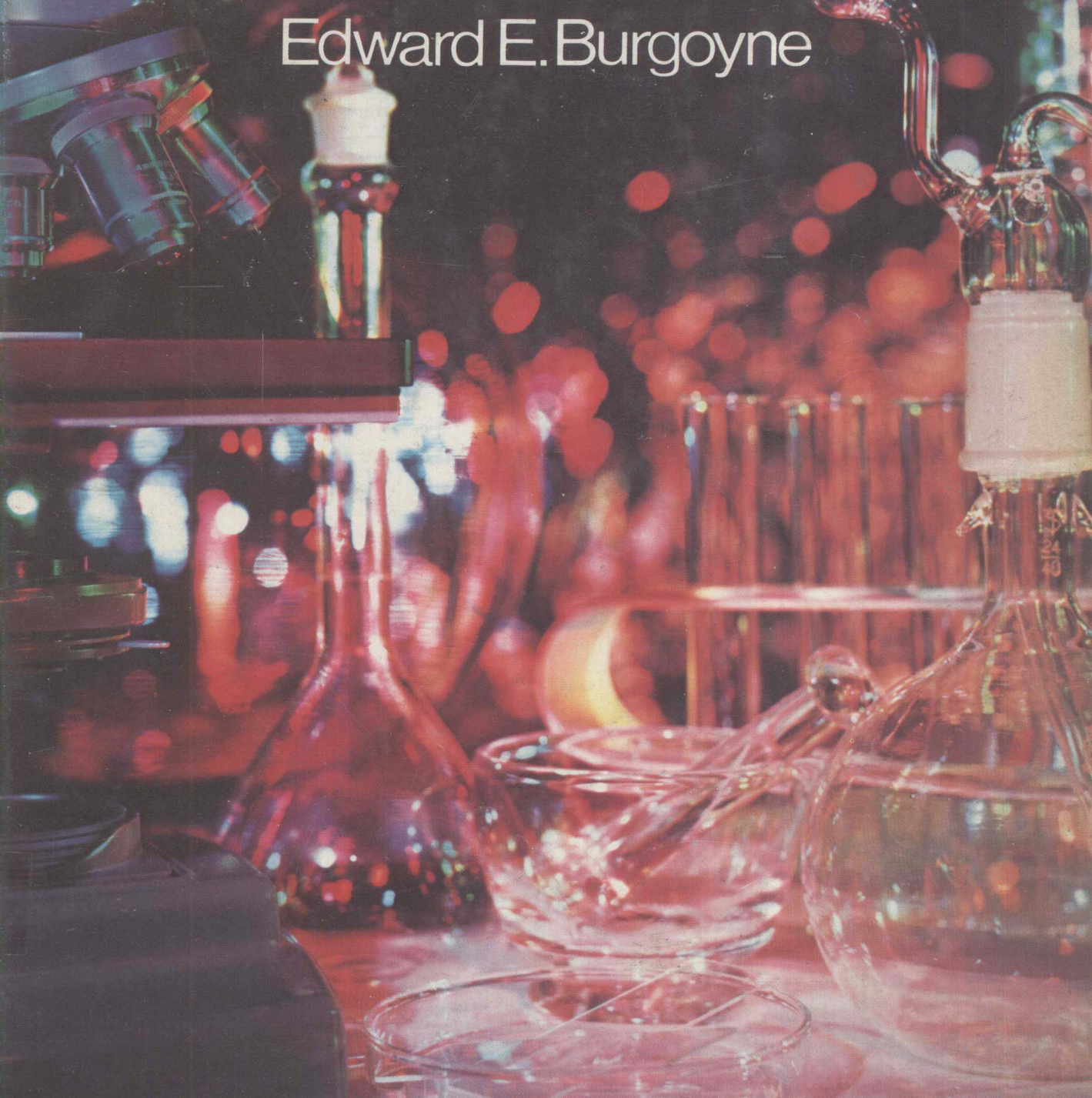


# A SHORT COURSE IN ORGANIC CHEMISTRY

Edward E. Burgoyne



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**EDWARD E. BURGOYNE**, Professor of Chemistry, Arizona State University

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## PREFACE

This text has been written for a one-semester or a one-quarter course to introduce students of nursing, biology, agriculture, forestry, and home economics to the principles of structure and reactions in organic chemistry and to the properties of organic compounds related to the various fields of study and life in general. At least a semester of general chemistry is assumed to have been previously completed; in it the principles of atomic and molecular theory, bonding, the periodic table, states of matter, solutions, acids and bases, and ionic equilibrium will have been studied. Some of those subjects are reviewed briefly in Chapter 1, but the discussion there is not adequate for an initial presentation.

The principles of structure and isomerism of molecules, functional groups, and nomenclature are introduced in Chapter 2. That should be considered only an introduction, and the student should not be expected to fully master those subjects at this time. The principles of Chapter 2 will be expanded, with learning in detail expected, as the chapters on the various functional groups are considered. The subject of organic chemistry cannot be arranged in one unique order of topics that can be followed as in going through a tunnel. The subject matter spreads out more like the surface of a sphere and has many related reactions and ideas. One could begin the study at several different places in the body of knowledge and spread out from there. One successful textbook used in the past began with the alcohols rather than with the alkanes. Since even the reactions and the preparation of the alkanes and alkenes cannot be discussed without some reference to alkyl halides and alcohols, it is useful to begin with a little knowledge of functional groups and nomenclature.

A brief introduction to the use of spectra is included in Chapter 2. It is intended to make the student aware of the use of spectra in analysis and structure determination, and not to make him or her proficient in using them. Some instructors will wish to omit the material altogether; others may wish to supplement it.

Although covering such a large field in one semester requires brevity, the presentation must be modern, as comprehensive as the fields of the students require, and as rational and palatable as possible within such a framework. Consequently, the simpler concepts of molecular orbitals,

resonance, stereoisomerism, and reaction mechanisms are included. My experience has been that students can master those concepts and that they do appreciate them as an aid in understanding the diverse properties and reactions of organic compounds rather than relying entirely on rote memorization of a mass of descriptive organic chemistry. Each instructor will make a decision as to depth of understanding and retention he or she will require for the reaction mechanisms given. In a course of this type, however, the chief value of the mechanisms is to facilitate understanding and learning of the important reactions; the mechanisms themselves have little importance to the students.

Some synthetic reactions are given not only as examples of reactions of organic compounds but also as a way of giving the student an appreciation of the sources of materials. Synthetic chemistry is involved in some of the problems as a drill to familiarize the student with important compounds, reactions, and concepts. However, the major emphasis is not on synthesis; it is on an understanding of properties through study of structure and reactions.

The chapters on fats, carbohydrates, proteins, enzymes, and metabolism apply the principles of organic chemistry to the more complicated compounds involved in biochemical reactions. In order for the contents to be covered in one semester, this introduction to biochemistry is necessarily brief. Some students will want to take an additional semester course in elementary biochemistry.

I am grateful to the following persons for their helpful comments upon reading the manuscript: Professor David L. Adams, North Shore Community College; Professor Jon Michael Bellama, University of Maryland; Professor Jack E. Leonard, Texas A&M University; Professor Lawrence T. Scott, University of Nevada at Reno; Professor Walter S. Trahanovsky, Iowa State University. I acknowledge with gratitude my colleagues at Arizona State University who read portions of the original manuscript and offered suggestions and encouragement. They are: Professor William J. Burke, Professor Wayne W. Luchsinger, and Professor Tom R. Thomson. I thank my son Edward R. Burgoyne for taking and finishing the photos of the molecular models from which the drawings were made. I wish to thank Sue Barnes for helping to develop this manuscript and Libby Forsyth for selecting the photographs.

Edward E. Burgoyne

## TO THE STUDENT

Organic chemistry has become a very complex, highly organized, and structured science, and reading a textbook or lecture notes over and over is not a very efficient method for learning it. Like physics and calculus, it can be learned thoroughly and in depth only by working problems. Before each lecture you should rapidly read the corresponding textual material as an introduction and to learn where the topics are discussed, so that you can later look the topics up again and consider them more carefully as you attempt the problems. Following the lecture, you should work out as many of the problems in the chapter and at the end of the chapter as you can. The work will go slowly at first because you will probably find it necessary to go back and consult the textual material and your lecture notes. Gradually, however, as your expertise increases, the work will go faster, and effective problem-oriented learning will take place.

There is emphasis on application of principles as well as mere understanding. How well would a football team play if it had heard the coach lecture on the plays in the locker room but had never tried the plays in scrimmage? How can a student demonstrate a knowledge of organic chemistry in the laboratory or on an examination if he or she has done nothing more than attend lectures and read the text? *About two-thirds of your study time should be devoted to working problems*, whether they are specifically assigned or not. You will find that working the problems can be interesting and fun. You will have a feeling of accomplishment when the problems are completed. Working on the problems with one or two other students may be mutually stimulating, and may make the task more interesting and efficient. But remember that although the old idea that two heads may be better than one has some merit, each of you should pull your own load.

Edward E. Burgoyne

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# INTRODUCTION TO ORGANIC CHEMISTRY

At about the time when the American colonists were declaring and fighting for their independence from England, chemistry was developing in Europe. *Chemistry* may be defined as the science that deals with the composition, structure, and properties of matter not only as matter may now exist but also as matter may change with respect to those aspects of its nature. *Organic chemistry* is the chemistry of the compounds of carbon. It is one of the most important branches of chemistry. Since carbon constitutes by weight less than 0.1% of the crust of the earth, it may seem strange that its compounds are so important. However, all things that are living, or that have lived, contain the element carbon. Carbohydrates, fats, and proteins are carbon compounds. An atom of carbon, because of its unique electronic arrangement, has the ability to unite with other atoms of carbon to form chains and rings of carbon atoms of great diversity. The number of known compounds of carbon (now about 3 to 4 million) is greater than the number of compounds of all of the rest of the elements put together. We shall find that carbon compounds are important in almost every phase of our existence.

Why the name  
“organic chemistry”?

We might now ask why the chemistry of the compounds of carbon is called organic chemistry. Berzelius first used the term *organic* in 1808 to apply to all compounds occurring in, or deriving from, living organisms or their remains. That was in accord with the vital force theory, which held that a living, or vital, force was essential to the production of all such compounds. The theory was discredited and finally overthrown. In 1828 Wöhler produced urea (a component of urine) by heating ammonium cyanate, and in 1845 Kolbe synthesized a derivative of acetic acid (a component of vinegar) from inorganic or nonliving source materials. In 1848 Gmelin noted that the only essential difference between organic and inorganic compounds is that organic compounds always contain carbon. Today, although our major sources of organic compounds are still the fossil remains of living things in the form of petroleum and coal, we have the knowledge and technology to produce a great many organic com-

pounds from simple carbon molecules and ions considered a part of the nonliving or inorganic world.

How organic chemistry has developed

Some organic compounds were actually prepared and studied when the science of chemistry was just beginning. In about 1776 the Swedish apothecary, Scheele (who discovered oxygen independently of Priestley), prepared oxalic acid by the action of nitric acid on sugar. Since oxalic acid had previously been isolated from rhubarb, his was an early example of conversion of one organic compound into another. The complexity and challenge of organic compounds was recognized by Wöhler in 1840 when he made the remark, "Organic chemistry gives me the impression of a primeval tropical forest, full of the most remarkable things."

It was not until the discovery of Kekulé and Couper, in 1858, that carbon has a valence of 4 and can unite with itself indefinitely that organic chemistry began to develop as an important branch of the science of chemistry. The concept of carbon uniting with itself, called *catenation*, was necessary for the foundation of the structural theory of organic chemistry. (Structural theory is concerned with how atoms are arranged to form molecules.) Also at about that time, organic chemistry received a most important economic stimulus. In England, in 1857, young William Henry Perkin accidentally discovered the first synthetic dye. He obtained a patent on his discovery and had the dye in production about a year later. It was a purple color called mauve, and it was so fantastically successful that it gave its name to a whole decade. More than that, it was an important factor in stimulating the beginning of the chemical industry in England and also in Germany. The practice of chemistry became a profitable profession which attracted investment, workers, and attention. The result was a relatively rapid growth of chemistry not only as an art and a science but also as a business.

The period when organic chemistry was beginning to develop in Europe coincided with the Civil War in the United States. After the war, population growth and the industrial revolution greatly increased consumer demand and products in the United States. Later, the two World Wars demonstrated the need for the United States to be independent of European chemicals. The result was the growth of the science of chemistry and the chemical industry in the United States to its present position of world prominence. Today huge chemical industries manufacture dyes, synthetic fibers, plastics, synthetic rubbers, fertilizers, insecticides, pharmaceuticals, cosmetics, explosives, fuels, lubricants, and all kinds of surface coatings. Most of those materials involve organic chemistry, and over half of all chemists are employed in the organic fields. You are now going to have the opportunity to learn something of this important and interesting subject.

# 1

## BASIC CONCEPTS OF CHEMISTRY: A REVIEW

Organic chemistry is the study of the 3 to 4 million carbon-containing compounds known. Although the large number and the kinds of reactions characteristic of organic compounds make the subject complex, some of the complexity is more apparent than real. There are indeed many, many more organic compounds than inorganic compounds; and many organic molecules are extremely large and complex. But the basic principles governing the formation and reaction of compounds are the same as those you have met previously in general chemistry.

In this chapter we shall review the most important of the basic principles and take a preliminary look at the application of those principles in organic chemistry. We shall consider chemical bonds, both covalent and ionic; intermolecular attractive forces; the nature of chemical reactions, including mechanisms and energy changes; and the nature of acids and bases and the application of acid-base theories to organic chemistry.

The concepts considered in this chapter will be of continuing importance as you progress through the course. If you find this brief review insufficient to help you recall them clearly, you may wish to study them in greater depth in a textbook of general chemistry.

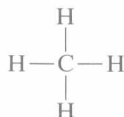
**1-1 Chemical bonds** How are the atoms comprising organic compounds held together? By the same types of chemical bonds you encountered in general chemistry. They are the covalent bonds and the ionic bonds. Let us review them briefly.

**Covalent bonds** The most common type of chemical bond is the *covalent bond*, which consists of a pair of shared electrons of opposite spin. Thus the hydrocarbon methane,  $\text{CH}_4$ , is held together by four equivalent covalent bonds

linking a single carbon atom with four hydrogen atoms. It may be represented by the formula



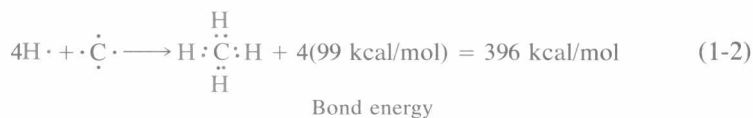
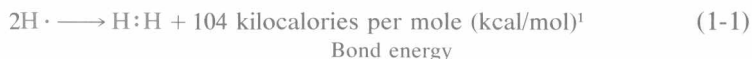
where the dots represent the outer, or valence, electrons which are paired up and shared. Methane may also be represented by the somewhat simpler formula



where the connecting lines represent the pairs of shared electrons.

You will note that the electron arrangement for methane effectively gives each hydrogen atom two electrons to complete its outer (and only) electron shell, while the carbon atom effectively completes its outer electron shell with eight electrons. Those electron configurations are possessed respectively by a helium atom and a neon atom—arrangements that have special stability and minimum energy.

**Bond energy.** Bond formation is usually an energy-releasing process. In the methane example, each hydrogen atom can be considered as contributing one electron to a bonding pair of electrons and the carbon atom as contributing its four valence electrons—one to each bonding pair—with attendant release of energy. The following equations illustrate the release of energy in bond formation for a mole of hydrogen and for a mole of methane.



**Pairing of electrons.** The concept of pairing of electrons is an important one. Each electron can be considered as spinning either clockwise or counterclockwise. Since each electron has a unit negative charge of electricity, its motion results in a magnetic field with poles located at the ends

<sup>1</sup> A note on units: In 1960, international agreement established the standard system of measurement called *Le Système International d'Unités*, abbreviated SI. The SI units are gradually being adopted in chemistry, but many older units continue to appear in the literature and in everyday use. The *calorie* and its multiple the *kilocalorie* are such units. The kilocalorie is retained in this text. You should know, however, that the SI unit for energy is the *joule* and that 1 kilocalorie (kcal) = 4.184 kilojoules (kJ).



of the axis of spin of the electron. Electrons that have the same direction of spin will possess magnetic fields of the same orientation. They will thus repel each other with a magnetic force, as well as with the electrostatic repulsion caused by possessing like charges. Such electrons could not pair up. However, electrons of opposite direction of spin will have opposed magnetic fields which will exert a magnetic force of attraction sufficient to counteract the inherent electrostatic repulsion. That makes it possible for two electrons of opposite spin to pair up and to occupy the same atomic orbital of an atom (unshared pair), or the same molecular orbital of a molecule (bonding pair). This is an application of Pauli's exclusion principle that no more than two electrons may occupy the same orbital and that two electrons occupying the same orbital must have opposite spins. Spins are of only two types, clockwise or counterclockwise. If more than two electrons (three, for example) were to occupy a given orbital, two of them would have to have the same spin. But electrons of the same spin would repel each other, so only two electrons of opposite spin could remain in the orbital. Thus the covalent bond consists of a pair of electrons of opposite spin shared by two atoms.

**PROBLEM 1-1** By using black dots and colored dots to represent the valence electrons, show electronic structures for (a) hydrogen peroxide,  $\text{H}_2\text{O}_2$ , (b) chlorine,  $\text{Cl}_2$ , (c) nitric acid,  $\text{HNO}_3$  ( $\text{HONO}_2$ ).



Note that in (c), nitric acid, the nitrogen atom contributes *both* electrons of the bonding pair to one of the oxygen atoms instead of each atom contributing one electron to the pair. This type of bond is termed a *coordinate covalent bond*.

**Geometry of single covalent bonds of carbon.** Compounds in which one or more of the hydrogen atoms of methane,  $\text{CH}_4$ , are replaced by some other atom or group of atoms can be formed; they are called *substituted methanes*. When one hydrogen is replaced by another element Y, only one product—one monosubstituted methane,  $\text{CH}_3\text{Y}$ —is formed. This indicates that all of the hydrogen atoms of the methane molecule are equivalent. If a disubstituted methane,  $\text{CH}_2\text{YZ}$ , is prepared, again only one product is formed. This indicates that the molecule cannot be planar. If it were planar, we would find two distinct compounds produced:

