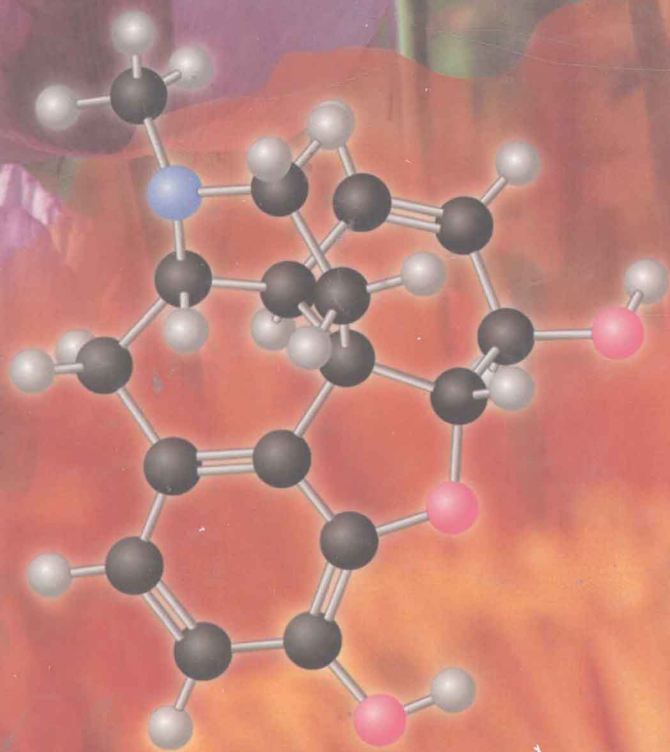


BROWN



# ORGANIC CHEMISTRY

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duction to  
**ORGANIC CHEMISTRY**

SECOND EDITION

**William H. Brown**  
*Beloit College*



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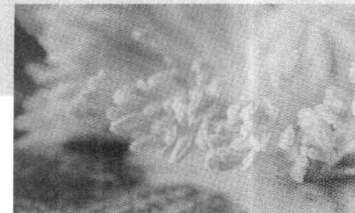
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# ABOUT THE AUTHOR



**W**illiam H. Brown is Professor of Chemistry at Beloit College, where he has twice been named Teacher of the Year. He is also the author of the college textbook *Organic Chemistry*, 2nd edition, published in 1998. His regular teaching responsibilities include organic chemistry, advanced organic chemistry, and, more recently, special topics in pharmacology and drug synthesis. He received his Ph.D. from Columbia University under the direction of Gilbert Stork and did postdoctoral work at California Institute of Technology and the University of Arizona.

Bill and his wife Carolyn enjoy hiking in the Southwest and the study of petroglyphs and pictographs. Twice he has been the Director of Beloit College's World Outlook Seminar, a program coordinated with the University of Glasgow in Scotland.



Bill Brown in Capitol Reef National Park, Utah (Carolyn S. Simonton)



# PREFACE



## THE AUDIENCE

This book provides an introduction to organic chemistry for students who are aiming toward careers in the sciences and who require a grounding in organic chemistry. For this reason, special effort is made throughout to show the interrelation between organic chemistry and other areas, particularly the biological and health sciences. While studying with this book, students will see that organic chemistry is a tool for these many disciplines and that organic compounds, both natural and synthetic, are all around us—in pharmaceuticals, plastics, fibers, agrochemicals, surface coatings, toiletry preparations and cosmetics, food additives, adhesives, and elastomers. Furthermore, students will experience that organic chemistry in a dynamic and ever-expanding area of science waiting openly for those who are prepared, both by training and inquisitive nature, to ask questions and to explore.

## ORGANIZATION: AN OVERVIEW

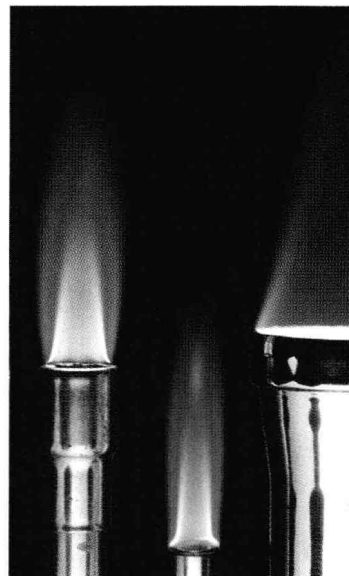
Chapters 1–14 lay a foundation for studying organic chemistry by first reviewing the fundamentals of covalent bonding, the shapes of molecules, and of acid/base chemistry. The structures and typical reactions of the important classes of organic compounds are then discussed; alkanes, alkenes, alcohols, benzene and its derivatives, amines, aldehydes, ketones, and finally carboxylic acids and their derivatives. Chapter 15 provides a brief introduction to organic polymer chemistry.

Chapters 16–20 present an introduction to the organic chemistry of carbohydrates, lipids, amino acids and proteins, and nucleic acids. Chapter 20, The Organic Chemistry of Metabolism, demonstrates how the chemistry developed to this point can be applied to an understanding of two major metabolic pathways— $\beta$ -oxidation of fatty acids and glycolysis.

Chapters 21–22 introduce  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, and IR spectroscopy. Discussions of spectroscopy require no more background than what students receive in general chemistry. These chapters are free-standing, and can be taken up in any order appropriate to a particular course. In the end-of-chapter problems of each functional group chapter, references are given to the appropriate end-of-chapter problems in the spectroscopy chapters.

## Chapter-by-Chapter

Chapter 1 begins with a review of the electronic structure of atoms and molecules, and the use of the VSEPR model to predict shapes of molecules and polyatomic





ions. The theory of resonance is introduced midway through Chapter 1 and, with it, the use of curved arrows and electron pushing. A knowledge of resonance theory combined with a facility for pushing electrons gives students two powerful tools for writing reaction mechanisms and understanding chemical reactivity. The discussion of resonance is followed by an introduction to the valence bond description of covalent bonding. Chapter 1 concludes with an introduction to the hydroxyl, carbonyl, carboxyl, and amino groups, the functional groups encountered most frequently in Chapters 1–14.

Chapter 2 contains a general introduction to acid-base chemistry and concentrates on two major themes. The first is the qualitative determination of the position of equilibrium in acid-base reactions. The second theme is the relationship between structure and acidity.

Chapter 3 opens with a description of the structure, nomenclature, and conformations of alkanes and cycloalkanes. The IUPAC system is introduced in Section 3.3A through the naming of alkanes, and, in Section 3.5, the IUPAC system is presented as a general system of nomenclature. Beginning here and continuing throughout the text, a clear distinction is made between IUPAC and common names. Where names are introduced, the IUPAC name is given and the common name or names, where appropriate, follow in parentheses. The concept of stereoisomerism is introduced in this chapter with a discussion of cis-trans isomerism in cycloalkanes.

Chapter 4 introduces the concepts of chirality, enantiomerism, and diastereomerism. This material, coupled with the liberal use of molecular models, both in the text and on the accompanying interactive CD-ROM, encourages students to think of organic molecules as three-dimensional objects and to treat them as such in order to gain a deeper understanding of the chemistry of organic and biochemical reactions.

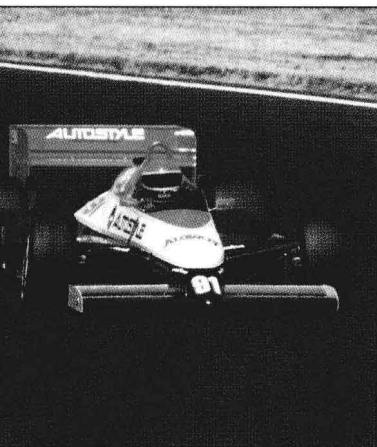
Chapter 5 presents the structure, nomenclature, and physical properties of alkenes and alkynes.

Chapter 6 opens with an introduction to chemical energetics and the concept of a reaction mechanism. The focus of this chapter is then on the reactions of alkenes, which are organized in the order: electrophilic additions, oxidation, and reduction. The twin concepts of regioselectivity and stereoselectivity are introduced in the context of electrophilic additions to alkenes.

Chapter 7 introduces alkyl halides and uses them as a vehicle for the discussion of nucleophilic substitution and  $\beta$ -elimination. The concepts of one-step and two-step nucleophilic substitutions along with  $S_N1$  and  $S_N2$  terminology are introduced first, and then the concepts of  $E1$  and  $E2$  reactions of alkyl halides.

Chapter 8 concentrates the structure and characteristic reactions of alcohols, including their conversion to alkyl halides, acid-catalyzed dehydration, and the oxidation of primary and secondary alcohols. There then follows a brief introduction to the structure, preparation, and acid-catalyzed ring opening of epoxides. This chapter concludes with a discussion of the acidity of thiols and their oxidation to disulfides.

Chapter 9 opens with the structure and nomenclature of aromatic compounds and several important heterocyclic aromatic compounds. Students are introduced to the unique properties of aromatic rings through the acid-base properties of phenols. The mechanism for electrophilic aromatic substitution, including the theory of directing effects, is then presented in detail.



Chapter 10 presents the structure and nomenclature of amines and concentrates on their most important chemical property, namely their basicity.

Chapters 11–14 develop the chemistry of carbonyl-containing compounds. First is the chemistry of aldehydes and ketones in Chapter 11, followed by carboxylic acids in Chapter 12 and their functional derivatives in Chapter 13. A major theme of these chapters is the addition of nucleophiles to the carbonyl group to form tetrahedral carbonyl addition products. Chapter 14 introduces the concept of an enolate anion and its involvement in aldol, Claisen, and Dieckmann reactions to form new carbon-carbon bonds.

Chapter 15, new to this edition, is a systematic introduction to organic polymer chemistry. Given the importance of organic polymers in the world around us, this material has been expanded in this edition.

Chapters 16–20 present the chemistry of carbohydrates in Chapter 16, lipids in Chapter 17, amino acids and proteins in Chapter 18, and nucleic acids in Chapter 19. Chapter 20 presents a discussion of two key metabolic pathways, namely  $\beta$ -oxidation of fatty acids and glycolysis. The purpose of this material is to show that the reactions of these pathways are the biochemical equivalents of organic functional group reactions already studied in previous chapters.

Chapters 21 and 22 present the fundamentals of the structure elucidation tools:  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectroscopy and then IR spectroscopy.

## SPECIAL FEATURES

### Full-Color Art Program

One of the most distinctive features of this text is its visual impact. The text's extensive full-color art program includes over 200 pieces of art by professional artists John and Bette Woolsey.

### Photo Art

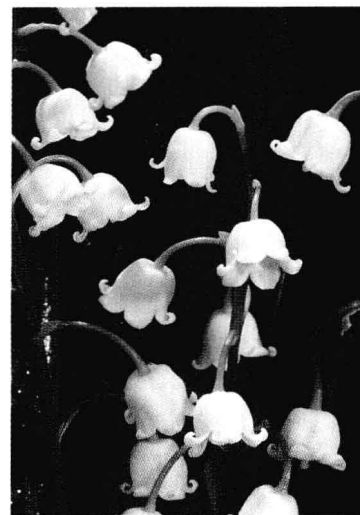
Photos, conceived and developed for this text, show organic chemistry as it occurs in the laboratory and in everyday life, and depict the natural sources of many organic compounds.

### Molecular Models


Developed by William Brown is a set of more than 275 molecular models for incorporation into this text. Their purpose is to assist students to visualize organic molecules as three-dimensional objects. All models have been prepared using CambridgeSoft Corporation ChemDraw and Chem3D software, and are energy-minimized to 0.01RMS.

### Interactive Organic Chemistry CD-ROM

Packaged with the text is a CD-ROM prepared by William Brown in conjunction with CambridgeSoft Corporation and containing over 300 molecular models rendered in Chem3D. With the plug-in supplied on the CD, students can rotate each





model, change model type from cylindrical bond to space-filling etc., measure bond angles, bond lengths, and the distance between nonbonded atoms. This icon [  ] signals students to go to the CD to view models seen in text.

## Chemical Connections Boxes

Each of the 36 boxes illustrates an application of organic chemistry to an everyday setting. Among the Chemical Connections are Chiral Drugs in Chapter 4, Morphine as a Clue to Drug Design and Discovery in Chapter 10, From Willow Bark to Aspirin and Beyond in Chapter 12, and Recycling Plastics in Chapter 15.

## Bioorganic Chemistry

Bioorganic chemistry is emphasized throughout the text, in the Chemical Connections Boxes, and in problems. For 116 compounds, there are references to *The Merck Index* (Susan Budavari, Editor, 12th Edition, Merck Research Laboratories, 1996), where students can read more about these compounds.

## In-Chapter Examples

There is an abundance of in-chapter examples, each with a detailed solution. Following each in-chapter example is a comparable practice problem designed to give students the opportunity to solve a related problem.

## End-of-Chapter Problems

There are plentiful end-of-chapter problems. All problems are categorized by topic. A tetrahedral icon indicates an applied problem, and a number set in blue indicates a more challenging problem.

## End-of-Chapter Summaries and Summaries of Key Reactions






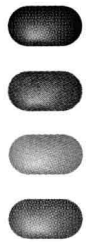





End-of-chapter summaries highlight all important new terms and concepts found in the chapter. In addition each new reaction is annotated and keyed to the section where it is discussed.

## Color






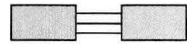
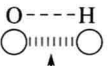



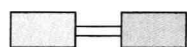
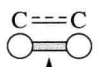




Color is used to highlight parts of molecules and to follow the course of reactions. The graphic here shows some of the colors used consistently in the artwork in this book.



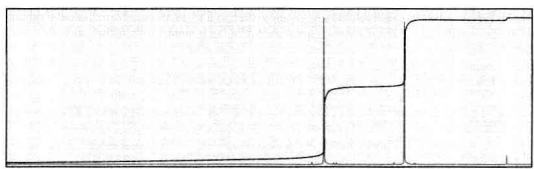
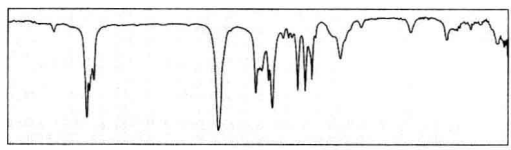
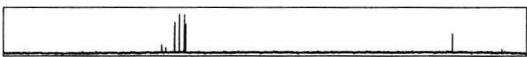


Elements									
					 Shapes like these are used for groups such as CH <sub>3</sub> , CH <sub>2</sub> CH <sub>3</sub> , and C <sub>6</sub> H <sub>5</sub> , where simplicity is important				
Carbon (C)	Hydrogen (H)	Oxygen (O)	Chlorine (Cl)	Bromine (Br)					
									
Nitrogen (N)	Phosphorus (P)	Sodium (Na)	Magnesium (Mg)	Fluorine (F)					

Bonds and Orbitals			Sugars		Nucleotides	
 Electron orbitals	 Electrons and electron pairs	 Single bond	 Fructose	 Glucose	 Cytosine    Guanine	
	 Hydrogen bond	 Double bond	 Mannose	 Galactose	 Thymine    Adenine	
	 Delocalized bond	 Triple bond	 Ribose	 Deoxyribose	 Uracil	

Spectroscopy	
 <sup>1</sup> H-NMR Spectra	 IR Spectra
 <sup>13</sup> C-NMR Spectra	

## Interviews

Four interviews with prominent scientists describe how these people became interested in chemistry as a college major, then as an educator and/or research professional. Their enthusiasm for their work is evident, and they invite students to pursue similar interests in the sciences.

## Margin Definitions and Glossary of Key Terms

Each new term has a free-standing definition placed in the margin adjacent to where the term is first introduced. All margin definitions are then collected in a

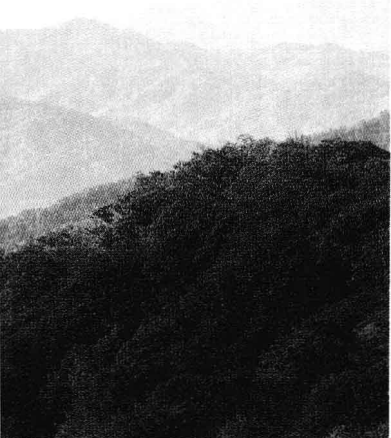


Glossary, with a notation added to show the section of the text in which the term is first introduced.

## NEW TO THIS EDITION

- Extensive use of the evolving software for viewing molecular models in the form of over which almost 275 molecular models created in Chem3D especially for this text. The inclusion of these models is to further convince students that organic molecules are three-dimensional objects, and their interaction is in large part governed by their shape and their polarities.
- The Interactive Organic Chemistry CD-ROM packaged on the inside cover of the text contains over 300 models rendered in Chem3D.
- Acids and Bases has been moved forward to Chapter 2, immediately following the review of covalent bonding and shapes of molecules in Chapter 1.
- Stereochemistry has been moved forward to Chapter 3 and now is placed immediately before the chemistry of alkenes. With the earlier introduction of stereochemistry, the regioselectivity and stereoselectivity of alkene reactions can now be discussed in greater depth.
- New to this edition is a chapter on organic polymer chemistry. Material on chain-growth polymerization and step-growth polymerization has been collected from the chapters on alkenes and functional derivatives of carboxylic acids and grouped to form this new chapter. In addition, the introduction to organic polymer chemistry has been expanded.
- Mechanisms, key elements in the organization of information in the study of organic chemistry, are now set apart and highlighted by a special design feature. All steps in each mechanism are presented together in its box. A list of the mechanisms presented in the text can be found following the table of contents.

## SUPPORT PACKAGE



- **PowerPoint™ Presentation.** Developed by William Brown is a pre-built set of approximately 700 PowerPoint™ lecture notes corresponding to every chapter in the text. These slides can be used in conjunction with the freely distributable PowerPoint™ Viewer, or edited and customized with the PowerPoint™ application program.
- **Student Solutions Guide** by David Benson, University of Kansas, and Brent and Sheila Iverson, University of Texas, contains detailed solutions to all problems.
- **Test Bank** by Jeffrey Elbert of South Dakota State University contains 25 multiple-choice questions per chapter for instructors to use as tests, quizzes, or homework assignments. Available also in computerized form for IBM-compatible and Macintosh computers.
- **Overhead Transparency Acetates.** A selection of 125 full-color figures from the text.

- **Instructor's Resource CD-ROM** contains all the images from this text as well as hundreds from other Saunders College Publishing chemistry texts.
- **CSC ChemOffice Limited, version 4.5.** Includes ChemDraw, Chem3D, and ChemFinder and is available at a very reasonable price from the publisher.
- **Pushing Electrons: A Guide for 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.

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## ACKNOWLEDGMENTS

Although one or a few persons are listed as "authors" of any textbook, the book is in fact the product of collaboration of many individuals, some obvious, others not so obvious. It is with gratitude that I acknowledge the contributions of the many. It is only fitting to begin with John Vondeling, Vice President and Publisher of Saunders College Publishing. John's keen sense of the marketplace has been primal in bringing this edition from rough manuscript to bound book form and to the development of the supplemental materials presented with this edition.

Sandi Kiselica has been a rock of support as Developmental Editor. I so appreciate her ability to set challenging but manageable schedules and her constant encouragement as I worked to meet those deadlines. She has also been an invaluable resource person with whom I could discuss everything from pedagogy to details of the art work.

Sarah Fitz-Hugh as Project Editor has been masterful in coordinating the transformation from manuscript to galleys and pages, along with incorporating the many components of the extensive art program. I have come to know Sarah well through this project and have great respect for her professionalism and judgment.

I also acknowledge the others at Saunders who contributed freely of their expertise to this project, in particular Caroline McGowan, Art Director; Pauline Mula, Marketing Strategist; and Charlene Squibb, Senior Production Manager.

Finally, I owe particular thanks to Professor Dana Chatellier, University of Delaware, for his involvement in this project, first as a reviewer of the entire manuscript, and then as an exceedingly careful and thorough proofer of both galleys and pages. Dana has provided a keen eye toward making sure that the book is as error-free as possible.





## List of Reviewers

The following reviewers provided valuable critiques of this book in its many stages.

Robert Badger, *University of Wisconsin, Stevens Point*

David R. Benson, *University of Kansas*

Dana Chatellier, *University of Delaware*

Robert Chesnut, *Eastern Illinois University*

Curtis Czerwinski, *University of Wyoming*

Chip Frazier, *Virginia Polytechnic Institute and State University*

Bryant Gilbert, *Portland State University*

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Ronald Starkey, *University of Wisconsin, Green Bay*

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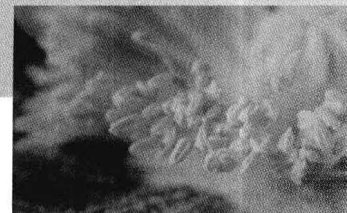
**William H. Brown**

*Beloit College, Beloit, WI*

*July 1999*



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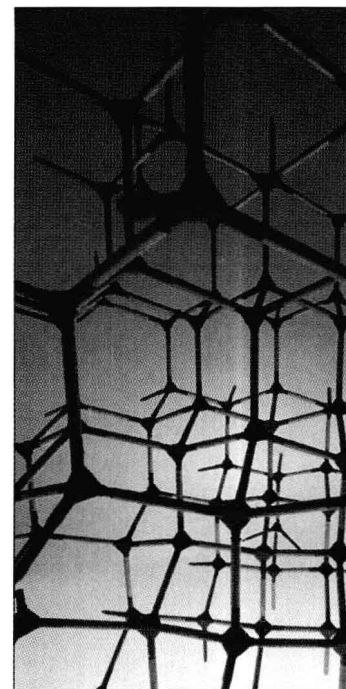
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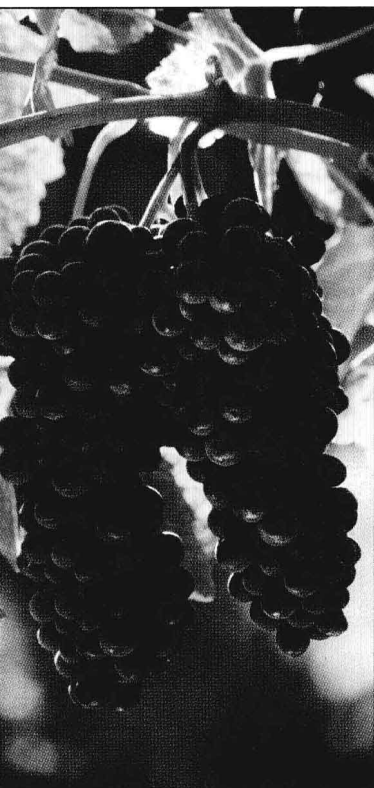
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