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Organic Chemistry

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James D. Morrison

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G. Tyler Miller, Jr.

Chemistry: A Contemporary Approach

G. Tyler Miller, Jr.

Chemistry: Principles and Applications

G. Tyler Miller, Jr.

Energy and Environment: Four Energy Crises

G. Tyler Miller, Jr.

The photomicrograph on the cover shows sodium potassium tartrate.

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Preface

This book is designed for one-quarter or one-semester organic chemistry courses. Its major goal is to teach the basic concepts in an interesting way. The hundreds of professors' responses to questionnaires and the more than 40 reviews indicated that most of you want a text for this course that is concise as well as interesting. Many complained that existing books for the one-term course are getting harder and longer with each new edition. So you want a flexible book that allows you to vary the course level and content. The following features in the book provide that kind of flexibility:

Two Texts in One The **basic text** of 10 chapters provides what most teachers consider the basics of organic chemistry for a one-term course. Those who want to enrich this basic material can use the **supplementary chapters and the essays**.

(1) Four optional *supplementary chapters* appear at the end of the basic text, but two, Synthetic Polymers and Spectrometric Methods, can be covered any time after Chapter 7 on amines.

(2) *End-of-chapter essays*. Most of the chapters are followed by one or two essays that provide interesting applications of principles or slightly more detailed material. Most essays deal with bioorganic chemistry.

Emphasis on Understanding Principles A serious deficiency of some one-term texts is the failure to build an appropriate background in simple structural organic chemistry. My first two chapters slowly and thoroughly cover the principles of bonding, chemical structure, and nomenclature with many illustrations and worked-out examples. Not only are correct solutions indicated through examples, but common errors are also pointed out.

Pacing and Readability Through several rewrites and their class testing, I deliberated over each chapter and each concept to ensure that the development of material is paced appropriately. Much thought was given to the appropriate concept and factual density for each chapter. I tried to avoid extraneous information that detracts from the main ideas, yet to give all necessary background material. Because even simple organic structures can be confusing to beginning students, I have avoided rushing into those interesting, but complex, examples.

Instead I first try to make sure students are comfortable with the basic structures early in the course.

After several drafts had been class-tested, Robert McNally, an excellent professional writer, read the manuscript from the point of view of a student as well as a gifted editor, and helped me continue to clarify the final version.

A Balance between the Basics and the Bioorganic Applications I have emphasized the basics of organic chemistry because they are crucial in preparing students for future course work in the life sciences and other fields. However, I believe in integrating *simple* bioorganic examples throughout the text. They not only motivate students by relating organic chemistry to the life sciences, but also clarify the basics. For those students who want slightly more depth in bioorganic applications, they will find many among the end-of-chapter essays.

Learning-Oriented System Many students have trouble with chemistry. In talking with students over 17 years of teaching introductory organic courses, I find that some of their troubles stem not from chemistry itself, but from texts that fail to help them learn systematically. Most books have some learning devices, but few have a complete and integrated system of them. Such a system helps in any text, but it is essential in a field as vast and as detailed as organic chemistry. In this book you will find:

A running summary of chapter content that can also serve as a preview. Within each chapter key points are stated in concise sentences that are boxed off and set in bold colored type. These sentences reinforce key concepts in the context of their development.

Key terms set in boldface and colored type.

Easy access to key terms. The pages on which key terms are defined appear in boldface type in the index. This feature lets students review the definition in context. A separate comprehensive glossary appears in the student study guide, as well as a list by chapter of key terms.

Accomplishments and review—lists of learning goals for each chapter. Arranged by section at the end of each chapter, they can be used both as pre-chapter objectives and as review questions. When students use these lists section by section, they get immediate feedback and approach the material in manageable segments.

Many end-of-chapter exercises. Again, arrangement by section lets students test their understanding immediately after completing each section. A separate study guide gives detailed solutions for all problems. This text contains approximately 1200 questions or exercises.

Key material reinforced three times. A combination of the key sentences, accomplishments and review, and exercises gives triple reinforcement of the important points.

Extensive Manuscript Review The detailed outline for this book was reviewed by more than 100 chemistry teachers from many kinds of schools. More than 40

teachers then reviewed all or part of the original and revised manuscripts and were extremely helpful in improving the basic text-supplement format. They also helped ensure that the text is accurate and up to date and provided many ideas for developing topics (see list of reviewers at the end of this preface).

Supplementary Materials

1. Student study guide that includes detailed solutions of all exercises, key terms listed by chapter, and an extensive glossary.
2. Laboratory manual, containing both classical experiments and ones concerning bioorganic chemistry.
3. Answer book for laboratory manual.

Acknowledgments Many people have contributed to the production of this book. Special thanks are due the many chemistry teachers (listed on the following page) who reviewed the manuscript and responded to questionnaires. These reviewers pointed out errors and suggested important improvements.

Bob McNally, Betty Adam, and Greg Hubit contributed their talents during the editing stages of production, and I thank them for helping me. Jack Carey, Chemistry Editor at Wadsworth Publishing Company, suggested this project many years ago. His persuasive powers are exceeded only by his creativity, patience, and dedication to excellence. Most important to me has been the support and understanding of my wife, Judy, who endured many evenings and weekends alone, as well as postponed vacations and other forms of neglect on my part during the writing and editing process. In spite of this, she was willing to help with the index.

Finally, you should recognize that much of what I say to you in this book was earlier said to me by my teachers. I was lucky to have been inspired to study organic chemistry by great teachers like Paul Johnson, Fred Suydam, Fred Snavely, Bob Letsinger, Howard Zimmerman, Fred Bordwell, and Harry Mosher. If this book helps you, they deserve some of the credit.

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Extensive Manuscript Review

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It all comes down to chemistry in the end, of course. Hydrogen, oxygen . . . What are the other things? God, how infuriating, how infuriating not to know!

Aldous Huxley, Point Counter Point

1-1 History, Matter, and Organic Chemistry

There was a time, now well past in terms of human lifespan but only yesterday in any longer perspective, when the living world was thought to be completely different from the nonliving. That distinction was apparent to anyone with eyes to see and a brain to think. A puppy, a daisy, and a scorpion, dissimilar as they seemed, shared an essential something that distinguished them absolutely from inanimate objects like rocks and water. That commonality was the life force. Destroy the life force, kill the daisy or puppy or scorpion, and they died and decayed. The mysterious something of life had been lost. But smash the rock to bits or pour the water onto the ground, and nothing like death occurred. The broken rock and spilt water simply mixed with the inanimate background. They had lost nothing but shape; otherwise they remained the same.

The gap between living and nonliving was bridged from time to time, but that feat was the work of divinity. When Zeus and his brothers and sisters, the gods of Greece, decided to fill the empty earth with people, they created them from metal. The first models came from gold and silver and brass, and they proved to be failures or, worse, potential rivals. The gods destroyed them. But when the gods made humans of iron, they were pleased with the result and set the iron-humans free on the earth. The Hebrew god Yahweh displayed his omnipotence by infusing life into the nonliving. "The Lord God formed man of the dust of the ground, and breathed into his nostrils the breath of life; and man became a living soul" (Genesis 2:7). In the world view of the Middle Ages divinity intruded less obviously than it had in Eden, but its power was undiminished. Frogs arose from the mud of ponds; mice, from piles of rags and laundry. Only God could bring the animate from the inanimate; creation continued, keeping the world supply of frogs and mice replenished.

Following the Renaissance, as thinkers and investigators turned increasingly to what we call science, the idea of a strict separation of living and nonliving

matter remained paramount. For example, at the end of the eighteenth century, urea (CON_2H_4) was first isolated from urine. Early chemists felt certain that only kidneys could produce urea, that the compound was the result of life and life alone. J. J. Berzelius, a Swedish chemist of the nineteenth century, classified compounds as organic—arising from living material—and *inorganic*—arising from *nonliving* material. Berzelius' distinction sprang from *vitalism*, the philosophical position that a mysterious life-force infused living matter and rendered it different from nonliving.

Chemistry itself, though, pulled the props out from under vitalism one by one. In 1828 Friedrich Wöhler, who had studied with Berzelius, mixed a solution of ammonium ions with one of cyanate ions. He expected to get only ammonium cyanate from the reaction, but found to his surprise that some urea was also produced under the conditions of his experiment. Wöhler had produced urea, an organic compound, in the laboratory (a decidedly inorganic setting) from nonliving materials. The vitalists clung to their position and pointed out that the cyanate in Wöhler's experiment came from dried blood, hoofs, and horns and that the urea, therefore, had an organic origin.

In 1845 Herman Kolbe, a student of Wöhler's, combined carbon, sulfur, chlorine, water, and a potassium-mercury alloy—all considered inorganic substances—and produced acetic acid (CH_3COOH), an organic compound. However, even this experiment did not destroy vitalism completely. It took many years, and many more experiments, before it became obvious to everyone that the same rules of chemical behavior apply to organic and inorganic compounds alike.

A pure organic compound isolated from a living thing is identical to the same compound synthesized from nonliving materials.

Today, the term *organic chemistry* refers to the study of carbon compounds. Vast numbers of carbon compounds occur in nature. Many others, though, are synthetic, created only by laboratory methods and not appearing in plants or animals. Increasingly, the distinction between organic and inorganic seems less and less useful to working chemists. Researchers find their investigations leading them back and forth across the old boundary often enough to blur the line between organic and inorganic chemistry.

Modern organic chemistry is the study of carbon compounds.

There is more to this blurring of distinctions than intellectual history. Our civilization is based on a high technology based in turn on contemporary science. We conceive of technology as artificial and contrast it with natural objects and processes. Thus, disaffection with modern farming technology and its reliance on chemicals to spur plant growth and kill pests has prompted interest in "organic" foods. Ironically, many of the pesticides and fertilizers shunned by the organicists are the products of organic chemistry. Organic chemistry is a major key to our civilization's technology. It provides us with plastics, petroleum products, drugs from aspirin to LSD, cosmetics, packaging materials, and synthetic fibers, among other things. Today, organic synthetics are fast replacing

plants and animals as the raw materials for clothing and shelter, and they may eventually provide a large part of our food supply. The world's capability for producing organic products has spiraled dizzily in the past few decades, and people have become more and more concerned about where that spiral will lead us and what the ride will cost.

Many common things are made up of organic chemicals.

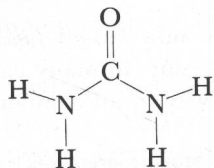
Organic chemistry also gives us a mode of self-knowledge. It helps us understand ourselves, for we are essentially complex aggregations of organic compounds. And it informs our understanding of the choices, prospects, and problems facing society.

1-2 Structural Formulas

To make a synthetic compound, an organic chemist in a laboratory combines various substances to get the one desired. That sounds almost childishly simple, like putting lettuce with radishes and onions and dressing to make a salad, but the process involves a sophisticated understanding of molecular processes. To put various compounds together and come out with the one you want, you first have to know how atoms and molecules combine.

By the middle of the nineteenth century, chemists had derived the molecular formulas of many organic compounds. They knew how many atoms of which elements made up one molecule of a given compound, but they had no way of figuring out how those atoms were arranged within the molecule.

The idea of a combining power, or *valence*, for each element gave chemists their first grasp of structure. The valence idea was that an atom of a given element, no matter what compound it appeared in, could combine only with certain fixed numbers of other atoms. The valence idea pictured the atom as a sort of Tinker Toy, the number of holes in it depending on its identity. Hydrogen had one such hole; oxygen, two; nitrogen, three; carbon, four; and so forth. With the valence idea, a structural formula could be deduced from the molecular formula. Thus, urea's molecular formula, CON_2H_4 , provided its structure:



This representation is a *structural formula*. The lines between the symbols for the chemical elements stand for chemical bonds (which, as we shall see, are shared electron pairs). The structural formula (read from left to right) says that two hydrogens are singly bonded to a nitrogen that is singly bonded to a carbon

that is doubly bonded to an oxygen and also singly bonded to another nitrogen that is singly bonded to two hydrogens. The structural formula gives the compound's constitution; it spells out the sequence in which the atoms are linked, and it shows how many chemical bonds are used for each linkage. The ideas that the valence of certain elements remains the same in all compounds and that valences may be used to form multiple bonds (double and triple bonds) represented giant steps forward in chemical theory.

Carbon, hydrogen, nitrogen, and oxygen are prevalent elements in organic compounds.

Organic compounds often have complex structures and contain many atoms.

A molecular formula gives only the elements and their ratios.

A structural formula shows molecular constitution, the sequence of atoms, and the bonds that connect them.

1-3 Organic Functional Groups

In the closing years of the nineteenth century, as chemistry shed the vestiges of vitalism, organic chemistry flourished. For the first time, chemists synthesized in the laboratory many compounds found in nature. In addition, as developing theories of chemical bonding showed that organic compounds not found in nature could also exist, chemists set to work to make these unknown compounds, with striking success.

However, laboratory research remained a matter of serendipity. Chemists allowed known elements or compounds to react, then assayed the reaction products to see what resulted. No theory existed that enabled them to predict results beforehand. Slowly this chaotic state of affairs changed. Researchers noted that certain structural units in various compounds, like the —NH_2 in urea, behaved in generally predictable ways no matter what compound they were part of. If chemists knew the groupings in the compounds they were studying, they had an approximate idea what would happen when those compounds reacted. Chemists started planning reactions before they went into the laboratory, predicting the results according to the known behavior of the groupings in the molecules. Such predictions proved astonishingly accurate.

The groupings that allow such predictability are now called *functional groups*. A functional group is a collection of atoms that occurs in many carbon compounds and that always behaves roughly the same way in all compounds.

Functional groups are ensembles of atoms that occur frequently in organic structures.

Why Functional Groups Are Useful Figure 1-1 illustrates a functional group called the *carboxyl group*, which occurs in the compounds called carboxylic acids. This