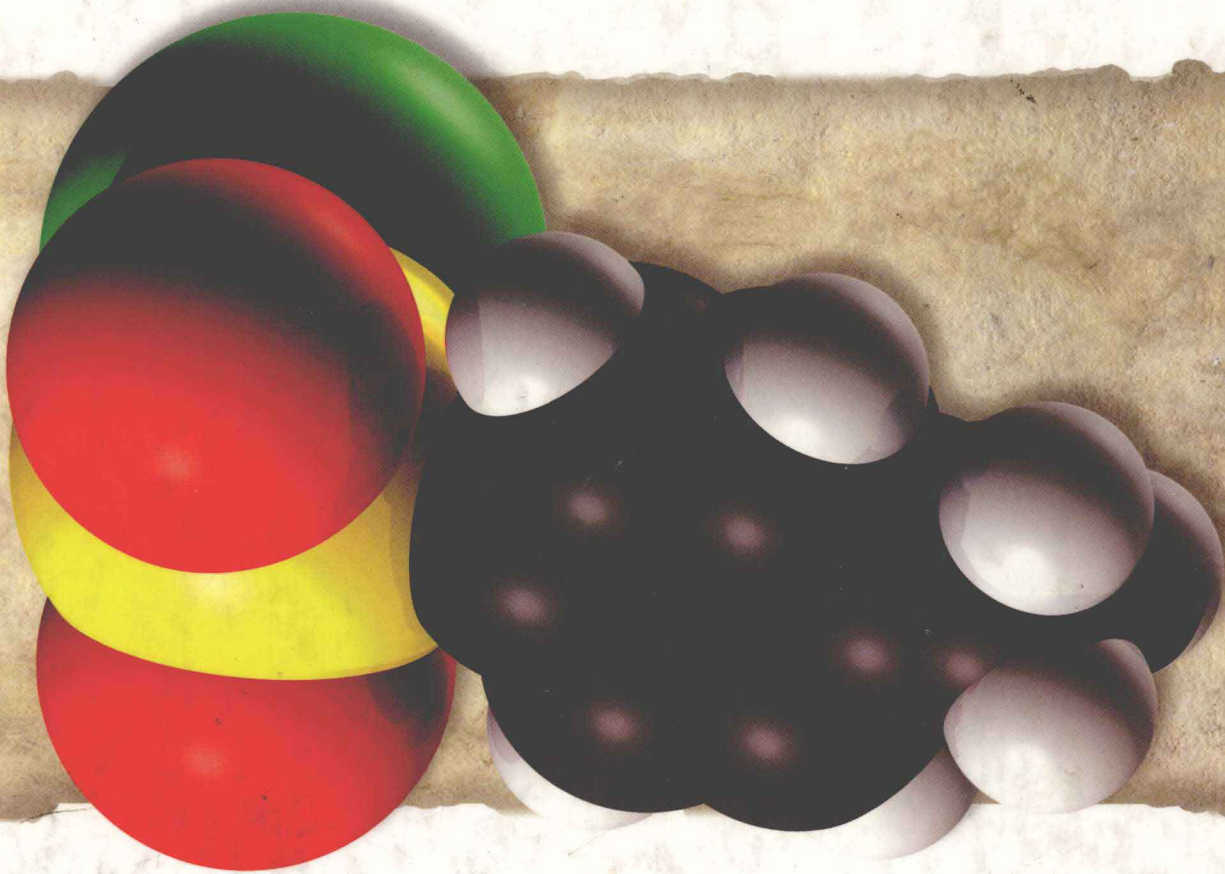


Organic Chemistry

Fourth Edition



L.G. WADE, JR.

FOURTH EDITION

Organic Chemistry

L. G. Wade, Jr.

Whitman College



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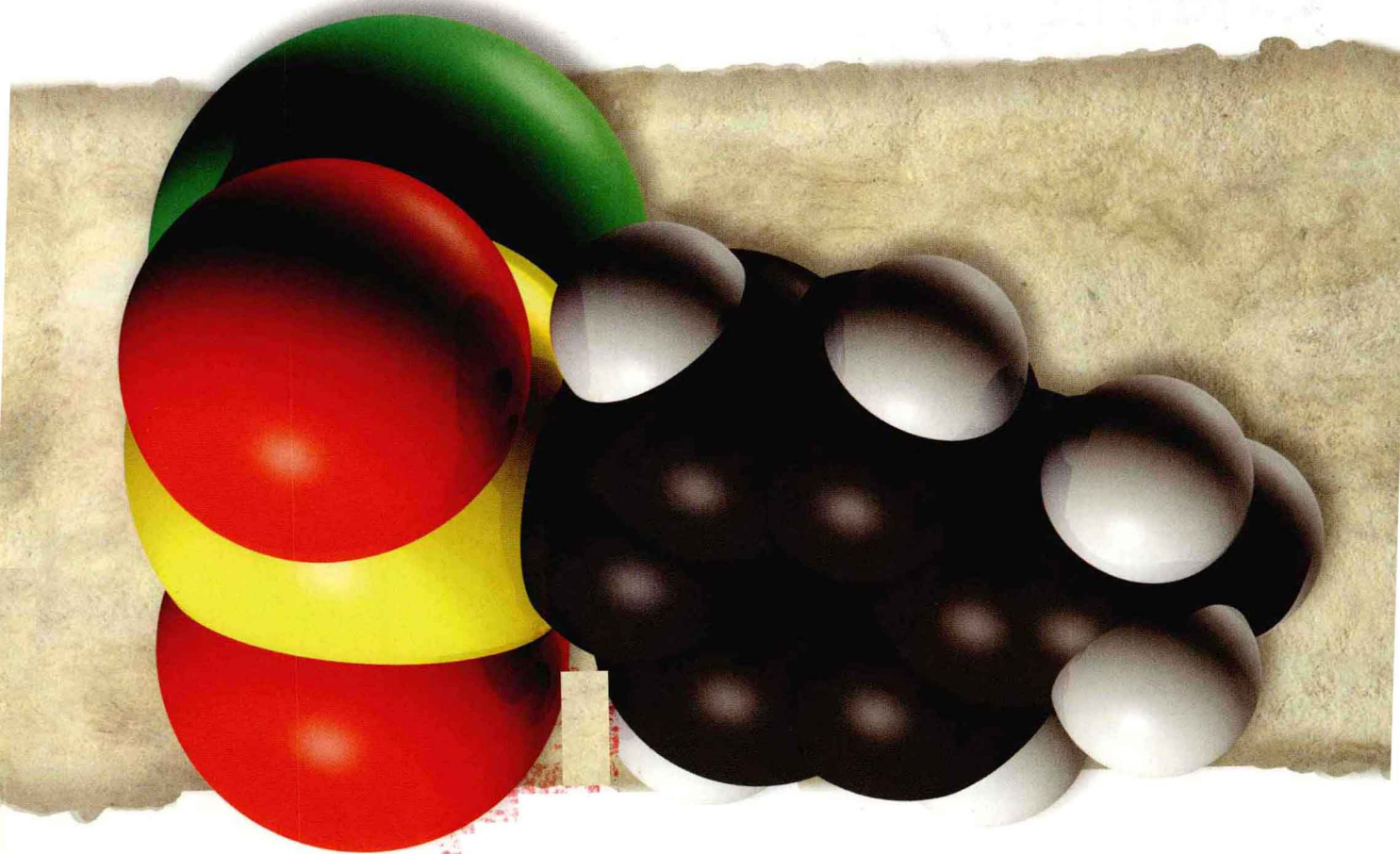
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Organic Chemistry



To my students and colleagues
at Whitman College

Preface

To the Student

As you begin your study of organic chemistry, you might feel overwhelmed by the number of compounds, names, reactions, and mechanisms that confront you. You may even wonder whether you can learn all this material in a single year. The most important function of a textbook is to organize the material to show that most of organic chemistry consists of a few basic principles and many extensions and applications of these principles. Relatively little memorization is required if you grasp the major concepts and develop flexibility in applying those concepts. Frankly, I have a poor memory, and I hate memorizing lists of information. I don't remember the specifics of most of the reactions and mechanisms in this book, but I can work them out by remembering a few basic principles, like "alcohol dehydrations usually go by E1 mechanisms."

Still, some facts and fundamental principles (probably about ten to twenty) in each chapter must be learned to serve as the working "vocabulary" of that chapter. As a student I learned this the hard way, when I made a **D** on my second organic chemistry exam because I had neglected to learn the important terms. In writing this book, I've tried to point out a small number of important facts and principles that should be learned to prepare for solving problems. For example, in studying nuclear magnetic resonance one might memorize thousands of chemical shifts, but Table 13-3 lists only about a dozen representative values that can be learned and used to solve most problems.

Don't try to memorize your way through this course. It doesn't work; you have to know what's going on so you can apply the material. Also, don't think (like I did) that you can get by without memorizing *anything*. Read the chapter, listen carefully to the lectures, and *work the problems*. The problems will tell you whether you know the material. If you can do the problems, you should do well on the exams. If you can't do the problems, you probably won't be able to do the exams, either. If you keep having to look up something to do the problems, that item is a good one to learn.

Here are some hints I give my students at the beginning of the course:

1. Read the material in the book before the lecture (expect 13–15 pages per lecture). Knowing what to expect and what is in the book, you can take fewer notes and spend more time listening and understanding the lecture.
2. Before the next lecture, review your notes and the book, and do the in-chapter problems. Also, read the material for the next lecture.
3. If you are confused about something, visit your instructor during office hours immediately, before you fall behind. Bring your attempted solutions to problems with you to show your instructor where you are having trouble.
4. To study for the exam, begin by reviewing each chapter and your notes, then concentrate on the end-of-chapter problems. Also use old exams for practice, if available.

Remember the two "golden rules" of organic chemistry.

1. **DON'T GET BEHIND!** The course moves too fast, and it's hard to catch up.
2. **WORK LOTS OF PROBLEMS.** Everyone needs the practice, and problems show where you need more work.

Study Aids

Several kinds of study aids are provided to emphasize and review the most important points.

Summary Tables. Whenever a large amount of material lends itself to a concise summary, a summary table is provided to compare and contrast this material. For example, the following summary table compares the factors affecting S_N1 and S_N2 reactions.

SUMMARY: Nucleophilic Substitutions

	S_N1	S_N2
promoting factors		
nucleophile	weak nucleophiles are OK	strong nucleophile needed
substrate (RX)	$3^\circ > 2^\circ$	$\text{CH}_3\text{X} > 1^\circ > 2^\circ$
solvent	good ionizing solvent needed	wide variety of solvents
leaving group	good one required	good one required
other	AgNO_3 forces ionization	
characteristics		
kinetics	first order, $k_t[\text{RX}]$	second order, $k_t[\text{RX}][\text{Nuc}^-]$
stereochemistry	mixture of inversion and retention	complete inversion
rearrangements	common	not possible

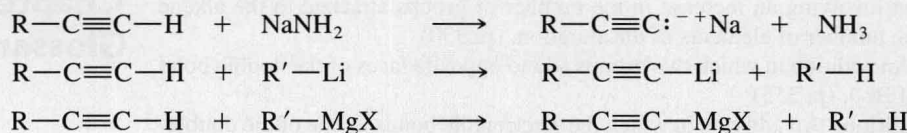
Reaction Summaries. At the conclusion of each section on syntheses or reactions of a functional group (“Reactions of Alkynes,” for example), a summary table is provided for efficient review. Each summary, highlighted by a beige background, includes cross-references to reactions that are discussed elsewhere.

SUMMARY: Reactions of Alkynes

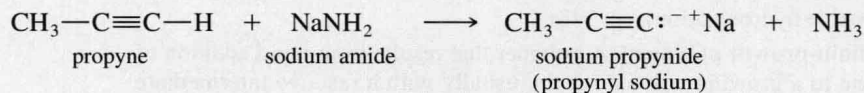
I. ACETYLIDE CHEMISTRY

1. Formation of acetylide anions (alkynides)

a. Sodium, lithium, and magnesium acetylides (Sections 9-6A and 10-9)



Example

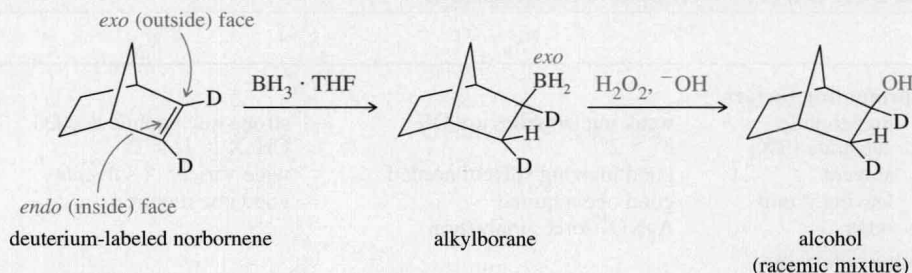


Problems. The in-chapter problems appear right after the relevant sections of the text. These problems provide immediate review and reinforcement of the material as you learn it, helping to make sure you understand each section well enough before moving on to the next. Later, end-of-chapter problems promote additional review and practice. Your instructor may choose to assign specific problems that reflect the emphasis of the lectures. Problems with red stars (*) are more difficult problems that require extra thought and perhaps some extension of the material presented in the chapter.

Solved Problems. Where appropriate, solved problems (highlighted by a beige background) are provided to show how you might approach a particular type of problem and what kind of answer is expected. For example, a solved problem might work through a mechanism to show how it is broken down into individual steps and how red curved arrows show movement of electrons.

SOLVED PROBLEM 8-4

A norbornene molecule labeled with deuterium is subjected to hydroboration–oxidation. Give the structures of the intermediates and products.



SOLUTION

The syn addition of BH_3 across the double bond of norbornene takes place mostly from the more accessible outside (*exo*) face of the double bond. Oxidation gives a product with both the hydrogen atom and the hydroxyl group in *exo* positions. (The less accessible inner face of the double bond is called the *endo* face.)

Glossaries. Each chapter ends with a glossary that defines and explains technical terms introduced in that chapter. New terms defined in the glossary are printed in bold-face the first time they appear in the chapter. The glossaries serve primarily as study aids for reviewing the material. They will help to jog your memory as you go over the definitions and make sure you understand and can use all the new terms.

addition A reaction involving an increase in the number of groups attached to the alkene and a decrease in the number of elements of unsaturation. (p. 330)

anti addition: An addition in which two groups add to opposite faces of the double bond (as in addition of Br_2). (p. 355)

electrophilic addition: An addition in which the electrophile bonds to one of the double-bonded carbons first, followed by the nucleophile. (p. 331)

syn addition: An addition in which two groups add to the same face of the double bond (as in osmium tetroxide hydroxylation). (p. 348)

addition polymer (chain-growth polymer) A polymer that results from rapid addition of one molecule at a time to a growing polymer chain, usually with a reactive intermediate (cation, radical, or anion) at the growing end of the chain. (p. 367)

alkoxymercuration The addition of mercuric acetate to an alkene in an alcohol solution, forming an alkoxymercurial intermediate. Demercuration gives an ether. (p. 343)

Chapter 8 Glossary

Problem-Solving Strategies. The problem-solving strategies (highlighted by a green background) suggest methods for approaching complicated problems, such as those that require proposing mechanisms and developing multistep syntheses. Students often have trouble seeing how to approach problem solving, and these strategies are meant to help you break problems down into simpler pieces. Although organic chem-

istry cannot be broken down into a rote process that guarantees an answer, experienced chemists instinctively approach problems in ways that are more likely to lead to solutions. The suggestions in the problem-solving discussions approximate what an experienced chemist is likely to do in approaching these problems. They serve as a starting point, not a guaranteed route to the answers.

PROBLEM-SOLVING

Multistep Synthesis

We use a systematic approach to solving multistep synthesis problems, working backward, in the “retrosynthetic” direction. We begin by studying the target molecule and considering what final reactions might be used to create it from simpler intermediate compounds. Comparing two or more pathways and the intermediates involved is usually necessary. Eventually, this retrosynthetic analysis should lead back to starting materials that are readily available or meet the requirements defined in the problem.

Problem-Solving Hints. These suggestions (green headings in the marginal column at the side of the page) are provided to remind you of facts or principles that are likely to be useful for solving common types of problems. These are the tips I give my own students when I help them work problems and review for exams. These hints highlight material that is sometimes overlooked but plays an important role in solving problems.

Essential Problem-Solving Skills. This list is provided at the end of each chapter to remind you of the kinds of skills needed to solve typical problems associated with the material in that chapter. When you finish a chapter, this list can point out concepts you might need to review, or it might suggest types of problems and solutions you have not considered. Reviewing the problem-solving skills is often a good prelude to doing the end-of-chapter problems.

PROBLEM-SOLVING HINT

To move a proton (as in a tautomerism) under basic conditions, try removing the proton from its old position, then adding it to the new position.

ESSENTIAL PROBLEM-SOLVING SKILLS IN CHAPTER 8

1. Predict the products of additions, oxidations, reductions, and cleavages of alkenes, including
 - (a) Orientation of reaction (regiochemistry)
 - (b) Stereochemistry.
2. Propose logical mechanisms to explain the observed products of alkene reactions, including regiochemistry and stereochemistry.
3. Use alkenes as starting materials and intermediates in devising one-step and multistep syntheses.
4. When more than one method is usable for a chemical transformation, choose the better method and explain its advantages.
5. Use clues provided by products of reactions such as ozonolysis to determine the structure of an unknown alkene.

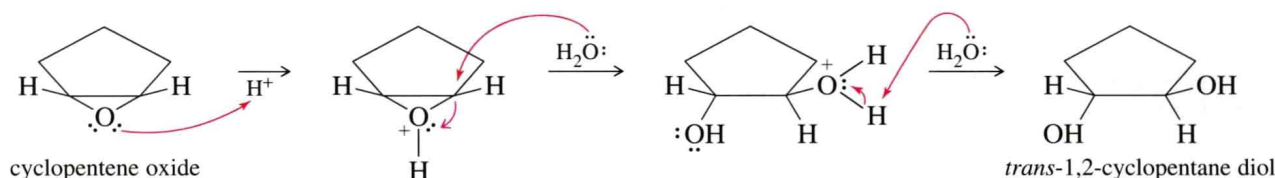
Four-Color Printing. This book is printed with four colors of ink to help you find and organize the material. Color is used to highlight major features for easy location; the beige backgrounds of summary tables and solved problems shown above are examples. The green backgrounds of problem-solving strategies and essential

problem-solving skills, and the green headings for problem-solving hints are further examples. Other features that are set off by color:

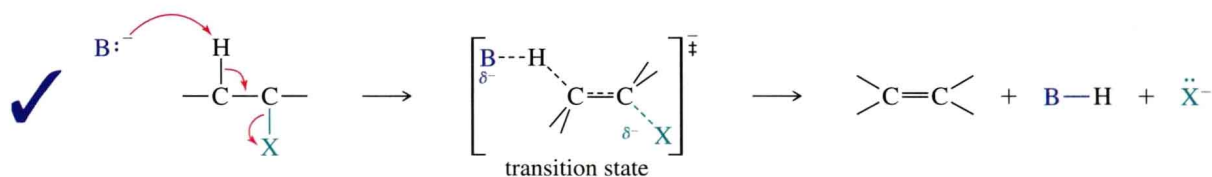
1. Key definitions and rules are in blue type.

MARKOVNIKOV'S RULE The addition of a proton acid to the double bond of an alkene results in a product with the acid proton bonded to the carbon atom that already holds the greater number of hydrogen atoms.

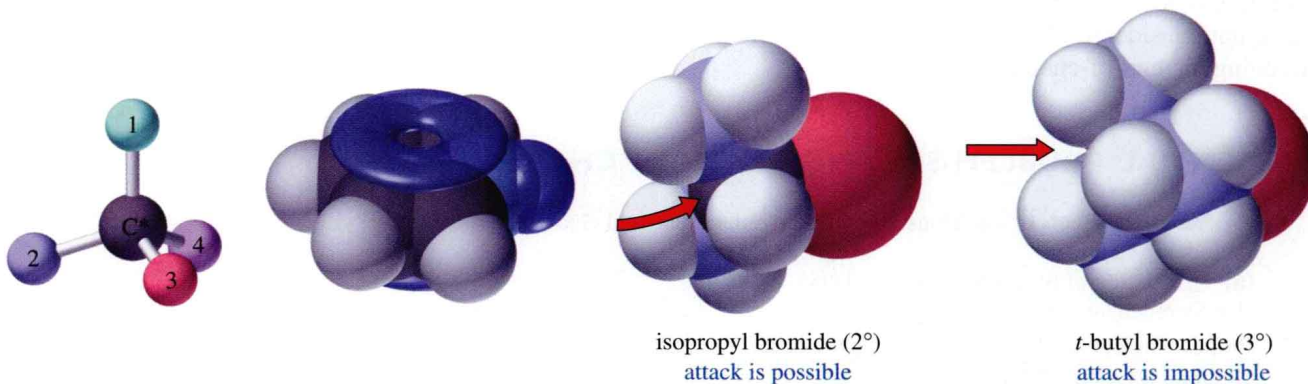
2. Curved red arrows are used throughout for “electron pushing,” to show the flow of electrons through the course of a reaction.



3. Important general reactions are highlighted by a check mark in the margin. Nucleophiles are often printed in blue and electrophiles in green.



The variety of available colors makes it possible to highlight and distinguish key aspects of reactions, structures, and molecular drawings, and to distinguish atoms and bonds within molecules and transition states.



I am always interested to hear from students using this book. If you have any suggestions about how the book might be made better, or if you've found an error, please let me know. (L. G. Wade, Whitman College, Walla Walla, WA, 99362; E-mail wadelg@whitman.edu). I take students' suggestions seriously, and hundreds of them now appear in this book. For example, Whitman student Brian Lian suggested Figure 21-9, and University of Minnesota student (and racing driver) Jim Coleman gave me the facts on methanol use at Indianapolis.

Good luck with your study of organic chemistry. I'm certain you will enjoy this course, especially if you let yourself relax and develop an interest in how organic compounds influence our lives. My goal in writing this book has been to make the process a little easier: to build the concepts logically on top of each other, so they flow naturally from one to the next. The hints and suggestions for problem-solving have helped my

students in the past, and I hope some of them will help you to learn and use the material. Even if your memory is worse than mine (highly unlikely), you should be able to do well in organic chemistry. I hope this will be a good learning experience for all of us.

Supplements

***Solutions Manual.* (ISBN: 0-13-974023-6)** Brief answers to many of the in-chapter problems are given at the back of this book. These answers are sufficient for a student on the right track, but they are of limited use to one who is having difficulty working the problems. The *Solutions Manual*, prepared by Jan W. Simek of California Polytechnic State University, contains many solutions to all the problems. Solutions also give helpful hints on how to approach each kind of problem. This supplement is a useful aid for any student, and it is particularly valuable for students who feel they understand the material but need more help with problem solving. Appendix 1 of the *Solutions Manual* summarizes the IUPAC system of nomenclature. Appendix 2 reviews and demonstrates how acidity varies with structure in organic molecules, and how one can predict the direction of an acid–base equilibrium.

The W@de Companion Website. This online center supports and enhances the text with interactive exercises, visualization exercises (hundreds of highly accurate 3-dimensional renderings of important molecules presented with mini-tutorials), current events features, relevant links, and animations—all organized according to the Wade table of contents. This useful website was created for Prentice Hall by Dr. Rainer Glaser and Dr. Mike Lewis of the University of Missouri, Columbia. Access this site at www.prenhall.com/wade.

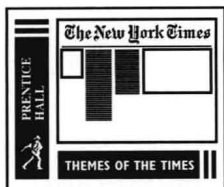
***Chemistry on the Internet.* (ISBN 0-13-758731-7)** This free book features a description of the Internet and suggestions for students who are planning to use Prentice Hall's chemistry Internet site, ChemCentral (www.prenhall.com/~chem). This book may be packaged with the text.

***ChemOffice Ltd. Software.* (ISBN: 0-13-082932-3)** This CD-ROM includes the student versions of ChemDraw and Chem3D. It can be bundled with the text for a discount. Each purchase of ChemOffice Ltd is accompanied by the *Tutorials in Modeling, Visualization, and Analyzing* workbook. This guide—created specifically for Wade 4/e—provides students with dozens of tutorials that require the use of ChemOffice Ltd; it is available for free downloading at www.prenhall.com/wade.

***Prentice Hall Molecular Model Kit.* (ISBN: 0-205-08136-3)** Every organic chemistry student needs a set of molecular models. These models are used to demonstrate a multitude of principles, including stereochemistry, ring strain, conformations of cyclic and acyclic systems, and many others. These principles are ideally presented with this durable model kit. The kit allows students to build space-filling and ball-and-stick models of organic molecules.

***Brumlik Framework Molecular Model Kit.* (ISBN: 0-13-330076-5)** Models constructed with this kit allow students to see the relationship between atoms in organic molecules, including precise interatomic distances and bond angles. The flexible bonds can form strained systems, with the amount of bend in the bonds giving a qualitative idea of the amount of strain.

***Brumlik Universal Molecular Model Kit.* (ISBN: 0-13-931700-7)** A scientifically accurate molecular model set that demonstrates the framework of a molecule, the space-filling capacity of a molecule, and molecular orbitals. This kit features color-coded atomic valence spheres and connectors. Its parts are fully interchangeable with the Brumlik Framework Molecular Model Kit.

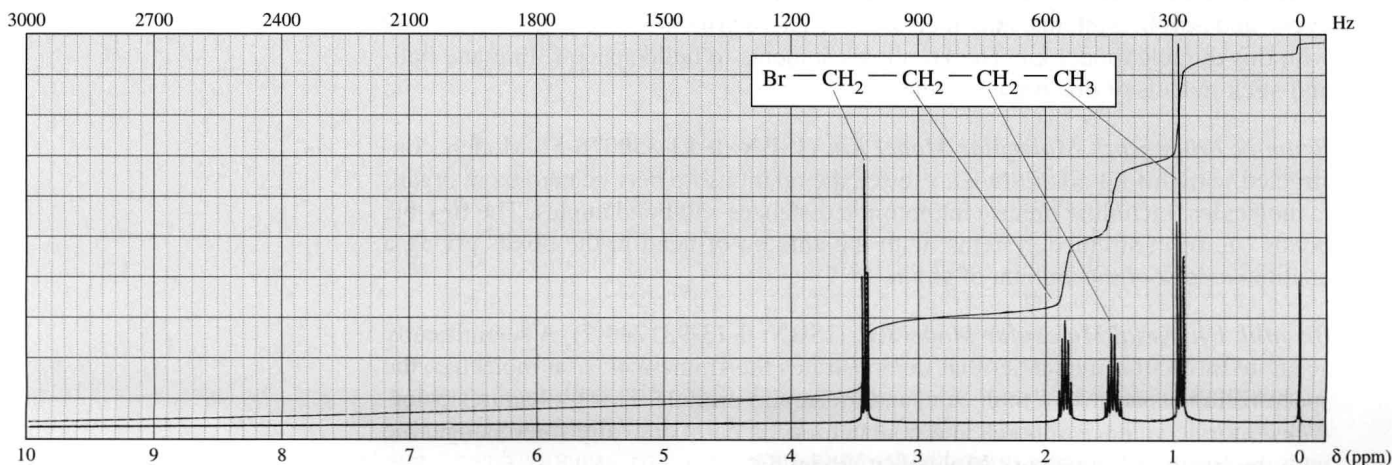
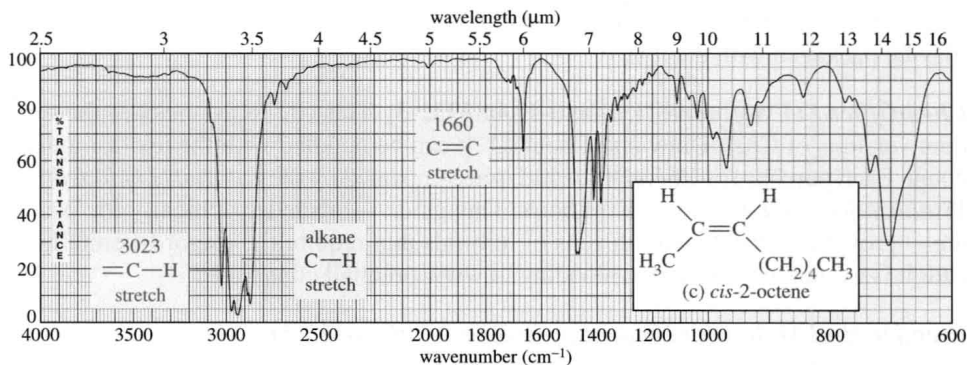


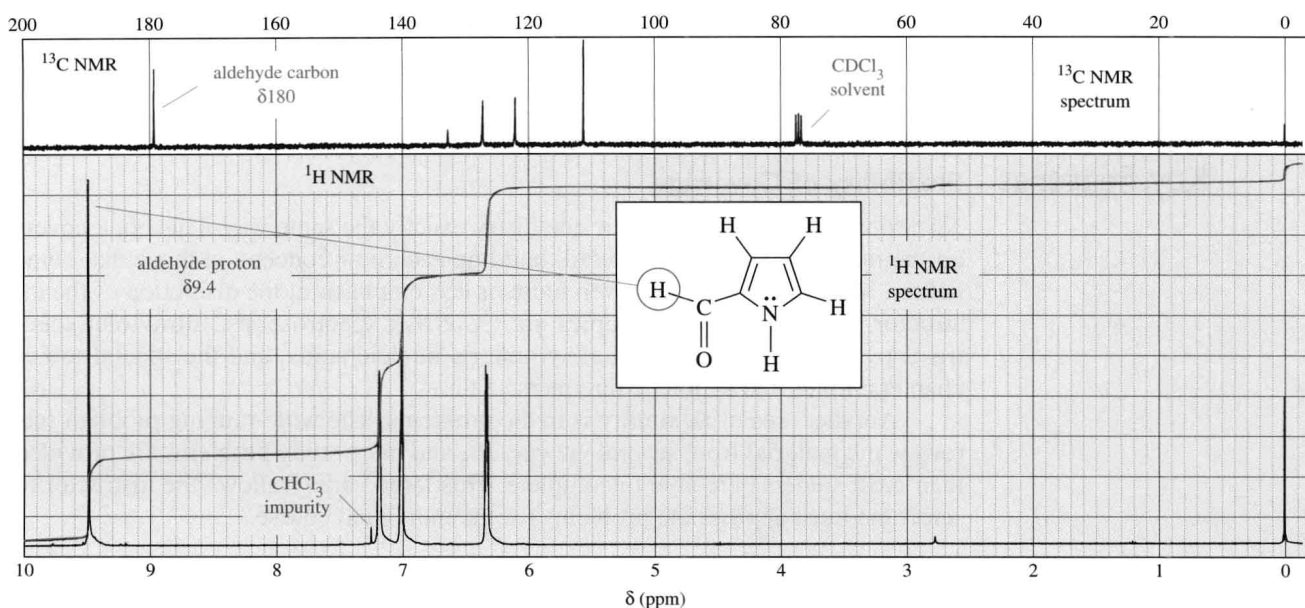
New York Times Themes of the Times. This newspaper supplement features recent articles on such topics as chemistry and health, environmental problems, and advances in chemistry as reported in the *New York Times*. It is available at no charge to users of Wade's *Organic Chemistry*.

To the Instructor

In writing the first edition of this text, my goal was to produce a modern, readable text that uses the most effective techniques of presentation and review. The second and third editions extended and refined that goal, with substantial rewriting and reorganization and with the addition of several new features. This fourth edition incorporates even more refinements than the third, with revisions in the organization, writing, and graphics. Some of the more obvious revisions are:

1. The chapters are reorganized to place alkynes immediately after alkenes, to reinforce the similarities between these two functional groups.
2. Much of the writing has been revised to enhance clarity and understanding, and to eliminate unnecessary repetition. Several new topics have been added, such as discussions of thiols, NMR imaging, and epoxy glues. Other topics have been expanded and updated, including polymer chemistry and biological applications.
3. All of the IR spectra and most of the NMR spectra are new, and many more ^{13}C NMR spectra have been added. The new IR spectra are taken from the Aldrich FT-IR catalog, with greatly enhanced resolution. The new proton NMR spectra are from the Aldrich FT-NMR catalog, taken at 300 MHz. A larger format is used for the new NMR spectra to allow the relatively smaller splittings to be fully resolved. A new section has been added comparing low-field and high-field NMR spectra.





4. The popular Problem-Solving Hints introduced in the third edition have been expanded to include more reminders and principles that help students solve specific types of problems.
5. The art program has been enhanced, using a large number of computer-generated three-dimensional structures. Fifty new color photographs have been added to increase student interest, while directly reinforcing the material. We hope you will agree that these photos are highly relevant.

The entire book has been edited, with many large passages rewritten to enhance clarity. As in the first edition, each new topic is introduced carefully and explained thoroughly. Many introductory sections have been rewritten to update them and make them more approachable for students. Whenever possible, illustrations have been added or modified to help students visualize the physical concepts.

The emphasis continues to be on *chemical reactivity*. Chemical reactions are introduced as soon as possible, and each functional group is considered in view of its reactivity toward electrophiles, nucleophiles, oxidants, reductants, and other reagents. "Electron-pushing" mechanisms are stressed throughout as a means of explaining and predicting this reactivity. Structural concepts such as stereochemistry and spectroscopy are thoroughly treated as useful techniques that enhance the fundamental study of chemical reactivity.

This book maintains the traditional organization that concentrates on one functional group at a time while comparing and contrasting the reactivity of different functional groups. Reactions are emphasized, beginning with Lewis acid–base reactions in Chapter 1, continuing with thermodynamics and kinetics in Chapter 4, and covering most of the important substitution, addition, and elimination reactions in the three chapters following stereochemistry.

Spectroscopic techniques (IR, MS, and NMR) are covered in Chapters 12 and 13, so that they will be covered in the first semester. This early coverage is needed to allow effective use of spectroscopy in the laboratory. Still, a large amount of organic chemistry has been covered before this digression into structure determina-

Organization

tion. The principles of spectroscopy are practiced and reinforced in later chapters, where the characteristic spectral features of each functional group are summarized and reinforced by practice problems.

Key Features **Flexibility of Coverage**

No two instructors teach organic chemistry exactly the same way. This book covers all the fundamental topics in detail, building each new concept on those that come before. Many topics may be given more or less emphasis at the discretion of the instructor. Examples of these topics are ^{13}C NMR spectroscopy, ultraviolet spectroscopy, conservation of orbital symmetry, nucleic acids, and the special topics chapters: lipids and synthetic polymers.

Another area of flexibility is in the problems. The wide-ranging problem sets review the material from several viewpoints, and more study problems are provided than most students are able to complete. This large variety allows the instructor to select the most appropriate problems for the individual course.

Up-to-Date Treatment

In addition to the classical reactions, this book covers many techniques and reactions that have more recently gained wide use among practicing chemists. Molecular-orbital theory is introduced early and used to explain electronic effects in conjugated and aromatic systems, pericyclic reactions, and ultraviolet spectroscopy. Carbon-13 NMR spectroscopy is treated as the routine tool it has become in most research laboratories. Many of the newer synthetic techniques are also included, such as the Birch reduction, Swern oxidations, alkylation of 1,3-dithianes, and oxidations using pyridinium chlorochromate.

Reaction Mechanisms

Reaction mechanisms are important in all areas of organic chemistry, but they are difficult for many students. Students fall into the trap of memorizing a mechanism while not understanding why it proceeds as it does. This book stresses the principles used to predict mechanisms. Problem-solving sections develop basic techniques for approaching mechanism problems, and they work to minimize rote memorization. These techniques emphasize deciding whether the reaction is acidic, basic, or free radical in nature, then breaking it down into Lewis acid–base interactions and using “arrow pushing” to illustrate these individual steps.

Introduction to Mechanisms Using Free-Radical Halogenation

The advantages and disadvantages of using free-radical halogenation to introduce reaction mechanisms have been debated for many years. The principal objection to free-radical halogenation is that it is not a useful synthetic reaction. But useful reactions such as nucleophilic substitution and additions to alkenes are complicated by participation of the solvent and other effects. Gas-phase free-radical halogenation allows a clearer treatment of kinetics and thermodynamics, as long as its disadvantages as a synthetic reaction are carefully discussed and the student is aware of the limitations.

Organic Synthesis

Organic synthesis is stressed throughout this book, with progressive discussions of the process involved in developing a synthesis. *Retrosynthetic analysis* is emphasized, and the student learns to work backward from the target compound and for-

ward from the starting materials to find a common intermediate. Several new problem-solving discussions of organic synthesis have been added, emphasizing how one approaches a multistep synthesis.

Typical yields have been provided for many synthetic reactions, although I hope students will not misuse these numbers. Too often students consider the yield of a reaction to be a fixed characteristic just as the melting point of a compound is fixed. In practice, many factors affect product yields, and literature values for apparently similar reactions often differ by a factor of 2 or more. The yields given in this book are *typical* yields that a good student with excellent technique might obtain.

Spectroscopy

Spectroscopy is one of the most important tools of the organic chemist. This book develops the theory for each type of spectroscopy and then discusses the characteristic spectral features. The most useful and dependable characteristics are summarized into a small number of rules of thumb that allow the student to interpret most spectra without looking up or memorizing large tables of data. For reference use, extensive tables of NMR and IR data and a more complete version of the Woodward–Fieser rules for UV are provided as appendices.

This approach is particularly effective with IR and NMR spectroscopy, and with mass spectrometry. Practical rules are given to help students see what information is available in the spectrum and what spectral characteristics usually correspond to what structural features. Sample problems show how the information from various spectra is combined to propose a structure. The emphasis is on helping students develop an intuitive feel for using spectroscopy to solve structural problems.

Nomenclature

IUPAC nomenclature is stressed throughout the book, but common nomenclature is also discussed and used to develop students' familiarity. Teaching only the IUPAC nomenclature might be justifiable, but such an approach would handicap students in their further study and use of the literature. Much of the literature of chemistry, biology, and medicine uses common names such as methyl ethyl ketone, isovaleric acid, methyl *t*-butyl ether, γ -aminobutyric acid, and ϵ -caprolactam. This book emphasizes why systemic nomenclature is often preferred, yet it encourages familiarity with common names as well.

Instructor Supplements

Wade Presentation Manager CD-ROM. (ISBN: 0-13-974080-5) This CD-ROM (runs on both Macintosh and IBM compatible machines) contains a wealth of images from the text, hundreds of 3-dimensional renderings of important organic molecules that can be manipulated with the Presentation Manager 3.0 software, and over 15 minutes of newly created animations. This program allows the user to search for images and animations by key terms, preview the selected pieces, edit the attached notes, and create transparency acetates. The user can also import his own multimedia assets into the program.

Transparency Pack. (ISBN: 0-13-974064-3) The package comprises 200 two- and four-color acetates of the most useful images, computer art, and line drawings from the text. The transparency pack is available at no charge to adopters of *Wade Organic Chemistry*.

Prentice Hall Custom Test. (Windows ISBN: 0-13-974049-X; Mac ISBN: 0-13-974031-7) This program contains a bank of over 1500 test questions prepared by Gary Hollis of Roanoke College. Based on the testing technology developed by Engineering Software Associates, Inc. (ESA), this supplement allows instructors to tailor exams to their own needs. With the Online Testing option, exams can be administered online, and data can be automatically transferred for evaluation. A comprehensive desk reference guide is included as well as online assistance.

Test Item File. (ISBN: 0-13-974056-2) This book is a printed version of all questions found on the Prentice Hall Custom Test software, organized according to the table of contents of Wade's *Organic Chemistry*.

Syllabus Builder. Syllabus Manager located at www.prenhall.com/wade. Extend the boundaries of your course with Syllabus Manager, a new online syllabus creation and management utility. The W@de Companion Website integrates Syllabus Manager, providing you with an easy, step-by-step process to create and revise your syllabus incorporating links into your text's Companion Website and other online content.

I've enjoyed working on this new edition, and I hope it's much better than the third edition. I've tried to make this book as error-free as possible, but I'm sure some errors have slipped by. If you find errors, or have suggestions about how the book might be made better, please let me know (L. G. Wade, Whitman College, Walla Walla, WA, 99362; E-mail wadelg@whitman.edu). Errors can be fixed quickly, in the next printing. I've already started a file of possible changes and improvements for the fifth edition, and I hope many of the current users will contribute suggestions to this file. I hope this book makes your job easier and helps more of your students to succeed. That's the most important reason I wrote it.

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