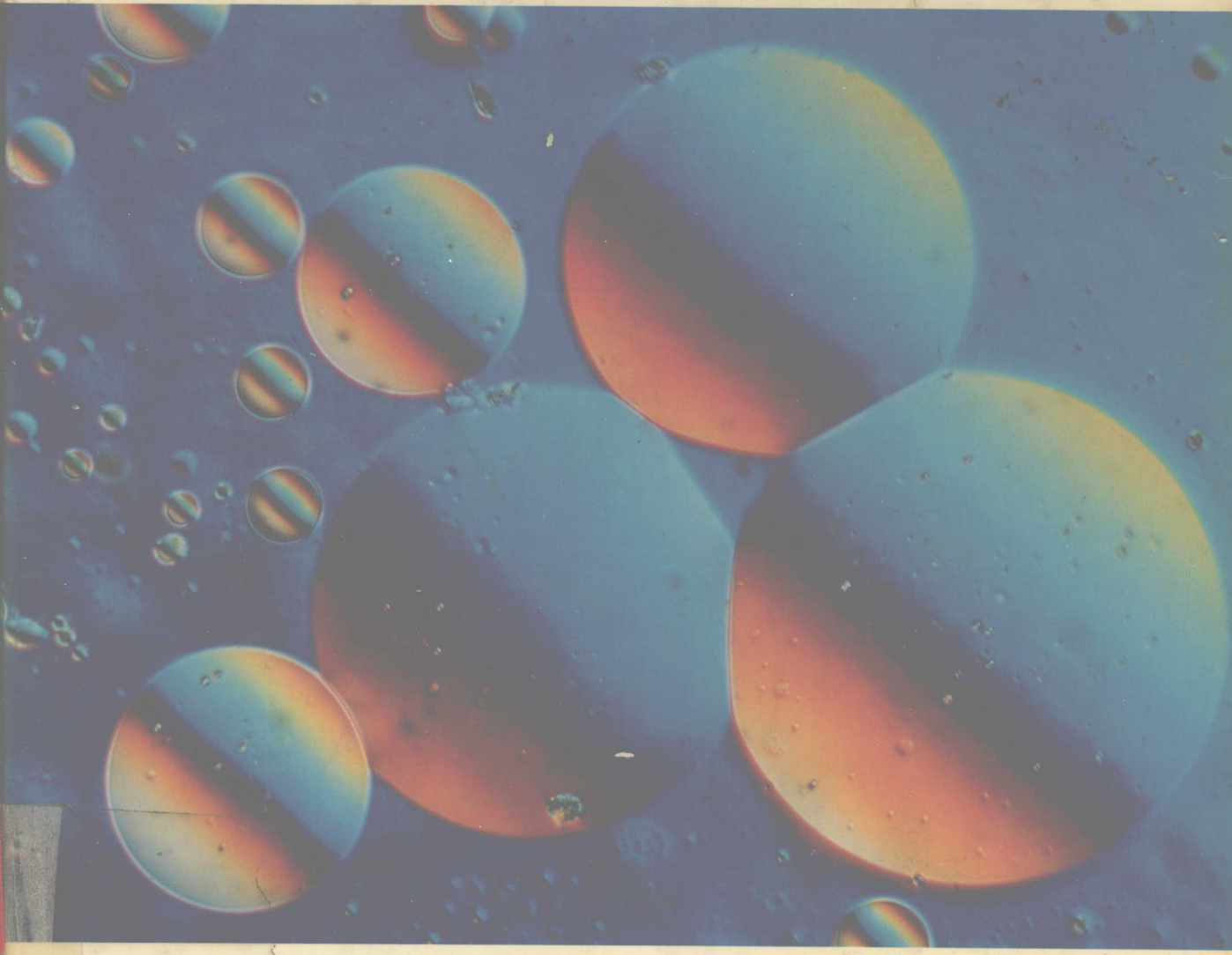
Second Edition

Elements of Organic Chemistry



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2nd edition

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Preface

This revision of *Elements of Organic Chemistry,* like its predecessor, is intended for a first course in organic chemistry. It is especially suited to the needs of students specializing in the life sciences, allied health fields, agricultural sciences, and other related curricula.

We have retained the basic philosophy of the first edition. Foremost, we wish this book to be a teaching text; one that students find readable, and can study and learn from with little dependence on the teacher. To this end, we have taken the same systematic, but *more selective,* approach to our material as in the earlier edition, keeping constantly in mind the student to whom this book is addressed. As in the first edition, the discussion of topics is organized around functional groups. In the selection of our material, we have stressed those aspects of organic chemistry pertinent to health, the environment, and biochemistry, areas of special interest to the career objectives of the students enrolled in the course. The practical uses of organic compounds as drugs, food additives, pesticides, plastics, and other products, as well as their occurrence in nature, are discussed throughout the text.

Nevertheless, a number of changes have been made in this second edition, with the hope to improve on the earlier one.

- The number of preparative methods and reactions presented has been purposely reduced. Some reactions, such as the Wurtz reaction for preparing alkanes, have been omitted because of their obsolescence or lack of practical applications. Others, such as the Gabriel synthesis of amines, have been deleted because of the time limitations inherent in a brief course and because we did not feel that they were important enough for nonchemistry majors.

Some mechanisms, such as those involving carbocation rearrangements, have been omitted because we felt they were beyond the scope of a short organic chemistry course. We trust we have been judicious in our selection of reactions and reaction mechanisms presented.

- The number of problems within the body of each chapter has been increased considerably. Problems within a chapter serve to test the student's mastery of the subject section by section. Selective answers to these problems are provided at the end of the book as a further learning tool.

  The exercises at the end of each chapter have also been expanded. These exercises cover material for the whole chapter and sometimes previous chapters. To guide the student in solving the end-of-chapter exercises we have indexed the exercises to the appropriate sections. This indexing should also help the instructor in choosing assignments.

  Answers to all problems and exercises, with detailed explanations, are given in the *Solutions Manual for Elements of Organic Chemistry.*
- To reinforce the mastery of new concepts as they are presented we have increased the number of worked-out examples.
- A summary of methods of preparation and reaction has been provided in a special display box in almost every chapter. The summary allows the instructor the freedom to choose which topics he or she wishes to deal with. The displays also helps the student to focus on the main reactions found in each chapter.
- New pedagogical aids are a detailed summary and a list of key terms at the end of each chapter.
- In addition to reorganizing and updating a number of chapters, we have written two new chapters, "Organic Halogen Compounds" (Chapter 8) and "Spectral Methods of Structure Determination" (Chapter 17).

Some of the highlights are:

In Chapter 1, after briefly reviewing atomic structure and bonding, we present in detail, and in a deliberate manner, the various methods of writing organic chemical formulas following the rules of covalence. Often, treatment of this topic is abbreviated. Our experience tells us that students taking the course are often confused when they encounter organic chemical formulas for the first time. We hope, by our methodical approach, to help students overcome their natural apprehension when faced with the strange and seemingly complex "hieroglyphics" of organic chemistry. To emphasize the orderliness of organic chemistry, we end the chapter with the classification of compounds into families according to functional groups.

Chapters 2–5 deal with hydrocarbons. In Chapter 2, on the alkanes, we consciously deleted the methods of preparation, primarily because alkanes are obtained most readily from natural sources rather than from the laboratory and because we did not wish to overwhelm the student in his/her first encounter with a family of organic compounds. Instead, we concentrated on physical properties, structural isomerism, and practical applications. Before introducing the few reactions that alkanes undergo, we wrote a separate section on the types of bond-breaking and bond-making.

In Chapter 3, dealing with alkenes, we have introduced a brief discussion of the *E,Z* system of nomenclature to supplement the treatment of the classical *cis-trans* method for naming geometric isomers. The chemistry of alkynes is treated in Chapter 4, with special stress on the similarities of this class of com-

pounds with the alkenes treated in the previous chapter. Dienes and the concept of resonance are also dealt with in Chapter 4. The resonance concept and how it helps us in understanding the chemistry of aromatic compounds is discussed again in Chapter 5.

To emphasize the three-dimensional nature of organic compounds we now present stereochemistry in Chapter 6. A new feature here is the methodical introduction of the *R,S* system of nomenclature in addition to the classical D,L system.

After having covered compounds containing only carbon and hydrogen, we reach Chapter 7, which deals with alcohols, phenols, and thiols. In the treatment of alcohols and phenols we consider them as organic derivatives of water. Special emphasis is placed on the chemistry common to both classes of compounds and what separates them from one another. By this time we are ready to deal with organic halogen compounds in Chapter 8. Chapter 8 correlates the material developed in the previous seven chapters with respect to the methods of preparing this class of compounds, the reactions they undergo, and their stereochemistry. A section on organometallic compounds provides the springboard for the application of Grignard reagents to the synthesis of compounds encountered earlier and to be found in the coming chapters.

Chapters 9–16 deal with ethers, aldehydes and ketones, carbohydrates, carboxylic acids and derivatives, lipids, amines, amino acids, peptides and proteins, and nucleic acids. The organization of these chapters is essentially the same as that of the earlier edition. However, we now treat aldehydes and ketones in one chapter (Chapter 10) and carboxylic acids and derivatives in one chapter (Chapter 12). In keeping with our philosophy of integrating the biochemical topics as soon as possible after discussion of the appropriate organic chemical families, carbohydrates are treated in Chapter 11 right after aldehydes and ketones; lipids in Chapter 13 immediately following carboxylic acids and derivatives; and amino acids, peptides, and proteins in Chapter 15 following treatment of amines.

Chapter 17 deals with uv–visible, ir, and nmr spectral methods of identification and structure determination. Bearing in mind that these topics are addressed to nonchemistry majors, we restricted ourselves to the key pieces of information that can be obtained from each technique. We deliberately omitted a discussion of mass spectrometry. Although this chapter is placed at the end of the book, the material can be taken up any time after the first few chapters, at the discretion of the instructor. To permit greater flexibility, we have written a number of additional exercises at the end of the chapter; these additional exercises are indexed to specific chapters in the text.

There is more material included in this book than is possible to cover in one semester. We feel this not to be a disadvantage. On the contrary, this allows a freedom of choice for subject matter on the part of the instructor.

Several of the changes in this edition were made in response to discussions, suggestions, and critical comments from colleagues, reviewers, and users of the previous edition. We thank them. In particular, we wish to express our gratitude to Professors Elmer E. Jones, Northeastern University; L. Salisbury, Kean College; M. Treblow, University of Pittsburgh; and G. Wilson, Western Kentucky University. Our thanks also go to those who reviewed our manuscript: Professors James O. Schreck, University of North Colorado; Wes Borden, University of Washington; Robert Coley, Montgomery College Maryland; Nathan Lerner, South Connecticut State College; and Daniel O'Brien, Texas A&M University.

Our colleagues at Bronx Community College, Professors J. Buckley,

D. Gracian, R. Miller, J. G. Riley, and H. Stein, and at New York City Technical College, O. Gaglione, Alla O. Romano, and S. Dreier, deserve our thanks for their encouragement and advice. A special thanks goes to Evelyn Shapiro whose words of advice were always a source of inspiration.

It has been a special pleasure to work with Elisabeth Belfer, our Production Supervisor, whose editorial thoroughness and excellent suggestions for improvement of the text we greatly appreciated. We are indebted to Greg Payne and Tom Vance, Editors, for their consistent interest and expert guidance in helping move the book through to its final form.

The nmr spectra in Chapter 17 were provided by Varian Associates, Inc., Palo Alto, California, and the ir spectra were provided by Sadtler Research Laboratories, Inc., Philadelphia. We thank them both for permission to use and adapt their materials.

We want especially to thank our wives and children for their patience and understanding during the long months of neglect while the manuscript was in preparation.

We shall be grateful for continued suggestions for improvement of the text in future editions.

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Contents

1

Bonding, Structural Formulas, and Molecular Shapes

The subject of organic chemistry is unique in that it deals with vast numbers of substances, both natural and synthetic, that directly influence our welfare and standard of living. Organic chemistry is crucial to our economy as the source of countless manufactured products that are essential to our comfort and well-being. The clothes we wear; the petroleum products we use to run our machines; the paper, rubber, wood, plastics, paint, cosmetics, insecticides, and vitamins and drugs that we use every day—all are examples of organic compounds. The chemical substances that make up the organs of our bodies, the food we eat for nourishment, and the chemical reactions that take place inside our bodies are also organic in nature. Organic chemistry is a subject that is fundamental to medicine, biology, and other related disciplines such as nursing, dental hygiene, and medical laboratory technology. Because it is almost impossible to think of an aspect of our daily lives that is not somehow influenced by organic chemistry, the relevance in your study of this exciting and dynamic subject should be quite apparent.

Organic Chemistry: A Modern Definition 1.1

From observation of the chemical makeup of many organic compounds it was recognized that one constituent common to all was the element **carbon.** Today **organic chemistry** is defined as the *study of carbon/hydrogen-contain-*