

# Organic Chemistry



John  
McMurry  
FIFTH EDITION

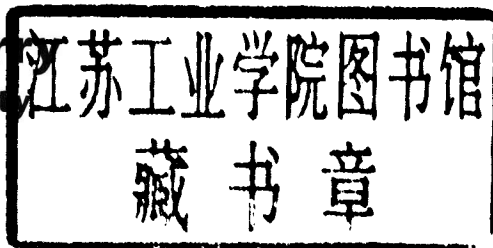
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# Organic Chemistry

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Fifth Edition

John McMurry  
Cornell University



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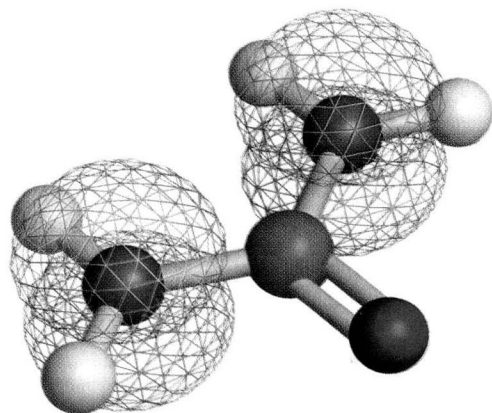
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# Organic Chemistry

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# Preface

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I wrote this book for one simple reason: 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 enthusiastic response to the four previous editions has been very gratifying and suggests that this book has served students well. I hope you will find that this fifth edition of *Organic Chemistry* builds on the strengths of the first four and serves students even better. I have made every effort to make this 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

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This fifth edition, like its predecessors, uses a dual organization that 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. Students new to the subject and not yet versed in the subtleties of mechanisms do better with this organization because it is straightforward. In other words, the *what* of chemistry is easier for most 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 for several reasons: It is relatively straightforward; it involves a common but important functional group; no prior knowledge of stereochemistry 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 in which the reaction steps are printed vertically while the changes taking place in each step are explained next to the reaction arrow. This format allows a reader to see easily what is occurring at each step in a reaction without having to flip back and forth between structures and text. This edition has numerous additional vertical mechanisms, all set off by an orange background.

**Organic Synthesis** Organic synthesis is treated in this text as a teaching device that helps 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 (Benzene), explain the thought processes involved in working synthesis problems and emphasize the value of starting from what is known and logically working backwards. In addition, new CHEMISTRY@WORK boxes on “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, 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 the 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* gives 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 for the Fifth 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 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, streamlining the presentation, improving explanations, and updating a thousand small



details. Some reactions have been deleted (the Clemmensen reduction, for instance), and a few new ones have been added (the synthesis of phenols from diazonium salts and the glycal-assembly method of polysaccharide synthesis, for instance).

Particularly noticeable are the changes in Chapter 2. A much expanded coverage of resonance structures has been added (Section 2.6), along with a useful new technique for generating resonance structures. A new section on acid–base strength (Section 2.8), another new section on organic acids and bases (Section 2.10), and a new section introducing the curved-arrow formalism (Section 2.11) have been added. The use of curved arrows for mechanisms is further reinforced several chapters later in a new Section 5.6.

Still other changes include the revised coverage of NMR in Chapter 13 to present  $^{13}\text{C}$  before  $^1\text{H}$  spectroscopy, and a return to the “steering-wheel” method of assigning *R,S* configuration to chirality centers in Chapter 9.

- **The order of topics**, while remaining basically the same, has been changed to move the coverage of phenols from Chapter 25 to Chapter 17, where it now appears along with the discussion of alcohols. In addition, the coverage of both alkylamines and arylamines has been integrated into a single new Chapter 24, and a new Chapter 31 on polymer chemistry has been added.
- **The problems** within each chapter and at the end of each chapter have been redone, and nearly 25% of them are new. Particularly noticeable are the new problem sections called “Visualizing Chemistry,” in which substances are shown as molecular models rather than as typical line structures. These questions are a good deal more challenging than they initially appear, and they provide excellent practice for thinking about chemistry on the atomic level. In addition, all chapters now end with a selection of problems that give students a chance to do their own molecular modeling using the accompanying SpartanView and SpartanBuild software from Wavefunction, Inc.
- **Practice problems** are more numerous in this edition and have been rewritten to make them more useful. They now begin with a “Strategy” discussion that focuses on general approaches to problem solving and on the thought processes used for finding solutions.
- **The artwork** has been completely redone, and a great many new computer-generated models have been added. The use of stereo views to facilitate three-dimensional perception of ball-and-stick molecular models was introduced in the fourth edition, and their number has been nearly doubled in this fifth edition. As before, a stereo viewer is bound into the back of the book.
- **Molecular modeling** receives greatly increased emphasis in this new edition. In addition to the large number of new ball-and-stick models and stereo views, there are approximately 90 images produced using SpartanView molecular modeling software from Wavefunction, Inc. Particularly useful are the many electrostatic potential maps, which show the calculated regions

of positive and negative charge within a molecule, thereby emphasizing the nucleophilic/electrophilic character of various functional groups. Many further images and animations are included on the accompanying CD-ROM, and problems at the end of each chapter, developed by Alan Shusterman and Warren Hehre for this edition, provide additional practice in using molecular modeling as a tool for learning organic chemistry.

- **CHEMISTRY@WORK 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 within the chapter. Topics new to this edition include “The Art of Organic Synthesis,” “Combinatorial Chemistry,” “Enantioselective Synthesis,” “DNA Fingerprinting,” and “Biodegradable Polymers.”
- **Biomolecules** have received particular attention in this edition to assure that coverage is up-to-date. Chapter 25, for instance, contains new material on the synthesis of polysaccharides (Section 25.10) and other new material on carbohydrate-based vaccines (Section 25.12). Chapter 26 contains a new section on the mechanism of enzyme action, using citrate synthase as the example (Section 26.16), and Chapter 27 contains updated material on cholesterol biosynthesis and on prostaglandins, including a discussion of the recently introduced COX-2 inhibitors. Finally, all the material on nucleic acids in Chapter 28 has been updated, with special treatment of the very latest DNA sequencing technology.
- **Polymer chemistry** is now drawn together in a new Chapter 31. Although much polymer chemistry is still interspersed throughout the text to ensure its full coverage, the new chapter brings a cohesiveness to the subject and makes it possible to relate structure with general physical properties.
- **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.
- **The biographies** of the chemists for whom so many organic reactions are named have been expanded. Rather than simply provide dry biographical data, more humanizing, sometimes offbeat, details of the lives of famous chemists have now been added.



## A Complete Ancillary Package

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*Organic Chemistry*, Fifth Edition, is supported by a complete set of ancillaries. Each piece has been designed to enhance student understanding. The following resources are available, free of charge, to adopters of the text.

**Printed Test Items** Over 1000 multiple-choice and matching questions, with detailed answers, in preprinted test forms corresponding to the main

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**<http://www.brookscole.com/chemistry>** At Brooks/Cole's Web site for chemistry, instructors and students can access a homepage for *Organic Chemistry*, Fifth Edition. All information is arranged according to the *Organic Chemistry* table of contents. Students can access flash cards for all glossary terms, practice quizzes for every chapter, and hyperlinks that relate to each chapter's contents. Instructors can download additional questions by chapter that require the use of either ChemOffice or HyperChem. In addition, students can research the accomplishments of past and present contributors to the field of chemistry in timeline format.

### **Student Resources**

A complete range of student ancillaries is also available, including print, CD-ROM, and online resources.

**Study Guide and Solutions Manual** Written by Susan McMurry, this manual provides answers and explanations for all in-text and end-of-chapter exercises. It also includes summaries of name reactions, functional-group synthesis and reactions, lists of reagents and abbreviations, and articles on topics ranging from infrared absorption frequencies to Nobel Prize winners in chemistry. This edition now includes all new artwork, expanded in-text problems, summary quizzes approximately every three chapters, more detailed explanations in solutions, and chapter outlines. ISBN 0-534-37192-2



**Organic Chemistry Online 2.0; and Wavefunction's SpartanBuild and SpartanView** This CD-ROM is included with this text and contains rich resources for problem solving, molecular visualization, and model building. *Organic Chemistry Online 2.0*, developed by Paul R. Young, contains a library of over 400 compounds commonly used in a lab, with Web links to a variety of databases such as NIST, NTP, MSDS, and IRIS; over 100 digitized spectra; 30 mechanisms and movies; extensive tutorials including electron pushing tutorials; and sample MCAT questions. In addition, it includes two professional software tools, SpartanView and SpartanBuild, from Wavefunction, for solving end-of-chapter molecular modeling problems in the main text. Spartan material for the text was developed by Alan Shusterman and Warren Hehre. ISBN 0-534-37364-X



**Organic Chemistry Online 2.0 Workbook** Written by Paul R. Young, this student workbook focuses on problem solving, and provides additional help, exercises, and practice problems corresponding to *Organic Chemistry Online 2.0* as well as supplemental topic information for a wide variety of organic compounds and reactions. ISBN 0-534-37191-4

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**Organic Chemistry Toolbox** This electronic study guide provides tutorials for the main concepts of the course—structure, nomenclature, reactions, bioorganic, and spectroscopy. The following visualization tools are included: a molecular modeler, a Lewis-dot structure drawing tool that can check formulas, reaction animation, a way to test knowledge of reactions, and spectral manipulation for infrared and  $^1\text{H}$  and  $^{13}\text{C}$  NMR. ISBN 0-534-35207-3

**Beaker™** This sophisticated yet easy-to-use software allows students to explore organic chemistry principles, study and solve problems, and sketch and analyze molecules. Using Beaker™ students can draw a molecule or simply type in an IUPAC name and let the software do the drawing. Beaker™ 2.1 for Macintosh ISBN 0-534-15973-7, Beaker™ 2.2 for Windows ISBN 0-534-13410-6

## Acknowledgments

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# A Note for Students

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We have the same goals. Yours is to learn organic chemistry; mine is to help you learn. I've 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 read the summary at the end of the chapter. 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 and some real challenges. Pay particular attention to the "Visualizing Chemistry" problems, which can help you begin to "see" molecules rather than think of them as vague abstractions. 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 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.
- **Use the Organic Chemistry Online CD and the Wavefunction Molecular Modeling Software Included with This Book** Both provide alternative, nontextual ways of approaching chemistry, using reaction animations and other computer-based approaches to learning.

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