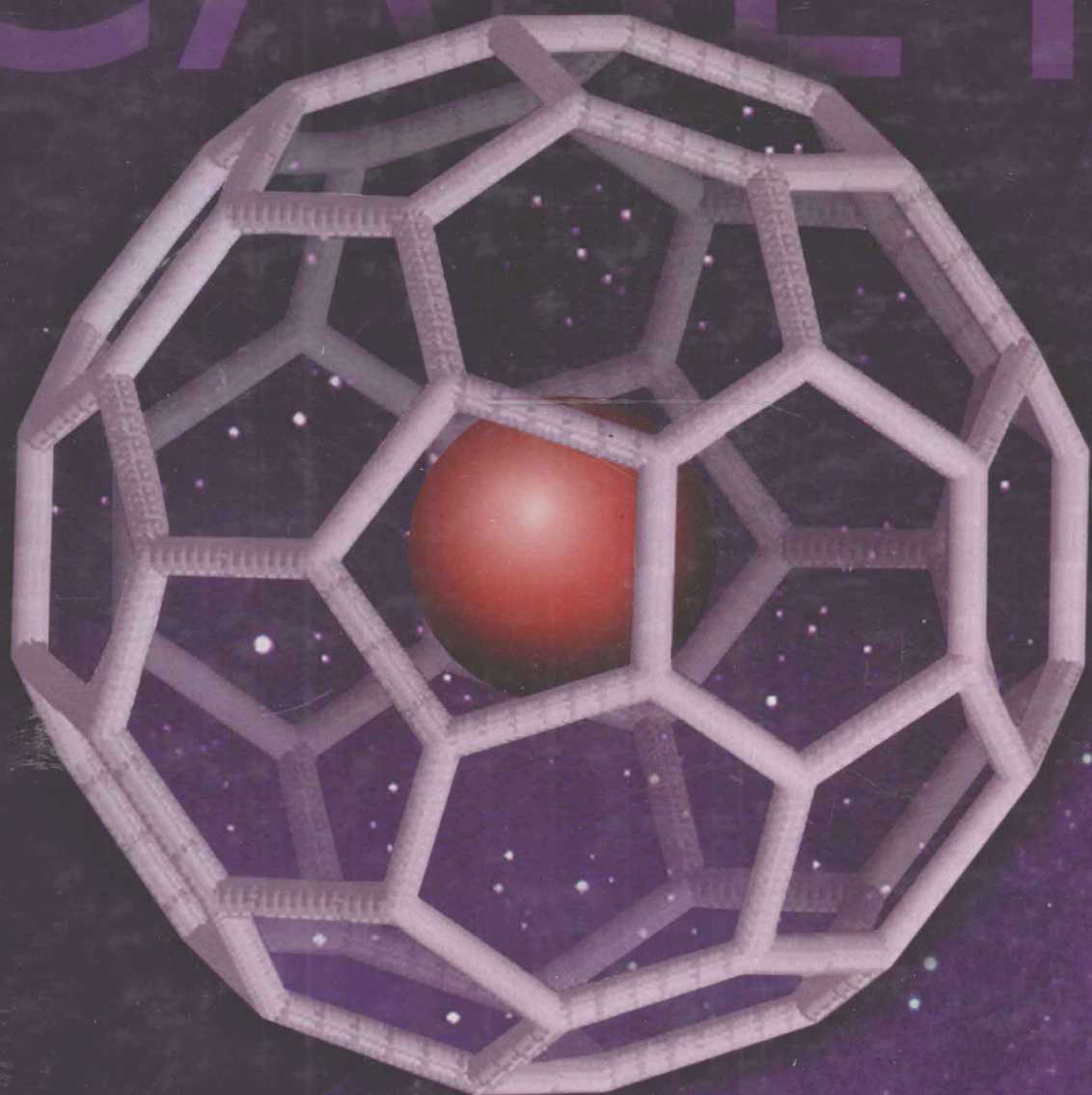


FRANCIS A.
CAREY



fifth edition

ORGANIC CHEMISTRY

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fifth edition

Francis A. Carey
University of Virginia

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ORGANIC CHEMISTRY, FIFTH EDITION

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A B O U T T H E A U T H O R

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 was appointed to the chemistry faculty of the University of Virginia in 1966. Prior to retiring in 2000, he regularly taught the two-semester lecture courses in general chemistry and organic chemistry.

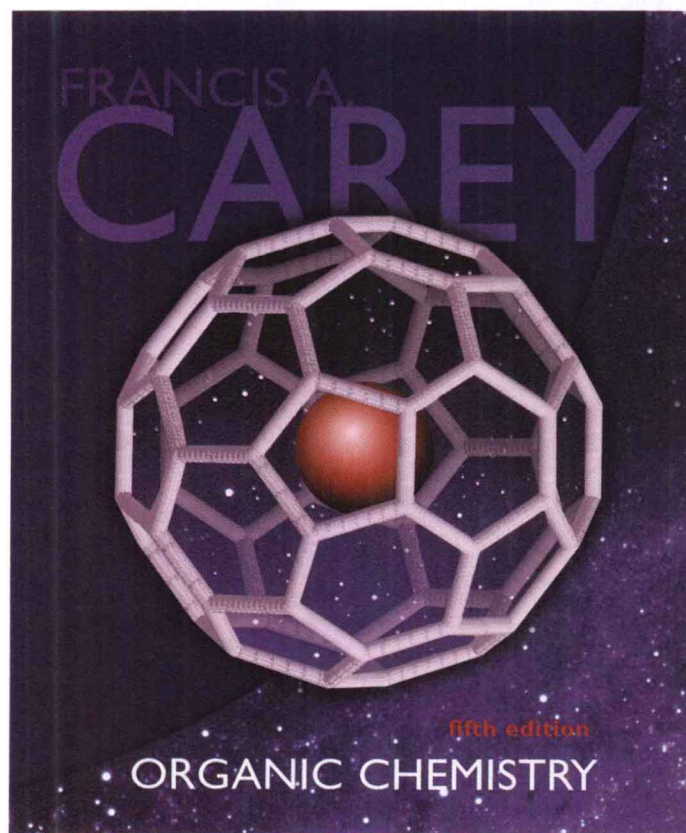
With his students, Professor Carey has published over 40 research papers in synthetic and mechanistic organic chemistry. In addition to this text, he is coauthor (with Robert C. Atkins) of *Organic Chemistry: A Brief Course* and (with Richard J. Sundberg) of *Advanced Organic Chemistry*, a two-volume treatment designed for graduate students and advanced undergraduates. He was a member of the Committee of Examiners of the Graduate Record Examination in Chemistry from 1993–2000.

Frank and his wife Jill, who is a teacher/director of a preschool and a church organist, are the parents of Andy, Bob, and Bill and the grandparents of Riyad and Ava.

ABOUT THE COVER

The cover shows a buckminsterfullerene (C_{60}) molecule traveling through interstellar space. A helium atom is trapped within the fullerene cage. Where the fullerene and helium atom came from, where they are going and when, combine to give the fascinating story of scientific detective work told on page 437.

We thank Dr. Luann Becker, a geochemist at the University of Hawaii and one of the lead investigators who discovered these “spacebuckys,” for providing the striking graphic displayed on the cover.



This edition is dedicated
with affection to my wife Jill.

P R E F A C E

From the first edition through this, its fifth, *Organic Chemistry* has been designed to meet the needs of the “mainstream,” two-semester undergraduate organic chemistry course. From the beginning and with each new edition, we have remained grounded in some fundamental notions. These include important issues concerning the intended audience. Does the topic appropriately take into consideration their interests, aspirations, and experience? Just as important is the need to present an accurate picture of the present state of organic chemistry. How do we know what we know? What makes organic chemistry worth knowing? Where are we now? Where are we headed?

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. Our objective has been to emphasize the connection between structure and properties, using the tools best suited to make that connection.

One tool is organizational. The time-honored *functional group approach* focuses attention on the *structural* units within a molecule that are most closely identified with its *properties*. The text is organized according to functional groups, but *emphasizes mechanisms* and encourages students to look for similarities in mechanisms among different functional groups.

Another tool relates to presentation. We decided to emphasize molecular modeling in the third edition, expanded its usefulness by adding Spartan electrostatic potential maps in the fourth, and continue this trend in the fifth. Molecular models, *and the software to make their own models*, not only make organic chemistry more accessible to students who are “visual learners,” they enrich the educational experience for all.

WHAT’S NEW FOR THE FIFTH EDITION?

Organization

Key changes appear at the beginning and at the end. The changes in Chapter 1 are major and send ripples through the book. Chapter 28 is new.

- **New!** Chapter 1 has been retitled “Structure Determines Properties” to better reflect its purpose and has been rewritten to feature a detailed treatment of *acids and bases*. Rather than a review of what students learned about acids and bases in general chemistry, Sections 1.12–1.17 discuss acids and bases from an organic chemistry perspective.
- To accommodate the new material on acids and bases in Chapter 1, the orbital hybridization model of bonding in organic compounds has been rewritten and placed in Chapter 2. In keeping with its expanded role, Chapter 2 is now titled “Hydrocarbon Frameworks. Alkanes.”
- Chapter 13, “Spectroscopy,” has been supplemented by an expanded discussion of ^1H and ^{13}C chemical shifts and a new section on 2D NMR. A **new box**, *Spectra by the Thousands*, points the way to websites that feature libraries of spectra and spectroscopic problems of every range of difficulty.
- Chapter 27 has been shortened by removing material related to nucleic acids and its title changed to “Amino Acids, Peptides, and Proteins.”
- **New!** Chapter 28 “Nucleosides, Nucleotides, and Nucleic Acids” is new. Its presence testifies to the importance of these topics and the explosive growth of our knowledge of the molecular basis of genetics.

Pedagogy

- **New!** The continuing positive response to the generous use of tables in *Organic Chemistry* has encouraged us to create new ones. The new tables are

Table 1.6 VSEPR and Molecular Geometry

Table 1.7 Dissociation Constants (pK_a) of Acids

Table 2.5 Oxidation Numbers in Compounds with More Than One Carbon

Table 28.2 The Major Nucleosides in DNA and/or RNA

- **New!** The number of boxed essays has been increased to 42 with the addition of

Electrostatic Potential Maps

Curved Arrows

Ring Currents: Aromatic and Antiaromatic

Spectra by the Thousands

Nonsteroidal Antiinflammatory Drugs (NSAIDs) and COX-2 Inhibitors

Oh NO! It's Inorganic!

"It Has Not Escaped Our Notice . . ."

RNA World

- The *Learning By Modeling* CD-ROM developed by Wavefunction, Inc. in connection with the fourth edition of this text accompanies the fifth as well. We were careful to incorporate Spartan so it would work with the textbook—from the Spartan images used in the text to the icons directing the student to opportunities to build models of their own or examine those in a collection of more than 250 already prepared ones.
- A number of **new** in-chapter and end-of-chapter problems have been added.

Art Program

- Instead of limiting molecular models to figures, "bonus" models have been integrated into the body of the text in places where they reveal key features more clearly than words or structural formulas alone can. (See page 175.)
- **New!** Attention is paid to the nodal properties of orbitals throughout the text in order to foster an appreciation for this important aspect of bonding theory. (See Figure 2.16 on page 90.)

Media

- *Learning By Modeling* for building, examining, and evaluating molecular models specific to organic chemistry
- **New!** Essential Study Partner (ESP) interactive student tutorial
- Improved Online Learning Center website for instructors and students
- **New!** Mechanism Animations CD-ROM for the instructor

INSTRUCTOR RESOURCES

McGraw-Hill offers various tools and technology products to support the fifth edition of *Organic Chemistry*. Instructors can obtain teaching aids by calling the Customer Service Department at 800-338-3987 or contacting your local McGraw-Hill sales representative.

Test Bank

Written by Bruce Osterby (University of Wisconsin-LaCrosse), this manual contains over 1,000 multiple-choice questions. The Test Bank is available under the Instructor Center on the Online Learning Center at www.mhhe.com/carey.

Computerized Test Bank

Written by Bruce Osterby (University of Wisconsin-LaCrosse), the Test Bank is formatted for easy integration into the following course management systems: PageOut, WebCT, and Blackboard.

Digital Content Manager

This presentation CD-ROM contains a multimedia collection of visual resources allowing instructors to use artwork from the text in multiple formats to create customized classroom presentations, visually-based tests and quizzes, dynamic course website content, or attractive printed support materials. The Digital Content Manager is a cross-platform CD containing an image library, a tables library, and a PowerPoint presentation.

Online Learning Center

The comprehensive website (www.mhhe.com/carey) is book-specific and offers excellent tools for both the instructor and the student. Instructors can create an interactive course with the integration of this site, and a secure Instructor Center stores your essential course materials to save you prep time before class. This center offers PowerPoint images, a PowerPoint lecture outline, mechanism animations, and more.

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 molecular models that reveal the interplay between electronic structure and reactivity in organic chemistry.

Solutions Manual

Written by Robert Atkins (James Madison University) and Francis Carey, this manual provides complete solutions to all of the problems in the text.

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.

Organic Chemistry Animations Library

Created by Rainer Glaser (University of Missouri), the animations are basic mechanisms that can be presented at full-screen size in your classroom. The animations on the CD can be played directly from the CD or can be imported easily into your own lecture presentation.

Course-Specific PageOut

Designed specifically to help you with your individual course needs, PageOut will assist you in integrating your syllabus with *Organic Chemistry* and with state-of-the-art new media tools. At the heart of PageOut you will find integrated multimedia and a full-scale Online Learning Center. You can upload your original test questions and create your own custom designs. More than 60,000 professors have chosen PageOut to create customized course websites.

WebCT, Blackboard

The Test Bank and Online Learning Center with self-assessments quizzes and review aids are available in the various course management systems. Please ask your sales representative for details if you are interested.

STUDENT RESOURCES

McGraw-Hill offers various tools and technology to support the fifth edition of *Organic Chemistry*. Students can order supplemental study materials by contacting the McGraw-Hill Customer Service Department at 800-338-3987.

Solutions Manual

Written by Robert C. Atkins and Francis A. Carey, the solutions manual provides step-by-step solutions guiding the student through the reasoning behind each problem in the text. There is also a self-test at the end of each chapter designed to assess the student's mastery of the material.

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 molecular models that reveal the interplay between electronic structure and reactivity in organic chemistry. Icons in the text point the way to where you can use this state-of-art molecular modeling application to expand your understanding and sharpen your conceptual skills.

OLC (Online Learning Center)

The Online Learning Center is a comprehensive, exclusive website that provides a wealth of electronic resources for instructors and students alike. For students, the OLC features tutorial, problem-solving strategies and assessment exercises for every chapter in the book that were developed by Ian Hunt and Rick Spinney from the University of Calgary. You can also access the Essential Student Partner from the OLC. Log on at www.mhhe.com/carey.

Schaum's Outline of Organic Chemistry

This helpful study aid provides students with hundreds of solved and supplementary problems for the organic chemistry course.

ACKNOWLEDGMENTS

No textbook is solely the creative work of the person whose name is on the cover. Left to their own devices, authors would include too much, address the wrong audience, and, worst of all, never finish. The indispensable people, the folks who keep us focused, are our editors. At McGraw-Hill, Shirley Oberbroeckling combines all the qualities an author appreciates in an editor. In developing “Carey 5/e,” Shirley never lost sight of the big picture, yet stayed on top of every detail. She was a consistent source of ideas and encouragement. Likewise, Kent Peterson, now publisher for the physical sciences, participated actively in shaping this edition, including identifying the content areas to emphasize. To use a sports metaphor, Kent was the coach of the team, Shirley was the captain. It was a pleasure to be on the field with them.

I also thank Linda Davoli, who has edited copy for most of our recent writing projects. In addition to being both professional and thorough, Linda makes a special effort to go beyond the words themselves to ensure that the ideas get through. As she did in the fourth edition, Peggy Selle oversaw the production of the text with skill and enthusiasm. Warren Hehre of Wavefunction, Inc., continues to support our efforts to expand the role of molecular modeling in the introductory organic chemistry course. He is generous with his time and a rich source of ideas.

I appreciate the help of Thomas Gallaher of the Department of Chemistry at James Madison University in obtaining the 2D NMR spectra that are new to this edition. As in every previous edition of this text, the contributions of Dr. Robert C. Atkins of James Madison University are beyond measure. I can’t think of anything connected with *Organic Chemistry* that hasn’t benefited from Bob’s efforts and insight.

The comments offered by an unusually large number of teachers of organic chemistry were especially helpful in developing this edition. I appreciate their help. A special thank you to the following participants in a McGraw-Hill organic chemistry summit held during the summer of 2000 for their insight into the needs of organic chemistry professors:

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Gary Gray, *University of Minnesota*
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J. Howard Hargis, *Auburn University*
Charles Kingsbury, *University of Nebraska*
Cary Morrow, *University of New Mexico*
Anne Padias, *University of Arizona*
Bradley Smith, *University of Notre Dame*

The reviewers listed below have reviewed for the fifth edition in various ways: sharing ideas on improving this edition from the fourth edition, helping fine-tune the manuscript of the fifth edition, giving direction on new art, and reviewing media including the *Learning By Modeling* CD and the Online Learning Center.

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 Hans Zimmer, *University of Cincinnati—Cincinnati*

My wife Jill, our sons Andy, Bob, and Bill, and daughter-in-law Tasneem, provide encouragement. Our grandchildren Riyadh and Ava provide inspiration. It all adds up.

Comments, suggestions, and questions—especially from students—are welcome. I invite you to contact me at fac6q@unix.mail.virginia.edu.

—Francis A. Carey

A GUIDE TO USING THIS TEXT

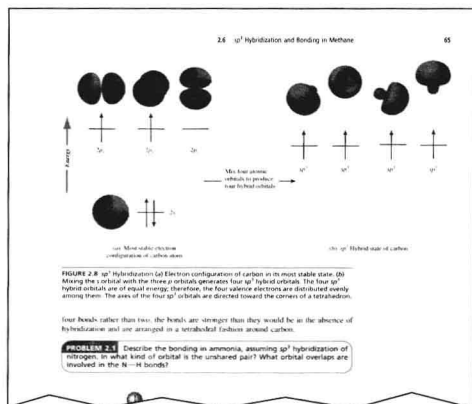
The following two pages walk you through some of the key features of this text. This book was designed with you, the student in mind—to help you succeed in organic chemistry. My main goal in writing this text was to make the material you study as accessible and appealing as possible. I hope you enjoy your study of organic chemistry.

Francis A. Carey

TEXT

Art Program

- Molecular models make organic chemistry more accessible and enrich the education experience for all.
- Molecular models are integrated into the content revealing key features more clearly than words or structural formulas alone.
- Nodal properties of orbitals are included to show this important aspect of bonding theory.



Tables and Summaries

- Summary tables allow the student easy access to a wealth of information in an easy to use format while reviewing information from previous chapters.
- End-of-Chapter Summaries highlight and consolidate all of the important concepts and reactions within a chapter.

626 CHAPTER FIFTEEN Alcohols, Ethers, and Thiols

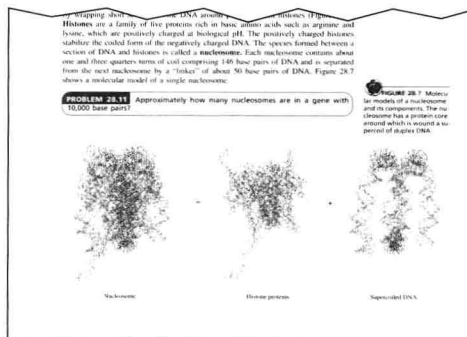
TABLE 15.1 Summary of Reactions Discussed in Earlier Chapters That Yield Alcohols

Reaction (section) and comments	General equation and specific example
Acid-catalyzed hydration of alkenes (Section 6.10) Water adds to the double bond in accordance with Markovnikov's rule.	$R_2C=CR_2 + H_2O \xrightarrow{H^+} R_2CH-CH_2R_2$ Alkene + Water \rightarrow Alcohol $(CH_3)_2C=CHCH_3 \xrightarrow{H_2O} (CH_3)_2CH-CH_2CH_3$ 2-Methyl-2-butene \rightarrow 2-Methyl-2-butanol (90%)
Hydroboration-oxidation of alkenes (Section 6.11) H and OH add to the double bond with regioselectivity opposite to that of Markovnikov's rule. This is a very good synthetic method; addition is syn, and no rearrangements are observed.	$R_2C=CR_2 \xrightarrow{1. BH_3, 2. H_2O_2, 3. NaOH} R_2CH-CH_2R_2$ Alkene \rightarrow Alcohol $CH_3(CH_2)_3CH=CH_2 \xrightarrow{1. BH_3, 2. H_2O_2, 3. NaOH} CH_3(CH_2)_3CH_2CH_2OH$ 1-Decene \rightarrow 1-Decanol (93%)
Hydrolysis of alkyl halides (Section 8.1) A reaction useful only with substrates that do not undergo $E2$ elimination readily. It is rarely used for the synthesis of alcohols, since alkyl halides are normally prepared from alcohols.	$R-X + H_2O \rightarrow R-OH + HX$ Alkyl halide \rightarrow Alcohol + Halide ion $H_3C-C(CH_3)_2-CH_2-Cl \xrightarrow{H_2O} H_3C-C(CH_3)_2-CH_2-OH$ 2,4,4-Trimethylbenzyl chloride \rightarrow 2,4,4-Trimethylbenzyl alcohol (93%)
Reaction of Grignard reagents with aldehydes and ketones (Section 14.8) A method that allows for alcohol preparation with formation of new carbon-carbon bonds. Primary, secondary, and tertiary alcohols can all be prepared.	$R'MgX + R''C(=O)R''' \xrightarrow{1. \text{aldehyde or ketone}, 2. H_2O} R'R''C(OH)R'''$ Grignard reagent + Aldehyde or ketone \rightarrow Alcohol Cyclopentylmagnesium bromide + Formaldehyde \rightarrow Cyclopentylmethanol (92-94%)

(Continued)

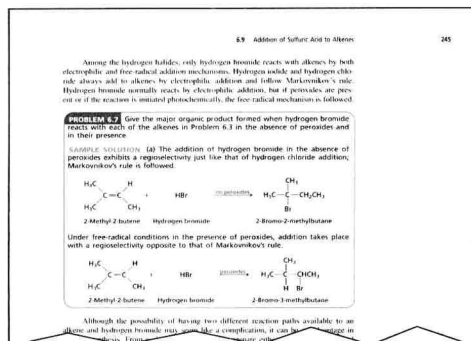
Biological Applications

- New chapter on *Nucleosides, Nucleotides, and Nucleic Acids* testifies to the explosive growth of the molecular basis of genetics.
- Numerous boxed essays throughout the text highlight biological applications of organic chemistry.



Problem-Solving

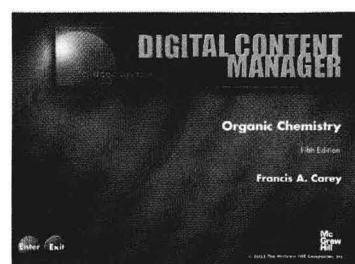
- Problem-solving strategies and skills are emphasized throughout. Understanding is continually reinforced by problems that appear within topic sections. For many problems, sample solutions are given.
- Every chapter ends with a comprehensive set of problems that give students liberal opportunity to master skills by working problems and integrating the use of Spartan modeling.



- Organic Chemistry Mechanism Animation Library—CD-ROM set includes 8 important and standard mechanisms that can be used directly from the CD or imported into your own lecture presentation.



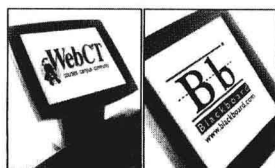
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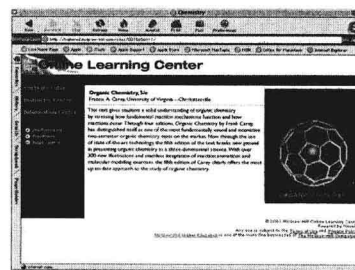
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