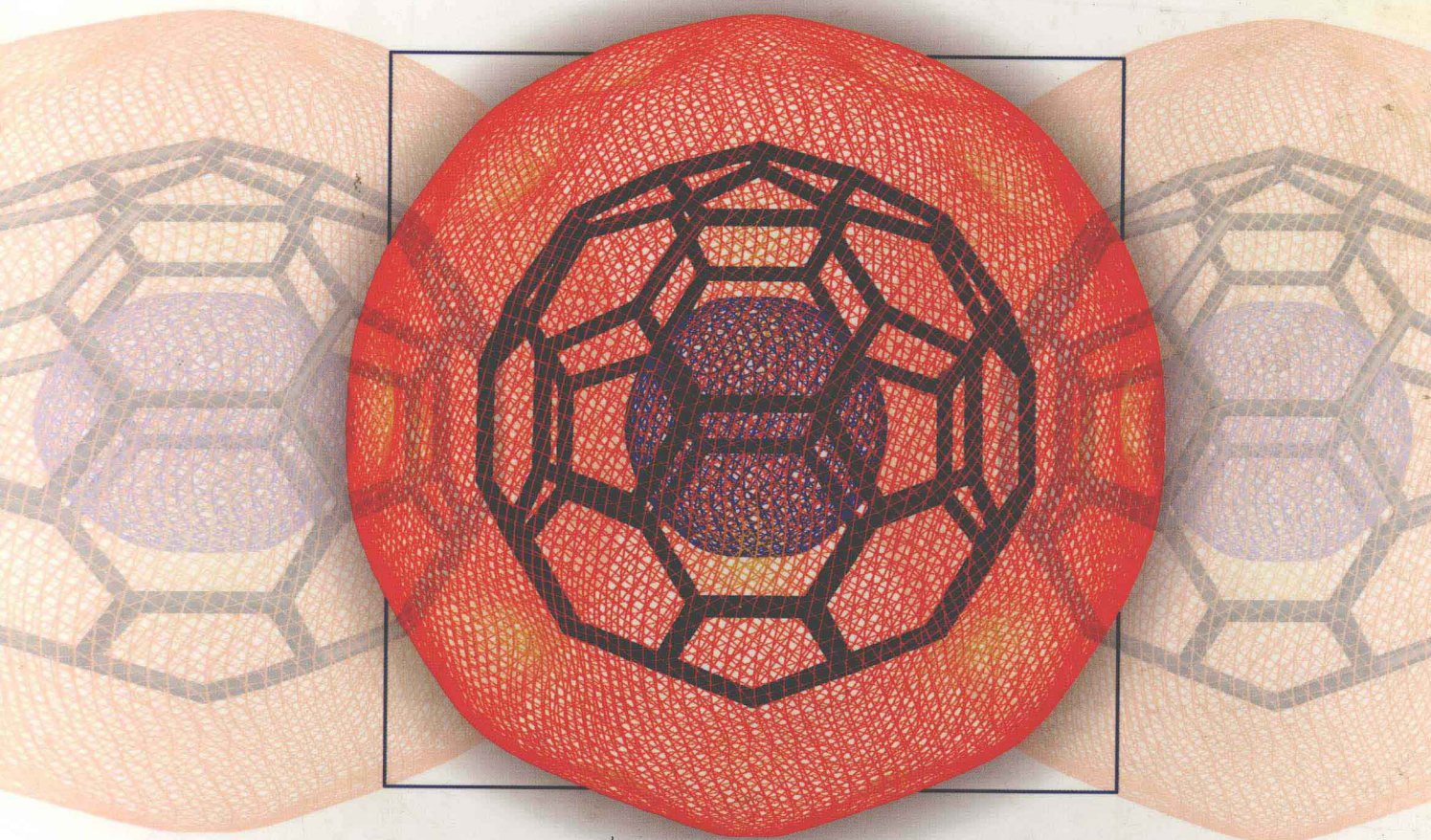


Francis A. Carey



fourth edition

ORGANIC CHEMISTRY

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Francis A. Carey
University of Virginia



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ORGANIC CHEMISTRY, FOURTH EDITION

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ABOUT THE AUTHOR

Francis A. Carey is a native of Pennsylvania, educated in the public schools of Philadelphia, at Drexel University (B.S. in chemistry, 1959), and at Penn State (Ph.D. 1963). Following postdoctoral work at Harvard and military service, he joined the chemistry faculty of the University of Virginia in 1966.

With his students, Professor Carey has published over 40 research papers in synthetic and mechanistic organic chemistry. He is coauthor (with Richard J. Sundberg) of *Advanced Organic Chemistry*, a two-volume treatment designed for graduate students and advanced undergraduates, and (with Robert C. Atkins) of *Organic Chemistry: A Brief Course*, an introductory text for the one-semester organic course.

Since 1993, Professor Carey has been a member of the Committee of Examiners of the Graduate Record

Examination in Chemistry. Not only does he get to participate in writing the Chemistry GRE, but the annual working meetings provide a stimulating environment for sharing ideas about what should (and should not) be taught in college chemistry courses.

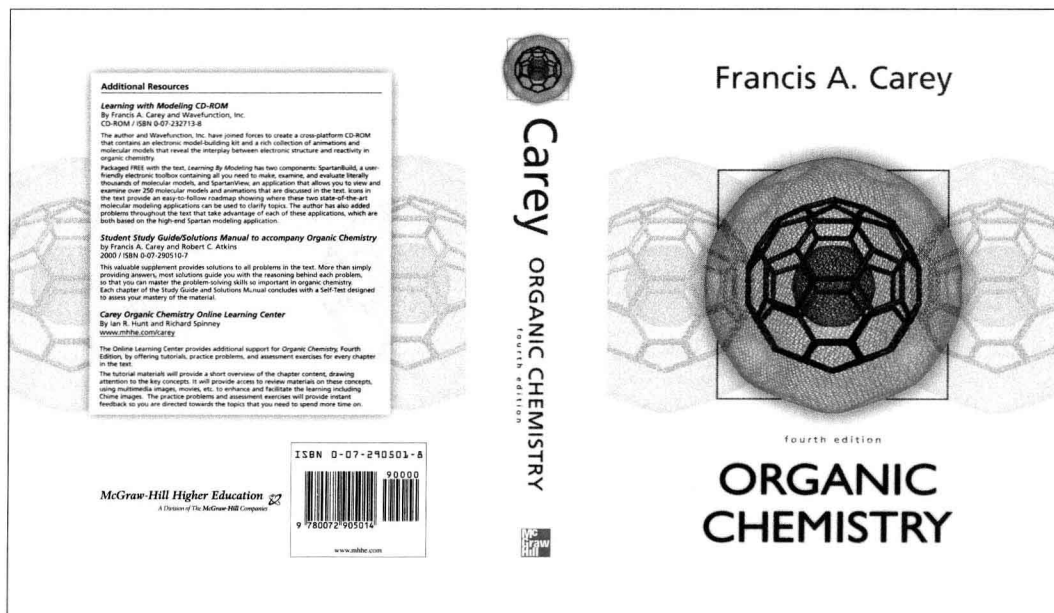
Professor Carey's main interest shifted from research to undergraduate education in the early 1980s. He regularly teaches both general chemistry and organic chemistry to classes of over 300 students. He enthusiastically embraces applications of electronic media to chemistry teaching and sees multimedia presentations as the wave of the present.

Frank and his wife Jill, who is a teacher/director of a preschool and a church organist, are the parents of three grown sons and the grandparents of Riyad and Ava.

ABOUT THE COVER

The cover image shows buckminsterfullerene (C₆₀) and its unusual electrostatic potential map as calculated using Spartan. It is best understood by first thinking about a sheet of fused benzene rings, such as occur in graphite. In such a sheet, negative electrostatic potential is equally distributed above and below the plane of the

atoms. Now curve the sheet, tending toward the ball. As the electrons inside the ball are brought closer together, they escape toward the outer surface where they are farther apart. The inside becomes a region of high positive potential (blue) and the outer surface a region of high negative potential (red).



This edition is dedicated to
my mother and father,
Julia and Francis W. Carey.

P R E F A C E

PHILOSOPHY

From its first edition through this, its fourth, *Organic Chemistry* has been designed to meet the needs of the “mainstream,” two-semester, undergraduate organic chemistry course. It has evolved as those needs have changed, but its philosophy remains the same. The overarching theme is that organic chemistry is not only an interesting subject, but also a logical one. It is logical because its topics can be connected in a steady progression from simple to complex. *Our approach has been to reveal the logic of organic chemistry by being selective in the topics we cover, as well as thorough and patient in developing them.*

Teaching at all levels is undergoing rapid change, especially in applying powerful tools that exploit the graphics capability of personal computers. Organic chemistry has always been the most graphical of the chemical sciences and is well positioned to benefit significantly from these tools. Consistent with our philosophy, this edition uses computer graphics to enhance the core material, to make it more visual, and more understandable, but in a way that increases neither the amount of material nor its level.

ORGANIZATION

The central message of chemistry is that the properties of a substance come from its structure. What is less obvious, but very powerful, is the corollary. Someone with training in chemistry can look at the structure of a substance and tell you a lot about its properties. Organic chemistry has always been, and continues to be, the branch of chemistry that best connects structure with properties. This text has a strong bias toward structure, and this edition benefits from the availability of versatile new tools to help us understand that structure.

The text is organized to flow logically and step by step from structure to properties and back again. As the list of chapter titles reveals, the organization is according to functional groups—structural units within a molecule most responsible for a particular property—because that is the approach that permits most students

to grasp the material most readily. Students retain the material best, however, if they understand how organic reactions take place. *Thus, reaction mechanisms are stressed early and often, but within a functional group framework.* A closer examination of the chapter titles reveals the close link between a functional group class (Chapter 20, Carboxylic Acid Derivatives) and a reaction type (Nucleophilic Acyl Substitution), for example. It is very satisfying to see students who entered the course believing they needed to memorize everything progress to the point of thinking and reasoning mechanistically.

Some of the important stages in this approach are as follows:

- The first mechanism the students encounter (Chapter 4) describes the conversion of alcohols to alkyl halides. Not only is this a useful functional-group transformation, but its first step proceeds by the simplest mechanism of all—proton transfer. The overall mechanism provides for an early reinforcement of acid-base chemistry and an early introduction to carbocations and nucleophilic substitution.
- Chapter 5 continues the chemistry of alcohols and alkyl halides by showing how they can be used to prepare alkenes by elimination reactions. Here, the students see a second example of the formation of carbocation intermediates from alcohols, but in this case, the carbocation travels a different pathway to a different destination.
- The alkenes prepared in Chapter 5 are studied again in Chapter 6, this time with an eye toward their own chemical reactivity. What the students learned about carbocations in Chapters 4 and 5 serves them well in understanding the mechanisms of the reactions of alkenes in Chapter 6.
- Likewise, the mechanism of nucleophilic addition to the carbonyl group of aldehydes and ketones described in Chapter 17 sets the stage for aldol condensation in Chapter 18, esterification of carboxylic acids in Chapter 19, nucleophilic acyl substitution in Chapter 20, and ester condensation in Chapter 21.

THE SPARTAN INTEGRATION

The third edition of this text broke new ground with its emphasis on *molecular modeling*, including the addition of more than 100 exercises of the model-building type. This, the fourth edition, moves to the next level of modeling. Gwendolyn and Alan Shusterman's 1997 *Journal of Chemical Education* article "Teaching Chemistry with Electron Density Models" described how models showing the results of molecular orbital calculations, especially electrostatic potential maps, could be used effectively in introductory courses. The software used to create the Shustermans' models was Spartan, a product of Wavefunction, Inc.

In a nutshell, the beauty of electrostatic potential maps is their ability to display the charge distribution in a molecule. At the most fundamental level, the forces that govern structure and properties in organic chemistry are the attractions between opposite charges and the repulsions between like charges. We were therefore optimistic that electrostatic potential maps held great promise for helping students make the connection between structure, especially electronic structure, and properties. Even at an early stage we realized that two main considerations had to guide our efforts.

- *An integrated approach was required.* To be effective, Spartan models and the information they pro-

vide must be woven into, not added to, the book's core.

- *The level of the coverage had to remain the same.* Spartan is versatile. We used the same software package to develop this edition that is used in research laboratories worldwide. It was essential that we limit ourselves to only those features that clarified a particular point. Organic chemistry is challenging enough. We didn't need to make it more difficult. If we were to err, it would therefore be better to err on the side of caution.

A third consideration surfaced soon after the work began.

- *Student access to Spartan would be essential.* Nothing could help students connect with molecular modeling better than owning the same software used to produce the text or, even better, software that allowed them not only to view models from the text, but also to make their own.

All of this led to a fruitful and stimulating collaboration with Dr. Warren Hehre, a leading theoretical chemist and the founder, president, and CEO of Wavefunction, Inc. Warren was enthusiastic about the project and agreed to actively participate in it. He and Alan Shusterman produced a CD tailored specifically to

NEW IN THIS EDITION

ALL-NEW ILLUSTRATIONS All figures were redrawn to convey visual concepts clearly and forcefully. In addition, the author created a number of new images using the Spartan molecular modeling application. Now students can view electrostatic potential maps to see the charge distribution of a molecule in vivid color. These striking images afford the instructor a powerful means to lead students to a better understanding of organic molecules.

FULL SPARTAN IMAGE INTEGRATION The Spartan-generated images are impressive in their own right, but for teaching purposes they are most effective when they are closely aligned with the text content. Because the author personally generated the images as he wrote this edition, the molecular models are fully integrated with text, and the educational value is maximized. Additionally, icons direct students to


specific applications of either the SpartanView or SpartanBuild program, found on the accompanying CD-ROM. Appendix 3 provides a complete guide to the *Learning By Modeling* CD-ROM.


ALL-NEW SPECTRA Chapter 13, Spectroscopy, was heavily revised, with rewritten sections on NMR and with all the NMR spectra generated on a high-field instrument.

IMPROVED SUMMARIES The end-of-chapter summaries are recast into a more open, easier-to-read format, inspired by the popularity of the accompanying summary tables.

NEW DESIGN This edition sports a new look, with an emphasis on neatness, clarity, and color carefully used to heighten interest and to create visual cues for important information.

accompany our text. We call it *Learning By Modeling*. It and *Organic Chemistry* truly complement each other. Many of the problems in *Organic Chemistry* have been written expressly for the model-building software SpartanBuild that forms one part of *Learning By Modeling*. Another tool, SpartanView, lets students inspect more than 250 already constructed models and animations, ranging in size from hydrogen to carboxypeptidase.

We were careful to incorporate Spartan so it would be a true amplifier of the textbook, not just as a stand-alone tool that students might or might not use, depending on the involvement of their instructor. Thus, the content of the CD provides visual, three-dimensional reinforcement of the concepts covered on the printed page. The SpartanView icon  invites students to view a molecule or animation as they are reading the text.

Opportunities to use SpartanBuild are similarly correlated to the text with an icon  directing students to further explore a concept or solve a modeling-based problem with the software.

In addition to its role as the electronic backbone of the CD component and the integrated learning approach, the Spartan software makes a visible impact on the printed pages of this edition. I used Spartan on my own computer to create many of the figures, providing students with numerous visual explorations of the concepts of charge distribution.

BIOLOGICAL APPLICATIONS AND THEIR INTEGRATION

Comprehensive coverage of the important classes of biomolecules (carbohydrates, lipids, amino acids, peptides, proteins, and nucleic acids) appears in Chapters 25–27. But biological applications are such an important part of organic chemistry that they deserve more attention throughout the course. We were especially alert to opportunities to introduce more biologically oriented material to complement that which had already grown significantly since the first edition. Some specific examples:

- The new boxed essay “Methane and the Biosphere” in Chapter 2 combines elements of organic chemistry, biology, and environmental science to tell the story of where methane comes from and where it goes.
- A new boxed essay, “An Enzyme-Catalyzed Nucleophilic Substitution of an Alkyl Halide,” in Chapter 8 makes a direct and simple connection between S_N2 reactions and biochemistry.

- Two new boxed essays, “How Sweet It Is!” in Chapter 25, and “Good Cholesterol? Bad Cholesterol? What’s the Difference?” in Chapter 26, cover topics of current interest from an organic chemist’s perspective.
- The already-numerous examples of enzyme-catalyzed organic reactions were supplemented by adding biological Baeyer-Villiger oxidations and fumaric acid dehydrogenation.

Chapters 25–27 have benefited substantially from the Spartan connection. We replaced many of the artist-rendered structural drawings of complex biomolecules from earlier editions with accurate models generated from imported crystallographic data. These include:

- maltose, cellobiose, and cellulose in Chapter 25
- triacylglycerols in Chapter 26
- alanylglycine, leucine enkephalin, a pleated β -sheet, an α -helix, carboxypeptidase, myoglobin, DNA, and phenylalanine tRNA in Chapter 27

All of these are included on *Learning By Modeling*, where you can view them as wire, ball-and-spoke, tube, or space-filling models while rotating them in three dimensions.

Both the text and *Learning By Modeling* include other structures of biological interest including:

- a space-filling model of a micelle (Chapter 19)
- electrostatic potential maps of the 20 common amino acids showing just how different the various side chains are (Chapter 27)

SPECTROSCOPY

Because it offers an integrated treatment of nuclear magnetic resonance (NMR), infrared (IR), and ultraviolet-visible (UV-VIS) spectroscopy, and mass spectrometry (MS), Chapter 13 is the longest in the text. It is also the chapter that received the most attention in this edition. All of the sections dealing with NMR were extensively rewritten, all of the NMR spectra were newly recorded on a high-field instrument, and all of the text figures were produced directly from the electronic data files.

Likewise, the IR and UV-VIS sections of Chapter 13 were revised and all of the IR spectra were recorded especially for this text.

After being first presented in Chapter 13, spectroscopy is then integrated into the topics that follow it. The functional-group chapters, 15, 16, 17, 19, 20, 22,

and 24, all contain spectroscopy sections as well as examples and problems based on display spectra.

INTEGRATION OF TOPICS

Too often, in too many courses (and not just in organic chemistry), too many interesting topics never get covered because they are relegated to the end of the text as “special topic chapters” that, unfortunately, fall by the wayside as the end of the term approaches. We have, from the beginning and with each succeeding edition, looked for opportunities to integrate the most important of these “special” topics into the core material. I am pleased with the results. Typically, this integration is accomplished by breaking a topic into its component elements and linking each of those elements to one or more conceptually related core topics.

There is, for example, no end-of-text chapter entitled “Heterocyclic Compounds.” Rather, heteroatoms are defined in Chapter 1 and nonaromatic heterocyclic compounds introduced in Chapter 3; heterocyclic aromatic compounds are included in Chapter 11, and their electrophilic and nucleophilic aromatic substitution reactions described in Chapters 12 and 23, respectively. Heterocyclic compounds appear in numerous ways throughout the text and the biological role of two classes of them—the purines and pyrimidines—features prominently in the discussion of nucleic acids in Chapter 27.

The economic impact of synthetic polymers is too great to send them to the end of the book as a separate chapter or to group them with biopolymers. We regard polymers as a natural part of organic chemistry and pay attention to them throughout the text. The preparation of vinyl polymers is described in Chapter 6, polymer stereochemistry in Chapter 7, diene polymers in Chapter 10, Ziegler–Natta catalysis in Chapter 14, and condensation polymers in Chapter 20.

INTEGRATING THE CHEMISTRY CURRICULUM

I always thought that the general chemistry course would be improved if more organic chemists taught it, and have done just that myself for the past nine years. I now see that just as general chemistry can benefit from the perspective that an organic chemist brings to it, so can the teaching and learning of organic chemistry be improved by making the transition from general chemistry to organic smoother. Usually this is more a matter of style and terminology than content—an incremental rather than a radical change. I started making such changes in the third edition and continue here.

I liked, for example, writing the new boxed essay “Laws, Theories, and the Scientific Method” and placing it in Chapter 6. The scientific method is one thing that everyone who takes a college-level chemistry course should be familiar with, but most aren’t. It normally appears in Chapter 1 of general chemistry texts, before the students have enough factual knowledge to really understand it, and it’s rarely mentioned again. By the time our organic chemistry students get to “Laws, Theories, and the Scientific Method,” however, we have told them about the experimental *observations* that led to Markovnikov’s *law*, and how our understanding has progressed to the level of a broadly accepted *theory* based on carbocation stability. It makes a nice story. Let’s use it.

FEWER TOPICS EQUALS MORE HELP

By being selective in the topics we cover, we can include more material designed to help the student learn.

Solved sample problems: In addition to a generous number of end-of-chapter problems, the text includes more than 450 problems within the chapters themselves. Of these in-chapter problems approximately one-third are multipart exercises that contain a detailed solution to part (a) outlining the reasoning behind the answer.

Summary tables: Annotated summary tables have been a staple of *Organic Chemistry* ever since the first edition and have increased in number to more than 50. Well received by students and faculty alike, they remain one of the text’s strengths.

End-of-chapter summaries: Our experience with the summary tables prompted us to recast the narrative part of the end-of-chapter summaries into a more open, easier-to-read format.

SUPPLEMENTS

For the Student

Study Guide and Solutions Manual by Francis A. Carey and Robert C. Atkins. This valuable supplement provides solutions to all problems in the text. More than simply providing answers, most solutions guide the student with the reasoning behind each problem. In addition, each chapter of the *Study Guide and Solutions Manual* concludes with a Self-Test designed to assess the student’s mastery of the material.

Online Learning Center

At www.mhhe.com/carey, this comprehensive, exclusive Web site provides a wealth of electronic resources for

instructors and students alike. Content includes tutorials, problem-solving strategies, and assessment exercises for every chapter in the text.

Learning By Modeling CD-ROM

In collaboration with Wavefunction, we have created a cross-function CD-ROM that contains an electronic model-building kit and a rich collection of animations and molecular models that reveal the interplay between electronic structure and reactivity in organic chemistry.

Packaged free with the text, *Learning By Modeling* has two components: SpartanBuild, a user-friendly electronic toolbox that lets you build, examine, and evaluate literally thousands of molecular models; and SpartanView, an application with which you can view and examine more than 250 molecular models and animations discussed in the text. In the textbook, icons point the way to where you can use these state-of-the-art molecular modeling applications to expand your understanding and sharpen your conceptual skills. This edition of the text contains numerous problems that take advantage of these applications. Appendix 3 provides a complete guide to using the CD.

For the Instructor

Overhead Transparencies. These full-color transparencies of illustrations from the text include reproductions of spectra, orbital diagrams, key tables, computer-generated molecular models, and step-by-step reaction mechanisms.

Test Bank. This collection of 1000 multiple-choice questions, prepared by Professor Bruce Osterby of the University of Wisconsin–LaCrosse, is available to adopters in print, Macintosh, or Windows format.

Visual Resource Library. This invaluable lecture aid provides the instructor with all the images from the textbook on a CD-ROM. The PowerPoint format enables easy customization and formatting of the images into the lecture.

The *Online Learning Center*, described in the previous section, has special features for instructors, including quiz capabilities.

Please contact your McGraw-Hill representative for additional information concerning these supplements.

ACKNOWLEDGMENTS

You may have noticed that this preface is almost entirely “we” and “our,” not “I” and “my.” That is because *Organic Chemistry* is, and always has been, a team effort. From the first edition to this one, the editorial and production staffs at WCB/McGraw-Hill have been committed to creating an accurate, interesting, student-oriented text. Special thanks go to Kent Peterson, Terry Stanton, and Peggy Selle for their professionalism, skill, and cooperative spirit. Linda Davoli not only copy edited the manuscript but offered valuable advice about style and presentation. GTS Graphics had the critical job of converting the copy-edited manuscript to a real book. Our contact there was Heather Stratton; her enthusiasm for the project provided us an unusual amount of freedom to fine-tune the text.

I have already mentioned the vital role played by Warren Hehre and Alan Shusterman in integrating Spartan into this edition. I am grateful for their generosity in giving their time, knowledge, and support to this project. I also thank Dr. Michal Sabat of the University of Virginia for his assistance in my own modeling efforts.

All of the NMR and IR spectra in this edition were recorded at the Department of Chemistry of James Madison University by two undergraduate students, Jeffrey Cross and Karin Hamburger, under the guidance of Thomas Gallaher. We are indebted to them for their help.

Again, as in the three previous editions, Dr. Robert C. Atkins has been indispensable. Bob is the driving force behind the *Study Guide and Solutions Manual* that accompanies this text. He is much more than that, though. He reads and critiques every page of the manuscript and every page of two rounds of proofs. I trust his judgment completely when he suggests how to simplify a point or make it clearer. Most of all, he is a great friend.

This text has benefited from the comments offered by a large number of teachers of organic chemistry who reviewed it at various stages of its development. I appreciate their help. They include

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 John Wasacz, Manhattan College

Finally, I thank my family for their love, help, and encouragement. The “big five” remain the same: my wife Jill, our sons Andy, Bob, and Bill, and daughter-in-law Tasneem. They have been joined by the “little two,” our grandchildren Riyad and Ava.

Comments, suggestions, and questions are welcome. Previous editions produced a large number of e-mail messages from students. I found them very helpful and invite you to contact me at:
fac6q@unix.mail.virginia.edu.

Francis A. Carey

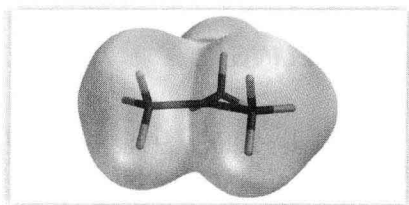
A GUIDE TO USING THIS TEXT

The following pages provide a walk-through of the key features of this text. Every element in this book has a purpose and serves the overall goal of leading students to a true understanding of the processes in organic chemistry.

INTEGRATED TEXT AND VISUALS

With All-new Figures

Because visualization is so important to understanding, illustrations work hand-in-hand with text to convey information. The author generated many of the figures himself as he wrote the text using Spartan software, so that images are fully coordinated with the text.



CHAPTER 4

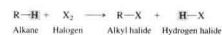
ALCOHOLS AND ALKYL HALIDES

Our first three chapters established some fundamental principles concerning the structure of organic molecules. In this chapter we begin our discussion of organic chemical reactions by directing attention to *alcohols* and *alkyl halides*. These two rank among the most useful classes of organic compounds because they often serve as starting materials for the preparation of numerous other families.

Two reactions that lead to alkyl halides will be described in this chapter. Both illustrate functional group transformations. In the first, the hydroxyl group of an alcohol is replaced by halogen on treatment with a hydrogen halide.



In the second, reaction with chlorine or bromine causes one of the hydrogen substituents of an alkane to be replaced by halogen.



Both reactions are classified as *substitutions*, a term that describes the relationship between reactants and products—one functional group replaces another. In this chapter we go beyond the relationship of reactants and products and consider the *mechanism* of each reaction. A *mechanism* attempts to show how starting materials are converted into products during a chemical reaction.

While developing these themes of reaction and mechanism, we will also use alcohols and alkyl halides as vehicles to extend the principles of IUPAC nomenclature, con-

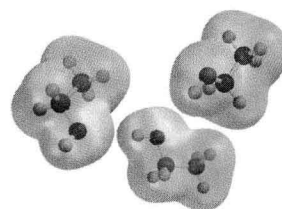


FIGURE 4.4 Hydrogen bonding in ethanol involves the oxygen of one molecule and the proton of an —OH group of another. Hydrogen bonding is much stronger than most other types of dipole-dipole attractive forces.

proton involved must be bonded to an electronegative element, usually oxygen or nitrogen. Protons in C—H bonds do not participate in hydrogen bonding. Thus fluoroethane, even though it is a polar molecule and engages in dipole-dipole attractions, does not form hydrogen bonds and, therefore, has a lower boiling point than ethanol.

Hydrogen bonding can be expected in molecules that have —OH or —NH groups. Individual hydrogen bonds are about 10–50 times weaker than typical covalent bonds, but their effects can be significant. More than other dipole-dipole attractive forces, intermolecular hydrogen bonds are strong enough to impose a relatively high degree of structural order on systems in which they are possible. As will be seen in Chapter 27, the three-dimensional structures adopted by proteins and nucleic acids, the organic molecules of life, are dictated by patterns of hydrogen bonds.

PROBLEM 4.5 The constitutional isomer of ethanol, dimethyl ether (CH_3OCH_3), is a gas at room temperature. Suggest an explanation for this observation.

Table 4.1 lists the boiling points of some representative alkyl halides and alcohols. When comparing the boiling points of related compounds as a function of the alkyl group, we find that the boiling point increases with the number of carbon atoms, as it does with alkanes.

Hydrogen bonds between —OH groups are stronger than those between —NH groups. As a comparison of the boiling points of water (H_2O , 100°C) and ammonia (NH_3 , -33°C) demonstrate.

For a discussion concerning the boiling point behavior of alkyl halides, see the January 1988 issue of the *Journal of Chemical Education*, pp. 62–64.

TABLE 4.1 Boiling Points of Some Alkyl Halides and Alcohols


Name of alkyl group	Formula	Functional group X and boiling point, °C (1 atm)				
		X = F	X = Cl	X = Br	X = I	X = OH
Methyl	CH_3X	-78	-24	3	42	65
Ethyl	$\text{CH}_3\text{CH}_2\text{X}$	-32	12	38	72	78
Propyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{X}$	-3	47	71	103	97
Pentyl	$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{X}$	65	108	129	157	136
Hexyl	$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{X}$	92	134	155	180	157

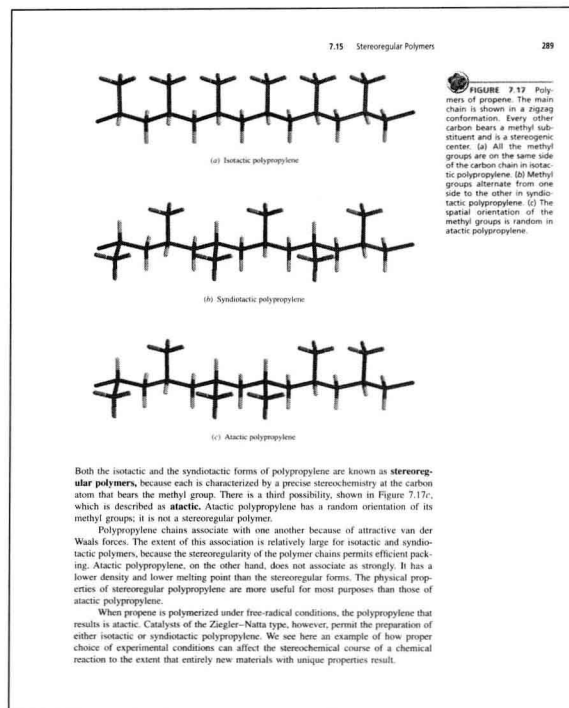
EFFECTIVE ORGANIZATION OF FUNCTIONAL GROUPS

Reaction mechanisms are stressed early and often, but within a functional framework. For example, Chapter 4 is the first chapter to cover a functional group (alcohols and alkyl halides) but it introduces *mechanism* simultaneously.

LEARNING BY MODELING

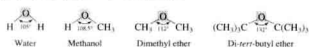
A Full Correlation

Not only can students view molecular models while using the book, but with the free CD-ROM that accompanies the text, they have access to the software that was used to create the images. With the SpartanView and SpartanBuild software, students can view models from the text and also make their own. The SpartanView icon  identifies molecules and animations that can be seen on the CD. Appendix 3 provides a complete tutorial guide to the CD.



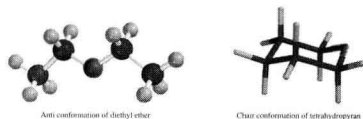
16.2 STRUCTURE AND BONDING IN ETHERS AND EPOXIDES

Bonding in ethers is readily understood by comparing ethers with water and alcohols. Van der Waals strain involving alkyl groups causes the bond angle at oxygen to be larger in ethers than alcohols, and larger in alcohols than in water. An extreme example is di-*tert*-butyl ether, where steric hindrance between the *tert*-butyl groups is responsible for a dramatic increase in the C—O—C bond angle.

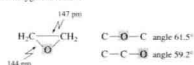


Typical carbon-oxygen bond distances in ethers are similar to those of alcohols (≈ 142 pm) and are shorter than carbon-carbon bond distances in alkanes (≈ 153 pm).

An ether oxygen affects the conformation of a molecule in much the same way that a CH_2 unit does. The most stable conformation of diethyl ether is the all-staggered anti conformation. Tetrahydropyran is most stable in the chair conformation—a fact that has an important bearing on the structures of many carbocyclic ethers.



Incorporating an oxygen atom into a three-membered ring requires its bond angle to be seriously distorted from the normal tetrahedral value. In ethylene oxide, for example, the bond angle at oxygen is 61.5° .




Thus epoxides, like cyclopropanes, are strained. They tend to undergo reactions that open the three-membered ring by cleaving one of the carbon-oxygen bonds.

PROBLEM 16.2 The heats of combustion of 1,2-epoxybutane (2-ethyloxirane) and tetrahydrofuran have been measured; one is 2459 kJ/mol (597.6 kcal/mol); the other is 2546 kJ/mol (609.1 kcal/mol). Match the heats of combustion with the respective compounds.

Ethers, like water and alcohols, are polar. Diethyl ether, for example, has a dipole moment of 1.2 D. Cyclic ethers have larger dipole moments; ethylene oxide and tetrahydrofuran have dipole moments in the 1.7- to 1.8-D range—about the same as that of water.

LEARNING BY MODELING

An Active Process

Many of the problems in this edition of the text have been expressly written to involve use of the SpartanBuild software on the *Learning By Modeling* CD-ROM. Students discover the connection between structure and properties by actually building molecules on their own. The SpartanBuild icon  directs them when to use this tool.

LEARNING BY MODELING

From Spartan to the Page

New in this edition's figures are molecular models that the author generated using the Spartan modeling application. Electrostatic potential maps give a vivid look at the charge distribution in a molecule, showing the forces that govern structure and properties in organic chemistry.

1.10 The Shapes of Some Simple Molecules

27

LEARNING BY MODELING

As early as the nineteenth century many chemists built scale models in order to better understand molecular structure. We can gain a clearer idea about the features that affect structure and reactivity when we examine the three-dimensional shape of a molecule. Several types of molecular models are shown for methane in Figure 1.7. Probably the most familiar are ball-and-stick models (Figure 1.7b), which direct approximately equal attention to the atoms and the bonds that connect them. Framework models (Figure 1.7a) and space-filling models (Figure 1.7c) represent opposite extremes. Framework models emphasize the pattern of bonds of a molecule while ignoring the sizes of the atoms. Space-filling models emphasize the volume occupied by individual atoms at the cost of a clear depiction of the bonds; they are most useful in cases in which one wishes to examine the overall molecular shape and to assess how closely two nonbonded atoms approach each other.

The earliest ball-and-stick models were exactly that: wooden balls in which holes were drilled to accommodate dowels that connected the atoms. Plastic versions, including relatively inexpensive student sets, became available in the 1960s and proved to be a valuable learning aid. Precisely scaled stainless steel framework and plastic space-filling models, although relatively expensive, were standard equipment in most research laboratories.

Computer graphics-based representations are rapidly replacing classical molecular models. Indeed, the term "molecular modeling" as now used in organic chemistry implies computer generation of models. The methane models shown in Figure 1.7 were all drawn on a personal computer using software that possesses the feature of displaying and printing the same molecule in framework, ball-and-stick, and space-filling formats. In addition to permitting models to be constructed rapidly, even the simplest software allows the model to be turned and viewed from a variety of perspectives.

More sophisticated programs not only draw molecular models, but also incorporate computational tools that provide useful insights into the electron distribution. Figure 1.7d illustrates this higher level approach to molecular modeling by using colors to display the electric charge distribution within the boundaries defined by the space-filling model. Figures such as 1.7d are called *electrostatic potential maps*. They show the transition from regions of highest to lowest electron density according to the colors of the rainbow. The most electron-rich regions are red; the most electron-poor are blue. For methane, the overall shape of the electrostatic potential map is similar to the volume occupied by the space-filling model. The most electron-rich regions are closer to carbon and the most electron-poor regions closer to the hydrogen atoms.

—Cont.

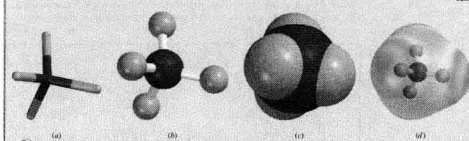


FIGURE 1.7 (a) A framework (tube) molecular model of methane (CH_4). A framework model shows the bonds connecting the atoms of a molecule, but not the atoms themselves. (b) A ball-and-stick (ball-and-spoke) model of methane. (c) A space-filling model of methane. (d) An electrostatic potential map superimposed on a ball-and-stick model of methane. The electrostatic potential map corresponds to the space-filling model, but with an added feature. The colors identify regions according to their electric charge, with red being the most negative and blue the most positive.

LEARNING BY MODELING

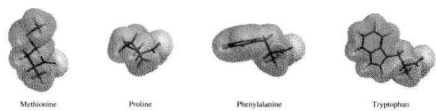
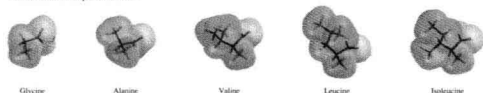
Build Biomolecules

In the biological-specific chapters, learning is once again enhanced by the access to Spartan model building. Carbohydrates, lipids, amino acids, peptides, proteins, and nucleic acid benefit from Spartan, and many for this edition were generated from imported crystallographic data. And students can view models of the 20 common amino acids on *Learning By Modeling*, and rotate them in three dimensions, or view them as ball-and-spoke, tube, or space-filling models.

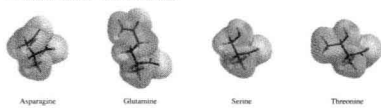
27.2 Stereochemistry of Amino Acids

1051

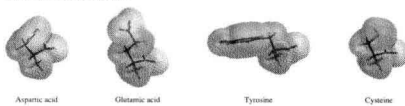
Amino acids with nonpolar side chains



Amino acids with polar but nonionized side chains



Amino acids with acidic side chains



Amino acids with basic side chains

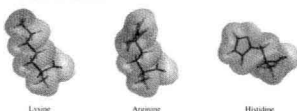
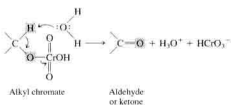


FIGURE 27.1 Electrostatic potential maps of the 20 common amino acids listed in Table 27.1. Each amino acid is oriented so that its side chain is in the upper left corner. The side chains affect the shape and properties of the amino acids.

This alkyl chromate then undergoes an elimination reaction to form the carbon-oxygen double bond.



In the elimination step, chromium is reduced from Cr(VI) to Cr(IV). Since the eventual product is Cr(III), further electron-transfer steps are also involved.

15.11 BIOLOGICAL OXIDATION OF ALCOHOLS

Many biological processes involve oxidation of alcohols to carbonyl compounds or the reverse process, reduction of carbonyl compounds to alcohols. Ethanol, for example, is metabolized in the liver to acetaldehyde. Such processes are catalyzed by enzymes; the enzyme that catalyzes the oxidation of ethanol is called *alcohol dehydrogenase*.



In addition to enzymes, biological oxidations require substances known as *coenzymes*. Coenzymes are organic molecules that, in concert with an enzyme, act on a substrate to bring about chemical change. Most of the substances that we call vitamins are coenzymes. The coenzyme contains a functional group that is complementary to a functional group of the substrate; the enzyme catalyzes the interaction of these mutually complementary functional groups. If ethanol is oxidized, some other substance must be reduced. This other substance is the oxidized form of the coenzyme *nicotinamide adenine dinucleotide* (NAD). Chemists and biochemists abbreviate the oxidized form of this

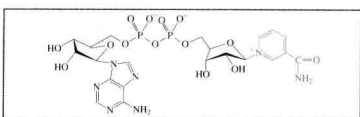


FIGURE 15.3 Structure of NAD⁺, the oxidized form of the coenzyme nicotinamide adenine dinucleotide.

SPECTROSCOPY

Spectroscopy coverage is up-to-date and thorough in this edition. Chapter 13, “Spectroscopy,” features NMR spectra that were newly recorded on a high-field instrument, and all the text figures were produced directly from electronic files. In addition, spectroscopy is integrated into all the functional group chapters that follow 13: Chapters 15, 16, 17, 19, 20, 22, and 24, which contain spectroscopy sections and examples and problems based on displayed spectra.

BIOLOGICAL APPLICATIONS THROUGHOUT

While biological topics receive greatest emphasis in Chapters 25–27, they are also introduced throughout the book, reflecting their growing role in the study of organic chemistry. Examples include:

- Biological oxidation of alcohols (p. 600)
- Epoxides in biological processes (p. 637)
- “Methane and the Biosphere” (boxed essay, p. 58)
- A biological dehydrogenation (new, p. 181)
- Figure 19.5, showing a realistic representation of a micelle (p. 744)
- “Chiral drugs” (boxed essay, p. 273)

