chemicals or **biochemicals**. These are considered under the topic of **biochemistry**, the chemistry of life processes. The topic of biochemistry and its relationship to green chemistry is addressed in more detail in later chapters, especially Chapters 9 and 13. At this point, however, it is useful to introduce several classes of the most important kinds of chemicals produced by organisms. Biochemicals are governed by the same laws of chemistry as are other kinds of organic chemicals. For example, many fats, oils, and waxes produced by organisms are esters, a class of organooxygen compounds described in Section 5.4 and shown in Reaction 5.4.1.

Many biochemicals are polymers, which may consist of huge macromolecules. One such material is DNA, the basic molecule of genetic material that may contain billions of atoms per molecule. Proteins are polymers of amino acids. Starch and cellulose are polymers of sugars. DNA, proteins, starch, and cellulose are condensation polymers which release a molecule of H2O for every monomer molecule bonded to the polymer. There are four major general groups of kinds of chemical species that are made and used by living organisms. These are proteins, carbohydrates, lipids, and nucleic acids, which are addressed in the sections that follow.

CARBOHYDRATES

Carbohydrates are biomolecules consisting of carbon, hydrogen, and oxygen having the approximate simple formula CH2O. One of the most common carbohydrates is the simple sugar glucose shown in Figure 5.7. Units of glucose and other simple sugars called **monosaccharides** join together in chains with the loss of a water molecule for each linkage to produce macromolecular **polysaccharides**. These include **starch** and **cellulose** in plants and starch-like glycogen in animals.



Glucose

Three units of the starch macromolecule

Figure 5.7. Glucose, a monosaccharide, or simple sugar, and a segment of the starch molecule, which

is formed when glucose molecules polymerize with the elimination of one H2O molecule per glucosemonomer.

Glucose carbohydrate is the biological material generated from water and carbon dioxide when solar energy in sunlight is utilized in photosynthesis. The overall reaction is

6CO2 + 6H2O → C6H12O6 + 6O2

LIPIDS: FATS, OILS, AND HORMONES

Lipids differ from most other kinds of biomolecules in that they are repelled by water. Lipids can be extracted from biological matter by organic solvents, such as diethyl ether or toluene. Recall that proteins and carbohydrates are distinguished largely by chemically similar characteristics and structures. However, lipids have a variety of chemical structures that share the common physical characteristic of solubility in organic solvents. Many of the commonly encountered lipid fats and oils are esters of glycerol alcohol, CH2(OH)CH(OH)CH2(OH), and long-chain carboxylic acids (fatty acids), such as stearic acid, CH3(CH2)16CO2H. The glycerol molecule has three -OH groups to each of which a fatty acid molecule may be joined through the carboxylic acid group with the loss of a water molecule for each linkage that is formed. Figure 5.9 shows a fat molecule formed from three stearic acid molecules and a glycerol molecule. Such a molecule is.

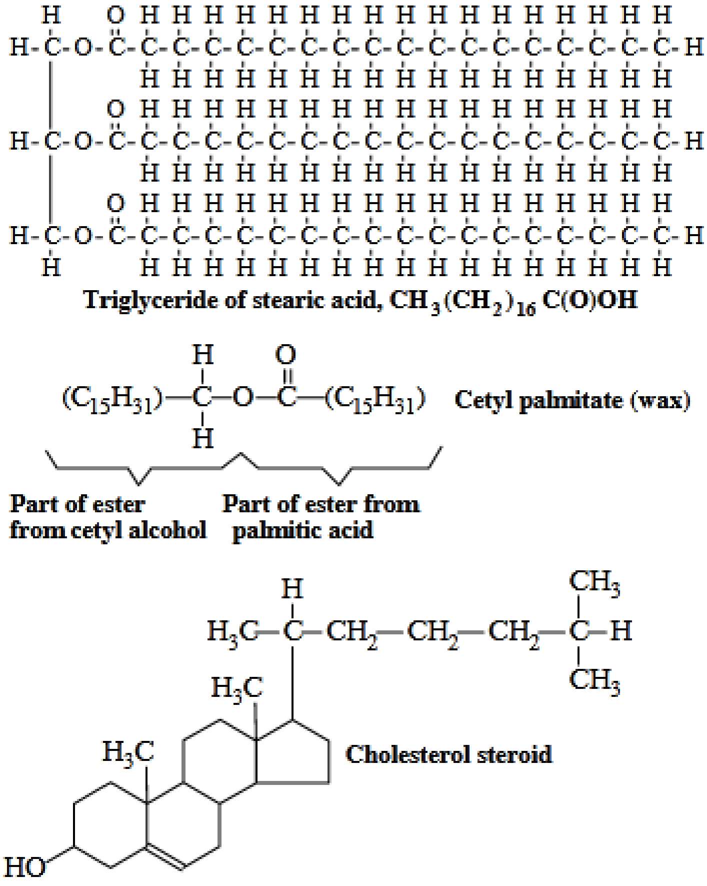


Figure 5.9. Three examples of lipids formed in biological systems. Note that a line structure is used to show the ring structure of cholesterol. The hydrocarbon-like nature of these compounds which makes them soluble in organic compounds is obvious.

one of many possible **triglycerides**. Also shown in this figure is cetyl palmitate, the major ingredient of spermaceti wax extracted from sperm whale blubber and used in some cosmetics and pharmaceutical preparations. Cholesterol shown in Figure 5.9 is one of several important lipid **steroids**, which share the ring structure composed of rings of 5 and 6 carbon atoms shown in the figure for cholesterol. Steroids act as **hormones**, in green chemistry. Poorly biodegradable substances, particularly organochlorine compounds, that are always an essential consideration in green chemistry, tend to accumulate in lipids in living organisms, a process called bioaccumulation. Lipids can be valuable raw materials and fuels. Therefore, the development and cultivation of plants that produce oils and other lipids is a major possible route to the production of renewable resources.

NUCLEIC ACIDS :

Nucleic acids are biological macromolecules that store and pass on the genetic information that organisms need to reproduce and synthesize proteins. The two major kinds of nucleic acids are **deoxyribonucleic acid**, **DNA**, which basically stays in place in the cell nucleus of an organism and **ribonucleic acid**, **RNA**, which is spun off from DNA and functions throughout a cell. Molecules of nucleic acids contain three basic kinds of materials. The first of these is a simple sugar, 2-deoxy-□-D-ribofuranose (deoxyribose) contained in DNA and □-D-ribofuranose (ribose) contained in RNA. The second major kind of ingredient consists of nitrogen-containing bases: cytosine, adenine,and guanine, which occur in both DNA and RNA, thymine, which occurs only in DNA, and uracil, which occurs only in RNA. The third consituent of both DNA and RNA is inorganic phosphate, PO4 3-.These three kinds of substances occur as repeating units called **nucleotides** joined together in astoundingly long chains in the nucleic acid polymer as shown in Figure 5.10.

The remarkable way in which DNA operates to pass on genetic information and perform other functions essential for life is the result of the structure of the DNA molecule. In 1953, James D. Watson, and Francis Crick deduced that DNA consisted of two strands of material counterwound around each other in a structure known as an □-helix, an amazing bit of insight that earned Watson and Crick the Nobel Prize in 1962. These strands are held together by hydrogen bonds between complementary nitrogenous bases. Taken apart, the two strands resynthesize complementary strands, a process that occurs during reproduction of cells in living organisms. In directing protein synthesis, DNA becomes partially unravelled and generates a complementary strand of material in the form of RNA, which in turn directs protein synthesis in the cell.

Nucleic acids have an enormous, as of yet largely unrealized, potential in the development of green chemistry. Much of the hazard of many chemical substances results from potential effects of these substances upon DNA. Of most concern is the ability of some substances to alter DNA and cause uncontrolled cell replication characteristic of cancer.

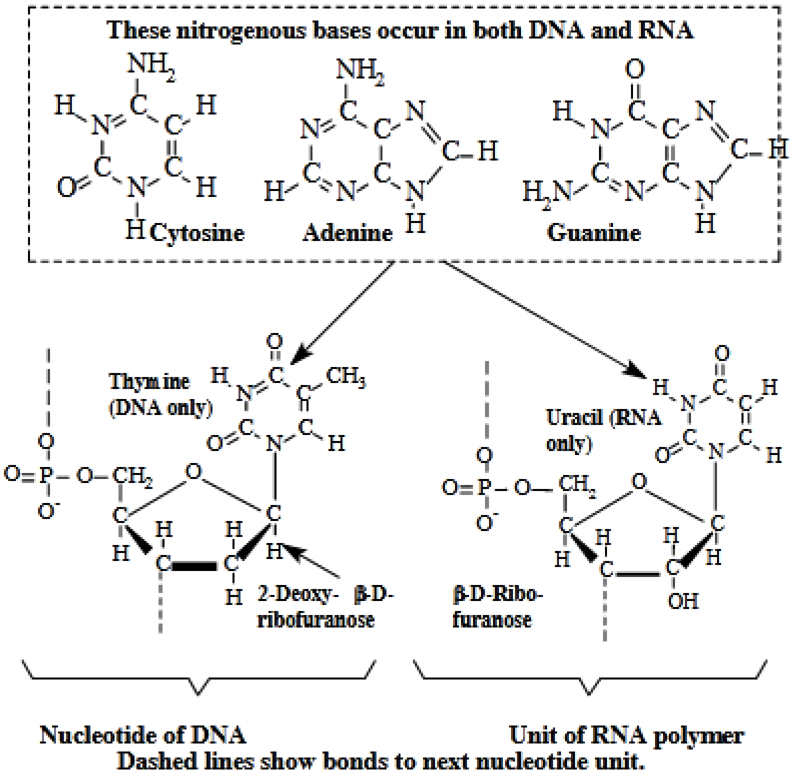


Figure 5.10. Basic units of nucleic acid polymers. These units act as a code in directing reproduction and other activities of organisms.

In recent years humans have developed the ability to alter DNA so that organisms synthesize proteins and perform other metabolic feats that would otherwise be impossible. Such alteration of DNA is commonly known as **genetic engineering** and **recombinant DNA** technology. Organisms produced by recombinant DNA techniques that contain DNA from other organisms are called **transgenic organisms**. The potential of this technology to produce crops with unique characteristics, to synthesize pharmaceuticals, and to make a variety of useful raw materials as renewable feedstocks is discussed in later chapters.

LITERATURE CITED

1. Barabási, Albert-László, “We’re all on the Grid Together,” *New York Times*, August 16, 2003, p. A25.

2. Barabási, Albert-László, *Linked: The New Science of Networks*, Perseus Publishing, Boulder, CO, 2002.

3. “Toxic *Chemicals* and Explosive Materials,” Chapter 4 in *Making the Nation Safer: The Role of Science and Technology in Countering Terrorism*, Bruce Alberts, William A. Wulf, and Kenneth I. Shine, Eds., The National Academies Press, Washington, DC, 2002, pp. 107–134.

4. Kolavic, Shellie A., Akiko Kimura, Shauna L. Simons, Laurence Slutsker, Suzanne Barth, and Charles E. *Haley*, “An Outbreak of *Shigella dysenteriae* Type 2 Among

Laboratory Workers Due to Intentional Food Contamination,” *Journal of the American Medical Association*, **278**, 396–8 (1997).

5. Derr, Mark, “With Dog Detectives, Mistakes Can Happen,” *New York Times*, Dec. 24, 2002, p. D1.

6. As quoted in “Green Solutions to Global *Problems*,” Stephen K. Ritter, *Chemical and Engineering News*, **81**, 31–33 (2003).