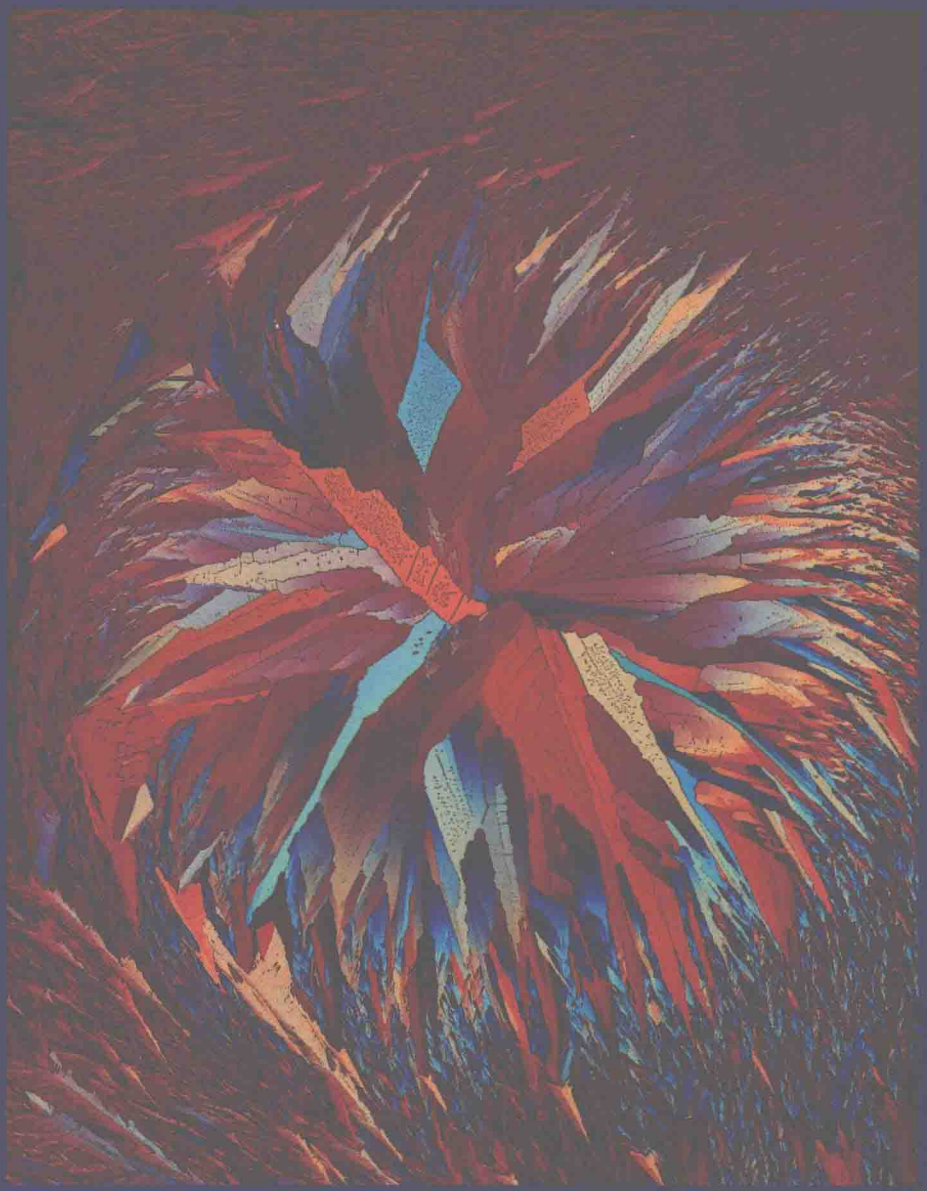
ORGANIC CHEMISTRY
SECOND EDITION



SEYHAN EGE

ORGANIC CHEMISTRY

SECOND EDITION

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D. C. HEATH AND COMPANY
LEXINGTON, MASSACHUSETTS TORONTO

ACKNOWLEDGMENTS

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Published simultaneously in Canada.

Printed in the United States of America.

International Standard Book Number: 0-669-18178-1

Library of Congress Catalog Card Number: 88-080264

10 9 8 7 6 5

To my teachers and my students

Preface

The pedagogical aim of *Organic Chemistry,* Second Edition is to educate students to think independently about organic chemistry. The first edition and now, the second edition, have the same philosophy of teaching: Students can truly learn organic chemistry only if they are actively involved in developing a practical understanding of the causes of chemical change, rather than trying to master organic chemistry through memorization. In both editions, I have presented organic chemistry by consistently emphasizing important themes and by returning to fundamentals again and again. In this way I have helped students to think as practicing chemists do in predicting reactivity from structure. Students have told me that they have learned an entirely new way of thinking—of analyzing problems, sorting facts, reasoning by analogy, looking for patterns—and that consequently their approach to all of their other work has changed.

Like the first edition, the second edition of *Organic Chemistry* has been designed to lead students quickly to the concept that structures of organic compounds determine their chemical reactivity. This theme is apparent immediately, even within the first two chapters of the book that introduce students to structure and bonding. Chapter 3, the first chapter devoted to chemical reactivity, uses the reactions of organic compounds as acids and bases to focus the student's attention on two simple reactions, protonation and deprotonation of organic compounds. Through the practice of solving problems on acidity and basicity, students gain confidence in their ability to predict reactivity as chemists do: by looking at structures of organic compounds and applying fundamental concepts such as atomic and ionic sizes, resonance stabilization of species, and pK_a values. In addition, students learn reactions that are important steps in many of the organic transformations they will study later.

Chapter 3 also introduces mechanisms of organic reactions and the convention of using curved arrows for symbolizing the motion of electrons. Coverage of the concepts of nucleophile and electrophile in Chapter 4 is built on the chemistry, and the language and symbolism of chemistry, learned in Chapter 3. In Chapter 4, the reactions of chloromethane with hydroxide ion and hydrogen bromide with propene are used to introduce thermodynamics and kinetics and the idea of reaction pathways.

Chapter 5 presents the nomenclature and conformation of both alkanes and cycloalkanes. Stereoisomerism is discussed in Chapter 6. With these first six chapters, students have most of the concepts they will need to understand the chemistry presented to them in the rest of the book. Extensive cross-referencing allows instructors considerable flexibility in choosing the order of subjects to follow.

NEW IN THE SECOND EDITION

Features

True mastery of organic chemistry requires that students learn to make discriminating use of their eyes and minds. To this end, several new features have been introduced in the second edition.

Visualizing the Reaction

As in the first edition, complete mechanisms are given for each type of reaction. These mechanisms are now highlighted in "Visualizing the Reaction" boxes set apart from the text. Students must practice developing their powers of imagination and following a process with the "inner eye," and these complete mechanisms, which feature the

judicious use of four colors, enhance the process of visualizing. Acidic or electrophilic sites are highlighted as red atoms, blue shading signifies basic or nucleophilic species, and grey shading emphasizes leaving groups. Color is used to indicate whether the reactive species on one side of an equation are converted into new reactive species after reaction, in order to show students the reversibility of many reactions, especially acid-base reactions.

Four Colors

While four-color printing appears primarily in the "Visualizing the Reaction" boxes, color is also used to enhance figures and to stress, with consistency, various important structural features. For example, in sections where students are just learning to see stereochemistry, green and red shading highlights stereochemical relationships.

Problem-Solving Skills Sections

In working with my students, I have become convinced that encouraging them to analyze problems systematically is the single most important factor in increasing their overall intellectual skills. These new Problem-Solving Skills sections, unique among organic chemistry texts, offer students a systematic, questioning approach to solving organic chemistry problems. These sections do not simply provide a way for students to learn to plug data into a prelearned formula; rather, students learn to reason their way to a solution.

- In Chapter 1, students are introduced to the idea that the solution to a problem in chemistry requires a step-by-step analysis of the problem. This analysis takes the form of questions that students pose to themselves in a systematic way.
- In Chapter 4, students are shown how to reason backwards in solving problems involving simple syntheses.
- In Chapter 7, students are led through the types of questions that help them to predict the product of a reaction and to transform a given starting material into a desired product. These are complex questions with many types of answers, depending on the particular problem being solved. Not all of the questions are directly applicable to the problem under consideration, but represent steps in the processes of deciding how to use the data given in the problem.
- The same method of questioning is applied in Chapter 9 to writing mechanisms. To reinforce this practice for students, in most chapters through Chapter 23, one or two problems are worked out using the same set of questions.
- The *Study Guide* further reinforces the questioning approach used in the book by applying it to solving some of the problems in and at the end of each chapter.

Concept Maps

Concept maps, which appear in the *Study Guide,* are a fourth innovation in this edition of *Organic Chemistry*. Conceived as a practical way to organize and summarize the material presented in the book, these concept maps present major ideas in outline form. Notes in the margin of the textbook alert students that the concept maps are available. While the concept maps provided can be quite helpful to students, students are encouraged to examine the maps and then create their own, because the process of creating a concept map requires them to give up a purely linear way of thinking about a subject and to explore interrelationships. My students who have used this method to organize their lecture notes and to outline related subjects have found the concept maps not only useful, but fun. Encouraging students to work in this way promotes an actively thinking approach to organic chemistry.

A package of transparency masters containing the complete set of concept maps that appear in the *Study Guide* is available to instructors.

In-Text Summaries
Besides the concept maps in the *Study Guide,* two other forms of summary appear in the textbook itself.

- An end-of-chapter *Summary* offers a concise review of the major concepts covered in the chapter.
- End-of-chapter *Tables* summarize the reactions that appear in the chapter. Organized so as to remind students of how the reactions proceed, they are not made up of general reactions to be memorized, but take students briefly through the stages of the reaction again, reminding them of the types of reagents needed, reactive intermediates involved, and the stereochemistry of the reaction. These tables are particularly helpful to students when they are used together with the concept maps in the *Study Guide*.

Easy-to-Use Cross-Referencing
The second edition is cross-referenced with page numbers to enable both students and teachers to locate related topics quickly.

Reorganization

This revision of *Organic Chemistry* has resulted in considerable rearrangement of topics. Important changes include:

- Early and separate chapters on infrared spectroscopy (Chapter 10) and nuclear magnetic spectroscopy (Chapter 11).
- The introduction to stereochemistry concentrated in a separate chapter (Chapter 6).
- Free radicals in a separate chapter. While free radicals are mentioned briefly in Chapter 5 in connection with the reactivity of alkanes, the separate chapter allows a fuller treatment of their use in synthesis and their biological significance.
- Separation of the contents of each of the longer chapters in the first edition into two shorter chapters. The first chapter in each pair contains the material on that topic commonly covered in most courses; the second chapter may either be omitted or taught in a different order. (Note that this edition retains the integration of biologically interesting examples of chemistry throughout the text.) For example, Chapter 14 concentrates on nucleophilic substitution reactions at the carbonyl group of carboxylic acids and their derivatives. Chapter 15 contains the reactions of carboxylic acids and their derivatives with metal hydrides and organometallic reagents. Chapter 16, which covers the chemistry of enolate anions, follows directly after the chemistry of carboxylic acid derivatives and emphasizes aldol and Claisen condensations. Chapter 18, the second chapter in the pair, involves the chemistry of α,β-unsaturated carbonyl compounds and ylides, and follows a chapter on polyenes (Chapter 17). Chapter 19 covers electrophilic aromatic substitution reactions, and the rest of aromatic chemistry comes in Chapter 23, after students have learned about free radicals (Chapter 20), mass spectrometry (Chapter 21), and diazotization reactions (Chapter 22). Aromatic chemistry is further reinforced by a study of heterocyclic compounds in Chapter 24.

The second edition is unchanged from the first edition in its emphasis on an understanding of reactivity rather than on an encyclopedic knowledge of reactions. Students suffer from an overload of different things to remember, and from not learning to think their way toward predicting the outcome of a reaction they have never seen before. Thinking for themselves is a skill that will be valuable to them as graduate students in chemistry, in other sciences with a strong chemical component, and in

medicine. A thorough understanding, with an emphasis on mechanism of a few major reactions, enables students to apply the principles they have learned and gives them the confidence to tackle new situations. I would rather teach students who are confident about their abilities than students who are overwhelmed by a mass of undigested material. Once the fundamental thought processes of chemistry have been learned, teachers find that they can introduce their own favorite reactions to their students.

The length of this book, thus, comes from meticulous explanations and fully detailed mechanisms for selected reactions, mechanisms that were chosen to represent many other reactions of the same type. My experience convinces me that only such an explicit, consistent approach gives students the reinforcement they need to learn a subject they perceive as being difficult.

Does this approach work? Feedback from students has been so positive that it has encouraged me to keep the same approach in this edition as I used in the first edition. I particularly cherish reports from faculty at various schools that students using the book receive better scores than before on the standardized ACS examinations at the end of the year and even complain that the examination was too easy! If the book is used as it is intended, students come to enjoy and be challenged by their intellectual competence. To watch this happen, is, of course, the ultimate satisfaction for a teacher.

SUPPLEMENTS

Study Guide

Roberta W. Kleinman of Lock Haven University, Pennsylvania, and Marjorie L. C. Carter of the University of Michigan are my coauthors for the first and second editions of the *Study Guide*. Both of them have given me invaluable help—especially Roberta Kleinman, who, with her skill at the computer, is responsible for transforming the material into camera-ready copy. As in the first edition, the second edition contains detailed solutions to every problem in the text as well as explanations of the reasoning processes behind the answers for many problems. Some problems in this edition are worked out using the questions developed in the Problem-Solving Skills sections of the text to reinforce students' understanding of this approach.

New concept maps, charts summarizing relationships between key ideas in a section or portion of a section, provide an innovative tool for practice and review. Notes in the margin of the text refer students to relevant concept maps in the *Study Guide*.

Transparency Masters

For classroom use by the instructor, a package of *Transparency Masters* contains the complete set of concept maps that appear in the *Study Guide*.

Transparencies

A complete set of *Transparencies* ($8\frac{1}{2} \times 11''$), many of them full color, is available free to college adopters of the textbook. Reproduced from selected figures and chemical structures in the text, the transparencies include spectra, molecular orbitals, space-filling models, stereochemistry, and reaction mechanisms.

Software

A variety of quality *software* programs are offered by arrangement with COMPress, a division of Queue, Inc. For information and demonstration disks, contact the Marketing Department at D. C. Heath at 1-(800)-235-3565.

ACKNOWLEDGMENTS

Many people have contributed to converting the first edition of *Organic Chemistry* into the second edition. Suggestions and corrections from colleagues and students who have used the book are particularly valuable. I owe special thanks to Brian Coppola, Richard Lawton, and John Wiseman of the University of Michigan; Sally Weersing, Muskegon Community College; Dorothy Goldish, Edwin Harris, and Tom Maricich, California State University, Long Beach; David Reingold, Juniata College; Hans Cerfontain, Henk Hiemstra, and Gerrit-Jan Koomen, University of Amsterdam; and Clarisse Habraken, University of Leiden.

Dr. Alex Aisen of the Department of Radiology at the University of Michigan supplied me with information on magnetic resonance imaging and the photograph that appears on page 416 of the text. Torin Dewey, a student of mine who is now doing graduate work at the University of California, Berkeley, took most of the proton magnetic resonance spectra. Frank Parker and James Windak helped with the spectra illustrating Fourier transform nuclear magnetic resonance and infrared methods.

I very much appreciate the suggestions of the reviewers for the second edition: R. G. Bass, Virginia Commonwealth University; George B. Clemans, Bowling Green State University; James H. Cooley, University of Idaho; William A. Donaldson, Marquette University; Richard R. Doyle, Denison University; Barbara V. Enagonio, Montgomery College; William A. Feld, Wright State University; Dorothy M. Goldish, California State University, Long Beach; Richard Jochman, St. John's University; Ronald H. Kluger, University of Toronto; Robert J. Newland, Glassboro State College; Daniel H. O'Brien, Texas A&M University; Suzanne T. Purrington, North Carolina State University; Harold R. Rogers and Robert Spenger, both at California State University, Fullerton; Joseph J. Tufariello, State University of New York at Buffalo.

No amount of thanks will repay my debt to Marjorie Carter and Roberta Kleinman. Not only have they contributed substantially to the *Study Guide,* but they have helped with the text itself too. All of the three-dimensional figures in the text originated with Roberta Kleinman, who combines artistic talent with an interest in how students visualize and learn. She joins me in struggling to see things as the student sees them and not as we, with years of experience, know them to be. I owe a great deal to her critical eye. Marjorie Carter also brings the viewpoint of the students and a questioning mind to the thankless task of proofreading. Many times she has insisted that Roberta and I try again in drawing structures or explaining our reasoning for greater clarity for the student. I value the help of both of these good friends.

Mary Le Quesne, Senior Acquisitions Editor at D. C. Heath, saw the book through revision with an openness toward my ideas, even when they were unconventional, for which I am grateful. Her knowledge of chemistry and her insight contributed greatly to this edition. Cathy Brooks, Senior Production Editor, has guided me patiently and with endless good humor through the traumatic process of the publication of a technical book in four colors. I am grateful for her expertise and her meticulous attention to detail.

Finally, none of this would have been possible without the encouragement of my family and friends. I thank them for their understanding during all of the times when I could not be with them and for their steady love that supports me.

Seyhan N. Eğe

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