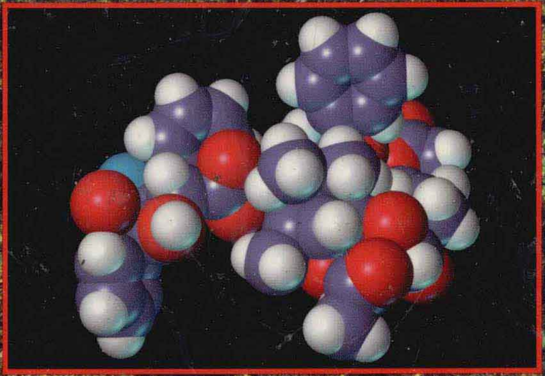
GRAHAM SOLOMONS
CRAIG FRYHLE



Organic Chemistry

seventh edition

ORGANIC CHEMISTRY

seventh edition

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For Judith, Allen, Graham, Jennie, Guido, and Cory. **TWGS**
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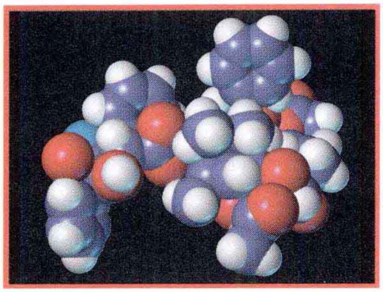
Preface



As with each new edition, there is one consistent goal: to bring the subject of organic chemistry to students in the comprehensible way that both they and it deserve.

ORGANIZATION

A central theme of our approach to organic chemistry is to emphasize the relationship between structure and reactivity. To accomplish this, we have chosen an organization that combines the most useful features of the traditional functional group approach with one based on reaction mechanisms. Our philosophy is to emphasize mechanisms and their common aspects as often as possible, and at the same time to use the unifying features of functional groups as the basis for most chapters. The structural aspects of our approach show students what organic chemistry is. Mechanistic aspects of our approach show students how it works. And wherever an opportunity arises, we show them what it does in living systems and the physical world around us.

Most important is for students to have a solid understanding of structure—of hybridization and geometry, steric hindrance, electronegativity, polarity, and formal charges—so that they can make intuitive sense of mechanisms. It is with these topics that we begin in Chapter 1. In Chapter 2 we introduce all of the important functional groups, and, new to this edition, we also introduce infrared spectroscopy. We have also added new, calculated structures throughout the book that enhance student's understanding of structure with models of electron density surfaces and maps of electrostatic potential.

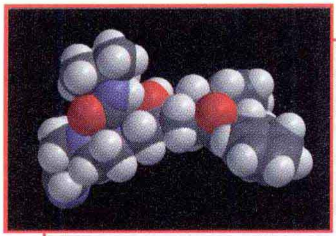
We begin our study of mechanisms in Chapter 3 in the context of acid-base chemistry. Why? Because acid-base reactions are fundamental. When looked at from the point of view of Lewis acid-base theory, the steps of most organic reaction mechanisms are acid-base reactions. Acid-base reactions, moreover, are relatively simple and they are reactions that students will find familiar. Acid-base reactions also lend themselves to an introduction of several important topics that students need to know about early in the course: (1) the curved arrow notation for illustrating mechanisms, (2) the relationship between free-energy changes and equilibrium constants, (3) how enthalpy and entropy changes affect reactions under equilibrium control, and (4) the importance of inductive and resonance effects and of solvent effects. In Chapter 3, we also begin to show students how organic chemistry works by presenting the first of many boxes called ***"A Mechanism for the Reaction."*** All through the book, these boxes highlight and bring forth the details of important reaction mechanisms.

Throughout our study we use various opportunities to show what organic chemistry does. As students come to realize that life and much of the world around us involves organic chemistry, their fascination with the subject cannot help but increase. We show what organic chemistry does in life, both in biological terms and in our physical environment, by including real world applications highlighted by chapter opening vignettes and "The Chemistry of . . ." boxes.

KEY FEATURES NEW TO THE SEVENTH EDITION

There are many changes in this edition but the most important ones are:

- **Chapter-opening vignettes to increase student interest**
- **Electrostatic potential maps and electron density surfaces—powerful new pedagogy**
- **An updated introduction to orbital hybridization and structure**
- **Learning Group Problems—active integration of concepts and opportunities for peer-led teaching**
- **A new introduction to retrosynthetic analysis and organic synthesis**
- **Highlights of biological and other real-world chemistry in "The Chemistry of . . ." boxes**
- **Mainstream coverage of certain special topics**
- **Early introduction of spectroscopy**
- **Pedagogical markers that focus attention on key tools and tips for learning**
- **CD for technology-based learning—molecular models in Spartan and .pdb (Protein Data Bank) formats, reaction animations, and teaching graphics**
- **Web Site to support faculty and students**



Chapter-Opening Vignettes

Students who find a subject interesting will be motivated to learn it. This idea was an innovation that made the first edition of this text the success that it became, and it is one that has been emphasized in every edition since. This edition takes this idea forward in an important new way: with vignettes that open each chapter and show students how the chapter's subject matter relates to "real-world" applications—to applications of biochemical, medical and environmental importance. For example, Chapter 2, the chapter that introduces functional groups, begins with an essay showing how certain functional groups are essential to the mechanism of action of Crixivan®, the HIV protease inhibitor. Chapter 3, on acid-base chemistry, is preceded by an essay that describes the role of the enzyme carbonic anhydrase in regulating blood acidity through the acid-base reactions involved in the mechanism of this enzyme. Opening Chapter 4 is an essay on the rotation of carbon–carbon single bonds in the muscle protein actin, one that sets the stage for the chapter's emphasis on conformational analysis. Other topics of similar engaging interest lead off each chapter in the text.

Electrostatic Potential Maps Illustrate Basic Principles of Structure and Reactivity

Two of the most helpful concepts that students can apply in organic chemistry are that opposite charges attract and that delocalization of charge is a stabilizing factor. As chemists, we know that many reactions occur because molecules with opposite charges are attracted to each other. We also know that reaction pathways are favored or disfavored partly on the basis of relative stability of charged intermediates. In order to fully utilize this pedagogy, we now use maps of electrostatic potential at the van der Waals surface of molecules in which colors indicate the charge distribution in the various regions of a molecule or ion.

For example, because an understanding of Brønsted–Lowry and Lewis acid-base reactivity is so essential for success in organic chemistry we have improved Chapter 3 (on acids and bases) by including a number of calculated electrostatic potential maps to illustrate how charge distribution influences the relative acidity of an acid and how it affects the relative stability of the conjugate base. These new graphics greatly assist visualization of charge separation, localization, and dispersal. Other examples in this chapter include illustrations of the acidity of terminal alkynes, of the charge distribution in acetate anion versus that of ethoxide anion, and in the Lewis acid-base reaction of boron trifluoride and ammonia.

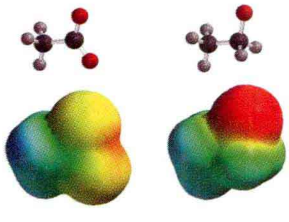


Figure 3.9 Acetate anion and ethoxide anion.

We also use electrostatic potential maps to focus attention on the complementary charges in nucleophiles and electrophiles, to show the relative charge distribution in asymmetric bromonium ions and asymmetric protonated epoxides, to compare the relative stability of arenium ion intermediates in electrophilic aromatic substitution, and to illustrate the electrophilic nature of carbonyl groups. In one of the early in-chapter boxes we also show how the LUMO of one reactant and the HOMO of another are important in reactions.

We generated the electron density surfaces and electrostatic potential maps in this book by ab initio quantum mechanical methods, using Spartan® software. Molecules we compare within a series are depicted over the same charge range to insure that comparisons are accurate and meaningful in relative terms. Structures are energy-minimized except for those where a particular higher energy conformation is desired.

Data files for most of the calculated structures we used in the book are included on the CD, and can be examined and manipulated in three dimensions using Spartan software. Many molecular structures are also provided in .pdb format for viewing with Rasmol or Chime. The CD icon denotes a structure whose data file is on the CD.

Orbital Hybridization and the Structure of Organic Molecules

In this edition we have chosen to use organic molecules to introduce all aspects of orbital hybridization. Hence, we begin with methane for sp^3 hybridization, and move directly to ethene for sp^2 hybridization, and then to ethyne for sp hybridization. (In the previous edition BF_3 and BeH_2 were used to introduce sp^2 and sp hybridization, respectively). By placing the emphasis directly on organic molecules we have been able to condense presentation of orbital hybridization and molecular structure from coverage in parts of two chapters to just one. Although our discussion of VSEPR still includes BF_3 and BeH_2 as examples, our emphasis is now on the three-dimensional structure of organic molecules, and this emphasis leads to an understanding of geometry and shape based on orbital hybridization. We also use calculated electron density surfaces to illustrate regions of bonding electron density, and overall molecular shape (the van der Waals surface) in representative molecules.

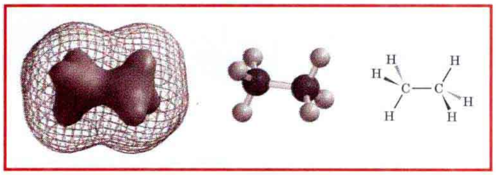


Figure 1.18 Structure of ethane.

Physical and Computer Molecular Models

Although we are strong proponents of technology in teaching, we also believe that hand-held molecular models are an essential complement to computer molecular models when students learn about structure. Indeed, some aspects of structure are best learned using physical molecular models. For this reason, we have included a set of 31 hands-on molecular model exercises in the *Study Guide* that are keyed to relevant sections of the text. Molecular models can be bundled with the text for an additional cost. Please ask your Wiley representative for details. We have also used marginal notes at several places in the text to suggest that students use hand-held molecular models to facilitate their studies at that specific point, just as we have used the CD icon to call attention to computer molecular models on the CD.

Active Integration of Concepts

LEARNING GROUP PROBLEMS

To facilitate active and collaborative student involvement in learning we have included problems at the end of each chapter that are designed to be solved by students working in small "Learning Groups." Each problem, called a Learning Group Problem (LGP), integrates concepts and requires gathering of information from the chapter for students to arrive at a complete solution. The problems can be worked inside or outside of class, with four to six students per group being a desirable size. The LGPs are a useful culminating activity to help students draw together what they have learned from each chapter and to integrate this knowledge with ideas they learned earlier.

Student-Led Teaching

The nature of the Learning Group Problems makes them useful as a vehicle for students to teach organic chemistry to their peers, as well. For example, because solutions to the problems draw out a variety of important concepts from each chapter, a group's classroom presentation of their Learning Group Problem can be the teaching mode for a given day in class. In this way, students can have the powerful experience of learning through teaching (a wonderful experience that we teachers already know first-hand). The instructor can coach the student presentations from the side of the classroom to insure that all the desired ideas are brought forth and articulated. Detailed suggestions for orchestrating a class involving Learning Group Presentations are given with information provided to instructors using this text. ■

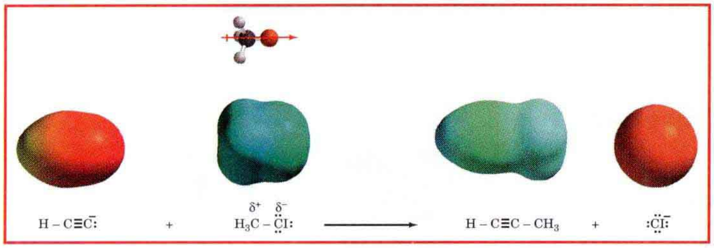


Figure 4.25 **Ethynide (acetylide) anion and chloromethane.**

Revised Introduction to Retrosynthetic Analysis and Organic Synthesis

In this edition the alkylation of alkynide anions replaces the Corey-House, Posner-Whitesides (lithium dialkylcuprate) sequence as the vehicle for introducing organic synthesis and retrosynthetic analysis (Chapter 4). One significant advantage of this change is that the reaction used to introduce organic synthesis is now one that is understood readily by students on an intuitive basis using concepts they will have learned up to that point. (This is something that could not be said for the coupling of alkyl halides with lithium dialkylcuprate reagents in previous editions.) Thus, several fundamental concepts presented in the very early chapters of the book are reinforced in the context of this new introduction to organic synthesis. For example, students will utilize Bronsted–Lowry acid-base chemistry when they outline syntheses that involve alkynide anions from alkynes, and they will recall Lewis acid-base concepts when they consider the interaction of an alkynide anion with an alkyl halide. And, here too, they will find reinforcement of the common theme of many organic reactions—the interaction between molecules bearing opposite charges.

Since carbon–carbon bond forming reactions are at the heart of organic synthesis, using the alkylation of alkynide anions as an introduction to synthesis gives students a method for making carbon–carbon bonds very early in their study of organic chemistry. Furthermore, using alkylations of alkynide ions gives students a product that contains a functional group—one they can use to make many other compounds. This is an aspect of synthesis that students will take advantage of later when their repertoire of reactions is larger. Finally, because "better" or "worse" retrosynthetic pathways using alkynide-anion alkylation are conceivable for a given molecule, this reaction is a realistic vehicle for teaching the logic of retrosynthetic analysis.

Substitution and Elimination Reactions

Substitution and elimination reactions provide an opportunity for students to encounter one of the important realities of organic chemistry. Reactions almost never follow exclusively one path, much as we would like them like to. We know very well how frequently one kind of reaction competes with another to complicate our synthetic plans. Therefore, bringing students to the point where they can propose reasonable syntheses using substitutions or eliminations requires a careful orchestration of topics. In this edition, as in the last, Chapter 6 focuses on substitution, but it also briefly introduces elimination reactions. We have done this because the two reactions nearly always occur together, and it is vitally important that students gain a chemically accurate understanding of this. Chapter 7 then rounds out the discussion by giving a detailed treatment of eliminations.

To smooth the flow of concepts and to keep the momentum going from the introduction of E2 and E1 reactions at the end of Chapter 6 to the full discussion of the stereochemistry and product distribution by elimination in Chapter 7, we have placed the discussion of elimination reactions very early in Chapter 7. Facilitating this change was the move of alkene and alkyne nomenclature from Chapter 7 to Chapter 4, where it is now included together with IUPAC nomenclature of alkanes. We also moved the hydrogenation of alkenes to the end of Chapter 7 from the beginning so that it does not delay further discussion of elimination reactions. Thus, Chapter 7 continues discussion of stereochemistry and product distribution in elimination reactions from Chapter 6 as soon as possible, yet it still provides the necessary background relating to relative alkene stability.

We took the discussion of kinetic versus thermodynamic control of product distribution out of Chapter 6 to save it for introduction in Chapter 13 at the discussion of 1,2- and 1,4-addition to conjugated dienes. In this context, the factors relating to overall product stability versus the relative stability of intermediates is easily grasped by students using concepts with which they have had long familiarity (relative alkene stability and relative carbocation stability). Kinetic versus thermodynamic product distribution also relates to discussion of the Diels-Alder reaction in Chapter 13.

Synthesis Updates

We have updated various sections so that they better illustrate the use of some important tools for synthesis. The Sharpless asymmetric epoxidation reaction is included in "The Chemistry of . . ." box in Chapter 11. Use of lithium enolates in organic synthesis is now a section in Chapter 17 (it had formerly been a Special Topic). Use of silyl ether protecting groups and silyl enol ethers is also discussed more clearly in the context of synthesis. The mechanism of primary alcohol dehydration has also been clarified. Discussion of the Diels-Alder reaction in Chapter 13 has been substantially updated. We have added enantioselective carbonyl reduction methods to Chapter 12, including the use of enzymes in organic synthesis (e.g., use of extremozymes from thermophilic bacteria for reduction reactions). Development of catalytic antibodies for aldol condensations is mentioned in relation to the Robinson annulation. Other reactions for which catalytic antibodies are being developed (such as Diels-Alder reactions, ester hydrolyses, etc.) are mentioned in Chapter 24 on proteins.

Spectroscopy

We have increased the opportunity for instructors, if they desire, to use spectroscopy as an early and integral part of their course. *We present infrared (IR) spectroscopy in Chapter 2, immediately after introduction of functional groups.* Placement of IR here shows students one of the important ways chemists actually obtain evidence about functional groups. It also supports the early experience that students may have with IR in the laboratory. Thus, as students study the important functional groups for the first time, they learn soon thereafter about the best method for detecting the presence of functional groups in a molecule.

We have given mass spectrometry (MS) mainstream coverage by placing it in the same chapter as NMR (mass spectrometry had been a Special Topic in earlier editions), *and we moved this chapter ahead in the book from Chapter 13 to Chapter 9.* We have also taken ultraviolet-visible (UV-Vis) spectrophotometry out of the NMR and MS chapter and placed it later in the context of conjugated unsaturated systems (Chapter 13). These changes provide emphasis for NMR and mass spectrometry as the two most powerful structure elucidation tools used by organic chemists, and they place these techniques squarely in the first part of a student's organic chemistry training. (This rearrangement also places mass spectrometry before free radical chlorination and bromination in Chapter 10, which allows use of mass spectrometry in exercises about radical halogenation, e.g., consideration of peak intensities with respect to isotopic natural abundance, etc.)

We also briefly introduce gas chromatography (GC) after mass spectrometry so that we can describe GC/MS as a tool for obtaining structural information on compounds in mixtures. The essence of our rationale for making all of these changes is that modern instrumental methods are central to the way chemists elucidate molecular structure, and NMR and mass spectrometry, together with IR, complete the typical analytical ensemble used by today's organic chemists. Early introduction of spectroscopic methods thus provides important support for the laboratory experiences of organic chemistry students, where instrumental methods play an increasing and early role in their training.

User-friendly NMR Spectra

All of the ^{1}H and ^{13}C NMR spectra were replaced with 300 MHz Fourier transform NMR spectra in the previous edition of the text. COSY and HETCOR two-dimensional NMR examples were added at that time, also. For this edition we have provided all of the 1D NMR data files (free induction decays) on our web site in both JCAMP format and NUTS format (an NMR software program from Acorn NMR, Inc.). The JCAMP format allows direct viewing of the NMR spectra using a web browser (but does not provide for extensive data manipulation). The NUTS format allows users to manipulate the data and prepare it for presentation in whatever manner they desire.

The NMR figures used to teach interpretation of spectra all have their signals color-coded to structural formulas, clearly showing which atoms are responsible for producing each signal in the NMR spectrum. Offset zoom expansions of all ^{1}H spectra are provided for clarity. Integrals are shown, as well. The ^{13}C NMR data are given with DEPT information, indicating the number of attached hydrogens on each unique carbon.

Mainstream Coverage for Some Former "Special Topics"

Several important areas that were "Special Topics" in previous editions are now included within the context of regular chapters as either chapter sections or "The Chemistry of . . ." boxes. For example, mass spectrometry now has coverage on equal footing with NMR in the "spectroscopy chapter," which also includes a brief introduction to two-dimensional NMR. Lithium enolates, because they are so central to organic synthesis, are covered as part of the general discussion of enolates. Chain growth polymers, because they are so important to our everyday lives, are placed in the chapter on radicals. Other Special Topics, such as "Biochemical Nucleophilic Substitution" and "The Photochemistry of Vision," though not essential to a student's knowledge of fundamental organic chemistry, are set as "The Chemistry of . . ." boxes in appropriate chapters. These boxes provide examples, embedded within the context of the fundamental chemistry surrounding them, of ways in which organic chemistry is central to life.

Relating Organic Chemistry to Biosynthesis

When an aspect of organic chemistry arises that has a biosynthetic counterpart we have juxtaposed that topic with the fundamental organic chemistry. An example is the biosynthesis of lanosterol from 2,3-oxidosqualene, a step along the pathway to cholesterol. Because this biosynthetic transformation is such a beautiful example of enzyme-mediated

The Chemistry of...

Example: Cholesterol Biosynthesis

In most chapters, one or more boxes called "The Chemistry of . . ." are used to provide enhanced coverage of a chapter topic, supply relevant biological, environmental, or material science examples, or expand upon concepts from the opening vignettes. Some examples are:

- **Radicals in Biology, Medicine, and Industry**
- **The Sharpless Asymmetric Epoxidation**
- **Epoxides, Carcinogens, and Biological Oxidation**
- **Nanotubes**
- **Sunscreens (Catching the Sun's Rays and What Happens to Them)**
- **Calicheamicin γ_1^I Activation for Cleavage of DNA**
- **Antibody-Catalyzed Aldol Condensations**
- **A Suicide Enzyme Substrate**
- **Artificial Sweeteners**

epoxide ring opening, alkene addition steps, and skeletal migrations, we placed "The Chemistry of . . . Cholesterol Biosynthesis" in Chapter 8, directly in relation to alkene addition reactions and shortly after students' acquaintance with hydride and methanide migrations. Another example of this approach is "The Chemistry of . . ." Polyketide Anticancer Antibiotic Biosynthesis" in Chapter 21, relating to phenols in that chapter and to the malonic ester synthesis and the Claisen condensation in Chapter 19. We believe that a student's appreciation of organic chemistry can be enhanced tremendously by showing the elegance of organic chemical reactions that take place in nature. Some other examples are:

- ***The Chemistry of . . .* Pyridoxal Phosphate**
- ***The Chemistry of . . .* Thiamine Pyrophosphate**
- ***The Chemistry of . . .* Biological Methylation**

OTHER PEDAGOGICAL FEATURES

We use the margins of the wide-format pages in this edition to note the central importance of certain topics, to provide study aids or practical tips for students where appropriate, and to add brief notes of a practical or historical nature where appropriate. Included in the margins are two types of icons.

Study Tip Icons

We have used "Study Tip" icons to highlight places in the text where a point is made that can be particularly helpful for a student learning organic chemistry. An example is the Study Tip icon in Section 1.8 regarding formal charges, pointing out that it will be necessary for students to keep track of formal charges later when they learn organic reactions. Another example is the Study Tip icon used to emphasize conventions used by chemists when we draw reaction and electron movement arrows (Section 1.8). Study Tip icons occur throughout the book.

Tool Box Icons

We have used "Tool Box" icons in the margin to emphasize concepts that are fundamental "tools" in organic chemistry. Some examples where the Tool Box icon is used are in Chapter 1, when we introduce the hydridization states of carbon and when we introduce VSEPR theory. These concepts are among the many essential "tools" for success in learning organic chemistry. We also use the Tool Box icon when a key process or reaction is described, such as the Robinson annulation for synthesis of carbocylic rings. Tool Box icons occur throughout the book.

Additional Features

In this edition we have refined and given added prominence to pedagogical features that existed in earlier editions:

A Mechanism for the Reaction

These boxes give detailed explanations for every key mechanism in the book. Curved arrows show precisely and unambiguously how electrons flow in each step of a mechanism. Text annotations under steps in the mechanisms further explain each transformation. At the end of chapters, **Summaries of Reactions** draw together the reactions from each chapter and help students see them in a unified context.

Additional features include:

- **Sample Problems with Solutions** show students how to approach problems in organic chemistry.
- **In-Chapter Problems** reinforce students' learning immediately after each topic is introduced.
- **Challenge Problems,** marked with an asterisk in the Additional Problems section of each chapter, are almost all new to this edition (approximately 75 have been added). The Challenge Problems are generally more difficult and involved than the majority of chapter-end problems. Challenge Problems typically require integration of several concepts to reach a solution.
- **Key Terms and Concepts,** listed at the end of each chapter with section references, allow students to test their memory regarding key ideas while also allowing easy reference back to a concept's full presentation in the chapter. The key terms and concepts listed are also defined in the Glossary.

Visualization Aids

Also, we've incorporated some significant new features to help students visualize structures and mechanisms.

- **Computer-generated models** Almost all ball-and-stick and space filling molecular models that previously had been artist's renderings have been replaced by computer-generated structures prepared by molecular modeling techniques. Most of these structures are included as a library of 3D-manipulable molecules on the CD in Spartan® or .pdb (Protein Data Bank) format.

- **Modernization of most graphics and illustrations** Many of the graphics and illustrations from previous editions (besides those that are new) have been modernized and updated.
- **Use of color in mechanisms** Consistent color schemes (implemented in previous editions, as well) are used to show changes in the bonding of atoms from reactants to products.

SUPPLEMENTS

OrganicView CD Every copy of the text includes the OrganicView CD. This fully integrated and interactive CD features Woodman Graphics with mechanism animations and other tutorials, IR Tutor, a library of the Spartan® molecular models found within the text, and .pdb molecular models for viewing with Rasmol® (also on the CD). Icons in the text indicate sections that are integrated with the CD.

Web Site The web site provides additional support for faculty and students who use the text. Included on the site is *Problem Assist!* which gives students further practice for mastering challenging problems. The web site also includes a complete collection of the Fourier transform NMR spectra used in the text. The NMR spectra are available in JCAMP format as well as in raw data format. Exciting links are also provided for each chapter.

Study Guide A *Study Guide* for **Organic Chemistry, 7th Edition** contains explained solutions to all of the problems in the text. The *Study Guide* also contains: an introductory essay called "Solving the Puzzle—or—Structure Is Everything" that serves as a bridge from general to organic chemistry; summary tables of reactions by mechanistic type and functional group; a review quiz for each chapter; a section describing the calculation of molecular formulas; and a set of 31 hands-on molecular model exercises keyed to relevant chapters in the text.

Modeling Kit In addition to computer modeling, we believe that hand-held molecular models are essential when students learn about structure. The Modeling Kit is available bundled with the text. Please ask your Wiley Representative for details.

Take Note! A notebook, containing key figures from the text, is provided so that students can take notes directly on the page during lecture. *Take Note!* is also available bundled with the text.

CD Resource Manager The CD Resource Manager includes figures and images from the text for use in lecture presentations. The Resource Manager has a built-in slide show and editing function. In addition, electronic images will be transferable into PowerPoint presentations.

Transparencies Full-color acetates of key illustrations are included. The images are enlarged and fonts are bolded for easier projection.

Test Bank The Test Bank includes over 1600 questions to aid instructors. The Test Bank is available in both a printed and computerized version.

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About the Authors

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T. W. Graham Solomons did his undergraduate work at The Citadel and received his doctorate in organic chemistry in 1959 from Duke University where he worked with C. K. Bradsher. Following this he was a Sloan Foundation Postdoctoral Fellow at the University of Rochester where he worked with V. Boekelheide. In 1960 he became a charter member of the faculty of the University of South Florida and became Professor of Chemistry in 1973. In 1992 he was made Professor *Emeritus.* In 1994 he was a visiting professor with the Faculté des Sciences Pharmaceutiques et Biologiques, Université René Descartes (Paris V). He is a member of Sigma Xi, Phi Lambda Upsilon, and Sigma Pi Sigma. He has received research grants from the Research Corporation and the American Chemical Society Petroleum Research Fund. For several years he was director of an NSF-sponsored Undergraduate Research Participation Program at USF. His research interests have been the areas of heterocyclic chemistry and unusual aromatic compounds. He has published papers in the *Journal of the American Chemical Society,* the *Journal of Organic Chemistry,* and the *Journal of Heterocyclic Chemistry.* He has received several awards for distinguished teaching. His organic chemistry textbooks have been widely used for 20 years and have been translated into Japanese, Chinese, Korean, Malaysian, Arabic, Portuguese, Spanish, and Italian. He and his wife Judith have a daughter who is a geophysicist and two younger sons.

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Craig Barton Fryhle is Associate Professor and Chair of the Department of Chemistry at Pacific Lutheran University. He earned his B.A. degree from Gettysburg College and Ph.D. from Brown University. Professor Fryhle's research interests relate to enzymes and metabolites of the shikimic acid pathway. His current research involves conformational studies of shikimate pathway substrates and analogues by molecular modeling and NMR spectrometry, and structure and reactivity studies of enzymes in the shikimic acid pathway. He has received research and instrumentation grants from the National Science Foundation, the M. J. Murdock Charitable Trust, and other private foundations. Professor Fryhle's work in chemical education has involved incorporation of active and computer-based learning strategies in organic chemistry, development of new experiments for undergraduate organic and instrumental analysis courses, and background work on the previous edition of this text. He is a volunteer with hands-on science programs in Seattle public schools. He was the 1999 Chair of the Puget Sound Section of the American Chemical Society. He lives in Seattle with his wife Deanna, and daughters Lauren and Heather.

To the Student

Contrary to what you may have heard, organic chemistry does not have to be a difficult course. It will be a rigorous course, and it will offer a challenge. But you will learn more in it than in almost any course you will take—and what you learn will have a special relevance to life and the world around you. However, because organic chemistry can be approached in a logical and systematic way, you will find that with the right study habits, mastering organic chemistry can be a deeply satisfying experience. Here, then, are some suggestions about how to study:

1. **Keep up with your work from day to day—never let yourself get behind.** Organic chemistry is a course in which one idea almost always builds on another that has gone before. It is essential, therefore, that you keep up with, or better yet, be a little ahead of your instructor. Ideally, you should try to stay one day ahead of your instructor's lectures in your own class preparations. The lecture, then, will be much more helpful because you will already have some understanding of the assigned material. Your time in class will clarify and expand ideas that are already familiar ones.
2. **Study material in small units, and be sure that you understand each new section before you go on to the next.** Again, because of the cumulative nature of organic chemistry, your studying will be much more effective if you take each new idea as it comes and try to understand it completely before you move on to the next concept. Many key concepts are emphasized by *Toolbox icons* in the margin and their accompanying captions. These concepts, once you learn them, will be part of your toolbox for success in organic chemistry. Similarly, tips or suggestions for studying and thinking about organic chemistry are highlighted by *Study Tip icons* and captions. Whether or not a concept is highlighted by a Toolbox or Study Tip icon, be sure you understand it before moving on.
3. **Work all of the in-chapter and assigned problems.** One way to check your progress is to work each of the in-chapter problems when you come to it. These problems have been written just for this purpose and are designed to help you decide whether or not you understand the material that has just been explained. If you can work the in-chapter problem, then you should go on; if you cannot, then you should go back and study the preceding material again. Work all of the problems assigned by your instructor from the end of the chapter, as well. Do all of your problems in a notebook and bring this book with you when you go to see your instructor for extra help.
4. **Write when you study.** Write the reactions, mechanisms, structures, and so on, over and over again. Organic chemistry is best assimilated through the fingertips by writing, and not through the eyes by simply looking, or by highlighting material in the text, or by referring to flash cards. There is a good reason for this. Organic structures, mechanisms, and reactions are complex. If you simply examine them, you may think you understand them thoroughly, but that will be a misperception. The reaction mechanism may make sense to you in a certain way, but you need a deeper understanding than this. You need to know the material so thoroughly that you can explain it to someone else. This level of understanding comes to most of us (those of us without photographic memories) through writing. Only by writing the reaction mechanisms do we pay sufficient attention to their details, such as which atoms are connected to which atoms, which bonds break in a reaction and which bonds form, and the three-dimensional aspects of the structures. When we write reactions and mechanisms, connections are made in our brains that provide the long-term memory needed for success in organic chemistry. We virtually guarantee that your grade in the course will be directly proportional to the