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ABSTRACT

This book is one in the series of Interdisciplinary Approaches to Chemistry (IAC) designed to help students discover that chemistry is a lively science and actively used to pursue solutions to the important problems of today. It is expected for students to see how chemistry takes place continuously all around and to readily understand the daily problems facing them and their environment. Contents include: (1) "Organic Chemistry"; (2) "Hydrocarbons"; (3) "Reactions of Hydrocarbons"; (4) "Alcohols: Oxidized Hydrocarbons"; (5) "Poisons and Chemical Warfare"; (6) "Aldehydes and Ketones"; (7) "Pesticides and Sex Attractants"; (8) "Esters and Acids"; (9) "Organic Bases: The Amines"; (10) "Polymers: The Linking of Molecules"; (11) "Photochemistry: Light and Heat"; and (12) "Drugs: From Aspirin to Hallucinogens". (KHR)

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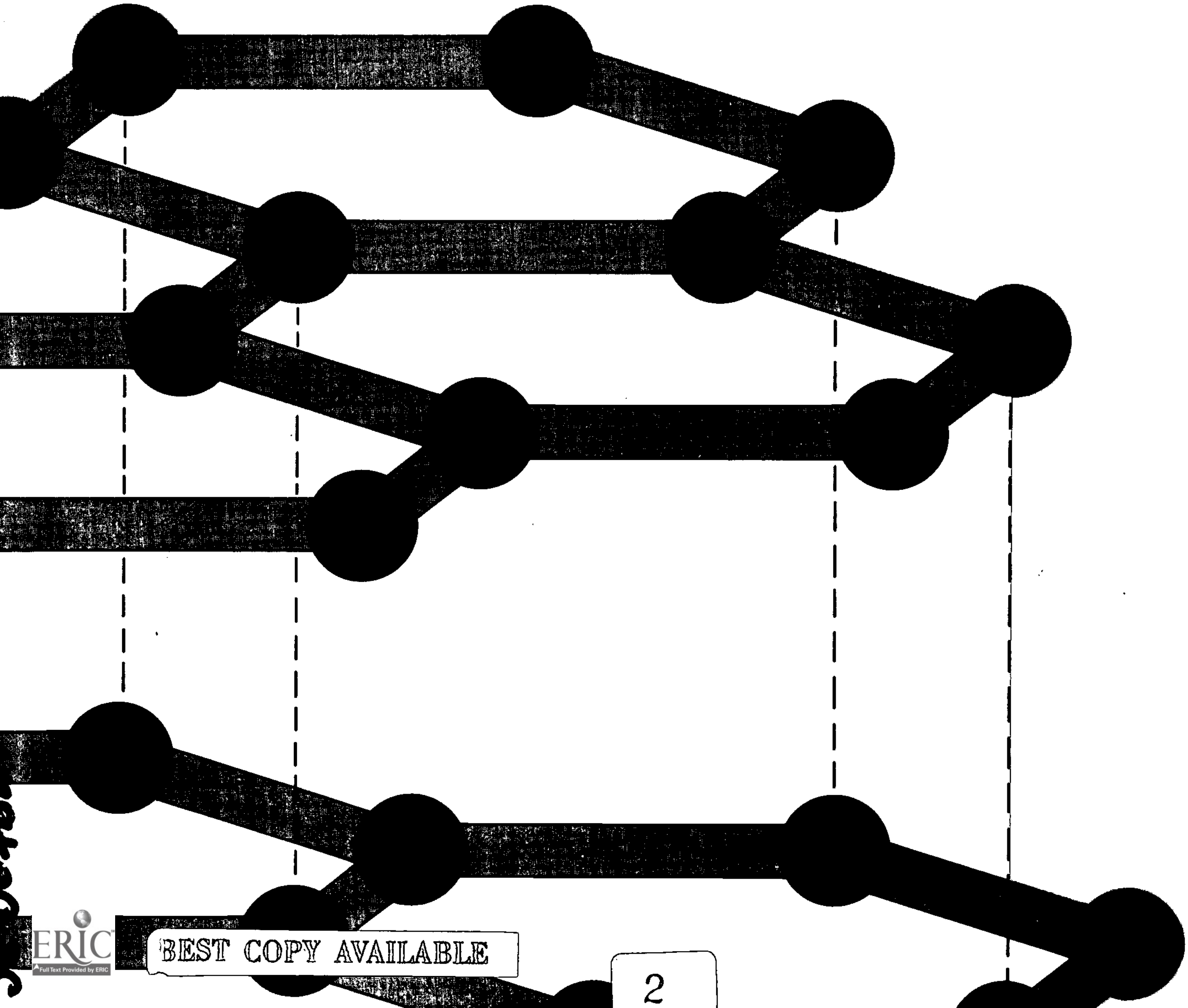
FORM AND FUNCTION

AN ORGANIC CHEMISTRY MODULE



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Paul Mazzocchi

1817
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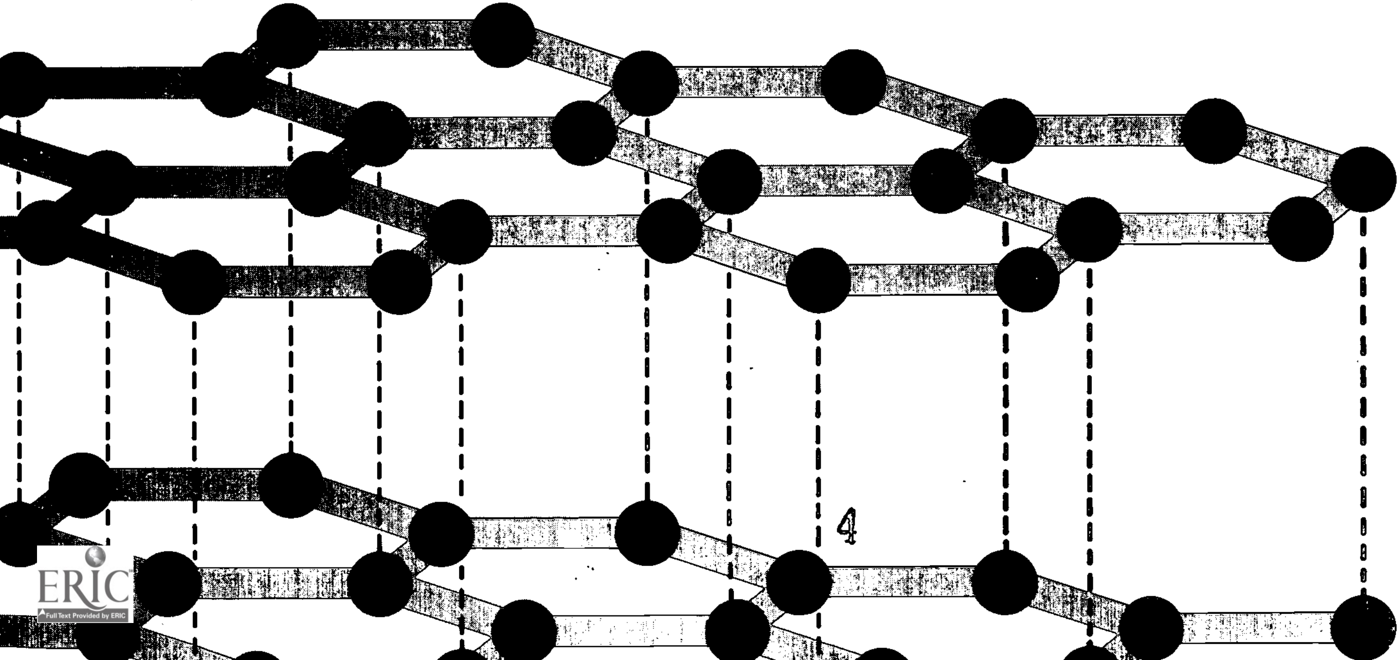

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FORM AND FUNCTION:
AN ORGANIC CHEMISTRY MODULE

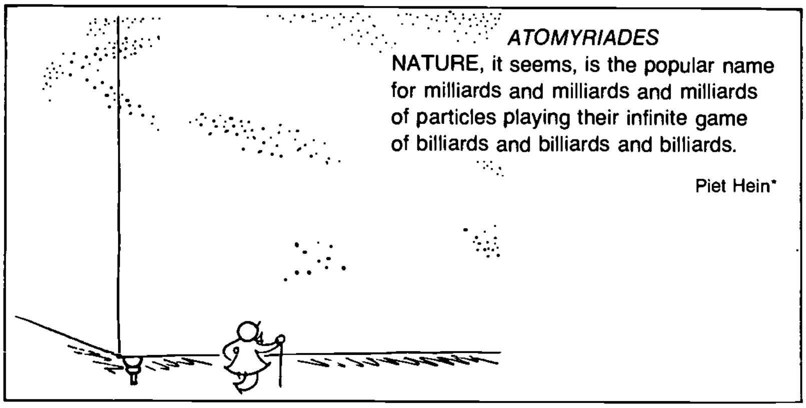
Bruce Jarvis and Paul Mazzocchi

BRUCE JARVIS

Bruce Jarvis arrived at the University of Maryland in 1967, and many people feel that the chemistry department will never be the same again. Sometimes embarrassing to his older colleagues, his graphic explanations during classes and seminars (they have, at times, taken the form of short, costumed one-act plays) are eagerly awaited by his students and coworkers. The exuberance and inquiring mind of Bruce Jarvis have brought a new dimension to chemistry research and teaching activities at the university.

PAUL MAZZOCCHI

Paul Mazzocchi came to the University of Maryland in 1967. Since then he has established himself in the chemistry department not only as a good scientist and teacher (winner of the university's Excellence in Teaching Award) but also as a master storyteller. As a young boy growing up on the streets of New York, "Mazzoc" rapidly learned to cope with all of the vagaries of life. More mature now, he continues to bring to the chemistry classroom a certain wisdom, understanding, and humor that go beyond the subject itself.



ATOMYRIADES

NATURE, it seems, is the popular name
for milliards and milliards and milliards
of particles playing their infinite game
of billiards and billiards and billiards.

Piet Hein*

© 1966 by Piet Hein

PREFACE

Welcome to IAC Chemistry. Enjoy this year as you explore this important area of science. Chemistry is to be enjoyed, cultivated, comprehended. It is part of our culture, of our everyday lives.

Polymers, paints, pharmaceuticals, people, and pollution all have something in common—a chemical base. IAC Chemistry is relevant, interdisciplinary, student centered, and filled with important concepts and processes.

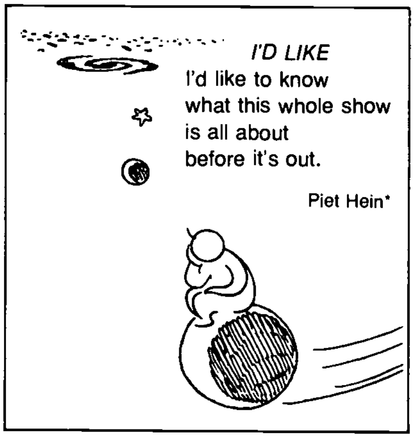
IAC will help you discover that chemistry is a lively science and being actively used to pursue solutions to the important problems of today. You will see how chemistry is taking place continuously all around. You will more readily understand the daily problems facing you and your environment.

Students throughout this country and in a number of other countries as well have let us know that they like and learn from the IAC modules. Classroom teachers have suggested changes to make them even better.

Since the IAC authors believe that student involvement in chemistry is very important, there are many activities that allow you to develop and apply chemistry concepts directly. We have tried to make the modules flexible, easy to read, and enjoyable, discussing everyday problems and adding a bit of humor that may help you remember some of the more important ideas. The Time Machines are intended to give you a sense of when the more important discoveries in chemistry happened in relation to other events.

Wonder—inquire—investigate. Think through all that you find here. But most of all—enjoy chemistry as you learn about the atoms, molecules, elements, and compounds that make up your universe. IAC is written for your learning pleasure.

Marjorie Gardner
Director
Interdisciplinary Approaches to Chemistry



I'D LIKE

I'd like to know
what this whole show
is all about
before it's out.

Piet Hein*

© 1966 by Piet Hein

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*Piet Hein is a Scandinavian poet who often served as a "mental Ping-Pong partner" for the famous chemist Niels Bohr.

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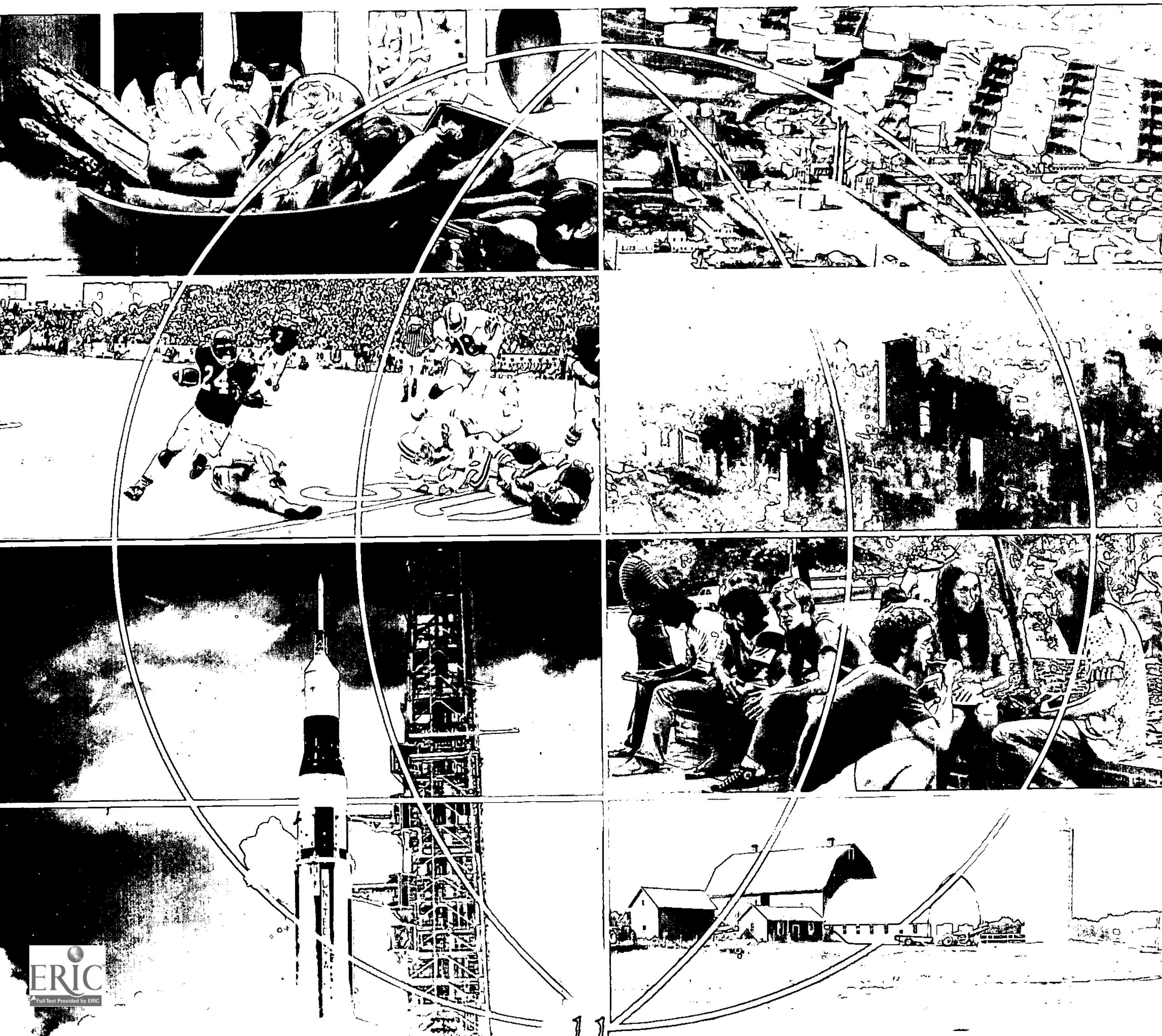
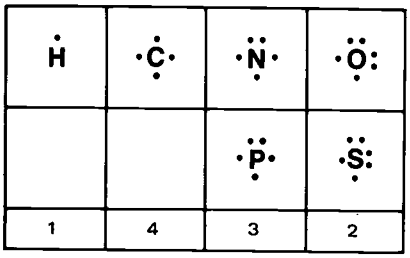
Organic Chemistry

Look around you. Observe the things in the room, outside the window, and in the street. Ask yourself, "What everyday materials are important to me and to everyone else?" If you examined the chemical makeup of those materials, you would find that most have at least one thing in common: they contain carbon. Organic chemistry is the study of compounds that contain carbon.

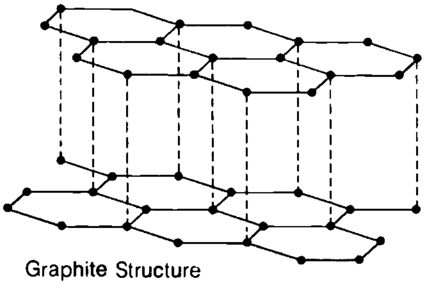




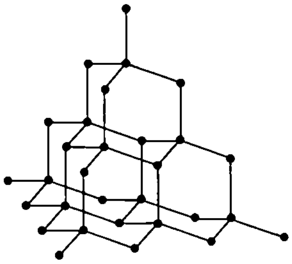
Numerals indicate electrons needed to complete outer shell

Each dot represents an electron in the outermost shell of an atom. Since the bonding potential is the number of electrons needed to complete the outermost shell, you can see why carbon is the most versatile element. It can accept or share four electrons.

TWO FORMS OF PURE CARBON



Graphite Structure



Diamond Structure

In the graphite structure, the bonding allows the layers to slip over each other, which is why graphite makes a good lubricant. The bonding in diamond accounts for its hardness.

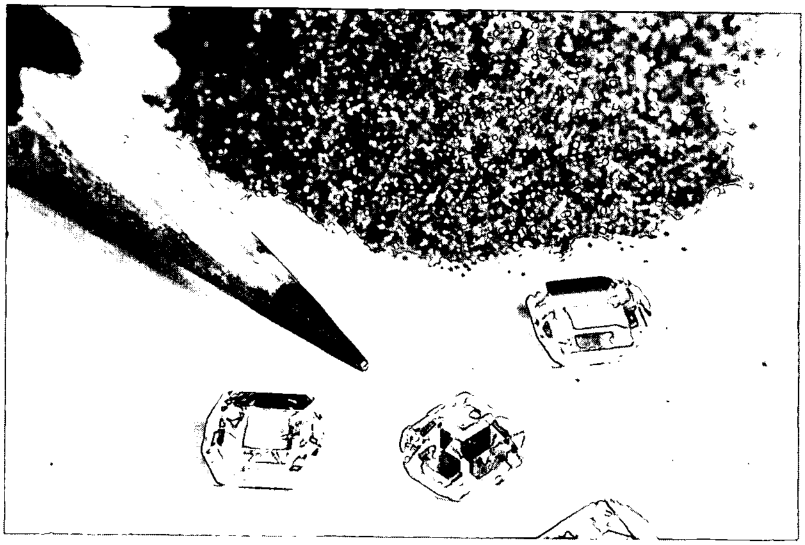
In your list of important items, you might have included fibers, fuels, food, coal, candy, clothes, candles, containers, cosmetics, paper, plastics, petroleum, rubber, wood, and ink. And these all contain carbon. But what is carbon?

Perhaps you already know that carbon is one of the lightest of the elements—a nonmetal located in the upper right section of the periodic table. Charcoal and coal contain carbon. Carbon black in the ink used to print this book contains carbon. Another form of carbon is graphite, which is the "lead" in lead pencils. A diamond, the hardest natural substance known, is a form of *pure* carbon found in nature. By itself carbon represents only one percent of all matter. Still, it can be found in millions of different materials. Carbon combines readily with itself and with other atoms and is part of every living thing—every plant and animal.

The tendency of carbon to form such diverse materials is the result of its ability to

- share its four valence electrons,
- form single, double, and triple bonds, and, most important,
- form seemingly endless arrays of bonds with itself.

The third property makes possible literally an infinite number of organic compounds. In addition to the millions of organic compounds that exist in nature, fifty thousand to one hundred thousand compounds containing carbon are being synthesized each year.



O-1 A Vital Force?

At one time it was believed that all organic compounds must have originated from living organisms. This was referred to as the *vital force theory*. According to this theory, there had to be a "vital force" in plants and animals that enabled them to synthesize (make) compounds of carbon. Accepting the vital force theory, the early chemists defined organic chemistry as the study of materials derived from living things. The vital force theory prevailed until the mid-nineteenth century when the chemist Marcellin Berthelot was able to produce several organic compounds without the aid of living organisms. He also introduced the term *synthesis* to describe the process of producing compounds in this way. We now realize that although living organisms can certainly synthesize fantastically complicated organic compounds, there is no such phenomenon as "vital force." Chemists now know that many substances commonly produced by living things can also be synthesized from inorganic substances. The rules and principles that guide such syntheses are common to both inorganic and organic compounds.

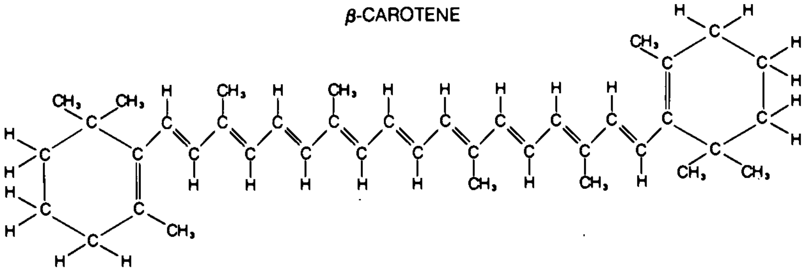
TIME MACHINE

1855	**Marcellin Berthelot produces organic compounds from inorganic compounds by a process he calls "synthesis."**
1856	Sir Henry Bessemer develops converter to reduce the amount of carbon in iron, producing stronger steel.
1857	First perforated postage stamps are used in the United States.
1858	Ottawa becomes the capital of Canada.
1859	Richard Wagner completes his tenth opera, *Tristan und Isolde.*
1860	**Marcellin Berthelot publishes his theories and methods in *Organic Chemistry Based on Synthesis*, finally disproving "vital force theory."**
1861	American Civil War begins.

O-2 Diversity of Organic Molecules

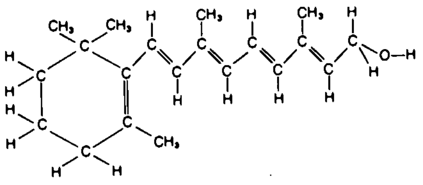
Almost all organic compounds contain hydrogen in addition to carbon. Organic molecules come in many sizes and shapes. They range from the simplest molecular compound, *methane,* which contains only one carbon atom and four hydrogen atoms (CH_4), to those containing many, many carbon atoms in complex arrangements. An example of one of the large molecules is β-carotene ($C_{40}H_{56}$).

β-CAROTENE



β-carotene gives carrots their orange color. In the human body this compound is easily *converted* to a simpler compound, vitamin A, an essential nutrient. Vitamin A provides resistance to infectious diseases and is also necessary for good eyesight. β-carotene is found in carrots, spinach, milk, liver, sweet potatoes, egg yolks, and fish-liver oils.

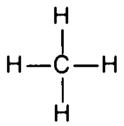
VITAMIN A



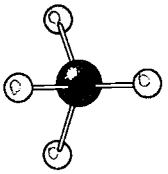
METHANE

CH_4

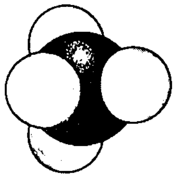
molecular formula



structural formula



ball-and-stick model

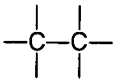


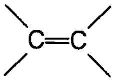
space-filling model

There are other organic compounds that have the same molecular formula as β-carotene ($C_{40}H_{56}$) but have different *structural formulas;* that is, the atoms in the molecules are arranged differently. Actually, there is an amazing number of ways of putting together forty carbon atoms and fifty-six hydrogen atoms. In your spare time, if you have a few years or a computer, you might see how many different structures you can create with forty carbon atoms and fifty-six hydrogen atoms.

Because of all the possible numbers and arrangements of carbon atoms, it is difficult to generalize about the properties of a "typical" organic compound. Some, such as Teflon, an organic polymer, are extremely stable. Others, such as nitroglycerin, are so unstable that they are explosive at room temperature. However, in studying the organic compounds, chemists have found that some classes of compounds react similarly. These have been grouped according to certain common characteristics (properties). Among the various classes of organic compounds are the hydrocarbons, alcohols, aldehydes, ketones, esters, and organic acids.

O-3 Carbon's Covalent Bonds

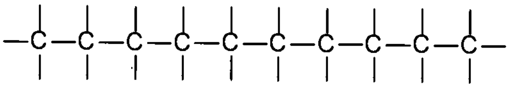

single bond


double bond

$-C\equiv C-$

triple bond

Organic compounds far outnumber inorganic compounds because carbon has the ability to link with itself and with other atoms in a great variety of ways. A carbon atom readily forms *covalent bonds.* It *shares* pairs of electrons with other carbon atoms or with atoms of a different element. A single carbon atom can form four covalent bonds with other atoms. With this four-way sharing—known as *tetravalence*—long chains of C—C bonds can easily be formed, resulting in the possible existence of large, bulky molecules. The carbon skeleton shown here illustrates a chain of covalent single bonds.



In many organic compounds carbon is linked to another atom by a *single covalent bond.* When a single bond is formed, the atoms share one pair of electrons. But the bonding capacity of carbon is not limited to a single covalent bond. The carbon atom can also be linked to another atom by means of a *double bond* or even by a *triple bond.* A double covalent bond is formed when atoms share two pairs of electrons. In a triple bond three pairs of electrons are shared. The ability of carbon to form multiple bonds is another reason for the large number of organic compounds. Let's look at the simplest of the organic compounds, the hydrocarbons.

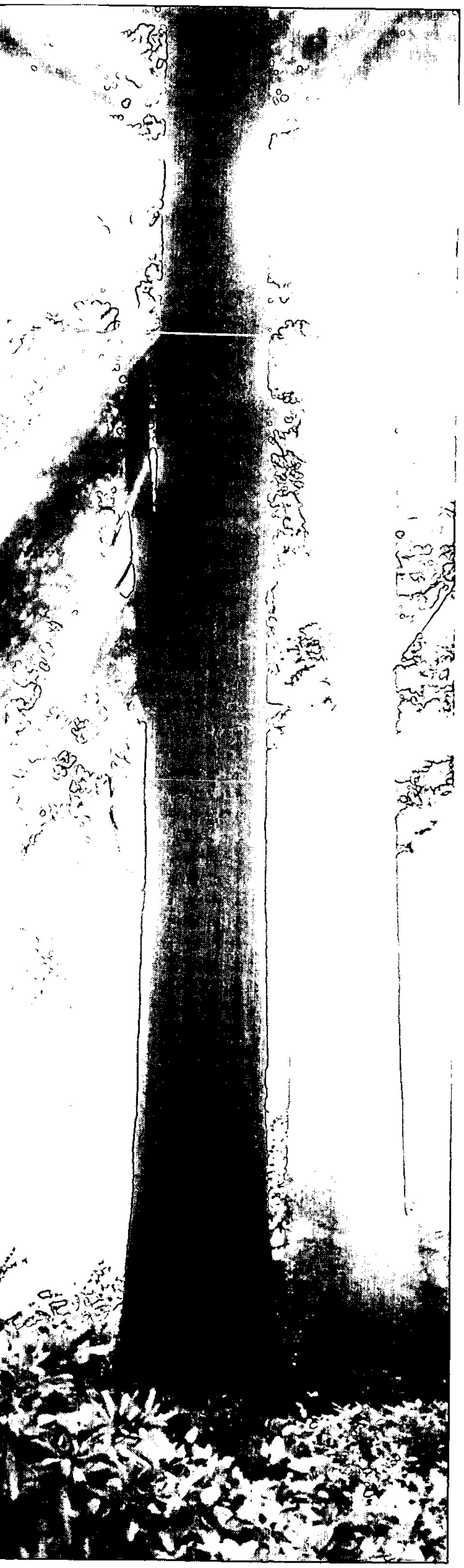
TIME MACHINE

1855	Walt Whitman publishes *Leaves of Grass.*
1856	Gail Borden patents condensed milk process.
1857	Elisha G. Otis installs world's first passenger elevator.
1858	**Kekule von Stradonitz and Archibald Couper formulate concept of tetravalent carbon.**
1859	Charles Darwin publishes *On the Origin of Species by Natural Selection.*
1860	Robert Bunsen and Gustav Kirchhoff discover new elements—cesium and rubidium.
1861	George Eliot publishes *Silas Marner.*

Hydrocarbons

A hydrocarbon is an organic compound that contains *only* carbon and hydrogen. β-carotene ($C_{40}H_{56}$) is a hydrocarbon, but as we mentioned before, it is a rather complex example. Methane (CH_4) —sometimes called marsh gas—is the simplest hydrocarbon. As the principal constituent of natural gas, it is of great importance to the fuel industry as a source of energy.

Great swamps such as this were in abundance over 250 million years ago. Through the years, the vegetation died, decayed, and decomposed to form hydrocarbon layers. Now after millions of years, we extract these hydrocarbons from beneath the surface of the earth for fuels.



O-4 Energy: From the Sun to You

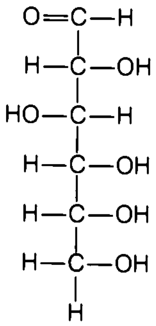
There are many hydrocarbons that are of interest to the chemist in determining the best and most economical sources of energy for our society. Although methane is the simplest of the hydrocarbons, would some of the more complex hydrocarbons serve as better sources of energy? And why is it that these hydrocarbons are such an important energy source? Let's examine where they all came from.

Like methane, almost all the organic compounds we know today are derived from living organisms—ones that lived in the past or that are living now. Plants have the ability to harness the sun's energy and put it to work. As a green plant lives and grows, it uses light, the energy of the sun, to convert carbon dioxide and water into the organic compound *glucose*—a sugar, used for food by plants and animals. This process is known as *photosynthesis* and can be represented by the equation

$$\underset{\text{(sunlight)}}{\text{energy}} + 6CO_2 + 6H_2O \longrightarrow \overset{\text{GLUCOSE}}{C_6H_{12}O_6} + 6O_2$$

The glucose in plants is a storehouse of chemical energy. Both animals and plants draw on this energy when they "burn" glucose in the cells of their bodies—a process known as *respiration*. Thus green plants, when they make glucose, are converting light energy to chemical energy. Other living organisms, including ourselves, do not have this capability and yet require chemical energy in order to live. Therefore, as consumers of this chemical energy, we are ultimately dependent on green plants for food. Some say that photosynthesis is the most important chemical reaction in the world. What do you think their reasons are for this statement?

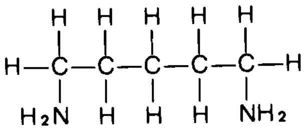
GLUCOSE



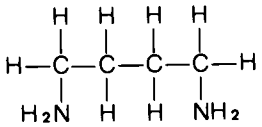
Living organisms have the ability to synthesize a vast number of different organic compounds. But, upon the death of the organism, all organic compounds suffer the same fate: they break down into smaller units, or *decompose*. Although the protein molecule is not a hydrocarbon, it is an easy example to use in explaining the process of decomposition. Protein molecules make up very large, diverse structures such as enzymes, vitamins, hormones, muscles, cell walls, and connective tissues. The large protein molecule decomposes into small units—amino acids. This is why amino acids are commonly defined as the "building blocks" of protein. Some proteins consist of thousands of amino acids strung together in large chains.

Amino acids contain the elements nitrogen, oxygen, hydrogen, and carbon. In time the amino acids themselves break down and decay, just as the parent protein molecule does. Some amino acids break down into distasteful organic compounds such as cadaverine and putrescine, which give decaying matter an unpleasant odor.

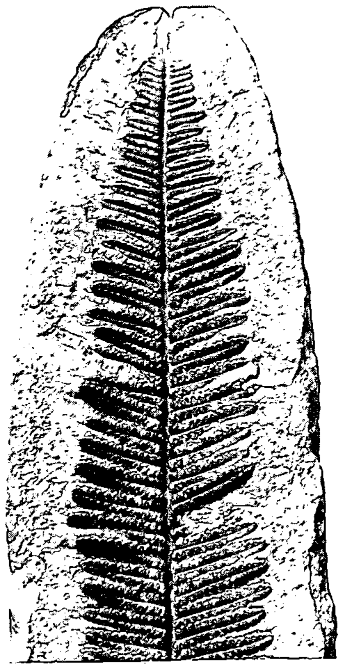
CADAVERINE



PUTRESCINE



Finally, these compounds can decompose to form simple hydrocarbons. It is important to note that the products of decomposition depend on the composition of the living organism and the conditions under which decay takes place. For example, as plant matter decays in swamp water, the simple hydrocarbon methane is formed. Although this type of decomposition is not the source of our natural gas supply today, it is an example of the complex process of plant material being converted to a simple hydrocarbon. Most of the natural gas that is used today—the main constituent of which is methane—is trapped in areas under the surface of the earth.



This fossil fern is one of the many types of plants that lived on the earth millions of years ago. Some underwent the change to hydrocarbons that provide us with modern fuels.

O-5 Fossil Fuels: Stored Organic Energy

Some decaying plant material such as the giant ferns, reeds, and grasses that grew millions of years ago "disappeared" into the earth. After millions of years these deposits formed peat, coal, and petroleum. These are often called *fossil fuels* to suggest that they came from living organisms. If left undisturbed, forms of carbon such as peat and coal eventually become graphite, a form of pure carbon. With sufficient heat, pressure, and time, diamonds may also be formed from the same material.

When we burn a hydrocarbon such as coal or gas, the compound combines with the oxygen in the air to give carbon dioxide (CO_2), water (H_2O), and energy. An equation for this reaction using the simplest hydrocarbon, methane, is

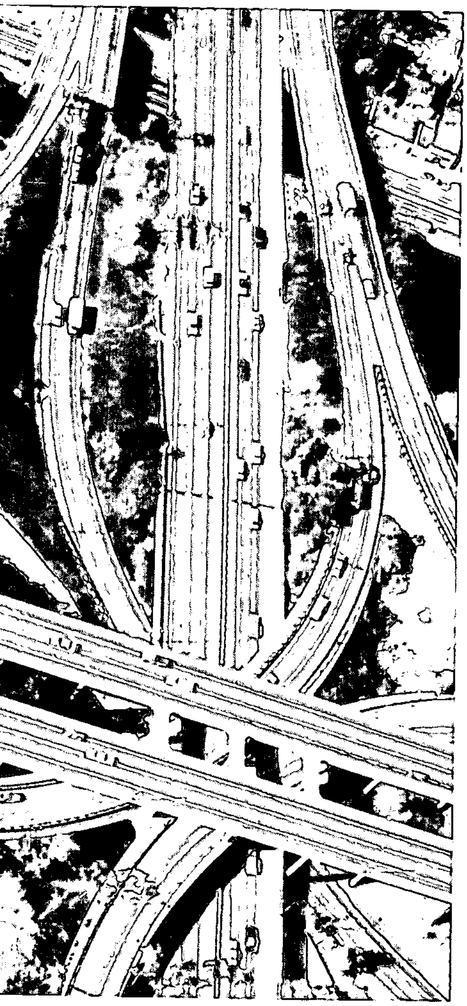
$$\begin{array}{ccccccc} \text{METHANE} & & \text{OXYGEN} & & \text{CARBON DIOXIDE} & & \text{WATER} \\ CH_4 & + & 2O_2 & \longrightarrow & CO_2 & + & 2H_2O + \text{energy} \end{array}$$

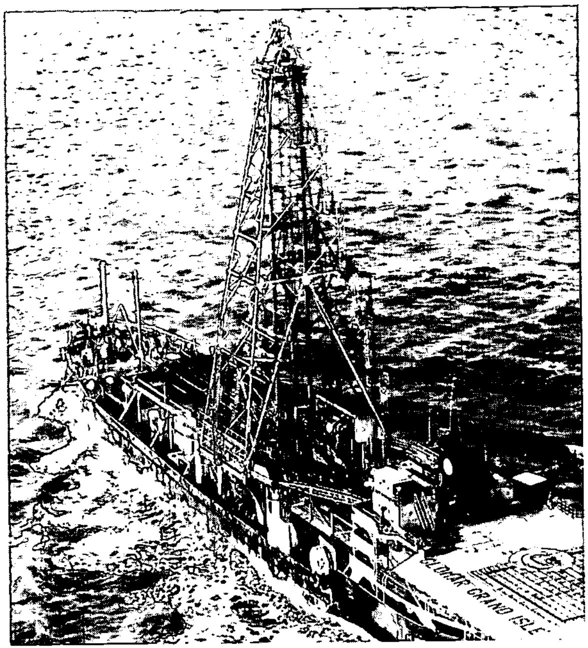
Compare this equation with the one representing the process of photosynthesis in section *O-4*. Can you see any relationship between the two reactions?

O-6 Energy Plus Problems

Three of the most important hydrocarbon fuels are represented on these pages in the form of coal, oil, and natural gas. Offshore oil exploration *(right-hand page)* is becoming a major source of our oil supply. A geologist examines material drilled from beneath the surface of the earth to determine its hydrocarbon fuel content. A simple formation of valves and pipes above ground is sometimes the only clue to a natural gas well. Coal is now being mined with modern automatic machines.

Let's look for a moment at the fossil fuels *coal* and *petroleum*. Petroleum products such as gasoline and fuel oil provide us with a substantial portion of the energy needed to sustain today's technological society. Petroleum also yields raw materials for the production of plastics, synthetic fibers, synthetic rubber, paints, cosmetics, drugs, fertilizers, and many organic chemicals. Coal, once a major fuel source in the United States, is slowly coming back into use now that we must conserve our supply of oil and natural gas. Through research we are discovering ways to improve the burning of coal, eliminating many of the problems of contaminants that once polluted the atmosphere. Coal is also important to us because it provides raw materials for the production of steel, drugs, insecticides, synthetic fibers, and ammonia and is used in the production of many other organic chemicals.

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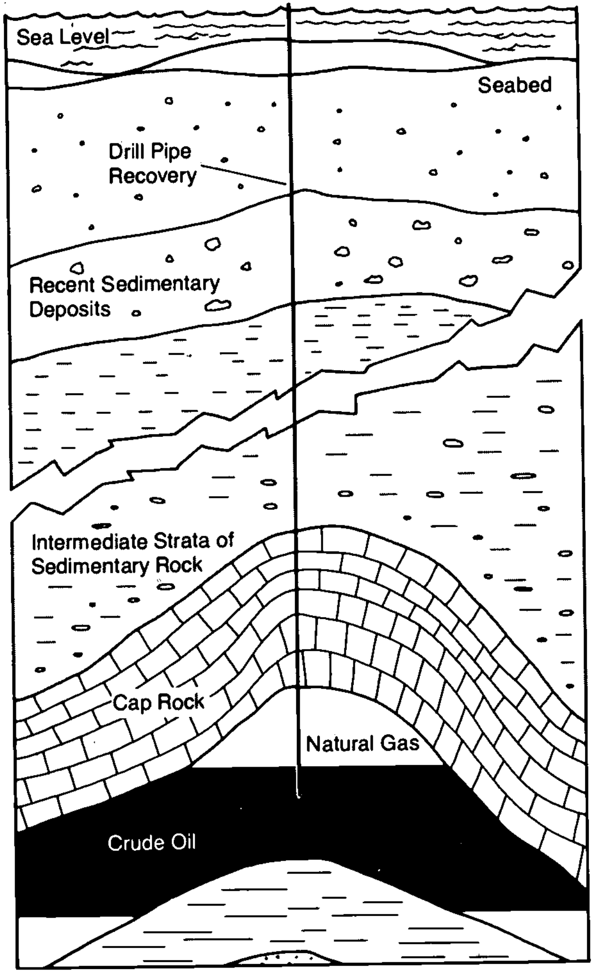
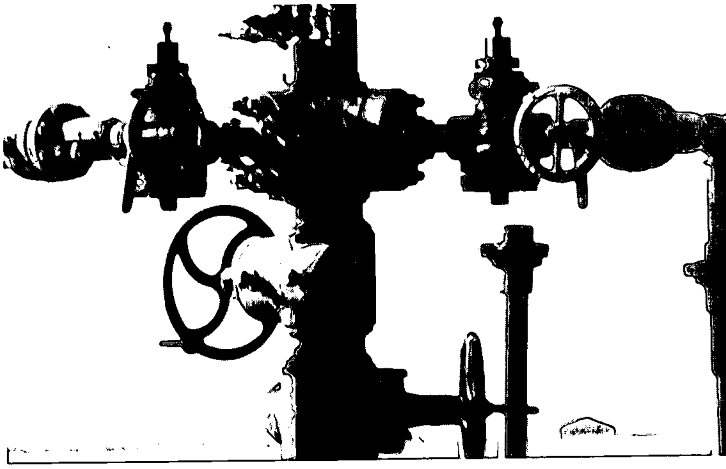
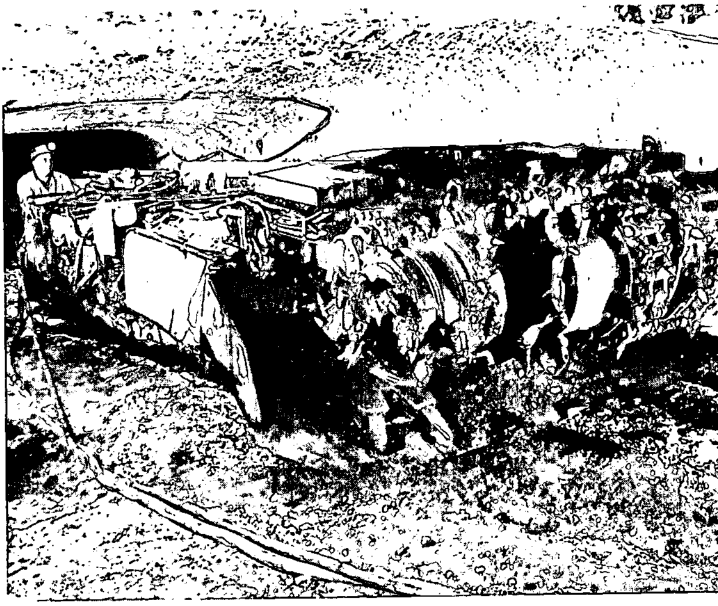

Sea Level
Seabed
Drill Pipe Recovery
Recent Sedimentary Deposits
Intermediate Strata of Sedimentary Rock
Cap Rock
Natural Gas
Crude Oil





Nearly all the compounds in coal and petroleum are hydrocarbons, but there are compounds other than hydrocarbons in petroleum—these are *contaminants*. The principal and most troublesome contaminants are organic sulfur compounds. When fossil fuels are burned, the sulfur is converted to sulfur dioxide (SO_2), which reacts with water vapor in the air to produce sulfurous acid, a corrosive compound.

Air pollutants are causing much damage to our environment as illustrated on the following page. Damage to living things can be seen in the photographs of the leaf and in the scene where vegetation growth has stopped. Even though pollution from an industrial site was curbed, this scene has remained unchanged for many years. Damage to nonliving things as well as to living things is all around us. The statue is an example of the corrosive action of air pollutants.

$$S + O_2 \longrightarrow SO_2$$

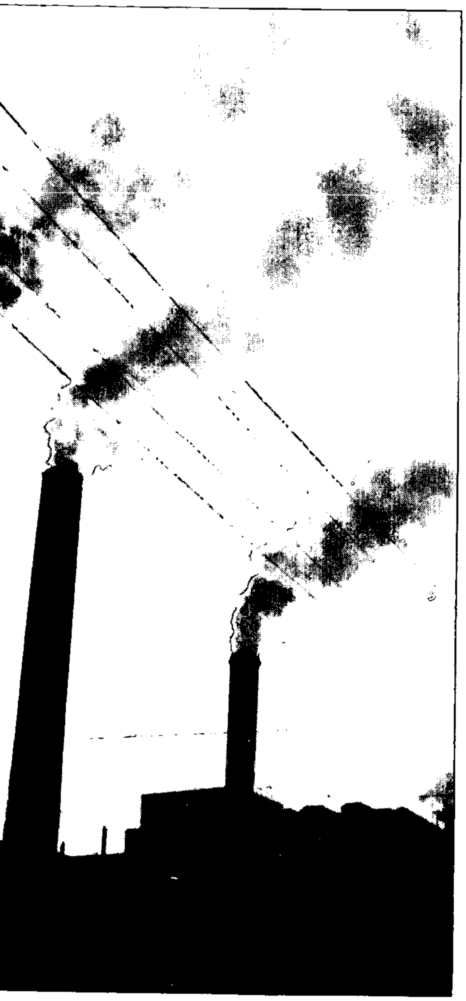
$$SO_2 + H_2O \longrightarrow H_2SO_3$$

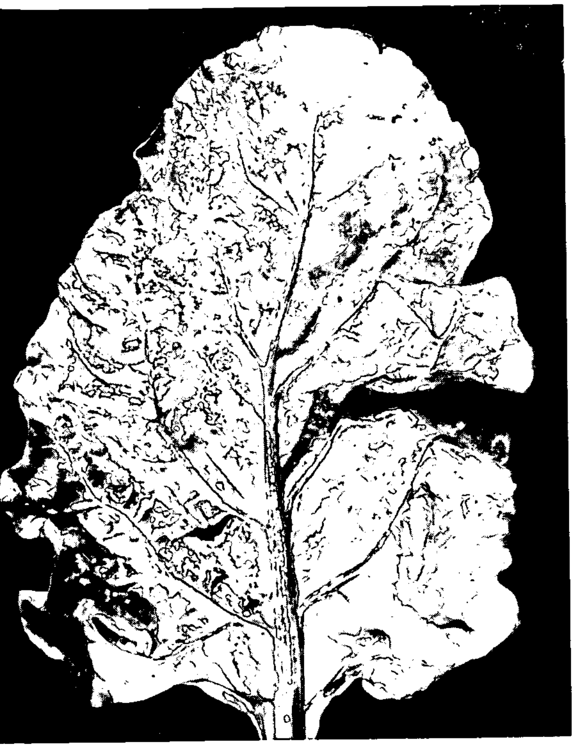
Worse yet, sulfur dioxide reacts with oxygen in the air to form sulfur trioxide (SO_3). Water vapor converts sulfur trioxide to sulfuric acid (H_2SO_4), which is highly corrosive.

$$2SO_2 + O_2 \longrightarrow 2SO_3 \xrightarrow{2H_2O} 2H_2SO_4$$

Pollution problems, such as smog and the corrosive action of the acid on materials in our environment—buildings, bridges, statues, plants, and our own bodies—result from the uncontrolled release of SO_2 into the atmosphere.

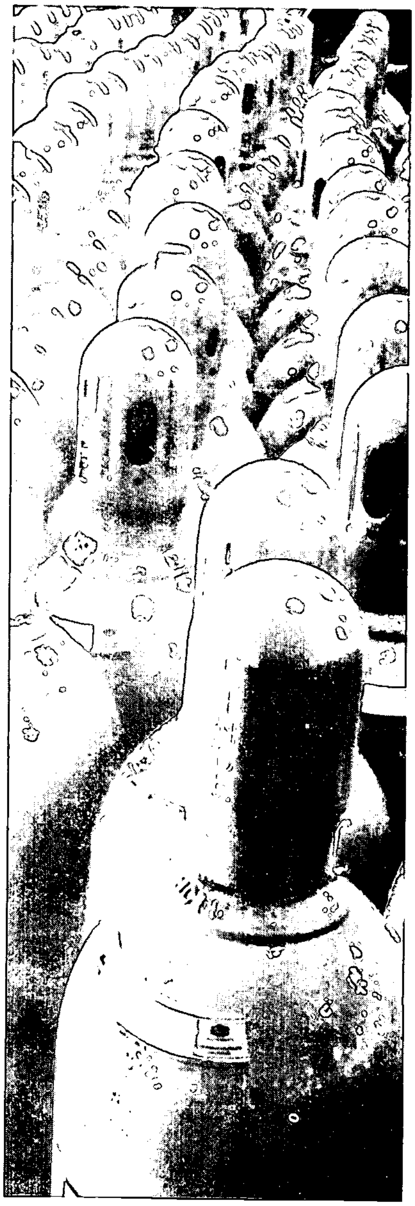
Metals also contaminate coal and petroleum in *trace* (minute) amounts. When the fuels are burned, these metals are released into the atmosphere. The burning of these fuels in large quantities pours thousands of tons of metals into the atmosphere annually. It is not yet clear how dangerous these metals may be to our health and environment, but some are suspected to be very harmful.



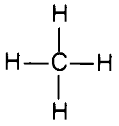


O-7 The Single-Bonded Alkanes

Chemists group the simplest of the hydrocarbons together and call this group the *alkanes*. Most of these are chain compounds. In some the carbons are linked in *straight chains;* in others the carbons are linked in *branched chains*. The carbon-carbon bonds in the alkanes are single covalent bonds—one pair of electrons is shared (C:C). The first six members of the alkane family are methane, ethane, propane, butane, pentane, and hexane.

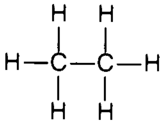


METHANE



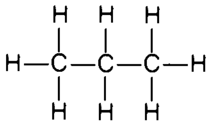
$\mathrm{H-\overset{H}{\underset{H}{C}}-H}$

ETHANE



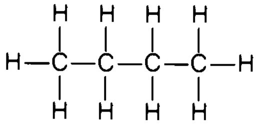
$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$

PROPANE



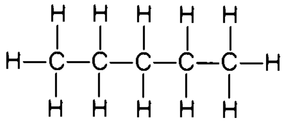
$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$

BUTANE



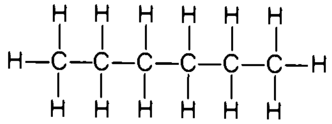
$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$

PENTANE



$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$

HEXANE



$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$

Methane (CH_4) is a colorless, odorless gas that does not become a liquid until its temperature drops to −161°C, far below any temperature reached naturally on the surface of the earth. The next members of the alkane series, ethane (C_2H_6) and propane (C_3H_8), are also gases. Butane (C_4H_{10}) is a gas at room temperature, but it changes into a liquid at about 0°C (the freezing point of water). Butane and propane are used in "bottled gases" and as fuels in some cigarette lighters. The C_5 (pentane) and C_6 (hexane) hydrocarbons are extremely *volatile* (they change easily from a liquid state to a gaseous state at room temperature). The pentanes and hexanes are used as solvents and as "dry cleaners." These liquids are highly flammable.

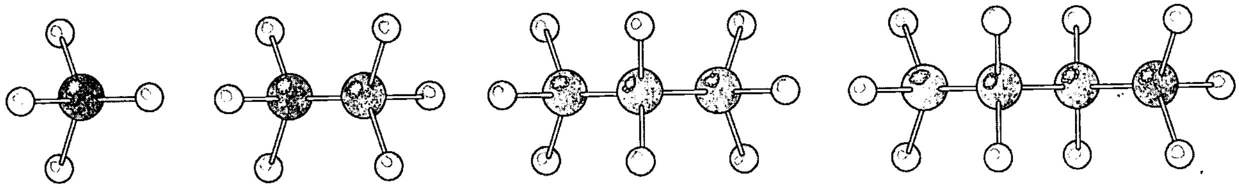
Note that each member of the series differs from the previous one by a multiple of CH_2; this generates the general formula for alkanes, C_nH_{2n+2} (see table *Some Compounds in the Alkane Series* in section *O-12*).

O-8 Straight-Chain Molecular Models

miniexperiment

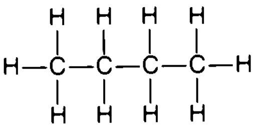
Obtain the materials to construct models of simple organic molecules. You will need to represent bonds, carbon atoms, and hydrogen atoms in your models. Construct as many different molecular structures as you can, using six or fewer carbon atoms. How many bonds to a carbon? to a hydrogen?

If you study the ball and stick models illustrated, you will note that they represent three-dimensional organic molecules. By now you will probably be able to recognize the hydrocarbon each model represents.



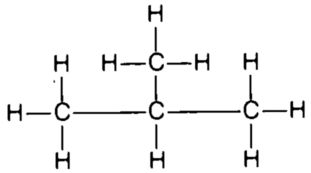
Let's stop for a moment and look at butane, because with its molecular formula C_4H_{10} a phenomenon known as *isomerism* arises. When the same number and types of atoms can be combined in more than one way to form different structures, the result is *isomers*. Or, to restate, isomers are two or more different compounds that have the same molecular formula but different structures. For example, there are two different butanes: normal butane (written as *n*-butane) and *iso*butane.

n-BUTANE



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

ISOBUTANE



Note that these two compounds have the same molecular formula and the same number of atoms of each kind—but different structural arrangements and therefore different properties. For example, isobutane remains a gas until the temperature has been lowered to −10°C, whereas *n*-butane liquefies at 0°C.

The *n*-butane is a *straight-chain* hydrocarbon. Each carbon atom lies along an imaginary straight line that connects the carbon atoms in the chain. Each carbon atom is connected to no more than two other carbon atoms. In isobutane one carbon atom lies off the main

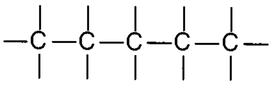
TIME MACHINE

1826	James Fenimore Cooper writes *The Last of the Mohicans.*
1827	Karl Baedeker issues first of his famous travel guides.
1828	Noah Webster publishes his first *American Dictionary of the English Language.*
1829	Andrew Jackson is inaugurated president of the United States.
1830	D. Hyde patents the first fountain pen.
1831	Cyrus H. McCormick demonstrates first practical reaper.
1832	**Jöns J. Berzelius proposes the name isomer for compounds of identical composition but with different properties.**
1833	Davy Crockett's autobiography is a bestseller.

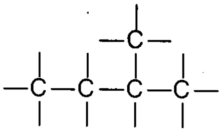
strand that connects the other carbons. This is referred to as *branching*. Thus isobutane, an isomer of butane, is said to be a *branched-chain* hydrocarbon. Note that in branched-chain hydrocarbons at least one carbon atom must have more than two carbon atoms connected to it. Can you find this carbon atom in the structure of isobutane?

Pentane (C_5H_{12}) has three isomers. The following carbon skeletons of the isomers of pentane illustrate other examples of straight- and branched-chain hydrocarbons.

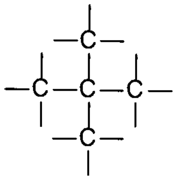
n-PENTANE



ISOPENTANE



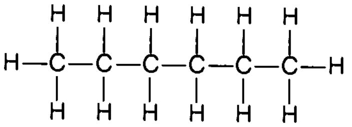
NEOPENTANE



Note the different properties of the isomers of pentane by examining their boiling points: *n*-pentane, 36°C; isopentane, 28°C; and neopentane, 9.5°C.

Hexane (C_6H_{14}) has five isomers. The structural formula for *n*-hexane is shown here. Write the structural formulas for the other four isomers.

n-HEXANE



miniexperiment

O-9 Branched-Chain Molecular Models

In miniexperiment *O-8* you constructed models of straight-chain molecules. Use the same materials to make models of the isomers of hexane and of other branched-chain molecules that you have been discussing.

As you continue your reading and discussion of the alkane series, you may wish to try to construct models of some more complicated molecules. Why is model making an important tool of the organic chemist? What kinds of information can a chemist learn from this type of activity? (See *Molecules in Living Systems: A Biochemistry Module* for photographs of scientists and the elaborate models of biomolecules they have constructed for study.)

Despite the vast array of organic compounds, almost all have several characteristics in common. One characteristic, the behavior of organic compounds when heated, makes an interesting study and an appropriate consideration for the chemist interested in the hydrocarbons. Most organic compounds burn, whereas typical inorganic compounds do not burn or even melt at the flame temperature of a Bunsen burner. Set up the following experiment to compare the behavior of organic compounds with the behavior of some common inorganic compounds when both are heated.

O-10 Comparing Properties

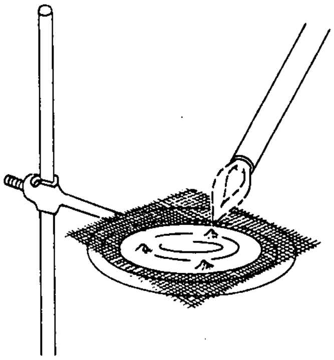
miniexperiment

This symbol represents three of the common hazards in a chemistry laboratory—flame, fumes, and explosion. It will appear with certain experiments in this module to alert you to special precautions in addition to those discussed in Appendix 1.

Distribute a small sample, the size of a match head, of the following materials around the outer edge of a tin can lid: sugar, paradichlorobenzene, calcium carbonate.

Place the lid on a ring attached to a ring stand. Direct the tip of a Bunsen flame directly onto each material and observe the result. **Caution:** *Keep your head and hair well back from the heating area.* Does the material tested melt or burn? Record your results.

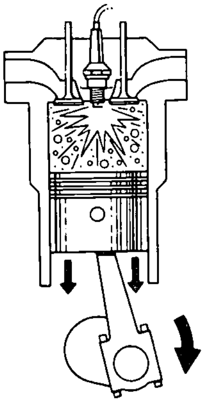
Repeat the setup, using another can lid and samples of the following: naphthalene, paraffin, salt (NaCl), a drop of mineral oil. Again record your results.

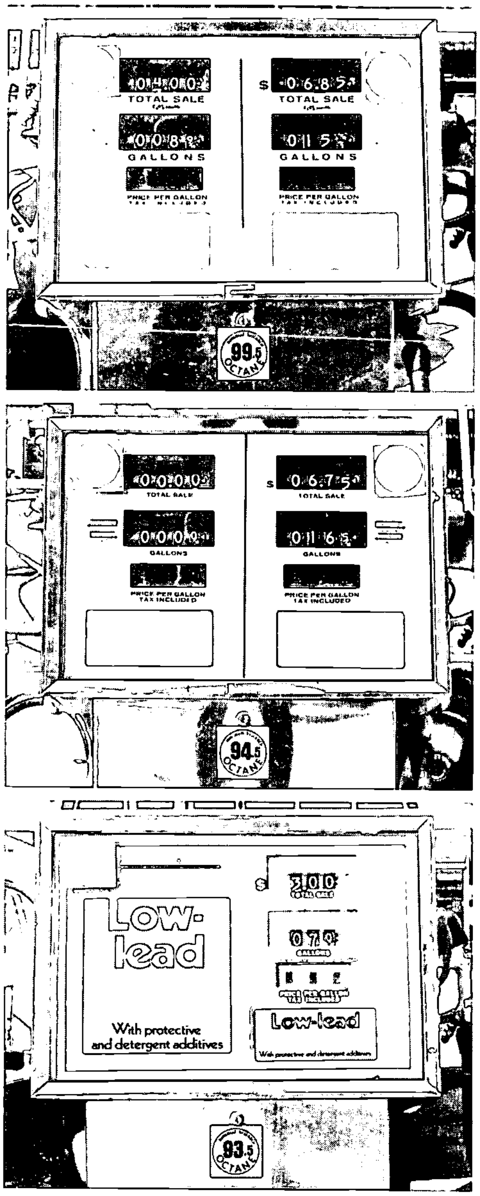


Questions: Which of the substances were organic compounds? How did the inorganic compounds react? Could you have tested in this manner any of the hydrocarbons you previously discussed? Why?

O-11 Fuels: How Well Do They Burn?

The C_7 (heptane), C_8 (octane), and C_9 (nonane) hydrocarbons are the main ingredients of gasoline. If you tried to burn heptane (C_7H_{16}) in an automobile engine, it would burn too rapidly and generate an explosion in the cylinder, upsetting the normal in-and-out motion of the pistons. This causes the "pinging" sound commonly referred to as engine knock. Fuels that are composed mostly of straight-chain hydrocarbons such as *n*-heptane perform poorly in a car engine. On the other hand, fuels composed of more branched hydrocarbons, such as an isomer of octane (C_8H_{18}) called isooctane, perform quite well in automobile engines. This compound burns in such a fashion that the piston moves smoothly up and down in the cylinder.





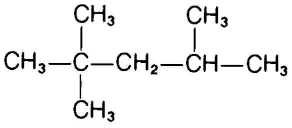
There are instruments that are used to measure accurately the degree of engine knock. An arbitrary scale rates *n*-heptane at 0 and isooctane at 100. The rating is called the *octane number*. Almost all automobiles run well on gasoline whose octane rating is between 89 and 100. An average rating of 89, which is the rating for a regular grade of gasoline, would be equivalent to a fuel made of 89 percent isooctane and 11 percent *n*-heptane. Premium gasolines have an average rating of about 95 octane.

n-HEPTANE

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

octane rating = 0

ISOOCTANE

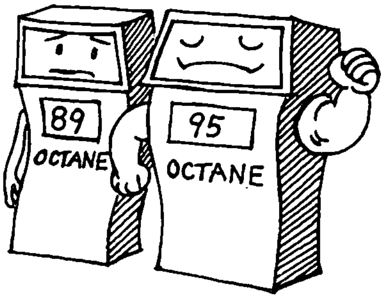


$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3$$

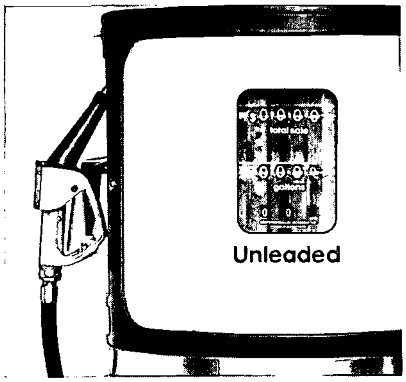
octane rating = 100

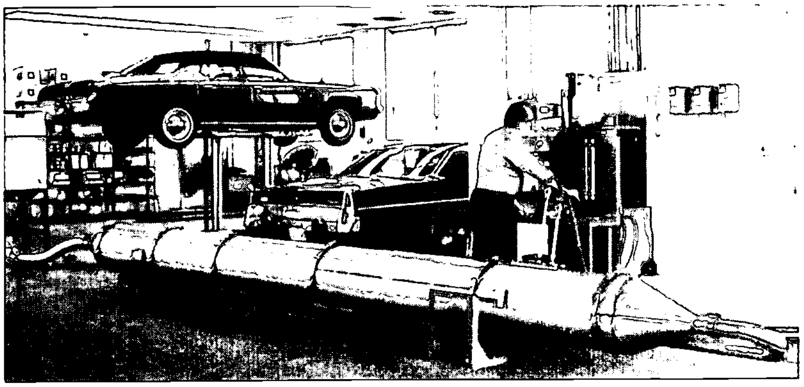
The higher-octane fuels are more difficult to produce and therefore more expensive than the lower-octane gasolines. To get around this problem, the petroleum industry developed *additives*. The most famous additive, tetraethyl lead (TEL), $Pb(C_2H_5)_4$, increased the octane rating of the poorer-grade fuels by slowing down the rate at which the hydrocarbons burn. This slowing down makes it possible for the engine to fire smoothly, without knocking.

Although TEL eliminates knocking, it is not without its problems. The most immediate problem for the motorist is that when TEL burns, it deposits lead in the engine. Lead fouls up the works. To get around this problem, petroleum chemists added 1,2-dibromoethane (CH_2BrCH_2Br) and 1,2-dichloroethane (CH_2ClCH_2Cl) to the fuel along with the tetraethyl lead. The bromine and chlorine in these compounds combine with the lead to produce inorganic lead halide salts. These salts are volatile enough to pass through the exhaust and into the air. Unfortunately, lead compounds are poisonous, and therefore they present a hazard when they escape into the atmosphere.

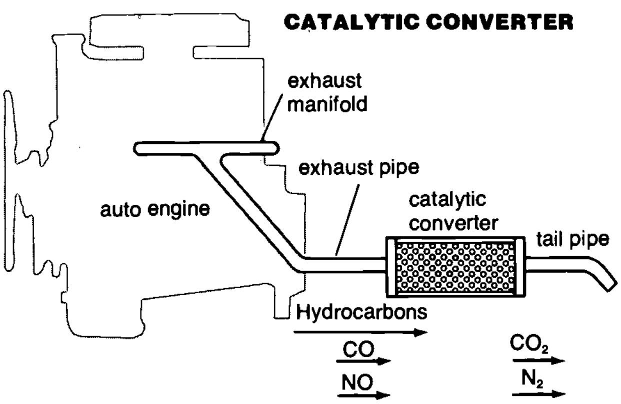


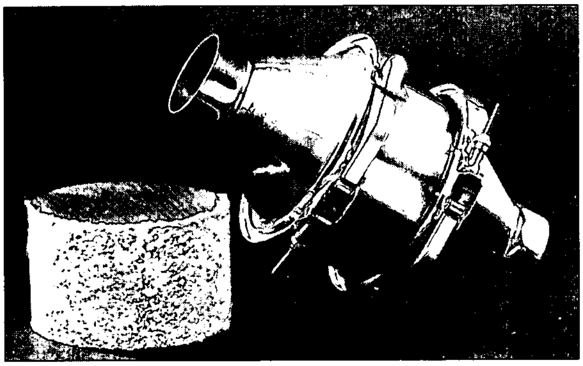
To cut down on other pollutants in the exhaust, engineers have fitted many new cars with antipollution devices. A metal catalyst in these devices ensures the maximum conversion of hydrocarbon fuel to carbon dioxide. Heavy metals, such as lead, poison these catalysts, just as they poison our body catalysts, the enzymes. As a result of this poisoning, many antipollution devices become useless after a short time *if* leaded gasoline is used. To prevent these devices from becoming useless, federal law now prohibits use of leaded gasolines in cars fitted with catalytic converters.





Federal law requires the use of unleaded gas and catalytic converters in cars sold today to control pollution.





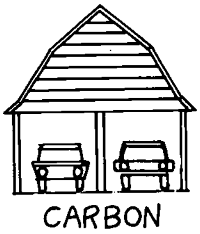
The trend today is away from leaded fuels and toward the more expensive high-octane fuels. The high-octane fuels usually contain aromatic or ring hydrocarbons such as toluene, which is normally used as an antiknock ingredient in aviation gas. However, even the aromatic (ring) hydrocarbons (see section *O-15*) are not without their problems, because they burn "dirtier" than chain hydrocarbons found in gasoline. Thus, we trade off one form of pollution for another. Solving problems such as these may well prove expensive. A great many chemists today are working hard to solve these and many other problems affecting our environment.

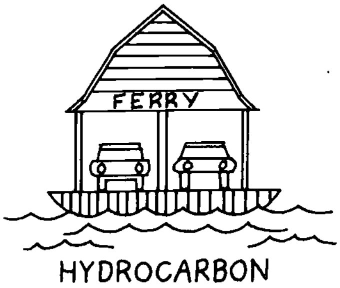
The internal combustion engine presents several other problems besides introducing lead into the atmosphere. When hydrocarbons are burned, they often undergo incomplete combustion—that is, all the hydrocarbons do not burn completely.

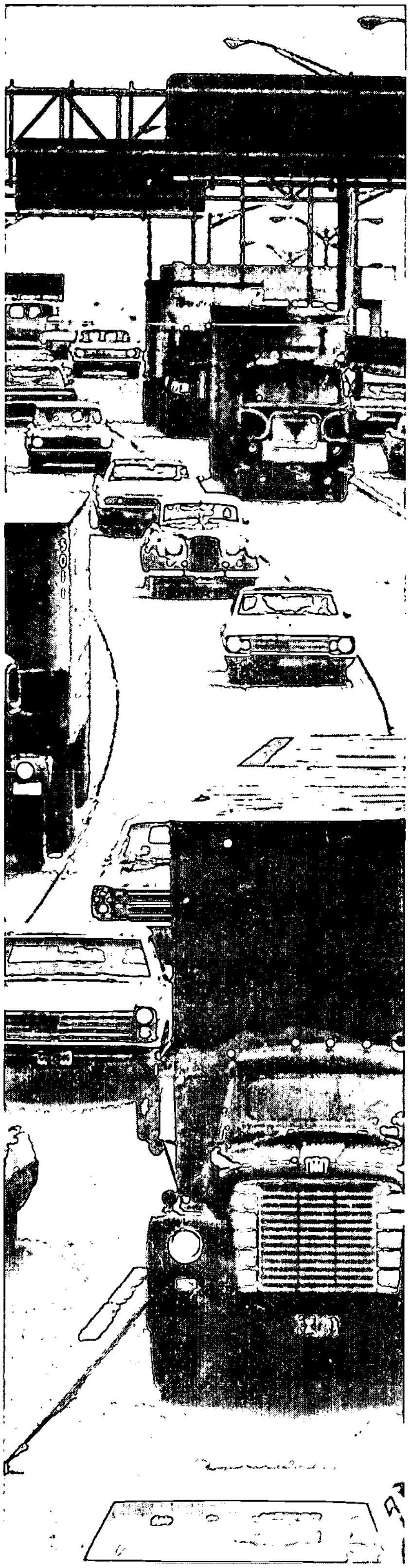
$$\underset{\text{(excess)}}{C + O_2} \longrightarrow CO_2$$

$$\underset{\text{(deficient)}}{C + O_2} \longrightarrow CO$$

Thus we introduce these unburned hydrocarbons and carbon monoxide into the air. In the human body carbon monoxide acts as a poison by competing with oxygen for hemoglobin, the oxygen-







carrying compound in the blood. People who die of carbon monoxide poisoning actually die of suffocation from lack of oxygen. Fortunately, carbon monoxide poisoning is reversible if caught in time.

Another problem of the internal combustion engine is that the heat produced inside the cylinders of an engine is sufficient to cause the oxidation of normally unreactive nitrogen gas. Nitrogen is present in the air that is introduced into the cylinder to aid the combustion of the fuel. It reacts with oxygen to form nitrogen oxides—particularly nitrogen dioxide, NO_2.

$$N_2 + O_2 \longrightarrow 2NO \xrightarrow{O_2} 2NO_2$$

Although nitrogen dioxide is not produced in great enough quantities to be an irritant in itself, it can act as a "trigger" for the production of some rather unpleasant organic compounds called peracyl nitrates (PAN). These are the ingredients in smog that irritate the eyes and the lining of the throat.

O-12 Separating Hydrocarbons

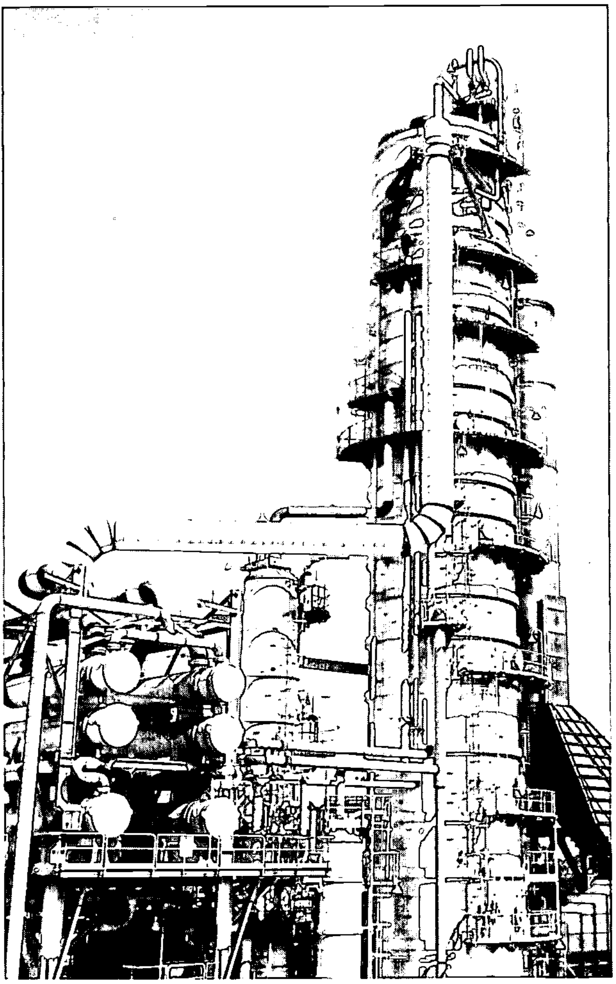
Because of the molecular makeup of hydrocarbons, they can usually be separated by *fractional distillation*. This is a rather simple and useful process for separating many of the hydrocarbon fractions of petroleum. The basic idea behind fractional distillation is that each compound in the hydrocarbon mixture has its own boiling point, as can be seen in the accompanying table.

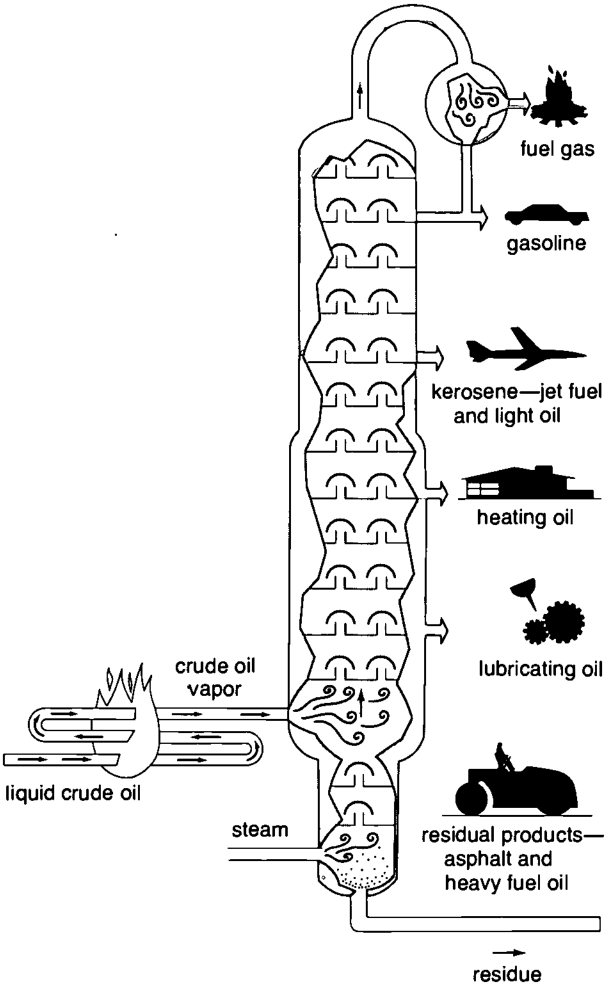
SOME COMPOUNDS IN THE ALKANE SERIES

General Formula: C_nH_{2n+2}

Name	Formula	Melting Point (°C)	Boiling Point (°C)	Possible Isomers
methane	CH_4	−183	−162	1
ethane	C_2H_6	−183	−89	1
propane	C_3H_8	−187	−42	1
n-butane	C_4H_{10}	−135	0	2
n-pentane	C_5H_{12}	−130	36	3
n-hexane	C_6H_{14}	−94	69	5
n-heptane	C_7H_{16}	−90	98	9
n-octane	C_8H_{18}	−57	126	18
n-nonane	C_9H_{20}	−54	151	35
n-decane	$C_{10}H_{22}$	−30	174	75
. . .				
n-pentadecane	$C_{15}H_{32}$	10	271	4347

Therefore, as a mixture of hydrocarbons is heated, each component boils at a different temperature. The mixture to be distilled is placed in a heating vessel which is attached to a cooling device called a condenser. As the material is heated, each component in the mixture reaches its boiling point, changes into a vapor, and "boils away." As the vapor encounters the cooling device (condenser), it recondenses as a liquid and is collected in another container.



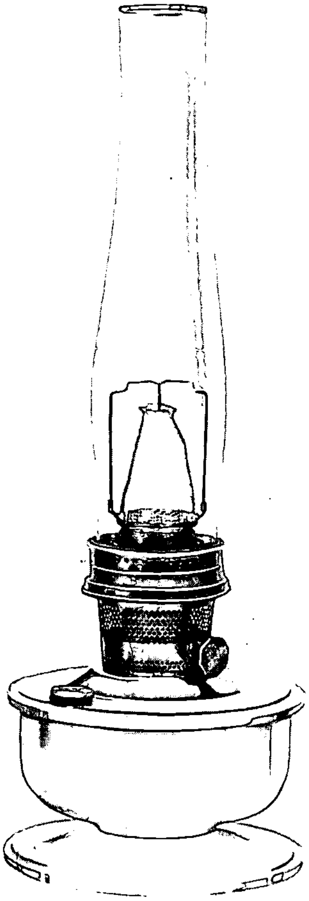


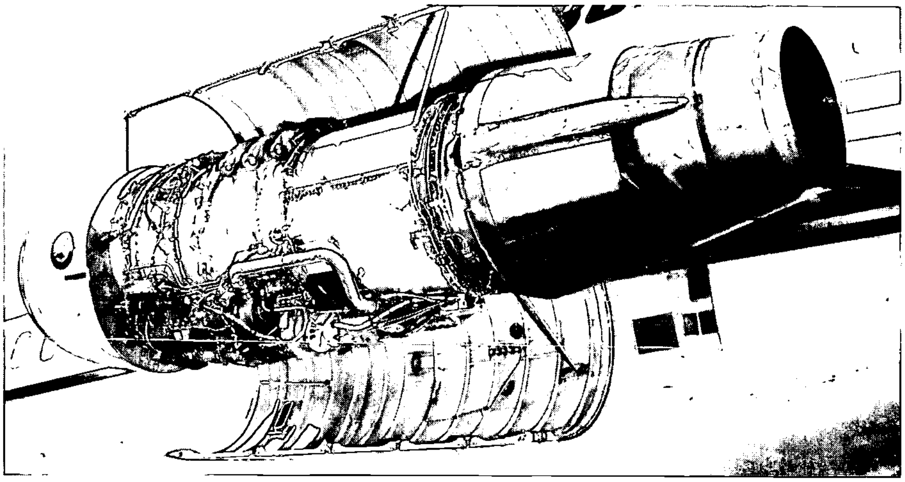
Kerosene, which was popular a century ago as a fuel for lamps and heaters, is the petroleum fraction containing the C_{10} to C_{14} hydrocarbons (boiling points from 175°C to 275°C). Today kerosene is used mainly as a jet fuel and in some home furnaces. Diesel oil, used in diesel engines (devised by the German engineer Rudolf Diesel), has a boiling point slightly higher than that of kerosene. Other fractions with higher boiling points produce useful substances such as mineral oil and lubricating oil.

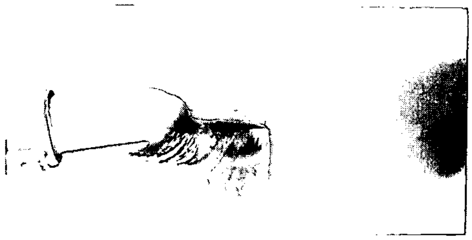
At about C_{22} in the series the alkanes become semisolid and are referred to as *petroleum waxes*. This fraction of petroleum yields paraffin, which is useful for making candles, waxed paper and liners for containers, and petroleum jelly. After the petroleum waxes are removed by distillation, the residue is a black, sticky goo called *petroleum asphalt*. Asphalt is useful for paving roads and for roofing buildings. It is also used in making paints and varnishes.

The following experiment will illustrate the separation of alkanes in a mixture.

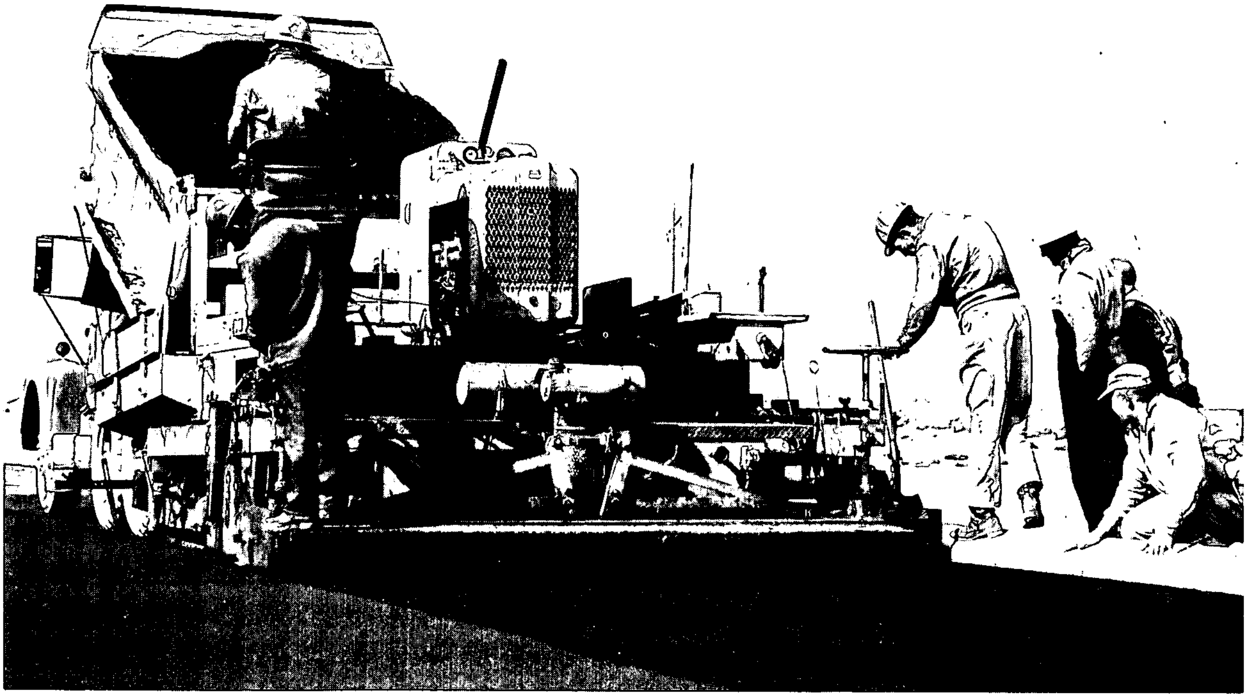
This stamp commemorates the diesel internal-combustion engine that Rudolf Diesel first patented in 1892.







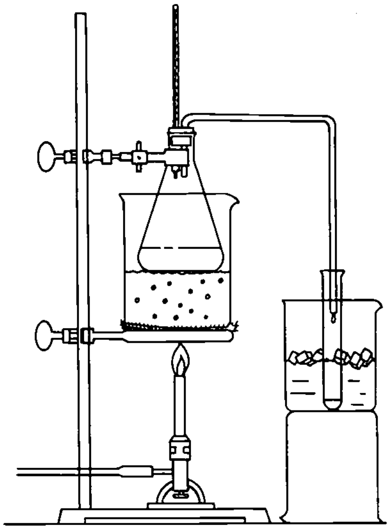
A few derivatives of petroleum—kerosene, jet fuel, motor oil, asphalt, and cosmetics are pictured here. There are hundreds more that you might name; the list alone could fill several of these pages.



O-13 Fractional Distillation

EXPERIMENT

Assemble the distillation apparatus as illustrated. Place 25 cubic centimeters (cm^3) of the mixture to be distilled in a 125-cm^3 Erlenmeyer flask and add two boiling chips. Place a receiving container (test tube) in an ice-water bath. This will help to minimize the loss of vapor. Carefully position the mercury bulb of the thermometer just below the opening in the air condenser tube. This placement is important for accurate temperature readings because the container and the amount of mixture are so small.



Clamp the flask in the water bath. Make sure that the surface of the water just touches the bottom of the flask. Install the tubing and stopper setup in the flask, insert the air condenser tube in the receiving container, and check to see that all the connections are tight. Before starting your distillation, have your instructor check your apparatus.

Begin heating the water bath slowly and record the temperature every 30 seconds. When the temperature levels off, it is an indication that one of the liquids in the mixture is boiling. You should see liquid beginning to collect in the receiving container. (Note: Because water will boil off in the water bath, you will have to adjust the flask to keep the bottom touching the water level.)

When the temperature begins to rise again, the first liquid should be almost completely distilled and the droplets entering the receiving container should stop. Change to a new receiving container when this happens. (Note: If one of the liquids in your mixture has a boiling point higher than that of water, it will be necessary to remove the water bath and heat the flask directly with the burner. Why?) Continue the procedure until there are only a few cubic centimeters of mixture in the flask. **Caution:** *Never heat to dryness!*

Questions: How many different liquids were in your mixture? What were the boiling points of each? What was the relative percent composition of each liquid? (Note: Use a graduated cylinder to measure the volume of each liquid.)

As we have seen, the different hydrocarbons are rich sources of both energy and useful chemicals. Through modern chemical technology chemists have been able to tap these sources so that today we depend on the fossil fuels not only for day-to-day energy needs but also for simple but important items such as clothing, food packaging, and building materials. In the future, however, chemists must find more efficient ways of utilizing hydrocarbons so that our reserves are not depleted or our environment polluted.

Reactions of Hydrocarbons

The alkanes are hydrocarbons formed by carbon atoms that are joined together by single bonds. They are the least reactive group of hydrocarbons. Many other hydrocarbons are more reactive than the alkanes. These other hydrocarbons contain double bonds and triple bonds between carbon atoms. What is there about the various kinds of bonds that makes carbon compounds differ so in reactivity?

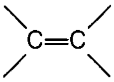
Engineers are using explosives to clear away unwanted buildings, bridges, and other areas much more quickly and safely than was possible in the past. This building collapsed in seconds, a fraction of the time it would have taken to do this by machine.

O-14 How Strong the Bond That Binds

A double bond is formed when two carbon atoms share two pairs of electrons (C::C). Since a carbon-carbon single bond is very strong and unreactive, it might seem logical that a carbon-carbon double bond would be even stronger and more unreactive than the single bond. It is true that it is more difficult to break *both* bonds of a double bond than to break a single bond. However, it is actually easier to break *one of the bonds* in a double bond than it is to break a single bond.

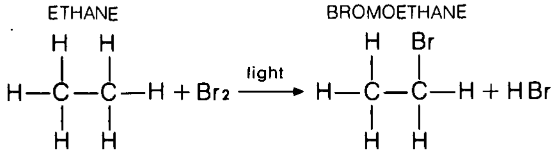
The unreactivity of the carbon-carbon single bond is one of the real strengths of organic compounds. It is this quality that allows nature as well as the chemist to construct such large and elaborate molecules.

Compounds with carbon-carbon multiple bonds such as the carbon double bond



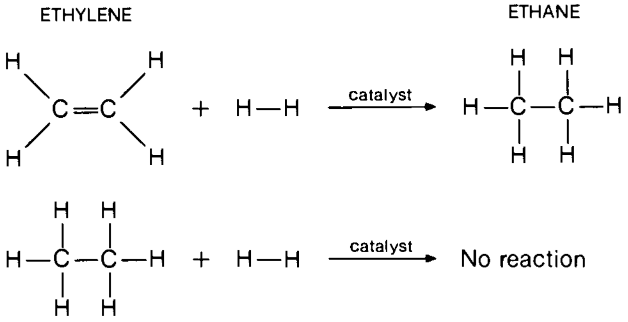
and the carbon triple bond $-C\equiv C-$ are said to be *unsaturated.* A compound with a double bond has two fewer hydrogen atoms than the corresponding alkane with the same number of carbons. A compound with a triple bond has four fewer hydrogens. More hydrogen or other atoms such as the *halogens*—fluorine (Fl_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2)—can be added to these compounds.

The single-bonded hydrocarbons such as methane, ethane, and propane are not able to accommodate any more atoms and are said to be *saturated*. That is, under normal conditions no more atoms can be added to them. For example, ethane, a saturated hydrocarbon, does not react with bromine under ordinary conditions—room temperature, atmospheric pressure, and no catalyst. But if a mixture of bromine and ethane is exposed to a bright light or sunlight a reaction occurs. Light acts as an energy source, causing the mixture to react. This is an example of a *substitution reaction.*



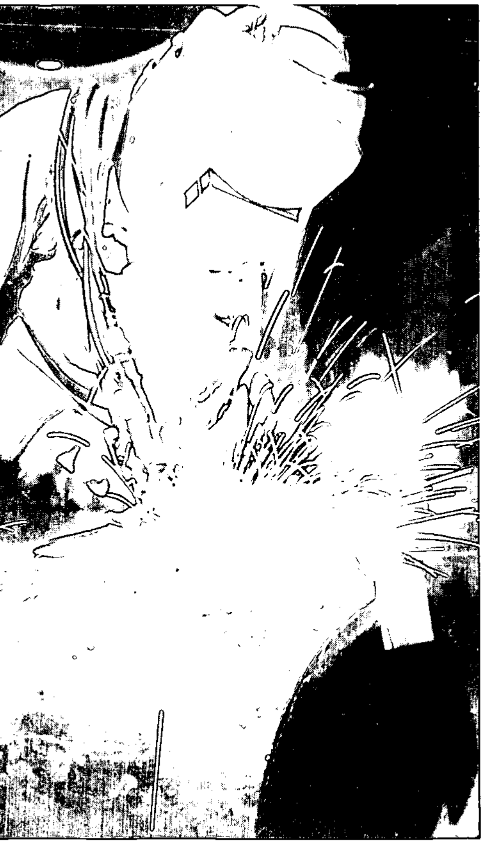
In a substitution reaction one atom in a molecule is replaced by another atom. In this example a bromine atom is substituted for a hydrogen atom in ethane. Note that in a substitution reaction there are two products.

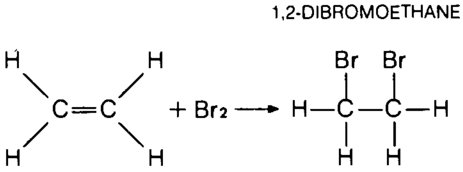
Let's look at another type of reaction. The following equations illustrate the addition of hydrogen atoms to the unsaturated hydrocarbon ethylene to form the saturated hydrocarbon ethane. Notice in the second equation what happens when hydrogen is introduced to the saturated hydrocarbon ethane.



The first equation in this section illustrates a saturated hydrocarbon, ethane, reacting with a halogen. Unsaturated ethylene also reacts with bromine to form a new compound, 1,2-dibromoethane, which results from the addition of bromine across the carbon-carbon double bond.

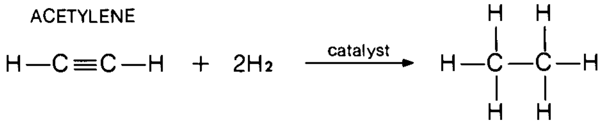
The use of acetylene is being replaced by other modern methods such as electric arc welding and the argon-gas shielded process to weld and cut steel.





In the unsaturated hydrocarbon reactions, two substances react to give a single product. This is called an *addition reaction*.

Compounds that contain two carbon atoms joined by a double bond belong to a group of hydrocarbons called *alkenes*. Alkenes are much more reactive than the alkanes. There is yet another group of hydrocarbons that contain carbon atoms joined by a triple bond, called the *alkynes*. Look at the following equation involving an example of a compound in the alkyne group, the hydrocarbon acetylene.



$$H{-}C{\equiv}C{-}H + 2H_2 \xrightarrow{\text{catalyst}} H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}H$$

Can you determine the types of bonding present in this equation? Which hydrocarbon would be saturated? Unsaturated? What is the name of the product of the acetylene and hydrogen reaction? What could you predict would happen when additional hydrogen or other atoms are introduced to the end product of the reaction? Acetylene is the most important triple-bonded compound of this series. It is a flammable gas useful for welding and cutting steel, and it is also used in the synthesis of other organic compounds.

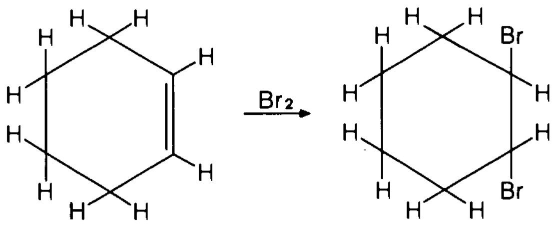
Remember that the alkanes participate in substitution reactions, while the double-bonded and triple-bonded carbon compounds undergo addition reactions. In substitution reactions there are two end products, whereas addition reactions form only one end product. These two types of reactions—addition and substitution—are among the most important reactions in organic chemistry.

O-15 Chains and Rings

As you have seen, carbon atoms readily link to one another and form chains. Since carbon tends to form bonds so readily, what is to keep the ends of a carbon chain from hooking up to each other? Sometimes they do link up, and the result is the formation of *rings* rather than chains. The names for these rings are derived from their straight-chain counterparts, with the addition of the prefix *cyclo-*. For example, the straight-chain hydrocarbon propane can link ends to form a ring called *cyclopropane* (C_3H_6)—the smallest that can be formed, the three-member carbon ring.

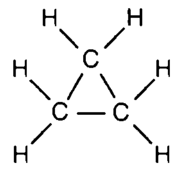
Cyclopropane is used as an anesthetic, although it is highly flammable. Anesthetics (from a Greek word meaning "no feeling") interfere with the transmission of nerve impulses in such a way that the patient feels no pain and usually loses consciousness. Anesthetics are organic compounds, with the exception of nitrous oxide (an inorganic compound sometimes called laughing gas and commonly used in dental surgery). Ether ($C_4H_{10}O$) is another organic compound used as an anesthetic. Chloroform ($CHCl_3$) was also once used as an anesthetic but is now considered too poisonous.

Rings may contain double bonds and triple bonds, just as the chain compounds do. In many regards, compounds that contain carbon-carbon single, double, or triple bonds react similarly, regardless of whether they are ring or chain compounds. Thus, one double bond behaves similarly whether it is in a ring or a straight chain. For example, cyclohexene (C_6H_{10}) reacts with bromine (Br_2) to produce 1,2-dibromocyclohexane, as illustrated in the following equation.

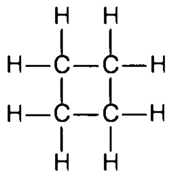


Is this an addition or a substitution reaction? Compare this reaction with that between bromine and ethylene discussed in section *O-14*.

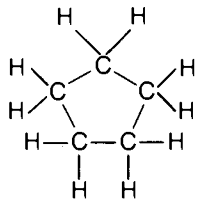
CYCLOPENTANE



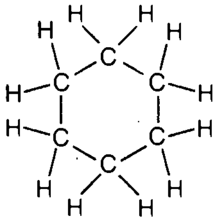
CYCLOBUTANE



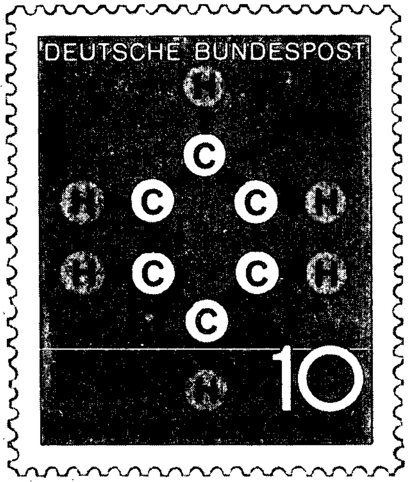
CYCLOPROPANE



CYCLOHEXANE



O-16 The Benzene Ring

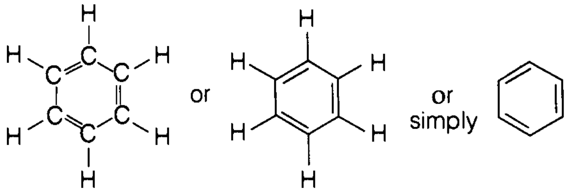


The benzene molecule puzzled scientists for generations because they could not determine how it bonded together. Friedrich August Kekulé, honored on this stamp, supplied the clue in 1864. In a dream he saw a snake grabbing its own tail. Upon awakening, the chemist quickly translated the image of the snake into a six-sided benzene ring.

If cyclohexane accumulates three double bonds, the compound formed is known as *benzene* (C_6H_6). Benzene belongs to a class of organic compounds called *aromatic hydrocarbons*. As you might guess, the term *aromatic* relates to odor. Before chemists knew the structures of compounds, they often classified them according to the effects of the compounds on the senses: smell, taste, and sight. Often this turned out to be a rather poor way of classification.* Nearly all aromatic compounds contain the benzene ring somewhere in the molecule, but not all compounds of this structure have pleasant odors.

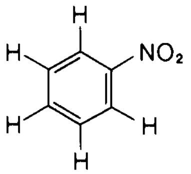
Benzene enters most frequently into the organic chemist's investigations. As its structural formula indicates, the benzene molecule is a regular hexagon. The first drawing of the structural formula of benzene shows that a carbon atom with an attached hydrogen atom is located at each corner of the ring. The structural formula of benzene can be represented in several ways. Can you see why some of the more simplified structures of benzene are used?

BENZENE C_6H_6

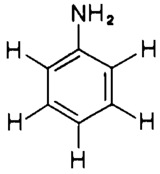


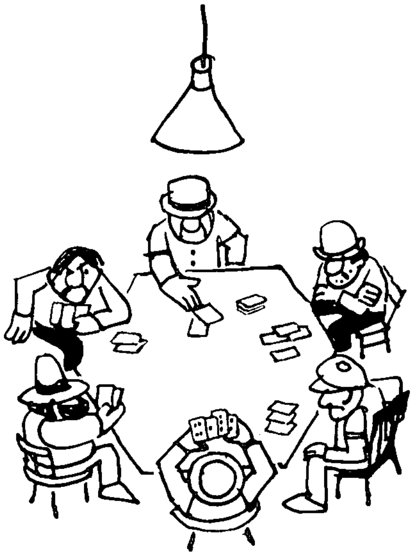
The familiar *benzene ring* shows up in thousands of organic compounds. Benzene enters into substitution reactions to produce many varied compounds. For example, when benzene combines with the nitro group (—NO_2), nitrobenzene is formed. In turn, nitrobenzene can be converted into aniline, another aromatic compound used in making dyes, perfumes, varnishes, and drugs.

NITROBENZENE



ANILINE





THE BENZENE RING

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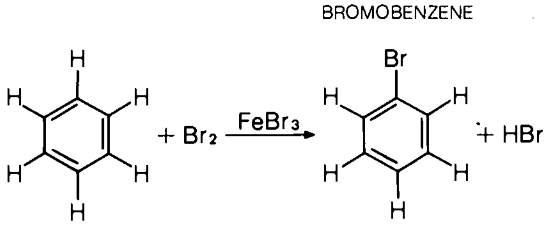
*In the "old days" it was standard operating procedure to smell and actually taste any unknown chemical in order to help identify it. This, in fact, was an accepted way to analyze for sugar in urine. You should never taste an unknown substance (for obvious reasons), however, and such a substance should be smelled, if necessary, only very carefully.

What is most unusual about aromatic compounds such as benzene is their high degree of stability and lack of reactivity. For example, when benzene and bromine are mixed there is no reaction. For a compound that possesses double bonds, this is most unusual. In comparison, bromine reacts vigorously with 1,3,5-hexatriene

$$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$$

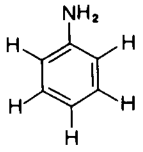
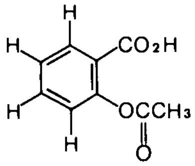
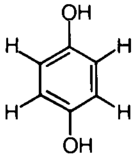
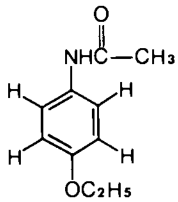
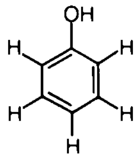
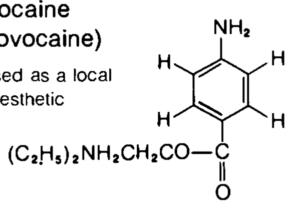
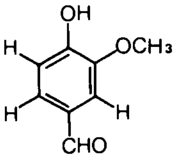
which, like benzene, is a six-carbon compound with three alternating double bonds. If benzene is combined with bromine in the presence of a suitable catalyst—iron(III) bromide ($FeBr_3$), for example—a reaction does take place. But the result is a substitution reaction rather than an addition reaction! Thus, benzene seems to behave more like ethane than ethylene—more like a saturated compound that undergoes substitution reactions than an unsaturated one.



It is characteristic of aromatic compounds to undergo substitution reactions rather than addition reactions. The reasoning behind this is somewhat complicated and need not concern us at this time. It is sufficient to point out that just as atoms and ions have filled shells of electrons (the inert gases, halide ions, and alkali metal ions), so do some organic molecules, including aromatic compounds. These special molecules do their utmost to maintain their "aromaticity." If the entire bromine molecule were *added* to benzene, the resulting molecule would lack aromaticity and would therefore be a more energetic (less stable) compound.

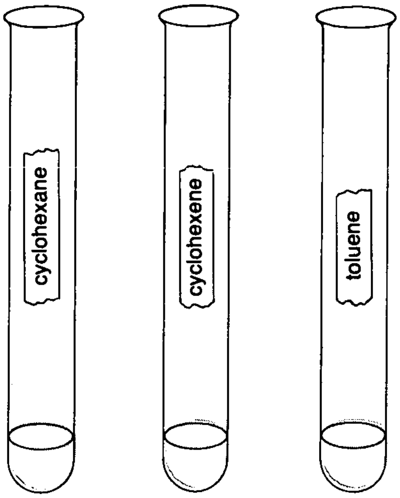
Whether a reaction is an addition reaction or a substitution reaction, a chemist is always interested in any changes that occur. Among the most powerful tools that a scientist has are the senses. Observation, although sometimes misleading, is one way of detecting whether a change has taken place in a system. Gas evolution, heat generation, precipitation, or color change often indicates a chemical change. In the following miniexperiment, which deals with reactions of specific hydrocarbons, rely on your senses to determine whether a chemical reaction has taken place.

A FEW BENZENE DERIVATIVES

Name/Uses	Structure
Aniline For production of dyes, perfumes, varnishes, and medicines	
Aspirin For relief of pain	
Hydroquinone For developing photographs	
Phenacetin For relief of headache	
Phenol Used in germicides and disinfectants	
Procaine (novocaine) Used as a local anesthetic	
Vanillin Used as a flavoring	

miniexperiment

O-17 Reactions of Hydrocarbons



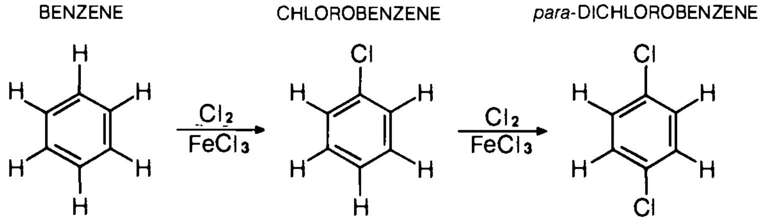
Add 1-cm^3 portions of cyclohexane, cyclohexene, and toluene to labeled test tubes. Then add 2 cm^3 of a 0.01 M potassium permanganate ($KMnO_4$) solution to each of the three test tubes containing the hydrocarbons. Be sure to dispense the reagents using proper laboratory technique.

Place a stopper in each tube and shake the tube gently. After 1 minute note any changes that occur in the tubes. Shake the tubes every few minutes and observe them again. After 5 minutes again note and record any changes. Be careful not to mix any of your samples.

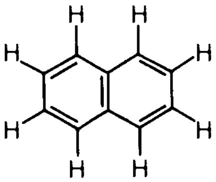
Questions: What do you conclude about the reactivity of these organic compounds with the inorganic compound potassium permanganate? Is there evidence that a chemical change has occurred? Which senses did you use to determine results in this miniexperiment?

O-18 Fused Rings: Bigger but Not Better

The reaction of chlorine with benzene in the presence of an iron-(III) chloride catalyst yields chlorobenzene (C_6H_5Cl). This may react further with chlorine to give *para*-dichlorobenzene ($C_6H_4Cl_2$). As a solid *para*-dichlorobenzene readily *sublimes* (goes directly from the solid state to the gaseous state without first liquefying).



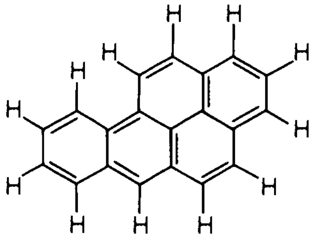
NAPHTHALENE

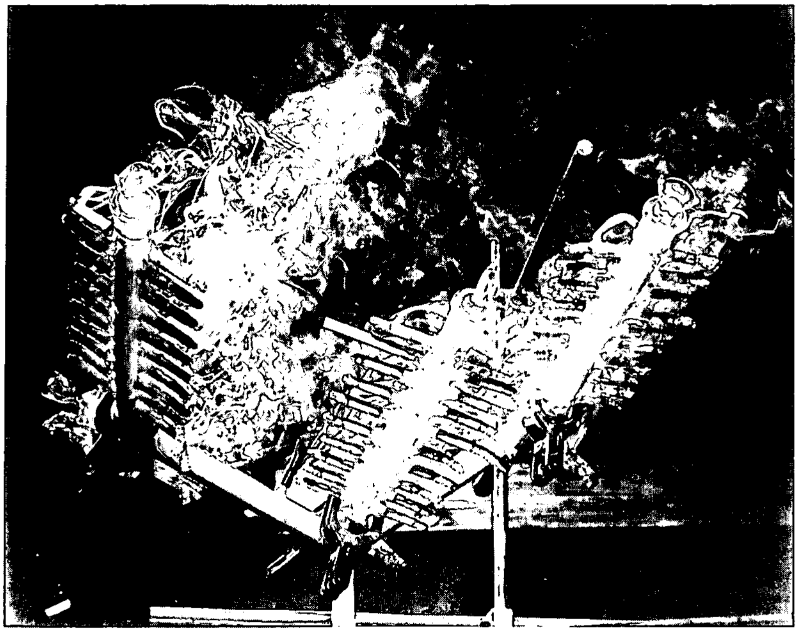


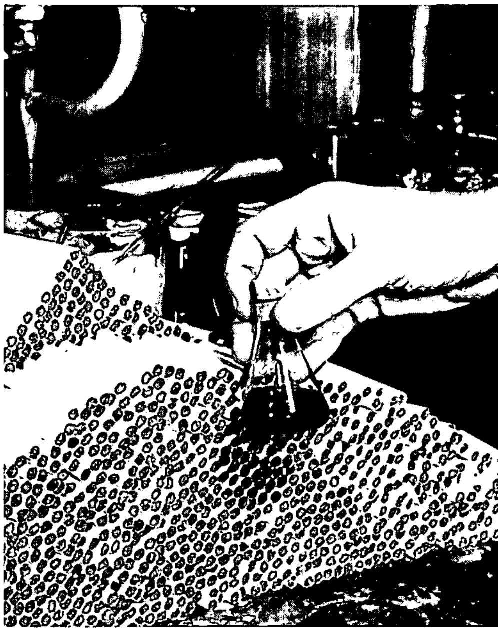
Some mothballs are made of *para*-dichlorobenzene. Mothballs are used to protect woolen clothes against moths. The aroma of the aromatic organic compound covers up the odor of the wool, making it difficult for the moth to locate. Mothballs can also be made of naphthalene ($C_{10}H_8$), another aromatic hydrocarbon. Naphthalene consists of two benzene rings fused together. Each ring in the structure shares two carbon atoms.

The principal source of aromatic compounds is *coal tar*. If coal is heated in the absence of air, a significant amount of unsaturated hydrocarbons is isolated. This black mixture, coal tar, is rich in aromatic compounds such as benzene and naphthalene. Among the aromatic compounds isolated from coal tar is benzopyrene ($C_{20}H_{12}$). Benzopyrene is a powerful *carcinogen* (cancer-causing agent). Along with at least a dozen other carcinogens, benzopyrene is one of the compounds in cigarette smoke.

BENZOPYRENE





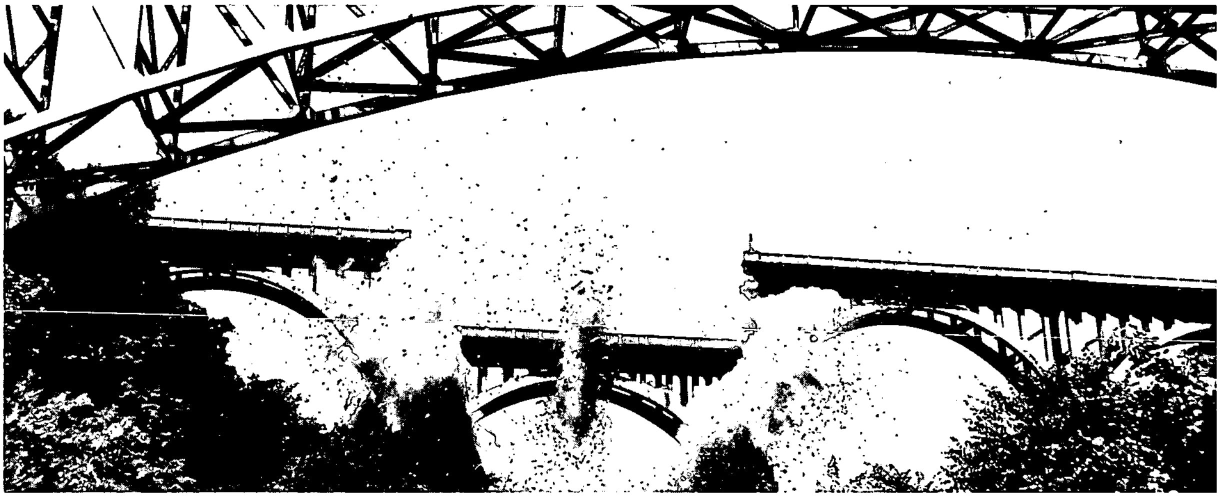


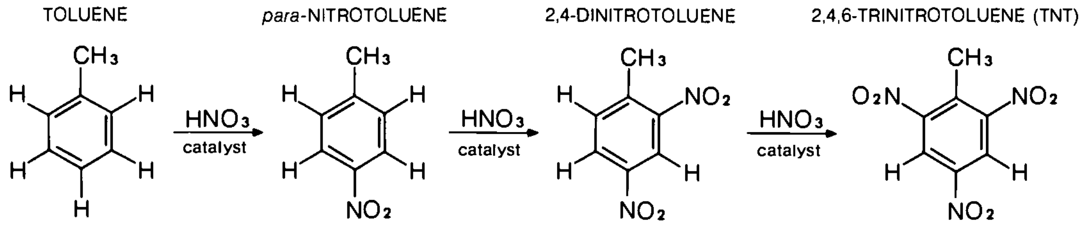
Cigarettes are being tested for carcinogens in this "smoking robot." The sample of tar on the right is the amount taken from two thousand cigarettes.

O-19 Molecules with a Bang

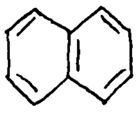
Another aromatic hydrocarbon compound is derived by replacing one of benzene's hydrogen atoms with a methyl group ($—CH_3$). The resulting compound is called *toluene* ($C_6H_5CH_3$). This hydrocarbon is important in the manufacture of industrial chemicals, explosives, aviation gas, antiknock additives, photographic chemicals, and drugs.

Toluene, like benzene, undergoes substitution reactions. One series of such reactions is with nitric acid (HNO_3). Again, the aromatic ring is so unreactive (stable) that a catalyst is necessary for the reaction to occur. This reaction, like many other organic reactions, takes place in steps. In this *stepwise reaction*, depending upon the reaction conditions, one, two, or three nitro groups ($—NO_2$) can be introduced. The end product, trinitrated toluene, $CH_3C_6H_2(NO_2)_3$, is the well-known explosive TNT—trinitrotoluene.

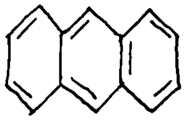




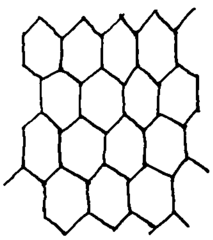
BENZENE



NAPHTHALENE



ANTHRACENE



CHICKEN WIRE

One characteristic of nearly all explosives and rocket fuels is that they contain nitrogen atoms. Gunpowder, which consists of a mixture of chemicals including potassium nitrate (KNO_3), was the most important explosive used in armaments until the twentieth century. The key to the reactivity of gunpowder is the reduction (loss of oxygen) of nitrate (NO_3) to molecular nitrogen (N_2). Since nitrogen is a very stable molecule, almost any chemical reaction that results in the formation of nitrogen also liberates a great amount of energy at the same time.

The principle that matter is neither created nor destroyed in chemical (not nuclear) reactions also applies to energy. Energy can neither be created nor destroyed in a chemical reaction. There is a large amount of stored energy in highly oxidized nitrogen-containing compounds, such as nitrates and polynitroaromatics*—one of which is TNT. But little energy is stored in molecular nitrogen. The less energy a material has, the more stable it is.

When nitrates are converted to molecular nitrogen, a good deal of energy is released. This energy is liberated in the form of light and heat. A reaction that gives off heat is called an *exothermic reaction*. A property of exothermic reactions is that, once started, they tend to continue on their own. If they are unusually exothermic, the reactions occur so rapidly that an explosion results.

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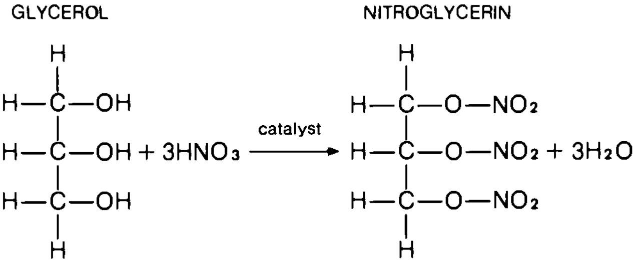
*The prefix *poly-* means "many." Therefore polynitroaromatics are aromatic compounds that contain many nitro groups.

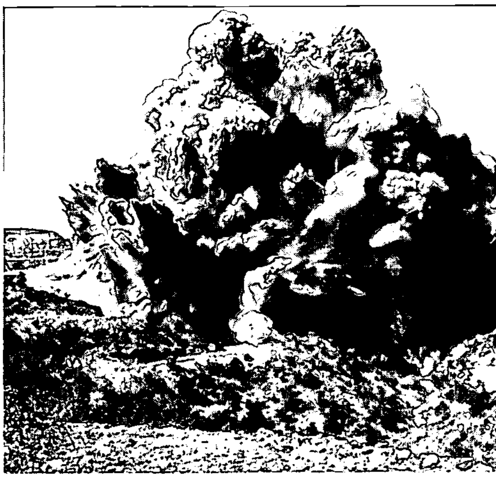
An explosive "explodes" because of the difference in the properties of liquids and solids versus the properties of gases. When TNT explodes, the solid (TNT) turns into very hot gases—nitrogen and carbon dioxide, for example—causing a rapid increase of pressure in a confined space. Because a solid is much denser than a gas, especially if the gas is hot, the container that held the solid cannot hold the gas that is given off. The container explodes and shatters. With care, TNT and gunpowder can be handled without risk of detonation. In fact, it is necessary to "shock" the sample (with the blow of a hammer, for example) or set off another small explosion in order to explode TNT or gunpowder. This initial small explosion takes place in a percussion cap. The material in the percussion cap is much more sensitive to shock than is the main explosive.

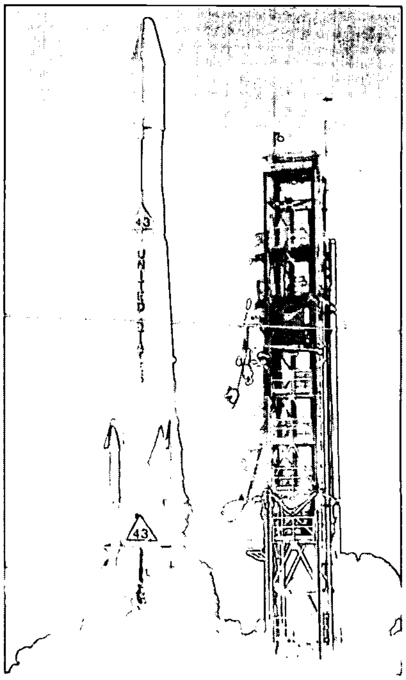
An explosive far more dangerous than TNT or gunpowder is *nitroglycerin*, $C_3H_5(ONO_2)_3$. Nitroglycerin is made from the organic compound glycerol, $C_3H_3(OH)_3$, and nitric acid, HNO_3, in the presence of a catalyst. The name nitroglycerin is somewhat misleading, because the compound really has three nitrate groups ($—ONO_2$) rather than nitro groups ($—NO_2$) attached to the carbon atoms. Nitroglycerin is extremely sensitive (a slight shock will set it off) and is highly explosive because there is more than enough oxygen present in the molecule to convert all the carbon and hydrogen into hot gaseous CO_2 and H_2O. People have been killed or seriously injured while carelessly handling nitroglycerin.



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H—C—OH} \\ | \\ \mathrm{H—C—OH} \\ | \\ \mathrm{H—C—OH} \\ | \\ \mathrm{H} \end{array} + 3HNO_3 \xrightarrow{\text{catalyst}} \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H—C—O—NO_2} \\ | \\ \mathrm{H—C—O—NO_2} \\ | \\ \mathrm{H—C—O—NO_2} \\ | \\ \mathrm{H} \end{array} + 3H_2O$$

In 1866 the Swedish chemist Alfred Nobel discovered that when nitroglycerin, a liquid, is absorbed by diatomaceous earth (which will absorb up to three times its own weight of a liquid and still appear to remain dry), the resulting solid is still explosive but is much less sensitive to shock. This he called dynamite, from a Greek word for "power." Nobel soon realized that diatomaceous earth, an inert substance composed of fossils of tiny prehistoric sea creatures, or diatoms, absorbed heat as well as the liquid nitroglycerin and thus reduced the blasting action of his invention. He replaced diatomaceous earth with wood pulp, which would absorb the liquid without absorbing heat. Dynamite is usually molded into





sticks and wrapped in paraffin paper. The sticks are fitted with percussion caps—Nobel invented the first of these in 1865—that contain shock-sensitive explosives.

One of the most powerful and shattering explosives known is blasting gelatin, a mixture of nitroglycerin and guncotton discovered by Nobel in 1875 and still used extensively for blasting rocks. Guncotton is made from cellulose (cotton is pure cellulose) and nitric acid, in the presence of a catalyst. If the percentage of nitroglycerin in blasting gelatin is decreased, the resulting formulation is slower burning and may be used for propellants.

The development of propellants is especially important for today's rocket technology. Propellants are fuels for rocket engines. Vast quantities of propellants are converted to hot gases by rapid but controlled combustion. The gases pass out through an opening, expand, and thus provide a forward thrust to the vehicle. In the early days of testing propellants, it was found that guncotton could provide the high-temperature gases needed to give smooth thrust to rocket boosters. Today, however, guncotton has been replaced by other rocket propellants.

COMMON ROCKET PROPELLANTS

Propellant	Specific Impulse*
90% H_2O_2	151
H_2NNH_2 (Hydrazine)	191
O_2, Ethyl alcohol	287
N_2O_4, CH_3NHNH_2	288
F_2, H_2NNH_2	364
O_2, H_2	391

*Time in seconds for burning one pound of fuel while generating one pound of thrust.

Dynamite, too, has many uses. Today, the peaceful uses of dynamite far outweigh its destructive uses. It can be used to clear terrain for tunnels and highways, to mine mineral deposits, and to safely and quickly demolish old buildings that are no longer useful.

Alfred Nobel made a great fortune from his inventions, but at the time he was greatly dismayed at the destructive use others made of his explosives. Upon his death he left nearly nine million dollars to establish the Nobel Foundation. Since 1901 the interest on this capital has been used for annual international prizes in physics, chemistry, physiology or medicine, literature, and peace, awarded to men and women who "have conferred the greatest benefit on mankind." A sixth Nobel Prize, for economics, was established by the Bank of Sweden in 1968. Although the Nobel Prize for Peace was not awarded in 1976, Americans won all the other Nobel Prizes that year—a sweep no other nation has achieved. Alfred Nobel, who spent four years in the United States when he was in his twenties, might have been pleased.

RECENT NOBEL PRIZES IN ORGANIC CHEMISTRY

1975	John W. Cornforth (Australia)
1974	Paul J. Flory (United States)
1969	Derek H. R. Barton (England) Odd Hassel (Norway)
1965	Robert B. Woodward (United States)
1963	Giulio Natta (Italy) Karl Ziegler (Germany)

Alcohols: Oxidized Hydrocarbons

Carbon can exist in a wide range of states. At one extreme is the fully oxidized form, carbon dioxide (CO_2). At the other extreme are the reduced forms of carbon: elemental carbon (graphite and diamonds), in which carbon atoms are bonded only to one another. Between these lies a host of oxygen-containing carbon compounds. The first of these compounds to be discussed will be the alcohols.

By burning methyl alcohol, this fondue pot keeps its contents hot throughout a meal. Sometimes called canned heat, methyl alcohol is used for many heating and warming purposes.

O-20 Oxidation and Reduction

To better understand the different states of carbon, we must learn more about oxidation and reduction. For the organic chemist these terms have a special meaning. For example, consider what happens when carbon burns. It combines with oxygen, forming CO_2. This reaction is an example of *oxidation*, because oxygen is added to carbon. The opposite reaction—the removal of oxygen from a carbon atom—is called *reduction*.

There are also types of oxidation and reduction reactions that do *not* involve oxygen. Whenever hydrogen is added to a carbon atom, the reaction is classified as a reduction reaction. Whenever hydrogen is removed from a carbon atom and replaced by another atom or group, the reaction is considered an oxidation reaction.

To summarize, then:

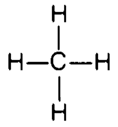
Oxidation = addition of oxygen or removal of hydrogen
Reduction = addition of hydrogen or removal of oxygen

$$2CH_4 + O_2 \xrightleftharpoons[\text{reduction}]{\text{oxidation}} 2CH_3OH$$

$$H_2C{=}O + H_2 \xrightleftharpoons[\text{oxidation}]{\text{reduction}} CH_3OH$$

Among the various oxidized hydrocarbons are the *alcohols*. An alcohol results when one of the hydrogen atoms of a hydrocarbon is replaced by a hydroxyl group (—OH). Since the hydrogen has been removed and replaced by another group of atoms containing oxygen, this is an oxidation reaction. As an example, remove a hydrogen from the hydrocarbon methane (CH_4), and add the hydroxyl group. The product of this reaction is *methyl alcohol*, CH_3OH. Methyl alcohol can also be called methanol. The *-ol* ending indicates that the hydroxyl group (—OH) is present. (See Appendix II for a discussion of the naming of organic compounds.)

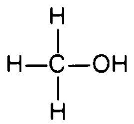
METHANE



$$\begin{array}{c} H \\ | \\ H{-}C{-}H \\ | \\ H \end{array}$$

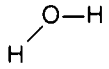
But we can also look at the alcohols in another way. Alcohols are closely related to the most common liquid of all, water. An alcohol is a water molecule in which a hydrocarbon group has replaced one hydrogen atom.

METHYL ALCOHOL
(METHANOL)

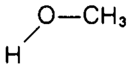


$$\begin{array}{c} H \\ | \\ H{-}C{-}OH \\ | \\ H \end{array}$$

WATER



METHYL ALCOHOL
(METHANOL)



Alcohols can therefore be regarded as either derivatives of hydrocarbons or derivatives of water. This can help us explain the chemical properties of the alcohols, some of which resemble the properties of water. Water, for example, has a high boiling point.

Similarly, alcohols have higher boiling points than the alkanes from which they are derived. Like water, alcohols can dissolve many substances, and the lighter alcohols themselves mix easily with water.

O-21 Methyl and Ethyl: Their Properties

The physical and chemical properties of alcohols are very different from those of the hydrocarbons. For example, it is often true that compounds of the same or nearly the same molecular weight have similar boiling points. The hydrocarbon ethane (C_2H_6), with a molecular weight of 30, has a boiling point of −89°C; but methyl alcohol (CH_3OH), with a molecular weight of 32, has a boiling point of +65°C, a difference of 154°! In fact, it is not until the hydrocarbon series reaches hexane (C_6H_{14}), with a molecular weight of 86, that the boiling point of the hydrocarbon (69°C) is near that of the much lighter methyl alcohol.

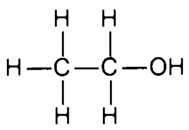
The solvent properties of alcohols also differ markedly from those of the hydrocarbons. Methyl alcohol, for example, is capable of dissolving several materials that are completely insoluble in hydrocarbon solvents. This is illustrated by the complete solubility of water in the lower-molecular-weight alcohols (methyl, ethyl, and propyl alcohols). Some inorganic salts are also soluble in these alcohols.

The fact that certain salts as well as water are soluble in methyl alcohol indicates that methyl alcohol is a polar molecule (see *Reactions and Reason: An Introductory Chemistry Module* for a discussion of polar molecules). The rule is that "like dissolves like." If two materials are nonpolar (for example, hexane and benzene), they will dissolve in one another. Similarly, polar compounds (or ionic compounds) will dissolve in polar solvents (water in alcohol, or sodium chloride in water).

The properties of methyl alcohol do not result solely from the presence of an oxygen atom in the molecule. Compare the properties of the structural isomers of C_2H_6O: ethyl alcohol, C_2H_5OH, and dimethyl ether, $(CH_3)_2O$.

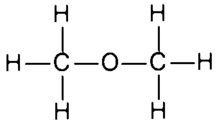
Alcohol is used as a solvent in many household products; one example is food flavorings. You might also find it in a medicine cabinet or first-aid kit in tincture of iodine. Can you think of other products in which alcohol is used as a solvent?

ETHYL ALCOHOL
(ETHANOL)



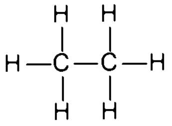
$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & OH \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

DIMETHYL ETHER



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

ETHANE



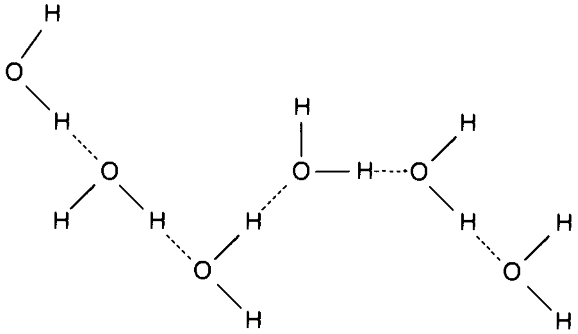
$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Ethyl alcohol (also called ethanol) has a boiling point of 78.5°C. In contrast, the boiling temperature of dimethyl ether is more than 100° lower than that of ethyl alcohol. Like methyl alcohol, ethyl alcohol can dissolve many inorganic salts, but dimethyl ether is a poor solvent for such purposes. Actually, dimethyl ether behaves physically much like a hydrocarbon, whereas methyl alcohol and ethyl alcohol more closely resemble water than hydrocarbons in their solvent properties. This suggests that it is the presence of the —OH in alcohols that makes the difference. But why should this be so?

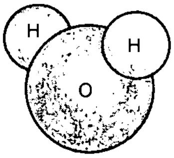
O-22 Another Type of Bonding

The reason why both methyl alcohol and ethyl alcohol have properties similar to those of water rests with an important type of bonding, *hydrogen bonding*. Hydrogen bonding is actually a weak bonding between molecules. In water, for example, a hydrogen bond links a hydrogen atom in one water molecule to an oxygen atom in another water molecule. Because of these bonds, water molecules group together and form clusters.

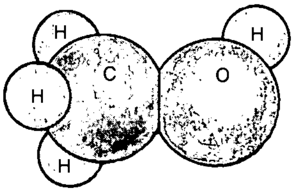
HYDROGEN BONDING OF WATER



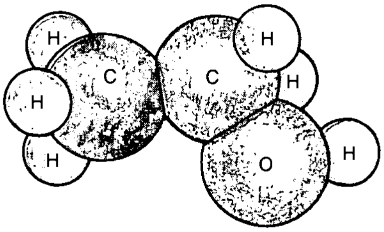
Normal oxygen-hydrogen bonds are solid lines.
Hydrogen bonds between water molecules are dashed lines.



WATER



METHYL ALCOHOL



ETHYL ALCOHOL

The peculiar properties of water depend chiefly on its tendency to form a large number of hydrogen bonds. Although water has a low molecular weight (18), it has a rather high boiling point (100°C). The reason for this high boiling point is that water molecules tend to cling to one another through their hydrogen bonds. Even though hydrogen bonds are only about one-twentieth as strong as normal covalent bonds, they are able to hold the light water molecules together below 100°C, so that they cannot fly off as vapor. Thus water remains a liquid below 100°C.

Like water, ethyl alcohol and methyl alcohol also have O—H bonds, and each is capable of hydrogen bonding. By contrast, ethers have no hydrogen atoms attached to oxygen atoms and therefore cannot hydrogen bond with themselves. Can you now explain the high boiling points of the alcohols when compared to the ethers, as well as the similarities between the alcohols and water?

Of course, the hydroxyl group is only part of the alcohol molecule. The hydrocarbon chain to which it is attached also has some effect on its physical properties. The longer the chain, the more the alcohol will resemble a hydrocarbon in various ways. Thus the higher alcohols are less like water and more like the corresponding alkanes from which they are derived. For example, they are much less soluble in water and more soluble in other alkanes.

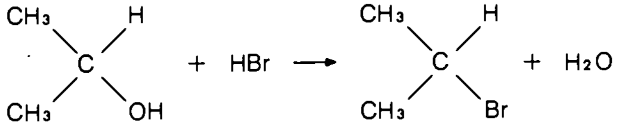
O-23 Functional Groups: Focus of the Matter

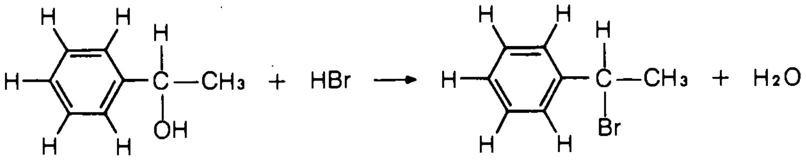
Organic molecules are numerous and often very complex. In order to be able to organize and make use of the vast amount of information about organic substances, chemists have had to find some way to classify various compounds. To do this they have derived the concept of the *functional group*. A functional group is a cluster of atoms covalently bonded together that functions as a unit in determining the physical and chemical properties of organic compounds. For example, —OH is a functional group known as a hydroxyl group. It consists of a hydrogen atom and an oxygen atom.

The same functional group shows up in many different molecules, but it usually reacts the same way with a reagent regardless of the nature of the rest of the molecule. For example, if you heat any of the alcohols in the following reactions with concentrated hydrobromic acid (HBr), you will obtain the corresponding bromo compound.

$$CH_3{-}OH + HBr \longrightarrow CH_3Br + H_2O$$

$$CH_3CH_2{-}OH + HBr \longrightarrow CH_3CH_2Br + H_2O$$





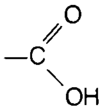
In all of these cases a substitution reaction takes place; bromine is substituted for the hydroxyl group. Note that the other groups attached to the carbon containing the hydroxyl group do not appear to be important to the reaction. They do not take part. Only the hydroxyl group has undergone a change.

In considering how a molecule will react, the chemist concentrates first on the functional groups, blocking the rest of the molecule from the mind. In fact, the letter *R* is often used to represent the part of the molecule that does not play an important role in the reaction. For example, in the case of the reaction of alcohols with hydrobromic acid, the general equation might be

$$R\text{—OH} + \text{HBr} \longrightarrow R\text{—Br} + H_2O$$

What would *R* be in each of the four previous equations?

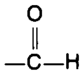
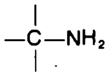
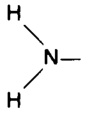
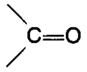
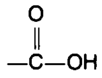
As you would expect, compounds that have the same functional groups also have the same kinds of properties. They not only have similar physical properties, such as solubility behavior in particular solvents, but they also exhibit similar chemical properties. For example, certain alcohols under similar conditions can be oxidized to form compounds called carboxylic acids, which are organic acids that contain the carboxyl group



Also, most alcohols react with hydrochloric acid to form the chloro compounds.

You will be working with all the functional groups listed in the accompanying table. Learn to locate and to identify the functional groups in a molecule. Become familiar with the properties that a functional group gives to the molecule.

FUNCTIONAL GROUPS WITHIN ORGANIC COMPOUNDS

Functional Group	Functional Group Name	Structural Formula	Compound Class	Compound Example and Formula	
—OH	hydroxyl	—OH	alcohols	ethyl alcohol	C_2H_5OH
—CHO	formyl	 $\text{—}\overset{\text{O}}{\overset{\Vert}{\text{C}}}\text{—H}$	aldehydes	formaldehyde	HCHO
 $\text{—}\underset{\vert}{\overset{\vert}{\text{C}}}\text{—}NH_2$	amino		amines	methylamine	CH_3NH_2
—O—	oxy	—O—	ethers	diethyl ether	$C_2H_5OC_2H_5$
—CO	carbonyl		ketones	acetone	CH_3COCH_3
—COOH	carboxyl	 $\text{—}\overset{\text{O}}{\overset{\Vert}{\text{C}}}\text{—OH}$	organic acids	acetic acid	CH_3COOH

O-24 Fermented and Distilled Alcohols

The most famous alcohol is ethyl alcohol, C_2H_5OH. Ethyl alcohol has been known for a long time. It was probably first discovered in overripened fruit. Some microorganisms live on the sugar produced by fruits. Unlike us, however, these microorganisms convert the sugar to ethyl alcohol, not to carbon dioxide.

Sugar is converted to ethyl alcohol through a process known as *fermentation*. Apparently people discovered fermented juices, sampled them, and liked them. They soon discovered how to ferment the juices squeezed from fruit and began to ferment them deliberately. From grapes came wine, from apples came hard cider, and from grain that had sprouted (malt) came beer and ale.

$$\underset{\substack{\text{(complex}\\\text{sugar)}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{enzyme}} \overset{\text{GLUCOSE}}{\underset{\substack{\text{(simple}\\\text{sugar)}}}{2C_6H_{12}O_6}}$$

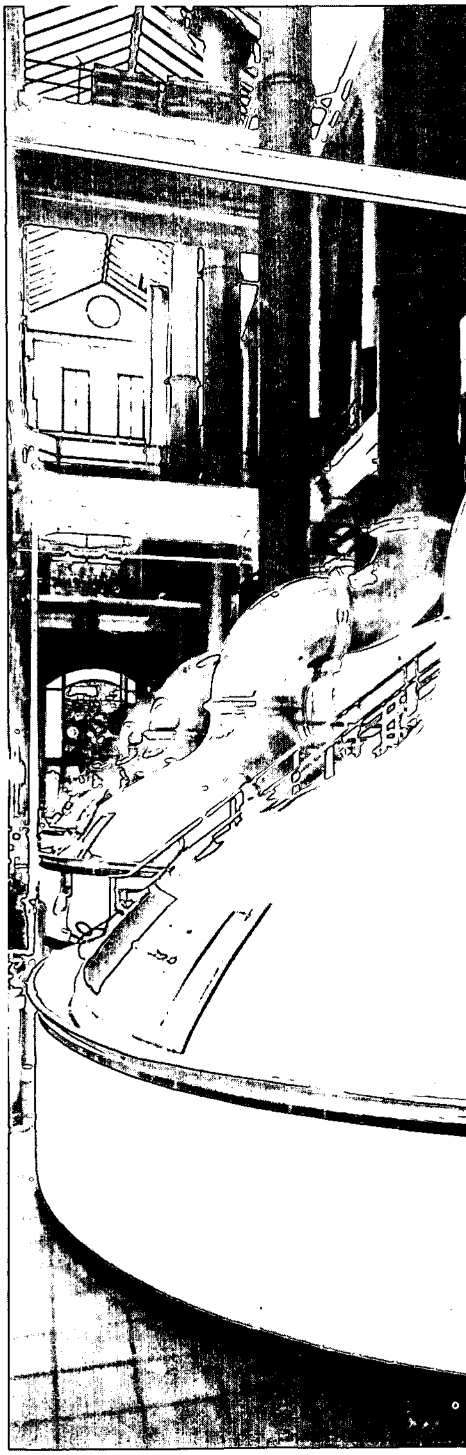
$$\overset{\text{GLUCOSE}}{C_6H_{12}O_6} \xrightarrow{\text{enzyme}} \overset{\substack{\text{ETHYL}\\\text{ALCOHOL}}}{2C_2H_5OH} + \overset{\substack{\text{CARBON}\\\text{DIOXIDE}}}{2CO_2}$$

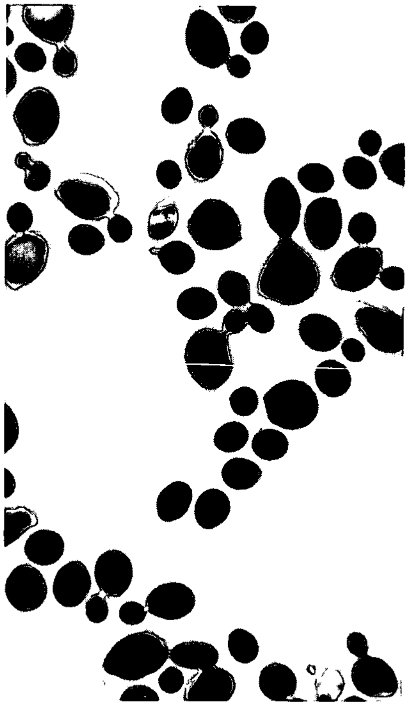
The alcohol content of these fermented mixtures may rise only to about 15 percent. At this point the microorganisms that produce alcohol die as a result of alcohol poisoning. (Alcohol is a fairly good antiseptic—it kills bacteria. A 70-percent solution of alcohol in water is usually used to swab the skin before you are given an injection.)

An alcohol can be obtained in a more concentrated form by *distilling* the fermented mixture. A chemist heats the liquid to its boiling point (78.5°C for ethyl alcohol), then transfers the vapors away from the solution and condenses the liquid in another vessel. The alcohol used in alcoholic beverages in itself is slightly sweet-smelling, but it has very little taste of its own. The flavor and the taste of alcoholic beverages come from the contaminants that distill along with the alcohol and from others produced by slow chemical reactions as the alcohol is aged in charred wooden barrels.

Ethyl alcohol is very inexpensive to produce, and most of it is intended for industrial purposes—it is the most important industrial solvent after water. By law, the inexpensive-to-produce ethyl alcohol is heavily taxed when used in beverages. To be used any other way, it must be denatured to prevent its being consumed as a beverage. A denatured alcohol such as you use in the laboratory is prepared from ethyl alcohol by adding chemicals that make it

Grain is converted into alcohol in giant fermenters.





unfit to drink and therefore not subject to taxation. The additives do not significantly change the important properties of ethyl alcohol.

Ethyl alcohol can also be synthesized from ethylene, which is obtained from petroleum and natural gas. Ethyl alcohol is also used in the synthesis of many different organic chemicals.

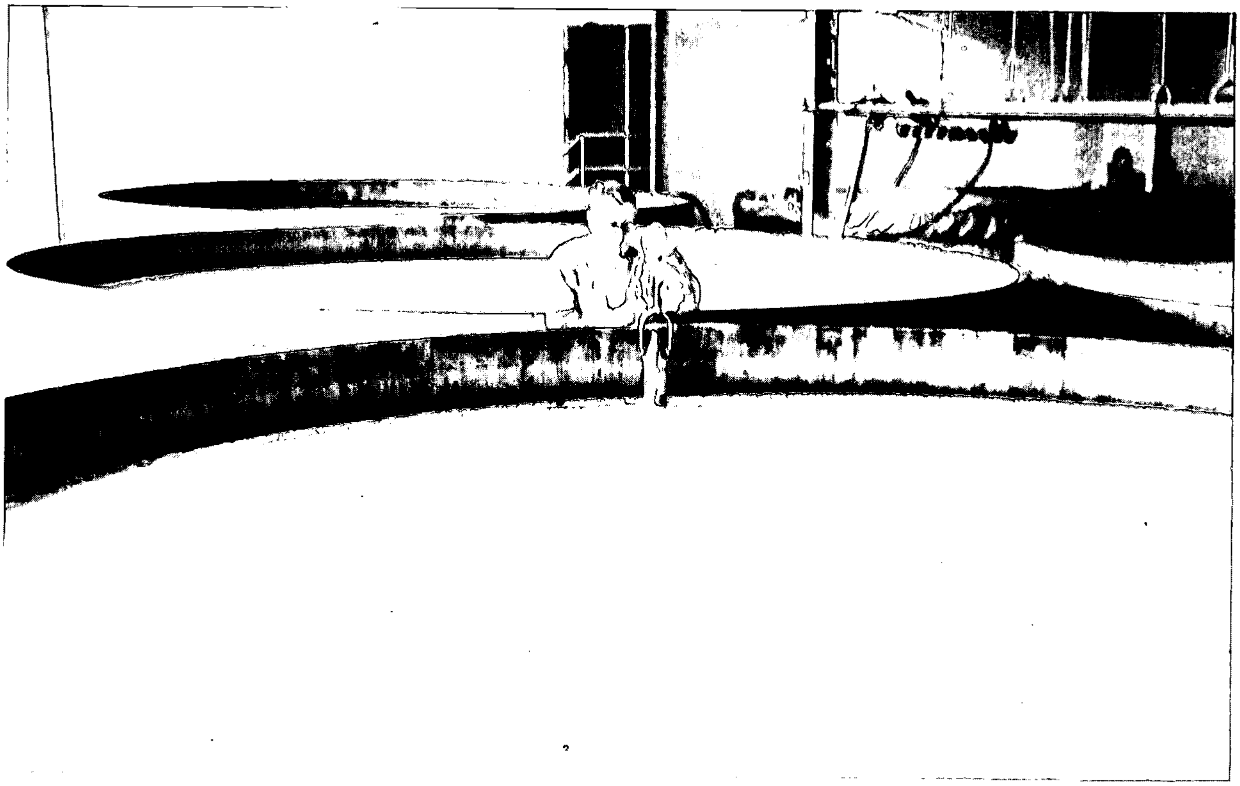
Methyl alcohol (or wood alcohol) was originally obtained by heating wood in the absence of air. This process, which also produced other useful chemicals such as acetone and acetic acid, is called *destructive distillation*. Methyl alcohol can also be obtained synthetically by a reaction of carbon monoxide and hydrogen.

$$CO + 2H_2 \xrightarrow{\text{catalyst}} CH_3OH$$

Methyl alcohol is also used to manufacture many organic chemicals and as a solvent. It is very poisonous if consumed, and the fumes are also quite toxic—they can cause blindness or even death.

The solubility of a substance in various liquids is a key property of the substance. In many instances a chemist first determines the solubility of a material when called upon to investigate it. (It would not do to manufacture raincoats made of a water-soluble material!) What determines whether one substance will dissolve in (mix with) another substance?

As yeast cells *(above)* grow and reproduce by budding, they change the sugar in grain to ethyl alcohol and carbon dioxide. Grain ferments in open wood tubs *(below)* to produce ethyl alcohol.



O-25 Comparing Solubilities

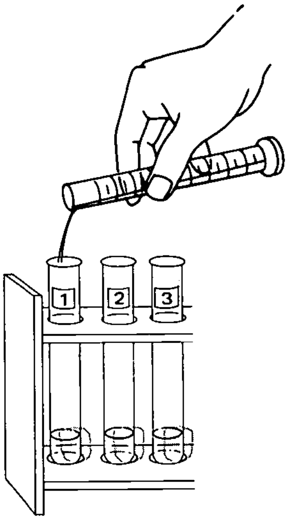
EXPERIMENT

You will be using the following solvents:

water (H_2O)
toluene ($C_6H_5CH_3$)
ethyl alcohol (C_2H_5OH)
n-hexane (C_6H_{14})

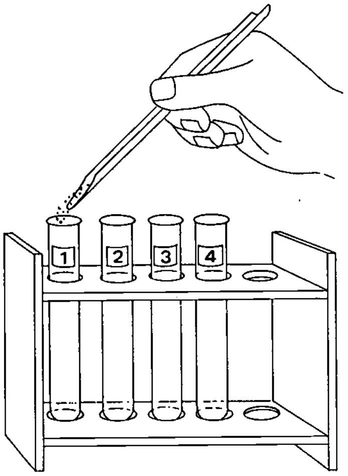
You will test these four compounds for solubility:

sugar ($C_{12}H_{22}O_{11}$)
salt (NaCl)
para-dichlorobenzene ($C_6H_4Cl_2$)
calcium carbonate ($CaCO_3$)



Test the solubility of the various solvents in each other. To do this, mix a 1-cm^3 portion of each solvent with a 1-cm^3 portion of each of the other solvents in test tubes. How many different combinations are there? Record the results.

Next, place enough of one compound to fill the end of a spatula into each of four test tubes. Add one of the solvents—enough to fill the test tube about one-third full. Repeat this procedure with each of the other compounds, using each of the remaining three solvents. How many different observations will there be? Observe and record each compound as being soluble, slightly soluble, or insoluble. Summarize your observations in a table. (List the four solvents along the left side of the table.)

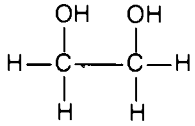


Questions: Which of the solvents were soluble in each other? Was any solvent unique in its solvent action compared with the others? Which of the solvents do you think are organic? Which of the solvents are polar? Which are nonpolar?

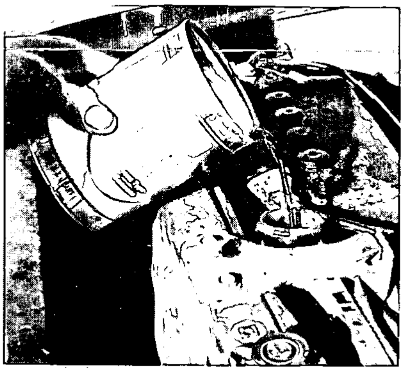
In 1920 and for the following twelve years, the United States prohibited the production and sale of ethyl alcohol for drinking purposes—Prohibition. One consequence of withdrawing alcoholic beverages (ethyl alcohol) from the public market was the substitution by unscrupulous people of poisonous alcohols for these beverages. Two such substitutes were methyl alcohol and ethylene glycol. As you recall, methyl alcohol is extremely poisonous. Some people died from consuming these substitutes; others were left physically handicapped. It should be noted that ethyl alcohol can also be toxic when consumed in large doses. More common, though, are the long-term effects of alcohol abuse such as cirrhosis (hardening) of the liver.

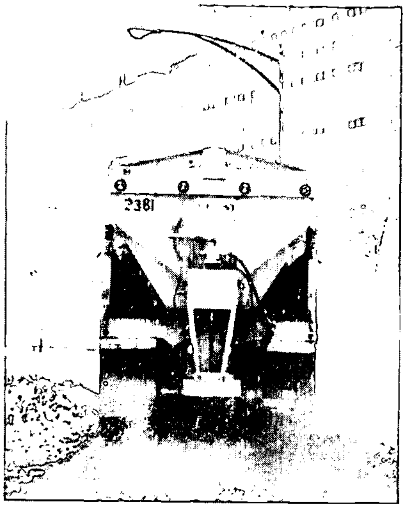
O-26 Polyalcohols

ETHYLENE GLYCOL



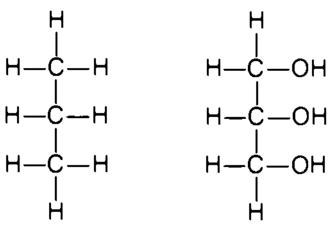
A *poly*alcohol contains more than one hydroxyl group (—OH). Methyl alcohol and ethyl alcohol each contain one hydroxyl group; therefore they are *mono*hydroxy alcohols and do not belong to the group of polyalcohols. Ethylene glycol is a *diol;* that is, it contains two hydroxyl groups. It is a *di*hydroxy alcohol. Ethylene glycol is best known as an antifreeze for car radiators. The water in a car radiator freezes when the temperature falls below 0°C. The freezing water expands, causing the engine block to crack. Therefore, it is necessary to add something to the water in order to lower the freezing point. Ethylene glycol is a good additive because it is noncorrosive and has a low melting point (−17°C) and a high boiling point (197°C). Other alcohols, such as ethyl alcohol and methyl alcohol, also prevent freezing at low temperatures and might be used in car radiators. Once the engine warms up, however, these alcohols evaporate easily and boil away.





It is interesting to note that, whereas water freezes at 0°C and ethylene glycol at −17°C, a mixture of four parts water and six parts ethylene glycol does not freeze until −49°C. This phenomenon is typical of liquids. Any soluble impurity lowers the freezing point (melting point) of a liquid. (This is why the highway department "salts" the roads in winter. Sodium chloride or the more often used calcium chloride lowers the freezing point of water, and the snow and ice then melt.) (See *A-13, Reactions and Reason: An Introductory Chemistry Module* and *P-18, Communities of Molecules: A Physical Chemistry Module.*)

Ethylene glycol is extremely poisonous, but if another carbon atom bearing a hydroxyl group is added to the chain, the nonpoisonous *triol* glycerol is obtained. Glycerol is sometimes called glycerin, but chemists prefer the name glycerol because, as we mentioned earlier, the suffix *-ol* indicates an alcohol. Glycerol is a sweet-tasting, viscous liquid with a boiling point of 290°C. Note that the boiling points of alcohols increase markedly as more hydroxyl groups are added to the molecules. Again, this is the result of the ability of the compound to form hydrogen bonds.



PROPANE GLYCEROL

Glycerol has a boiling point of 290°C, whereas propane boils at −45°C.

Glycerol, $C_3H_5(OH)_3$, is classified as a *tri*hydroxy alcohol; three hydroxyl groups (—OH) are attached to each glycerol molecule. The three —OH groups in each glycerol molecule enable the molecule to associate strongly with its neighbors. This raises the boiling point and also makes the liquid slow to flow (viscous). What might you predict about the solubility of glycerol in water?

Because glycerol is sweet but does not crystallize or evaporate at room temperature, it is used in making candy. It is also added to tobacco and hand lotions as a moisturizing agent.

The series of polyalcohols can be extended to four, five, six, seven, or more functional groups.

Poisons and Chemical Warfare

People and animals use certain organic chemicals for defensive purposes. Examples of these are tear gases, poisonous gases, and the irritants of insect stings. Although these substances may inflict damage on others, they have often helped scientists discover more about the working of the human body and its relationship to the intricate world of organic chemicals.

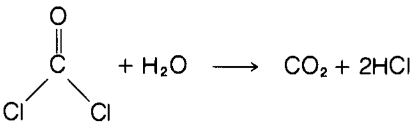
When threatened, the sea hare protects itself by squirting "ink" into the water. How do you suppose this protects the animal? Can you think of other animals that protect themselves in this manner?

O-27 Tears and More Tears

Each human body is a unique chemical laboratory, and chemicals react in our bodies in different ways. Too much sugar can be poisonous for one person, while too little can be poisonous to another. Many drugs are also poisons, but in prescribed doses they can cause reactions within the human body that cure illness (see *Drugs: From Aspirin to Hallucinogens*). Some chemicals react differently, depending on the way they contact the human body. A chemical may come in contact with a person's skin and cause a rash, whereas if it is inhaled or ingested it may cause death or illness.

Phosgene, a by-product of using carbon tetrachloride to put out electrical fires, was used as a war gas during World War I. When this gas is inhaled, it reacts with the moisture in the lungs to form hydrochloric acid. The acid irritates the lung tissue, which in turn reacts by giving off water. The water fills the lungs and prevents oxygen from entering and carbon dioxide from leaving, and the person suffocates.

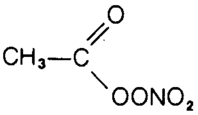
PHOSGENE



Some acids and bases damage body tissues. Bases are corrosive and break down body tissues, and acids cause irritation and inflammation as well as corrosive damage.

Earlier we discussed the burning of fuel with sulfur contaminants, which go into the air as pollutants. Sulfur dioxide can combine with the oxygen and moisture in the air eventually to produce sulfuric acid (see section *O-6*). Both acids and bases react with body tissues and alter the complex protein molecules to the extent that they cannot carry out the specified body functions.

PAN

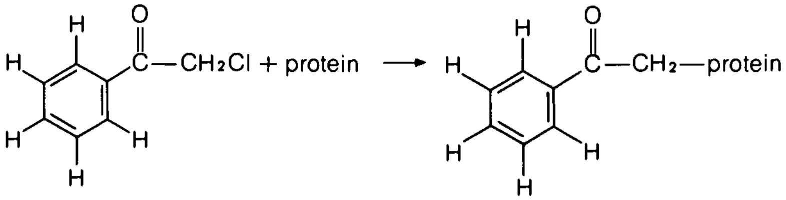


We have also discussed PAN, an organic compound in smog that acts as an oxidizing agent to our body cells (see section *O-11*). This chemical causes enzymes to become deactivated and they cease to work. It is no wonder that many agencies around the country are monitoring such things as food production, drugs, air pollution, water pollution, the ozone layer, and weather changes.

The tear gases, which act as lacrimators (from Latin—*lacrima*, "a tear"), are sometimes used as riot control agents. These gases irritate the sensitive mucous membranes of the eyes, nose, and throat. This irritation seems to be enough to disarm a rioting crowd and help bring it under control without damaging the human body permanently. Mace (α-chloroacetophenone) is an example of a lacrimator that irritates the eyes and skin but does not usually have a lasting harmful effect.

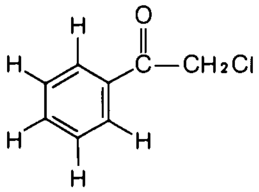
O-28 Alkylating Agents

Several common lacrimators used in tear gases are α-chloroacetophenone, chloropicrin, and *o*-chlorobenzalmalononitrile. Although these organic compounds do not appear to be related to one another in any systematic fashion, upon examination of their reaction behavior, one common characteristic shows up: they are *alkylating agents*. This means that they can react easily with the chemicals found in human tissue—especially proteins or nucleic acids—to add carbon groups. Acids are often generated by this reaction along with foreign (modified) proteins, and this gives rise to local irritation, ranging from hay fever to a skin reaction such as hives.



(alkylating agent)   (foreign protein)

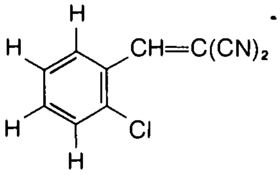
CHLOROACETOPHENONE



CHLOROPICRIN

Cl_3CNO_2

o-CHLOROBENZALMALONONITRILE



Normally the body protects itself against invaders such as bacteria or viruses by attacking and removing the intruders, but this ability varies from one individual to another and may also depend on the person's general health. Complications arise when our protective system overreacts (allergies) or, more dangerously, when the protective system (antibodies and white blood cells) considers part of its own body as alien. Some diseases such as rheumatic fever result when our antibodies actually attack and destroy cells in the body as though they were foreign.

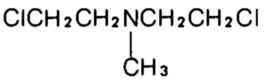
Some of the most powerful and dangerous alkylating agents are the so-called mustard gases, the *sulfur mustards* and the *nitrogen mustards*. These materials cause large and painful boils on the skin and any other tissue they reach. Sulfur mustard was used as a poison gas during World War I. Chlorine and phosgene, although not mustards, also were used extensively as poison gases in that war. Phosgene is particularly deceptive because it has a rather pleasant odor (like that of new-mown hay).

The mustards, however, have proved useful in the treatment of leukemia, cancer of the blood. Because most cancer cells grow much faster than ordinary cells, they are more sensitive than normal cells to chemicals that interrupt cellular processes (for example, cell division). The mustards may also kill healthy cells, however, so, like many other powerful cancer treatments, they must be used carefully. Sulfur mustards are too reactive (destructive of healthy tissue), but several nitrogen mustards have proved very useful in cancer treatment.

SULFUR MUSTARD

$ClCH_2CH_2SCH_2CH_2Cl$

NITROGEN MUSTARD

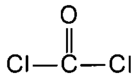


$ClCH_2CH_2\underset{CH_3}{\underset{|}{N}}CH_2CH_2Cl$

CHLORINE GAS

Cl—Cl

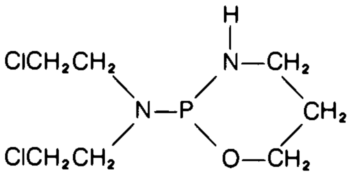
PHOSGENE



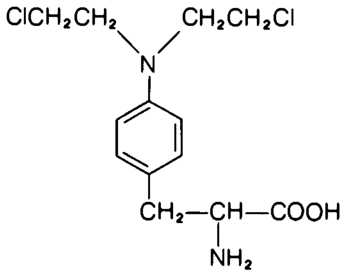
$Cl—\overset{\overset{O}{\parallel}}{C}—Cl$

NITROGEN MUSTARDS USED IN CANCER CHEMOTHERAPY

CYCLOPHOSPHAMIDE



L-PAM



Alkylating agents have other dangerous properties. Many of these can act as carcinogens. Others are known to be chemical *mutagens*, which alter chromosomes and create genetic abnormalities. Chemical mutagens may also produce cellular changes that cause skin cancer or genetic changes that could result in the birth of a malformed baby.

Several common compounds are also *suspected* of being mutagens, at least for certain strains of bacteria and mice. Among these compounds are tranquilizers (Librium and Valium), antidepressants (Marplan, Niamid, and Nardil), and antibiotics (Chloromycetin, Streptomycin, Micomycin C, and Actinomycin D). Sodium nitrite, certain pesticides, and air pollutants (ozone and benzopyrene) from smoke may also cause mutations in humans or animals. Another dangerous mixture is the solvent used in airplane glue. This solvent is a mixture of toluene, acetone, hexane, and ethyl acetate and is dangerous to inhale because it can lead to asphyxiation. The geneticist also looks upon LSD (lysergic acid diethylamide), marijuana, and even caffeine with suspicion because some research suggests that these compounds produce permanent damage to cells that may be transmitted to succeeding generations (see *Drugs: From Aspirin to Hallucinogens*).

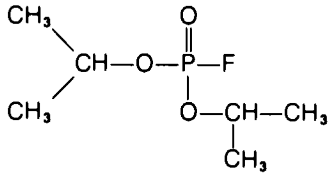
Of the compounds just listed only benzopyrene has been shown to be a definite carcinogen in humans. Researchers have discovered that benzopyrene causes skin cancer. Several of the other compounds, however, are known to cause a breakdown of chromosomes in white blood cells in the human body. Just what effect this has on an individual is not clear.

O-29 Nerve Gases

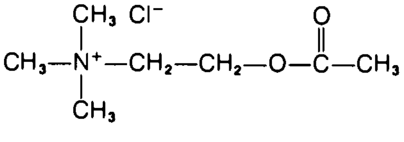
After World War II a new class of war gases was developed: the *nerve gases*. Scientists in wartime Germany developed these gases as an outgrowth of their research on insecticides. The Soviet Union captured the plant where Germany's nerve gas was produced and moved it to Russia to continue research and production. The United States became aware of this and began to produce its own nerve gas.

As the name implies, nerve gases affect the nervous system. They do this by interfering with the breakdown of acetylcholine, a chemical compound in the body that is involved in the transmission of nerve impulses. Under the influence of the gases, the nerve impulses continue with no control, resulting in paralysis and eventually death. (Many common insecticides operate in a similar way.) The circumstance that makes nerve gases especially dangerous is not only their extreme toxicity but the fact that they can be absorbed through the skin. The whole body, not just the breathing system, must be protected against them.

A NERVE GAS



ACETYLCHOLINE

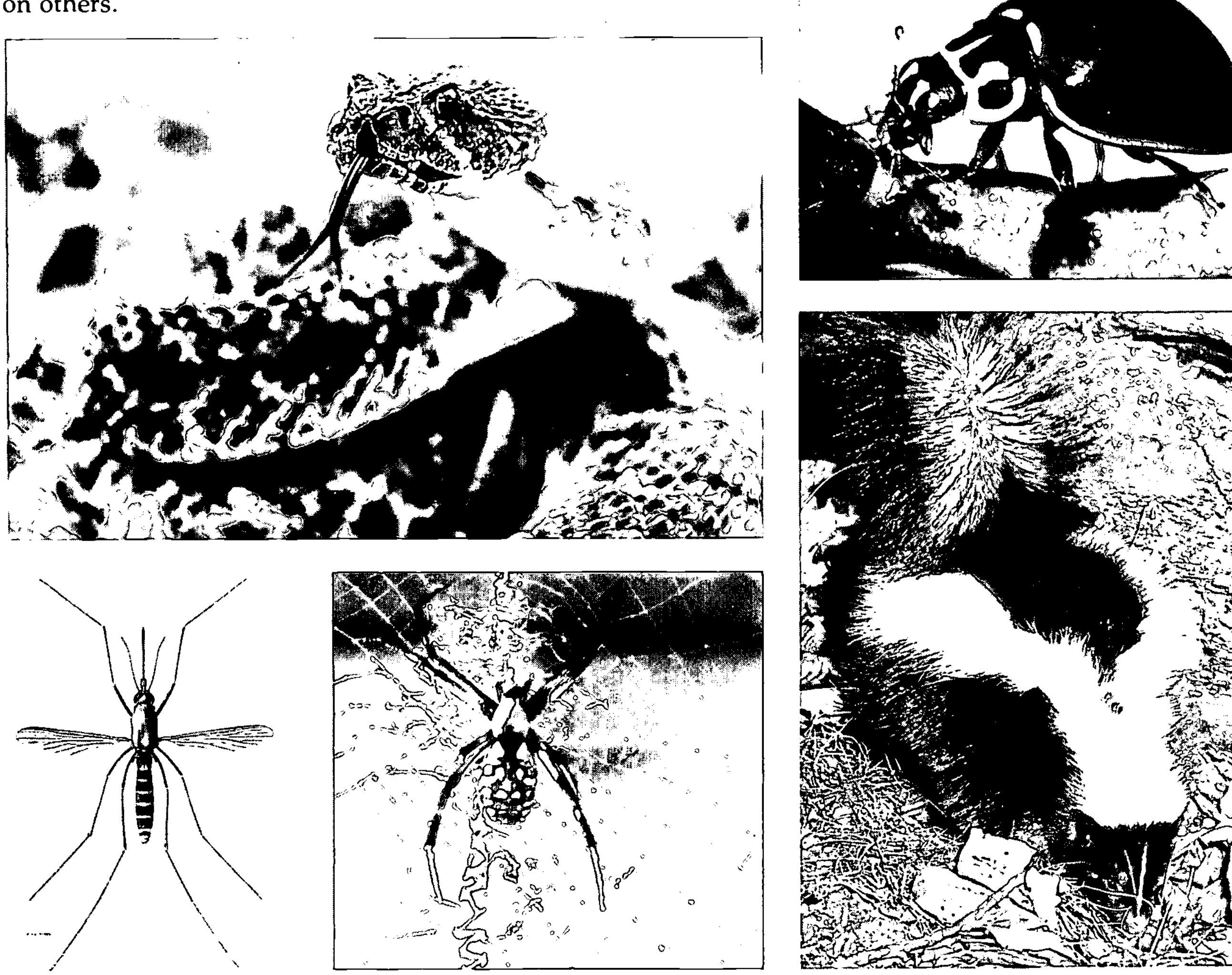


$$CH_3-\overset{CH_3\ Cl^-}{\underset{CH_3}{N^+}}-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3$$

O-30 Chemical Warfare in the Animal World

Human beings may think that they originated the use of chemicals in warfare, but they really did not. Animals carried out chemical warfare long before humans made their appearance. The classic example is the familiar skunk, which uses a group of sulfur-containing organic compounds (see Appendix III) as an effective deterrent against potential predators. All but the most foolish adversaries take warning when the skunk begins a kind of foot-stamping dance, which usually precedes the use of the yellowish chemical spray secreted from glands under its tail. The skunk's spray when ejected may reach more than three meters. As with many compounds in nature, the skunk's secretion has other uses; it sometimes forms the base of perfumes used by human beings. There are dozens of animals—reptiles, mammals, fish, insects—that make some use of poison in protecting themselves or preying on others.

Snake, beetle, mosquito, spider, and skunk all protect themselves by using various means of chemical warfare.

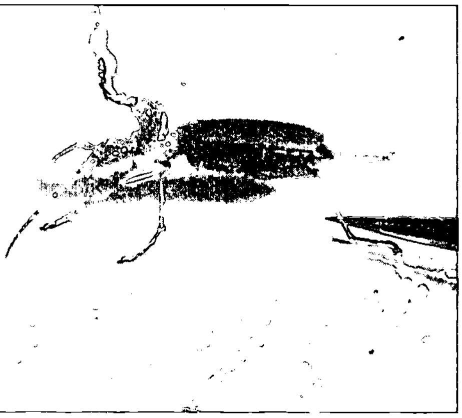


But the arthropods, which include the insects and spiders, probably have the most ingenious means of defending themselves. Most of these creatures are small and without a backbone and can hardly exchange blows with an attacking enemy. These animals simply do not have the "muscle power" to protect themselves. Yet, they've been able to exist essentially unchanged from prehistoric times. Nature has endowed many of the arthropods with a sophisticated defense system—a system of chemical defense.

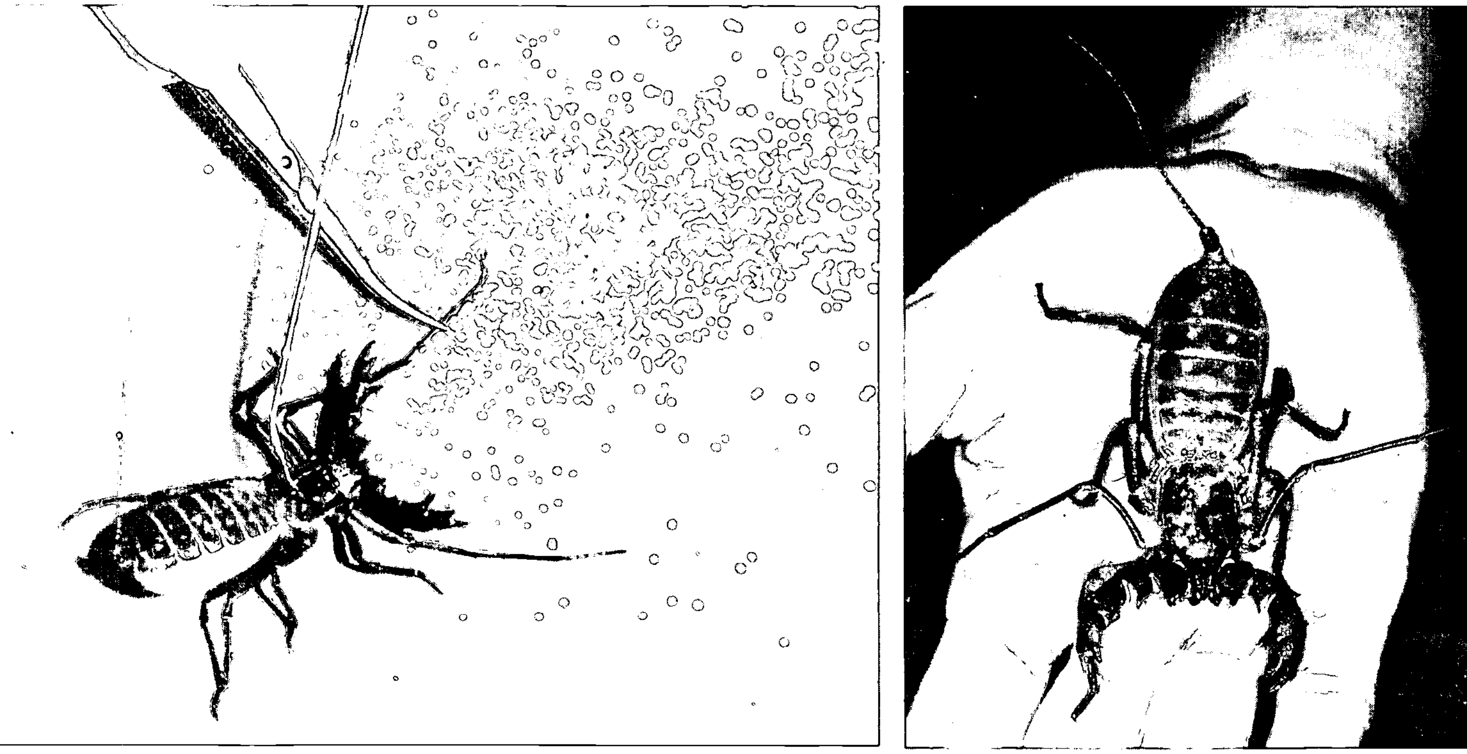
For example, when the beetle *Galerita janus* is attacked by a predator, it reacts quickly and effectively. The little beetle sprays the attacker with a secretion that contains large amounts of formic acid ($HCOOH$). This spray soon drives the intruder away. The beetle aims the spray from one of a pair of glands at the rear of its abdomen. Although very effective, this formic acid attack is among the simpler measures that insects use to protect themselves.

Another interesting example of chemical defense in the animal world is exhibited by an arthropod called the whip scorpion, or *Mastigoproctus giganteus*. The whip scorpion has a peculiar structure at the base of its tail. It consists of a turretlike mechanism that the scorpion can rotate at will. This turret has two glandular openings. When the scorpion is threatened, it rotates the turret into position, aims, and fires. The spray contains a mixture of 84 percent acetic acid (CH_3COOH), 5 percent caprylic acid [$CH_3(CH_2)_6COOH$], and water.

For the purpose of observation, the beetle *Galerita janus (below)* is temporarily attached to a wire with a piece of wax. When threatened, the beetle aims and fires an acid spray at its "attacker." It does this by revolving its abdominal tip where the discharge glands are located.

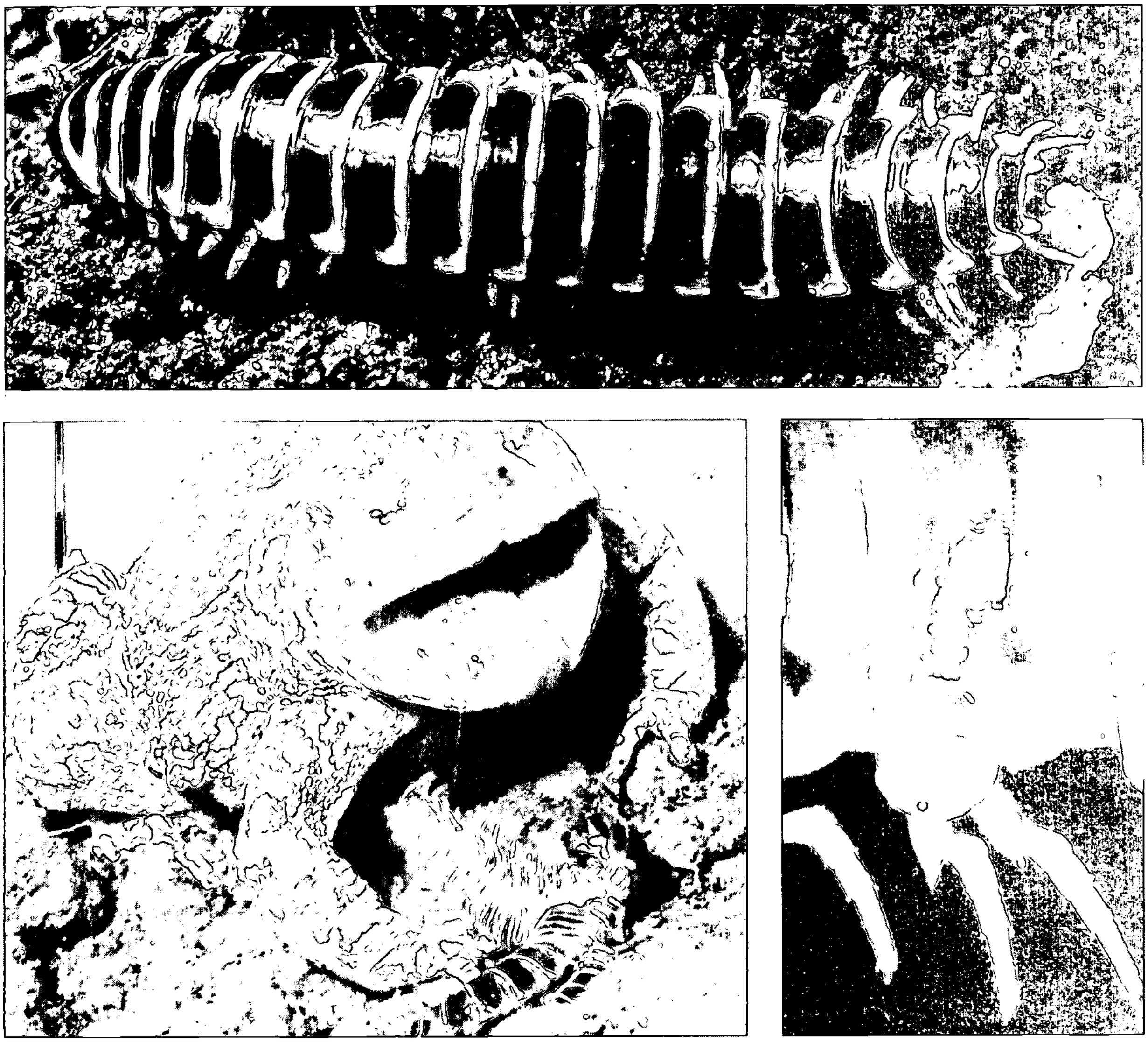


Whip scorpion *(below)*



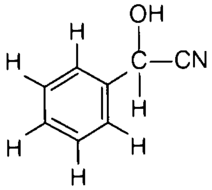
The millipede *Apheloria corrugata* really has a surprise for its enemies. When attacked, this millipede defends itself with gas warfare. Through glands in the side of its body, the *Apheloria corrugata* gives off rather large amounts of the gas hydrogen cyanide (HCN). This lethal gas convinces almost all potential enemies that they should search elsewhere for their next meal.

The toad *(bottom left)* found its prospective meal of *Apheloria corrugata* to be quite distasteful. The enlargement shows the glands on the side of the millipede's body—the opening has been marked for clear identification.



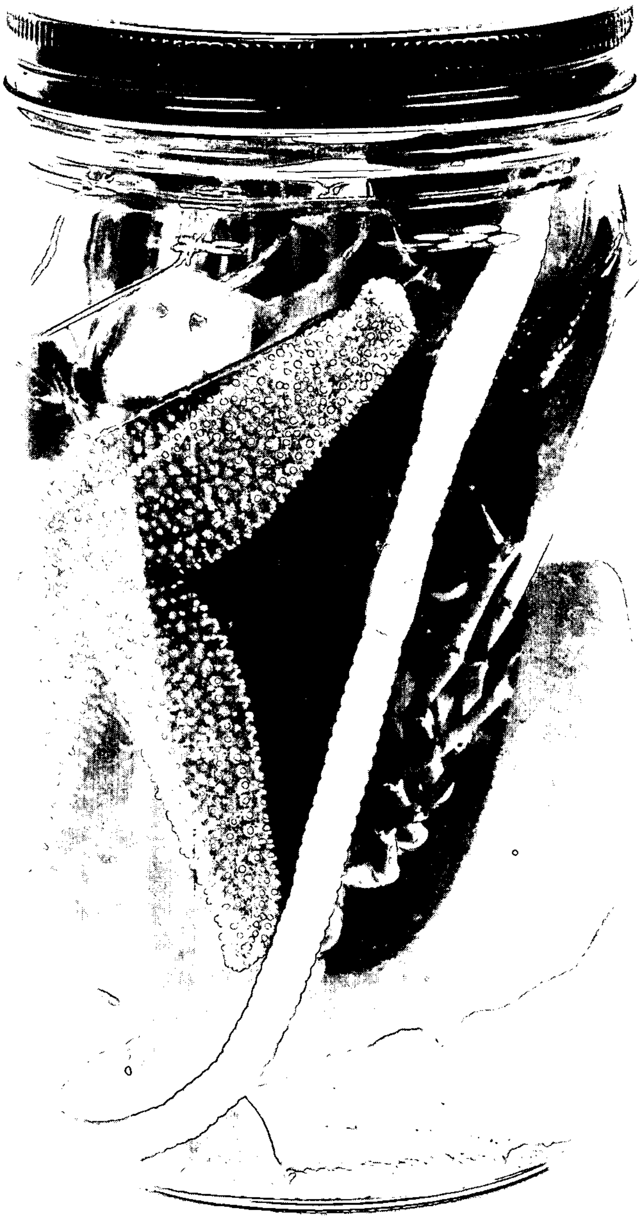
The surprising thing about *Apheloria corrugata* is that in itself it contains no hydrogen cyanide. Upon dissecting the millipede, you will find no hydrogen cyanide in the gland from which the emission comes. Instead, you will find the chemical mandelonitrile, $C_6H_5CH(OH)CN$. To the organic chemist, the presence of mandelonitrile is a red flag, a giveaway as to the real source of the hydrogen cyanide. This we will discuss further in the next section.

MANDELONITRILE



Aldehydes and Ketones

Some alcohols can be partially oxidized to form two other kinds of oxidized hydrocarbons—aldehydes and ketones. The sharp odor you smell when you walk past a biology laboratory comes from the simplest of the aldehydes—formaldehyde. The simplest compound in the ketone group is acetone, an excellent but highly flammable solvent.



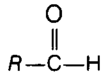
Formaldehyde, one of the most common aldehydes, was once a familiar odor in the biology laboratory but is now being replaced by odorless and much safer preservatives.

O-31 The Carbonyl Clan

Many organic compounds contain oxygen in the form of the carbonyl group, carbon bound to oxygen by a double bond, C═O. In this case, the carbon atom is in a higher oxidation state than the carbon atom in alcohols. In the carbonyl group carbon has two bonds to the oxygen (C═O), whereas in alcohols the carbon atom bonds only once to oxygen.

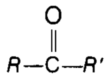
In carbon dioxide (O═C═O) the carbon atom is in its highest oxidation state. In this state the carbon atom shares all four of its bonds with oxygen. As you might expect, there are compounds in which carbon shares three of its bonds with oxygen; these will be discussed later.

The carbonyl group is found in several classes of compounds, including *aldehydes* and *ketones*. Aldehydes have the grouping



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

and ketones have



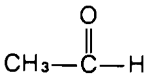
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R'$$

where *R* and *R′* stand for carbon-containing groups, as illustrated in the following examples.

ALDEHYDES

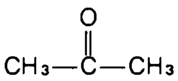
KETONES

ACETALDEHYDE



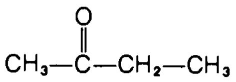
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

ACETONE



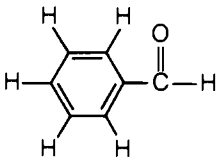
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

2-BUTANONE

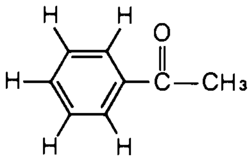


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3$$

BENZALDEHYDE

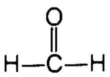


METHYL PHENYL KETONE



Aldehydes are so named because they can be derived from *al*cohols by *dehyd*rogenation—an oxidation process. As an example, look at the simplest of all aldehydes, formaldehyde. It is formed from the dehydrogenation of methyl alcohol.

FORMALDEHYDE



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

METHYL ALCOHOL FORMALDEHYDE HYDROGEN

$$CH_3OH \xrightarrow[\text{catalyst}]{\text{heat}} CH_2O + H_2$$

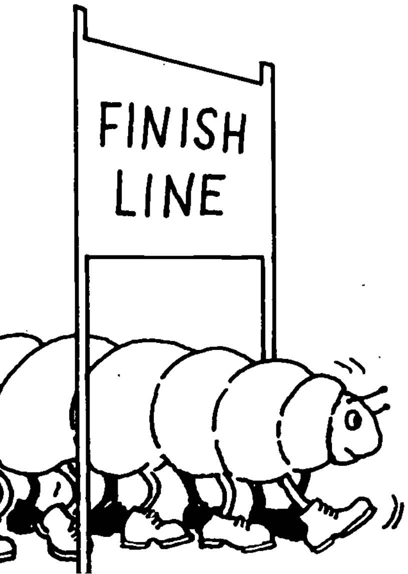
You may have noticed that, although a name such as methyl phenyl ketone has some relationship to the structure of the compound (it is a ketone; it has a methyl group and a phenyl group), names such as formaldehyde and acetone give no hint of the structure of the compounds. These names are historically derived.

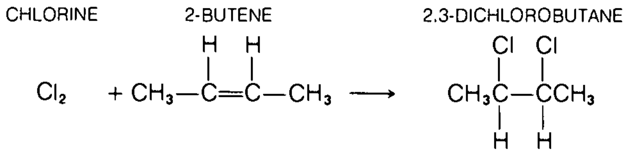
Nomenclature in organic chemistry is filled with these so-called common names, or derived names. Although a more systematic approach to naming chemical compounds has been accepted for years (see Appendix II), many compounds are still known by the names that were given to them a long time ago. Furthermore, many compounds have such complicated formal names that using the common simple names is the only sensible way to identify them.

Aldehydes and ketones are not what you would call common household items, nor would you see them on the general consumer market. The most familiar are formaldehyde and acetone. Formaldehyde is a gas at room temperature, but when dissolved in water it is an excellent preservative for biological specimens, a disinfectant, and a fungicide. It is very important to the plastics industry and in manufacturing other organic chemicals. The most important industrial ketone is acetone. It is a solvent and is used in manufacturing many industrial solvents, in cleaning metals, and in the manufacture of other organic compounds. Acetone is one of the important chemicals used in the manufacture of the polymer rayon.

O-32 Carbonyl Chemistry and the Millipede

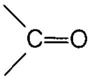
Do you recall our previous reference to the two kinds of reactions—substitution reactions and addition reactions? In a substitution reaction one group or one atom replaces another atom or group as the reaction proceeds. In an addition reaction groups or atoms are added to a multiple bond. For example, consider the addition of chlorine (Cl_2) to a carbon-carbon double bond.



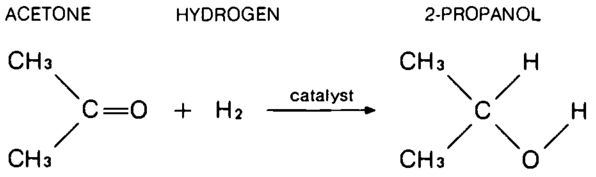


$$Cl_2 + CH_3-\overset{H}{C}=\overset{H}{C}-CH_3 \longrightarrow CH_3\underset{H}{\overset{Cl}{C}}-\underset{H}{\overset{Cl}{C}}CH_3$$

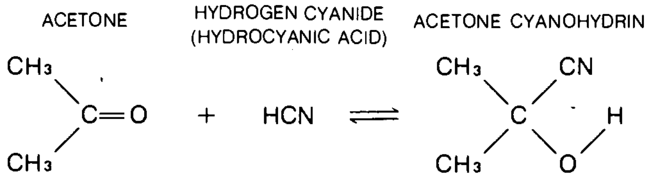
Aldehydes and ketones also have a multiple (double) bond because they contain a carbonyl group



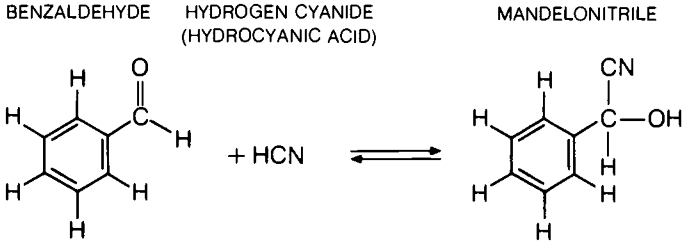
In the carbonyl group the double bond is not between two carbon atoms, as it is in 2-butene, but between a carbon atom and an oxygen atom. Reagents will add to carbon-oxygen double bonds, just as they do to carbon-carbon double bonds. Consider the following example in which acetone reacts with hydrogen.



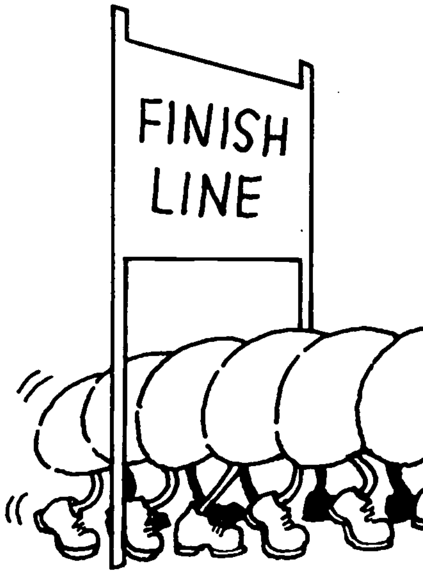
In fact, another reagent, hydrogen cyanide (HCN), adds to carbonyl compounds very effectively to form what are known as *cyanohydrins*. One example is the formation of acetone cyanohydrin.



If you recall the previous discussion of the millipede *Apheloria*, you will remember that, although glands in this millipede contained no hydrogen cyanide (HCN), they did contain mandelonitrile, $C_6H_5CH(OH)CN$. The mandelonitrile reveals the source of the hydrogen cyanide to the chemist. Mandelonitrile itself is the addition product of hydrogen cyanide and benzaldehyde.

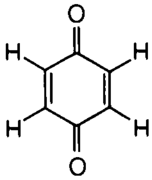


Note that the reaction is reversible. Benzaldehyde and hydrogen cyanide can combine to form mandelonitrile, and mandelonitrile can decompose to produce benzaldehyde and hydrogen cyanide. The millipede makes use of this reversible reaction. Its war gas, hydrogen cyanide, is produced on demand from the mandelonitrile stored in the glands. Mandelonitrile is harmless to the millipede. But when the millipede is attacked, an enzyme causes the mandelonitrile to decompose. The mandelonitrile decomposes to benzaldehyde and hydrogen cyanide. It is this mixture that is the millipede's defensive secretion.



O-33 The Bombardier Beetle

BENZOQUINONE

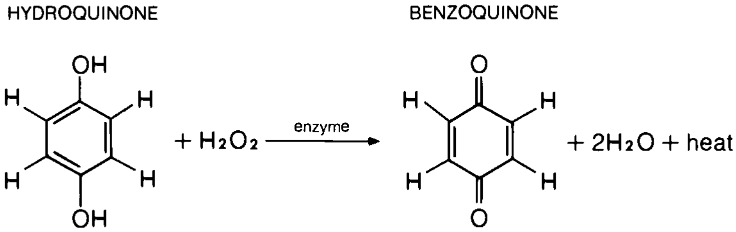


The bombardier beetle employs an even more dramatic means of defending itself. When the bombardier beetle is attacked, a rather strange phenomenon occurs. There is a slight but audible cracking sound and a little cloud of smoke appears from the rear of the beetle. When this cloud of smoke is collected and analyzed, it is found to contain water and benzoquinone.

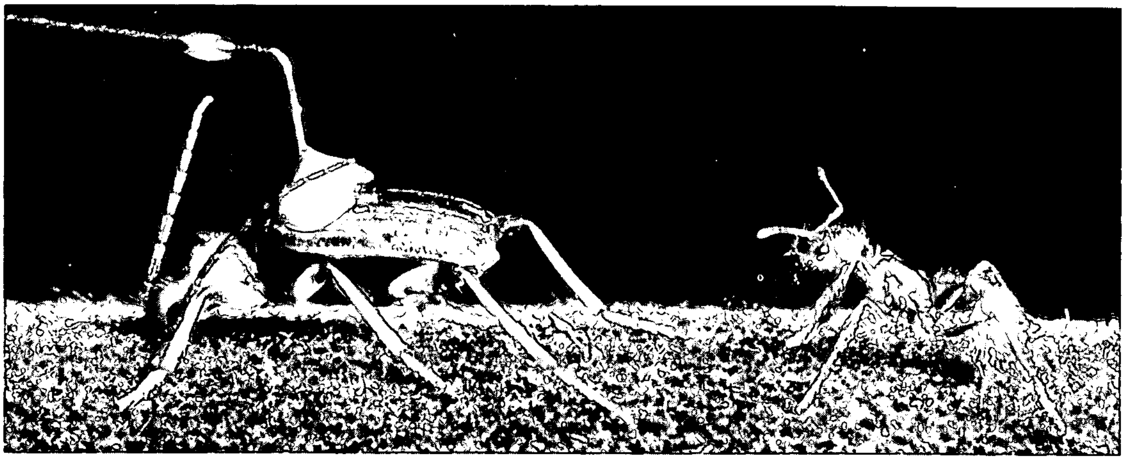
Benzoquinone and other compounds related to it are commonly found in the defensive secretions of insects and arthropods. These quinones have a tendency to stain the human skin black or brown. Apparently the quinones are irritating to the insects and small animals that prey upon the bombardier beetle. The bombardier beetle derives its name from the cracking sound that can be heard when the smoke is emitted.

An investigation of the bombardier beetle reveals that it contains no benzoquinone. The beetle has a pair of glands at the rear of its abdomen. These glands consist of two chambers: an upper chamber, which serves as a *storage chamber;* and a lower chamber, which functions as a *reactor chamber*. The storage chamber contains a mixture of hydroquinone and hydrogen peroxide. Hydrogen peroxide is a well-known oxidizing agent. When the bombardier beetle is attacked, the beetle allows the hydroquinone–hydrogen peroxide mixture to flow from the storage chamber to the reactor chamber. In the reactor chamber other glands release an enzyme that catalyzes the oxidation of hydroquinone to benzoquinone.

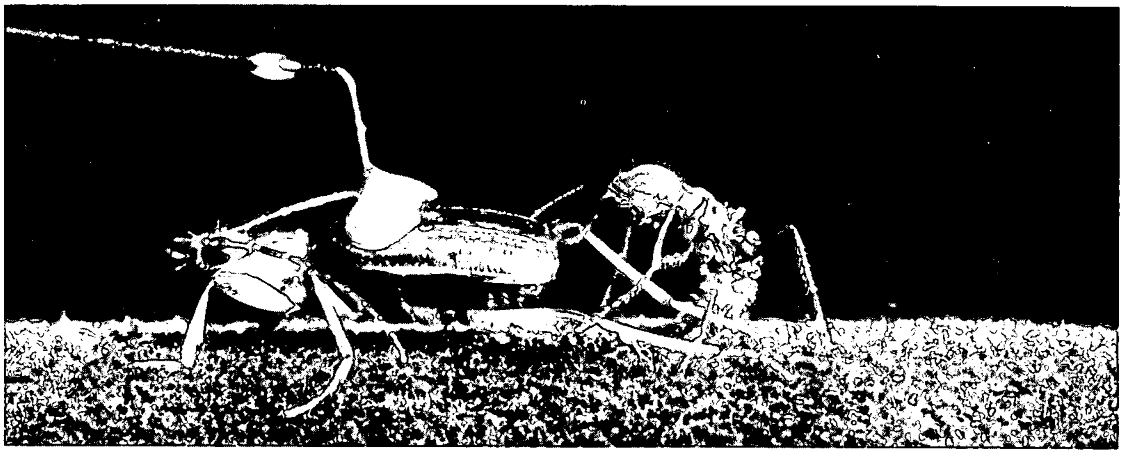
The reaction is an exothermic one—a chemical reaction that gives off heat. The reaction gets started and proceeds at an amazing speed. In fact, the reaction is so fast that it amounts to an explosion, and this is what causes the cracking sound.



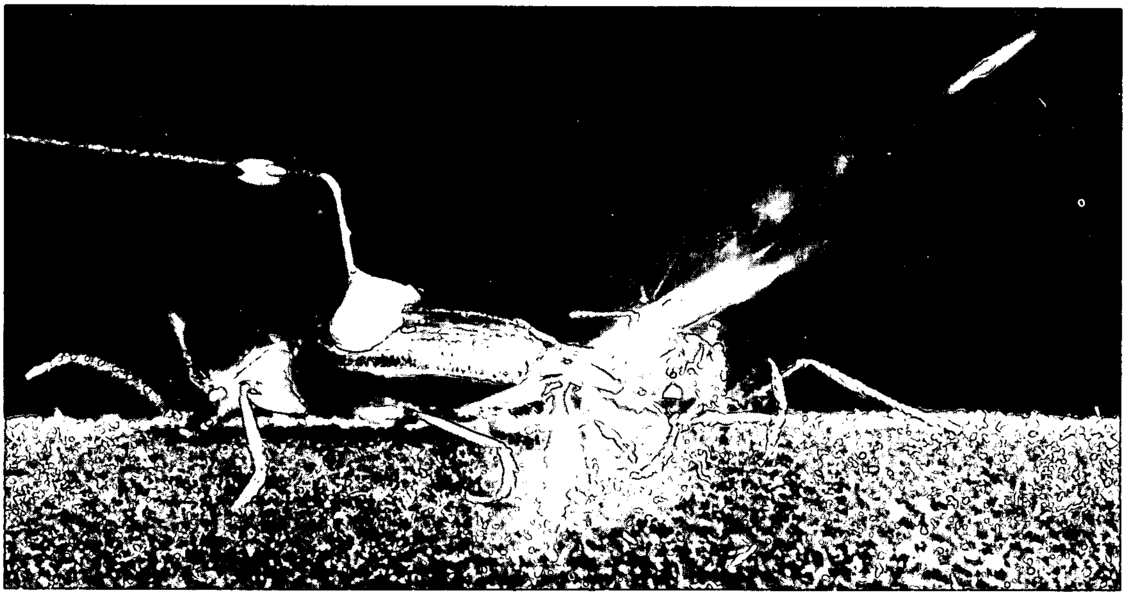
The bombardier beetle's "artillery" actually consists of a mixture of *steam* and *benzoquinone*. The temperature of the discharge is near 100°C, a warm but uncomfortable welcome for any predator—insect or animal.



The brightly colored bombardier beetle (held in place with a drop of wax) attracts an ant.



The ant moves in and seizes the beetle's leg.

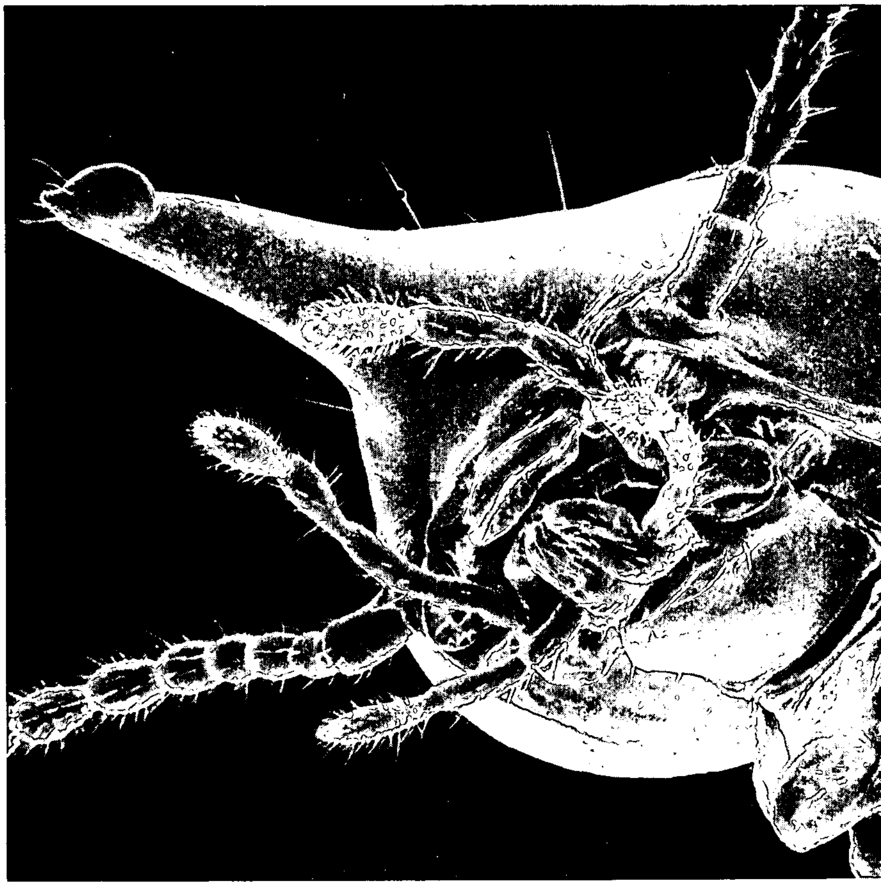


Rotating its abdomen, the beetle aims and fires!

The species of termite *Mastotermes darwiniensis* is similar to the bombardier beetle because it, too, gives off a sticky spray that contains benzoquinone. These animals are little more than walking "spray guns." The globe-shaped head contains the defensive gland that discharges its contents through the pointed end. The sticky fluid contains the chemical irritants α-pinene, β-pinene, and limonene in combination with benzoquinone. Once the assailant is sprayed, the odor of the liquid becomes a signal to other termite soldiers. They then converge on the assailant and add their spray to the target. Besides quickly driving away most predators with the odor and irritation, this liquid also gradually turns rubbery. If an assailant is not careful, it can simply become stuck in the goo.

As we have seen, aldehydes and ketones are used not only by chemists in organic syntheses, but also by some insects in defending themselves. In each case the reactions of these compounds are of the same basic types—oxidation-reduction reactions and addition reactions. It is the properties of the carbonyl group that determine the kinds of reactions that aldehydes and ketones will undergo.

Termite soldiers attack an ant *(below left)*. The head of a termite soldier *(below right)* seen under the electron microscope suggests how it directs the chemical spray at its attacker.



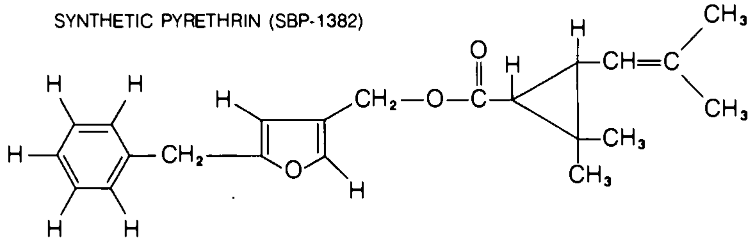
Pesticides and Sex Attractants

Of all the creatures on Earth that affect human affairs, insects can be our closest allies or our worst enemies. Though most insects contribute to human well-being, a small percentage cause disease and destruction. Our ancestors simply had to tolerate these pests until the nineteenth century, when the widespread use of pesticides began to bring these insects under control.

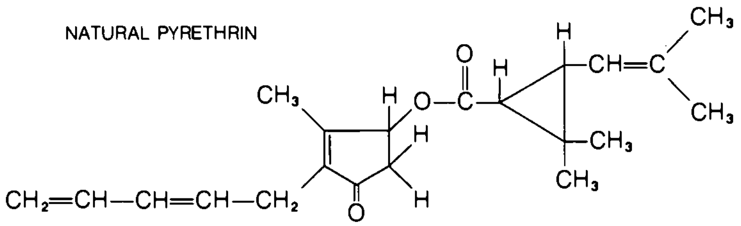
O-34 Insecticides: Chlorinated Hydrocarbons

Except for nicotine (see *O-58*) and pyrethrin, insecticides before 1943 were inorganic materials. Nicotine and pyrethrin are the products of plants. Nicotine is found in tobacco. Pyrethrin comes from pyrethrum flowers, which grow in Africa and which are related to chrysanthemums. As an insecticide, natural pyrethrin is rather expensive. But a close relative of natural pyrethrin has now been synthesized and is much less expensive.

SYNTHETIC PYRETHRIN (SBP-1382)



NATURAL PYRETHRIN



Many of the earlier inorganic insecticides were poisonous compounds containing arsenic (As). In 1943 chemists introduced a new class of insecticides, the *chlorinated hydrocarbons*. The first of these was DDT (*d*ichloro*d*iphenyl*t*richloroethane). DDT and the related hydrocarbons proved to be effective in the war against insects, but they have their drawbacks. Although these chemicals have a low toxicity for human beings, they are toxic for many animals such as fish, shellfish, and useful insects. Furthermore, many insect pests can develop a resistance to the chlorinated hydrocarbons.

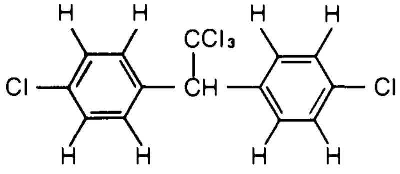
Another unforeseen development has disturbed the ecologists. Chlorinated hydrocarbons are broken down very slowly by nature and thus can persist in our environment for many years. Furthermore, these insecticides tend to become more concentrated in the organisms at the higher end of the food chain. The lower organisms, such as algae and insects, may contain only small amounts of DDT, but the higher animals eat these lower forms of life and so build up the concentration of DDT in their bodies. DDT permeates the bodies of almost all animals, including human beings. The buildup of DDT in humans has become high enough that if the milk of nursing mothers were a salable item, it would be banned by the Food and Drug Administration (FDA). The DDT content of human milk exceeds the allowable limit in cow's milk.

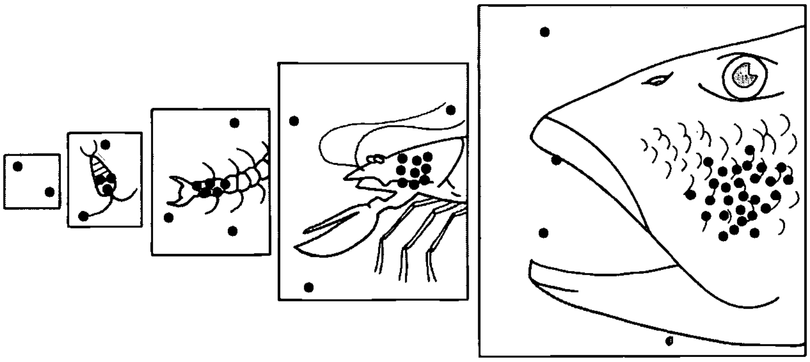
Insect pests have completely eaten away all the foliage from these trees.

TIME MACHINE

1936	Margaret Mitchell publishes *Gone with the Wind.*
1937	The burning of the dirigible *Hindenburg* over Lakehurst, N.J., is reported in first transcontinental radio broadcast.
1938	Thornton Wilder's *Our Town* opens on Broadway.
1939	**Paul Müller discovers that DDT is an effective pesticide.**
1939	World War II begins in Europe.
1939	Howard Florey and Ernest Chain first isolate pure penicillin.
1940	John Steinbeck's *The Grapes of Wrath* wins Pulitzer Prize.
1940	Americans Philip Abelson and Edwin McMillan discover new element—neptunium.

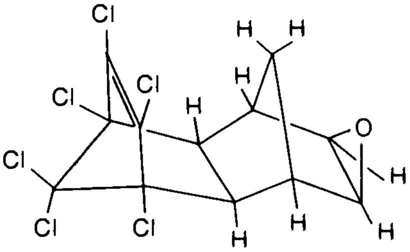
DDT



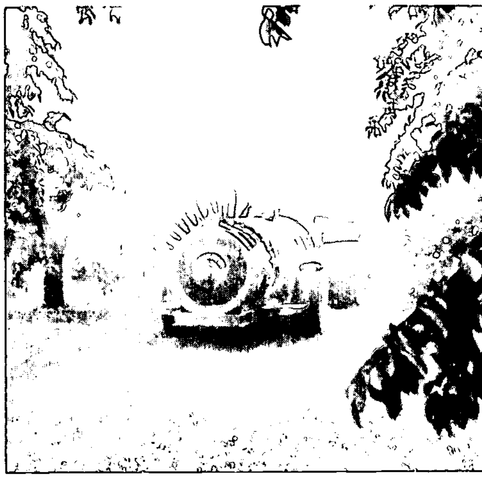


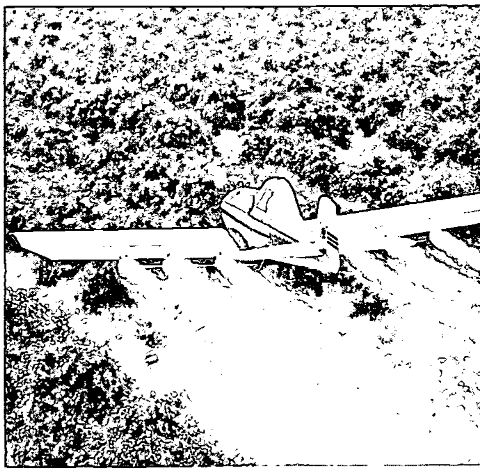
DDT is an example of an insecticide that has been so widely used that it is now a more or less permanent pollutant in our environment. Other chlorinated insecticides, too, have come under investigation as pollutants. Some, such as dieldrin and aldrin (a close relative of dieldrin), have been banned, not only because they are highly toxic but also because, like DDT, they take years to decompose into less toxic compounds.

DIELDRIN



*1,2,3,4,10,10-HEXACHLORO-6,7-EPOXY-1,4,4a,5,6,7,8,8a-OCTAHYDRO-1,4-*endo-exo*-5,8-DIMETHANONAPHTHALENE





Unfortunately, it is difficult, time-consuming, and very expensive to test adequately a single compound for toxicity and carcinogenicity. To test the hundreds of thousands of organic compounds already in the environment, as well as new compounds synthesized each year, would involve a staggering amount of time and money.

Nevertheless, the public as well as those who work in the chemical industry are now demanding adequate protection from unnecessary exposure to potentially dangerous chemicals. Because of unsafe practices in the production of the insecticide kepone in Hopewell, Virginia, a number of workers who came into direct contact with the chemical have been incapacitated. Also, a large segment of the James River, and probably the Chesapeake Bay as well, has become dangerously contaminated with kepone. The

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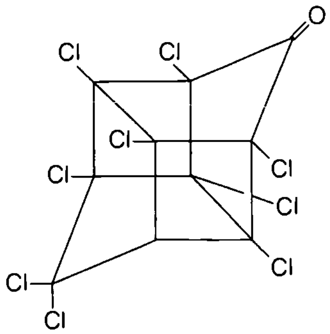
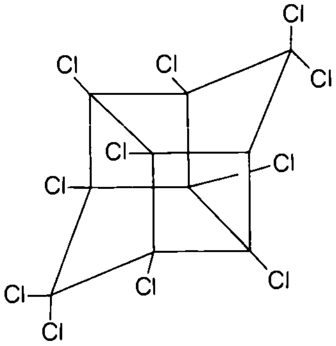
*Here is a clear example of the appeal for common names over formal, complicated compound names. For most people, the common name *dieldrin* is easier to remember and pronounce.

result of this contamination is not yet fully understood, but there will certainly be bad if not disastrous effects on the local fishing industry. Recently, the government banned the use of mirex, a close relative of kepone. For years mirex has been used as the only effective insecticide for control of the highly noxious fire ant in the South.

KEPONE



MIREX

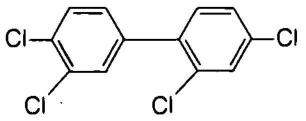


Fire ants feeding on the bud of an unopened okra plant.

O-35 Chlorinated Hydrocarbon Problems

The problems caused by chlorinated hydrocarbons are not confined to insecticides; these compounds have many other important uses. It is becoming more and more clear that chlorinated organic compounds in general present a significant hazard. Vinyl chloride ($CH_2{=}CHCl$), for example, has been implicated in cases of a rare form of liver cancer. Polychlorinated biphenyls (PCBs) have been used extensively for years as plasticizers, as hydraulic fluids, as heat transfer fluids, and in electric transformers. PCBs are fairly volatile and consequently have shown up in unexpected places

A POLYCHLOROBIPHENYL
(PCB)

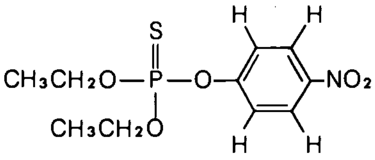


in our environment. They also have been produced industrially on a significantly higher scale than DDT. PCBs appear to be particularly toxic to some forms of marine life, including shellfish and fish, but seem to exhibit little immediate toxicity for mammals. Their long-term effects are unknown. (See Appendix III for other structures.) Fortunately, scientists are discovering and synthesizing compounds that appear to be much safer to replace some of these.

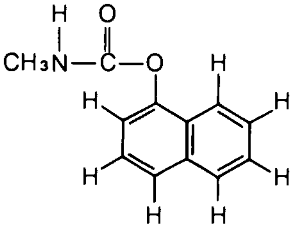
O-36 Ban All Insecticides?

We may use alternative chemicals in place of some of the chlorinated hydrocarbons, but we cannot afford to ban all insecticides. The result would be economic loss and medical misery for the majority of the world's population. Nonpersistent insecticides (that is, insecticides that break down easily into less harmful compounds) have been developed, but most of them are considerably more poisonous to human beings than the more persistent ones, such as the chlorinated hydrocarbons. In fact, many of them are closely related to the nerve gases. Insects seem to have a difficult time in developing a resistance to these poisons. Compare the following structures of nonpersistent insecticides with those of the nerve gases discussed in section *O-27*.

PARATHION

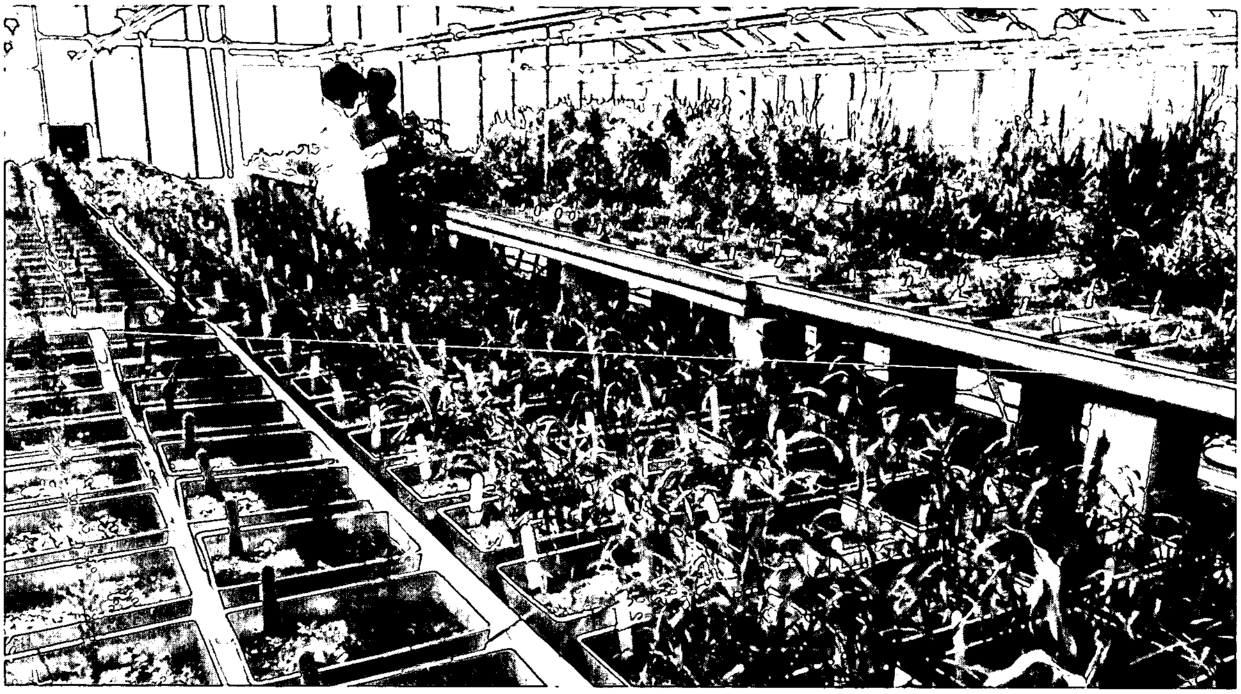


CARBARYL



One solution to the problems created by both types of insecticides would be to do away with all insecticides and return to the "natural" state. The results of this course of action, as pointed out earlier, are probably as bad as the damage caused by the indiscriminate use of insecticides. Is there any other solution? Many scientists believe that an alternative is to use our knowledge of organic chemistry in a more imaginative manner. One way that is now being tried is described in section *O-37*.

The war on insects has produced many problems in maintaining the balance in other areas of the animal world.



Commercial insecticides are being tested in a laboratory greenhouse for their effect both on insects and the environment.

O-37 Sex Attractants: An Alternative

Insects have many real enemies and many potential enemies, but still they survive. Nature has built into them a survival mechanism that explains their large numbers: reproduction. Insects give birth to huge numbers of offspring, so that they have managed to survive simply because they are so numerous.

In the mating process there must be some way for the members of any given species to find and to identify one another. This is no easy task, in view of the many different kinds of insects that inhabit the earth. How do they do it? *Entomologists* (scientists who study insects) and chemists working together have come up with the answer: the insects send messages to each other. In most cases these messages are not sight messages or sound messages, as they are with human beings. They are chemical messages; chemicals used to transmit information are called *pheromones*.

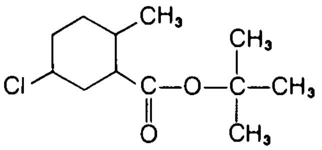
What does an insect do when it wants to attract a mate? The female fruit fly, as an example, makes use of a "perfume" that can be looked upon as a super Chanel No. 5. To attract a mate the female fruit fly gives off a small amount of a pheromone, a chemical substance that is classified as a sex attractant. An unsuspecting male fruit fly that happens to be downwind of the female detects the sex attractant. The male fruit fly simply follows its "nose," flying upwind. If it is moving in the wrong direction, it loses the scent. The male fruit fly then changes direction until it is back on the right track. With a little searching, it finds the female fruit fly and the male and the female mate. Soon a whole new batch of little fruit flies are around to pester us.

Because members of different species cannot mate, the sex attractants must be specific. That is, a sex attractant acts only upon members of the same species. Furthermore, the sex attractants can be detected in extremely minute quantities. The receptor (detector) sites in insects are so sensitive that they are able to detect unbelievably minute quantities of a sex attractant.

Scientists have found that the sex attractants now offer a remarkably effective means of insect control. With an appropriate attractant it is possible to "call in" all of the males (or females) of a species to a small area. With trapping techniques or the use of insecticides in this limited area, the selective control of a single species can be achieved. Thus, selective control of a species is possible without destruction of all wildlife in an area by the widespread use of insecticides.

Selective control by means of a sex attractant is still in an experimental stage. But, in some instances, it has been carried out successfully. U.S. Department of Agriculture scientists have used a sex attractant against the Mediterranean fruit fly to which they have given the name Trimedlure. Using Trimedlure in combination with insecticides, Department of Agriculture entomologists have eradicated the Mediterranean fruit fly from Florida.

TRIMEDLURE

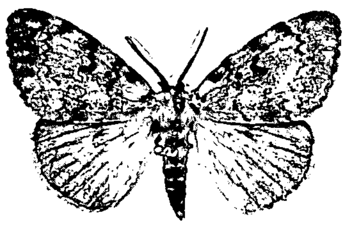


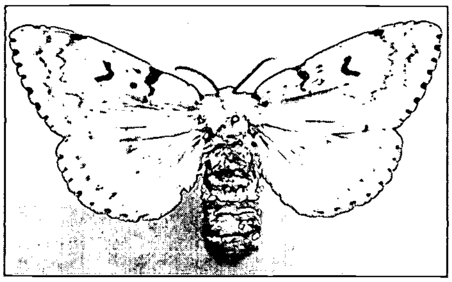
Many tons of rice each year are damaged by insect pests such as the rice weevil.

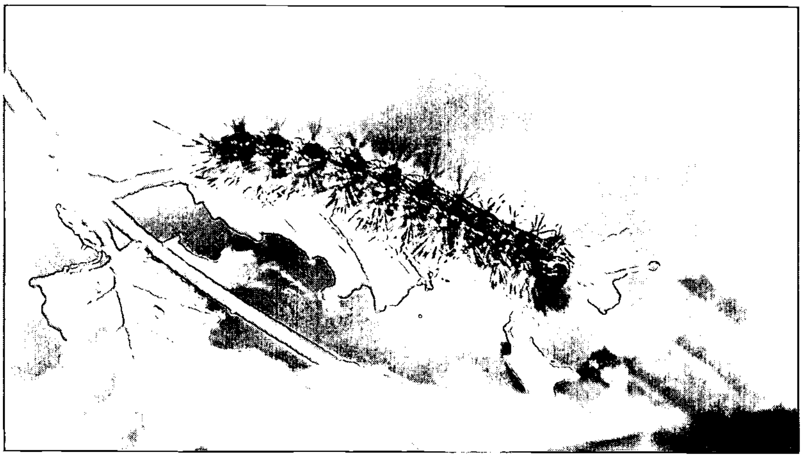
The chemist and entomologist work together to isolate the sex attractants. First, the entomologist removes the portion of the insect in which the attractant is believed to be stored. (In at least one case an entomologist treated half a million insects in a search for the sex attractant.) Once the entomologist isolates the sex attractant, the chemist analyzes it.

A sex attractant often consists of many compounds. Each compound must be tested on the insect to determine which is the active one. When the active compound is identified, the chemist then tries to determine its structure. Then it can be synthesized in large quantities in the laboratory. This is a difficult, painstaking series of tasks; but, hopefully, when the job is finally completed, another insect pest will be easier to control.

The larvae of the gypsy moth are especially troublesome pests. They can chew away a million acres of forest and orchards in a year.

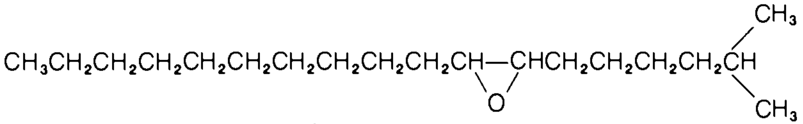






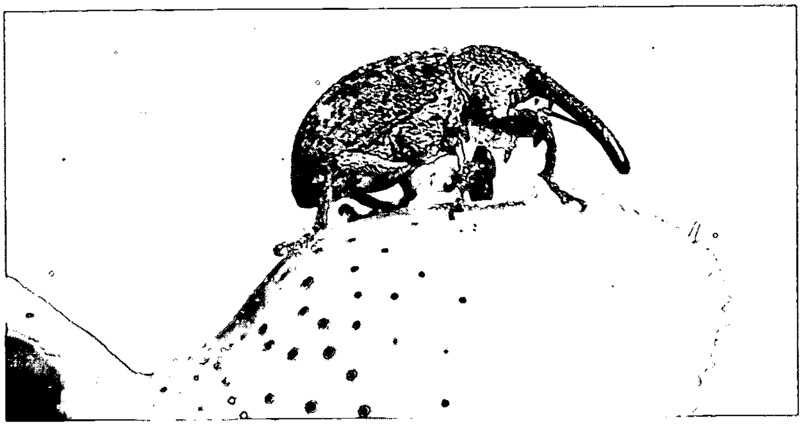
Disparlure, the sex attractant of the gypsy moth, has been isolated; it is now available in quantity and is being used against this pest in various areas of this country.

DISPARLURE

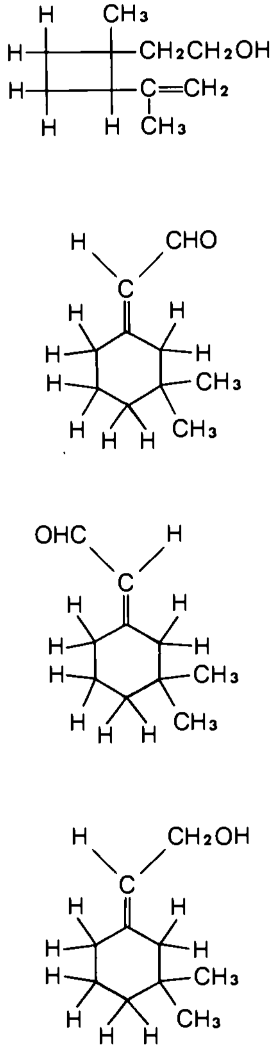


$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH\overset{O}{—}CHCH_2CH_2CH_2CH_2CH(CH_3)_2$$

The sex attractant of the boll weevil is a combination of four materials. It is hoped that these materials will someday be used to halt the destruction of cotton crops by ridding the fields of the boll weevil without the widespread use of insecticides.



BOLL WEEVIL SEX ATTRACTANTS



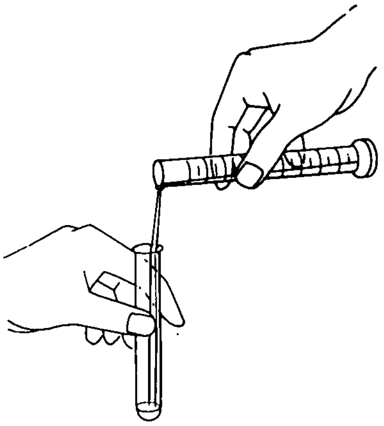
Esters and Acids

Many chemicals that insects produce to communicate with one another belong to a class of compounds called *esters*. Esters are formed in the reactions of acids with alcohols. Just as insects find some of these esters "irresistible," human beings, too, find certain esters pleasant-smelling. Esters give rise to several common odors such as those of fruits and flowers.

O-38 Preparation of Esters

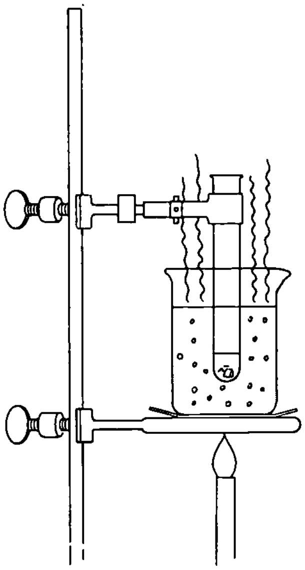
EXPERIMENT

Caution: *Review items 11 and 13 in* Appendix I: Safety *before proceeding with this experiment.* Before mixing any of your reagents together, be sure to smell each carefully. Use the technique that your teacher demonstrates. Then proceed as outlined:



A. Amyl Acetate

1. Pour about 2 cm^3 of glacial (100 percent) acetic acid (CH_3COOH) into a test tube.
2. Add to the acetic acid an equal volume of *n*-pentyl alcohol [$CH_3(CH_2)_3CH_2OH$].
3. Cautiously add about 1 cm^3 of concentrated sulfuric acid (H_2SO_4).
4. Stir the mixture slightly and then place the test tube in a boiling water bath.
5. After a few minutes note the odor of the new product by wafting a little of the vapor toward you. If you fail to detect an odor, pour the contents of the test tube into a beaker containing 25 to 50 cm^3 of warm water. The ester that you formed results from the reaction of the carboxyl group (—COOH) with the hydroxyl group (—OH) of an alcohol.
6. What fruit does this ester smell like? Why is sulfuric acid used in this reaction?



B. Octyl Acetate

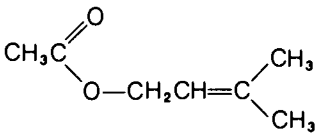
Repeat the preceding procedure, using glacial acetic acid and octyl alcohol. (Note: Warming the solution may be necessary.) What odor does the product have?

C. Methyl Salicylate

Repeat the same procedure, using about 1 gram (g) of salicylic acid and 2 cm^3 of methyl alcohol.

Although each of the esters you have just made may be the principal fragrance of a particular fruit, natural as well as commercial fragrances are often complex mixtures of esters, aldehydes, and ketones. In fact, Juicy Fruit fragrance is one that comes from a single compound, while one formulation of imitation blackberry fragrance contains twenty different esters.

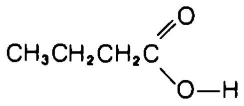
3-METHYL-2-BUTENYL ACETATE



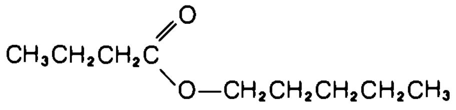
(Juicy Fruit)

It is interesting that small structural differences make large differences in properties. Butyric acid has a putrid odor, yet conversion to its methyl and *n*-propyl esters produces materials that smell like apricot and apple.

BUTYRIC ACID

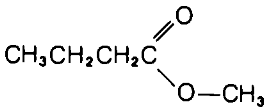


PENTYL BUTYRATE



(Apricot)

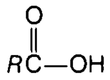
METHYL BUTYRATE



(Apple)

O-39 Organic Acids

The last class of organic compounds on the way up the oxidation chain to carbon dioxide is the *carboxylic acids.*



$$R\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{—OH}$$

These are weak acids, which means that in a water solution only a small, but significant, percentage of the molecules dissociate into ions.

ACETIC ACID

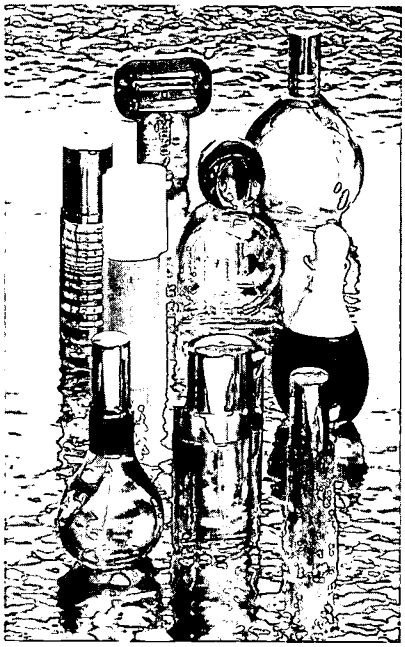
$$\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{—O—H} \rightleftharpoons \mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{—O^-} + \mathrm{H^+}$$

acetate ion
(a carboxylate ion)

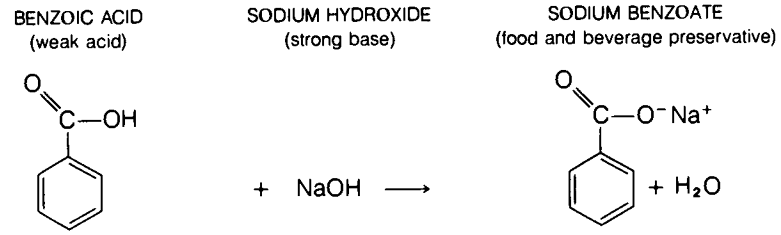
The fact that acetic acid is a weak acid is indicated by the larger arrow pointing to the side of the equation more favored—the left side, in this instance. Of one thousand molecules of acetic acid (CH_3COOH) in solution, only about four dissociate to form acetate ions and hydrogen ions. Almost all of the inorganic acids—hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4)—that have crossed your path so far in chemistry are strong acids. This means that they are completely dissociated in water.

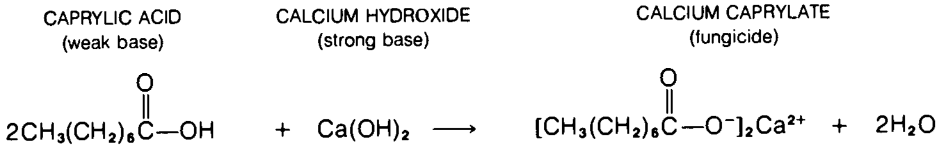
$$\mathrm{HCl} \longrightarrow \mathrm{H^+} + \mathrm{Cl^-}$$

Colognes and perfumes were used in ancient times, but research on esters and acids has vastly increased the variety of fragrances available today.

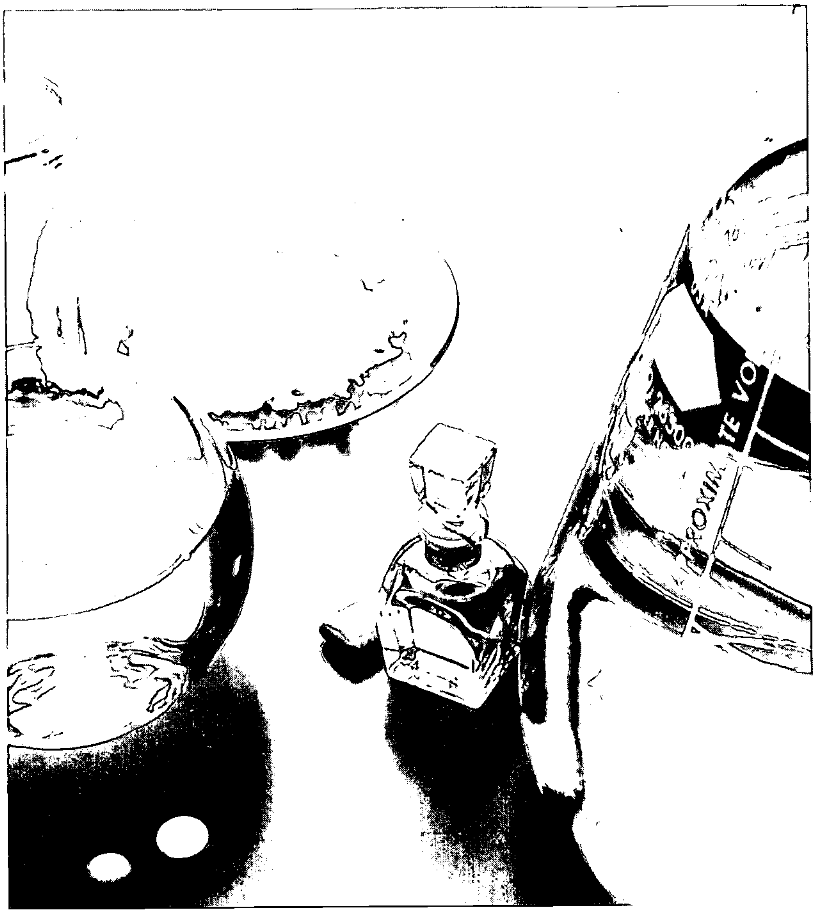


Weak organic acids react with strong bases to produce salts. Some of these salts can be used as preservatives and antifungal agents. Note the list of ingredients on the labels of such foods as carbonated beverages, breads, cookies, and crackers. Some of them will contain sodium benzoate as a preservative.





$$2CH_3(CH_2)_6\overset{\overset{\displaystyle O}{\|}}{C}—OH + Ca(OH)_2 \longrightarrow [CH_3(CH_2)_6\overset{\overset{\displaystyle O}{\|}}{C}—O^-]_2Ca^{2+} + 2H_2O$$



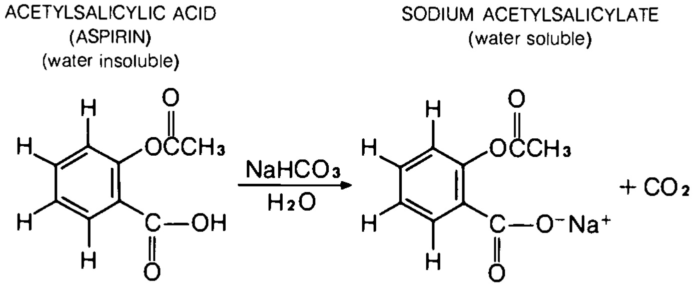
Industrial chemicals, soaps, aspirin and drugs, and colognes and perfumes are all a result of the growing field of ester and acid formations.

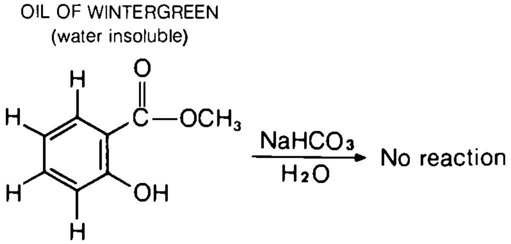
The acids from C_1 to C_4 are water soluble, but after C_8, the carboxylic acids are virtually insoluble in water.

CARBOXYLIC ACIDS

Name	Formula	Melting Point °C	Boiling Point °C	Solubility in g/100 g H_2O
Formic	$HCOOH$	8	100.5	∞
Acetic	CH_3COOH	16.6	118	∞
Propionic	CH_3CH_2COOH	−22	141	∞
Butyric	$CH_3(CH_2)_2COOH$	− 6	164	∞
Valeric	$CH_3(CH_2)_3COOH$	−34	187	3.7
Caproic	$CH_3(CH_2)_4COOH$	− 3	205	1.0

The alkali metal salts (Na^+, K^+) of carboxylic acids are much more soluble in water than the acids. This increased solubility is a property that has many practical uses. For example, suppose you wished to separate acetylsalicylic acid and oil of wintergreen from each other. Both are water insoluble, but the acid will dissolve in a sodium bicarbonate solution, whereas the other compound will not.





Acetylsalicylic acid is the chemical name for the most commonly used drug, aspirin. Aspirin is sometimes commercially packaged in a mixture of citric acid and sodium bicarbonate (Alka-Seltzer), so that when it is put into water it becomes a soluble salt, the form in which it is most easily absorbed. The mixture fizzes because carbon dioxide gas is given off when aspirin reacts with the bicarbonate ion (HCO_3^-).

The organic chemist's main claim to fame is synthesis. Some syntheses are extremely complicated, expensive, and time-consuming.

Others, such as the synthesis of aspirin, are relatively simple. Yet, for the novice, even simple syntheses can prove interesting and challenging. In the following experiment you will synthesize aspirin.

O-40 Synthesis of Aspirin

EXPERIMENT

Place approximately 5 g of salicylic acid in a clean, dry 250-cm^3 flask. From a 50-cm^3 buret (see Figure 1), located on the side shelf in the laboratory, add 10 cm^3 of acetic anhydride, and swirl the flask for a minute or two.

Now add 10 cm^3 of glacial acetic acid from a 50-cm^3 buret, also located on the side shelf. From a small dropping bottle add 3 drops of concentrated sulfuric acid. Swirl the contents of the flask for 3 or 4 minutes.

When the liquid is clear (or nearly so—when there is no visible solid present), empty the contents of the flask into a clean 250-cm^3 beaker containing 100 cm^3 of water. Place the beaker in an ice bath (see Figure 2) until thoroughly chilled. If crystallization has not already begun, scratch the side of the beaker beneath the surface of the solution with a stirring rod. Allow crystallization to become complete.

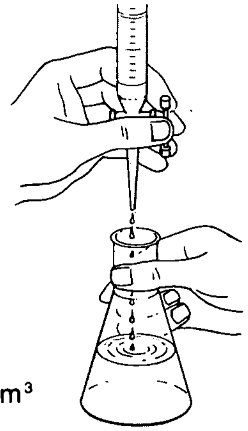


FIGURE 1

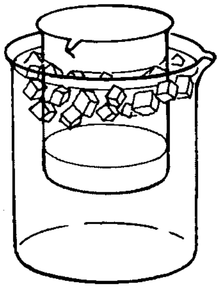


FIGURE 2

Set up a funnel fitted with filter paper (see Figure 3). Filter the product from the beaker, and wash it three times with 10-cm^3 portions of water. Remove the filter paper from the funnel, unfold it, and place it on a paper towel. Place the marked samples in an area designated by your teacher. Leave the samples in this area for drying.

Suggested tests:

1. Determine the melting point of your sample in a melting-point tube. Determine the melting point of commercial aspirin in another tube. Your teacher will demonstrate the proper techniques for determining the melting point of an organic solid.
2. Place a small sample of your aspirin on a small can lid. About 2 to 3 cm away on the lid place an equal-size sample of commercial aspirin (see Figure 4). Place the can lid on the ring of a ring stand. With a low Bunsen flame, heat the lid from below at a point between the two samples. Compare the melting points of the two samples.
3. Test the solubility of your sample. Add a few crystals (about the size of a match head) of your sample to 3 cm^3 of toluene in a beaker. Repeat, using hot water instead of the toluene.
4. Try dissolving a few crystals of your aspirin sample in 5 cm^3 of cold 0.5 M sodium bicarbonate solution. Does it dissolve? Add 0.5 M hydrochloric acid to the solution until it becomes acid.

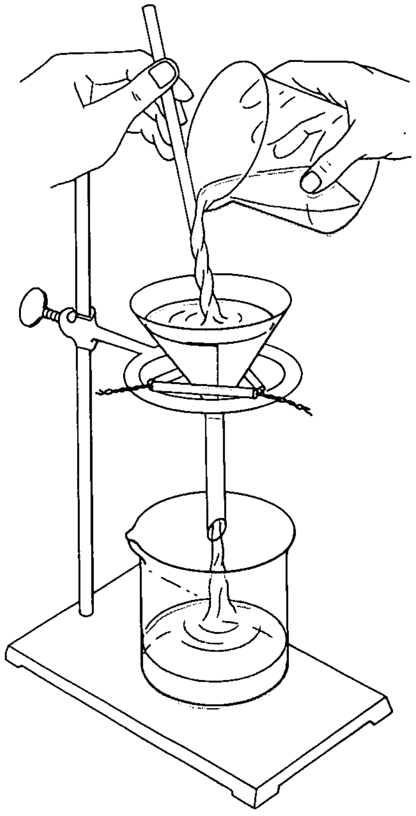


FIGURE 3

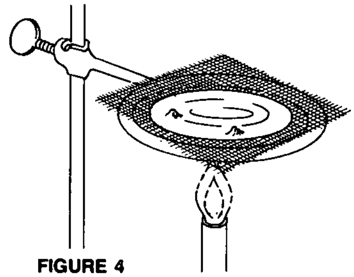
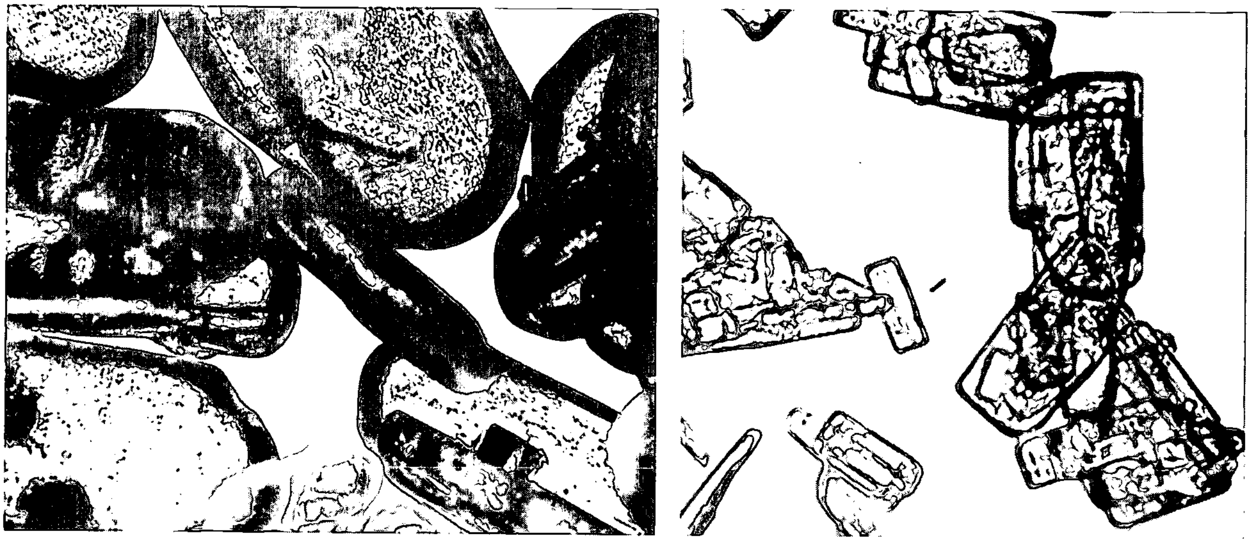


FIGURE 4

Use litmus paper to test the acidity. Chill in an ice bath. What do you conclude about the solubility of aspirin in an acidic solution? In a basic solution?

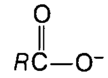
5. To a few milligrams of salicylic acid in a clean, dry test tube, add 1 cm^3 of methanol and 1 drop of 0.1 M iron(III) chloride. Observe the color. Repeat, using milligram samples of your aspirin and commercial aspirin. Do you observe the same color? If so, what could this mean?



Two kinds of aspirin crystals as seen under the microscope—plate type used for dull headaches and needle type for sharp headaches.

O-41 Soaps and Detergents

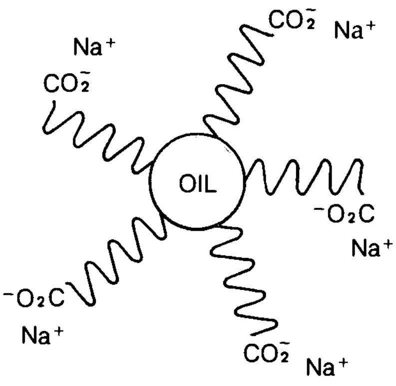
An increase in the length of the hydrocarbon chain increases the size of a carboxylic acid molecule. With this increase in size, the carboxylic acid molecule takes on a solubility that is much like the solubility of pure hydrocarbons. As we mentioned, the metal salts of carboxylic acids tend to be much more soluble in water than the acids themselves. Still, there is a limit to the ability of the carboxylate ion



$$RC(=O)O^-$$

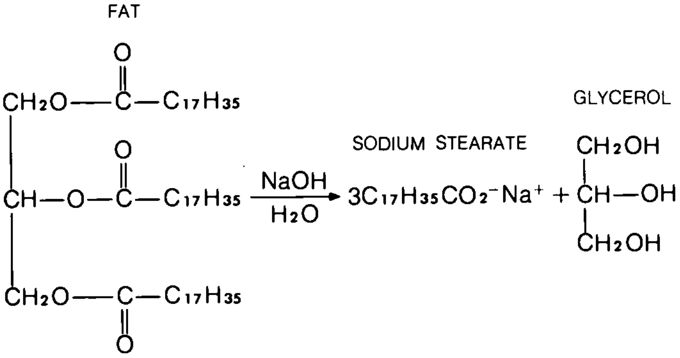
to dissolve in water.

If the rest of the molecule (the *R* group) is a large hydrocarbon chain, the carboxylate ion may not be sufficiently influential to cause the whole molecule to dissolve. The result of this is that the sodium salts of high-molecular-weight carboxylic acids act as wetting agents. In other words, the carboxylate end of the molecule holds onto water, whereas the hydrocarbon end of the molecule clings to oil or grease. This has the effect of "wetting" the surface of the oil or grease (see the diagram *Action of Soaps*).

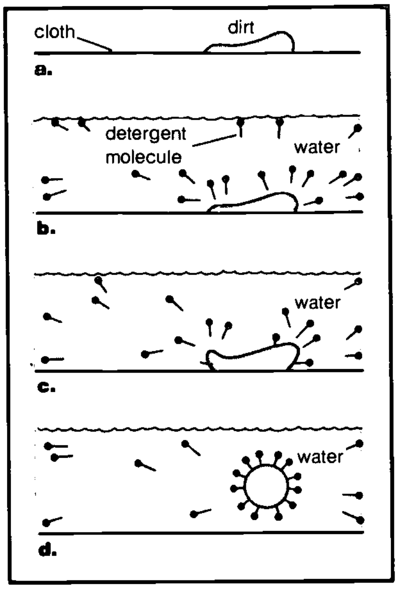


ACTION OF SOAPS

All this is a technical explanation of soap and how it works. One kind of soap is sodium stearate ($C_{17}H_{35}COONa$). To make this soap, boil a mixture of fat and sodium hydroxide ($NaOH$). When the mixture cools, it forms a thick glop that contains soap in suspension.



$$\begin{array}{l} CH_2O{-}C({=}O){-}C_{17}H_{35} \\ CH{-}O{-}C({=}O){-}C_{17}H_{35} \\ CH_2O{-}C({=}O){-}C_{17}H_{35} \end{array} \xrightarrow[H_2O]{NaOH} 3C_{17}H_{35}CO_2^-Na^+ + \begin{array}{l} CH_2OH \\ CH{-}OH \\ CH_2OH \end{array}$$

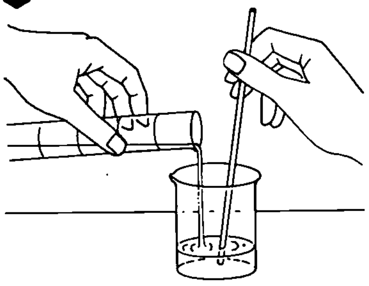


The action of detergent ions on dirt. (a) Dirt on cloth. (b) Detergent molecules attach their ends to dirt and (c) begin to lift it off. (d) Detergent molecules surround dirt and hold it in suspension to be washed away.

The making of soap is one of the oldest known synthetic organic processes. The ancient Egyptians treated animal fats with alkali to make soap. Although technology has enabled us to make soap in quantities undreamed of by the pharaohs, the chemistry is basically the same as that used in Egypt five thousand years ago. In the following experiment you will use vegetable oil rather than animal fat, but the result will be the same—soap.

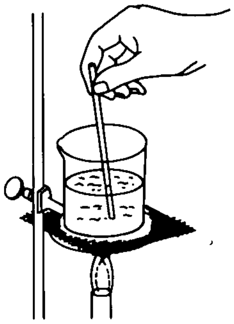
O-42 Preparation of Soap

EXPERIMENT



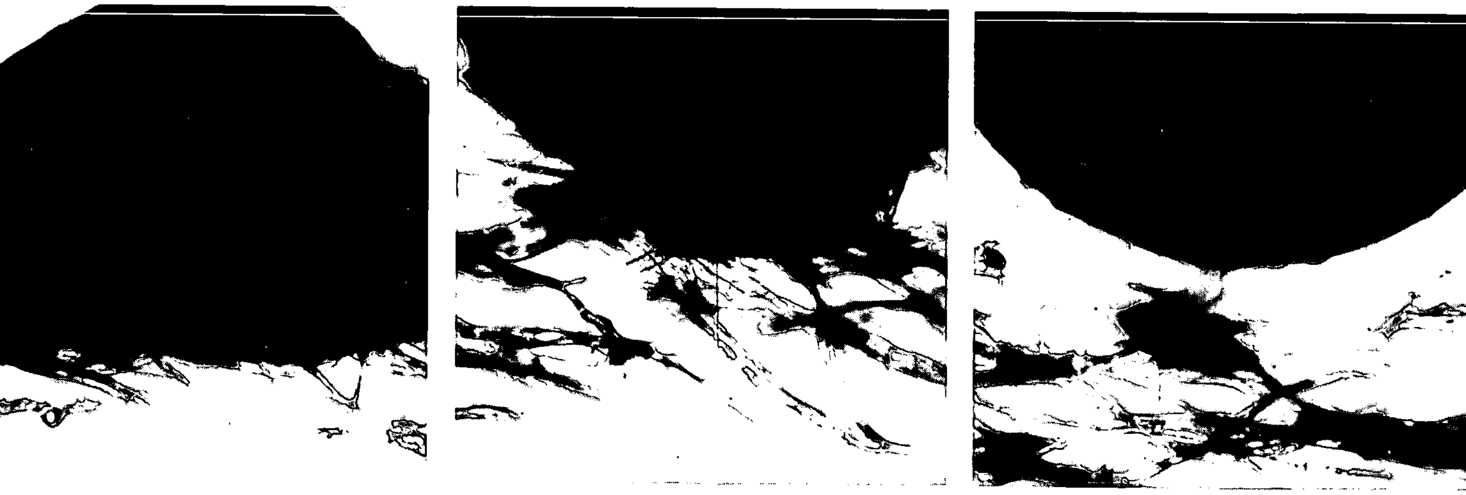
Pour about 5 cm³ of vegetable oil (or animal fat) into a beaker. Add about 20 cm³ of denatured ethyl alcohol and 15 cm³ of 40-percent sodium hydroxide ($NaOH$). ***Caution:*** *Be careful when handling the sodium hydroxide. It is extremely caustic. Also note that you are using alcohol that is flammable in this reaction. Have several wet paper towels ready to smother the flame if the alcohol should catch fire.* Gently heat the mixture, stirring constantly, until the mixture becomes viscous (pasty).

While you are heating the mixture, heat about 150 cm³ of water in another beaker. When the mixture has become a pasty mass, add the boiling water to it. Stir the reaction mixture in the beaker and add about 50 g of sodium chloride. Let the mixture in the water cool. Then skim off the product, which is soap. Rinse the soap with cold water.



Questions: Based on your knowledge of solubility, why did you add the ethyl alcohol? What, besides soap, is a product of this reaction?

Testing the soap:
Fill a test tube one-third full of water and add a few drops of oil. Shake the mixture. Observe. Does it stay mixed? Add some of your soap to the mixture. Then shake the mixture. Note the difference. What name is given to the mixture of oil, soap, and water?



In this photomicrograph, a spot of dirt is seen being removed from a piece of fabric by a detergent. In the final photo, you can see the dirt floating away from the surface of the fabric.

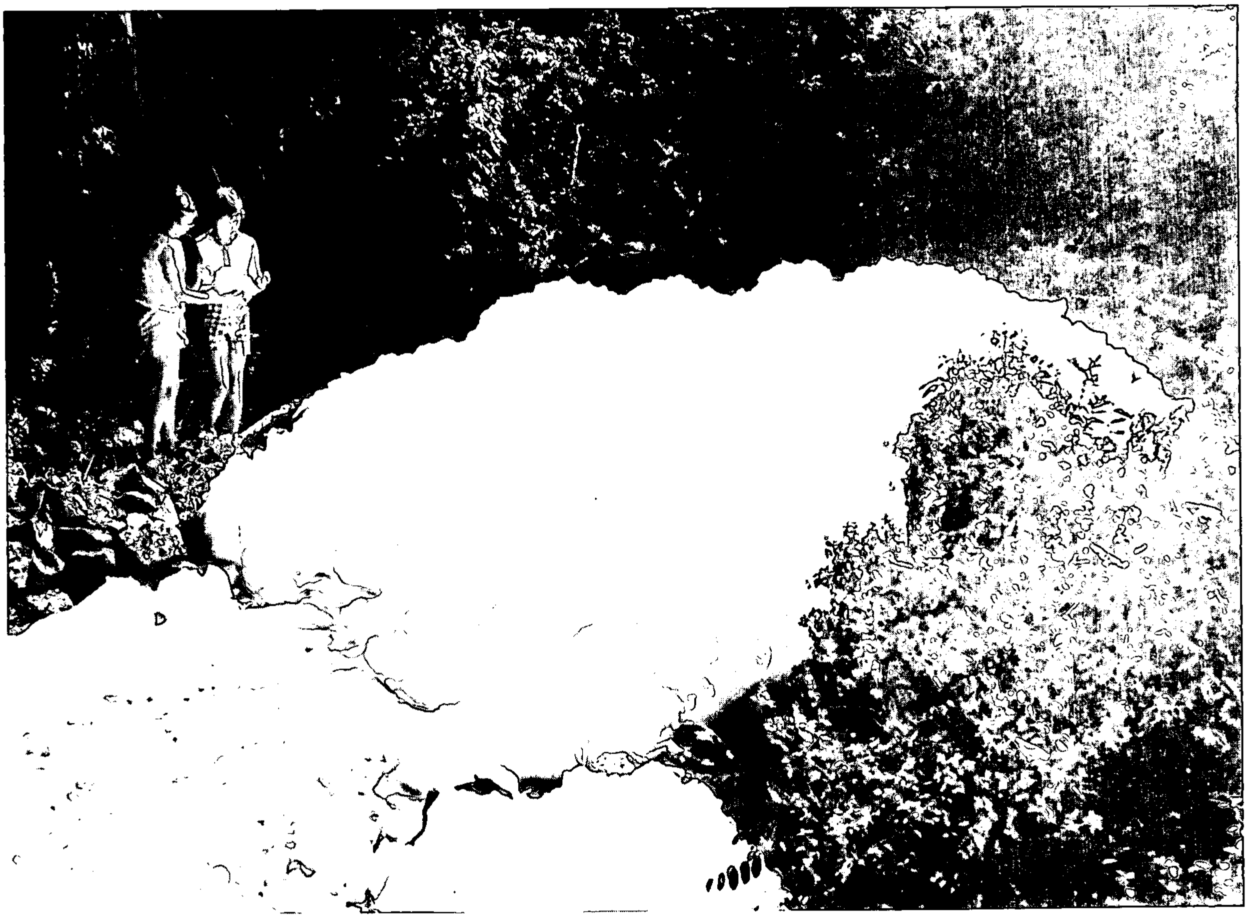
Soaps effectively remove dirt and oil from objects being cleaned. Still, they have their disadvantages. For one thing, several common metal ions can reduce the effectiveness of soap. Among such ions are calcium and magnesium. Calcium and magnesium are found in "hard" water. These ions form insoluble salts in a reaction with fatty acids such as sodium stearate (see *Diversity and Periodicity: An Inorganic Chemistry Module*). The salts decrease the soap's cleaning power. In addition, the insoluble salts form a scum in a tub or in a pan.

An obvious way to avoid this interference with soap is to use "soft" water. Soft water contains much lower concentrations of ions such as calcium and magnesium. In many communities, however, soft water is unavailable, and devices known as *water softeners* are expensive. An easy substitute is to use inexpensive detergents. A *detergent* is a synthetic agent that can be used as a substitute for soap. Like soap, a detergent holds dirt in suspension by emulsifying the oils and water. The advantage that many commercial detergents have over natural soaps is that they contain polyphosphate ions. The polyphosphate ions tie up calcium and magnesium ions so that the detergent can do its cleaning job.

Detergents, however, are not without their faults. In the future we may well have to go back to using "grandma's lye soap" and soften the water in many communities. Common detergents consist of the salts of sulfonic acids ($RSO_3^-Na^+$) and polyphosphate ions. The massive introduction of phosphates in detergents has created an environmental pollution problem (see *The Delicate Balance: An Energy and the Environment Chemistry Module*). The detergents along with their phosphates drain into sewer systems and eventually pour into lakes and streams. (Fertilizers containing phosphates also drain into lakes along with runoff water from the soil.) Algae feed upon the phosphates and soon begin to multiply. Thick mats of algae spread across the surface of the water, with a costly drain on its supply of oxygen. Fish cannot get enough oxygen to remain alive. As a result, many communities have banned the sale of phosphate detergents.

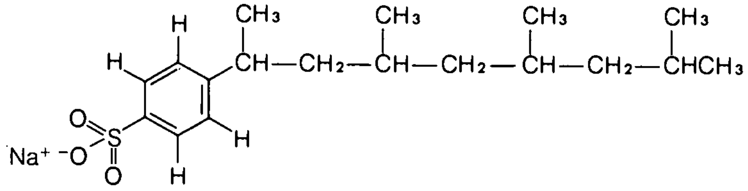
One additional problem accompanies the introduction of synthetic sulfonates such as sodium dodecylbenzenesulfonate. Microorganisms cannot break down this compound into usable fragments. As a result, our streams and lakes rapidly become clogged with bubbles. This particular problem has been solved by switching to biodegradable detergents.

Foam caused by soaps and detergents polluted our waterways before the development of biodegradable detergents.

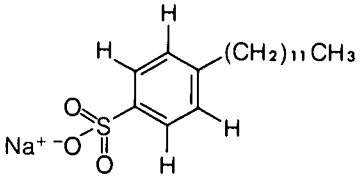


The structural formulas for sodium dodecylbenzenesulfonate and for a biodegradable detergent are shown here.

SODIUM DODECYLBENZENESULFONATE



BIODEGRADABLE DETERGENT



At first glance the two benzenesulfonates depicted in the structural formulas look very much the same. In fact, they are isomers of each other; the two compounds have identical molecular formulas. To bacteria, however, one is a meal, and the other is unusable. Bacteria are incapable of breaking down sodium dodecylbenzenesulfonate and removing it from the water. On the other hand, the biodegradable isomer is readily consumed and taken apart by the hungry bacteria.

O-43 Maintaining the Cycle

Chemists are now synthesizing materials that in the past were never seen in nature. With the production of many synthetics, people are now coping with a problem that they never had to face before—*the inability to recycle*. Life, before the human race inhabited the earth, was the continual buildup and breakdown of carbon compounds in an endless cycle.

Soap is a good example of a substance that can be recycled. For years we took animal fat, converted it into soap, used the soap, and discarded it. Bacteria degraded and assimilated the discarded soap, producing water and carbon dioxide, which make their way into plants through photosynthesis. Animals consume the plants. This is a never-ending cycle, with carbon constantly being returned to the earth and to the atmosphere.

Our modern society is now interfering with this cycle. By altering the structure of compounds, we are assembling products that are completely foreign to nature. Such is the case with plastics, synthetic rubbers, chlorinated hydrocarbons, and, as we have seen, dodecylbenzenesulfonate. To solve the recycling problem, we must synthesize materials that nature can use—that is, we must make them biodegradable. Or we can alter nature so that it is capable of degrading the compounds. An example is the development of strains of bacteria and yeast that are able to "eat" crude oil and thus convert it to usable protein. The development of oil-consuming bacteria holds great promise for eliminating the problem of oil slicks.

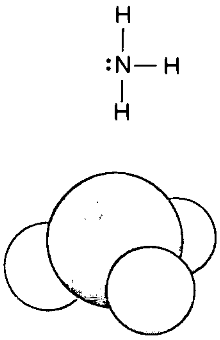
Chemists continue to test lakes and streams to determine the cause and effect of pollutants such as soaps and detergents. The development of biodegradable detergents, which is required by many communities, will help alleviate many of these problems.

Organic Bases: The Amines

Nitrogen, the most abundant gas in our atmosphere, is also one of the least reactive. In synthesizing compounds that contain nitrogen, chemists generally rely on ammonia (NH_3). If the hydrogen atoms in the ammonia molecule are replaced with carbon-containing groups, the resultant organic compounds are called *amines*.

Research with nitrogen compounds has provided us with fertilizers that are responsible for greatly increased crop yields and vast improvements in the world's food supply.

AMMONIA

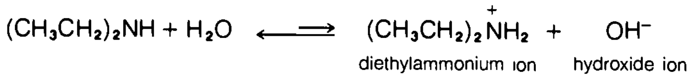


O-44 Ammonia's Offspring

Amines are related to ammonia in the same manner that alcohols and ethers are related to water. Amines are formally derived from ammonia by replacing the hydrogen atom(s) with *carbon-containing* groups.

The lower-molecular-weight amines are water soluble, but amines with more than six carbon atoms are much less soluble in water. Like ammonia, the amines are weak bases by virtue of their slight tendency to react with water to produce hydroxide ions. Again, the longer arrow in the following equation indicates that the majority of diethylamine does not react with water to give hydroxide and diethylammonium ions.

DIETHYLAMINE

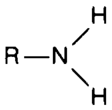


$$(CH_3CH_2)_2NH + H_2O \rightleftharpoons \underset{\text{diethylammonium ion}}{(CH_3CH_2)_2\overset{+}{N}H_2} + \underset{\text{hydroxide ion}}{OH^-}$$

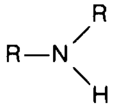
Diethylamine, $(C_2H_5)_2NH$, is such a weak base that only about three molecules in one hundred react with water to give hydroxide ions. However, owing to their basic character, almost all amines dissolve in solutions of acid and water. The amine functional group (RNH_2, R_2NH, R_3N) is essentially the only functional group that imparts this basic character to organic molecules. Thus, when an organic compound is referred to as being a base, the compound usually contains an amine group.

Amines are classified as *primary*, *secondary*, or *tertiary* amines, depending upon how many carbon chains are attached to the nitrogen atom. Methylamine and aniline are primary amines. Diethylamine is a secondary amine, and triethylamine is a tertiary amine.

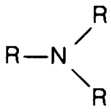
A PRIMARY AMINE



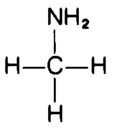
A SECONDARY AMINE



A TERTIARY AMINE

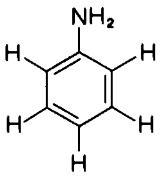


METHYLAMINE



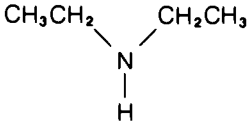
$R\text{NH}_2$

ANILINE



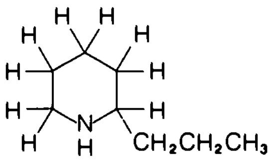
$R\text{NH}_2$

DIETHYLAMINE



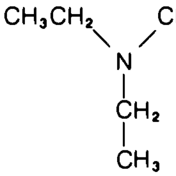
$R_2\text{NH}$

2-*n*-PROPYLPIPERIDINE
(CONIINE)



$R_2\text{NH}$

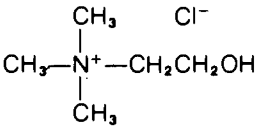
TRIETHYLAMINE



$R_3\text{N}$

The nitrogen atom in amines generally has three groups bound to it. When a fourth group binds to nitrogen an ammonium salt is formed. If all four groups bonded to the nitrogen atom are carbon groups, the resulting ion is called a *quaternary ammonium compound*, of which choline chloride is an example. These salts are water soluble, and they have many applications in industry.

CHOLINE CHLORIDE



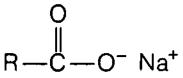
$$\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{CH_3{-}N^+{-}CH_2CH_2OH}}\quad Cl^-$$

R_4N^+

$$\underset{\text{water insoluble}}{C_{10}H_{21}NH_2 + HCl} \longrightarrow \underset{\text{water soluble}}{C_{10}H_{21}NH_3^+Cl^-}$$

Some detergents known as *invert soaps* contain quaternary ammonium groups. An example of such an invert soap is cetyltrimethylammonium chloride. The term *invert soap* arises because in ordinary soaps the anion is an organic ion and the cation is an inorganic ion, whereas in an invert soap the reverse is the case: the organic ion is a cation and the inorganic ion is the anion. (Remember that a *cation* is an ion that has a positive charge; an *anion* is an ion that has a negative charge.) The quaternary ammonium salts are also used in disinfectants, mouthwashes, and throat lozenges.

ORDINARY SOAP

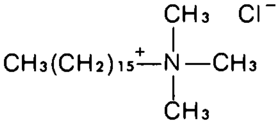


$$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O^-\ Na^+$$

INVERT SOAP

$R_4N^+Cl^-$

CETYLTRIMETHYLAMMONIUM CHLORIDE

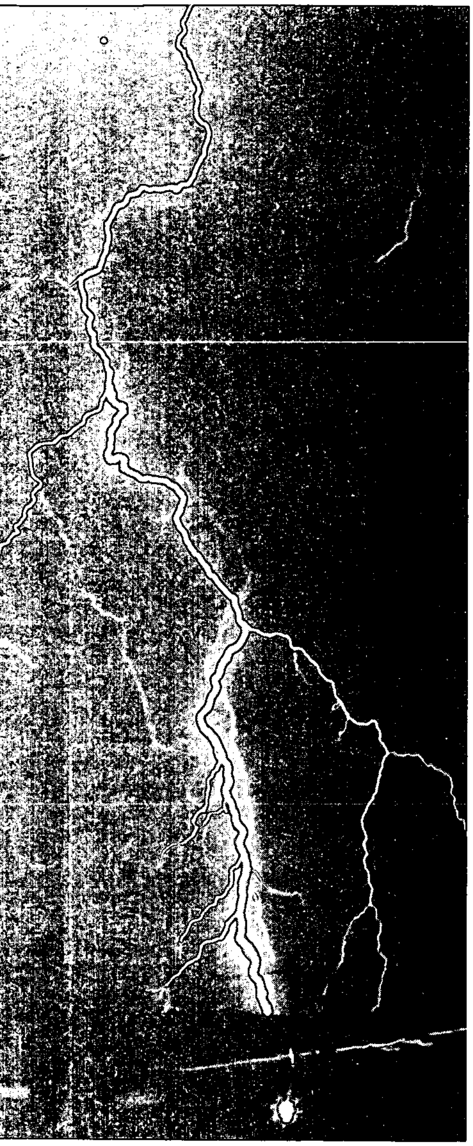


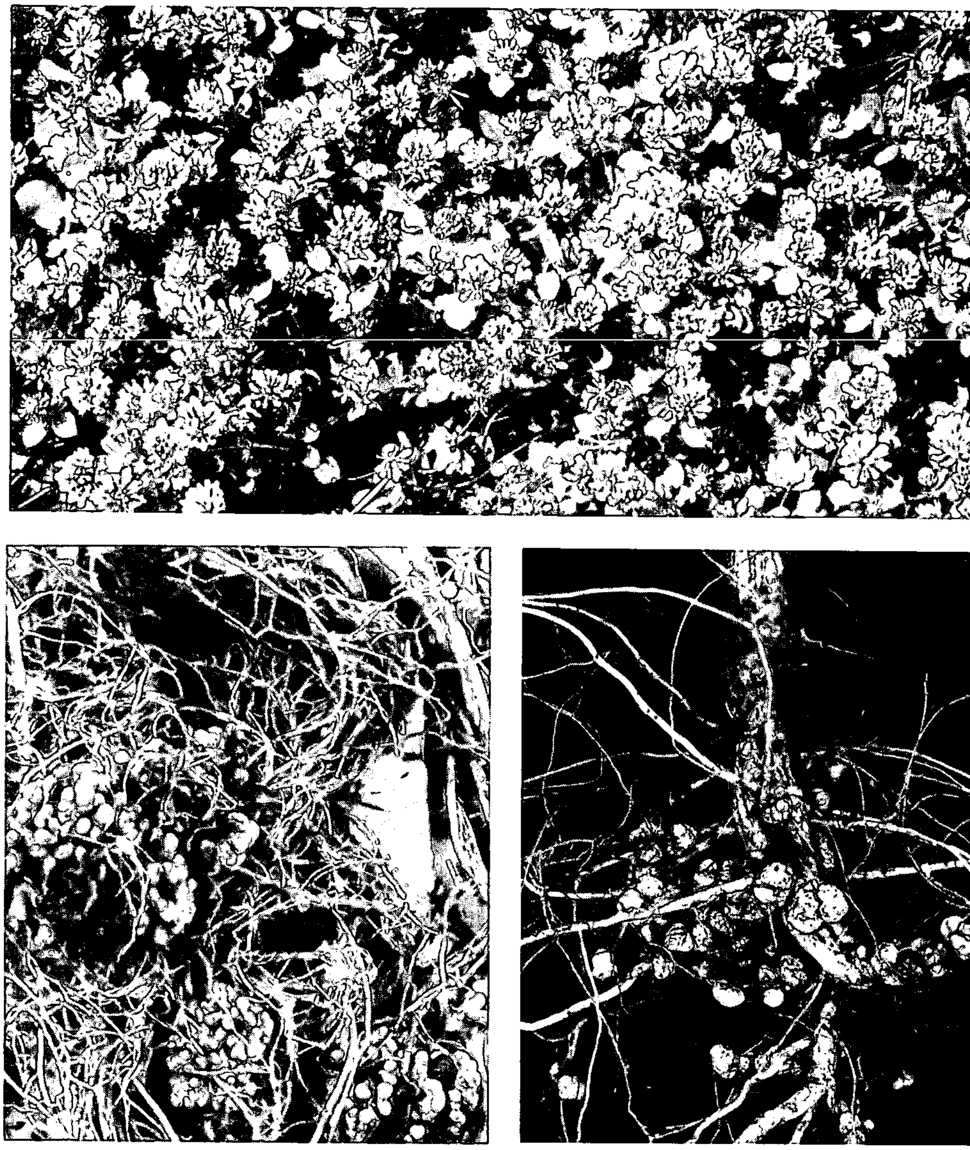
$$\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{CH_3(CH_2)_{15}{-}\overset{+}{N}{-}CH_3}}\quad Cl^-$$

O-45 Molecular Nitrogen

All the oxygen found in organic compounds (alcohols, aldehydes, ketones, acids, esters, and so forth) comes directly or indirectly from molecular oxygen (O_2). In the case of nitrogen-containing organic compounds (amines), the ultimate source for the nitrogen atoms is molecular nitrogen (N_2). Virtually all the earth's nitrogen is now or has been in the form of molecular nitrogen. The reason for this is the great stability of the molecule.

Like carbon, nitrogen has a cycle. However, because of the stability of molecular nitrogen, there are few ways that it is taken



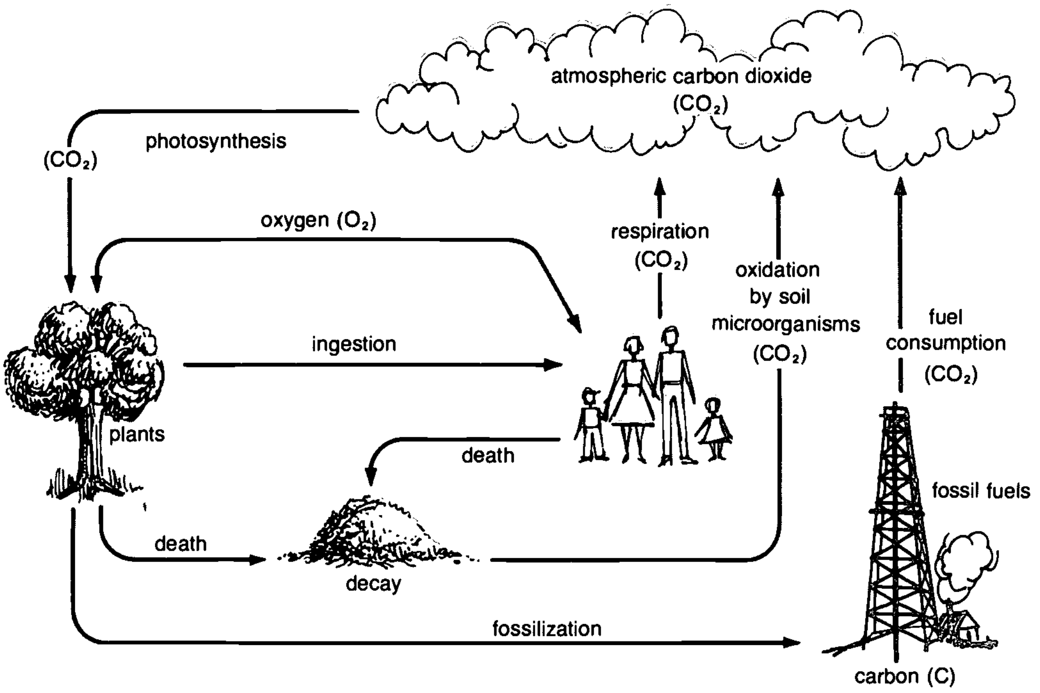


Bacteria in the nitrogen-fixating root systems of clover *(top right)*, winter peas *(bottom left)*, and soybeans *(bottom right)* provide necessary nitrogen compounds for the soil building process. Notice the nodules in the root systems of peas and soybeans where the nitrogen-fixating process takes place.

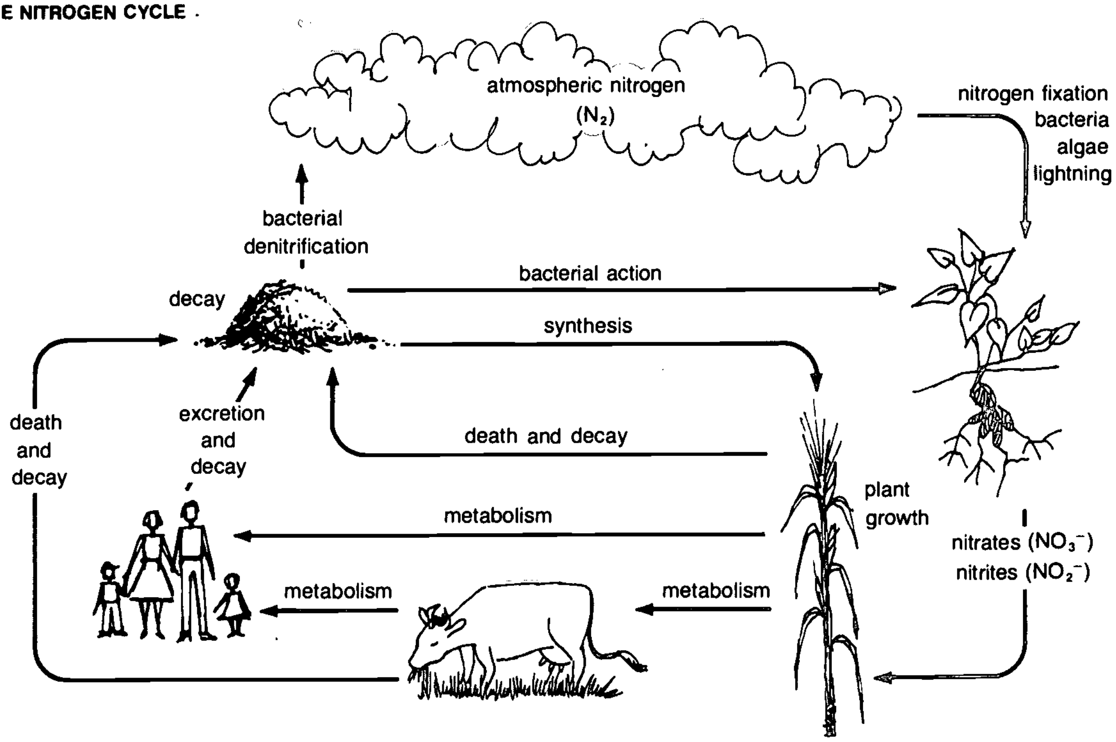
out of that chemical form naturally. The two principal ways are by oxidation during electrical storms ($N_2 \rightarrow$ nitrates) and by reduction to ammonia ($N_2 \rightarrow NH_3$) brought about by certain kinds of bacteria. This latter process is essential for life. Without it, complex molecules such as proteins and nucleic acids could not be synthesized, and thus life, as we know it, could not exist.

All this was known in a vague way to the nineteenth-century chemist. At that time there were two main commercial uses for nitrogen: it was used for fertilizing plants and for manufacturing explosives. The procurement of fertilizers was no problem in the nineteenth century; there was a good deal of compost readily available. But the manufacture of explosives was another problem. The

THE CARBON CYCLE



THE NITROGEN CYCLE



Fertilizers *(opposite page)* in both liquid and powder form are used to supply the nitrogen needed to build up the soil.

principal source of nitrates for making explosives was Chilean saltpeter ($NaNO_3$). No one knew how long the supply from Chile would last.

Before World War I Germany became concerned about the availability of Chilean nitrates. If war broke out, presumably the British could easily cut off Germany's nitrate supplies. The German leaders asked Fritz Haber (1868–1934), a German chemist, to develop a process for making nitrates from raw materials then available to Germany.

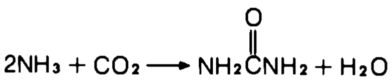
Haber developed a process for the conversion of N_2 to NH_3, ammonia. To make the conversion, he brought about a reaction between nitrogen and hydrogen. When mixed at room temperature, nitrogen and hydrogen do not react with each other. But extreme heat and extreme pressure cause the two elements to react. Haber heated the mixture to a temperature of about 600°C with a pressure of about two hundred times the pressure of the atmosphere in the presence of an iron catalyst (see *Diversity and Periodicity: An Inorganic Chemistry Module).*

HABER PROCESS

$$N_2 + 3H_2 \xrightarrow[450\text{–}600\,°C]{Fe} 2NH_3$$

Ammonia (NH_3) can easily be oxidized to nitrates—used in both fertilizers and explosives. Or it can be combined with carbon dioxide to produce urea, also a good fertilizer. Ammonia itself is often used as a fertilizer.

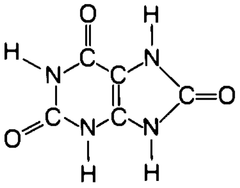
UREA



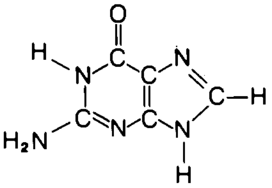
$$2NH_3 + CO_2 \longrightarrow NH_2\overset{\overset{\displaystyle O}{\|}}{C}NH_2 + H_2O$$

In most mammals, including humans, urea is one of the products of the breakdown of proteins (see *Molecules in Living Systems: A Biochemistry Module*). By forming urea, we are able to excrete the nitrogen in our urine, since urea is water soluble. For land reptiles and birds, on the other hand, uric acid is the main excretory product of protein breakdown. These animals have no liquid waste system, since uric acid is not water soluble. Most aquatic animals excrete nitrogen in the form of ammonia. Spiders excrete nitrogen as guanine, and some fish excrete nitrogen as trimethylamine oxide.

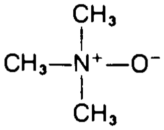
URIC ACID



GUANINE

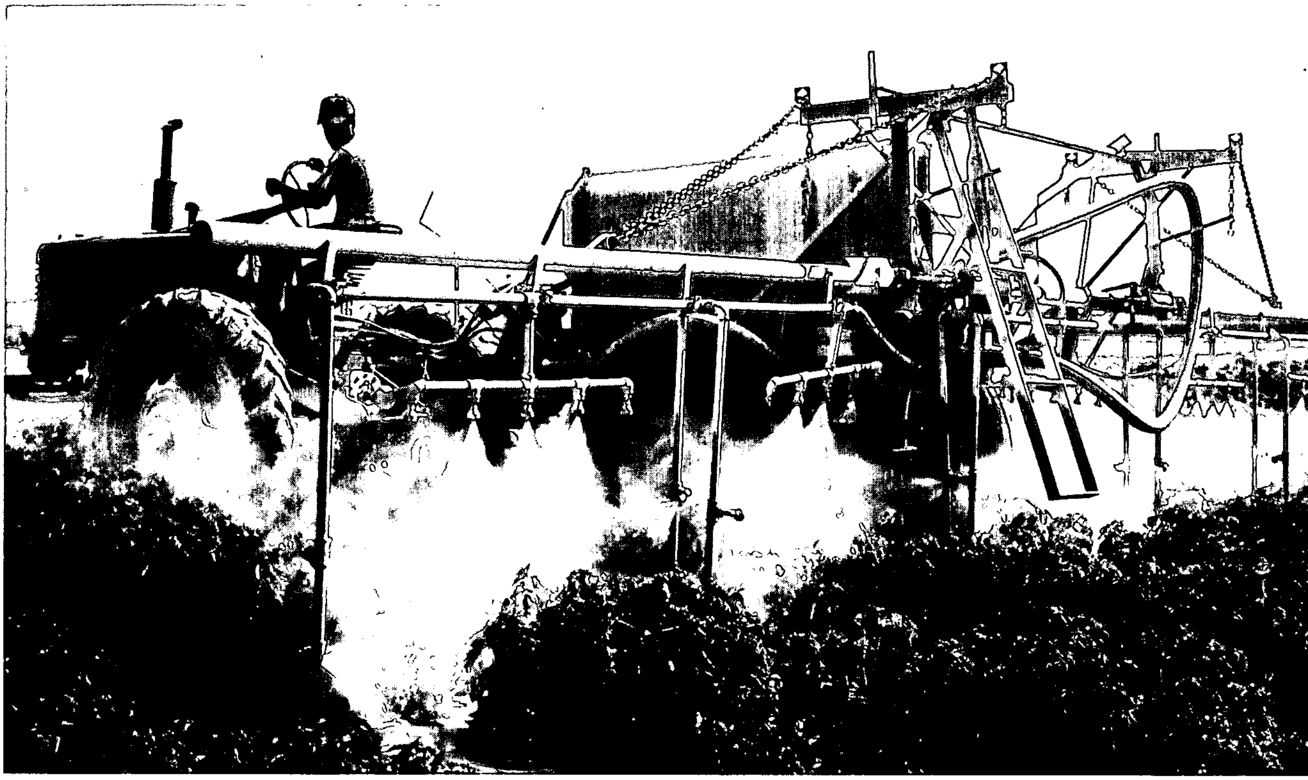


TRIMETHYLAMINE OXIDE



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}-O^-$$

Carbon dioxide (CO_2), the end product of respiration, is the principal vehicle by which we excrete carbon. Life on earth is based on carbon chemistry. It is possible (but highly unlikely) that life on another planet could be based on an element of the same family as carbon, such as silicon. If this were the case, what would be the principal vehicle by which silicon would be excreted?



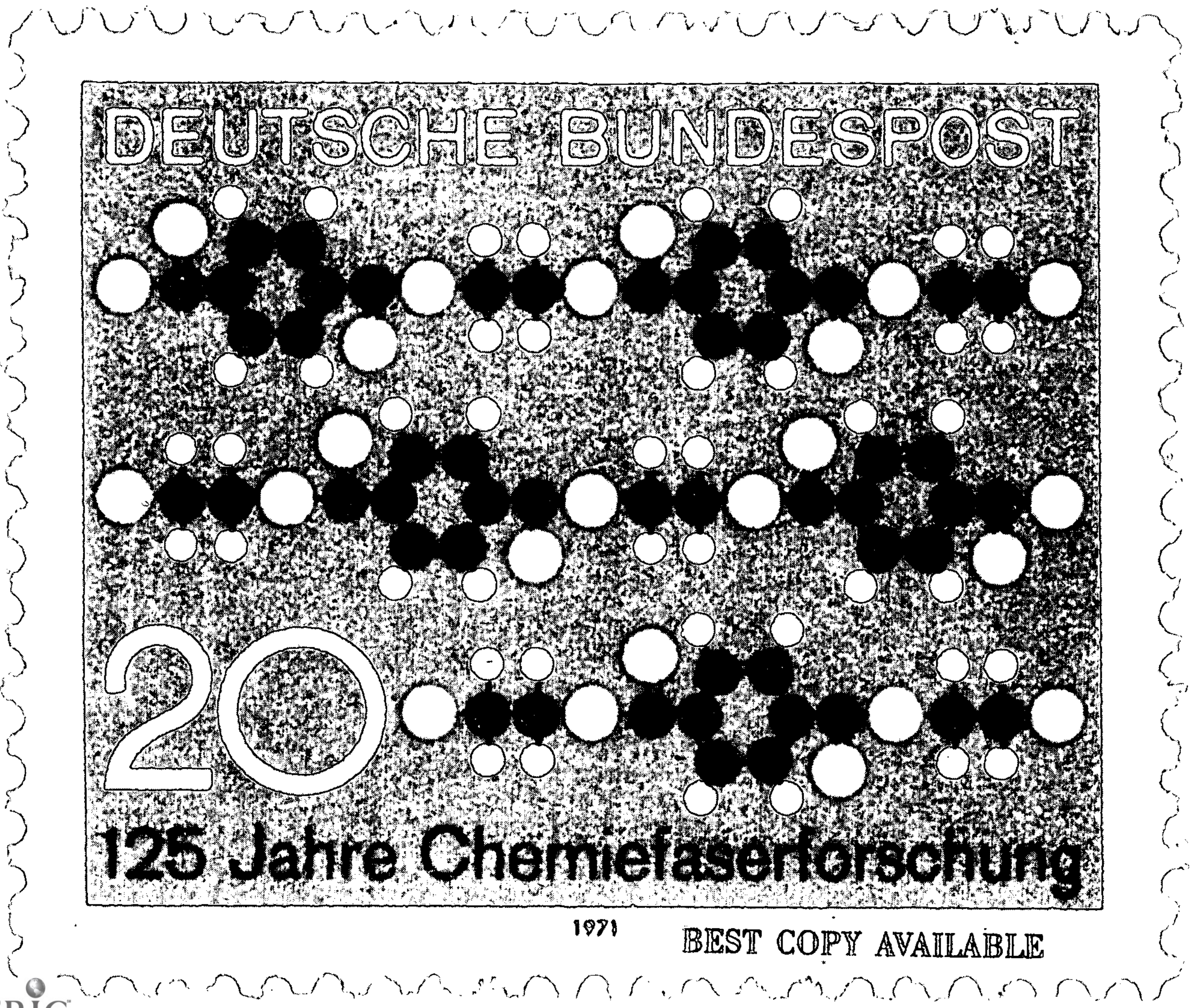

FERTILIZER
GRO-GREEN
UREA 46
GUARANTEED ANALYSIS
NITROGEN 46%
UREA 46

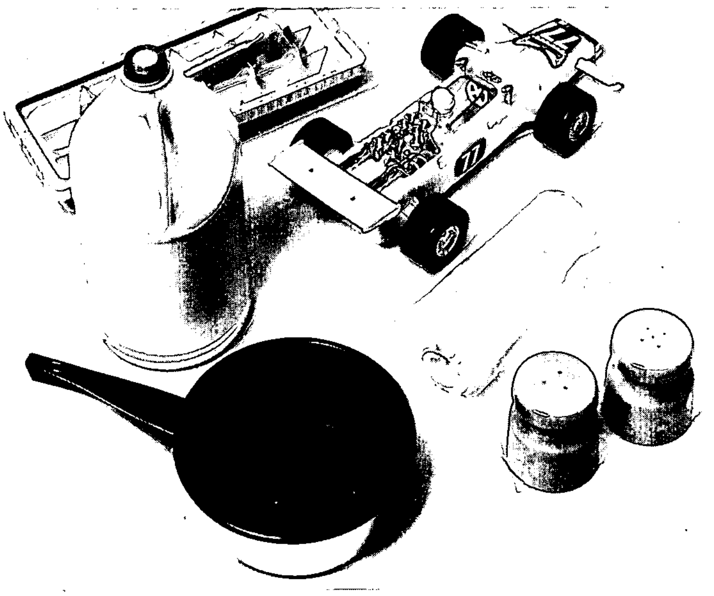

SQUARE DEAL
PELLEFORM
3-9-18

Polymers: The Linking of Molecules

Almost all the molecules we have talked about so far are exceedingly small. Because the molecules are small, their properties are often determined by such things as a single polar atom or a functional group. As molecules get larger and larger, however, size alone seems to determine their properties. Many materials we know and use every day are made up of larger molecules.

This stamp commemorates 125 years of research on polymers and illustrates the idea of the macromolecule.





You will not be able to remember what life was like without the ever present "plastics." Yet the plastics industry is still in its youth. Even though research on polymers has gone on for over 100 years, many of the popular plastics that we know today are the result of recent research. There are many kinds of polymers on the market each with a different property and a different use. Many more are continuing to be developed.

O-46 The Making of Macromolecules

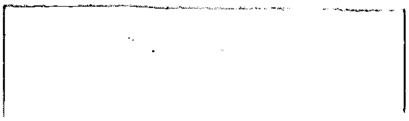
Plastics, rubber, cotton, wool, and nylon are some examples of substances made of compounds that chemists refer to as macromolecules. A *macromolecule* is a large molecule made up of smaller, simpler molecules. An ordinary molecule has a molecular mass of perhaps a few hundred. In contrast, macromolecules have masses in the thousands or millions. Although we call these materials macromolecules, they are large only on a molecular scale. Stretched out, the largest of the macromolecules would be only a fraction of an inch long.

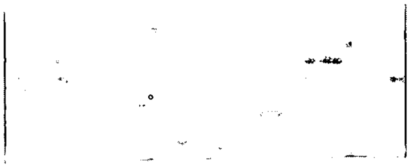
How are these materials obtained? Many of them occur naturally, but chemists have synthesized macromolecules as well. They have combined molecules in their laboratories and have come up with many different kinds of materials. Among such materials are nylon and Dacron. The making of macromolecules is one of the key activities in an industrial chemistry laboratory. New macromolecules are constantly being produced.

A chemist usually works with materials having molecular masses ranging from 50 to 400. Let us imagine a molecule with a molecular mass of 50, which we shall designate as molecule A. We can increase the mass of this material by combining two molecules of A to form A—A with a new mass of 100 (2 × 50). If we now join another A, we get molecule A—A—A with a mass of 150 (3 × 50).

Suppose we were to put together a molecule made of twenty A units. It would be tedious to write out A—A—A—A—A—A—A—A—A—A—A—A—A—A—A—A—A—A—A—A. Instead, we can use the formula $A\text{—}(A)_{18}\text{—}A$. This formula indicates that

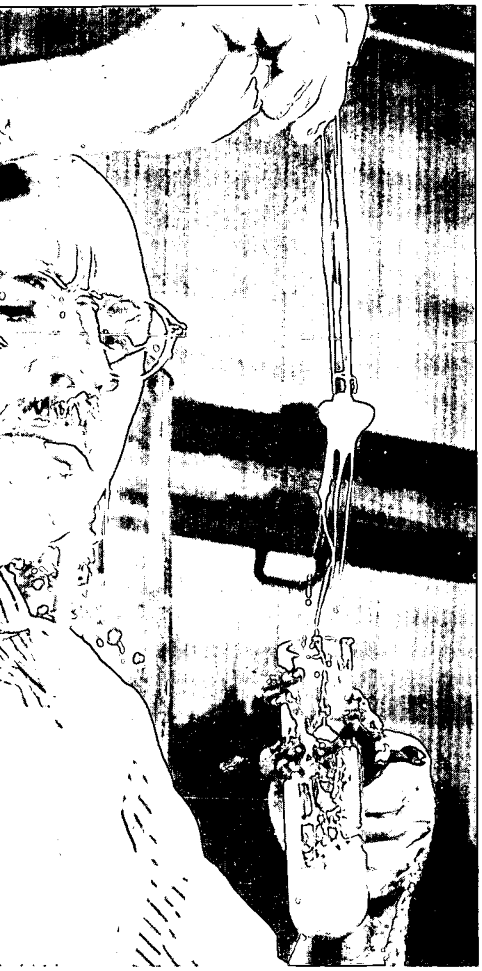
In the following photomicrographs, you will note that a wool fiber *(top right)* is made up of flat scales which overlap. Cotton *(middle)*, a natural cellulose fiber, is similar to flattened tubes with irregular twists. Synthetic fibers such as nylon *(bottom)* are cylindrical and smooth.





COURTESY CAROLINA BIOLOGICAL SUPPLY COMPANY we have a molecule made up of twenty A units, the two end A units and the eighteen internal A units. The general formula would be $A—(A)_n—A$, where the subscript n can be any number. The molecular mass then is $(n + 2)(A)$. If the unit A has a mass of 50 and n equals 25, the molecule will have a mass of 1350.

We could describe this material as *poly*-A, because it is made up of many units of A. (Remember, the prefix *poly-* suggests that a quantity contains more than two or three units.) In fact, compounds of this type are called *polymers*. A polymer is a compound consisting of repeated structural units. Each single unit in a polymer is known as a *monomer*. In the example to which we referred, $A—(A)_n—A$ is the formula of the polymer, and A is the formula of the monomer. The monomer is like a single link in a chain, the polymer molecule.



Reenactment of the discovery of the first synthetic polymer.

TIME MACHINE

1933	**Giulio Natta synthesizes polymers in a predictable fashion.**
1933	First all-star baseball game is played in Chicago.
1934	Dionne sisters become first known surviving quintuplets.
1935	Frédéric and Irène Joliot-Curie receive Nobel Prize in chemistry for synthesis of new radioactive elements.
1935	George Gershwin's opera *Porgy and Bess* is performed for the first time.
1936	Charlie Chaplin stars in the movie *Modern Times*.
1937	Golden Gate bridge is opened to the public in San Francisco.

O-47 From Monomer to Polymer

What properties must a molecule have in order to be useful as a monomer? The most important property of the monomer molecule is that it be *difunctional*; that is, it must have two reactive groups. A polymer molecule, remember, can be looked upon as a chain. The links in this chain are monomer molecules. Like the links in a normal chain, the monomer must be able to react at two ends. Each link must be able to attach to two other links. Otherwise, no chain would form.

All monomer units must be able to form bonds—link up—at both ends. But all of the monomer units do not have to be identical. You can easily imagine a chain with alternating red links and blue links. When a polymer chain is made of more than one kind of monomer, or "link," it is a *copolymer*. For example, we could have a system in which two monomers, B and C, react.

$$\begin{aligned} B + C &\longrightarrow B—C \\ B—C + B &\longrightarrow B—C—B \\ B—C—B + C &\longrightarrow B—C—B—C \end{aligned}$$

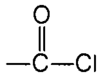
The reaction could be carried on until a polymer with the formula $B—(C—B)_n—C$ is formed.

As an exercise, try to calculate a general formula for the molecular mass of this polymer. Remember, the corresponding formula for the polymer $A—(A)_n—A$ was $(n + 2)(A)$.

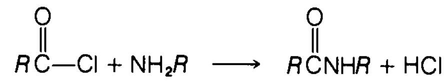
Calculate the molecular mass of the copolymer if

mass of B unit = 25
mass of C unit = 30
$n = 20$

Let us examine a real reaction now, that of an acid chloride with an amine to form an amide. The acid chloride is a new functional group that is derived from the acid group. The —OH of the acid has been replaced by the —Cl to give

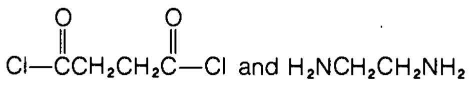


$$-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Cl}$$



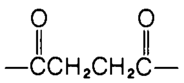
$$R\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Cl} + \mathrm{NH_2}R \longrightarrow R\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NH}R + \mathrm{HCl}$$

In the preceding reaction a new bond has formed between a carbonyl group and a nitrogen atom. We can change the structure of the amine and make it difunctional simply by adding another amine group. We can do the same thing with the acid chloride. By adding another reactive group, we end up with molecules like



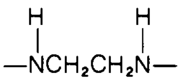
$$\mathrm{Cl}-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_2CH_2}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Cl} \text{ and } \mathrm{H_2NCH_2CH_2NH_2}$$

Both can react at two ends. They should make good monomers. If we allow them to react together, we should get a polymer of the B—C—B—C—B—C type. The B unit might be



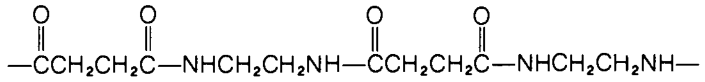
$$-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_2CH_2}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-$$

and the C unit



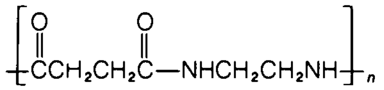
$$-\overset{\overset{\displaystyle \mathrm{H}}{|}}{\mathrm{N}}\mathrm{CH_2CH_2}\overset{\overset{\displaystyle \mathrm{H}}{|}}{\mathrm{N}}-$$

The formula for part of the polymer would be



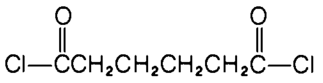
$$-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_2CH_2}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{NHCH_2CH_2NH}-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_2CH_2}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{NHCH_2CH_2NH}-$$

which could be represented by the general formula



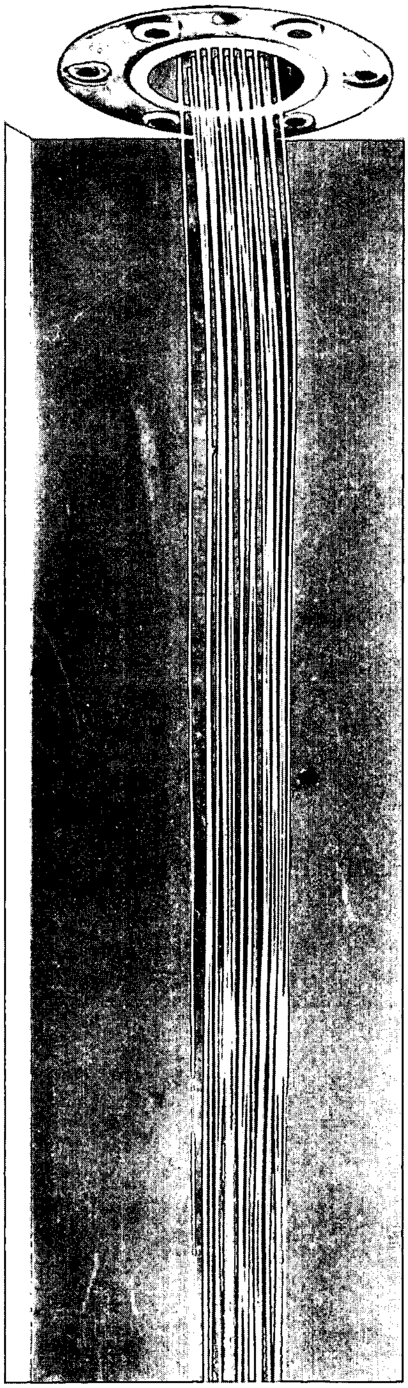
$$\left[\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_2CH_2}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{NHCH_2CH_2NH}\right]_n$$

In the following experiment you will actually prepare a polymer very similar to this one: nylon 66. The reagents you will use are adipyl chloride



$$\mathrm{Cl}-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_2CH_2CH_2CH_2}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Cl}$$

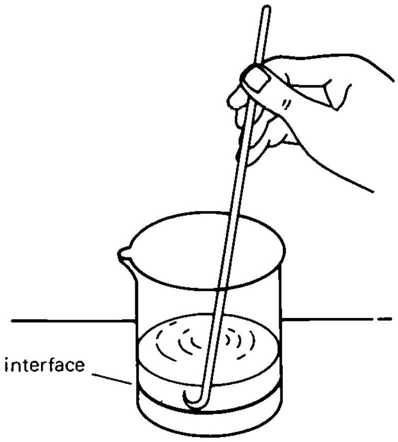
and hexamethylene diamine, $\mathrm{H_2NCH_2CH_2CH_2CH_2CH_2CH_2NH_2}$. Why do you think the polymer is called nylon 66? Can you write the formula for the polymer?



From tiny holes in a spinneret, a polymer is formed into fine filaments that are twisted together into a single thread. This is how fibers such as nylon, Dacron, and Orlon are formed.

EXPERIMENT

O-48 Synthesis of Nylon 66



Obtain from your teacher solutions of adipyl chloride in hexane (0.25 M) and 0.5 M hexamethylene diamine in 0.5 M sodium hydroxide (NaOH) solution. Bend a piece of copper wire into a hook, the shaft of which is long enough to reach the bottom of a 50-cm^3 beaker.

Place 3 cm^3 of diamine solution into the beaker and carefully pour 3 cm^3 of the adipyl chloride solution onto the surface of the diamine solution. These solutions are *immiscible,* that is, incapable of being mixed together. You will notice the immediate formation of an opaque white film where the two immiscible liquids meet—the *interface.*

Insert the wire into the beaker and hook the film. Slowly withdraw the hook from the beaker, carrying the film with it. You will notice that, as soon as the film (a polymer) is pulled off, a new film is formed.

If you continue to withdraw the film, a long thread of nylon 66 will be formed. When the thread breaks, place it in a beaker or on a watch glass, and then wash it with water. Next, wash the thread with either acetone or alcohol. Allow it to dry. ***Caution:*** *Alcohol, acetone, and hexane are flammable. Do not throw waste materials into the sink.* Consult your teacher for disposal instructions.

O-49 Properties of Polymers

In the nylon experiment the choice of solvents was carefully made so that the two solvents were *immiscible.* This resulted in the polymer forming only at the interface of the two liquids. The diamine (polar) is soluble in water (polar), and the acid chloride (nonpolar) is soluble in hexane (nonpolar). The molecules can react with each other only when they come in contact. They do this only at the interface of the liquids.

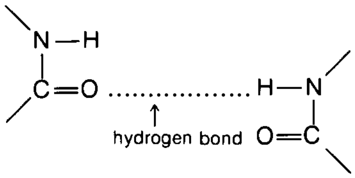
Both of the reactants—diamine and acid chloride—would dissolve in other solvents that are available. What do you think the result would be if you mixed hexamethylene diamine and adipyl chloride in the same solvent? If you are to obtain nylon thread, is it absolutely necessary to use solvents that are immiscible?

In the experiment you easily withdrew strands of nylon. As you did so, additional molecules continued to react at the interface, thereby reforming the film. Is the nylon you withdrew like the nylon you are used to? Examine the properties of your polymer.

Now that you have made your own fiber, how can you use it? How about making a shirt or a dress from it? Not a very good idea, is it? The nylon you made is just not like the nylon you are used to. Instead of being strong and flexible, it is weak and brittle.

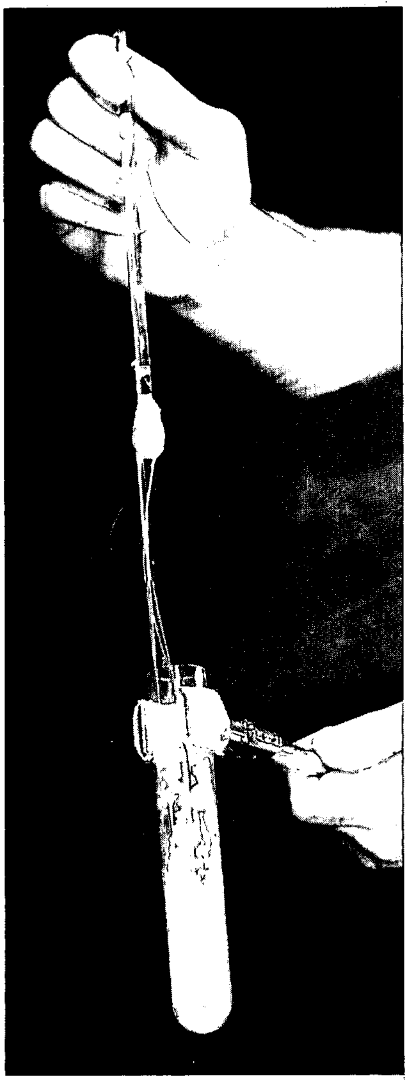
The properties of the nylon 66 you prepared can be improved. Heat the nylon 66 to a temperature just below its melting point, and then stretch it. Be careful not to break the nylon when you stretch it. The stretching is a tricky procedure. Don't try it unless you have a lot of patience. Once it is stretched, the nylon 66 is more like the nylon to which you are accustomed.

How does stretching improve the fiber? The answer lies in how a polymer links together. Remember, even large polymer molecules are only a fraction of an inch long. Somehow these molecules must stick together to form a fiber or thread. In the case of nylon, that's just what the molecules do—they stick together. The nylon molecules make use of hydrogen bonds much like the hydrogen bonds previously described for water and alcohols.

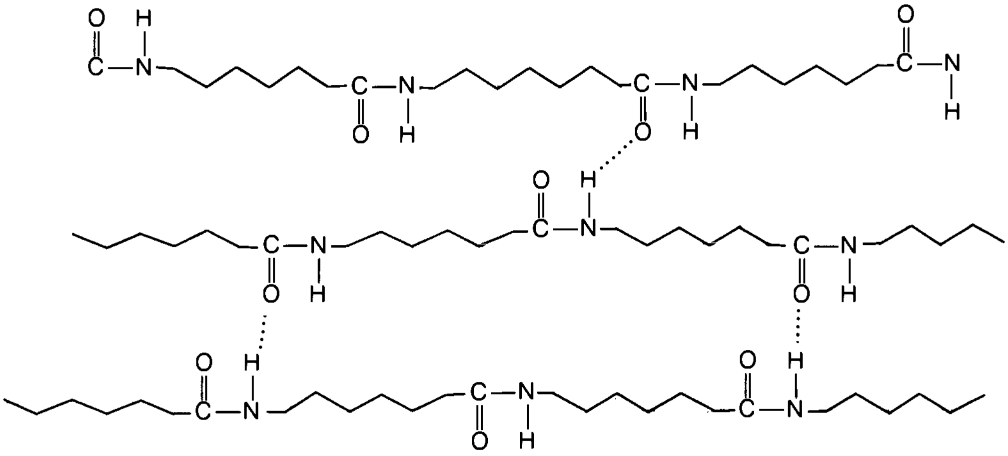


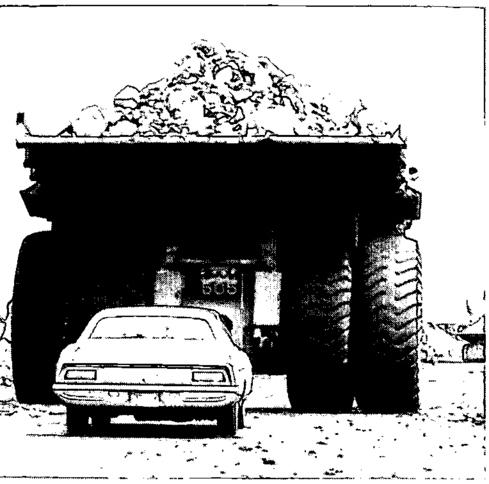
In your sample of nylon the individual polymer molecules twist and turn; they are randomly oriented, or *disordered.* The fiber is weak. As the fiber is stretched, the molecules line up like tin soldiers and cling together strongly. With this clinging together the properties of the fiber improve; the polymer has become *ordered.*

Chemists have expended much effort in trying to prepare ordered polymers similar to the ones found in nature. But these ordered polymers are hard to duplicate.

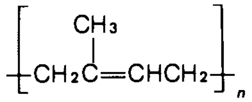


STRETCHED NYLON FIBER



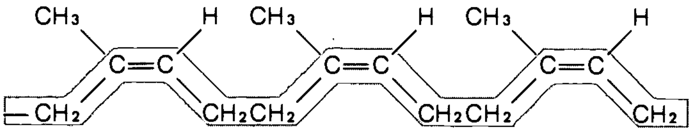


One example of a natural polymer is rubber (natural as opposed to synthetic). Not only is it a natural polymer; it is an ordered polymer. Natural rubber has the molecular structure



$$\left[-CH_2\overset{CH_3}{\overset{|}{C}}=CHCH_2- \right]_n$$

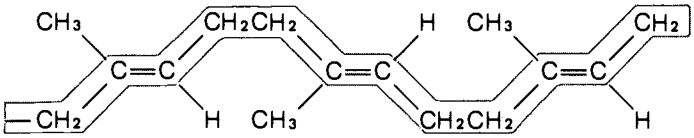
Notice how these natural rubber molecules form a chain.



NATURAL RUBBER

You are probably familiar with the properties of natural rubber: it is strong and pliable; stretch it, and it soon regains its shape.

There is another naturally occurring polymer that looks very much like natural rubber and is also produced from the milky fluid of a tree. This material is called *gutta-percha*.



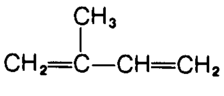
GUTTA-PERCHA

Natural rubber and gutta-percha are isomers of each other. They are not structural isomers, as are ethanol and dimethyl ether. Instead, they are geometric isomers. The only difference between rubber and gutta-percha is that in rubber the methyl group ($-CH_3$) and hydrogen atom are on the same side of the double bond. Such an isomer is known as a *cis* isomer. In gutta-percha the methyl group and hydrogen atom are on opposite sides of the double bond. Such an isomer is called a *trans* isomer. This little difference means a lot. Instead of being a soft, elastic substance, gutta-percha is hard and tough. It is most commonly used in insulation, waterproofing, and golf balls.

Chemists' first attempts to copy natural rubber failed. The materials made in the laboratory contained a mixture of *cis* and *trans* double bonds. This polymer did not have the desirable properties of natural rubber. It is only recently that it has been possible to make synthetic rubber that is nearly identical to natural rubber.

By the use of catalysts, scientists were able to make synthetic rubber by joining isoprene molecules in chains. In this kind of synthesis there are cross-links between chains, which allow the polymer to be stretched or bounce back but prevent the chains from being pulled apart. Chemists have developed many kinds of rubber, each with its own properties and uses. Knowing the structures of the monomer of rubber and the kinds of catalysts that help polymerize this monomer, as well as the way it links to form chains, chemists have been able to create new molecules and specific properties.

ISOPRENE



$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH{=}CH_2$$

KINDS OF RUBBER	PROPERTIES AND USES
Styrene-butadiene	Abrasion resistant—minimizes tire skid
Polybutadiene	Has more bounce than natural rubber
Neoprene	Heat resistant
Nitrile	Resistant to oil and chemicals
Butyl	Used for inner tubes and tubeless tires
Polysulfide	Good sealant for fuel tanks
Silicon	Chemically inert—used in artificial heart valves, medicine-bottle stoppers, and packaging for the food industry

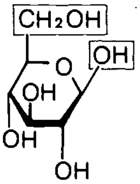
This stamp was issued to commemorate one country's contribution to the production of natural rubber. Notice one section of the molecular chain that is responsible for the properties of rubber.

While chemists were looking for synthetic rubber, they discovered many other chemicals and products. For example, chicle, the rubbery substance used to make chewing gum, was found in the sapodilla tree while chemists were searching for a suitable replacement for natural rubber. Today, the gum we chew is no longer made from chicle but from synthetic polymers created by the magic of polymer chemistry.

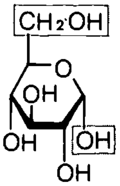
O-50 Natural and Synthetic Polymers

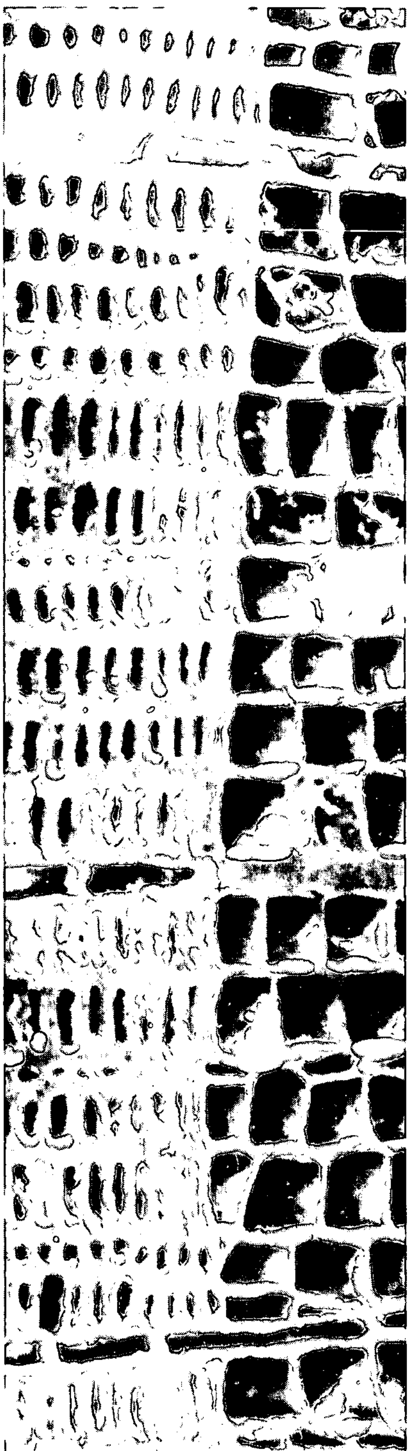
There are many other chainlike polymers, both artificial and natural. For example, starch is a natural polymer that is made of glucose. Glucose is found in two forms, which are called α-glucose and β-glucose. The glucose structures are complex, but we need only consider a small portion of the molecules. Consider the —CH_2OH group and the —OH group. Notice that the only difference between α-glucose and β-glucose is that in β-glucose these groups are on the same side of the ring. In α-glucose they are on opposite sides.

β-GLUCOSE



α-GLUCOSE

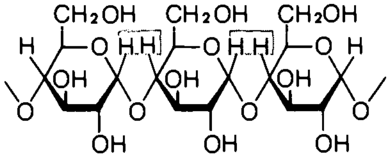




A microphoto of the cellulose cells in wood (magnified about 300 times). Would you agree that cellulose is a major constituent of wood?

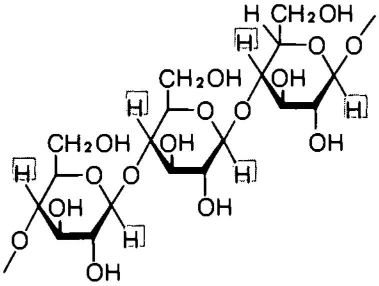
Glucose is a sugar that can be oxidized to carbon dioxide (CO_2) and water (H_2O). The body uses glucose as a fuel. Starch is a polymer of α-glucose. It is formed by splitting out a molecule of water from between adjacent glucose molecules. Starch can be used as a "storehouse" of energy. The body can break down starch to glucose by the use of an enzyme as a catalyst. The enzyme splits the bonds between glucose units by the addition of water.

STARCH



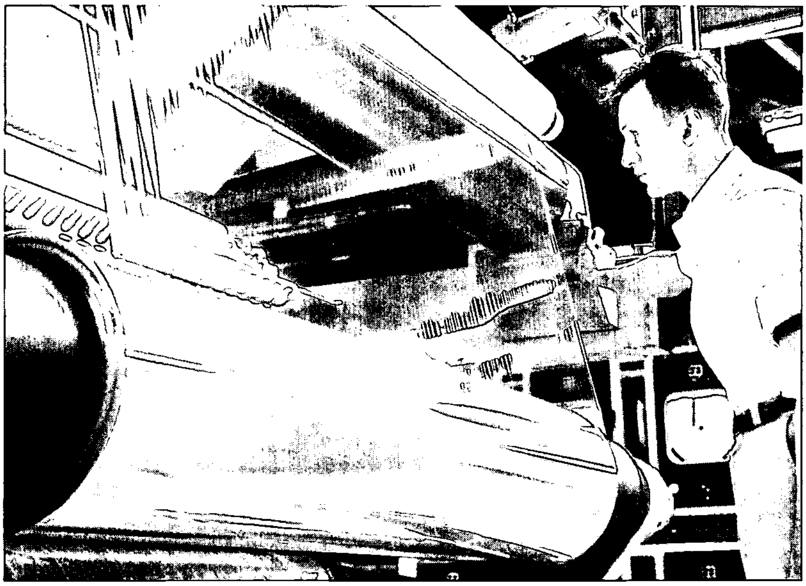
Cellulose, a major constituent of wood, is closely related to starch. It is also a polymer of glucose, but of β-glucose rather than α-glucose. These polymers are similar; in fact, you might have trouble telling them apart. Again, look at the relationship between the hydrogens. These natural polymers have different shapes. They also have different properties.

CELLULOSE



Unless you are a termite, *don't swallow toothpicks*. This bit of advice is based on the fact that although human beings are able to convert starch to glucose, we cannot accomplish this with the cellulose in wood. Termites are lucky enough to have bacteria that produce an enzyme capable of converting cellulose to glucose. We possess neither the bacteria or the enzyme. Cellulose is not a source of energy for humans.

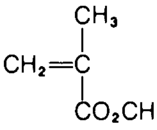
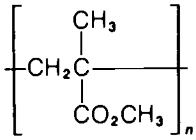
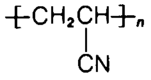
Cellulose was the basis for the first successful synthetic fiber, rayon. Developed late in the 19th century, rayon is made by several different processes. The two most important commercial forms are viscose rayon, a pure cellulose product; and acetate rayon, which is made from a combination of cellulose and acetic acid. The viscose process, in which a thick liquid is forced through holes or between rollers into an acid bath, was also used to produce the



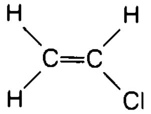
Cellophane, invented in 1912, displaced wax paper as the most popular food wrapper and is still important in packaging today.

first cellophane. Although it is still widely used, cellophane today competes with some of the modern synthetic products (such as Saran and other forms of polyethylene) for display and packaging use. The liquid form of acetate rayon is used to make photographic film and sound-recording tape.

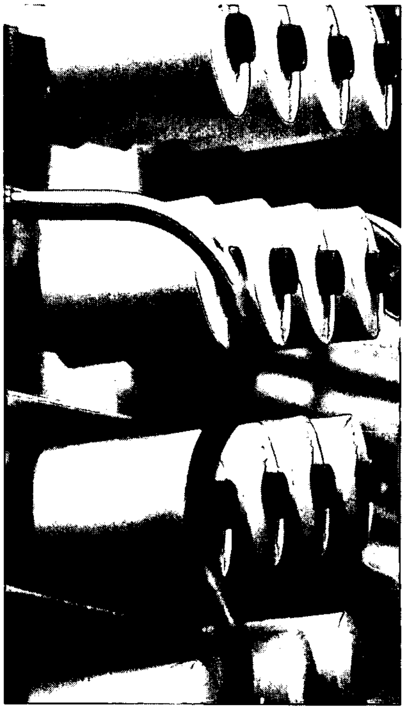
There are many other synthetic and natural polymers with which we come in contact daily. Some examples are:

MONOMER	**POLYMER**	**COMMON NAME**
ETHYLENE $CH_2{=}CH_2$	POLYETHYLENE $\left[CH_2CH_2\right]_n$	
METHYL METHACRYLATE  $CH_2{=}C(CH_3)CO_2CH_3$	POLYMETHYL METHACRYLATE  $\left[CH_2C(CH_3)(CO_2CH_3)\right]_n$	Lucite Plexiglas
TETRAFLUOROETHYLENE $CF_2{=}CF_2$	POLYTETRAFLUOROETHYLENE $\left[CF_2CF_2\right]_n$	Teflon
VINYL CHLORIDE $CH_2{=}CHCl$	POLYVINYLCHLORIDE $\left[CH_2CHCl\right]_n$	Vinyl
ACRYLONITRILE $CH_2{=}CHCN$	POLYACRYLONITRILE  $\left[CH_2CH(CN)\right]_n$	Orlon

PVC



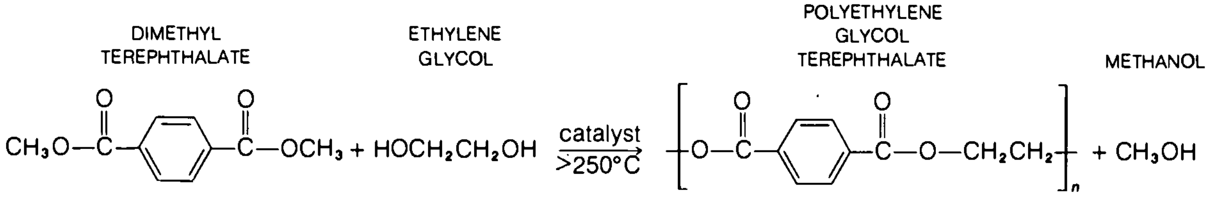
Polyester textile filament yarn is very important to the world's textile market.



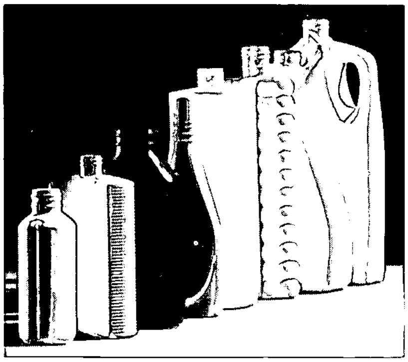
Toys and many other plastic objects are made of polyethylene. Polyethylene is also used for insulation and for films, whereas polymethyl methacrylate forms Plexiglas and Lucite sheets. Polyacrylonitrile is known as Orlon and is used in woollike fabrics. Polyvinyl chloride (PVC) has many useful qualities and is extensively used in making corrosion-resistant pipe and other molded articles. When combined with softening agents called plasticizers, PVC can be formulated into the soft leatherlike material called vinyl which is used in upholstery and clothing. Unfortunately, although PVC is harmless, the vinyl chloride monomer has been found to be a powerful carcinogen, and extreme care must be taken in the manufacture of PVC to ensure that trace quantities of the vinyl chloride vapor do not escape into the environment.

Scientists have discovered many of these materials by means of carefully planned experiments. They have discovered others accidentally. The discovery of Teflon at E. I. du Pont de Nemours & Company came quite by accident. Chemists using a tank of the gas tetrafluoroethylene found that although the tank seemed to be empty, it had not delivered the quantity of gas promised on the label. Curious, they opened the tank to investigate and found a white, greasy solid. Somehow, the tetrafluoroethylene had polymerized. Teflon was discovered. After some investigation, the chemists were able to polymerize tetrafluoroethylene in the laboratory. As you probably know, polytetrafluoroethylene, or Teflon, is used as a nonstick coating on pans, skillets, cookie sheets, and steam irons. By further modifying the Teflon molecule, chemists came up with a liquid coating for paper and fabric that resists oil and water. An accident had given birth to a startling variety of convenience products.

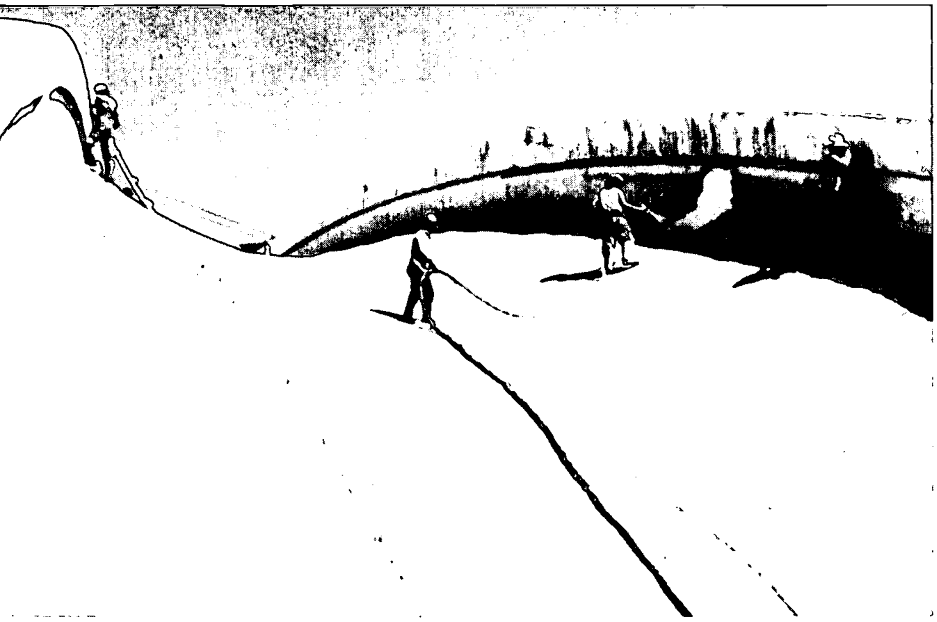
Another class of polymers is the polyesters. These polymers are prepared by reacting a diacid (or diester) with a dialcohol.

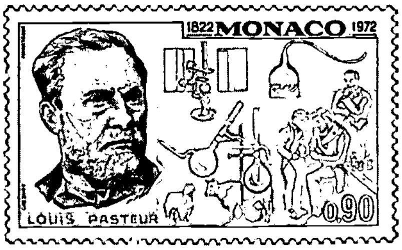


The reaction of the diester dimethyl terephthalate with the dialcohol ethylene glycol produces the polymer called Dacron when it is formed as a fiber and Mylar when it is cast as a film. It might be interesting to compare the structures of Dacron and nylon. Do you notice similarities and differences? Are there major structural differences that might alter the properties of the polymer?



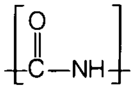
There are many different polymers, and each has its own different properties and uses—solid, liquid, hard, soft, flexible, brittle. Some polymers can be poured; some can be applied like paint; some can be molded and formed into various shapes; and some can be sprayed—as illustrated in the photo where a polymer is being used on the roof of a new sports dome for insulation.





Several naturally occurring polymers—wool, silk, human hair—are proteins. Proteins are complex macromolecules that are made up of amino acids joined together by what is called the peptide bond

PEPTIDE BOND

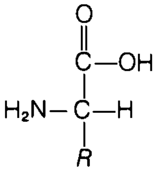


$$\left[\begin{array}{c} \mathrm{O} \\ \| \\ -\mathrm{C}-\mathrm{NH}- \end{array}\right]$$

the same bond we encountered in the nylon molecule.

There are many different amino acids, but they have one property in common. They all have a central carbon atom that contains a carboxyl group, a hydrogen, and an amino group. The nature of the *R* group is what makes the various amino acids different. In one case it is hydrogen, in another case a methyl group, and in still other cases other groups.

AMINO ACID



R = H, *R* = CH_3, etc.

There is one other property of these amino acids that is important to the structure of the polymers and to life itself. They exhibit a subtle kind of isomerism which is called *mirror-image isomerism*. Prove it to yourself by carrying out the following experiment.

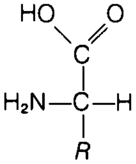
TIME MACHINE

1845	American inventor E. B. Bigelow constructs power loom for manufacturing carpets.
1846	War between United States and Mexico begins.
1847	First use of adhesive postage stamps in United States.
1848	**Louis Pasteur identifies optical isomers.**
1848	California Gold Rush begins.
1849	Amelia Bloomer campaigns for women's rights, wearing "bloomers" as part of new relaxed fashion.
1850	Nathaniel Hawthorne publishes *The Scarlet Letter.*

EXPERIMENT

O-51 Mirror Image Molecular Models

1. Make a model of ethylene ($CH_2{=}CH_2$).
2. Make a model of dichloroethylene ($C_2H_2Cl_2$).
   How many different models of dichloroethylene can you make? What are the differences?
3. Make a model of an amino acid

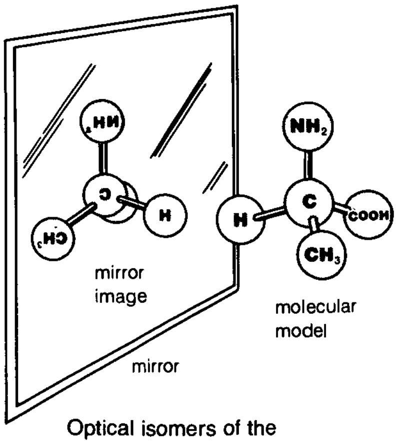


where *R* = H (that is, the central atom will have an amine group, a carboxylic acid group, and two hydrogens). Compare your model with your neighbor's model. Are they the same? Poll the class.

Now replace one of the hydrogens bound to the central carbon atom in your model with a methyl group. Compare it with your neighbor's model. Are they the same? Can you place one model over the other so that all the atoms superimpose? Poll the class. Look at the reflection of your model in a mirror.

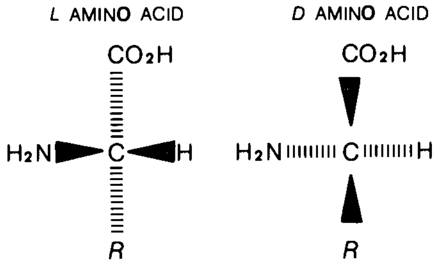
Exchange the methyl group and the hydrogen. Are the models still the same? Poll the class. Now look in a mirror. Rub your right eye with your right hand. Imagine that you are the person in the mirror (behind the glass). Which hand must you use to imitate the "mirror image"?

Does your neighbor's model superimpose on yours? If not, how does it relate to yours? It has the same four "groups." If they are not superimposable, they are mirror images.

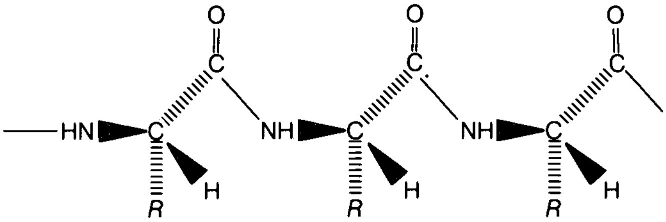


Optical isomers of the amino acid alanine.

These two mirror-image isomers of a single amino acid are called *L* and *D* isomers. Although many of the properties of the *L* and *D* amino acids are the same, some are quite different. These isomers are not identical. They are not superimposable. Moreover, nearly all the amino acids found in nature are of a single type. They are essentially all *L* amino acids; very few *D* amino acids are found. Why this is true is an important and unanswered question.

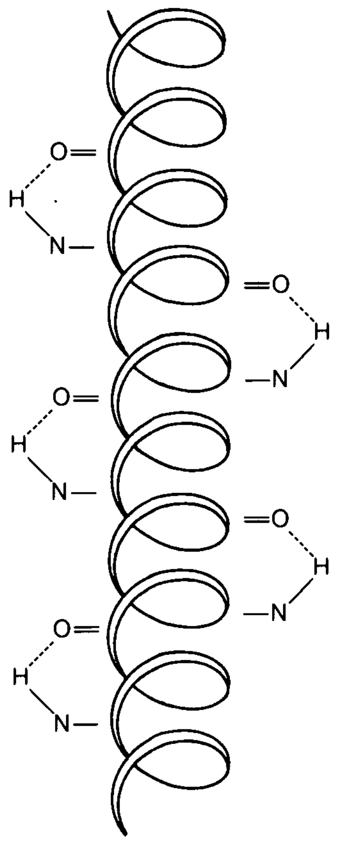


In a protein molecule the amino acid molecules are joined together by amide bonds or peptide bonds.



Obviously, the protein molecule is an ordered molecule. As in the nylon molecule, hydrogen bonding takes place, not only between molecules but within a given protein molecule. This hydrogen bonding causes the protein molecule to exist in special ways. They tend to exist as a *helix* (coil) or as sheets. The hydrogen bonds act to hold the loops in the coil in the correct position. You will learn more about proteins in *Molecules in Living Systems: A Biochemistry Module.*

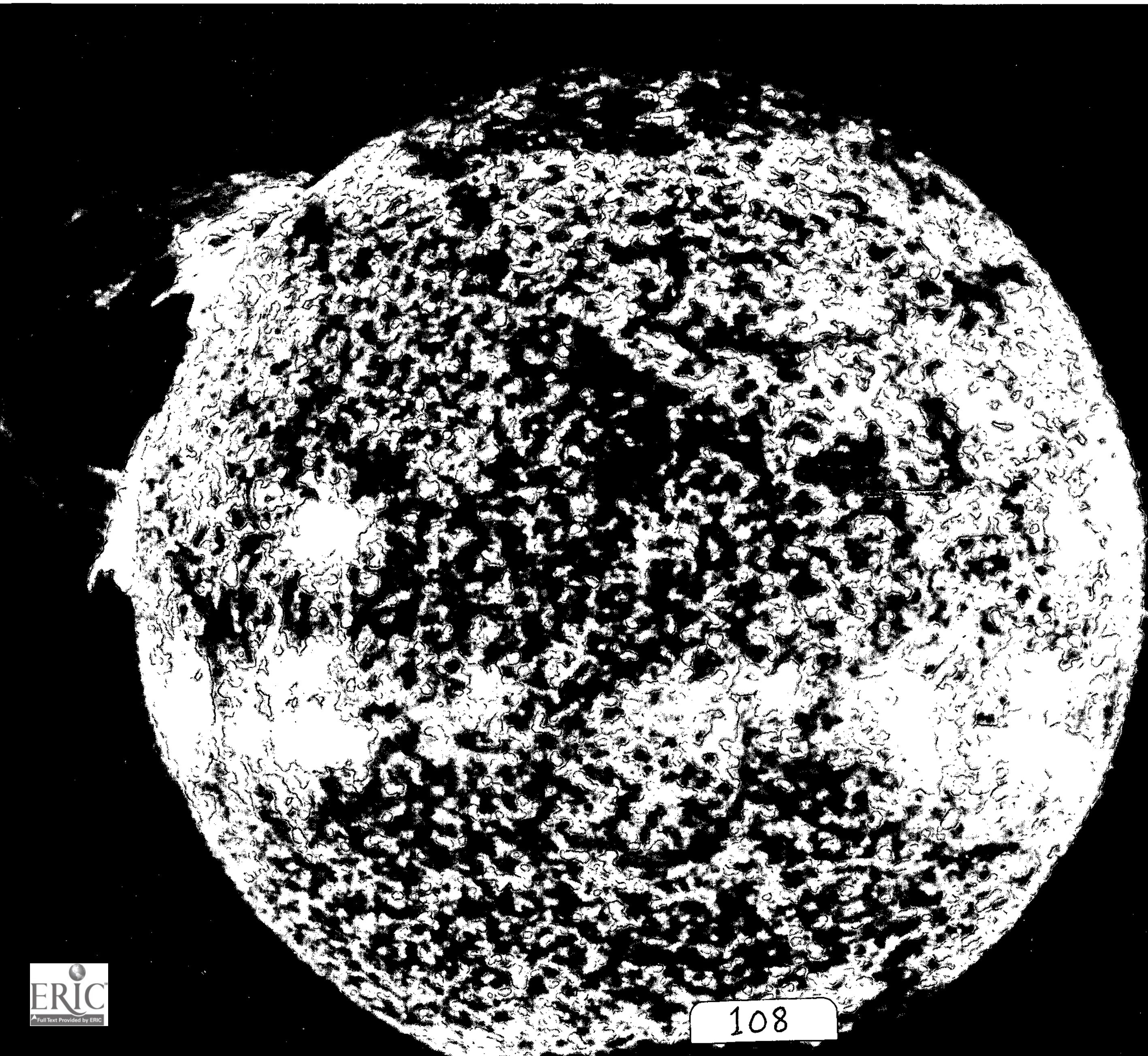
Protein Molecule



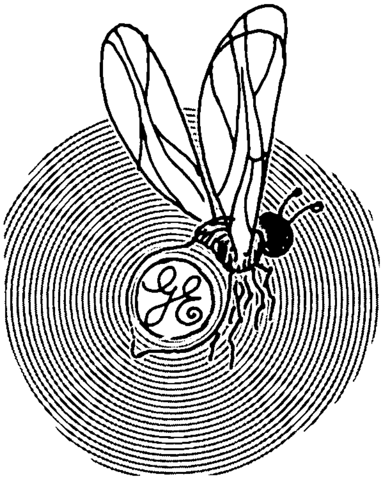
Photochemistry: Light and Heat

We learn to associate heat with light at an early age. When an object emits light, it usually releases a certain amount of heat. You can easily observe the light and feel the heat from the sun, a light bulb, a red-hot iron, and a blazing fire. The object is actually giving off energy in the form of light and heat to its surroundings.

A solar flare *(upper left)*, one of the largest ever recorded, spans more than 588 000 kilometers across the surface of the sun.

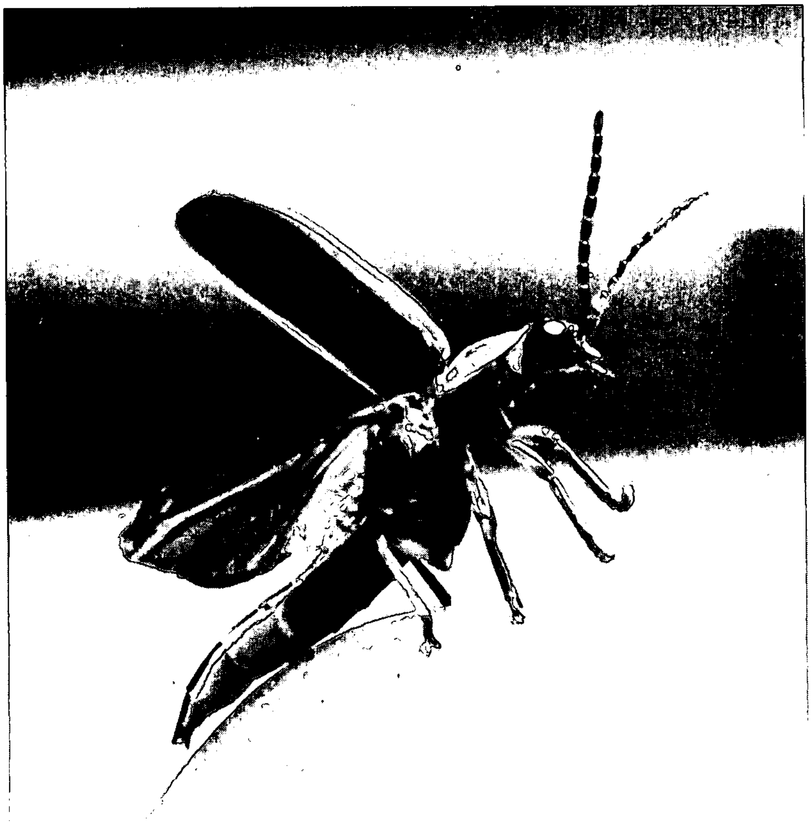


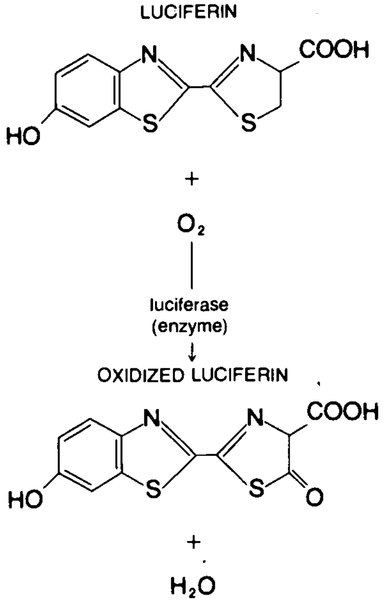
O-52 Cold Light: Its Sources



It is possible for an object to give off energy only in the form of light. Although rare, such occurrences are known to be possible; this property is referred to as *luminescence*. In these cases the light is "cold"; that is, no detectable amount of heat is observed. A common example of this is the phosphorescence of certain minerals. These minerals glow in the dark. A wide variety of living organisms exhibit biological luminescence, which is called *bioluminescence*, because it arises from living organisms. The best-known bioluminescent species is the firefly.

The bioluminescence of the firefly has a definite function. When the male firefly flashes its light, it is actually sending out a mating signal. Any female in the vicinity that sees the light responds by flashing in turn. When this happens, the male approaches the female, and they mate. The chemistry of this ritual is actually quite simple. A single compound, *luciferin*, is oxidized under the influence of the enzyme *luciferase*. It is the oxidation of luciferin that produces the light (see sections *B-33* and *B-34* in *Molecules in Living Systems: A Biochemistry Module*).





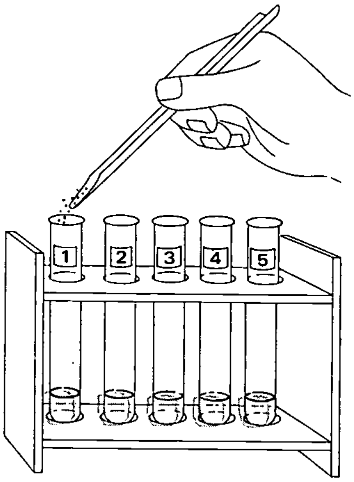
Almost all organic compounds are flammable. When they burn they give off both heat and light. The combustion of petroleum products (gasoline, kerosene, natural gas, and diesel fuels) is our major source of commercial heat energy. But a few chemicals undergo reactions with the liberation of "cold" light, so-called *chemiluminescence*. One compound known to undergo chemiluminescence is luminol. The products of the reaction, except for nitrogen gas, are not yet completely identified. In order for luminol to chemiluminesce in water, there must be oxygen, hydrogen peroxide, alkali (sodium hydroxide), and small amounts of a catalyst such as iron, copper, or cobalt compounds. The object of the following experiment is to determine which compound will act most effectively as a catalyst for the chemiluminescence of luminol.

EXPERIMENT

O-53 Chemiluminescence of Luminol

Dissolve 0.2 g of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) in 10 cm^3 of 2.5 M sodium hydroxide. Dilute the solution with water to 200 cm^3. Add 15 cm^3 of 3-percent hydrogen peroxide. This will serve as your stock luminol solution.

Transfer 3-cm^3 portions of the stock solution to five test tubes. Arrange the test tubes in a test-tube rack. Prepare to add a few crystals of the following compounds to each test tube: (1) copper(II) sulfate, (2) chromium(III) chloride, (3) potassium chloride, (4) potassium iron(III) cyanide, (5) magnesium sulfate.



In near darkness (or in a specially prepared "dark box") add the crystals to the luminol solution, watching carefully as the crystals are added. What do you observe? If the metal in the crystalline compound is acting as a catalyst, which one appears to be the best?

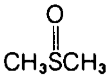
Dissolve 0.5 g of potassium iron(III) cyanide in 100 cm^3 of water in a 500-cm^3 flask. Add 100 cm^3 of the remaining luminol stock solution to this solution after darkening the room. Take 5 cm^3 of this solution and add a few drops of 40-percent sodium hydroxide. Add a few drops of concentrated hydrochloric acid to a separate 5-cm^3 sample. What can you conclude about the ability of the luminol solution to luminesce in the presence of an acid or a base?

O-54 Cold Light: Its Uses

Cold light can be extremely useful in many situations, particularly when flame and heat are dangerous. During World War II Japanese soldiers used a dried clam, *Cypridina*, as a source of light. Holding the dried clam in his hand, the soldier poured water over it. The resulting reaction produced enough light (bioluminescence) to read a message or a map in the dark. The dim light did not disclose the soldier's position.

The light from *Cypridina* has its disadvantages. For one thing, this light is of low intensity; it is not bright. In addition, the light from a *Cypridina* or from luminol lasts for only a short time. In view of these limitations, luminol is not considered a good commercial source of cold light. Few chemicals are capable of producing cold light efficiently for prolonged periods of time. Such light seldom lasts for more than one hour.

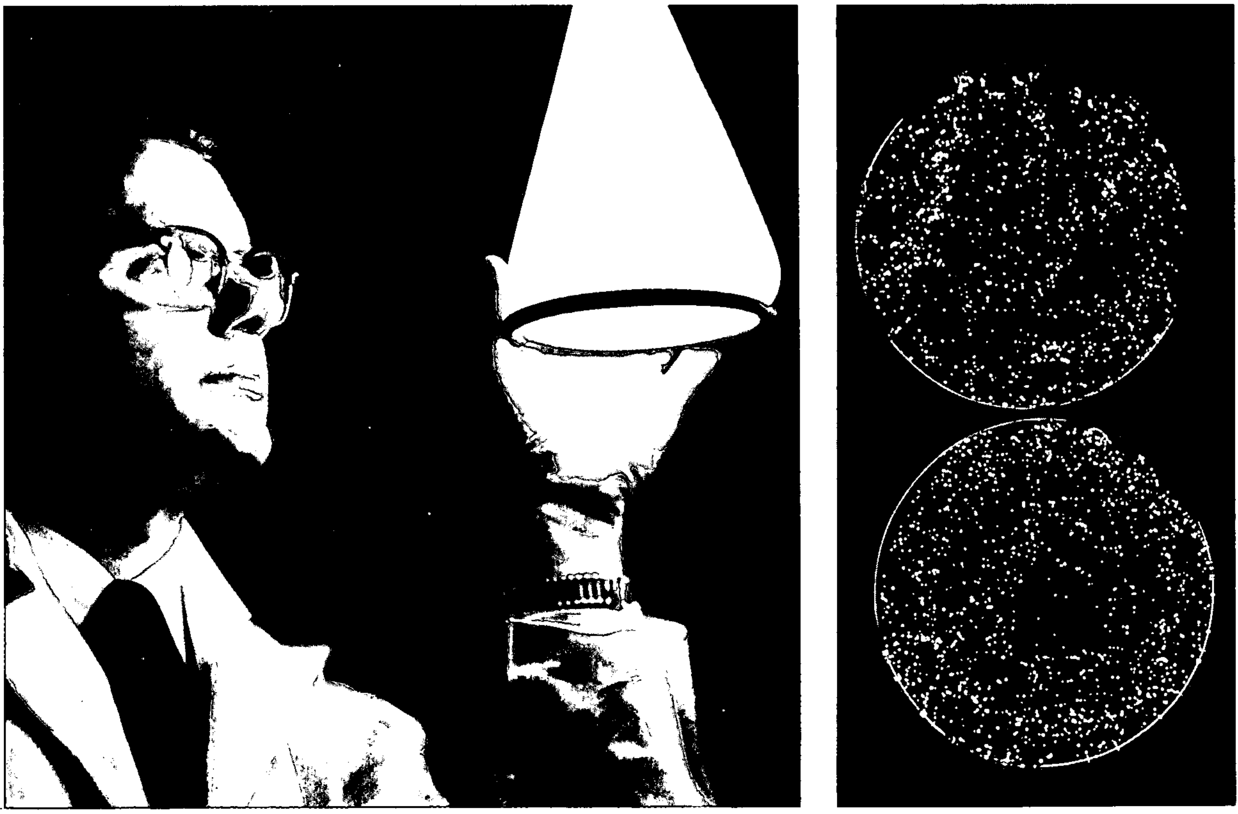
Luminol reacts with concentrated sodium hydroxide (NaOH) solution in the organic solvent dimethyl sulfoxide (DMSO)

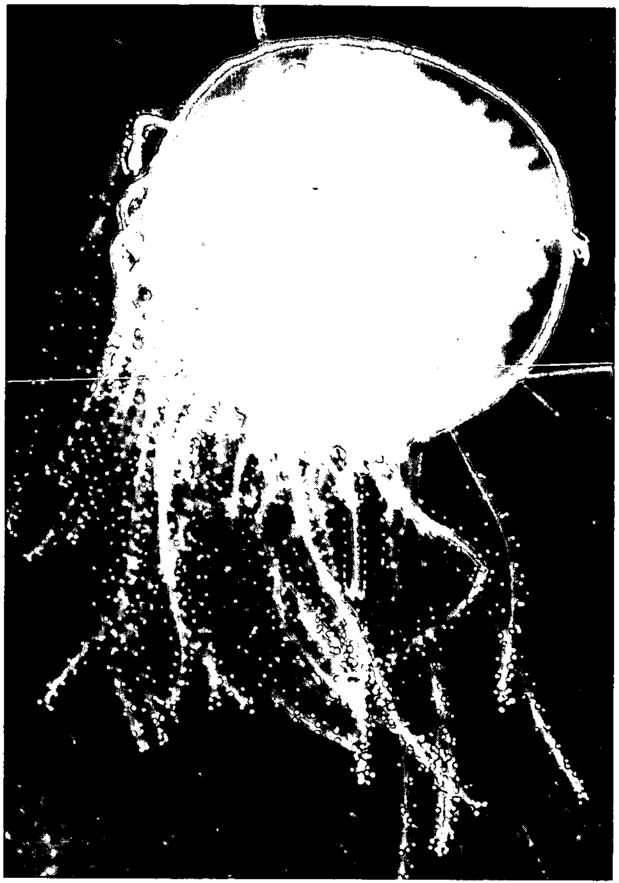


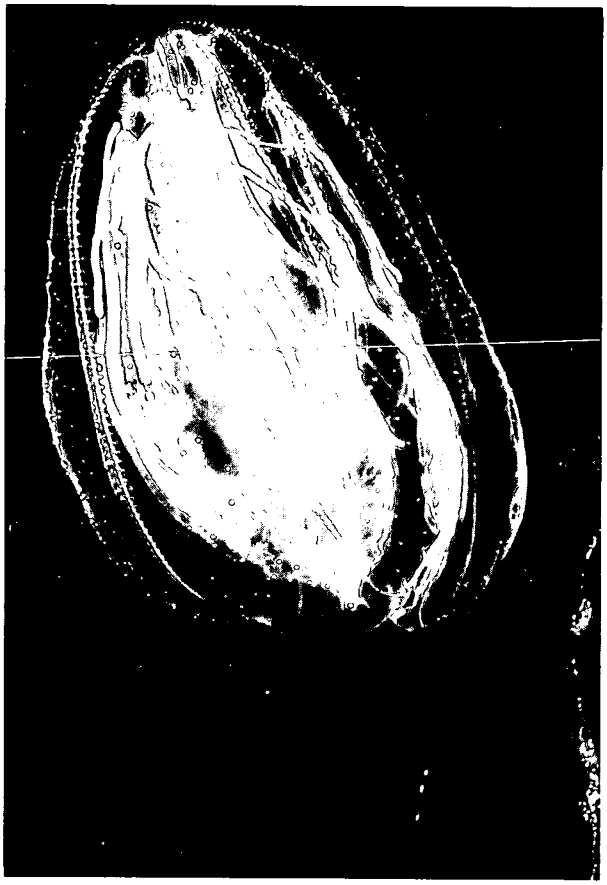
$$\mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{CH_3}$$

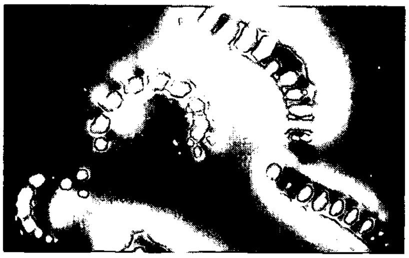
in the presence of oxygen. The chemiluminescence that results is brighter and longer lasting than that observed in the hydroxide-catalyst system. When sealed in a Mylar plastic bag, this luminol solution emits cold light for as long as thirty days if air (O_2) is admitted slowly to the bag.

Bioluminescent bacteria growing in a flask *(left)* and in culture dishes *(right)* produced enough light to make these photographs. Scientists study these organisms to learn more about the phenomena of cold light.

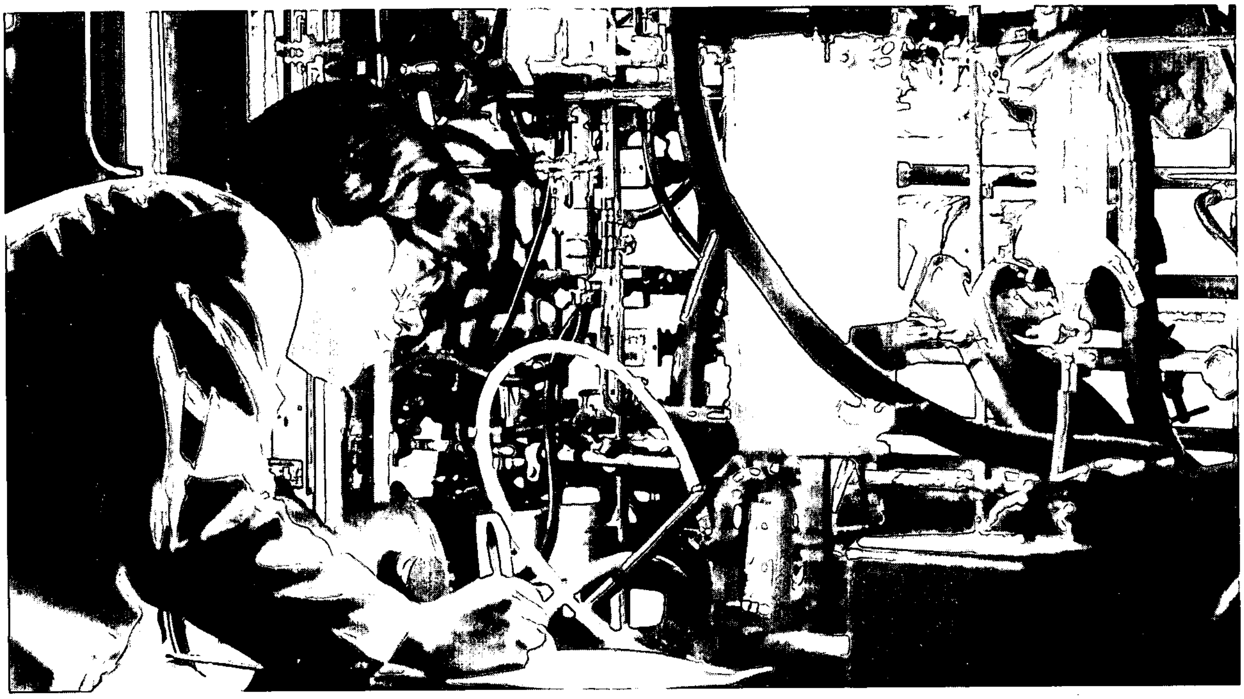








Many animals such as *(left to right, clockwise)* jellyfish, comb jelly, anemone, sea pansy, and glow worm have the ability to produce cold light. They ripple and undulate eerily in their world of silence.



Scientists study bioluminescent material to determine how the photooxidation process may be applied to other areas of chemistry, biology, and related sciences.

O-55 Chemistry of Vision

For years chemists have been studying what affects us more than any other factor, our environment. The environment really includes many things—the oceans, the atmosphere, the earth, plants, animals—and human beings.

Consider, for example, the activity in which you are now engaged. You are reading this book. In order to read, you must be able to see. This means that your eyes must be able to detect light, and a message that light has been detected must somehow get to your brain. Both the detection of light and the transmission of messages in the human nervous system are in part chemical events. And the chemistry of vision is organic chemistry. Its study and explanation illustrate several important principles.

You can look upon light as small "blips" or particles. The particles of energy are called *photons*. Each photon has a certain amount of energy. One index of this energy is called the *wavelength* of light. For example, red light has a wavelength of around 700 nanometers.* Violet light has a wavelength of 400 nm. A photon of red light has less energy than a photon of violet light.

How can light be detected by a molecule? An obvious example is the process that takes place on photographic film. In this reaction

TIME MACHINE

1889	John L. Sullivan goes 75 rounds to beat Jack Kilrain in last official bare-knuckles bout.
1891	**Leo Baekeland produces the first photographic paper that can be developed under artificial light.**
1892	Tchaikovsky's *The Nutcracker* ballet is first staged in St. Petersburg (now Leningrad), Russia.
1892	Rudolf Diesel receives patent for Diesel engine, and Frank Duryea makes first American automobile.
1893	Shredded Wheat becomes the first patented breakfast cereal.
1894	Model-car racing begins.
1895	William Konrad Roentgen discovers X rays.
1896	Henri Becquerel discovers radioactivity.

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*A nanometer (nm) is 10^{-9} meters—that is, a billionth of a meter.

SHAKING A TEST TUBE OF LUMINOL IN THE DARK WITHOUT THE CORK

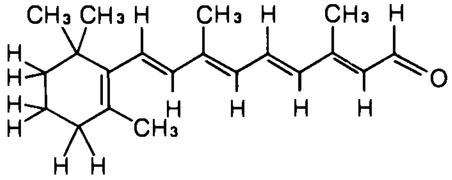
light alters silver ions in a manner that allows the developing solution to reduce them to silver metal, which appears as a black spot on the film negative.

Light can cause chemical reactions. However, in order for the light to be effective, it must be absorbed. For example, have you ever held a piece of paper in the sunlight under a magnifying glass? By focusing the sunlight on the paper, you can set fire to the paper. In this instance light energy is converted to heat energy. When the temperature of the paper reaches its kindling temperature, the paper combusts spontaneously. The light causes the paper to burn. At the same time the light passes through the glass without raising the temperature of the glass.

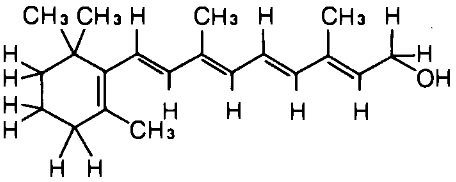
What happens in the eye? Is the light absorbed and changed to heat energy? Is the message that heat has been released somehow then transmitted to the brain? The processes that take place in vision are much more subtle and complex.

The chemistry of vision involves complex molecules. The key molecule is retinal—a molecule that is closely related to vitamin A. The difference is only two hydrogen atoms. Both the retinal molecule and the vitamin A molecule are closely related to β-carotene, the pigment that causes carrots to be orange. The β-carotene molecule roughly corresponds to two molecules of retinal (minus the oxygen) joined together end to end. The other molecule in the vision process is the *opsin molecule,* one of a series of complex biochemical macromolecules called proteins. Like all proteins, the opsin molecule is made up of a long chain of amino acids. We know that the opsin chain tends to exist in a folded form. Unfortunately, the precise structure of opsin is not known.

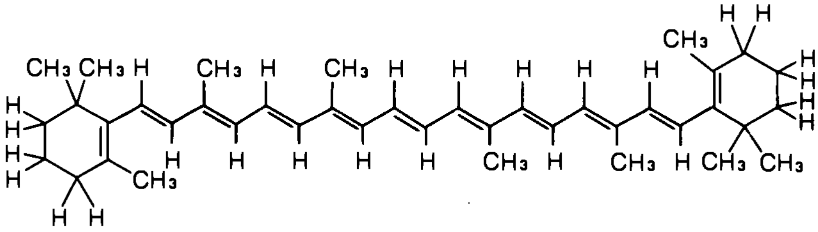
RETINAL



VITAMIN A

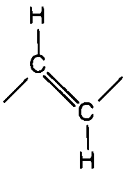


β-CAROTENE

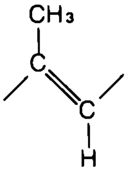


The structure we have shown for retinal is really only one of many possible *cis* and *trans* isomers. If we look at the double bonds in retinal, we see that each double bond has either two hydrogens or a methyl group and a hydrogen attached to it.

trans

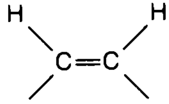


trans

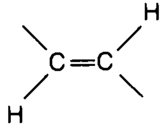


In the arrangement shown, these groups are on opposite sides of the double bond, and we call this *trans*. If they are on the same side, they are called *cis*.

cis

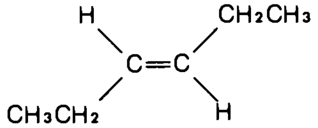


trans

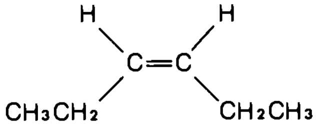


These are called *geometric isomers* because in going from *cis* to *trans* the geometry, or shape, of the molecule changes.

trans-3-HEXENE

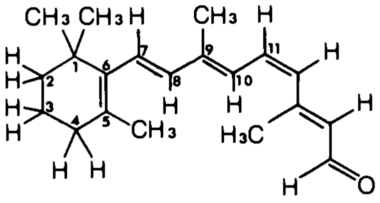


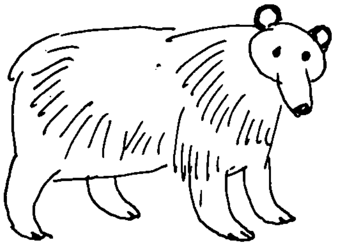
cis-3-HEXENE



In the retina of the eye an isomer of retinal (11-*cis*-retinal) is bound to the opsin molecule to give a pigment called *rhodopsin*. In the pigment the *cis*-retinal is curled up and sits nicely in one of the folds of the opsin molecule. When light hits the rhodopsin molecule, the 11-*cis*-retinal isomerizes (changes) to all *trans*-retinal. When this happens, the shape of the retinal also changes; it can no longer fit in its old home. The opsin molecule must uncoil to let out the *new* retinal molecule. All that light does in the process of vision is to change the shape of retinal. This results in a chain reaction that sends a message to your brain and you "see."

11-*cis*-RETINAL





POLAR

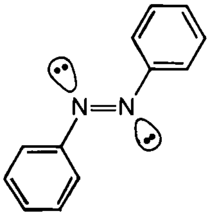
NON-POLAR

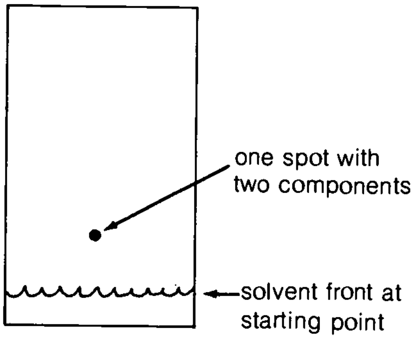
How does this "isomerization" take place? Is it common for light to cause reactions like this to take place? Can we show that light can cause a *cis* double bond to change to a *trans* double bond? The azobenzene molecule demonstrates this very nicely. The azobenzene molecule exists in *cis* and *trans* forms, both of which are yellow and therefore easily visible.

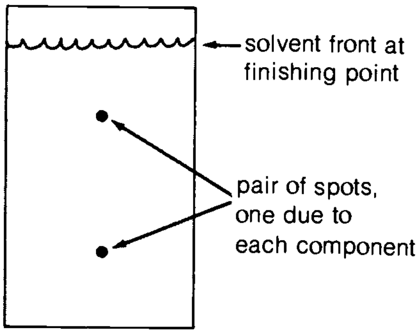
We can demonstrate the existence of each of these molecules by using a technique called *thin-layer chromatography* (TLC). A "thin-layer plate" is spread with an adsorbent substance called silica gel. If a molecule such as azobenzene is applied to the surface of the silica gel, it sticks to the gel, and the strength with which it sticks is a measure of its polarity. Polar molecules stick to the surface of the gel more strongly than nonpolar ones. This can be demonstrated by standing the plate in a solvent and allowing the solvent to "run" or "creep" up the plate. Nonpolar compounds will be dragged along by the solvent better than polar compounds will be. *Cis*-azobenzene is more polar than *trans*-azobenzene, so it should move up the TLC plate more slowly.

Light causes *trans*-azobenzene to rearrange to *cis*-azobenzene. We should be able to demonstrate this by using thin-layer chromotography. If the plate is allowed to stand in a small amount of solvent, the solvent flows up the plate, and it tends to drag along any other material that is on the surface of the adsorbent. Different materials are dragged along with different efficiencies, so that if you place a spot of two components on a plate and allow the solvent to flow past that point, two spots will be formed further along the direction of the solvent flow, indicating that the original spot was a mixture of two components.

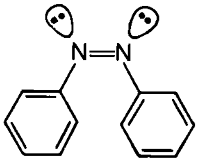
trans-AZOBENZENE







cis-AZOBENZENE



In the following experiment you will use thin-layer chromotography to show that a reaction has occurred. The reaction is one that occurs by shining a light on the pure component.

O-56 Photochemical Reaction

EXPERIMENT

Obtain from your teacher two TLC plates (2.5 cm × 10 cm), a developing jar, and a piece of capillary tubing. On each of the TLC plates make a mark with a pencil, not a pen, at the edge of the plate 1 cm from each end. Label the plates A and B. Plate A will be used as a control to demonstrate that no reaction takes place without strong irradiation.

Dip the capillary into a bottle marked *trans*-azobenzene in toluene, which will be furnished by your teacher. (Note that the brown bottle excludes light.) Tap the capillary against the inside lip of the bottle so that only a few millimeters of solution remain in the capillary. Carefully lower the tip of the capillary against the surface of the adsorbent on plate A so that a spot is formed 1 cm from the bottom and centered on the plate. Try not to scratch or mar the adsorbent surface. Keep the spot as small as possible.

Repeat with plate B. Place plate B where it is exposed to full sunlight or some other ultraviolet source (a lamp). One full day of exposure to sunlight is needed. A shorter time may be used if an ultraviolet light source is available (10 to 20 minutes).

While plate B is being irradiated, develop plate A. Pour developing solvent, 3:1 cyclohexane-toluene, into your developing jar to a depth of about 0.5 cm. Cap the jar and swirl it for a few seconds. Stand plate A in the solvent, recap the jar, and allow the solvent to flow up the plate until it reaches the upper mark. Remove the plate, allow it to dry, and then inspect it.

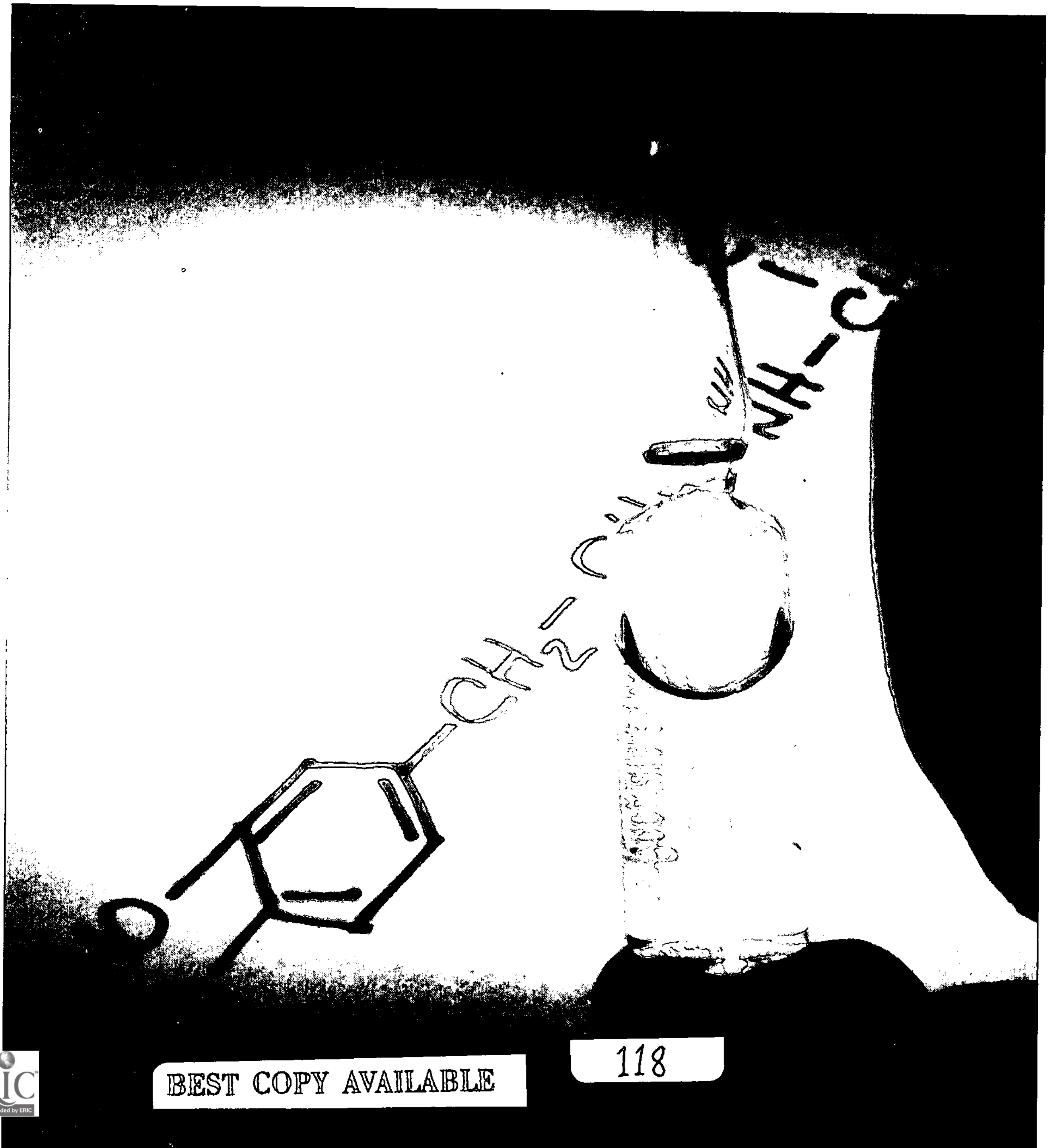
What has happened to the original spot? Is there a new spot? If so, where is the new spot? Measure the distance that the solvent has traveled past the point where you originally spotted the azobenzene. Now measure how far the spot has traveled. The ratio of these two distances is called an R_f value. The ratio relates the distance a material has traveled to the distance the solvent has traveled from the initial point.

After appropriate irradiation time, develop TLC plate B. Examine it for spots and calculate R_f values. What can you say about the irradiated and nonirradiated materials? Is there any evidence of a chemical reaction?

As we have seen, some chemical compounds are capable not only of absorbing light and changing their structures but also of emitting light without producing heat. Chemists, having recognized the practical importance of these two properties, are working to put them to use.

Drugs: From Aspirin to Hallucinogens

Organic chemists are very much involved in the analysis and synthesis of drugs. Our society uses vast quantities of different kinds of drugs each year, and it is not easy to find a single, simple definition of the word *drug* that covers all of them. Dictionaries generally define *drug* as a medicine or an ingredient of a medicine. Today, however, we often use the term to include many chemicals that are not, strictly speaking, medicines at all.



Shown in powder, crystalline, and tablet form, aspirin (acetylsalicylic acid) is the most widely used nonprescription pain reliever in the world.

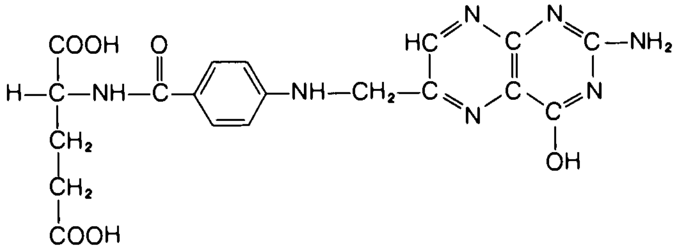
O-57 Let's Start with Aspirin

The action of many drugs in the body is somewhat of a mystery. There is much that we do not yet understand. Aspirin, a drug you synthesized in one of your laboratory experiments, is the most widely used drug. More than twenty billion tablets are consumed each year. Aspirin, as you know, can reduce pain, stop swelling, and lower a fever. But even after 75 years of research, we still do not know how aspirin accomplishes all this. Moreover, we know very little about what else it may do in the body, or what its long-term effects might be. Even today, doctors are still finding new uses for aspirin.

Chemists and pharmacologists have a better understanding of some other drugs than they do of aspirin. A good example is the first of the modern wonder drugs, sulfanilamide. Sulfanilamide belongs to a class of drugs known as *sulfa drugs*. Pharmacologists introduced sulfanilamide before the now more widely used antibiotics such as penicillin (see Appendix III).

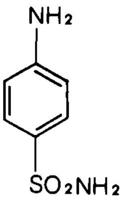
Sulfanilamide kills off a bacterial infection in the human body by depriving the bacteria of an essential substance needed for their metabolism. This compound is folic acid, one of the B vitamins.

FOLIC ACID

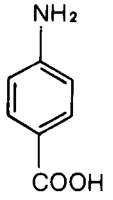


The growth of a fungus that produces an antibiotic is being studied to determine the potential use of the antibiotic in fighting disease. Research chemists try to establish the chemical structure of the antibiotic in order to synthesize it for mass production. Even after synthesis and preliminary testing, the drug undergoes elaborate animal tests before being used on humans.

SULFANILAMIDE



p-AMINOBENZOIC ACID



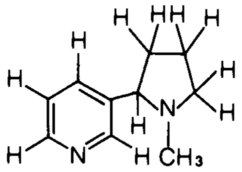
Bacteria must have folic acid in order to live, but they can use *only* the folic acid that they make themselves. They cannot use folic acid from outside sources. To synthesize folic acid, bacteria use another chemical called *p*-aminobenzoic acid. The key to the effectiveness of sulfanilamide is its close structural resemblance to *p*-aminobenzoic acid. The chemical "factories" of the bacteria cannot tell the two substances apart. But when bacteria try to use sulfanilamide to make folic acid, the sulfanilamide sabotages the entire process. It ties up an enzyme that plays a vital role in the synthesis of folic acid. With this enzyme out of action, no more folic acid can be produced and the bacteria cannot grow or multiply.

Folic acid is also important to the metabolism of cells other than bacteria. In fact, it is an essential nutrient for the human body. Fortunately, human beings can take sulfanilamide, the bacteria killer safely—unless they are allergic to it—because it is not necessary for the human body to synthesize its own folic acid. Unlike bacteria, we can obtain folic acid from the food we eat.

O-58 Alkaloids

Aspirin is an *analgesic*, or pain killer. Sulfanilamide, an *antibiotic*, works against bacterial infections. But there are many other kinds of drugs. Among those that will be discussed are the opiates, which are classed as *narcotics* (powerful pain killers that numb the senses), and the *hallucinogenic*, or mind-altering, drugs. Almost all the opiates and hallucinogens are chemically related. They belong to the class of substances known as *alkaloids*.

NICOTINE



Alkaloids are natural organic chemicals found in plants. An alkaloid always contains *at least one nitrogen atom*. Although many alkaloids have intensive physiological effects on animals, they apparently serve no essential purpose for plants. For example, *nicotine* is an alkaloid found in the tobacco plant. Tobacco normally contains nicotine, but botanists have learned that a tobacco plant can survive without nicotine. In fact, botanists have actually bred tobacco plants that contain no nicotine.

Botanists also have shown that a plant that normally has no nicotine can survive when nicotine is added to its cells. Tobacco plants are closely related to tomato plants, and the two have been successfully grafted together. A tomato plant ordinarily contains no nicotine, but once it is grafted onto a tobacco root, nicotine begins circulating through its system. The nicotine appears to have no adverse effect on the tomato plant.

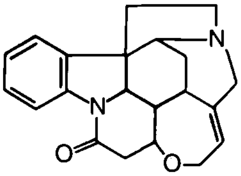
Although scientists have been unable to document the biochemical role of alkaloids, these chemicals still may be important in the evolutionary development of some plants. It has been sug-

When Columbus reached the New World, he found Native Americans cultivating tobacco for its medicinal properties. Here modern growers examine tobacco leaves prior to harvest. The next steps include grading, curing, and selling at auction before final processing.

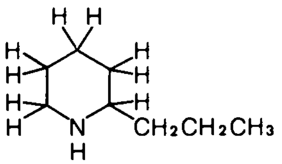
gested that because many of the alkaloids are quite toxic to animals, plants containing these poisons have an advantage against predators. Nicotine is a powerful insecticide, and few insects therefore bother tobacco plants. Also, we have made use of nicotine as an insecticide.

Many alkaloids are poisons—coniine and strychnine, for example. Coniine is one of the lethal compounds in the hemlock plant. The ancient Greeks brewed hemlock into a potion and forced those condemned to death to drink it. The most famous victim of this poison was the Greek philosopher Socrates. Strychnine is best known as a rat poison and was very popular in mystery novels and movies as an easily available murder weapon. Nicotine, too, is poisonous, but its harmful effects vary greatly, depending on how it enters the body. It is very deadly if injected directly into the bloodstream, but much less dangerous when swallowed. Even so, the tobacco in a single cigarette contains enough nicotine to make you quite sick if you eat it. Inhaling nicotine is also dangerous. But in small doses nicotine functions as a stimulant. This stimulant effect is probably one of the reasons some people still smoke tobacco despite its grave health hazards.

STRYCHNINE

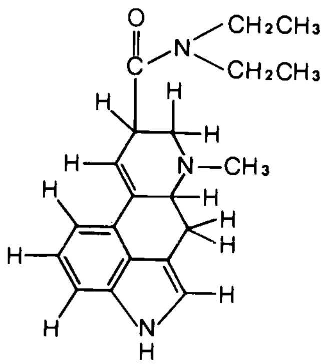


CONIINE



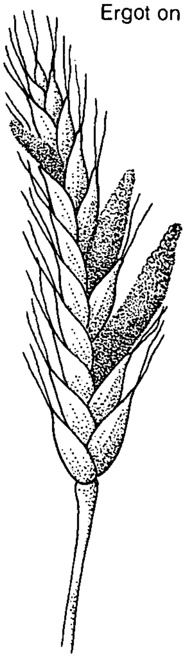
O-59 Hallucinogens: The "Dream Makers"

LSD



People have been interested in the hallucinogenic drugs for thousands of years—since long before recorded history. At one time or another people have attempted to eat everything that moved or grew. They soon learned that there are many plants that cause extreme physical and mental changes. As a result, the human race has cataloged a long list of plants that are useful as poisons, medicines, and "dream makers." Among the most remarkable are the *hallucinogens*—drugs that alter or distort the perception of reality. These substances open the doors of the mind to bizarre experiences and strange (often frightening) visions.

One well-known hallucinogenic drug is lysergic acid diethylamide, commonly referred to as LSD. Although LSD does not occur naturally, it can be synthesized from lysergic acid. The compound lysergic acid is found in ergot, a fungus that attacks rye. Ergot contains a number of other alkaloids, many of which are poisonous as well as hallucinogenic.

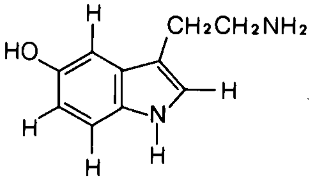


Ergot on Rye

During the Middle Ages a pestilence known as Holy Fire, or Hell's Fire, swept whole communities. The symptoms of this disease varied from extreme itching and burning sensations to gangrene, psychosis, physical deformity—and even death. To deal with the problem the Order of Saint Anthony was founded. Hence, the affliction came to be known as Saint Anthony's Fire. Later it was established that the malady arose from eating rye infected with the fungus ergot. The disease was called ergotism or simply ergot poisoning.

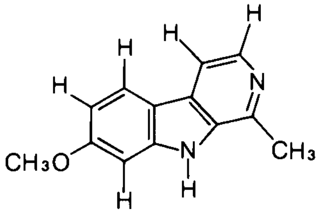
LSD, thought to be useful in the treatment of mental patients and in the study of clues to nerve-cell chemistry, has fascinated scientists for many years. It also has important medical uses in controlling muscle contraction and bleeding. The LSD molecule contains a section that resembles the serotonin molecule. It is thought that serotonin may be one of the chemicals naturally occurring in the human brain that help transfer signals from one nerve cell to another. One theory states that the LSD molecule can fool a nerve cell into accepting it as a signal-carrying serotonin molecule. But the LSD cannot forward impulses the way serotonin does. Therefore the signals are altered, increased, or distorted, causing sensations exaggerated beyond ordinary experience.

SEROTONIN

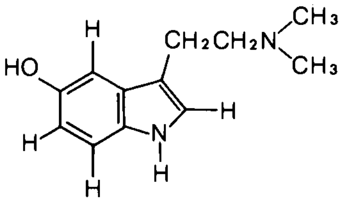


Other compounds related to LSD and to serotonin are harmine, bufotenine, dimethyltryptamine (DMT), and psilocybine.

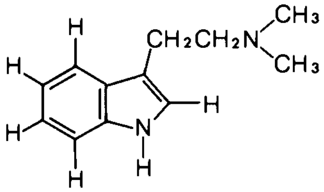
HARMINE



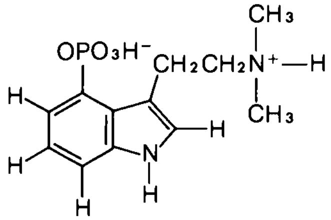
BUFOTENINE



DMT

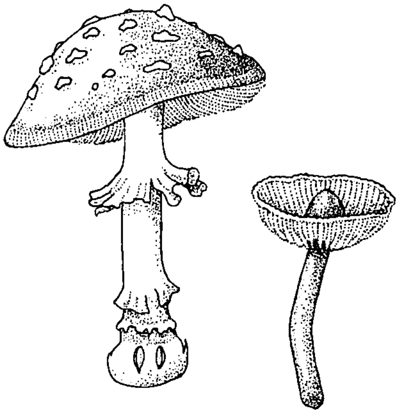


PSILOCYBINE



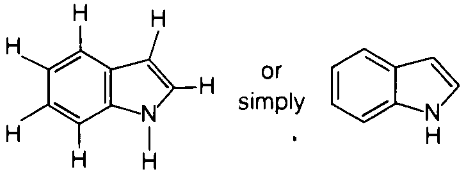
Harmine is an organic compound found in several varieties of plants in South America. Natives make a brew of the plants for the purpose of prophecy and to prepare young boys for the painful initiation into manhood. Another hallucinogenic drug, bufotenine, is one of the few alkaloids that also occur in animal cells—it has been isolated from the tissues of toads. DMT is an active ingredient in hallucinogenic snuff prepared and used by South American natives. Psilocybine is a compound found in the hallucinogenic mushrooms of Mexico.

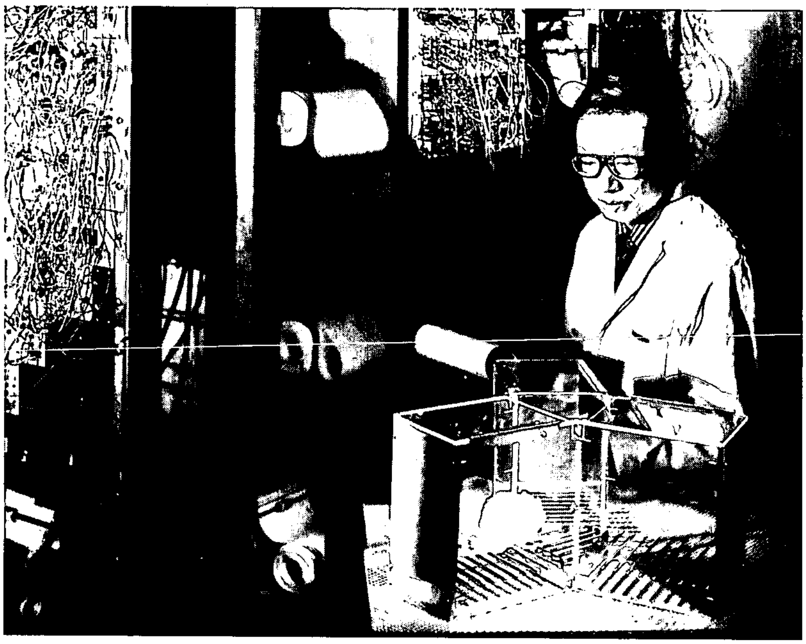
If you note the manner in which the preceding structures for hallucinogens have been drawn, you will see that they are closely related to serotonin. All of these compounds possess a certain ring structure known as the *indole ring* system. There are many alkaloids that contain the indole ring structure, composed of a five-membered ring fused to the familiar benzene ring. The presence of the indole ring in a compound gives chemists a clue to the properties and reactivity of the compound.



Hallucinogenic Mushrooms

INDOLE



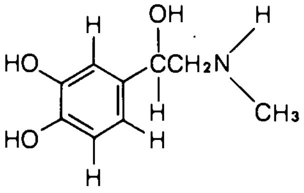


A researcher tests the effects that a potential psychoactive drug may have on the human body. By using electronic equipment and trained rats, scientists can predict the relationship between behavior and drugs on the central nervous system of humans.

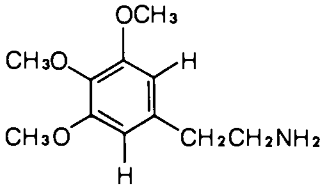
The biochemical action of serotonin and other amine-containing compounds in the brain is not yet fully understood. We know, however, that these compounds are very important in the behavior of animals. We also know that the hallucinogenic drugs alter the brain's normal chemistry in some way. It seems likely that their structural similarity to serotonin is the key to their ability to do this. But exactly how they work is still unclear.

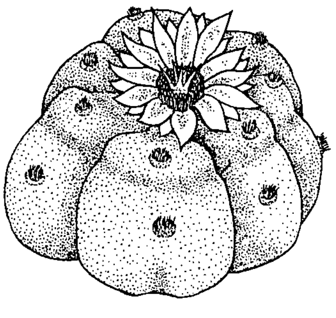
Another important substance that plays a major role in the brain's functioning is *epinephrine* (formerly called adrenaline). Not surprisingly, some drugs that are structurally related to epinephrine also are hallucinogens; one of these is mescaline.

EPINEPHRINE



MESCALINE





Peyote Cactus

Mescaline is found in the peyote cactus of the southwestern United States. The Mescalero Apaches (hence the name mescaline) were the first to use this drug. The hallucinogenic amine mescaline (β-3,4,5-trimethoxyphenethylamine) can be extracted from the surface tops or "buttons" of the peyote cactus. It can also be synthesized in the laboratory. The dangers of using the drug are similar to those of using LSD, but it is not yet known what organic damage the drug may cause to the cells of the human body.

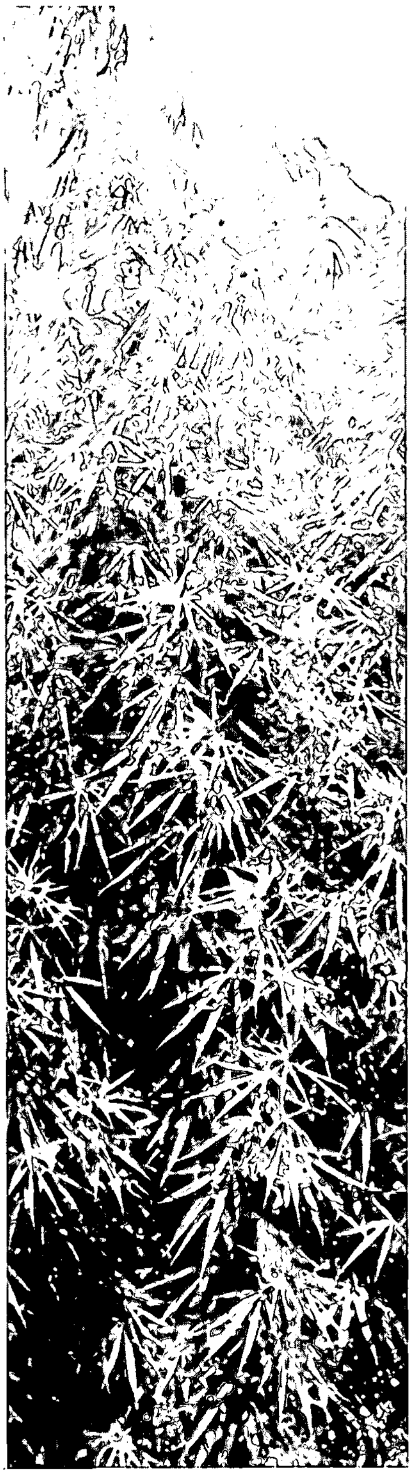
O-60 Marijuana: Psychoactive Plant

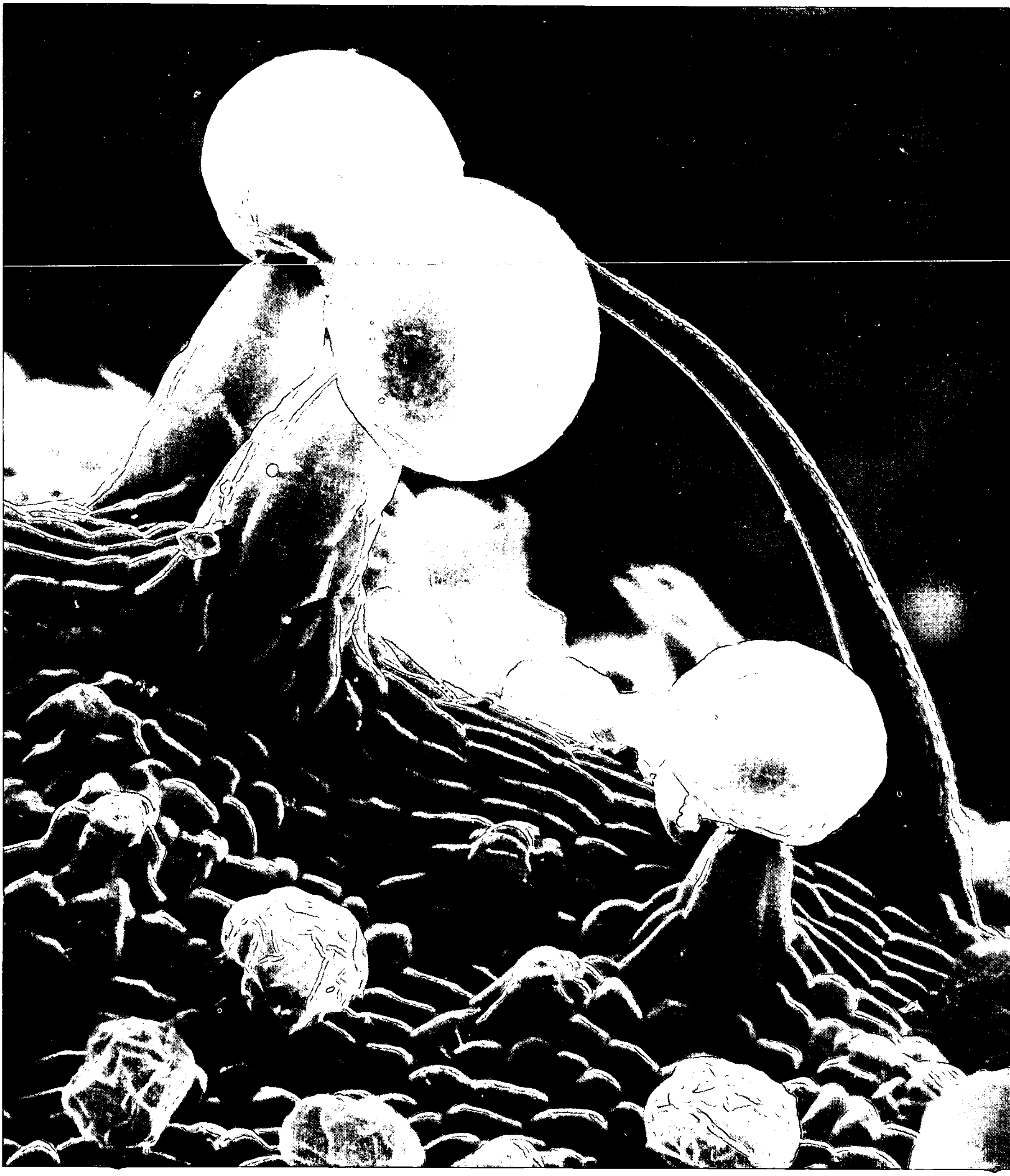
Marijuana, another mind-altering drug, comes from the Indian hemp plant *(Cannabis sativa)*. Hemp once had great commercial value because it was used to make rope. The Japanese cut off the United States' source of hemp in Southeast Asia during World War II. To maintain an adequate supply for making rope, the United States began growing the plant in a number of midwestern states. This hemp is no longer of any commercial value because most of the rope used today is made from synthetics.

Like many of the other psychoactive (mind-altering) plants, marijuana has a long and interesting history. Probably the most spectacular rumored use of marijuana was by the Hashishin, a semireligious group located in the rugged mountains of what is now northern Iraq. Local rulers hired the leader of this group to have assassinations committed. As part of a religious ceremony, the leader's followers were plied with hashish, the sticky resin that covers the flower of the marijuana plant. When they were under the influence of the drug they were promised Paradise if they died while carrying out their mission. In the thirteenth century the Mongols wiped out the colony, but hashish survived and gave us our word *assassin*, which is derived from the Arabic *hashish*.

The active ingredient in marijuana is Δ^9-tetrahydrocannabinol (THC). Interestingly, THC is not an alkaloid, because the molecule contains no nitrogen. The amount of THC in the plant varies in different subspecies grown in different parts of the world.

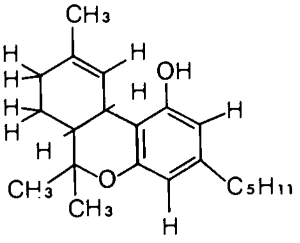
As with aspirin, little is known about what marijuana actually does in the human body. In fact, until just recently—the late 1960s—it has been difficult for scientists to do research on the effects of marijuana. This drug, along with aspirin, is an example of one of the many controversial drugs that scientists are studying today. One of the reasons research was difficult was that the strength of marijuana differed so widely that it was impossible to scientifically measure and compare data. Another reason was that until just recently, scientists were not sure of the exact active components of marijuana. Several things happened in 1967 to change this. The Center for Study of Narcotics and Drug Abuse was established. This has now become the National Institute on Drug Abuse. In the same year an Israeli chemist, Raphael Mechoulam, synthesized the active ingredient in marijuana, THC. Now scientists could prepare a standardized measure of this ingredient to use in controlled experimental work. NIDA set up a research center at the University of Mississippi where they established the only legalized marijuana farm in the United States.


The School of Pharmacy at the University of Mississippi conducts studies on the effect of marijuana on humans. For its research, it grows the only legal marijuana in the United States.

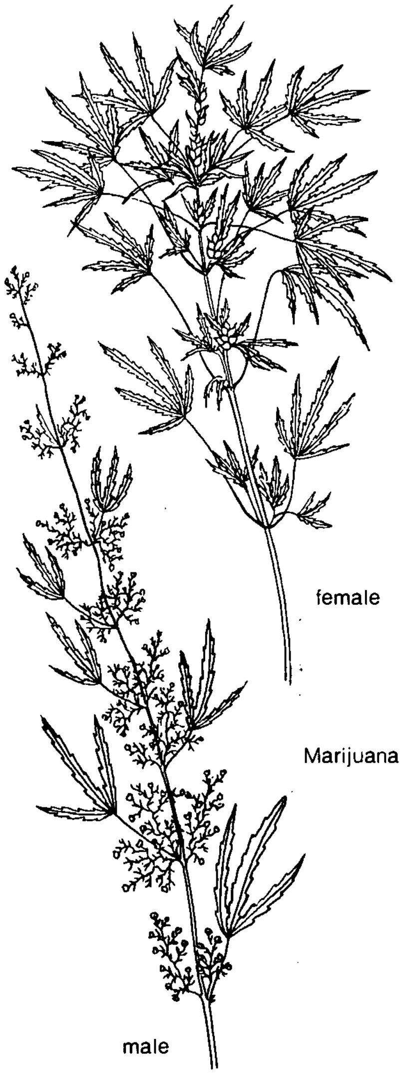


Much is still unknown about the effects of marijuana, but some initial findings to date suggest that THC is more dangerous than other common drugs because it takes much longer than alcohol or caffeine to be eliminated from the body, and it remains in areas of the body that are highly sensitive to chemical action.

THC



Scientists have some evidence that relatively high doses of marijuana over a period of time may cause specific reactions in the body chemistry of males and more general effects on the bodies of both males and females, and it may have some effect on mental attitudes and behavior. There is some evidence that smoking marijuana can cause damage to the lungs similar to that caused by cigarettes. Scientists also believe that marijuana may affect the growth-control hormone in the human body. Through continuing research, scientists are able to understand more fully the long-range effects of drugs and can better educate the public on the use and abuse of all drugs.



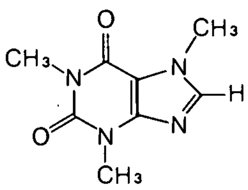
Marijuana

O-61 Stimulants

Earlier we mentioned the fact that the nicotine in tobacco is a stimulant. So is *caffeine*, found in tea and coffee. Caffeine is used in several common medications designed to help people avoid drowsiness and stay alert. Since caffeine has been considered a relatively mild and safe substance, these preparations can be bought in drugstores without prescriptions.

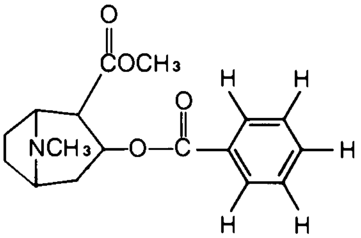
A much stronger and more dangerous stimulant is *cocaine*. Cocaine is an alkaloid extracted from the leaves of the coca plant, a shrub native to Peru and Bolivia. Cocaine produces an intense stimulation, making the user talkative, confident, active and euphoric, although with a large dose it has been reported that the user may experience hallucinations and is likely to become confused, anxious, and hostile. When the drug wears off, the feeling of power and elation is usually followed by depression.

CAFFEINE



The photomicrograph *(opposite page)* shows the glandular hairs on a marijuana plant (magnified over 550 times). Hashish comes from the resin that oozes from these hairs.

COCAINE

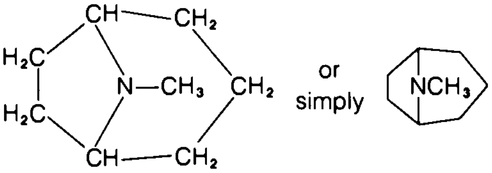


Like many drugs, cocaine has been used for medical purposes —mainly as an anesthetic. Physically, cocaine constricts blood vessels and stimulates the central nervous system. It can cause inflammation of the nasal passages and local-tissue death. Not much is known about the effects of cocaine on the cells of the human body, but although it is not as harmful as heroin, use of cocaine *can* result in death.

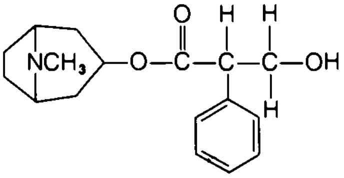
There is an interesting note in the history of cocaine. When cola syrup was first developed, in the 1880s, it was intended as a tonic. One of its ingredients was an extract of coca leaf which contained a trace amount of cocaine. When the manufacturer became concerned about public suspicions of his cola drink, he had it analyzed by a chemist who reported that a person would have to consume more than five and a half quarts of the beverage at once to experience any effect from its trace cocaine content. Despite this reassurance, chemists were assigned to remove the cocaine from the leaves, and this popular drink has not had any cocaine in it since 1905. A more controversial ingredient of cola syrup *at the time* was caffeine, but the chemist who analyzed the contents found that caffeine was present in very small amounts—perhaps one-fifth the amount found in coffee.

Cocaine belongs to a class of alkaloids known as *tropanes*. Two other well-known members of this class are atropine and scopolamine. Atropine is found in several plants including belladonna, henbane, and deadly nightshade. Optometrists use dilute solutions of atropine to dilate eye pupils. Also, atropine can be used as an antidote to nerve gas poisoning. Scopolamine was used many years ago in the original "truth serum." Today, scopolamine can be found, although in very low amounts, in several sleeping aids sold without a prescription.

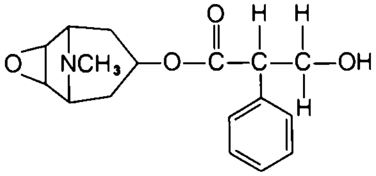
TROPANE
RING STRUCTURE



ATROPINE

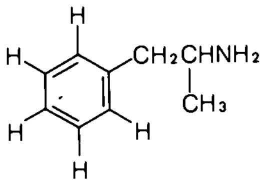


SCOPOLAMINE



Synthetic stimulants such as the *amphetamines* produce effects similar to those of cocaine. The amphetamines are habit-forming and their prolonged use is known to cause damage to the brain. These drugs affect the central nervous system, probably by mimicking the action of epinephrine. (Compare for yourself the structural formulas of epinephrine and amphetamine.)

AMPHETAMINE



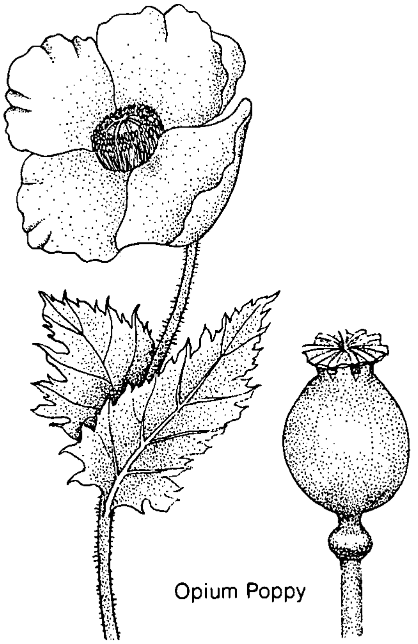
O-62 Narcotics: Analgesic but Addictive

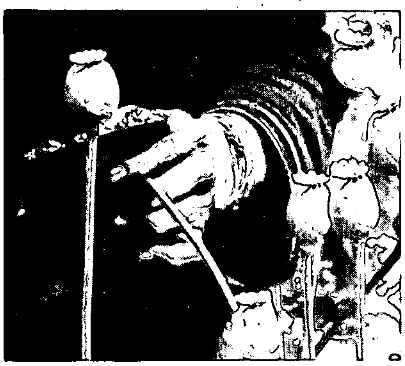
Among the drugs that are commonly used as medicines are the *analgesics.* An analgesic is a chemical or drug that can relieve pain. Technically, both aspirin and morphine are analgesics. An analgesic such as morphine is also classified as a *narcotic.* A narcotic is a drug that depresses the central nervous system, thereby reducing pain very markedly. In larger doses narcotics generally induce sleep, or even coma and death. As pain killers, narcotics are beneficial. Unfortunately, though, narcotics tend to be addictive—that is, they are dangerously habit-forming. An addict not only has a powerful craving for the drug to which he/she is addicted but will become physically ill if deprived of it.

The *opiates* are among the narcotics that are strongly addictive. They are derived from opium, which is obtained from the dried juice of the opium poppy. Opium contains some twenty alkaloids (nitrogen-containing organic bases) of which *morphine* is usually the principal constituent. Other opiates include *codeine* (also found in opium) and *heroin,* both of which are structurally similar to morphine.

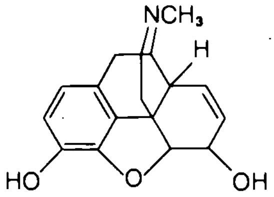
For years chemists have attempted to alter the chemical structure of morphine to obtain a new drug that would possess its desirable pain-killing properties but would lack the properties that lead to addiction. They have had little success, though—as the structure of morphine was altered to make it less addictive, its power to ease pain was also reduced. Among the narcotics, at least, nonaddictive drugs are only weak pain relievers.

Heroin is made from morphine. Chemists originally synthesized it as part of their search for a nonaddictive analgesic. In fact, heroin proved to be as effective as morphine in fighting pain. Unfortunately, it also proved to be even *more* addictive than morphine.

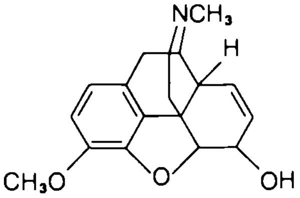

Opium Poppy



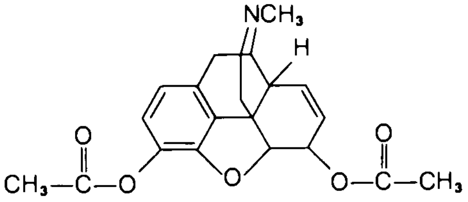
MORPHINE



CODEINE



HEROIN

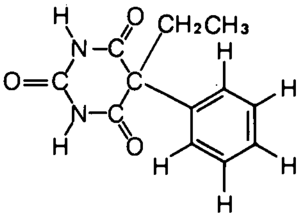


O-63 Barbiturates: The Synthetics

The *barbiturates* are a purely synthetic class of drug—they are made in the laboratory rather than obtained from plants. A chemist produced the first barbiturate in 1864 by combining urea (an animal waste product) with malonic acid. The chemist gave the name barbituric acid to the compound he had synthesized. The derivation of the name is not known for certain. One story suggests that the chemist who made this new compound went to the local tavern to celebrate his discovery. At the tavern some soldiers were celebrating the day of Barbara, the patron saint of the artillerists. Out of this gathering came the name for the new drug: barbituric acid, a combination of *Barbara* and *urea.*

Today, barbiturates are among the most popular and useful of drugs. More than 2500 different barbiturate compounds have been synthesized. Barbiturates are used chiefly as sedatives (that is, sleeping pills). They make the user feel calm, relaxed, and drowsy. One common barbiturate is *phenobarbital.*

PHENOBARBITAL



Barbiturates are depressants that operate on the central nervous system. The brain is more sensitive to barbiturates than is any other organ in the body. The barbiturates apparently interfere with the consumption of oxygen in the brain. In addition, these drugs also interfere with the mechanism that enables the cells to take in energy, store the energy, and use it. Because barbiturates are highly addictive, they are prescription drugs and should be used only with utmost care, as prescribed by a doctor.

It is interesting to note that most drugs appeared at their conception in history as pain relievers. Many have gone through periods of history during which they have received wide acclaim. There was a time when the tea leaf, coffee bean, tobacco leaf, and coca plant, to name a few, received glowing testimonials for their medicinal powers. Even alcohol was introduced as a medicine in the 1300s. Because there is so little known about how drugs affect the human body, it is important that we treat drugs with great respect. Only those trained in the many facets of the human body and the effects of drugs on it are qualified to prescribe their use.

TIME MACHINE—Drugs

1806	Morphine is the first plant drug to be isolated.
1820	F. Runge isolates the alkaloid chemical compound caffeine from the coffee bean.
1898	John J. Abel isolates the hormone epinephrine.
1903	The first barbiturate, barbital, is introduced.
1910	Paul Ehrlich introduces chemotherapy, a method of treating infectious diseases by using chemicals to attack the disease-causing bacteria.
1925	Sir Robert Johnson identifies, with the exception of one atom, the structure of morphine.
1928	Alexander Fleming discovers the first antibiotic—penicillin.
1930s	Amphetamines are first used medically.
1935	Gerhard Domagk discovers the first sulfa drug—Prontosil.
1937	United States government outlaws sale, use, or possession of marijuana, except for approved research.
1938	Arthur Stoll and Albert Hofmann first synthesize LSD.
1942	Selman Waksman coins the term *antibiotics* for the family of bacteria-killing drugs.

It is interesting that the oldest known prescription, written 4000 years ago on this section of an ancient clay tablet, calls mostly for the use of plant material.

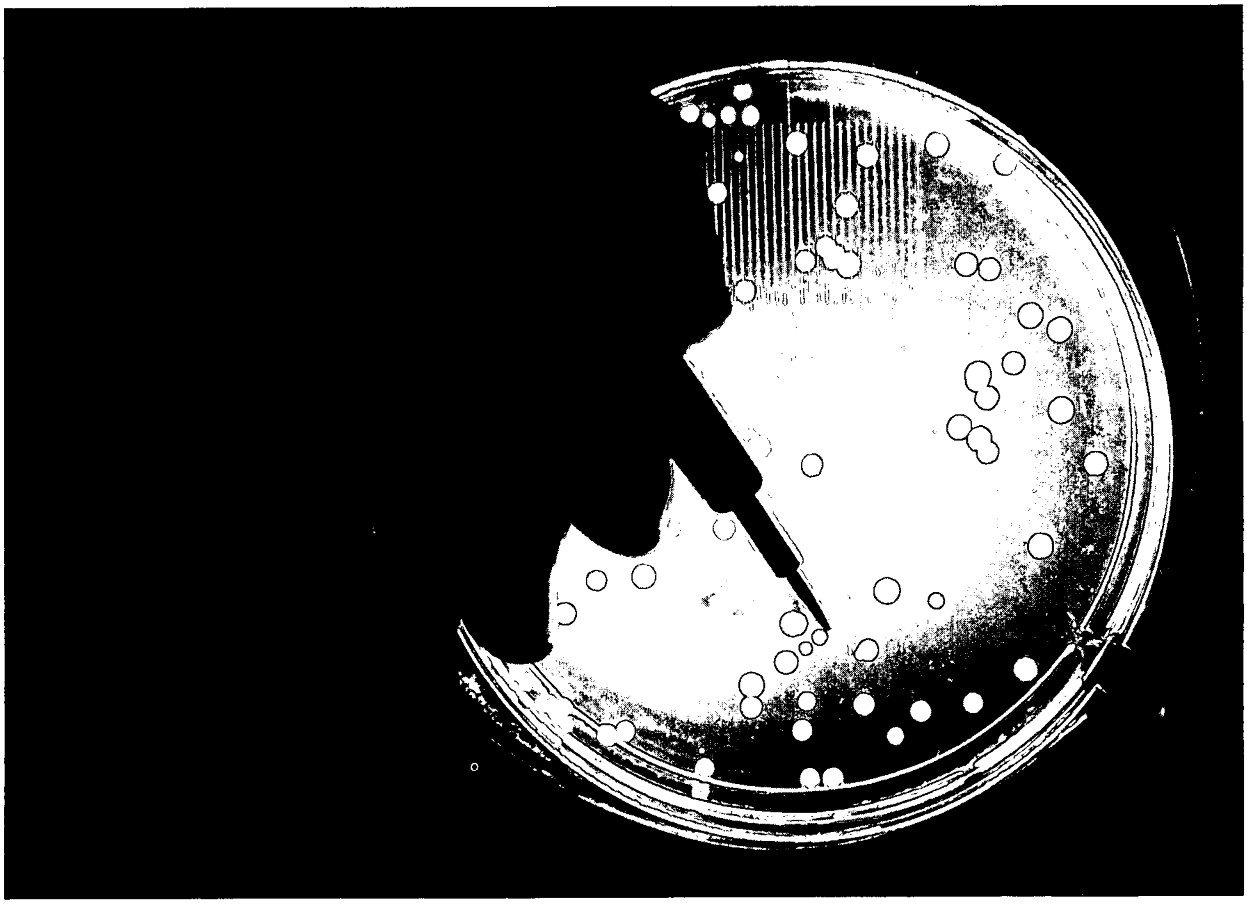
Summing Up

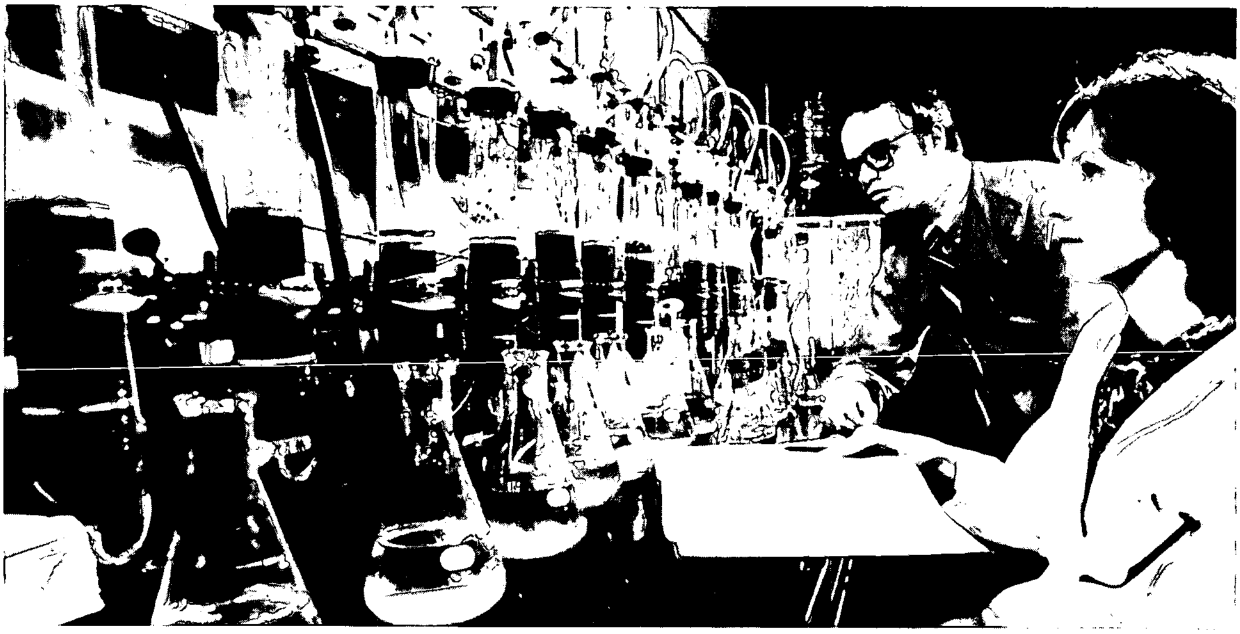
You are probably aware by now that *Form and Function* has barely scratched the surface of the vast subject of organic chemistry. Although we have briefly discussed a number of areas in organic chemistry, there are a number that have not been mentioned at all.

Many areas of organic chemistry will be of paramount importance in the years to come. One, for instance, is that of energy. Much research is being done on the conversion of coal and vegetable matter to liquid fuels to provide power for industry. The recovery of shale oil by extraction is a related area of research that will receive much attention.

The synthesis of new drugs—either totally new molecules or derivatives of existing materials—that are effective against new diseases or resistant viral and bacterial strains will be a continuing task. For example, drugs that are effective against such diseases as cancer and heart disease will continue to be sought.

The effects of a new drug are being tested against disease-producing organisms. Here a research scientist measures the growth pattern of disease-producing organisms that have come in contact with a new drug.





Research scientists are checking various biodegradable detergents in simulated sewage treatment systems to determine the effect that they may have on the environment.

With increasing frequency, various chemicals of industrial importance are being implicated as having long-term (chronic) toxic or carcinogenic properties. For safety reasons we will have to severely limit the use of many of these materials in the future. To maintain our quality of life, huge sums of money and scientific effort must be expended in attempts to modify these existing materials or find replacements that have the desired properties but lack undesirable, toxic properties.

Another large area of organic chemistry is the study of reaction mechanisms. A reaction mechanism is a description, in minute detail, of how a reaction proceeds from beginning to end. This description includes how the bonds are formed and broken, how in some cases the intermediate compounds are formed, and how the exact sequence of these reactions occurs. A knowledge of the reaction mechanisms allows the chemist to predict the results of various reactions in detail. This information is important in the study of both classical organic chemistry and molecular biology.

A great deal of research is being conducted in a new subdiscipline —bioorganic chemistry, which involves the study of molecules and systems important to biological processes (see *Diversity and Periodicity: An Inorganic Chemistry Module.)* There is often significant overlap between investigations in bioorganic chemistry and the study of organic reaction mechanisms.

By simply reading our daily newspapers, it is evident that the future of organic chemistry is brighter than ever; and, as long as there is life on our earth, this will continue to be so. The serious student of organic chemistry will indeed find the future both challenging and rewarding.

Appendix I: Safety

SAFETY IN THE LABORATORY

Proper conduct in a chemistry laboratory is really an extension of safety procedures normally followed each day around your home and in the outside world. Exercising care in a laboratory demands the same caution you apply to driving a car, riding a motorbike or bicycle, or participating in a sport. Athletes consider safety measures a part of playing the game. For example, football players willingly spend a great deal of time putting on equipment such as helmets, hip pads, and shoulder pads to protect themselves from potential injury.

Chemists must also be properly dressed. To protect themselves in the laboratory, they commonly wear a lab apron or a coat and protective glasses. Throughout this course you will use similar items. Hopefully their use will become second nature to you, much as it becomes second nature for a baseball catcher to put on a chest protector and mask before stepping behind home plate.

As you read through a written experimental procedure, you will notice that specific hazards and precautions are called to your attention. Be prepared to discuss these hazards with your teacher and with your fellow students. Always read the entire experimental procedure thoroughly before starting any laboratory work.

A list of general laboratory safety procedures follows. It is not intended that you memorize these safety procedures but rather that you *use* them regularly when performing experiments. You may notice that this list is by no means complete. Your teacher may wish to add safety guidelines that are relevant to your specific classroom situation. It would be impossible to anticipate every hazardous situation that might arise in the chemistry laboratory. However, if you are familiar with these general laboratory safety procedures and if you use common sense, you will be able to handle potentially hazardous situations intelligently and safely. Treat all chemicals with respect, not fear.

GENERAL SAFETY GUIDELINES

1. Work in the laboratory only when the teacher is present or when you have been given permission to do so. In case of accident, notify your teacher immediately.
2. Before starting any laboratory exercise, be sure that the laboratory bench is clean.
3. Put on a laboratory coat or apron and protective glasses or goggles before beginning an experiment.
4. Tie back loose hair to prevent the possibility of its contacting any Bunsen burner flames.
5. Open sandals or bare feet are not permitted in the laboratory. The dangers of broken glass and corrosive liquid spills are always present in a laboratory.
6. Fire is a special hazard in the laboratory because many chemicals are flammable. Learn how to use the fire blanket, fire extinguisher, and shower (if your laboratory has one).
7. For minor skin burns, immediately immerse the burned area in cold water for several minutes. Then consult your teacher for further instructions on possible additional treatment.
8. In case of a chemical splash on your skin, immediately rinse the area with cold water for at least one minute. Consult your teacher for further action.
9. If any liquid material splashes into your eye, wash the eye immediately with water from an eyewash bottle or eyewash fountain.
10. Never look directly down into a test tube—view the contents of the tube from the side. (Why?)
11. Never smell a material by placing your nose directly at the mouth of the tube or flask. Instead, with your hand, "fan" some of the vapor from the container toward your nose. Inhale cautiously.
12. Never taste any material in the laboratory.
13. Never add water to concentrated acid solutions. The heat generated may cause spattering. Instead, as you stir, add the acid slowly to the water or dilute solution.
14. Read the label on a chemical bottle at least *twice* before removing a sample. H_2O_2 is not the same as H_2O.
15. Follow your teacher's instructions or laboratory procedure when disposing of used chemicals.

This symbol represents three of the common hazards in a chemistry laboratory—flame, fumes, and explosion. It will appear with certain experiments in this module to alert you to special precautions in addition to those discussed in this Appendix.

Appendix II: Nomenclature

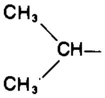
Naming organic compounds is an important part of organic chemistry. The huge number of different compounds makes it necessary for the chemist to use a reasonably organized method for naming them. Historically, as organic compounds were discovered, the discoverer gave them names. We call these names *trivial names*, or *common names*. It soon became apparent that things were getting out of hand. The number of compounds to be named increased so rapidly that a systematic way of naming them had to be developed.

The system we will use is essentially the IUPAC (International Union of Pure and Applied Chemistry) system. This system of nomenclature is based on

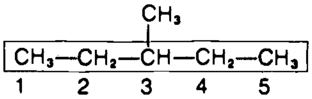
- defining the longest carbon chain in a molecule,
- giving a number to each carbon atom,
- defining the "groups" that are attached to the carbon chain, and
- numbering those groups with regard to the carbon to which they are attached.

ALKANES

The names of all of the saturated alkanes (four carbons or hydrogens connected to each carbon) end with *-ane*. Those past butane in the series start with the prefixes *pent-*, *hex-*, *hept-*, *oct-*, *non-*, *dec-*, and so on. These prefixes mean 5, 6, 7, 8, 9, and 10. There are 5, 6, 7, 8, 9, and 10 carbon atoms, respectively, in the chain.

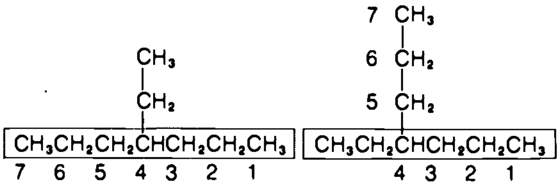
Alkane	Name and No. of Carbons		Group	Name
CH_4	methane	1	CH_3—	methyl
CH_3CH_3	ethane	2	CH_3CH_2—	ethyl
$CH_3CH_2CH_3$	propane	3	$CH_3CH_2CH_2$—	propyl
				isopropyl
$CH_3CH_2CH_2CH_3$	butane	4	$CH_3CH_2CH_2CH_2$—	butyl
$CH_3CH_2CH_2CH_2CH_3$	pentane	5		
$CH_3CH_2CH_2CH_2CH_2CH_3$	hexane	6		
$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	heptane	7		
$CH_3—(CH_2)_6—CH_3$	octane	8		
$CH_3—(CH_2)_7—CH_3$	nonane	9		
$CH_3—(CH_2)_8—CH_3$	decane	10		

The carbon atoms in the chain are assigned numbers. The "groups" attached to the main chain are then named and their positions designated by the number of the carbon atoms to which they are attached. For example, in the following compound the longest single chain contains five carbon atoms. The single group attached to the main chain is a methyl group. The name of the compound is methylpentane.


$$\boxed{CH_3—CH_2—\overset{CH_3}{\overset{|}{C}H}—CH_2—CH_3}$$

To show that the methyl group is attached to carbon number 3, we write "3-methylpentane." The lowest numbers possible are always used.

It should be noted that it is not necessary for the main chain to be written horizontally. Both of the following structures are correctly named 4-ethylheptane because they are the same compound.



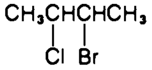
Remember, the main chain in a compound is the longest possible continuous chain of carbon atoms in that compound.

Other groups that are named in the same manner as an alkyl group are

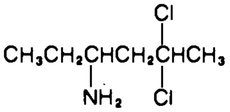
$—NH_2$	amino	—Br	bromo
—F	fluoro	—I	iodo
—Cl	chloro	$—NO_2$	nitro

Some examples include the following:

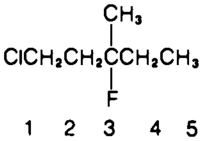
2-CHLORO-3-BROMOBUTANE


$$CH_3\underset{Cl}{\underset{|}{C}H}\underset{Br}{\underset{|}{C}H}CH_3$$

2,2-DICHLORO-4-AMINOHEXANE


$$CH_3CH_2\underset{NH_2}{\underset{|}{C}H}CH_2\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}HCH_3$$

1-CHLORO-3-FLUORO-3-METHYLPENTANE

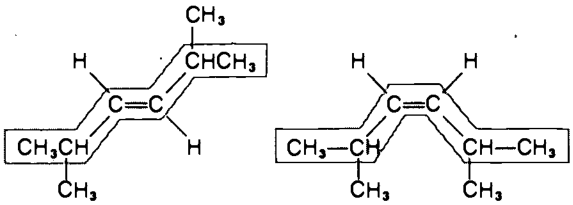

$$ClCH_2CH_2\underset{F}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2CH_3$$

ALKENES

Alkenes are named by defining the position of the double bond in that chain. For example, in $CH_3CH{=}CHCH_2CH_3$ the double bond is between carbons 2 and 3; the compound is named 2-pentene. Note that all alkene compounds end in *-ene*.

The name of $CH_3CH(CH_3)CH{=}CH(CH_3)CHCH_3$ is 2,5-dimethyl-3-hexene. Because there are two isomers of this compound, this is not its complete name.

2,5-DIMETHYL-3-HEXENE



If we look at the main chain of carbon atoms in the first isomer, we see that the chain branches off from the double bond in opposite directions and is known as a *trans-* ("across from") alkene. The complete name of this isomer is 2,5-

dimethyl-*trans*-3-hexene. In the second isomer, the main chain branches off from the double bond in the same direction and is known as a *cis*- ("same side") alkene. The complete name of this isomer is 2,5-dimethyl-*cis*-3-hexene.

ALCOHOLS

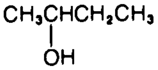
Compounds containing other functional groups are named in the same way. The hydroxyl, or alcohol, group is —OH. Compounds containing this group are known as *alcohols*. The presence of the —OH group is indicated by the ending *-ol* on the name of the compound. Thus, ethanol is an alcohol containing the "ethyl" group.

ETHYL	ETHANOL
$CH_3CH_2—$	CH_3CH_2OH

When there are four carbon atoms, the group is a butyl group. The alcohol is butanol.

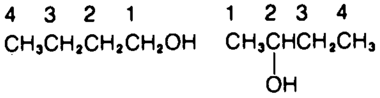
BUTYL	BUTANOL
$CH_3CH_2CH_2CH_2—$	$CH_3CH_2CH_2CH_2OH$

However, in this case there are two different substances possible. We can have the substance as shown previously and also an isomeric butanol



$$CH_3\underset{\mathrm{OH}}{\underset{|}{C}}HCH_2CH_3$$

We can name this compound simply by numbering the carbon atoms as we did before.

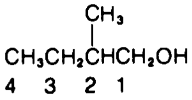


$$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2OH \qquad \overset{1}{C}H_3\underset{\mathrm{OH}}{\underset{|}{\overset{2}{C}}}H\overset{3}{C}H_2\overset{4}{C}H_3$$

In this way we obtain the names of 1-butanol and 2-butanol. (Is there a compound 3-butanol? Why not?)

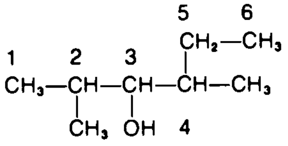
More complicated alcohols can be named by first identifying the alkyl group and then assigning the hydroxyl group a position. For example, note the following:

2-METHYL-1-BUTANOL



$$\overset{4}{C}H_3\overset{3}{C}H_2\overset{\mathrm{CH_3}}{\overset{|}{\overset{2}{C}}}H\overset{1}{C}H_2OH$$

2,4-DIMETHYL-3-HEXANOL



In the case of 2,4-dimethyl-3-hexanol, the name was obtained by first finding the longest chain of carbon atoms in the compound. In this case there are six carbon atoms; thus the compound is a derivative of hexane and is so indicated by "3-hexanol." Then the alkyl groups that are connected to the main chain must be identified; and in this case they are indicated by "dimethyl." After this is done, the alcohol is further identified by the position of its alkyl groups; in this case, the alkyl groups are in position 2 and 4 in the chain. Thus, the complete name for the alcohol is "2,4-dimethyl-3-hexanol."

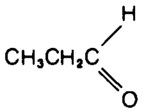
ETHERS

Ethers are derivatives of water, H—O—H, where the H's are replaced by alkyl groups. Ethers are named by identifying the groups on either side of the oxygen and then adding the names of these groups to the word ether. Thus, $CH_3—O—CH_2CH_3$ is methyl ethyl ether; $CH_3CH_2—O—CH_2CH_2CH_3$ is ethyl propyl ether; and $CH_3CH_2—O—CH_2CH_3$ is diethyl ether.

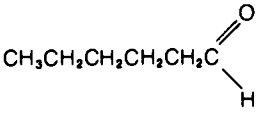
ALDEHYDES AND KETONES

Aldehyde functional groups must always come at the end of a chain. The compound names end in *-al*.

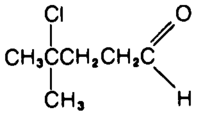
PROPANAL



HEXANAL



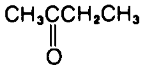
4-CHLORO-4-METHYLPENTANAL



Note that in the case of 4-chloro-4-methylpentanal the numbering *always* starts with the aldehyde group.

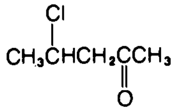
Ketones are named by the *-one* ending.

2-BUTANONE



$$CH_3\underset{\mathrm{O}}{\underset{\|}{C}}CH_2CH_3$$

4-CHLORO-2-PENTANONE



$$CH_3\overset{\mathrm{Cl}}{\overset{|}{C}}HCH_2\underset{\mathrm{O}}{\underset{\|}{C}}CH_3$$

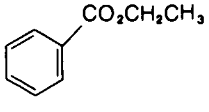
ACIDS AND ESTERS

The naming of acids follows from the names of the compounds from which they are derived. The acid group is $—CO_2H$. In naming acids we determine the name of the alkane, drop the *e* in the corresponding alkane, and add the ending *oic*, as in pentanoic acid.

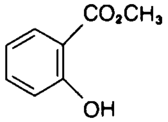
PENTANE	PENTANOIC ACID
$CH_3CH_2CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2CO_2H$

The naming of esters follows from the name of the acid. An ester is prepared from an alcohol and an acid, and it is named as such. We name the alcohol first, and then we name the acid, using the ending *-ate*, as in

ETHYL BENZOATE
(from ethyl alcohol and
benzoic acid)

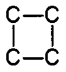


METHYL SALICYLATE
(from methyl alcohol and
salicylic acid)



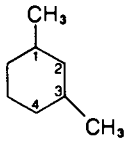
CYCLIC COMPOUNDS

When several carbon atoms are joined together they can be joined not only as a chain but also in the form of a ring. Thus, four carbon atoms may be connected as a chain, C—C—C—C, as in butane (C_4H_{10}), or as a ring

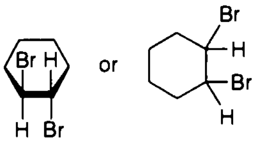


We would show this by using the prefix *cyclo-*. The name is *cyclo*butane (C_4H_8). The cyclic forms of pentane, hexane, and heptane are called *cyclo*pentane, *cyclo*hexane, and *cyclo*heptane, respectively. Because there is no end to a ring or circle, it is impossible to number the carbons by starting from one end of the chain with cyclic compounds; we simply start with the carbon to which a group is attached, give it the number 1, and then continue numbering around the ring. Of course, when there are two possible ways of numbering, we choose the way that gives us the lower set of numbers. For example,

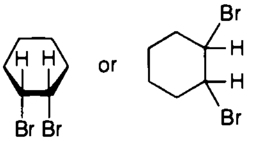
1,3-DIMETHYLCYCLOHEXANE



A ring compound differs from a chain compound not only because it is impossible to number the carbons by starting from one end of the chain but also because the ring compound generates a structure with a plane that has an upper and lower face. This means that there are more than one 1,2-dibromocyclohexanes. There is one compound in which both bromines are on the same side of the plane and one in which they are on the opposite side of the plane. The two compounds are *trans* 1,2-dibromocyclohexane

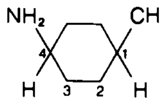


and *cis* 1,2-dibromocyclohexane.

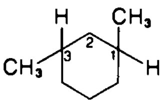


The *cis* is used here to mean "same side of the ring," and *trans* is used to mean "opposite side of the ring." For example,

cis-4-AMINOMETHYLCYCLOHEXANE

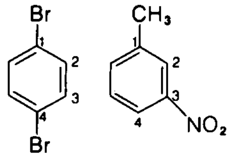


trans-1,3-DIMETHYLCYCLOHEXANE



BENZENE COMPOUNDS

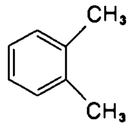
If numbers are used to indicate the position of groups, the nomenclature of the compounds of benzene follows the same general rule that we outlined earlier. For example, the compounds illustrated here could be named 1,4-dibromobenzene and 3-nitromethylbenzene.



It would be equally correct to name the second compound 3-methyl nitrobenzene, but 5-methylnitrobenzene would be an *incorrect* name since the number (position) of the methyl group is higher than necessary. It should be noted that because there is only *one* hydrogen at each carbon of the benzene ring, only *one* can be replaced. There can be only one group at each position.

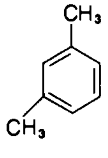
There is another way of naming benzene compounds that is used as often as the number system. This method makes use of the prefixes *ortho-*, *meta-*, and *para-*. In this system of nomenclature we start with *one* group connected to the benzene ring and see how close the other group is to it. This method of naming is used only with compounds of benzene in which *two* hydrogens in the benzene ring have been replaced with other groups—the so-called *disubstituted* benzenes. If the second group is on an adjacent carbon, it is called an *ortho*-compound.

ortho-DIMETHYLBENZENE

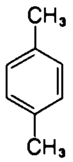


If the second group is on the second carbon atom away (either clockwise or counterclockwise around the ring), the compound is called *meta*-dimethylbenzene. If the second group is on the third carbon atom away (directly across the ring), it is called *para-*, as in *para*-dimethylbenzene. In writing out these names we use a shorthand *o-*, *m-*, and *p-*, to indicate *ortho-*, *meta-*, and *para-* in the compound name.

1,3-DIMETHYLBENZENE
(or *m*-DIMETHYLBENZENE)



1,4-DIMETHYLBENZENE
(or *p*-DIMETHYLBENZENE)



Of course, as the structures of compounds become more complex, systematic names become more and more complicated and inconvenient. In fact, for many complex materials we use the common names such as cholesterol and vitamin D_2 because they are far simpler to write and remember than systematic names. (see *Appendix III*).

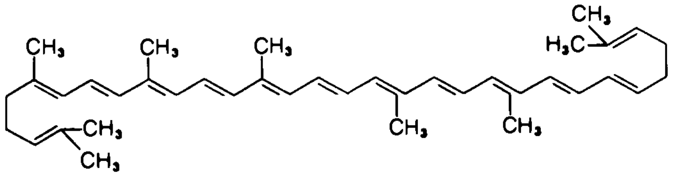
Appendix III: Interesting Molecular Structures

The following is a list of compounds and their molecular structures with recognizable names and/or uses. It is likely that you have heard about, read about, or have even made use of many of them in your daily life. Many are very simple compounds while others are exceedingly complex. As you study these compounds, look for the familiar structures that place them in each class or category. Also see if you can recognize any other familiar structures in their formulas that give the chemist a clue to their properties and reactivity.

HYDROCARBONS

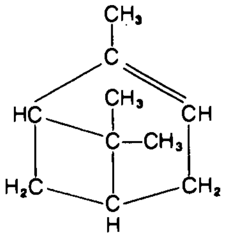
Lycopene, a naturally occurring hydrocarbon, gives tomatoes their characteristic red color. This substance, similar to β-carotene, is converted into vitamin A in the liver. Lycopene belongs to a group of plant hydrocarbons known as *terpenes,* the substances that give plants their characteristic colors and fragrances.

LYCOPENE



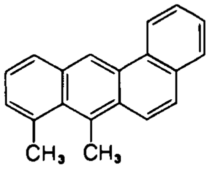
Another terpene found in nature is *α-pinene,* the principal hydrocarbon in turpentine. In its pure form, α-pinene is used as a solvent for coatings and wax formulas, as well as an additive for lubricating.

α-PINENE



5,10-Dimethyl-1,2-benzanthracene is the most potent carcinogenic (cancer-causing) hydrocarbon known. It has been synthesized from anthracene, an important component of coal tar. 5,10-Dimethyl-1,2-benzanthracene belongs to a class of hydrocarbons known as *polynuclear aromatic* compounds.

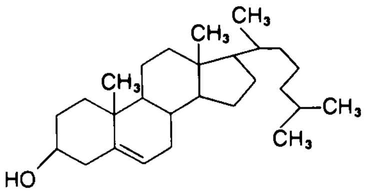
5,10-DIMETHYL-1,2-BENZANTHRACENE



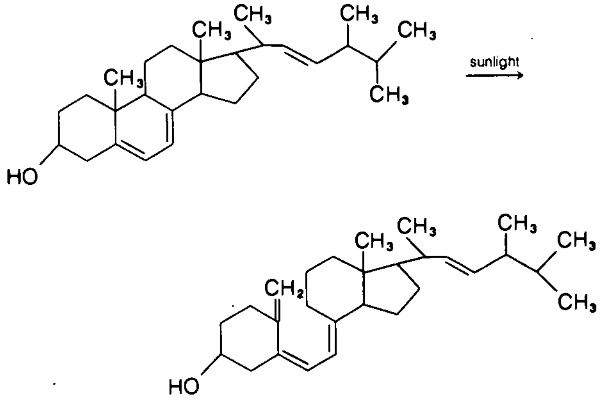
ALCOHOLS

Cholesterol, a special kind of alcohol called a *sterol,* is known to be the major constituent of gallstones, and has recently been gaining notoriety for its alleged connection to hardening of the arteries and other circulatory ailments. It is synthesized in the human body, and its true function is not yet known.

CHOLESTEROL

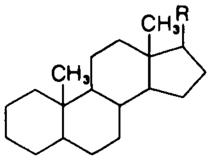


Another sterol of importance in human biology is *ergosterol.* When this substance is irradiated with sunlight—that is, ultraviolet light—it is transformed into vitamin D_2. When this vitamin is lacking, human beings develop what is known as *rickets,* which is the result of the improper deposit of calcium in the bones, causing them to become soft and weak.



Sterols such as cholesterol belong to a larger class of compounds known as *steroids:* compounds with the following general structure.

STEROID STRUCTURE



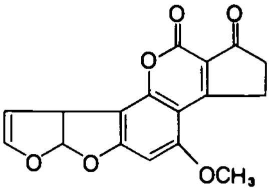
NATURALLY OCCURRING POISONS (TOXINS)

There are a number of substances found in nature that are extremely poisonous. One of the more familiar ones is sodium cyanide. Although not an organic poison, sodium cyanide is a useful basis of comparison in determining relative toxicities of other poisons that are organic. As you can see in the following table, organic poisons exhibit high levels of toxicity.

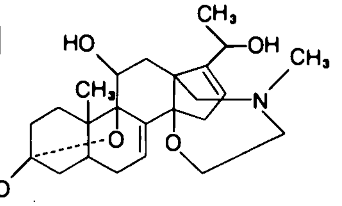
Toxic Substance	Natural Source	Relative Toxicity
Sodium cyanide (NaCN)	An inorganic salt	.1
Cobra venom	Cobra (snake)	500
Aflatoxin B	A fungus *(Asperquillos flavus)*	1000
Tetrodotoxin	Puffer fish California newt Frog (Costa Rica) Blue-ringed octopus	2500
Batrachotoxin A	Frog (South America)	50 000
Tetanus toxin	A bacterium *(Clostridium tetani)*	6 000 000
Botulinus toxin	A bacterium *(Clostridium botulinum)*	15 000 000

Three of the naturally occurring toxic compounds which appear in the table have the following highly complicated structures:

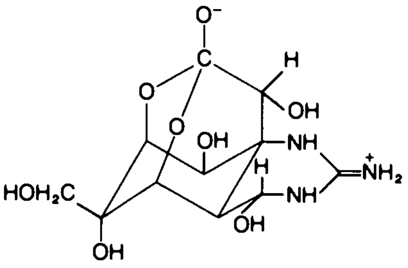
AFLATOXIN B



BATRACHOTOXIN A



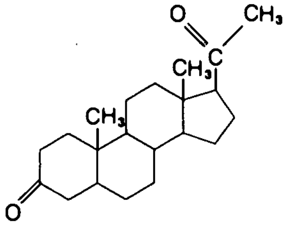
TETRODOTOXIN



KETONES

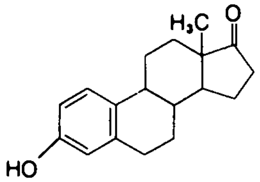
Steroids have many important functions in the body. One group of steroids regulates fertility in the human female. This group is the *estrogens*. *Progesterone* is the estrogen that prepares the uterus for implantation of the fertilized egg. As you will notice in the following structure, progesterone contains the carbonyl group. The suffix *-one* is added to designate this compound as a steroid with a ketone functional group.

PROGESTERONE



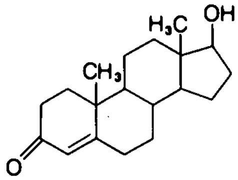
Another estrogen that contains a carbonyl group is *estrone*. Estrone, like progesterone, regulates fertility in females.

ESTRONE



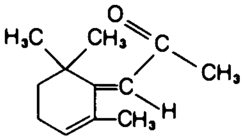
Androgens are male sex hormones, and one of the most important androgens is *testosterone*. Testosterone, like progesterone and estrone, is a steroid.

TESTOSTERONE

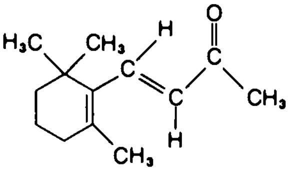


Two ketones far simpler than those so far discussed are *irone* and *ionone*. Irone is the odoriferous substance in violets. Ionone is a synthetic chemical used to produce the fragrance of violets in certain perfumes.

IRONE

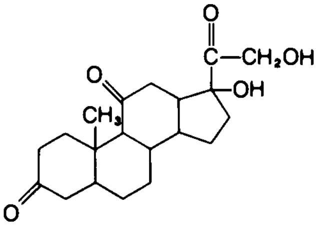


IONONE



Cortisone, the steroid which is used to treat arthritis and other inflammatory diseases, is a ketone with the following structure:

CORTISONE

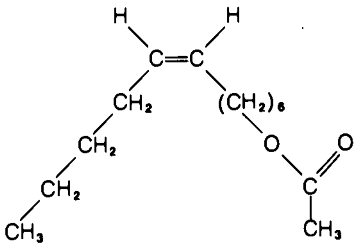


SEX ATTRACTANTS

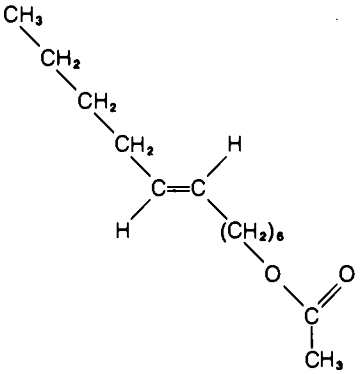
Dodec-7-enyl acetate is a compound that exists in *cis*- and *trans*-forms. Examples include the *trans*-isomer that attracts the false coddling moth and the *cis*-isomer that attracts the cabbage looper.

DODEC-7-ENYL ACETATE

cis-ISOMER



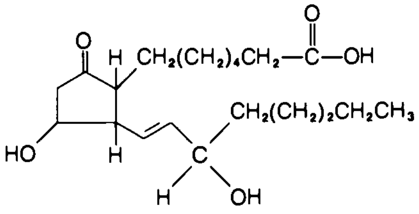
trans-ISOMER



ESTERS AND ACIDS

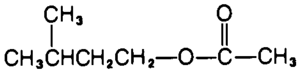
Another important group of hormones that functions in human reproductive physiology is the *prostaglandin* group. These compounds are lipid acids found in extremely minute quantities in a variety of body tissues and biological fluids. Research is now being carried out to develop these compounds as birth-control agents.

PROSTAGLANDIN E



Isopentyl acetate, an ester, is the "odor substance" in bananas.

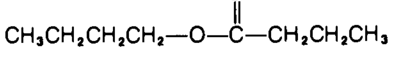
ISOPENTYL ACETATE



$$\mathrm{CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2CH_2{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3}$$

The ester *n-butyl butyrate* is the "odor substance" in pineapple.

n-BUTYL BUTYRATE

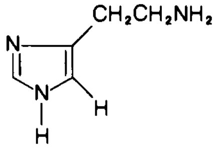


$$\mathrm{CH_3CH_2CH_2CH_2{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_2CH_2CH_3}$$

AMINES

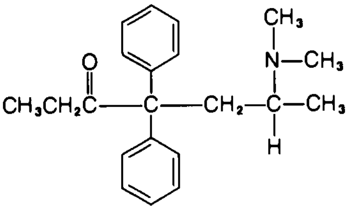
Histamine is one of the amines found in the human brain. The biological function of histamine is, for the most part, unknown. However, histamine is know to be one of the agents responsible for some unpleasant allergy symptoms: inflamed eyes, congested sinuses, and runny noses. When a person with hay fever comes into contact with ragweed pollen, for instance, certain cells in the body called *mast cells* release huge quantities of histamine. To relieve the symptoms of hay fever, antihistamine drugs are often used.

HISTAMINE



Methadone, a complex amine is a synthetic narcotic widely used for the treatment of heroin addiction.

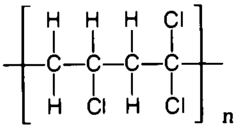
METHADONE



POLYMERS

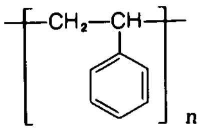
Saran, the familiar material we use to wrap foods, is a copolymer of vinyl chloride and vinylidene chloride ($CH_2{=}CCl_2$).

SARAN



Polystyrene is a versatile plastic used for electrical insulation, packing insulation for delicate instruments, and for manufacturing many kinds of plastic objects. Polystyrene may also be fabricated in the form of a rigid foam by whipping air into the semiliquid plastic. The product is the familiar "styrofoam," used to make thermo-cups for hot/cold drinks.

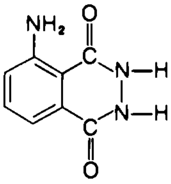
POLYSTYRENE



LUMINESCENCE

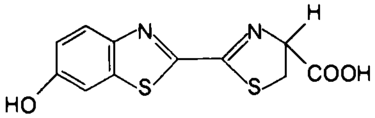
Luminol, the substance responsible for chemiluminescence, has the following structure:

LUMINOL



Luciferin is the substance fireflies manufacture to produce light.

LUCIFERIN

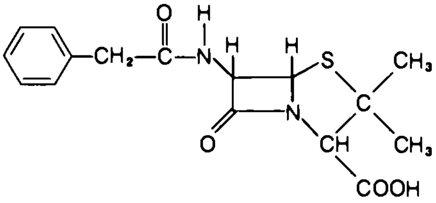


DRUGS

Antibiotics

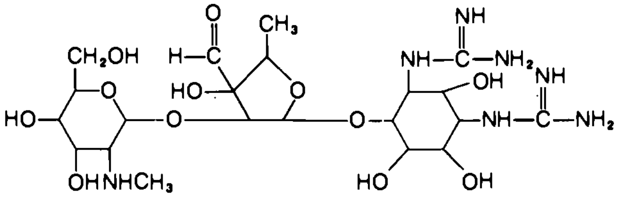
Penicillin G is the first and one of the most effective of the antibiotic drugs. Penicillin and many antibiotics are isolated from fungi, where they apparently serve as protection against bacteria.

PENICILLIN G



Streptomycin, a substance isolated from a soil microorganism, is a powerful antibiotic that has proved effective against tuberculosis and other infectious diseases.

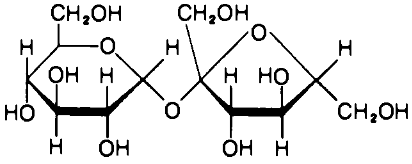
STREPTOMYCIN



MISCELLANEOUS

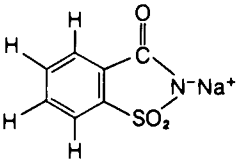
Sucrose, or natural sugar, is derived from sugar cane or sugar beet.

SUCROSE (NATURAL SUGAR)



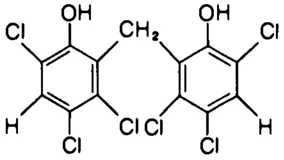
Saccharin is a synthetic compound used as an artificial sweetener. It is 700 times sweeter than sugar and leaves a slightly bitter aftertaste. Saccharin, however, is now under close scrutiny because it has been linked to cancer in mice.

SOLUBLE SACCHARIN



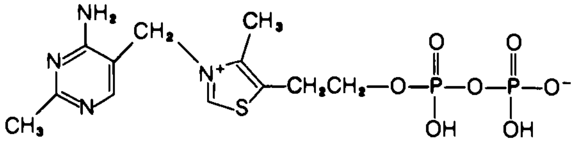
Hexachlorophene is a mild antiseptic used in soaps and deodorants. The government placed a partial ban on the use of this chemical when it was found to cause brain damage if used in large quantities.

HEXACHLOROPHENE



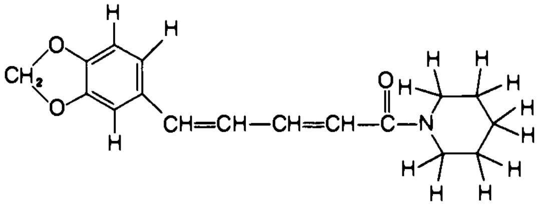
Vitamin B₁, also called *thiamine,* is a water soluble vitamin found in many foods. A deficiency of this vitamin in the diet produces the disease *beri-beri,* a condition characterized by poor growth, irritability, depression, and weakness.

VITAMIN B₁



Piperine is the alkaloid in black pepper responsible for the characteristic taste of this spice.

PIPERINE



Diallyl sulfide (allyl—from the Latin word for "garlic") is found in garlic. *Divinyl sulfide* is found in onions. These organosulfide compounds are responsible, in part, for the unmistakable taste and smell of these vegetables.

DIALLYL SULFIDE $(CH_2{=}CHCH_2)_2S$

DIVINYL SULFIDE $(CH_2{=}CH)_2S$

Allylisothiocyanate is the compound responsible for the sharp taste of mustard and horseradish.

ALLYLISOTHIOCYANATE

$H_2C{=}CHCH_2{-}N{=}C{=}S$

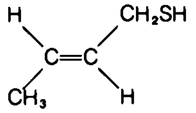
Thiols, commonly called *mercaptans,* have distinctive odors, and some occur naturally in animals and vegetables. Because of its odor, the compound *propyl mercaptan* (C_3H_7SH) is added to natural gas, which is odorless, to aid in the detection of pipeline leaks.

PROPYL MERCAPTAN

$CH_3CH_2CH_2{-}S{-}H$

The odor of skunks is due to the presence of the following organosulfur compounds:

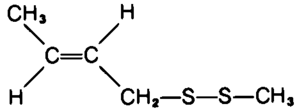
trans-2-BUTENE-1-THIOL



3-METHYL-1-BUTANETHIOL

$(CH_3)_2CHCH_2CH_2SH$

METHYL-1-*trans*-2-BUTENYL DISULFIDE



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One of America's leading science writers introduces the basics of organic chemistry in an easy to read style—ideal for the layman.

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In addition, discussion of new developments in chemistry relevant to the topics covered in this module will be found in *Chemistry, Journal of Chemical Education, Scientific American,* and *Science News Letter.*

Acknowledgments

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Index

TABLE OF INTERNATIONAL RELATIVE ATOMIC MASSES*

Element	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	227.0
Aluminum	Al	13	27.0
Americium	Am	95	(243)**
Antimony	Sb	51	121.8
Argon	Ar	18	39.9
Arsenic	As	33	74.9
Astatine	At	85	(210)
Barium	Ba	56	137.3
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01
Bismuth	Bi	83	209.0
Boron	B	5	10.8
Bromine	Br	35	79.9
Cadmium	Cd	48	112.4
Calcium	Ca	20	40.1
Californium	Cf	98	(251)
Carbon	C	6	12.0
Cerium	Ce	58	140.1
Cesium	Cs	55	132.9
Chlorine	Cl	17	35.5
Chromium	Cr	24	52.0
Cobalt	Co	27	58.9
Copper	Cu	29	63.5
Curium	Cm	96	(247)
Dysprosium	Dy	66	162.5
Einsteinium	Es	99	(254)
Erbium	Er	68	167.3
Europium	Eu	63	152.0
Fermium	Fm	100	(257)
Fluorine	F	9	19.0
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.3
Gallium	Ga	31	69.7
Germanium	Ge	32	72.6
Gold	Au	79	197.0
Hafnium	Hf	72	178.5
Helium	He	2	4.00
Holmium	Ho	67	164.9
Hydrogen	H	1	1.008
Indium	In	49	114.8
Iodine	I	53	126.9
Iridium	Ir	77	192.2
Iron	Fe	26	55.8
Krypton	Kr	36	83.8
Lanthanum	La	57	138.9
Lawrencium	Lr	103	(260)
Lead	Pb	82	207.2
Lithium	Li	3	6.94
Lutetium	Lu	71	175.0
Magnesium	Mg	12	24.3
Manganese	Mn	25	54.9
Mendelevium	Md	101	(258)
Mercury	Hg	80	200.6
Molybdenum	Mo	42	95.9
Neodymium	Nd	60	144.2
Neon	Ne	10	20.2
Neptunium	Np	93	237.0
Nickel	Ni	28	58.7
Niobium	Nb	41	92.9
Nitrogen	N	7	14.0
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	16.0
Palladium	Pd	46	106.4
Phosphorus	P	15	31.0
Platinum	Pt	78	195.1
Plutonium	Pu	94	(244)
Polonium	Po	84	(209)
Potassium	K	19	39.1
Praseodymium	Pr	59	140.9
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.0
Radium	Ra	88	226.0
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.9
Rubidium	Rb	37	85.5
Ruthenium	Ru	44	101.1
Samarium	Sm	62	150.4
Scandium	Sc	21	45.0
Selenium	Se	34	79.0
Silicon	Si	14	28.1
Silver	Ag	47	107.9
Sodium	Na	11	23.0
Strontium	Sr	38	87.6
Sulfur	S	16	32.1
Tantalum	Ta	73	180.9
Technetium	Tc	43	(97)
Tellurium	Te	52	127.6
Terbium	Tb	65	158.9
Thallium	Tl	81	204.4
Thorium	Th	90	232.0
Thulium	Tm	69	168.9
Tin	Sn	50	118.7
Titanium	Ti	22	47.9
Tungsten	W	74	183.8
Uranium	U	92	238.0
Vanadium	V	23	50.9
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.0
Yttrium	Y	39	88.9
Zinc	Zn	30	65.4
Zirconium	Zr	40	91.2

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*Based on International Union of Pure and Applied Chemistry (IUPAC) values (1975).

**Numbers in parentheses give the mass numbers of the most stable isotopes.

PERIODIC TABLE OF THE ELEMENTS

200.6 — atomic mass
Hg — symbol
Mercury — name
80 — atomic number

IA	IIA	IIIB	IVB	VB	VIB	VIIB	← VIIIB →			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1.008 **H** Hydrogen 1																	4.00 **He** Helium 2
6.94 **Li** Lithium 3	9.01 **Be** Beryllium 4											10.8 **B** Boron 5	12.0 **C** Carbon 6	14.0 **N** Nitrogen 7	16.0 **O** Oxygen 8	19.0 **F** Fluorine 9	20.2 **Ne** Neon 10
23.0 **Na** Sodium 11	24.3 **Mg** Magnesium 12											27.0 **Al** Aluminum 13	28.1 **Si** Silicon 14	31.0 **P** Phosphorus 15	32.1 **S** Sulfur 16	35.5 **Cl** Chlorine 17	39.9 **Ar** Argon 18
39.1 **K** Potassium 19	40.1 **Ca** Calcium 20	45.0 **Sc** Scandium 21	47.9 **Ti** Titanium 22	50.9 **V** Vanadium 23	52.0 **Cr** Chromium 24	54.9 **Mn** Manganese 25	55.8 **Fe** Iron 26	58.9 **Co** Cobalt 27	58.7 **Ni** Nickel 28	63.5 **Cu** Copper 29	65.4 **Zn** Zinc 30	69.7 **Ga** Gallium 31	72.6 **Ge** Germanium 32	74.9 **As** Arsenic 33	79.0 **Se** Selenium 34	79.9 **Br** Bromine 35	83.8 **Kr** Krypton 36
85.5 **Rb** Rubidium 37	87.6 **Sr** Strontium 38	88.9 **Y** Yttrium 39	91.2 **Zr** Zirconium 40	92.9 **Nb** Niobium 41	95.9 **Mo** Molybd'm 42	(97) **Tc** Technetium 43	101.1 **Ru** Ruthenium 44	102.9 **Rh** Rhodium 45	106.4 **Pd** Palladium 46	107.9 **Ag** Silver 47	112.4 **Cd** Cadmium 48	114.8 **In** Indium 49	118.7 **Sn** Tin 50	121.8 **Sb** Antimony 51	127.6 **Te** Tellurium 52	126.9 **I** Iodine 53	131.3 **Xe** Xenon 54
132.9 **Cs** Cesium 55	137.3 **Ba** Barium 56	138.9 **La*** Lanthanum 57	178.5 **Hf** Hafnium 72	180.9 **Ta** Tantalum 73	183.8 **W** Tungsten 74	186.2 **Re** Rhenium 75	190.2 **Os** Osmium 76	192.2 **Ir** Iridium 77	195.1 **Pt** Platinum 78	197.0 **Au** Gold 79	200.6 **Hg** Mercury 80	204.4 **Tl** Thallium 81	207.2 **Pb** Lead 82	209.0 **Bi** Bismuth 83	(209) **Po** Polonium 84	(210) **At** Astatine 85	(222) **Rn** Radon 86
(223) **Fr**† Francium 87	226.0 **Ra** Radium 88	(227) **Ac**** Actinium 89	‡ 104	‡ 105	‡ 106												

*	140.1 **Ce** Cerium 58	140.9 **Pr** Praseody'm 59	144.2 **Nd** Neodymium 60	(145) **Pm** Promethium 61	150.4 **Sm** Samarium 62	152.0 **Eu** Europium 63	157.3 **Gd** Gadolinium 64	158.9 **Tb** Terbium 65	162.5 **Dy** Dysprosium 66	164.9 **Ho** Holmium 67	167.3 **Er** Erbium 68	168.9 **Tm** Thulium 69	173.0 **Yb** Ytterbium 70	175.0 **Lu** Lutetium 71
**	232.0 **Th** Thorium 90	231.0 **Pa** Protactinium 91	238.0 **U** Uranium 92	237.0 **Np** Neptunium 93	(242) **Pu** Plutonium 94	(243) **Am** Americium 95	(245) **Cm** Curium 96	(245) **Bk** Berkelium 97	(251) **Cf** Californium 98	(254) **Es** Einsteinium 99	(254) **Fm** Fermium 100	(256) **Md** Mendel'm 101	(254) **No** Nobelium 102	(257) **Lr** Lawrencium 103

†The most stable known isotopes are shown in parentheses.

‡The discovery of elements 104, 105, and 106 has been claimed by both American and Soviet scientists. The Americans have suggested the name *rutherfordium* and *hahnium* for 104 and 105; the Soviets have suggested the names *kurchatovium* and *nielsbohrium* for these same elements. No name has yet been proposed for element 106.

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