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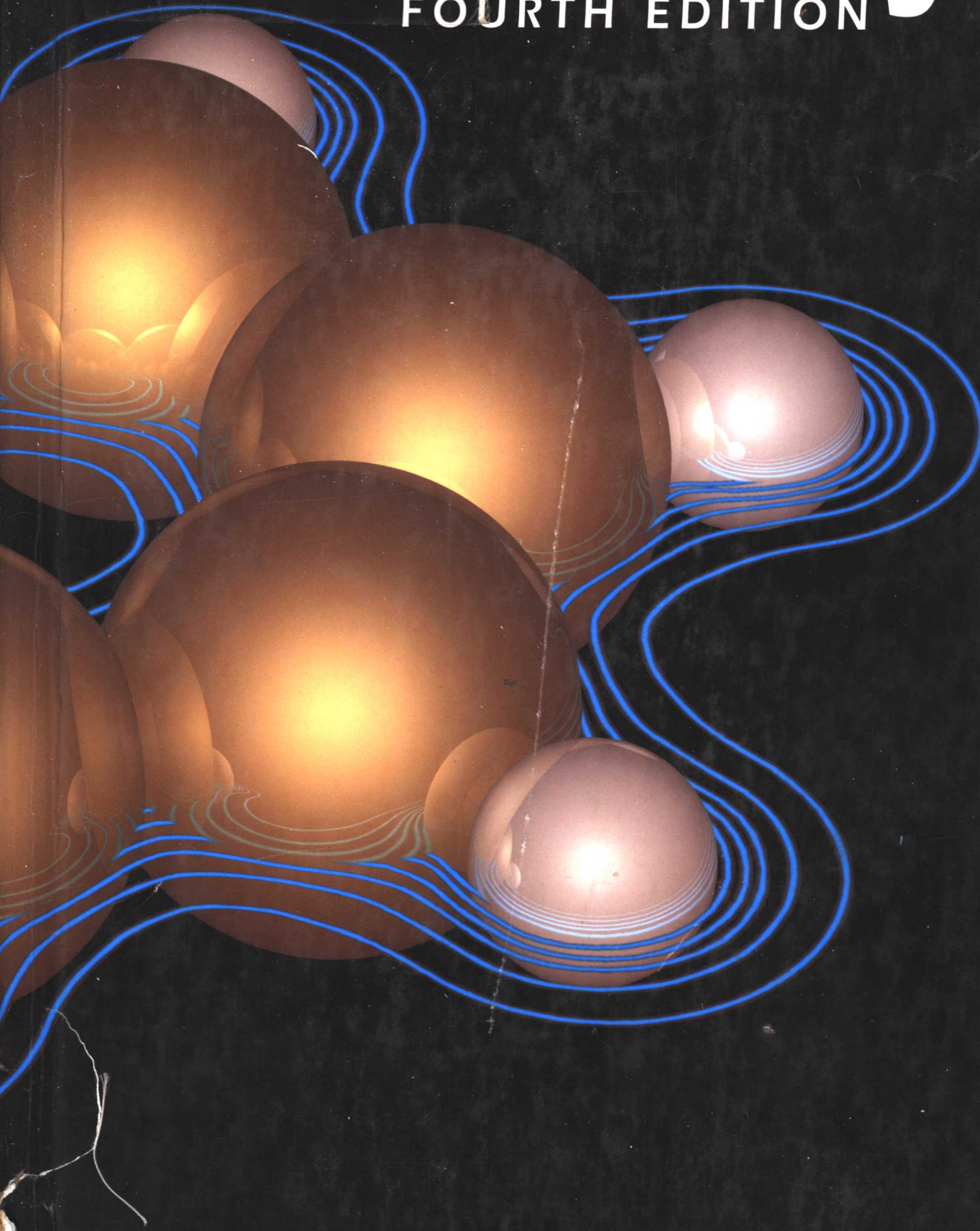
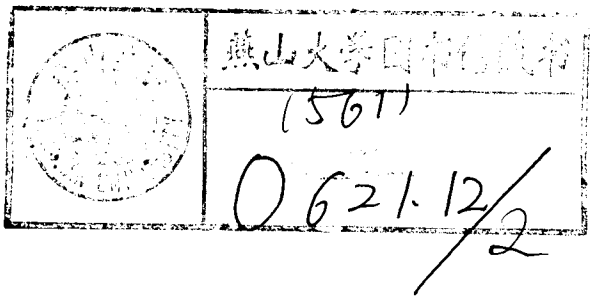
FOURTH EDITION



Organic Chemistry

Fourth Edition

John McMurry
Cornell University



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Preface

I've been asked hundreds of times over the past ten years why I wrote this book. It wasn't because there aren't other perfectly acceptable organic chemistry textbooks out there, and it wasn't because I thought I'd get rich. I wrote this book because I love writing. I get great pleasure and satisfaction from taking a complicated subject, turning it around until I see it clearly from a new angle, 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 tremendous response to three previous editions has been very gratifying and suggests that this book has served students well. I hope you will find that this fourth edition of *Organic Chemistry* builds on the proven strengths of the first three and serves students even better. I have made every effort to make this fourth edition as effective, clear, and readable as possible, to show the beauty and logic of organic chemistry, and to make it enjoyable to learn.

Organization and Teaching Strategies

As in the previous editions, I use a dual organization in this fourth edition, blending the traditional functional-group approach with a mechanistic approach. The primary organization of this book is by functional group, beginning with the simple (alkenes) and progressing to the more complex. Students new to the subject and not yet versed in the subtleties of mechanisms prefer this organization because it is straightforward. In other words, the *what* of chemistry is easier for most new students 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 naturally 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 because it has many advantages: it is relatively straightforward; it involves a common but important functional group; no prior knowledge of chirality or kinetics is needed to understand it; and, most importantly, 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, I introduced an innovative format for explaining reaction mechanisms that met with an enthusiastic response. Now set off by a color panel, mechanisms shown in this format have the reaction steps printed vertically while the changes taking place in each step are explained next to the reaction arrow. This format allows the reader to see easily what is occurring at each step in a reaction without having to jump back and forth between structures and text. Pages 157 and 198 show examples.

Organic Synthesis Organic synthesis is treated as a teaching device that helps students organize and deal with a large body of factual information (the same kind of 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. The value of starting from what is known and logically working backwards is given particular emphasis.

Modular Presentation Topics are arranged in a modular way wherever possible. Thus, the chapters on simple hydrocarbons are grouped together (Chapters 3–8), the chapters on spectroscopy are grouped together (Chapters 12–14), and the chapters on carbonyl-group chemistry are grouped together (Chapters 19–23). 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 this book.

Basic Learning Aids Clarity of explanation and smoothness of information flow are crucial requirements for any textbook. In writing and revising this text, I consistently aim for summary sentences at the beginning of paragraphs, lucid explanations, and smooth transitions between paragraphs and between topics. New concepts are introduced only when they are needed, not before, and are immediately illustrated with concrete examples. Frequent cross-references to earlier (but not later) 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 most in-text problems. For still further aid, an accompanying *Study Guide and Solutions Manual* provides a summary of name reactions, a summary of methods for preparing functional groups, a summary of functional-group reactions, and a summary of the uses of important reagents.

Changes and Additions in the Fourth Edition

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

- **The writing** has again been revised at the sentence level, paying particular attention to such traditionally difficult subjects as stereochemistry and nucleophilic substitution reactions.
- **The artwork** has been redone, and many new computer-generated molecular models have been added to aid in three-dimensional perception. Figures frequently present structures in several different formats, side by side, so that students learn structures thoroughly and become used to the various ways in which chemists graphically represent their work. Look at pages 27 and 121 to see some examples.
- **Stereo views** of computer-generated ball-and-stick molecular models have been added as an aid for three-dimensional perception, using the stereo viewer bound into the back of the book. There are examples on pages 29 and 111.
- **The organic chemistry of metabolic pathways** is presented in an entirely new chapter (Chapter 30). Several of the most important pathways—glycolysis, the citric acid cycle, gluconeogenesis, and others—are dissected and analyzed according to the organic reaction mechanisms by which the various steps occur. This new chapter will be of particular interest to the large number of premedical and biology students who take the organic chemistry course.
- **Interlude boxes** at the end of each chapter present interesting applications of organic chemistry relevant to the main chapter subject. Including topics from science, industry, and day-to-day life, these applications enliven and reinforce the material presented in each chapter. Some Interlude topics address environmental concerns and examine popular assumptions about chlorinated organic compounds or chemical toxins in food and the water supply. Other Interludes discuss such topics as the 1995 announcement of a polyyne form of carbon, the development of insect antifeedants for use as pesticides, a look at the facts about vitamin C, and the chemistry of chiral drugs.

- **Biologically important organic reaction mechanisms** are specially identified by the use of a margin icon. Students often wonder about what topics are "important," and this icon helps biologically inclined students answer that question. See page 412, for example.
- **Spectra** are all new, have been redrawn for clarity and accuracy, and are presented with a light color background, coded by type of spectra. Some examples are on pages 428 and 436.
- **NMR spectroscopy** (Chapter 13) has been completely revised and updated. Proton NMR spectroscopy is now presented first, and the use of the DEPT technique for carbon NMR is emphasized.
- **New problems** have been added at the end of each chapter, including a new kind of problem called "A Look Ahead," in which students are challenged to extend their thinking by applying concepts just learned in one chapter to the subject of a future chapter.
- **A review of reaction mechanisms** is given in a new Appendix C in which mechanisms are referenced to their presentation in the main text.

To facilitate the changes outlined above, some material from the previous edition has been compressed, several infrequently used reactions (such as the Hunsdiecker reaction) have been deleted, and other material has been moved. The material on polymer chemistry, formerly in a late, separate chapter, is now integrated into Chapters 7, 14, and 21 to ensure its coverage.

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For Students

Study Guide and Solutions Manual
by Susan McMurry
- Includes answers to all in-text and end-of-chapter problems and explains in detail how answers are obtained.
- Also contains a summary of name reactions, a summary of methods for preparing functional groups, a summary of functional-group reactions, a summary of the uses of important reagents, and tables of spectroscopic information.

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- A text-specific program for constructing molecular models, drawing Lewis dot structures, creating animations of reactions, solving chemistry problems, and studying structures.
- Available for DOS/Windows and Macintosh platforms.

Acknowledgments

It is a great pleasure to thank the many people whose help and suggestions were so valuable in preparing this fourth edition. Foremost is my wife, Susan, who read, criticized, and improved the manuscript, and who was my constant companion throughout all stages of this book's development. Among the reviewers providing valuable comments were Clair Cheer, San Jose State University; Dale Drueckhammer, Stanford University; Douglas Dyckes, University of Colorado, Denver; Kent Gates, University of Missouri, Columbia; Dan Harvey, University of California, San Diego; John Hogg, Texas A & M University; Jack Kampmeier, University of Rochester; John A. Landgrebe, University of Kansas; James Long, University of Oregon; Guy Mattson, University of Central Florida; David McKinnon, University of Manitoba; Kirk McMichael, Washington State University; Roger Murray, University of Delaware; Carmelo Rizzo, Vanderbilt University; Peter W. Slade, University College of Fraser Valley; Ronald Starkey, University of Wisconsin, Green Bay; J. William Suggs, Brown University; Michelle Sulikowski, Texas A & M University; Joyce Takahashi, University of California, Davis; Bruce Toder, State University of New York, Brockport; and Barbara J. Whitlock, University of Wisconsin, Madison.

A Note for Students

We have the same goals. Yours is to learn organic chemistry; mine is to help you learn. I've already done the best I can with my part, and now it's going to take some work from you. The following suggestions should prove helpful.

- **Don't Read the Text Immediately.** As you begin each new chapter, look it over first. Read the introductory paragraphs, find out what topics will be covered, and then turn to the end of the chapter and read the summary. You'll be in a much better position to learn the material if you know where you're going.
- **Work the Problems.** There are no shortcuts; working problems is the only way to learn organic chemistry. The practice problems show you how to approach the material, the in-text problems at the ends of most sections provide immediate practice, and the end-of-chapter problems provide both additional drill as well as some real challenges. Short answers to in-text problems are given at the back of the book; full answers and explanations for all problems are given in the accompanying *Study Guide and Solutions Manual.*
- **Use the Study Guide.** The *Study Guide and Solutions Manual* that accompanies this text gives complete solutions to all problems as well as a wealth of supplementary material. Included are a summary of how to prepare functional groups, a summary of the reactions that functional groups undergo, a summary of important reagents, a summary of name reactions, and much more. This material can be extremely useful, both as a source of information and as a self-test, particularly when you're studying for an exam. Find out now what's there so you'll know where to go when you need help.
- **Ask Questions.** Faculty members and teaching assistants are there to help you. Most of them will turn out to be genuinely nice people with a sincere interest in helping you learn.
- **Use Molecular Models.** Organic chemistry is a three-dimensional science. Although this book uses stereo views and many careful drawings to help you visualize molecules, there's no substitute for building a molecular model and turning it around in your own hands.

Good luck! I sincerely hope you enjoy learning organic chemistry and come to see the beauty and logic of its structure. I've heard from many students who used the first three editions of this book and would be glad to receive more comments and suggestions from those who use this new edition.

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On the Cover: A molecular model of benzene showing electrostatic potential in the equatorial plane of the molecule (gold = carbon, white = hydrogen). The isobars, which denote electrostatic potential much as the contour lines on a geographic map denote altitude, were calculated using the AM1 semi-empirical method and later smoothed.

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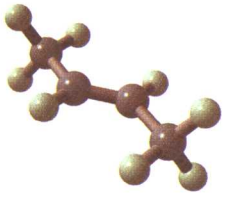

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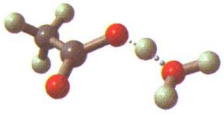

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