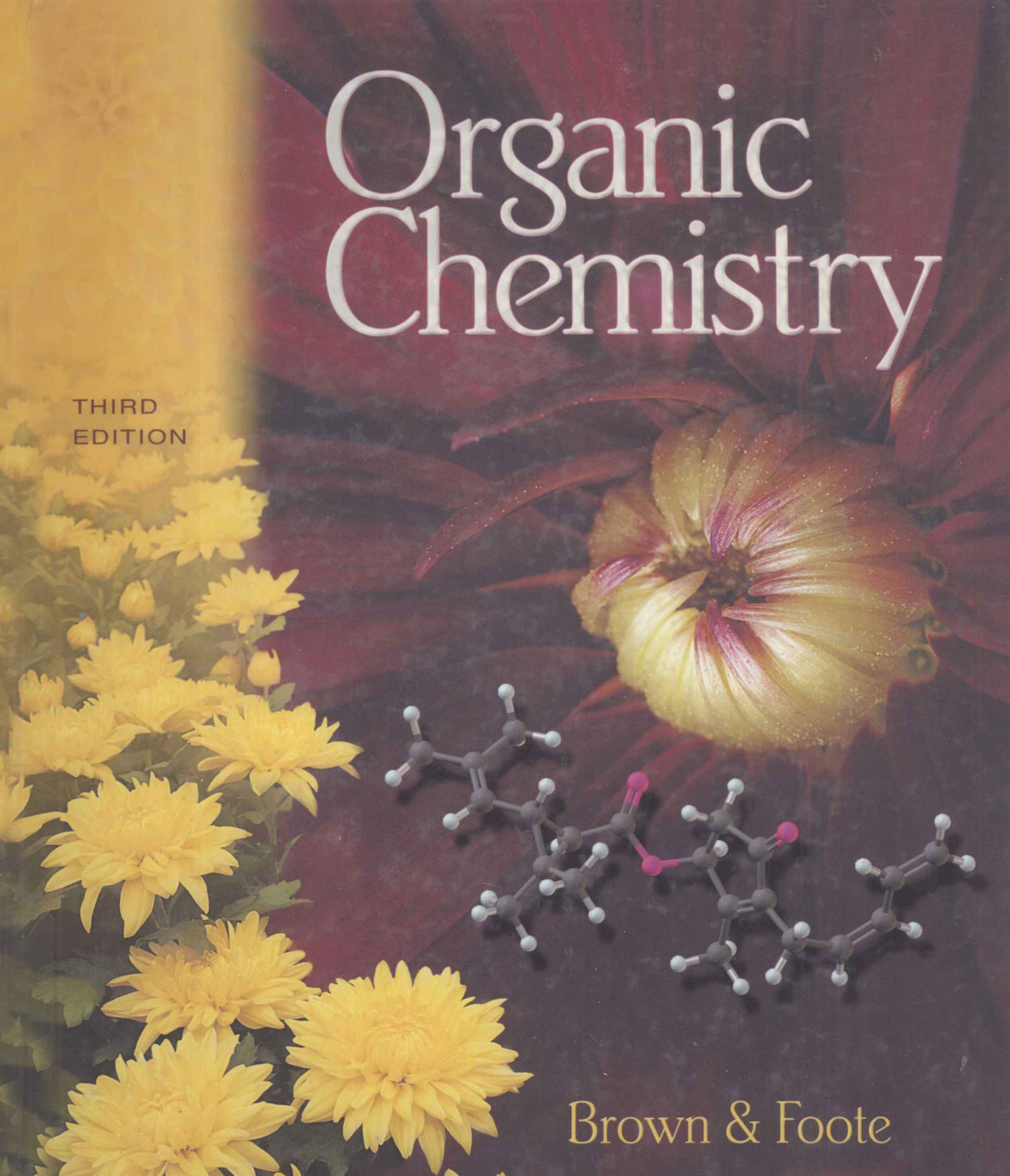
Organic Chemistry

THIRD EDITION



Brown & Foote

Organic Chemistry

Third Edition

William H. Brown

Beloit College

Christopher S. Foote

University of California, Los Angeles

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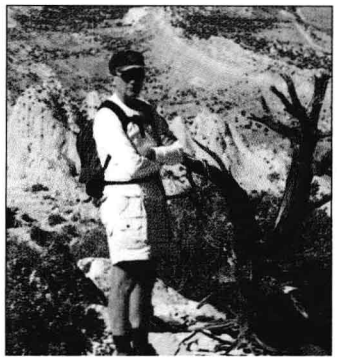
For John Vondeling
Mentor and Friend

BIOGRAPHIES

William H. Brown William 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 *Introduction to Organic Chemistry 2/e*, published in 2000. His regular teaching responsibilities include organic chemistry, advanced organic chemistry, and, more recently, special topics in pharmacology and drug synthesis. He received his PhD from Columbia University under the direction of Gilbert Stork and did postdoctoral work at California Institute of Technology and the University of Arizona.

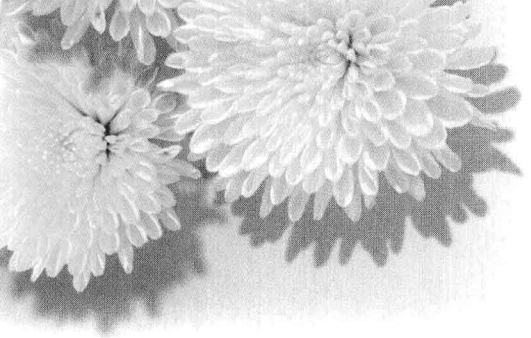
Bill Brown and his wife Carolyn enjoy hiking in the Southwest and the study of petroglyphs and pictographs. Twice he has been the Director of Beloit College's World Outlook Seminar, a program coordinated with the University of Glasgow in Scotland.



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

Christopher S. Foote Christopher S. Foote is Professor of Chemistry at the University of California, Los Angeles. He received his BS degree from Yale University and his PhD in Organic Chemistry from Harvard University. In 1995, he received the Tolman Award of the ACS Southern California Section for his contributions to chemistry. Foote's research has focused on the chemistry of oxygen in organic and biological systems and on the chemistry of fullerenes. Other awards he has received include the Yale Science and Engineering Award for the Advancement of Basic and Applied Science, the ACS North Jersey Sections' Leo Hendrick Baekeland Award, and the 2000 American Society of Photo Biology Distinguished Research Award. He was also an ACS Cope Scholar in 1994 and is the author of more than 250 research papers.

Christopher S. Foote



PREFACE

The Audience

This book provides an introduction to organic chemistry for students majoring in chemistry and in related disciplines, especially the health and biological sciences. Fundamental to our approach to the material of this course is the fact that organic chemistry has an underlying rationale, namely the mechanistic themes that unify it. With an appreciation for the power of mechanisms to provide an underpinning for its information content, organic chemistry can become an exciting area for exploration in its own right. We hope students will see organic chemistry as 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.

New to the Third Edition

In this edition, we have made major changes to unify the approach, to add new material that is at the forefront of organic synthesis, and to make the treatment of energy and mechanisms more complete. For almost every reaction for which a mechanism can be written, we present it. The treatment of reaction energetics has been expanded. Most importantly, we have incorporated feedback from students and users throughout this revision.

We now use SI units. Almost all elementary chemistry texts and most biochemistry texts now prefer kJ to kcal, and it seems time to begin the transition for organic chemistry texts as well. However, many users of the book will have learned to think in kcal. For this reason, we give energies as kJ (kcal)/mol throughout.

We have removed stereoviews from this edition and replaced them with computer models generated by CambridgeSoft's Chem3D. All models are also available on the bundled CD-ROM. Computed electrostatic potential maps and orbitals generated with Wavefunction's MacSpartan computer program are used in the text where relevant.

Chapters 3 and 4 have been switched to put stereochemistry/chirality immediately following the introduction to structure. Chapter 4 introduces acids and bases, followed by the alkenes chapter, which now uses the acid/base concepts more effectively.

The spectroscopy chapters (12–14) have been expanded somewhat, and have been made modular in that material for all functional groups has been introduced. In the present form, IR and NMR could be used as early as after Chapter 2, but could also be introduced at any convenient point in a course, including much later. Topicity has been added to the NMR chapter.

A separate chapter on organometallics (15) has been added. This chapter alerts students to the enormous advances in this area of chemistry. The Heck, Simmons-Smith, and alkene methathesis reactions are used as examples of important organometallic reactions. Synthesis and concepts of stereocontrol have been greatly expanded and stereospecific or enantiospecific syntheses are used in many places.

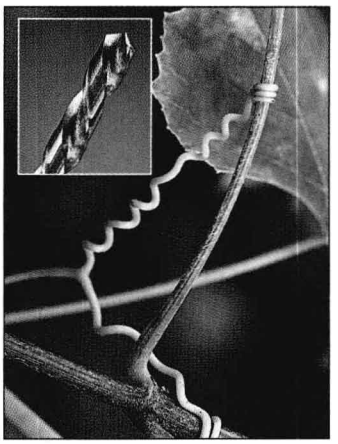
A new interchapter on medicinal chemistry unifies and reinforces the reactions introduced previously in the text by using them in problems on synthesis of important medicinal compounds. Explanatory material with these problems introduces more material on medicinal chemistry. Many of these problems can be introduced earlier to deepen the synthesis component of the course.

Major changes have been made in the detailed treatment of mechanisms in the carboxyl and enolate chapters (18 and 19). The chapter on conjugated systems (23) has been expanded, and limited coverage of UV/Vis spectroscopy has been moved to this chapter. There is expanded coverage of the Diels-Alder reaction. The chapter on proteins (27) has been updated with the use of mass spectra in sequencing, and a section on the genome decoding has been added to the DNA chapter (28).

Chapter-by-Chapter Overview

Chapter 1 begins with a review of the electronic structure of atoms and molecules, the Lewis model of bonding, and use of the VSEPR model to predict shapes of molecules and ions. Within this discussion, we introduce the functional groups encountered most frequently in the text along with the theory of resonance and the use of curved arrows and electron pushing. A knowledge of resonance theory combined with a facility for moving electrons gives students two powerful tools for writing reaction mechanisms and understanding chemical reactivity. Chapter 1 concludes with an introduction to quantum mechanics and the molecular orbital theory of covalent bonding.

Chapter 2 opens with a description of the structure, nomenclature, and conformational analysis of alkanes and cycloalkanes. Beginning here and continuing throughout the text, a clear distinction is made between IUPAC and common names. Where names are introduced, IUPAC names are given first and common names, where appropriate, follow in parentheses. The IUPAC system is introduced in Section 2.3A through the naming of alkanes, and in Section 2.5, it is presented as a general system of nomenclature. The concept of stereoisomerism is introduced in this chapter with a discussion of cis,trans isomerism in cycloalkanes.



(Charles D. Winters)

Chapter 3 begins with a review of constitutional, conformational, and cis,trans/E,Z isomerism and then introduces the concepts of chirality, enantiomerism, and diastereomerism.

Chapter 4 contains a general introduction to acid-base chemistry with emphasis on both qualitative and quantitative determination of the position of equilibrium in acid-base reactions. We include an in-depth discussion of relationships between molecular structure and acidity. With an understanding of the structural basis for these relationships, students can then deal with questions such as "Why is a carboxylic acid a stronger acid than an alcohol", and "Why is acetylene a stronger acid than ethane?"

Chapters 5 and 6 cover the chemistry of alkenes. Their structure and physical properties are presented in Chapter 5. The chapter concludes with the structure of ter-

penes and an introduction to one theme in the molecular logic of biomolecules. The focus in Chapter 6 is on the chemical reactivity of alkenes. It opens with an introduction to the concept of a reaction mechanism, energy diagrams, Gibbs free energy, activation energy, and reactive intermediates. Reactions of alkenes are organized in the following order: electrophilic additions, hydroboration, oxidation, and reduction. The twin concepts of regiospecificity/selectivity and stereospecificity/selectivity are introduced in the context of electrophilic additions. This chapter builds on the concepts of acid-base reactions introduced in Chapter 4 and develop the concepts of carbocation stability and rearrangement.

Chapter 7 introduces the haloalkanes and their structure and nomenclature. It has as its central theme the radical halogenation of alkanes and provides an introduction to the mechanistic concepts of chain initiation, propagation, and termination. Regioselectivity of radical bromination compared with radical chlorination is interpreted in terms of Hammond's postulate. Free radical autoxidation is introduced.

Chapter 8 presents what, in our experience, is one of the most formidable and anxiety-producing aspects of introductory organic chemistry, namely S_N1, S_N2, E1, E2 mechanisms and the attendant concepts of stereochemistry, kinetics, and relationships between structure and chemical reactivity. The difficulty does not lie in any single part of this material, but in the number of concepts to be assimilated at one time. This introduction is made much simpler because the key concepts of carbocation stability and rearrangements have already been introduced in Chapter 6. By this stage in the course, students have a good grounding in the structure of organic molecules, the theory of resonance, electron pushing, and reaction mechanisms. Nucleophilic substitution and β-elimination then become a vehicle for integration of previously covered chemistry into a larger pattern.

(Charles D. Winters)

Chapter 9 continues the theme of the relationships between structure and reactivity by considering the chemistry of alcohols. A significant body of the chemistry of alcohols can be understood using the concepts of nucleophilic substitution, β-elimination, and the relative stability of carbocations, all of which have been developed in previous chapters.

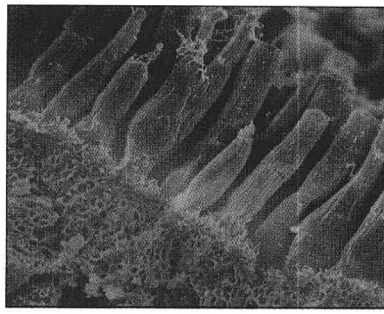
Chapter 10 opens with the structure and nomenclature of alkynes followed by the acidity of terminal alkynes. It then emphasizes the usefulness of alkynes as building blocks in organic synthesis through alkylation of acetylide anions, reduction, hydroboration-oxidation, and electrophilic additions. The chapter concludes with an introduction to the strategy of organic synthesis, namely retrosynthetic analysis.

Chapter 11 is a logical extension of nucleophilic substitutions as applied to the synthesis and reactions of ethers and epoxides. The value of epoxides in organic synthesis is stressed, including the regio- and stereochemistry of their reactions with a variety of nucleophiles. Sharpless stereospecific epoxidation is introduced.

Chapters 12–14 examine the molecular spectroscopy of the most common functional groups presented in the course. First is infrared spectroscopy in Chapter 12, followed by ^{1}H-NMR and ^{13}C-NMR spectroscopy in Chapter 13, and then mass spectrometry in Chapter 14. While this material is presented as a cluster of chapters mid-

way through the text, the chapters have been made free-standing and can be used in different order as appropriate to a particular course.

Chapter 15 new in this edition, begins with the preparation and structure of Grignard and organolithium reagents, followed by their basicity, reaction with proton acids, and reaction with oxiranes. Next we show the preparation of lithium diorganocopper (Gilman) reagents and their coupling with alkyl and alkenyl halides to form new carbon-carbon bonds. This chapter introduces carbenes and carbenoids, including the Simmons-Smith reaction. In keeping with our desire to give even greater emphasis to the chemistry of organometallic compounds, we introduce both the Heck and olefin metathesis reactions and demonstrate their usefulness in forming new carbon-carbon bonds.



(Omikron/Photo Researchers Inc.)

Chapters 16–19 concentrate on the chemistry of carbonyl-containing compounds. First is the chemistry of aldehydes and ketones in Chapter 16 followed by the chemistry of carboxylic acids and their functional derivatives in Chapters 17 and 18. Collected in Chapter 19 are various carbonyl condensation reactions, including the aldol reaction, and the Claisen and Dieckmann condensations as well as alkylation and acylation reactions of acetoacetic esters, malonic esters, and enamines. Mechanistic treatment of these reactions is enhanced.

Chapters 20 and 21 present the chemistry of aromatic compounds. The first of these chapters concentrates on structure and nomenclature of aromatic compounds, the concept of aromaticity, and the structure and acid-base properties of phenols. The second is devoted to aromatic substitution reactions.

Chapter 22 presents the chemistry of aliphatic and aromatic amines.

Chapter 23 completes the introduction to organic functional groups with the particular chemistry of conjugated dienes, including both 1,2- and 1,4-addition and the Diels-Alder reaction. This discussion is followed by an overview of pericyclic reactions and the concept of transition state aromaticity. The chapter concludes with an introduction to UV-Vis spectroscopy.

Problems in Medicinal Chemistry With completion of Chapter 23, we have covered the chemistry of the major functional groups and, in this interchapter section, we present a set of problems in organic synthesis. In recognition of the fact that many students taking introductory organic chemistry are interested in careers in the health and biological sciences, we have chosen problems entirely from the area of medicinal chemistry. Problems are grouped by their therapeutic category, and for several we include information on drug design and discovery. Many of them may be introduced earlier to deepen the synthesis component of the course.

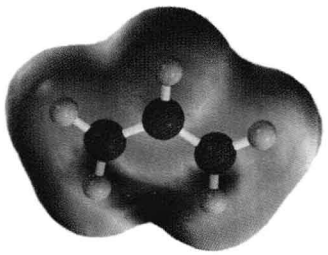
Chapter 24 is a systematic introduction to organic polymer chemistry. New to this edition is a discussion of ring-opening metathesis polymerization (ROMP). Given the importance of organic polymers in the world around us, we have made this chapter more extensive than that found in most other organic textbooks.

Chapters 25–28 present an introduction to the chemistry to carbohydrates, lipids, amino acids and proteins, and nucleic acids. Emphasis in this chapter is on the

structure of these biomolecules. These chapters have been updated to include cutting-edge topics related to proteomics and genomics.

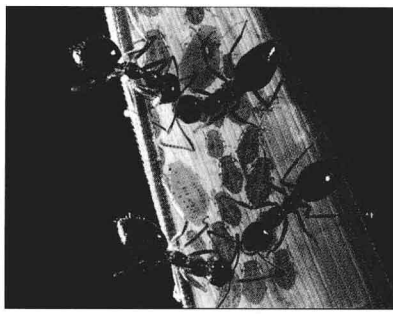
Chapter 29 presents a discussion of two key metabolic pathways, namely glycolysis and β-oxidation of fatty acids. It is our purpose in this chapter to show that the reactions of these pathways are biochemical equivalents of organic functional group reactions we have already studied in detail.

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 250 pieces of art by professional artists John and Bette Woolsey. A large number of molecular models have been generated and energy minimized in CambridgeSoft's Chem3D, and then rendered by these artists to provide easily visualized pictures of molecular structures. All of these models are available on the bundled CD-ROM. Computed electrostatic potential maps generated by Wavefunction's MacSpartan are provided at appropriate places throughout the text to illustrate the important concepts of resonance, electronegativity, and nucleophilicity.
- **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.
- **Using ChemOffice Web with Organic Chemistry, Third Edition** Packaged with the text is a CD-ROM prepared by the authors in conjunction with CambridgeSoft Corporation and containing over 300 models rendered in Chem3D. Their purpose is to assist students in visualizing organic molecules as three-dimensional objects. With the plug-in supplied on the CD-ROM, students can rotate each model, change from ball-and-stick to space-filling, measure bond angles and interatomic distances, and invert configuration at a stereocenter in a cyclic molecule. With the plug-in, students can also build models in ChemDraw, assign *R,S* configuration to each stereocenter, and import ChemDraw structures into other documents. Icons  in the text alert students to use the CD.
- **Bioorganic Chemistry** Bioorganic chemistry is emphasized throughout the text, in the Chemistry in Action boxes, in end-of-chapter problems, and in the 50 medical chemistry problems collected in the interchapter section following Chapter 23. Merck Index references are from *The Merck Index* (Susan Budavari, editor, 12th edition, Merck Research Laboratories, 1996).
- **Chemistry in Action Boxes** These boxes illustrate applications of organic chemistry to everyday settings. Topics range from "Radical Autoxidation" to "Drugs That Lower Plasma Levels of Cholesterol."
- **In-Chapter Examples** There are an abundance of in-chapter examples, all with detailed solutions. Following each in-chapter example is a comparable in-chapter problem designed to give students the opportunity to solve a problem related to the example.
- **End-of-Chapter Summaries and Summaries of Key Reactions** End-of-chapter summaries highlight all important new terms found in a chapter. In addition, each reaction is annotated and keyed to the section where it is discussed.

- **End-of-Chapter Problems** There are plentiful end-of-chapter problems. The majority of problems are categorized by topics. A problem number set in red indicates a more challenging problem.
- **Glossary of Key Terms** Throughout the book we place definitions for new terms in the margin. In addition, all definitions are collected in a glossary at the end of the text. Each glossary listing is keyed to the section of the text where the term is introduced.
- **Color** Color is used to highlight parts of molecules and to follow the course of reactions.
- **Interviews** Four interviews with prominent scientists describe how each of these people became interested in chemistry, then insights into their careers as educators and research professionals. Their enthusiasm for their work is evident, and they invite students to pursue similar interests in the sciences.



(Photo Asscociates)

Support Package

For the Student

- **Student Study Guide** by Brent and Sheila Iverson of the University of Texas, Austin. Contains detailed solutions to all in-text and end-of-chapter problems.
- **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.
- **Problem Book for Organic Chemistry** by Andrew Ternay (University of Denver) contains more than 800 additional problems with explanations about the important concepts in organic chemistry. Keyed to the textbook.
- **Interactive Organic Chemistry CD-ROM** by William Vining and Vincent Rotello, University of Massachusetts. This dual-platform tutorial CD-ROM includes 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. The text is keyed by an icon  shown in the margin. An accompanying **workbook** by Steven Hardinger, University of California, Los Angeles, contains questions to guide students through the CD-ROM modules.
- **CSC ChemOffice Limited, version 4.5** includes ChemDraw, Chem3D, and ChemFinder and is available at a very reasonable price from the publisher.
- **Organic Chemistry Web Site** (http://www.brookscole.com) contains tutorials, animations, molecular modeling, and practice problems. **PowerPoint**™ lecture slides by William H. Brown can be found on the Web site for organic chemistry.

For the Instructor

- **Test Bank** A multiple-choice bank of over 1000 problems for instructors to use for tests, quizzes, or homework assignments. Also available in computerized form for Windows™ and Macintosh® platforms.

- **PowerPoint™** lecture slides by William H. Brown can be found on the Web site for organic chemistry.
- **Instructors' Resource CD-ROM** contains all images and tables from the text for instructors to incorporate into lectures.
- **Overhead Transparency Acetates** A selection of 150 full-color figures from the text.

To the Student

ChemOffice Web — CD-ROM

How to Use the CD-ROM

The CD-ROM enclosed in your text is your exploration to molecular structure. In the text you will find CD-ROM icons, which direct you to specific models and exercises on the CD-ROM. Icons are located next to particular models, examples, practice problems, or additional problems at the end of each chapter.

When you find an icon in the text, mount the CD-ROM, locate the menu of chapters on the left side of your screen, and open (click on) the appropriate chapter. You will then see a menu of models for that chapter along with a brief descriptive title of each model. Select (click on) the appropriate title. The screen that appears shows you the model you have selected and, under it, one or more exercises related to that model. In addition, there are molecular modeling exercises at the end of many of the in-text chapters.

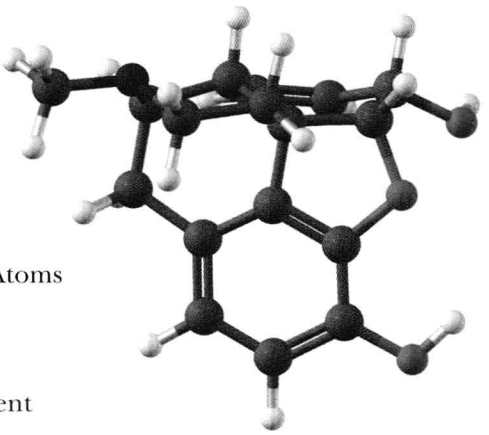
The purpose of the CD-ROM, along with its models and exercises, is to help you appreciate that organic molecules are three-dimensional objects. With the CD-ROM, you can measure bond lengths, bond angles, and examine molecular sizes and shapes. You can rotate the models in space and view them from any perspective you choose. You can display the models as ball-and-stick, cylindrical bond, wire frame, or space-filling.

Tutorials

Included on the CD-ROM is a set of tutorials. We suggest that you work through these tutorials first before you try any of the interactive exercises on the CD-ROM. The tutorials will introduce you quickly to the tools.

Tutorial Contents

A. Measure Bond Lengths
B. Measure Bond Angles
C. Determine Bond Order
D. Rotate a Molecule
E. Change Among Model Types
F. Resize a Model or Models
G. Resize and Center a Model or Models
H. Rotate About a Bond
I. Measure Distance Between Nonbonded Atoms
J. Hide/Show all Hydrogens (H's)
K. Create Mirror Images
L. Invert Configuration
M. Paste a Chem3D Structure into a Document
N. Play a Movie
O. Assign Formal Charges



We do not provide solutions in the accompanying Study Guide for the Interchapter problems. We do, however, provide solutions on our Web site to instructors who have the option of supplying them to the students. Select Organic Chemistry from our Web site at http://www.brookscole.com

Acknowledgments

While one or a few persons are listed as "author" 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 we herein 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 contribution began with the faith that we could do this book and then marshaling the support systems necessary to bring it from rough manuscript to bound book form, assembling the elements of the supplemental materials, and finally bringing to bear his keen sense of the marketplace.

Sandi Kiselica has been a rock of support as Senior Developmental Editor. We so appreciate her ability to set challenging but manageable schedules for us and her constant encouragement as we worked to meet those deadlines. She was also an invaluable resource person with whom we could discuss everything from pedagogy to details of art work. We also want to acknowledge others at Saunders who contributed to this project, in particular, Ellen Sklar, Project Editor; Jonel Sofian, Art Director; Pauline Mula, Senior Marketing Strategist; and Charlene Squibb, Senior Production Manager.

We are also indebted to the many reviewers of our manuscript who helped shape its contents. With their guidance we have revised this text to better meet the needs of their students. A special thanks goes to William Vining (University of Massachusettes) who keyed our textbook by icon to the Interactive organic chemistry CD-ROM. Also, we are grateful to Gary Lyon (Louisiana State University) who read all the galleys and page proofs for accuracy.

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We have enjoyed writing this text, and hope that instructors and students alike find in it a measure of the excitement we feel for organic chemistry.

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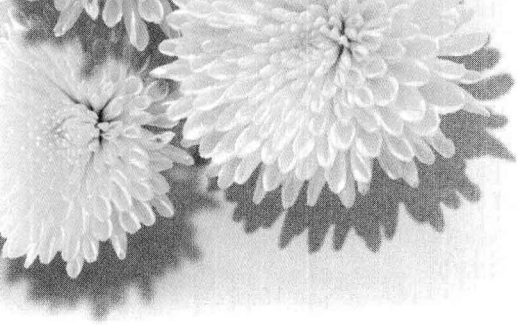

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