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ORGANIC CHEMISTRY

John McMurry
Cornell University

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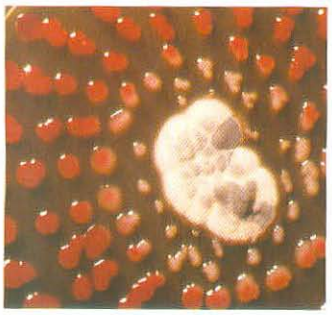

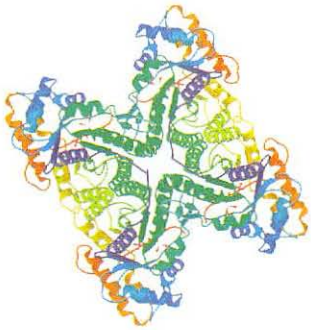

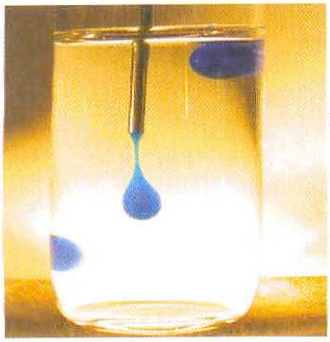

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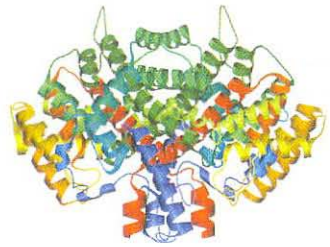

Preface

I love to write. I get real pleasure from taking a complicated subject, turning it around until I see it clearly, and then explaining it in simple words. I write to explain chemistry to students today the way I wish it had been explained to me years ago.

The enthusiastic response to the six previous editions has been very gratifying and suggests that this book has served students well. I hope you will find that this seventh edition of *Organic Chemistry* builds on the strengths of the first six and serves students even better. I have made every effort to make this new edition as effective, clear, and readable as possible; to show the beauty and logic of organic chemistry; and to make organic chemistry enjoyable to learn.

Organization and Teaching Strategies This seventh edition, like its predecessors, blends the traditional functional-group approach with a mechanistic approach. The primary organization is by functional group, beginning with the simple (alkenes) and progressing to the more complex. Most faculty will agree that students new to the subject and not yet versed in the subtleties of mechanism do better this way. In other words, the *what* of chemistry is generally easier to grasp than the *why*. Within this primary organization, however, I place heavy emphasis on explaining the fundamental mechanistic similarities of reactions. This emphasis is particularly evident in the chapters on carbonyl-group chemistry (Chapters 19–23), where mechanistically related reactions like the aldol and Claisen condensations are covered together. By the time students reach this material, they have seen all the common mechanisms and the value of mechanisms as an organizing principle has become more evident.

The Lead-Off Reaction: Addition of HBr to Alkenes Students usually attach great importance to a text's lead-off reaction because it is the first reaction they see and is discussed in such detail. I use the addition of HBr to an alkene as the lead-off to illustrate general principles of organic chemistry for several reasons: the reaction is relatively straightforward; it involves a common but important functional group; no prior knowledge of stereochemistry or kinetics in needed to understand it; and, most important, it is a *polar* reaction. As such, I believe that electrophilic addition reactions represent a much more useful and realistic introduction to functional-group chemistry than a lead-off such as radical alkane chlorination.

Reaction Mechanisms In the first edition of this book, I introduced an innovative format for explaining reaction mechanisms in which the reaction steps are printed vertically, with the changes taking place in each step described next to the reaction arrow. This format allows a reader to see easily what is occurring at each step without having to flip back and forth between structures and text. Each successive edition has seen an increase in the number and quality of these vertical mechanisms, which are still as fresh and useful as ever.

Organic Synthesis Organic synthesis is treated in this text as a teaching device to help students organize and deal with a large body of factual information—the same skill so critical in medicine. Two sections, the first in Chapter 8 (Alkynes) and the second in Chapter 16 (Chemistry of Benzene), explain the thought processes involved in working synthesis problems and emphasize the value of starting from what is known and logically working backward. In addition, *Focus On* boxes, including The Art of Organic Synthesis, Combinatorial Chemistry, and Enantioselective Synthesis, further underscore the importance and timeliness of synthesis.

Modular Presentation Topics are arranged in a roughly modular way. Thus, certain chapters are grouped together: simple hydrocarbons (Chapters 3–8), spectroscopy (Chapters 12–14), carbonyl-group chemistry (Chapters 19–23), and biomolecules (Chapters 25–29). I believe that this organization brings to these subjects a cohesiveness not found in other texts and allows the instructor the flexibility to teach in an order different from that presented in the book.

Basic Learning Aids In writing and revising this text, I consistently aim for lucid explanations and smooth transitions between paragraphs and between topics. New concepts are introduced only when they are needed, not before, and they are immediately illustrated with concrete examples. Frequent cross-references to earlier material are given, and numerous summaries are provided to draw information together, both within and at the ends of chapters. In addition, the back of this book contains a wealth of material helpful for learning organic chemistry, including a large glossary, an explanation of how to name polyfunctional organic compounds, and answers to all in-text problems. For still further aid, an accompanying *Study Guide and Solutions Manual* gives summaries of name reactions, methods for preparing functional groups, functional-group reactions, and the uses of important reagents.

Changes and Additions for the Seventh Edition

The primary reason for preparing a new edition is to keep the book up to date, both in its scientific coverage and in its pedagogy. My overall aim is always to refine the features that made earlier editions so successful, while adding new ones.

- **The writing** has again been revised at the sentence level, streamlining the presentation, improving explanations, and updating a thousand small details. Several little-used reactions have been deleted (the alkali fusion of arenesulfonic acids to give phenols, for instance), and a few new ones have been added (the Sharpless enantioselective epoxidation of alkenes, for instance).

- Other notable **content changes** are:

  Chapter 2, *Polar Covalent Bonds; Acids and Bases*—A new Section 2.13 on noncovalent interactions has been added.

  Chapter 3, *Organic Compounds: Alkanes and Their Stereochemistry*—The chapter has been revised to focus exclusively on open-chain alkanes.

  Chapter 4, *Organic Compounds: Cycloalkanes and Their Stereochemistry*—The chapter has been revised to focus exclusively on cycloalkanes.

  Chapter 5, *An Overview of Organic Reactions*—A new Section 5.11 comparing biological reactions and laboratory reactions has been added.

Chapter 7, *Alkenes: Reactions and Synthesis*—Alkene epoxidation has been moved to Section 7.8, and Section 7.11 on the biological addition of radicals to alkenes has been substantially expanded.

Chapter 9, *Stereochemistry*—A discussion of chirality at phosphorus and sulfur has been added to Section 9.12, and a discussion of chiral environments has been added to Section 9.14.

Chapter 11, *Reactions of Alkyl Halides: Nucleophilic Substitutions and Eliminations*—A discussion of the E1cB reaction has been added to Section 11.10, and a new Section 11.11 discusses biological elimination reactions.

Chapter 12, *Structure Determination: Mass Spectrometry and Infrared Spectroscopy*—A new Section 12.4 discusses mass spectrometry of biological molecules, focusing on time-of-flight instruments and soft ionization methods such as MALDI.

Chapter 20, *Carboxylic Acids and Nitriles*—A new Section 20.3 discusses biological carboxylic acids and the Henderson–Hasselbalch equation.

Chapter 24, *Amines and Heterocycles*—This chapter now includes a discussion of heterocycles, and a new Section 24.5 on biological amines and the Henderson–Hasselbalch equation has been added.

Chapter 25, *Biomolecules: Carbohydrates*—A new Section 25.7 on the eight essential carbohydrates has been added, and numerous content revisions have been made.

Chapter 26, *Biomolecules: Amino Acids, Peptides, and Proteins*—The chapter has been updated, particularly in its coverage of solid-phase peptide synthesis.

Chapter 27, *Biomolecules: Lipids*—The chapter has been extensively revised, with increased detail on prostaglandins (Section 27.4), terpenoid biosynthesis (Section 27.5), and steroid biosynthesis, (Section 27.7).

Chapter 28, *Biomolecules: Nucleic Acids*—Coverage of heterocyclic chemistry has been moved to Chapter 24.

Chapter 29, *The Organic Chemistry of Metabolic Pathways*—The chapter has been reorganized and extensively revised, with substantially increased detail on important metabolic pathways.

Chapter 30, *Orbitals and Organic Chemistry: Pericyclic Reactions*—All the art in this chapter has been redone.

- **The order of topics** remains basically the same but has been changed to devote Chapter 3 entirely to alkanes and Chapter 4 to cycloalkanes. In addition, epoxides are now introduced in Chapter 7 on alkenes, and coverage of heterocyclic chemistry has been moved to Chapter 24.

- **The problems** within and at the end of each chapter have been reviewed, and approximately 100 new problems have been added, many of which focus on biological chemistry.

- ***Focus On* boxes** at the end of each chapter present interesting applications of organic chemistry relevant to the main chapter subject. Including topics from biology, industry, and day-to-day life, these applications enliven and reinforce the material presented within the chapter. The boxes have been updated, and new ones added, including Where Do Drugs Come From? (Chapter 5),

Green Chemistry (Chapter 11), X-Ray Crystallography (Chapter 22), and Green Chemistry II: Ionic Liquids (Chapter 24).

- **Biologically important molecules and mechanisms** have received particular attention in this edition. Many reactions now show biological counterparts to laboratory examples, many new problems illustrate reactions and mechanisms that occur in living organisms, and enhanced detail is given for major metabolic pathways.

More Features

NEW!

- Why do we have to learn this? I've been asked this question so many times by students that I thought that it would be appropriate to begin each chapter with the answer. The *Why This Chapter?* section is a short paragraph that appears at the end of the introduction to every chapter and tells students why the material about to be covered is important.

NEW!

- Thirteen Key Ideas are highlighted in the book. These include topics pivotal to students' development in organic chemistry, such as Curved Arrows in Reaction Mechanisms (Chapter 5) and Markovnikov's Rule (Chapter 6). These Key Ideas are further reinforced in end-of-chapter problems marked with a ▲ icon. A selection of these problems are also assignable in OWL, denoted by a ■.

- Worked Examples are now titled to give students a frame of reference. Each Worked Example includes a Strategy and a worked-out Solution, and then is followed by problems for students to try on their own. This book has more than 1800 in-text and end-of-chapter problems.

- An overview chapter, *A Preview of Carbonyl Chemistry,* follows Chapter 18 and highlights the author's belief that studying organic chemistry requires both summarizing and looking ahead.

NEW!

Organic KNOWLEDGE TOOLS

- Thorough media integration with Organic Knowledge Tools: ThomsonNOW for Organic Chemistry and Organic OWL are provided to help students practice and test their knowledge of the concepts. ThomsonNOW is an online assessment program for self-study with interactive tutorials. Organic OWL is an online homework learning system. Icons throughout the book direct students to ThomsonNOW at **www.thomsonedu.com**. A fee-based access code is required for Organic OWL.

NEW!

- About 15 to 20 end-of-chapter problems per chapter, denoted with a ■ icon, are assignable in the OWL online homework system. These questions are algorithmically generated, allowing students more practice.

- OWL (Online Web-based Learning) for Organic Chemistry, developed at the University of Massachusetts, Amherst; class-tested by thousands of students; and used by more than 50,000 students, provides fully class-tested questions and tutors in an easy-to-use format. OWL is also customizable and cross-platform. The OWL Online Web-based Learning system provides students with instant grading and feedback on homework problems, modeling questions, and animations to accompany this text. With parameterization, OWL for Organic Chemistry offers nearly 6000 different questions as well as MarvinSketch for viewing and drawing chemical structures.

- A number of the figures are animated in ThomsonNOW. These are designated as **Active Figures** in the figure legends.
- The Visualizing Chemistry Problems that begin the exercises at the end of each chapter offer students an opportunity to see chemistry in a different way by visualizing molecules rather than by simply interpreting structural formulas.
- Summaries and Key Word lists help students by outlining the key concepts of the chapter.
- Summaries of Reactions, at the ends of appropriate chapters, bring together the key reactions from the chapter in one complete list.

Companions to This Text

Supporting instructor materials are available to qualified adopters. Please consult your local Thomson Brooks/Cole representative for details.

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Ancillaries for Students

Study Guide and Solutions Manual, by Susan McMurry, provides answers and explanations to all in-text and end-of-chapter exercises. (0-495-11268-2)

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ThomsonNOW Website To further student understanding, the text features sensible media integration through **ThomsonNOW**, a powerful online learning companion that helps students determine their unique study needs and provides them with individualized resources. This dynamic learning companion combines with the text to provide students with a seamless, integrated learning system. The access code that is required for ThomsonNOW may be included with a new copy of the text or purchased separately. Visit **www.thomsonedu.com** to register for access (or to purchase access) to ThomsonNOW.

OWL for Organic Chemistry, authored by Steve Hixson and Peter Lillya of the University of Massachusetts, Amherst, and William Vining of the State University of New York at Oneonta. Class-tested by thousands of students and used by more than 50,000 students, OWL (Online Web-based Learning) provides fully class-tested content in an easy-to-use format. OWL is also customizable and cross-platform. The OWL Online Web-based Learning system provides students with instant analysis and feedback on homework problems, modeling questions, and animations to accompany this text. With parameterization, OWL for Organic Chemistry offers more than 6000 questions as well as MarvinSketch, a Java applet for viewing and drawing chemical structures.

This powerful system maximizes the students' learning experience and, at the same time, reduces faculty workload and helps facilitate instruction. OWL also uses the MDL Chime application to assist students with viewing structures of organic compounds. New to this edition are 15 to 20 end-of-chapter problems per chapter, denoted by a ■ icon, which are assignable in OWL. A fee-based access code is required for OWL.

Pushing Electrons: A Guide for Students of Organic Chemistry, third edition, by Daniel P. Weeks. A workbook designed to help students learn techniques of electron pushing, its programmed approach emphasizes repetition and active participation. (0-03-020693-6)

NEW! **Spartan Model Electronic Modeling Kit**, A set of easy-to-use builders allow for the construction and 3-D manipulation of molecules of any size or complexity—from a hydrogen atom to DNA and everything in between. This kit includes the SpartanModel software on CD-ROM, an extensive molecular database, 3-D glasses, and a *Tutorial and Users Guide* that includes a wealth of activities to help you get the most out of your course. (0-495-01793-0)

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