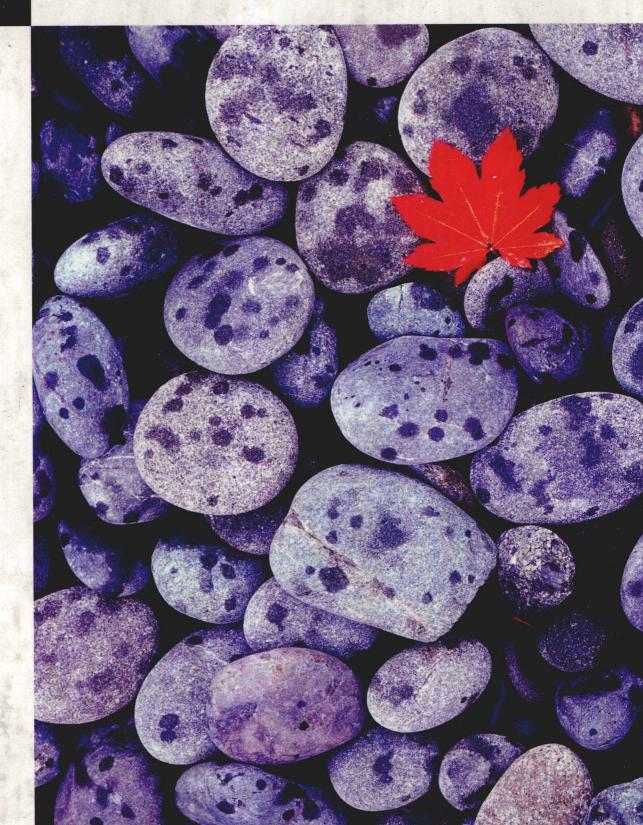
# Organic Chemistry





# Organic Chemistry

Sixth Edition

John McMurry

Cornell University





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Printed in the United States of America 4 5 6 7 07 06 05 04

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#### Library of Congress Control Number: 2002111603

Student Edition with InfoTrac College Edition: ISBN 0-534-38999-6

Preview Book: ISBN 0-534-42003-6

International Student Edition: ISBN 0-534-42005-2 (not for sale in the United States)

Production Service: Graphic World Inc.
Text Designer: Patrick Devine Design
Photo Researcher: Stuart Kenter

Copy Editor: Graphic World Inc. Illustrators: Academy Artworks,

Dovetail Publishing Services, Graphic World Inc.

Cover Designer: Patrick Devine Design Cover Image: Grant V. Faint/Getty Images

Cover Printer: Lehigh Press
Compositor: Graphic World Inc.
Text Printer: R.R. Donnelley/Willard

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#### **Preface**

I wrote this book for the simple reason that I love writing. I get real pleasure 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 five previous editions has been very gratifying and suggests that this book has served students well. I hope you will find that this sixth edition of *Organic Chemistry* builds on the strengths of the first five and serves students even better. I have made every effort to make this sixth 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 This sixth 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 mechanism 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 a 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 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, 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. Now set off by a colored screen, each successive edition has seen an increase in the number of these vertical mechanisms.

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 (Aromatic Compounds), 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, 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 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 Sixth Edition



The primary reason for preparing a new edition is to keep the book up-todate, 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.

In addition, the Sixth Edition is supported by an unparalleled array of technology teaching and learning tools. The way icon in the text leads students to a variety of new online resources, including **Organic Chemistry Direct** (accessible at <a href="http://chemistry.brookscole.com/mcmurry6e">http://chemistry.brookscole.com/mcmurry6e</a>), which is the first assessment-centered system to help organic chemistry students determine their unique study needs by providing them with individualized resources. The text is also supported by an electronic homework and assessment system called Organic Chemistry Direct Powered by OWL.

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 reduction of acid chlorides to aldehydes, for instance), and a few new ones have been added (the Knowles enantioselective synthesis of amino acids, for instance). Changes are particularly noticeable in:

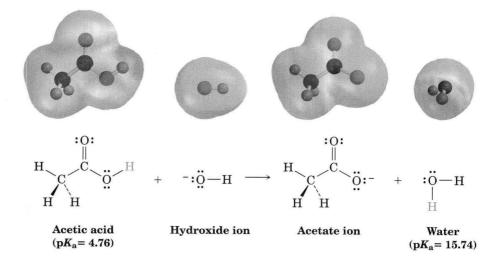
■ Chapter 2, where Section 2.10 on organic acids and bases has been enhanced to include biological acids.

- Chapter 9, where a new Section 9.19 discusses prochirality.
- Chapter 13, where a new Section 13.8 covers the NMR behavior of homotopic, enantiotopic, and diastereotopic hydrogens.
- Chapter 14, where a new Section 14.11 on the chemistry of vision has been added.
- Chapter 20, where Section 20.9 now covers the chemistry of nitriles.
- Chapter 21, where Section 21.8 now covers biological acyl phosphates as well as thioesters.
- Chapter 26, where a new Section 26.4 covers the enantioselective synthesis of amino acids.
- Chapter 27, where Sections 27.6 on terpenoid biosynthesis and Section 27.9 on steroid biosynthesis have been expanded and updated.
- Chapter 29, where Sections 29.2, 29.5, and 29.7 on metabolic pathways have been substantially expanded and more stereochemical detail of individual steps has been included.

The order of topics remains basically the same but has been changed to move the coverage of nitriles from Chapter 21 to Chapter 20, where it now appears along with the discussion of carboxylic acids. In addition, Chapter 14, on Dienes, has been reorganized, with the Diels-Alder reaction placed more prominently.

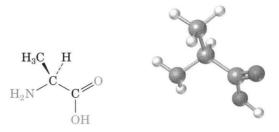
The problems within and at the end of each chapter have been reviewed, and approximately 100 new problems have been added. Particularly noticeable is the increase in visualization problems based either on molecular models or on interpreting the polarity patterns evident in electrostatic potential maps.

**Molecular modeling** receives further emphasis in this new edition, particularly with respect to electrostatic potential maps. These maps show the calculated regions of positive and negative charge within a molecule, thereby emphasizing the nucleophilic/electrophilic character of various functional groups.



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. All the boxes have been updated, and several have been completely rewritten. In addition, students are now prompted by the www icon to view corresponding *CNN* videos at Organic Chemistry Direct and to explore Web links correlated to the topic at hand, expanding learning into a multimedia environment, and illustrating organic chemistry in action in the real world.

Biologically important molecules and mechanisms have received particular attention in this edition. Chapter 2, for instance, contains new material on biological acids and bases (Section 2.10). Chapter 5 contains a discussion of reaction energy diagrams in biological reactions (Section 5.9). Chapter 9 introduces the concept of prochirality, particularly as it applies to biological molecules (Section 9.19). Chapter 21 has added coverage on acyl phosphates (Section 21.8). Chapter 26 now discusses the Knowles enantioselective method of amino acid synthesis (Section 26.4). Chapter 27 has a greatly expanded coverage of terpenoid biosynthesis (Section 27.5) and cholesterol biosynthesis (Section 27.9). Finally, Chapter 29 has been rewritten to provide substantially more detail on the mechanisms and stereochemistry of individual steps in important metabolic pathways (Sections 29.2, 29.5, and 29.7).



Alanine, an amino acid



A unique, class-tested electronic homework and assessment system called **Organic Chemistry Direct Powered by OWL** contains the following features:

- Molecular Structure Building exercises and problems that allow you to test your students' understanding of molecular structure.
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- An automatic grading system allows you to easily grade students by pass/fail or percentages. You can also alter existing content and create your own questions.

#### **Features**

- More than 150 new electrostatic potential maps are placed throughout the text, providing students with a vibrant portrayal of electron density within a molecule. These maps emphasize the polarity patterns in organic functional groups and the importance of these patterns for chemical reactivity.
- Engaging biographies of the chemists for whom so many organic reactions are named are included to humanize the discipline, such as Stanislao Cannizzaro in Chapter 19, and Roger Adams and H. C. Brown in Chapter 7.
- Consistent color is used in displayed reactions to show the progress of the reactions more clearly.
- More than 1800 in-text and end-of-chapter problems are included to give students ample practice with problem solving. *Visualizing Chemistry* problems help students match structural formulas with ball-and-stick models and enhance students' ability to bridge the gap between the microscopic level of molecules and the macroscopic level of daily life. *A Look Ahead* problems bridge the concepts learned in a chapter with future chapters.
- In-text practice problems are designed with strategies for how to tackle a problem in organic chemistry.
- Chemistry@Work essays highlight important applications of organic chemistry in the real world, such as the new interludes, Terpenes: Naturally Occurring Alkenes in Chapter 6 and Unusual Elements in Organic Chemistry in Chapter 22. Many of these essays are linked to CNN videos at Organic Chemistry Direct http://chemistry.brookscole.com/mcmurry6e.
- Summaries and Key Word lists help students by outlining the key concepts of the chapter.
- Summary of Reactions brings together all the key reactions from the chapter in one complete list.

#### KEY IDEAS

- Key Ideas are highlighted in the text with this icon to further reinforce major topics.
- Mechanisms are consistently designed for easy identification and use Mc-Murry's copyrighted vertical format.
- Two overview chapters highlight McMurry's ideas that studying organic chemistry requires constant summarizing and looking ahead. They include A Brief Review of Organic Reactions (following Chapter 16) and A Preview of Carbonyl Compounds (preceding Chapter 19).



■ Because so many of the students in the course are on a premedical track and taking biology courses concurrently, Biological Connections were added to reinforce organic chemistry as a discipline associated with other sciences.



- The World Wide Web icon alerts students to use Organic Chemistry Direct (accessible at http://chemistry.brookscole.com/mcmurry6e) for additional problems and tutorials associated with the text.
- A new design and layout gives the book a more aesthetically pleasing look.

#### A Complete Support Package

#### For Students

*Study Guide and Solutions Manual* by Susan McMurry, Cornell University This manual provides answers and explanations for all in-text and end-of-chapter exercises. It also includes self-tests, chapter outlines, summaries of name reactions, functional-group synthesis and reactions, and lists of reagents and abbreviations. (0-534-40934-2)

NEW!



Organic Chemistry Direct at http://chemistry.brookscole.com/mcmurry6e is the first assessment-centered system to help organic chemistry students determine their unique study needs and provide them with individualized resources designed to enhance their conceptual and problem-solving skills. For example, a student may enter Organic Chemistry Direct to review his or her general understanding of reaction mechanisms. The student answers a series of diagnostic review questions created by David Collard, Georgia Institute of Technology, to create a personalized study plan. If the student answers one of these review problems incorrectly, he or she may be directed, depending on the question, to a substitution and elimination tutorial and corresponding text files. In one unique environment, the text, problems, and media are all integrated! Developed in association with Paul R. Young, University of Illinois, Chicago, Organic Chemistry Direct also contains a library of more than 400 compounds commonly used in a lab, with additional links to a variety of databases such a NIST, NTM, MSDS, and IRIS; more than 100 digitalized tutorials, including electron pushing tutorials; and sample MCAT questions. Media flags in the text alert students to the corresponding animations and tutorials available at Organic Chemistry Direct.

NEW/



Organic Chemistry Direct Powered by OWL This fully integrated testing, tutorial, and course-management software is accessible by instructors and students via a browser-based format. The assessment portion features more than 1000 Problem Solving practice problems, as well as Hot Topic essay questions. The homework system provides students with instant analysis and feedback to quizzes, modeling questions, animations created specifically for the text, and more and is accessible to students via the Web. With this unique class-tested system, students can construct gradeable molecular structures. Feedback to problems supports the approach of the text. (Passcode is required for access. Please contact your Thomson • Brooks/Cole sales representative for details.)

Interactive Organic Chemistry CD-ROM 2.0 with Workbook by William J. Vining and Vincent Rotello, University of Massachusetts This dual-platform tutorial CD-ROM included six modules to help students learn organic chemistry in an interactive fashion. The modules include mechanisms, Nomenclature, Reactivity Explorer, Multistep Synthesis, Spectroscopy, and Supporting Concepts. (0-03-033481-0)

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



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#### For Instructors

These ancillary materials are available to qualified adopters. Please consult your local Thomson • Brooks/Cole sales representative for details.

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#### **Acknowledgments**

It is my great pleasure to thank the many people whose help and suggestions were so valuable in preparing this sixth edition. Foremost is my wife, Susan, whose critical eye and expertise greatly improved this manuscript.

Particular thanks go to Erik Simanek of Texas A & M University, who served as an accuracy reviewer reading all the page proofs and to the staff at Brooks/Cole, including senior developmental editor Sandi Kiselica and publisher David Harris.

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Chapter	Organic Interactive	Organic Process	Active Figure
Chapter 1 Structure and Bonding	Identifying Hybridization		• Figure 1.10 • Figure 1.11
Chapter 2 Polar Covalent Bonds; Acids and Bases	<ul><li>Calculation of Formal Changes</li><li>Drawing Resonance Forms</li><li>Drawing Chemical Structures</li></ul>		• Figure 2.5 • Figure 2.6
Chapter 3 Organic Compounds: Alkanes and Cycloalkanes	<ul> <li>Identifying Functional Groups</li> <li>Recognizing Isomerism</li> <li>Drawing Structures from IUPAC Names—Alkanes</li> <li>Drawing Structures from IUPAC Names—Cycloalkanes</li> </ul>		• Figure 3.4 • Figure 3.5
Chapter 4 Stereochemistry of Alkanes and Cycloalkanes	Conformational Analysis     Conformations of     Cyclohexanes		• Figure 4.5 • Figure 4.21
Chapter 5 An Overview of Organic Reactions	<ul> <li>Identifying Reaction Types</li> <li>Identification of Nucleophilic and Electrophilic Centers</li> <li>Polar Reaction Mechanisms</li> <li>Bond Dissociation Energies</li> </ul>	Addition of HBr to an Alkene	• Figure 5.5 • Figure 5.6
Chapter 6 Alkenes: Structure and Reactivity	<ul> <li>Calculating Degrees of         Unsaturation</li> <li>Drawing Structures from         IUPAC Names—Based on         Nomenclature</li> <li>E,Z Sequence Rules</li> <li>Addition of HX to Alkenes</li> <li>Markovnikov Regiochemistry</li> <li>Predicting Carbocation Stability</li> <li>Carbocation Rearrangements</li> </ul>	Addition of HCl to 2-Methylpropene	• Figure 6.14
Chapter 7 Alkenes: Reactions and Synthesis	Addition of Halogens to Alkenes     Oxymercuration of Alkenes     Reduction of Alkenes	<ul> <li>Addition of Br<sub>2</sub> to an Alkene</li> <li>Formation of a Bromonium Ion</li> <li>Addition of HOBr to an Alkene</li> <li>Addition of BH<sub>3</sub> to an Alkene</li> <li>Reaction of Dichlorocarbene with an Alkene</li> </ul>	• Figure 7.5 • Figure 7.6



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Chapter	Organic Interactive	Organic Process	Active Figure
Chapter 8 Alkynes: An Introduction to Organic Synthesis	<ul> <li>Addition of HX and Halogens to Alkynes</li> <li>Enol Interconversion</li> <li>Alkylation of Alkyne Anions</li> </ul>	S <sub>N</sub> 2 Reaction Between Acetylide Anion and Chloromethane	• Figure 8.6
Chapter 9 Stereochemistry	<ul> <li>R,S Sequence Rules</li> <li>Determining R,S Sequence in Organic Molecules</li> <li>Alkene Addition Reactions Generating Chiral Centers</li> </ul>		<ul><li>Figure 9.16</li><li>Figure 9.17</li></ul>
<b>Chapter 10</b> Alkyl Halides	<ul> <li>Drawing Structures from IUPAC Names—Alkyl Halides</li> <li>Synthesis of Alkyl Halides</li> <li>Organometallic Reagents</li> </ul>		• Figure 10.3 • Figure 10.4
Chapter 11 Reactions of Alkyl Halides: Nucleophilic Substitutions and Eliminations	<ul> <li>S<sub>N</sub>2 Reactions</li> <li>Elimination Reactions</li> <li>Substitution and Elimination in Synthesis</li> </ul>	Stereochemistry of the S <sub>N</sub> 2 Reaction The S <sub>N</sub> 1 Reaction of 2-Methyl-2-propanol with HCl The S <sub>N</sub> 1 Solvolysis of 2-Methyl-2-chloropropane Mechanism of the E2 Elimination Reaction Mechanism of the E1 Elimination Reaction	• Figure 11.20
Chapter 12 Structure Determination: Mass Spectrometry and Infared Spectroscopy	Mass Spectrometry     Infrared Spectroscopy		• Figure 12.4 • Figure 12.5
Chapter 13 Structure Determination: Nuclear Magnetic Resonance Spectroscopy	• <sup>13</sup> C NMR Spectroscopy • <sup>1</sup> H NMR Spectroscopy		• Figure 13.3 • Figure 13.19
Chapter 14 Conjugated Dienes and Ultraviolet Spectroscopy	Electrophilic Additions     to Conjugated Dienes     Cycloaddition Reactions		• Figure 14.2 • Figure 14.3
<b>Chapter 15</b> Benzene and Aromaticity	Drawing Structures from IUPAC Names—Arenes     Aromaticity		<ul><li>Figure 15.4</li><li>Figure 15.5</li><li>Figure 15.11</li></ul>



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Chapter	Organic Interactive	Organic Process	Active Figure
Chapter 16 Chemistry of Benzene: Electrophilic Aromatic Substitution	<ul> <li>Mechanisms of Electrophilic Aromatic Substitution</li> <li>Electrophilic Aromatic Substitution</li> <li>Nucleophilic Aromatic Substitution</li> <li>Oxidation and Reduction of Aromatic Compounds</li> </ul>	Electrophilic Aromatic Substitution     Nucleophilic Aromatic Substitution	• Figure 16.10
Chapter 17 Alcohols and Phenols	<ul> <li>Drawing Structures from IUPAC Names—Alcohols</li> <li>Grignard Reactions</li> <li>Reactions of Alcohols</li> <li>Reactions of Phenols</li> </ul>	<ul> <li>Acid-Catalyzed Dehydration of an Alcohol</li> <li>Dehydration of an Alcohol with POCl<sub>3</sub></li> </ul>	• Figure 17.8
Chapter 18 Ethers and Epoxides; Thiols and Sulfides	<ul> <li>Drawing Structures from IUPAC Names—Ethers</li> <li>Reactions Yielding Ethers</li> <li>Reactions of Ethers and Epoxides</li> </ul>		• Figure 18.1 • Figure 18.2
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