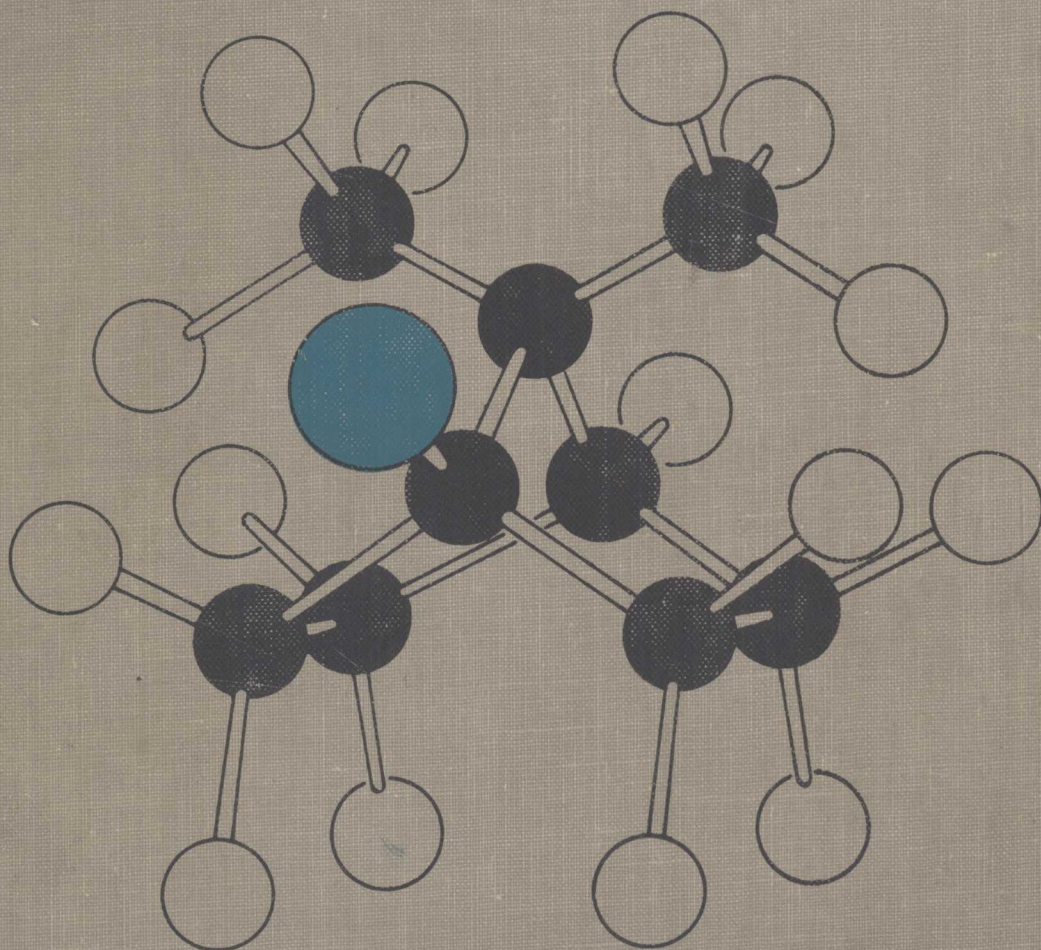


FOURTH EDITION

# PRINCIPLES OF Organic Chemistry

T. A. Geissman



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PRINCIPLES OF  
**Organic Chemistry**

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## Preface

This revision of *Principles of Organic Chemistry* is designed to meet what I believe are the changing needs of instruction in the modern one-year college or university course in organic chemistry. The last decade has seen some pronounced changes in the teaching of the subject. It was not long ago that many universities offered two kinds of courses: a rigorous two-semester or three-quarter course for students majoring in chemistry, and a less intensive and usually abbreviated course for students in the biological and medical sciences.

It is becoming increasingly apparent that the educational needs of students in the life sciences can no longer be met by the kind of organic chemistry courses that once fulfilled their curricular requirements. The growing sophistication of modern instruction in biology, with its emphasis upon the details of processes at the molecular level, requires a background in organic chemistry that consists of more than a descriptive presentation of the subject. A thorough understanding of the chemical events in biological systems now requires the student to pursue a course of study in organic chemistry that possesses much of the rigor of the traditional course for chemistry majors. That this is now recognized is shown by the increasing proportion of biology majors in regular one-year organic chemistry courses.

At the same time, students whose professional activities will lie within the area described as organic chemistry are faced with new developments and departures in the field. In recent years there have been many new and important developments in the chemistry of living organisms and of biologically active substances. Many of these are the products of the research of organic chemists, most of whom have been led by their work into realms that are as much biological chemistry as organic chemistry. Indeed, such terms as "bioorganic chemistry" and "molecular biology" are applied to fields of study in which expertise in both chemistry and biology is essential.

These considerations have led to this revision, in which the biological aspects of organic chemistry and the organic chemistry of biological transformations have been combined in a textbook that, it is hoped, will serve the educational needs of students of both biological and physical sciences. Although distinctions can be seen between the extremes of these, there can be no doubt that the middle ground is expanding, and that what was once a discrete interface between biological and organic chemistry is rapidly losing its definition.

This book is nevertheless a textbook of organic, not "bio-organic," chemistry. It presents the subject as a blend of theory and experimental observation, describing organic reactions as expressions of the properties and characteristic behavior of functional groups. But such general concepts as the making and breaking of chemical bonds, the theory of acid-base reactions, stereochemical relationships, the recognition of the reactive sites of organic compounds, and so on are as much within the province of biochemistry as of organic chemistry; and many of the principles of organic chemical reactivity can be illustrated by examples drawn from the realm of biological chemistry as well as—and often better than—by the more abstract examples drawn from classical organic chemistry.

The use and interpretation of physical data are again emphasized. The widespread use of modern spectroscopic instrumentation in undergraduate laboratories requires that the beginning student be instructed in the principles and practice of ultraviolet, infrared, nuclear magnetic resonance, and mass spectrometry. These techniques are discussed in their own chapters, but frequent references are made throughout the text to such physical data as they reflect and explain chemical properties and reactivity.

The application of chemical and physical evidence and degradative and synthetic procedures to the determination of the structures of organic compounds is presented in a separate chapter. This is the last chapter in the book because the structural study of even a simple compound usually requires the chemist to bring to bear knowledge of many aspects of physical and chemical properties. The instructor may wish to use this chapter by assigning for study those separate examples that are especially relevant to one or another of the earlier chapters. For example, the chemistry of the simple terpenes, ocimene and myrcene, could be studied in connection with the chemistry of olefinic compounds; of shikimic acid with carbohydrates; and of nicotine with amines or heterocyclic compounds. It did not seem advisable to make these associations

in the text, for no one of the compounds described represents solely one class of functionality.

This revision has not been greatly expanded in size, for it is not intended to be encyclopedic or even to cover everything that the graduate in chemistry is expected to know about organic chemistry. Certain theoretical topics are dealt with briefly or omitted, chiefly because the chemistry major will encounter them in further courses for which this one-year course serves as a foundation and prerequisite; the student of the life sciences will find more valuable those topics that have been added. Moreover, students should be encouraged to do additional reading, and there are available for this purpose reference works, excellent monographic paperbacks, and the limitless literature of the periodical journals.

Finally, a word about the content and organization of this book. Although it is generally agreed that the presentation of a subject should proceed in a progressive and cumulative manner, so that topics discussed early in the book provide a basis for a rational development, there are certain topics so essential to the understanding of organic chemistry that they must be introduced even before the student has the background to master them fully. Three such topics are stereochemistry, the concepts of which pervade the entire field; the energy relationships embodied in reaction rate and equilibrium; and "resonance," or charge delocalization. It will be obvious to the teacher of organic chemistry that to introduce these at an early point requires the use of specific examples of compound classes that the student may not find familiar. There is, however, no reason why these earlier chapters cannot be referred to when their content is again relevant. In the same way, it is seldom possible to discuss a compound class in isolation from others. For example, the preparation of olefins necessarily involves a discussion of alcohols; esters and saponification could be introduced either along with the chemistry of alcohols or later, with carboxylic acids. The choice of the sequence of topics is entirely by the preference of the author, but it is not ineluctable. If the user of the book prefers to present the chemistry of alcohols before that of olefins, there is no reason why chapter study assignments cannot be altered. A later chapter is not necessarily more complex or difficult of comprehension than an early one.

For these reasons there is necessarily—and advisedly—some duplication to be found throughout the text. The student studying a given chapter cannot be expected to recall everything contained in the chapters preceding it, and a recapitulation of a topic or the rewriting of a structural formula will be both an aid to the student's understanding and a concession to his natural reluctance to interrupt his thoughts to search the Index or an earlier chapter to refresh his memory.

On the other hand, in some of the textual material and in some of the Problems and Exercises compounds are given by name only. In certain cases the formulas for these compounds are not to be found in the chapter or section where the names appear, or even not in the book at all. This is done purposely: it is hoped that it will encourage the student to have frequent recourse to the library and to become familiar with the

reference books (and eventually with the monographic and periodical literature) that are there for him to use.

There are three reference works that are unexcelled for ready information about names, structures, and properties of organic compounds, and that will be found in most chemistry libraries:

*Dictionary of Organic Compounds*, 4th edition. Edited by I. Heilbron. Oxford University Press, New York. 1963.

*Chemistry of Carbon Compounds*, 2nd edition. Edited by E. H. Rodd and S. Coffey. Elsevier, New York. 1964, continuing.

*Merck Index*, 8th edition. Merck & Company, Rahway, New Jersey. 1968.

Answers to selected problems are provided in an appendix.

Los Angeles, California

1 March 1976

T. A. Geissman



PRINCIPLES OF  
**Organic Chemistry**



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## **Introduction.**

### **Characteristics of organic compounds**

It is well for a student of any organized discipline of learning to become aware of its origins and its evolution into modern form, for this will enlarge his perspective and permit him to appreciate the facts and theories he encounters in his study as the end products of decades or even centuries of inquiry and debate.

Organic chemistry is an experimental science: its theories have grown out of experimental observations and have been tested and verified by experimental means. It is not an empirical science but it is in large measure a pragmatic one, and resorts finally to the observed behavior of discrete substances. For this reason, this chapter dwells at some length upon the general properties of organic compounds, upon the ways in which they are purified and analyzed, and upon the early stages of their experimental manipulation.

Sections 1-12 and following deal with the specific analytical procedures that are universally employed by organic chemists. These basic procedures have in recent times been augmented by sophisticated methods of physical measurement, but they have not been superseded by modern instrumentation. The student is urged to cultivate an attitude of recognition that he is always dealing with actual substances, and that their physical properties and elementary composition are not simply pieces of numerical data, but represent information that is fundamental to the development of his understanding of their chemical behavior.

## 1-1 What is organic chemistry?

With the rapid growth of the science of chemistry in the past half-century has come its separation into a number of special areas: physical chemistry, analytical chemistry, biological chemistry, organic chemistry, and others. These areas are not mutually exclusive, for each permeates the others; yet each is characterized by the emphasis that is placed upon it, by some special approach in the techniques utilized, or by the kinds of compounds that are dealt with. *Organic chemistry* deals with the chemical compounds of carbon, and principally with compounds in which carbon is combined with hydrogen, oxygen, nitrogen, sulfur, and the halogens. It is a special area of chemistry because of the enormous number of carbon compounds—over a million are known, and the number is increasing at the rate of about five percent per year. More than ninety percent of these are synthetic substances, the remainder having been isolated from living organisms (animals, plants, fungi, microorganisms) and their fossil remains (coal, petroleum).

The *naturally occurring* organic compounds are of concern to the biochemist as well as to the organic chemist, and indeed it is in dealing with such substances that biochemistry and organic chemistry come together and lose their individual identity. The naturally occurring compounds include the proteins, fats, carbohydrates, vitamins, and hormones that compose living cells; many of the drugs used to control disease and relieve suffering; the perfumes and colors of the plant world; and thousands of other substances that participate in the metabolic activities of living things.

The *synthetic* organic compounds are derived largely from natural sources of carbon—coal and petroleum—but are the products of man's voluntary ingenuity rather than of the involuntary activities of living organisms. There is no limit to the number of organic compounds that can be made, and indeed the known synthetic compounds include many naturally occurring compounds that have been prepared synthetically as final confirmation of their structures. The only *kinds* of compounds that have so far resisted the attack of the synthetic organic chemist are the complex carbohydrates, the nucleic acids, and the complex combinations of these that make up the essential stuff of the living cell. Although the complete synthesis of only a few substances identical in structure and function with these natural materials has been accomplished, further achievement will surely come in time. It is to the new generations of scientists who will pursue these goals that this book is addressed, in the hope that it will help to impart that basic understanding of the scientific principles of organic chemistry that must underlie future progress in both chemistry and biology.

## 1-2 The development of organic chemistry

The scientific revolution of the sixteenth and seventeenth centuries was characterized by the birth of a spirit of inquiry and skepticism that marked a new phase of the

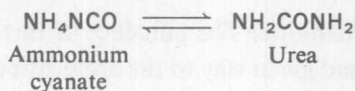


intellectual development of mankind. The influence of this spirit upon chemistry was felt at a time when alchemy had given way to the application of chemistry to medicine, and the dominance of an earlier mysticism was crumbling. The new approach to chemistry was the experimental attack, and through its chief proponent, Robert Boyle (1627–1691), this new philosophy gave to chemistry the status of an independent science. The chemists of the seventeenth and eighteenth centuries soon began the task of systematizing the growing body of empirical facts that their experiments revealed, and began to create generalizations into which numbers of facts could be grouped. The early theories and much of the work devoted to their study did a great deal to define the area of intellectual activity that is the science of chemistry, and thus to attract to these new studies the attention of men of an inquiring turn of mind.

Toward the end of the eighteenth century chemists began to turn to the examination of living organisms, and a great many compounds were isolated from plant and animal sources. Plants had been used in medicine since ancient times, and enlargement of interest in chemistry led in the first years of the nineteenth century to the study of plants of medicinal importance and to the isolation in crystalline form of such complex substances as strychnine ( $C_{21}H_{22}O_2N_2$ ), quinine ( $C_{20}H_{24}O_2N_2$ ), and morphine ( $C_{17}H_{19}O_3N$ ), the structures of which were to remain unknown for another hundred years.

A bar to progress during these early stages of what was known as “organic” chemistry was the persistent belief that compounds formed in living organisms had properties, and owed their formation to laws, that set them apart from compounds of inanimate origins. This doctrine of a *vital force* persisted through the first quarter of the nineteenth century. It can be readily understood how such a belief could prevent the development of a rational theory. It could not, however, prevent the progress of experimental studies, and important developments took place, starting with Lavoisier’s (1743–1794) recognition of the fact that organic compounds could be burned, and that by weighing the products of the combustion accurately it was possible to determine the *composition* of a compound. Lavoisier had at his disposal only a limited number of compounds, most of them from vegetable sources, so his experiments led him to believe that organic compounds were composed of carbon, hydrogen, and oxygen. His contemporaries and followers soon discovered the presence of nitrogen, sulfur, and phosphorus in organic compounds of animal origin, yet before long it was realized that there is no sharp distinction between organic substances that is based upon their origin. The importance of Lavoisier’s contribution was that it introduced the *quantitative* element into the study of chemistry, and it so influenced further development of the subject that his work marks a real chemical revolution and can be regarded as the beginning of the modern science.

An important early discovery was that of Wöhler (1800–1882), who in 1828 found that urea, an organic substance that derives its name from urine, in which it is found, could be prepared by heating the “inorganic” compound ammonium cyanate:



Wöhler's discovery did not immediately demolish vitalism, but the disintegration of that enervating doctrine continued from that time on, with the increasing number of syntheses of other organic compounds from inorganic materials.

### 1-3 The introduction of analytical methods

Developed chiefly by Gay-Lussac (1778–1850) and Liebig (1803–1873), quantitative analysis of organic compounds by combustion became a powerful tool for the discovery of many new facts. By 1830, improvements in the methods of determining the carbon and hydrogen content of organic compounds, as well as the analytical method for nitrogen (Dumas, 1800–1884), had made it possible to ascertain the composition of these substances with a high degree of accuracy. From then on, the development of organic chemistry proceeded with amazing rapidity. In less than fifty years thousands of new compounds were discovered and synthesized; an enormous chemical industry developed in Europe; and there evolved a valid structural theory, which survives to the present day.

Thus we have seen how the scientific revolution of the seventeenth century set mankind on the road of free inquiry; how Lavoisier's chemical revolution a century later established the importance of accurate quantitative observations; and how, another century later, chemistry was at last firmly based on experimental method and the beginnings of theory. The stage was now set for the twentieth-century discoveries on the nature of atoms and molecules and the forces that bind them together, and for the growth of the modern theories of organic chemistry around which this book is constructed.

### 1-4 Isomerism and the concept of structure

One of the most important discoveries that resulted from the development of accurate quantitative analysis of organic compounds was that it is possible for two or more compounds to have identical chemical *composition*, yet to be quite different in their chemical and physical properties. Liebig found that both silver cyanate and silver fulminate, two quite distinct substances, have the composition  $\text{AgCNO}$ . Wöhler observed that both ammonium cyanate and urea were represented by the formula  $\text{CH}_4\text{N}_2\text{O}$ , and in 1828 he discovered that ammonium cyanate could be converted into urea simply by heating it. Up to this time it had been regarded as self-evident that substances of the same composition were identical. The observations of Liebig and Wöhler were soon followed by others, and the Swedish chemist Berzelius (1779–1848)

proposed the term *isomerism* for the relationship between two substances with different properties but identical composition. Since then these criteria have been refined by the concept of molecular weight, so that we now define isomers as *compounds having different properties but identical molecular formulas*.

The recognition of isomerism was the first step toward the solution of the problem of the molecular structure of organic compounds. Berzelius recognized that isomerism could be explained only by supposing that the relative positions of the atoms in isomeric compounds must be different. The *fact* of difference—the experimental observations of composition and chemical behavior—led to the question of the *reason* for the difference, and thus the concept of isomerism has within it the concept of structure.

### 1-5 Molecular and structural formulas

It will be seen that the molecular formula of a compound does not define either its chemical properties or the class to which it belongs. As simple a molecular formula as  $C_2H_6O$  represents two quite different compounds: ethyl alcohol ( $C_2H_5OH$ ) and dimethyl ether ( $CH_3OCH_3$ ). Three quite different compounds are represented by  $C_3H_8O$ , and  $C_4H_{10}O$  is the molecular formula for seven compounds.

It is evident that even though carbon, hydrogen, and oxygen atoms possess definite and invariable combining powers, there can be more than one way in which a certain number of these atoms can be joined together; but there cannot be an unlimited number of ways. There exists, for example, only one compound  $CH_4O$ , only one  $C_2H_6$ , one  $CH_2O$ , one  $C_2H_2O_2$ , and one  $C_2H_2O_4$ . But as the number of carbon atoms increases, the number of isomers increases rapidly, as the examples in the preceding paragraph have shown.

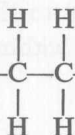
The problem that confronted the chemists of Liebig's time was to express the constitution of organic compounds in terms of their internal nature and to devise formulas that not only clearly distinguished isomers but suggested the chemical differences between them. One of the earliest observations contributing to the solution of this problem was made in 1832 by Liebig and Wöhler, who showed that there exist certain groups of atoms that behave as unchanging units when passing through a series of chemical transformations. The compound benzaldehyde,  $C_7H_6O$ , was converted to benzoic acid,  $C_7H_6O_2$ , and this in turn was transformed into benzoyl chloride,  $C_7H_5OCl$ , benzamide,  $C_7H_7ON$ , and methyl benzoate,  $C_8H_8O_2$ . All of these compounds can be regarded as consisting of the group of atoms  $C_7H_5O$ , called the benzoyl group, in combination with H, OH, Cl,  $NH_2$ , or  $CH_3O$  in the compounds mentioned. Gay-Lussac had observed earlier that the cyanogen group could appear in the compounds HCN,  $(CN)_2$ , BrCN, ClCN, and so on.

The discoveries and theories of the next twenty-five years culminated in 1858 with the publication by Kekulé (1829–1896), and independently by Couper (1831–1892), of

a structure theory that for the first time represented the individual atoms in organic compounds and showed how they were joined. Kekulé proposed that the "combining power" of the elements was fixed, and that carbon had four, nitrogen had three, oxygen had two, and hydrogen had one combining unit (or, as we would say, a *valence*

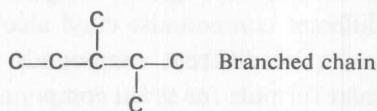
of four, three, two, and one). Thus methane,  $\text{CH}_4$ , could be represented by  $\text{H}-\text{C}-\text{H}$ ,  
 $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H} \end{array}$

ethane by  $\text{H}-\text{C}-\text{C}-\text{H}$ , and carbon *chains* could be constructed by linking together

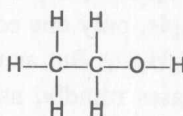


carbon atoms and filling with other atoms or groups the remaining combining capacities of the carbon atoms.

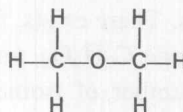
$\text{C}-\text{C}-\text{C}-\text{C}-\text{C}$  "Straight" or unbranched chain



We can now represent ethyl alcohol and dimethyl ether, both  $\text{C}_2\text{H}_6\text{O}$ , in a way that clearly shows the difference between them:



$\text{CH}_3\text{CH}_2\text{OH}$   
Ethanol  
(ethyl alcohol)



$\text{CH}_3\text{OCH}_3$   
Dimethyl ether

These formulas are *structural formulas*. Those in which all the bonds are shown are *graphic structural formulas*; the others (for example,  $\text{CH}_3\text{CH}_2\text{OH}$ ) are *condensed structural formulas*. Note that in both of the above structural formulas the *group* of

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### Exercise 1

Write graphic structural formulas for the three isomeric compounds  $\text{C}_3\text{H}_8\text{O}$ .

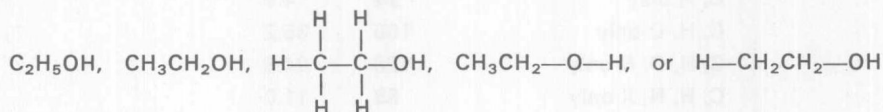
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atoms  $\text{CH}_3-$  appears. This is called the *methyl group*. The word *group* denotes a structural entity only; it is not a substance, but a component part of a substance.

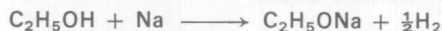


The short lines that join the atoms together in the graphic formulas are symbols for the *bonds* between the atoms. We speak of the carbon-carbon bond, the carbon-hydrogen bond, and the oxygen-hydrogen bond, and often abbreviate these by the terms C—C bond, C—H bond, and O—H bond.

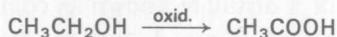
It is important to recognize that structural formulas are only conventional symbols for molecules. Ethanol is one compound, whether it be written



Each way of writing the formula for a given compound may have particular advantages in describing one or more aspect of its behavior. For example, if we wished to depict the reaction of ethanol with sodium, we might write



On the other hand its oxidation to acetic acid, in which the methyl group remains unchanged, could be written



to show the kind of change that takes place. As we grow more familiar with ways of writing structural formulas we shall feel at ease even with symbols such as Me for  $\text{CH}_3-$  (methyl), *n*-Pr for  $\text{CH}_3\text{CH}_2\text{CH}_2-$  (normal-propyl), and others.

## 1-6 The nature of organic compounds

Let us examine a list of 6,500 organic compounds that was compiled for a well-known chemical handbook. Of these, only about 70 (1%) contain no hydrogen, and most of these are derived from hydrogen-containing compounds by the replacement of hydrogen by halogen atoms. Of those compounds that contain six carbon atoms only, we find the distribution listed in Table 1-1. While this table represents an arbitrary sample that includes only a small percentage of all of the known six-carbon-atom compounds, it does show that the preponderance of organic compounds contain hydrogen, and that the bulk of these also contain oxygen or nitrogen.

Everyday experience has made us familiar with other characteristics of many organic compounds. The burning of wood, paper, coal, and petroleum is evidence of the susceptibility of organic substances to oxidation. The end products of such oxidations are carbon dioxide (the ultimate oxidation state of carbon), water, and other oxides or their corresponding elements. The charring of paper, the caramelization of sugar, and the roasting of foodstuffs show us that heat can change and decompose organic substances. Extreme temperatures cause *pyrolysis*, in which extensive decomposition