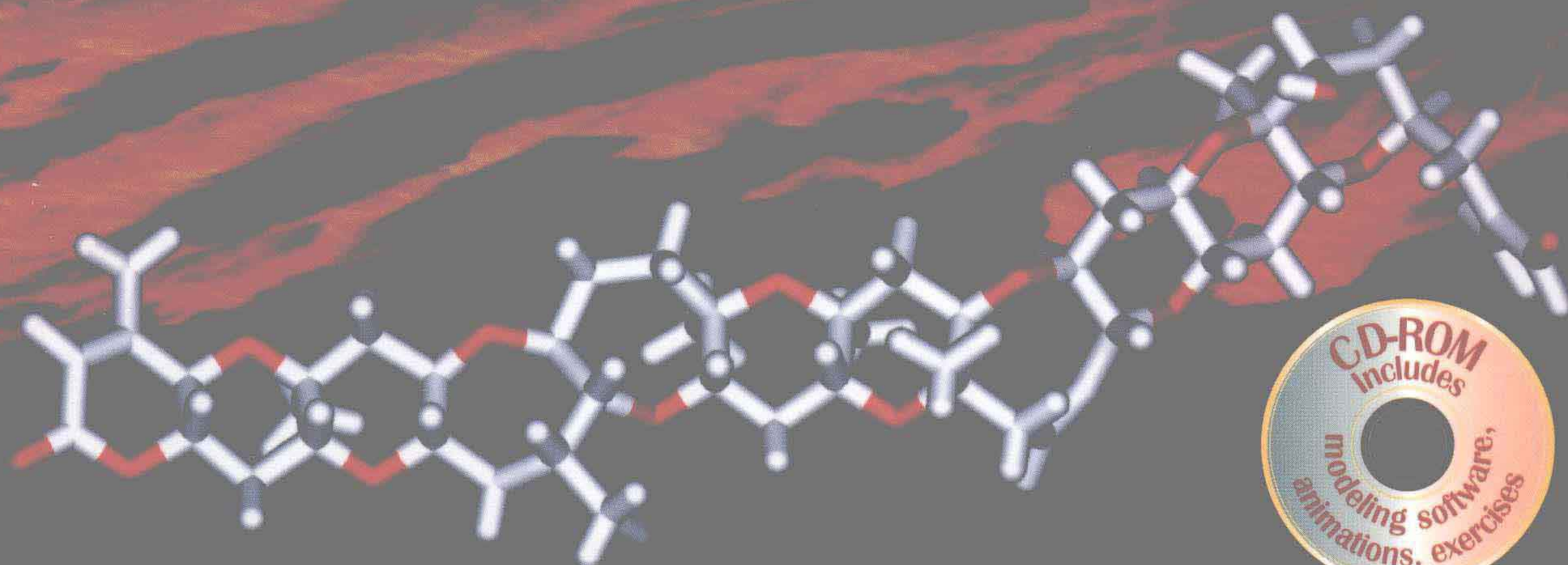


Third Edition

ORGANIC CHEMISTRY

Structure and Function

K. Peter C. Vollhardt Neil E. Schore



Third Edition

ORGANIC CHEMISTRY

Structure and Function

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University of California at Berkeley

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W. H. Freeman and Company
NEW YORK

About the Cover: *Brevetoxin B* (shown as a ball-and-stick model) is a potent marine neurotoxin responsible for massive fish kills, mollusk poisoning, and human food poisoning along the coast of Florida, the Gulf of Mexico, and many other parts of the world. It is associated with the explosive growth, or bloom, of the algae dinoflagellate *Ptychodiscus brevis* under certain favorable conditions of temperature, salinity, and sunlight, causing a phenomenon called "red tide." The front cover depicts a red tide on May 6, 1976, approaching the coast of Oshima Island, Japan. The back cover shows space-filling and bond-line formulas of the unique structure of brevetoxin B consisting of a single carbon chain arranged in a rigid ladder-like framework and composed of 11 contiguous trans fused ether rings. Brevetoxin B was made in the laboratory by total synthesis in 1994, requiring 83 steps from 2-deoxyribose and 12 years of effort, spearheaded by Professor Kyriacos Costa Nicolaou (who also supplied the original photograph) at the Scripps Research Institute and the University of California at San Diego. Synthetic strategies are discussed in Chapter 8 and subsequently throughout the text.

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ORGANIC CHEMISTRY

Structure and Function

PREFACE

A USER'S GUIDE TO "ORGANIC CHEMISTRY: STRUCTURE AND FUNCTION"

Structure and Function Motif

Too many students find that organic chemistry is an overwhelming parade of facts. Our goals are to dispel this notion and, more important, to help students learn and understand organic chemistry. The best way to do this is to provide a framework, or scaffolding, around which students can organize their thoughts. The framework that we provide is the accessible notion that an understanding of structure will lead to an understanding of function.

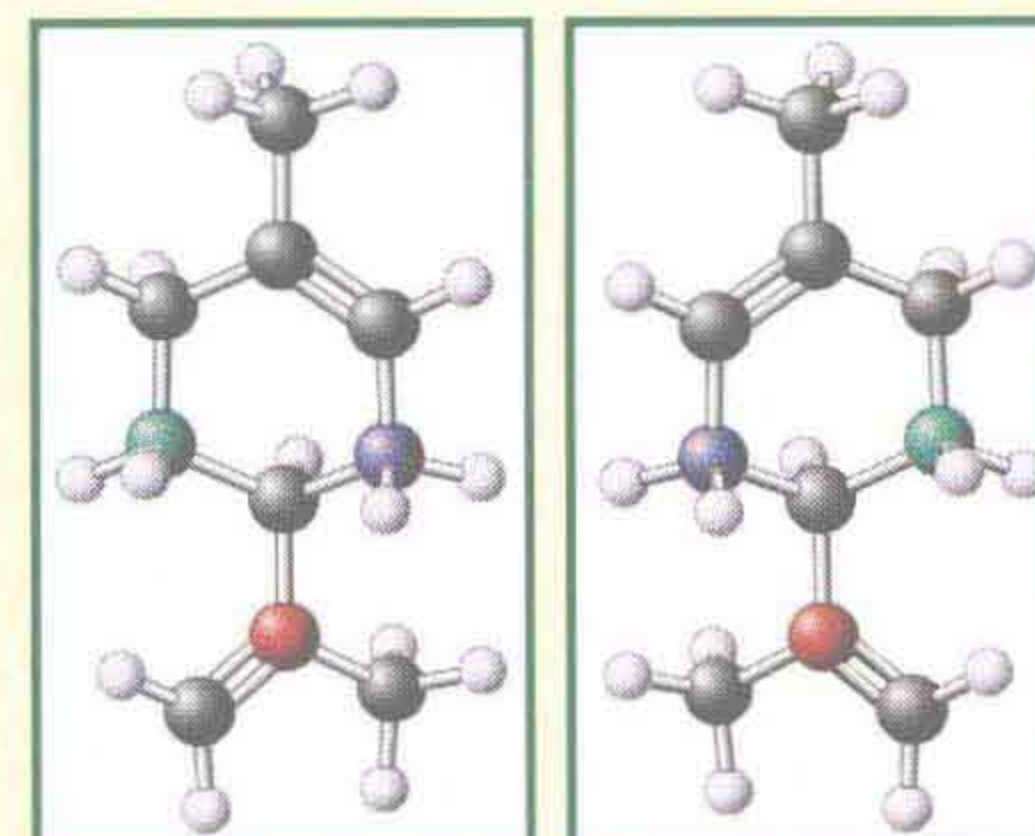
A Uniform Organization Emphasizes the Relation Between Structure and Function

Much like a language, in which grammar would be dangling without the "meat" of vocabulary, the text develops material as a juxtaposition of structure and function. Thus, Chapter 1 provides the fundamentals of structure and bonding, specifically as they will become useful in understanding organic chemistry. Chapter 2 then follows with an introduction to the structural features of the alkanes and how they "function" in the simplest sense—namely, conformational mobility. Chapter 3 relates bond-dissociation energies to the lead reaction: radical halogenation (functionalization) of alkanes. Chapter 4 repeats the motif of Chapter 2 but with cycloalkanes as its center of focus.

The structure of the haloalkanes and how it determines their fate in its nucleophilic substitution and elimination reactions are the topics of Chapters 6 and 7. Each subsequent functional group is covered according to the same scheme: naming, structure, spectroscopy, preparations, reactions, and biological and other applications.

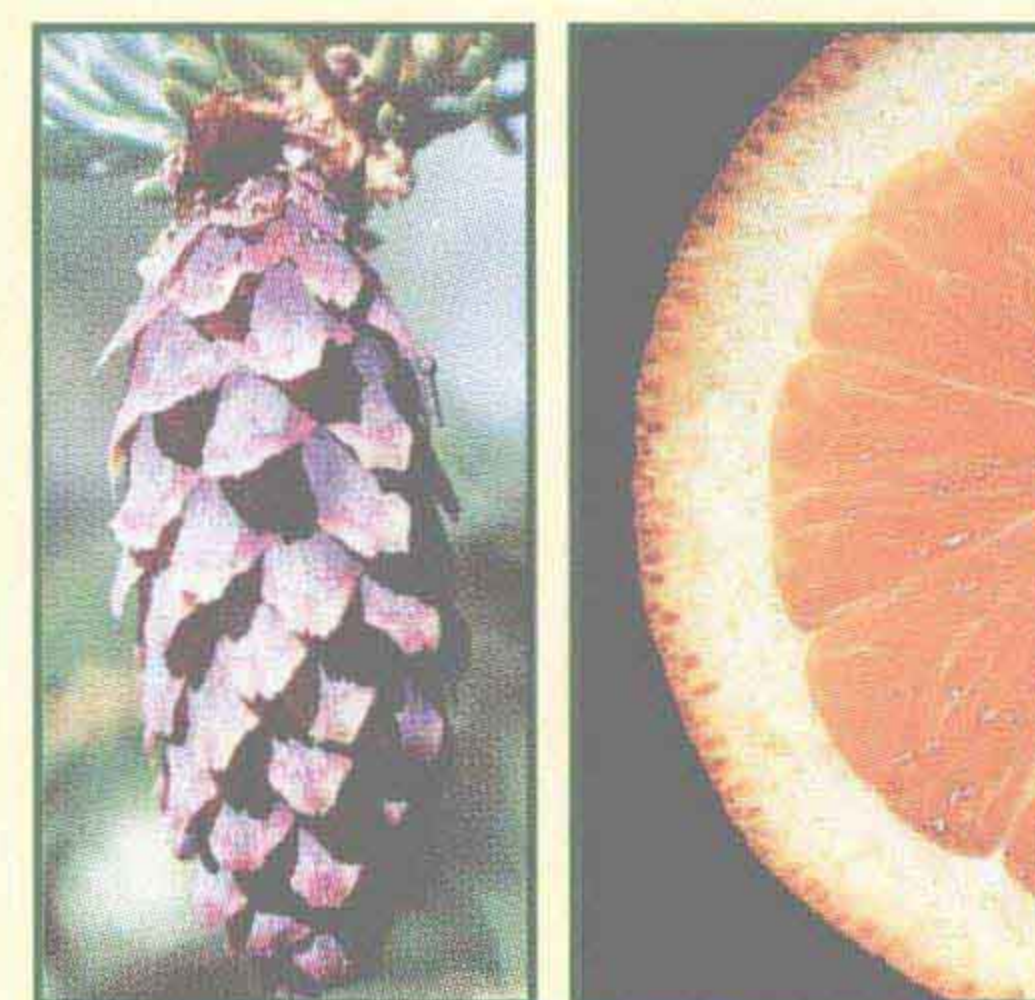
Students Are Given the Structural "Tools" They Need to Understand Function

The interplay between structure and function that gives a hierarchy to individual chapters also confers a hierarchy on the text as a whole. This is why we introduce stereochemistry in Chapter 5. Students learn about stereochemical principles so that they are prepared to understand the substitution and elimination reactions of haloalkanes (Chapters 6 and 7) and the addition reactions of alkenes (Chapter 12). Moreover, this hierarchy allows the mechanistic discussion of all new important reactions to take place concurrently rather than being scattered in different places throughout the text. Such a unified presentation of mechanisms benefits the student enormously.



S(-)-Limonene

R(+)-Limonene

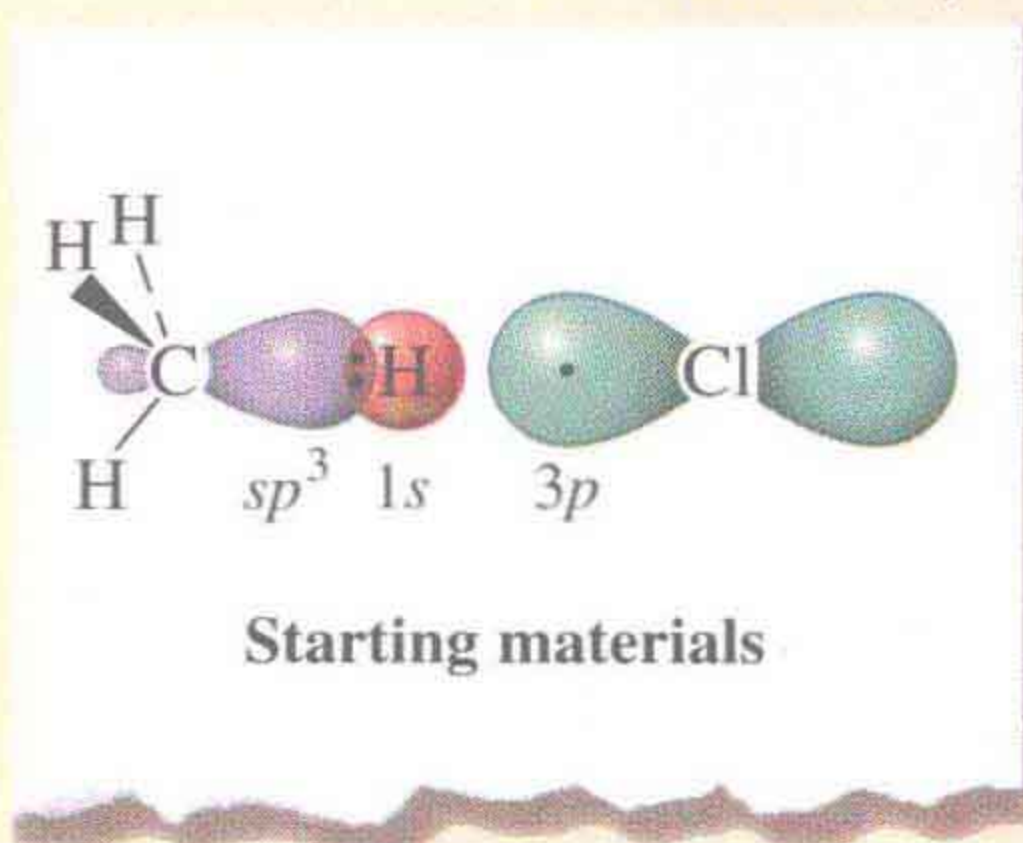


Silver fir tree cone Orange peel

Alcohols (Chapters 8 and 9) with the simplest oxygen-containing function are treated early because their chemistry sets the stage for understanding their central role in synthesis. Similarly, carbocations (and their rearrangements; see Section 9-3) appear before a discussion of the Markovnikov rule, alkenes (Chapter 12) before conjugated polyenes (Chapter 14), and conjugated polyenes before aromatic systems. Early coverage of spectroscopy reinforces the interplay between structure and function. This organization allows students to apply spectroscopic techniques in the context of the functional group. Infrared spectroscopy, for example, is introduced in Chapter 11 on alkenes.

The Lead Reaction: Radical Halogenation of Methane

The first, more detailed discussion of a reaction and its mechanism, the “lead reaction,” is presented very early in Chapter 3. For several reasons, the best (most logical)



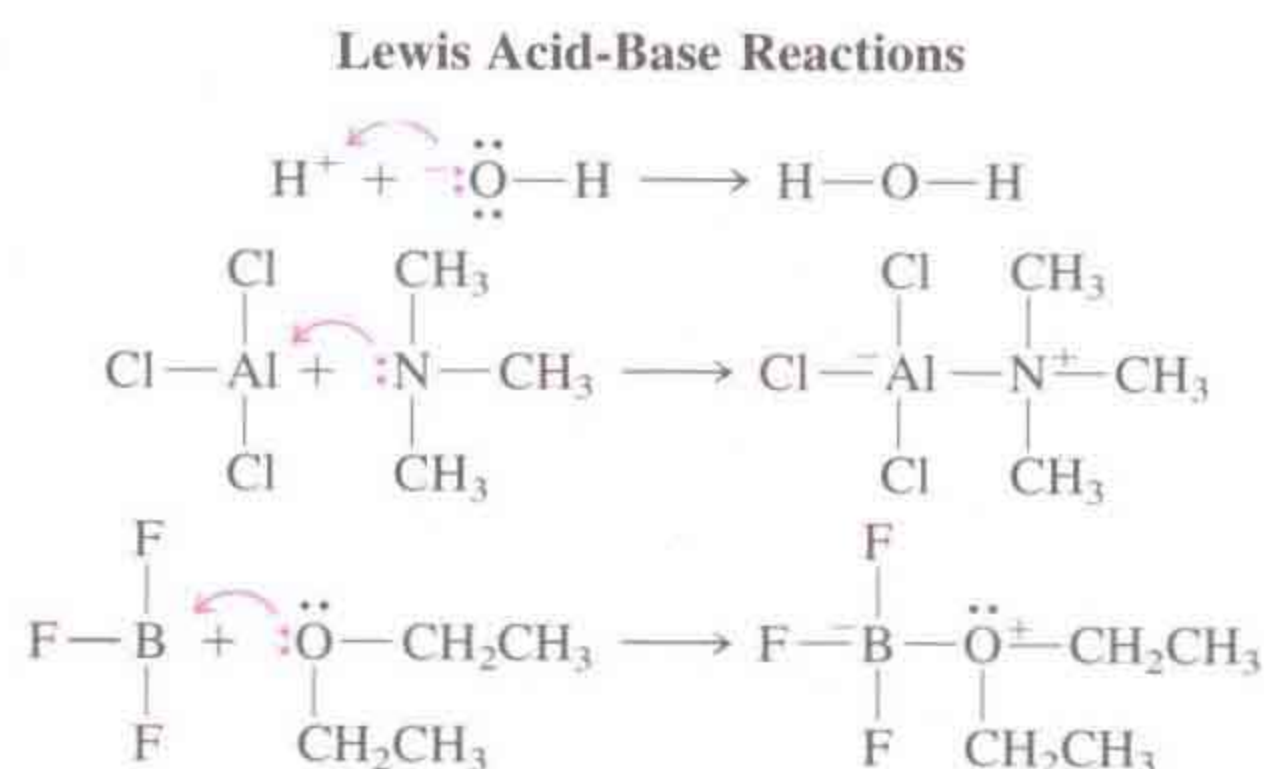
choice is the chlorination of methane. First, all chemical reactions require bond making and bond breaking. The radical halogenation of methane allows the introduction of the concepts of bond-dissociation energies and the stability and structure of the ensuing radicals. This leads to an understanding of the thermal stability of the simplest organic bonds, C—H and C—C, and, hence, of why organic materials are capable of existence. The students learn that to “activate” a C—H bond, a reactive agent is required. Second, the lead reaction, because it purposely does not include ionic species, can be analyzed thermodynamically

by calculating enthalpies of the overall process, as well as individual steps. This exercise is fundamental and gives the student the basic tool of “eyeballing” the relative feasibility of all future transformations. It also serves as a first application of potential energy diagrams to a chemical process. Third, the generalization of the chlorination of methane to the halogenation of other alkanes permits the simple introduction of the concepts of reactivity and selectivity, a feeling for the statistics needed to deal with molecules endowed with several equally reactive sites, and practical applications of these principles.

A Book for Real Students

We are aware of the challenges this course presents to students. Our students have taught us what these challenges are and we have applied this understanding in the following ways:

Early Coverage of Acids and Bases

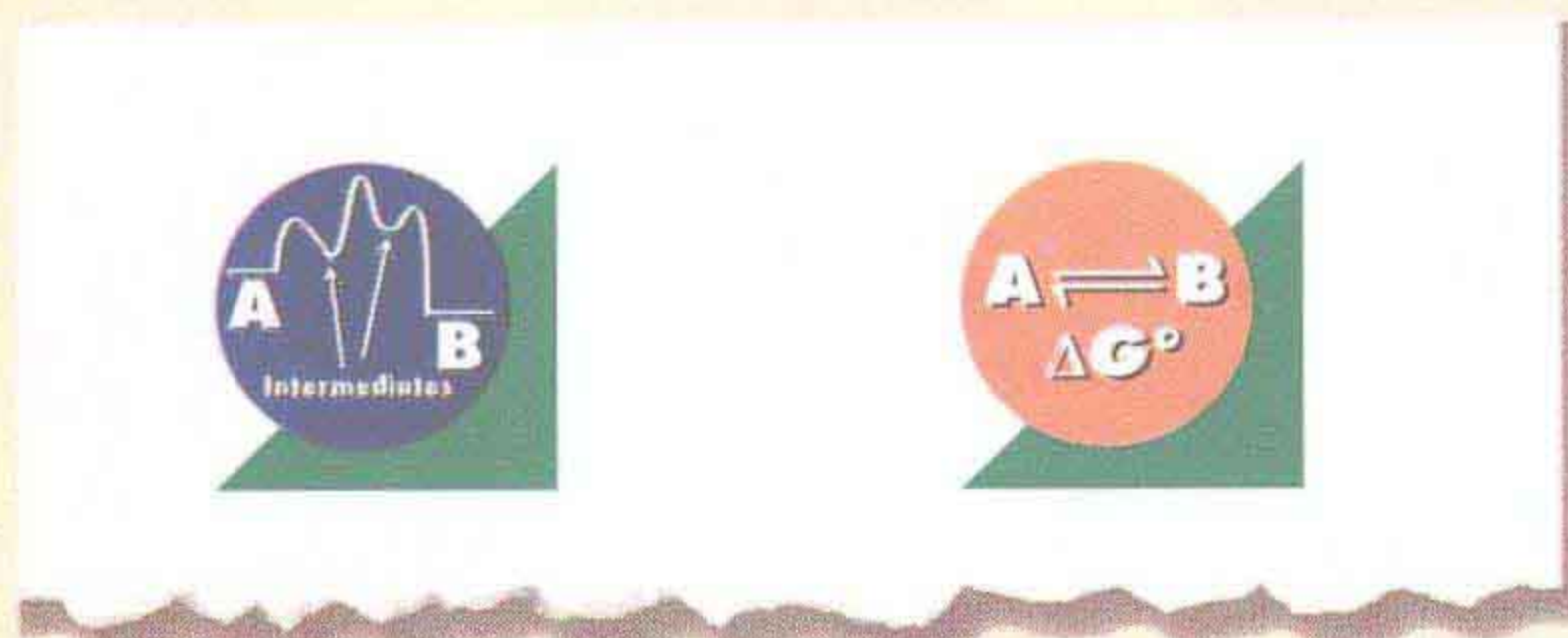


We have moved the discussion of acids and bases to Section 2-9 and expanded it to provide the student with an early review of this aspect of general chemistry as it applies to organic systems. This treatment now includes explicitly Lewis acids and bases and sets the student up for a general understanding of the similarity between such

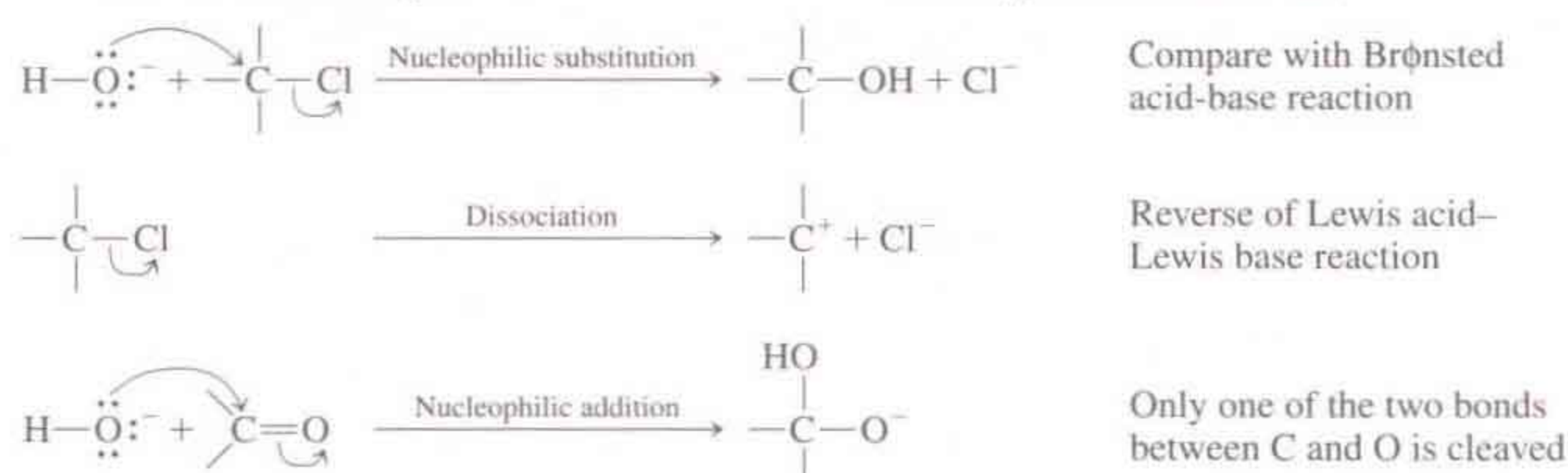
diverse processes as nucleophilic trapping of carbocations and solvation (e.g., of Grignard reagents or by crown ethers or ionophores) and for the role of metal halides in Friedel-Crafts alkanoylation.

Improved Presentation of Reaction Mechanisms

The presentation of reaction mechanisms has been improved by the increased use of arrows to better show electron flow. The introduction of icons for a “reaction” and its “mechanism” serves to emphasize the “vocabulary-grammar” duality of the two types of schemes. In addition, we have added a new section on electron-pushing arrows (Section 6-4) to familiarize the student explicitly with this technique.



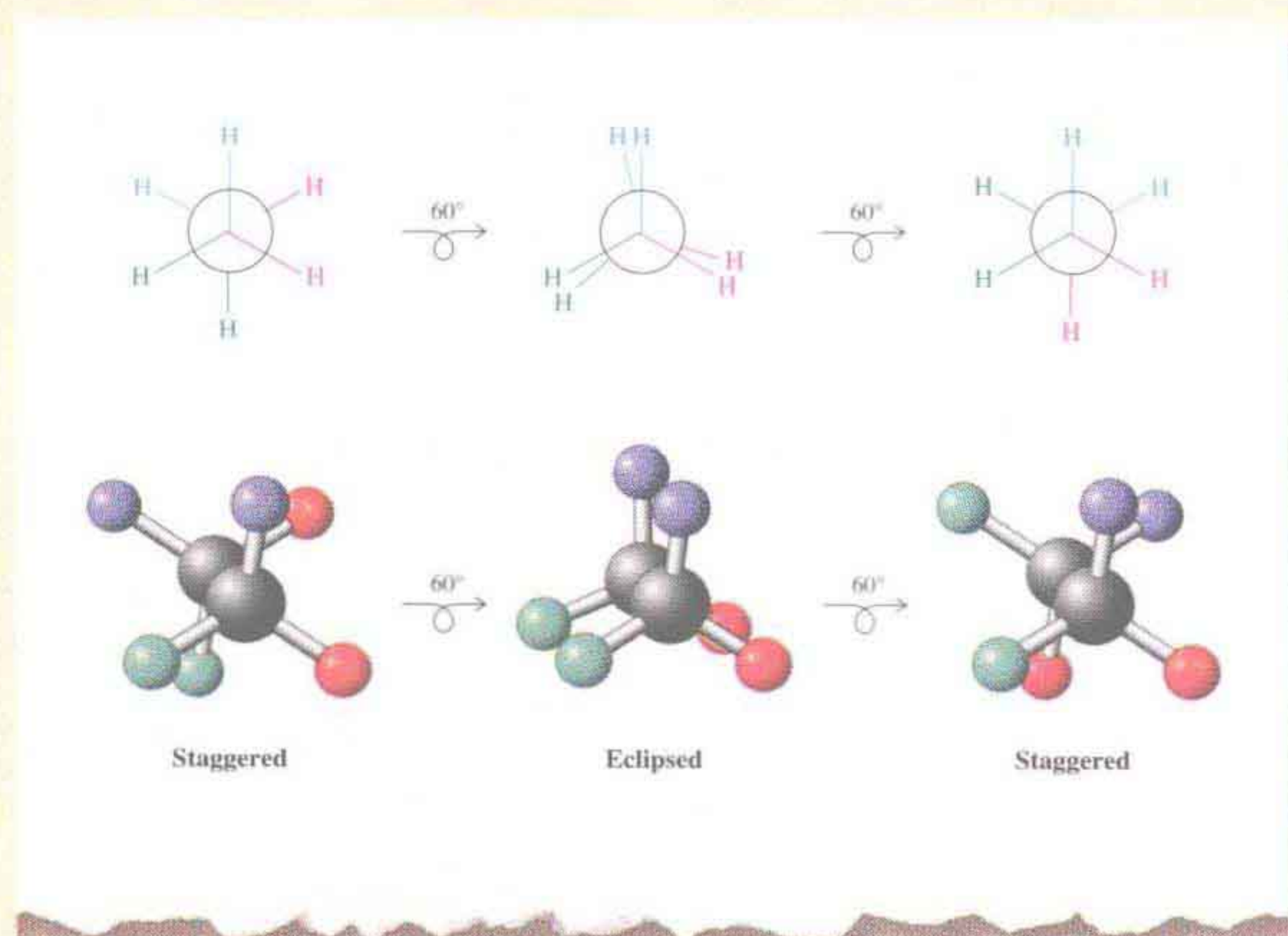
Curved-Arrow Representations of Several Common Types of Mechanisms



New Ways to Visualize Organic Chemistry

We have now included computer-generated pictures of ball-and-stick and space-filling models. These pictures encourage students to build actual models. They also provide students with lowest-energy conformations, guiding them in the construction of realistic assemblies. Finally, space-filling renditions create a more accurate impression of size, shape, and the extent of orbitals.

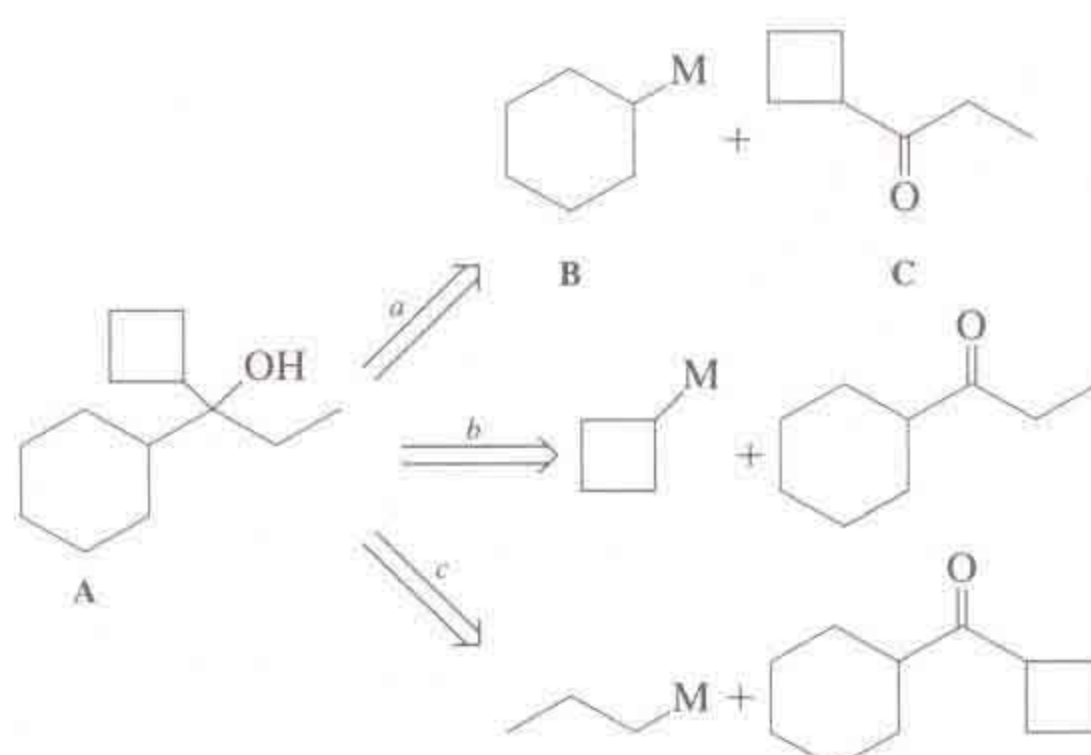
The first and second editions emphasized the importance of building molecular models as an aid in visualizing three-dimensional structure and dynamics. We have highlighted this emphasis by a new icon at numerous locations. Ball-and-stick model kits are available for purchase through the publisher.



Innovative Approaches to Problem Solving

SOLUTION

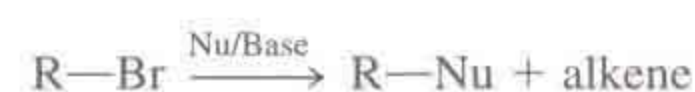
Before we start a random trial and error approach to solving this problem, it is better to take an inventory of what is given. First, we are given cyclohexane, and we note that this unit shows up as a substituent in tertiary alcohol A. Second, a total of seven additional carbons appears in the product, so our synthesis will require some additional stitching together of smaller fragments because we cannot use compounds containing more than four carbons. Third, target A is a tertiary alcohol, which should be amenable to the retrosynthetic analysis introduced in Section 8-9 (M = metal):



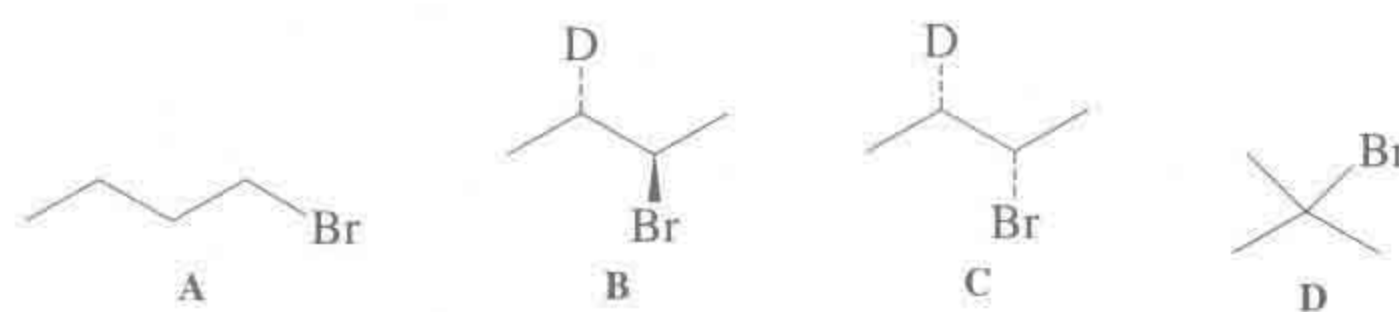
• *New Chapter Integration Problems* are solved problems that emphasize concept integration both within and between chapters. The solution is worked out step-by-step, teaching the art of problem solving in general and specifically demonstrating how one set of learned skills builds on and interacts with preceding ones. Particular emphasis is placed on problem analysis, deductive reasoning, and logical conclusions.

Team Problem

47. Consider the general substitution-elimination reactions of the bromoalkanes.



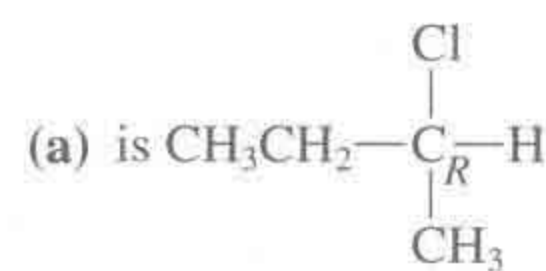
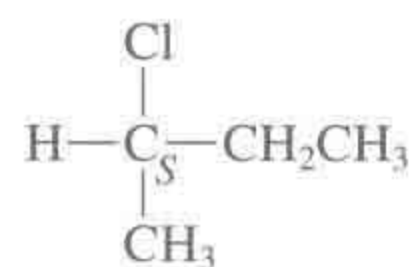
How do the reaction mechanisms and product formation differ when the structure of the substrate and reaction conditions change? To begin to unravel the nuances of bimolecular and unimolecular substitution and elimination reactions, focus on the treatment of bromoalkanes A through D under conditions (a) through (e). Divide the problem evenly among yourselves so that each of you tackles the questions of reaction mechanism(s) and qualitative distribution of product(s), if any. Reconvene to discuss your conclusions and come to a consensus. When you are explaining a reaction mechanism to the rest of the team, use curved arrows to show the flow of electrons. Label the stereochemistry of starting materials and products as *R* or *S*, as appropriate.



• *The Team Problem* is also new to each chapter. Team Problems encourage discussion and collaborative learning among students. Although these problems could be assigned in a classroom setting, they are written so as to be perfectly workable in an unstructured, casual setting, such as a library, coffee shop, study hall, or home. The idea is to stimulate “cross-talk,” an exchange of information and ideas, and support among students.

Preprofessional Problems

55. The enantiomer of



(c) is nonisomeric

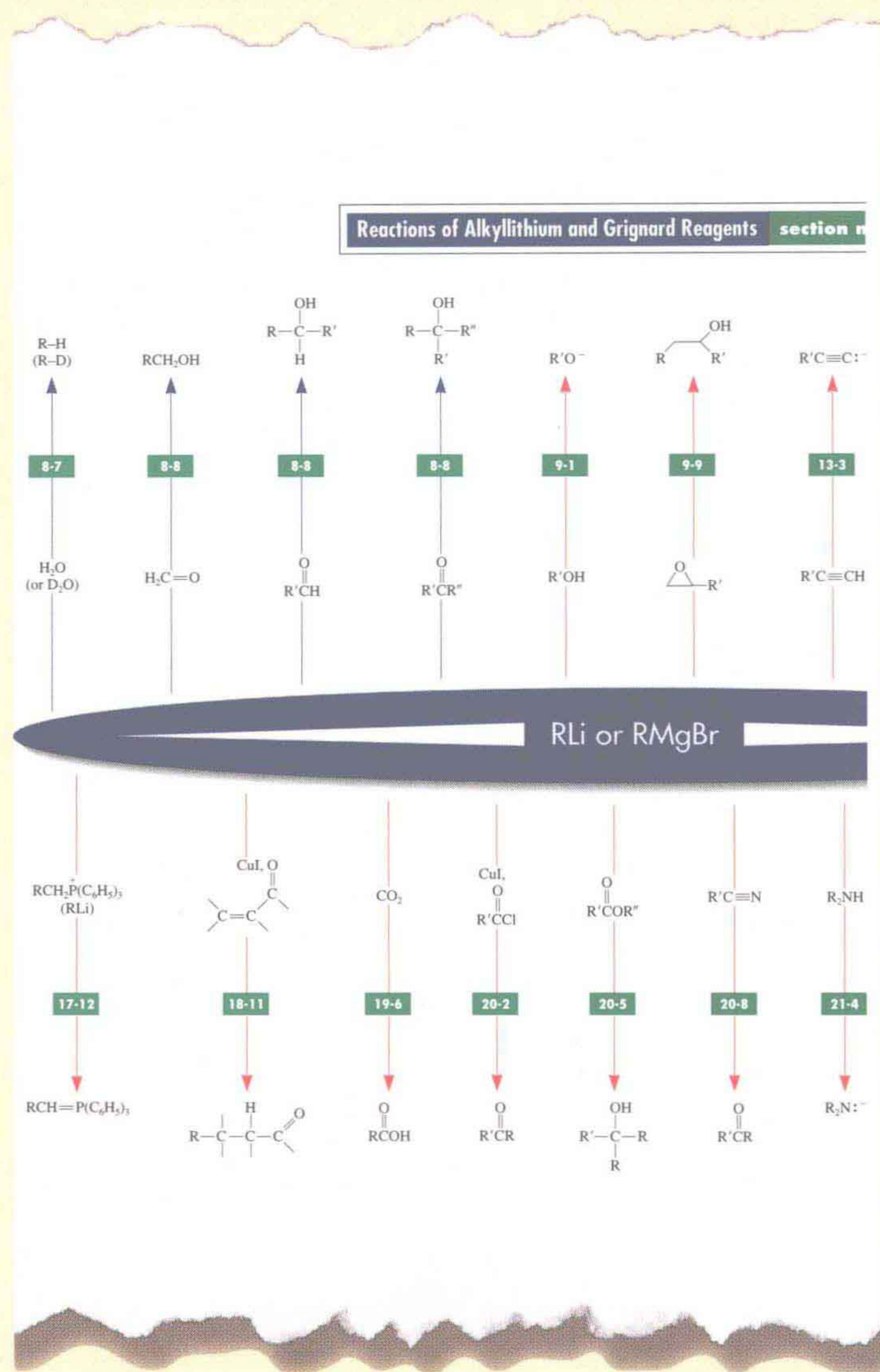
(b) can exist only at low temperatures

(d) is incapable of existence

• *Preprofessional Problems* will be appreciated by students who are planning careers in medicine or related fields. In a new multiple-choice format, they are typical of those that appear on the MCAT, GRE, and DAT.

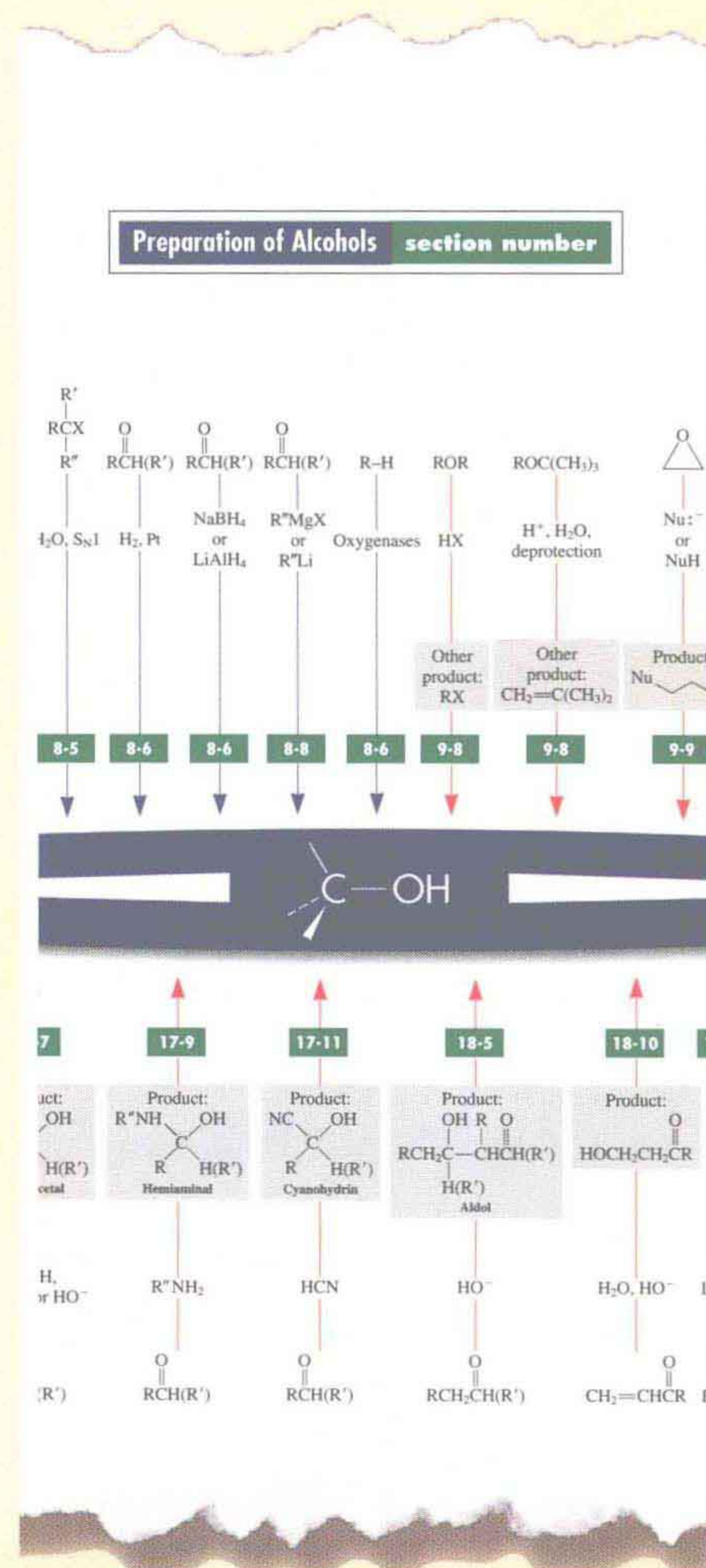
New Reaction Summary Road Maps

From Chapter 8 onward, the chemistry of each functional group is shown in condensed form through two types of **reaction summary road maps**, providing “the functional group at a glance.” The first type depicts the function as the origin of multiple reaction arrows, each labeled with a particular reagent, ending in a specific product. Section numbers indicate where the transformation is discussed in the text,



and color distinguishes past from future chemistry. This map provides information about the reactions of the functional group—that is, what it does. The second type of map is very similar, but the reaction arrows are reversed—that is, pointing toward the functionality. This map provides information about the function’s possible origins—that is, its precursor functional groups. Thus, a specific reaction $A \rightarrow B$ may appear in two separate schemes, one with A and the other with B as the center. These maps are an important aid in synthetic-retrosynthetic analysis and a check on the student’s “vocabulary” of synthetic methodology.

the functional group at a glance.” The first type depicts the function as the origin of multiple reaction arrows, each labeled with a particular reagent, ending in a specific product. Section numbers indicate where the transformation is discussed in the text,



A Book for the Real World

Modern Biological and Industrial Applications

In every chapter of this textbook you will find many references to biological, medical, and industrial applications of organic chemistry. Much of this material is new to

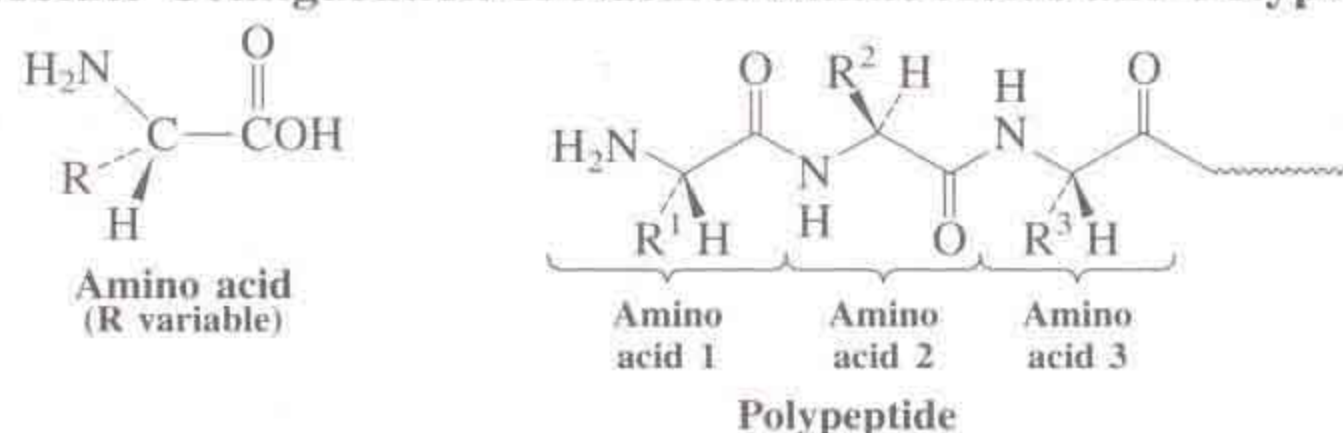
CHEMICAL HIGHLIGHT 5-5

Why Is Nature "Handed"?

In this chapter, we have seen that many of the organic molecules in nature are chiral. More importantly, most natural compounds in living organisms not only are chiral, but also are present in only one enantiomeric form. An example of an entire class of such

compounds consists of the *amino acids*, which are the component units of *polypeptides*. The large polypeptides in nature are called *proteins* or, when they catalyze biotransformations, *enzymes*.

Absolute Configuration of Natural Amino Acids and Polypeptides



Being made up of smaller chiral pieces, enzymes arrange themselves into bigger conglomerates that also are chiral and show handedness. Thus, much as a right hand will readily distinguish another right hand from a left hand, enzymes (and other biomolecules)

have "pockets" that, by virtue of their stereochemically defined features, are capable of recognizing and processing only one of the enantiomers in a racemate. The differences in physiological activity of the two enantiomers of a

this edition. For instance, in Chapter 3 there is a new section on the effects of chlorine compounds on the atmosphere. In Chapter 5 you will find new Chemical Highlights on chiral drugs and the handedness of nature. New material on polyethers and their medical uses is found in Chapter 9. We have expanded our coverage of polymers, including polymer synthesis using dienes and nitriles (Chapter 14), and biodegradable polyester plastics (Chapter 19). Chapter 26 discusses the mechanism of chymotrypsin activity. Finally, in keeping with our emphasis on synthesis,

throughout the text students are guided through the syntheses of many biologically important compounds, including norethynodrel (Chapter 17), steroids (Chapter 18), and Prozac (Chapter 21).

New Chapter Introductions

When you hear or read the word *steroids*, two things probably come to mind immediately: athletes who illegally "take steroids" to develop their muscles and "the pill" used for birth control. But what do you know about steroids aside from this general association? What is their structure? How does one steroid differ from another? Where are they found in nature?

An example of a naturally occurring steroid is diosgenin, obtained from the Mexican yam and used as a starting material for the synthesis of several commercial steroids. Most striking is the number of *rings* in the compound.

The introduction to each chapter has been "spiced up" with thought-provoking questions relating the relevance of the chapter's material to everyday experience. These general questions find answers on further reading, thus prompting the student's interest and participation.

A Book About Real Chemistry

Emphasis on Synthetic Strategy

The importance of synthesis is stressed starting on page 3, and the considerations entering into the development of a good synthetic strategy and the avoidance of pitfalls are developed throughout the text. Since the innovative introduction of Section 8-9 on retrosynthetic analysis in the first edition, this aspect of the text has received much positive feedback from teachers and students. The present edition has added a

slightly more explicit treatment of linear versus convergent synthesis to this section. Multistep partial and total syntheses are pointed out where appropriate in the various functional-group treatments. Particular emphasis is placed on stereo- and regioselectivity (Chapter 12 and Section 16-5), biological and medicinal relevance (e.g., Sections 9-11, 12-16, 18-12, and 19-4 and Chapters 24 through 26), and the importance of materials synthesis (e.g., Sections 12-13 through 12-15, 13-11, 14-10, and 21-12). These discussions are then extensively reinforced in the In-Chapter Exercises and End-of-Chapter Problems and highlighted in numerous Chemical Highlights.

Retrosynthetic analysis simplifies synthesis problems

Many compounds that are commercially available and inexpensive are also small, containing six or fewer carbon atoms. Therefore, the most frequent task facing the synthetic planner is that of building up a larger, complicated molecule from smaller, simple fragments. The best approach to the preparation of the target is to work its synthesis *backward* on paper, an approach called **retrosynthetic analysis*** (*retro*, Latin, backward). In this analysis, strategic carbon-carbon

Early and More Unified Presentation of Spectroscopy

Our first edition broke ground by introducing spectroscopy right after alcohol chemistry. Early coverage, beginning with NMR in Chapter 10, offers opportunities to practice the application of spectroscopic methods to many kinds of compounds. After NMR, we cover IR- and UV-visible spectroscopy in Chapters 11 and 14 in the context of functional groups. Courses can include each of the principal types of spectroscopy in the first half of the text.

Early coverage of spectroscopy reinforces the interplay between structure and function. This organization allows students to apply spectroscopic techniques in the context of the functional group. Infrared spectroscopy, for example, is introduced in Chapter 11 on alkenes.

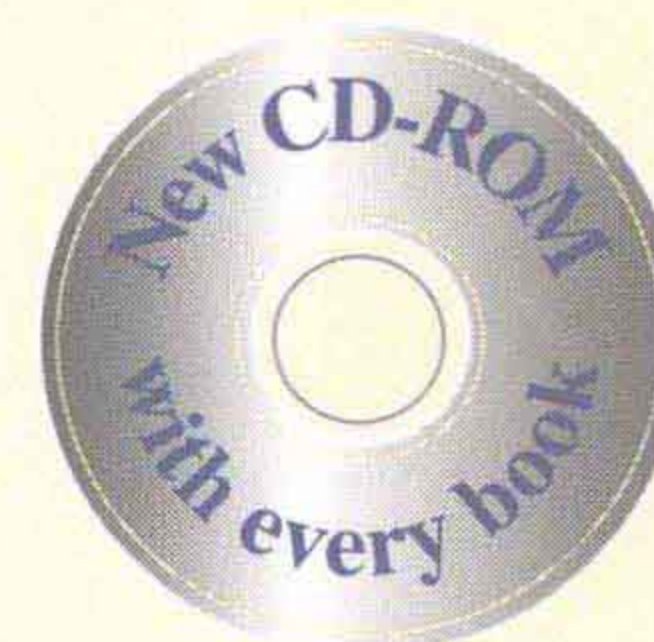
We have also added new discussions (e.g., Section 10-9) and problems that unify the application of spectroscopic techniques in structure determination.

An Innovative Package:

SUPPLEMENTS AND LABORATORY MANUALS

The CD-ROM found in the back of this text is a multimedia learning tool developed by W. H. Freeman and Company in conjunction with Sumanas, Inc. All the features of the CD function within the context of the book's coverage. Many of the structures mentioned in the book are depicted as three-dimensional animations with multiple-display options through a molecular-modeling program. These animations and many other molecular-level simulations bring the concepts of the book to life. Practice tools, such as interactive quizzes in every chapter and a preprofessional examination, help students review for exams. Spectroscopy and NMR exercises along with other interactive exercises help students master difficult concepts. Presentation software for instructors allows them to prepare a series of illustrations and animations for lecture.

- *The Study Guide* is written by Neil Schore, providing a direct link from the text to the supplement. Sample problems are worked out, and the solutions to the End-of-Chapter Problems are given. "Keys to the Chapter" sections point out pitfalls



Available
in ground glass
and
flexible connector
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of faulty logic and help students visualize the solution steps for various exercises. Tables summarize the spectral features associated with each functional group. A glossary of key terms is also provided.

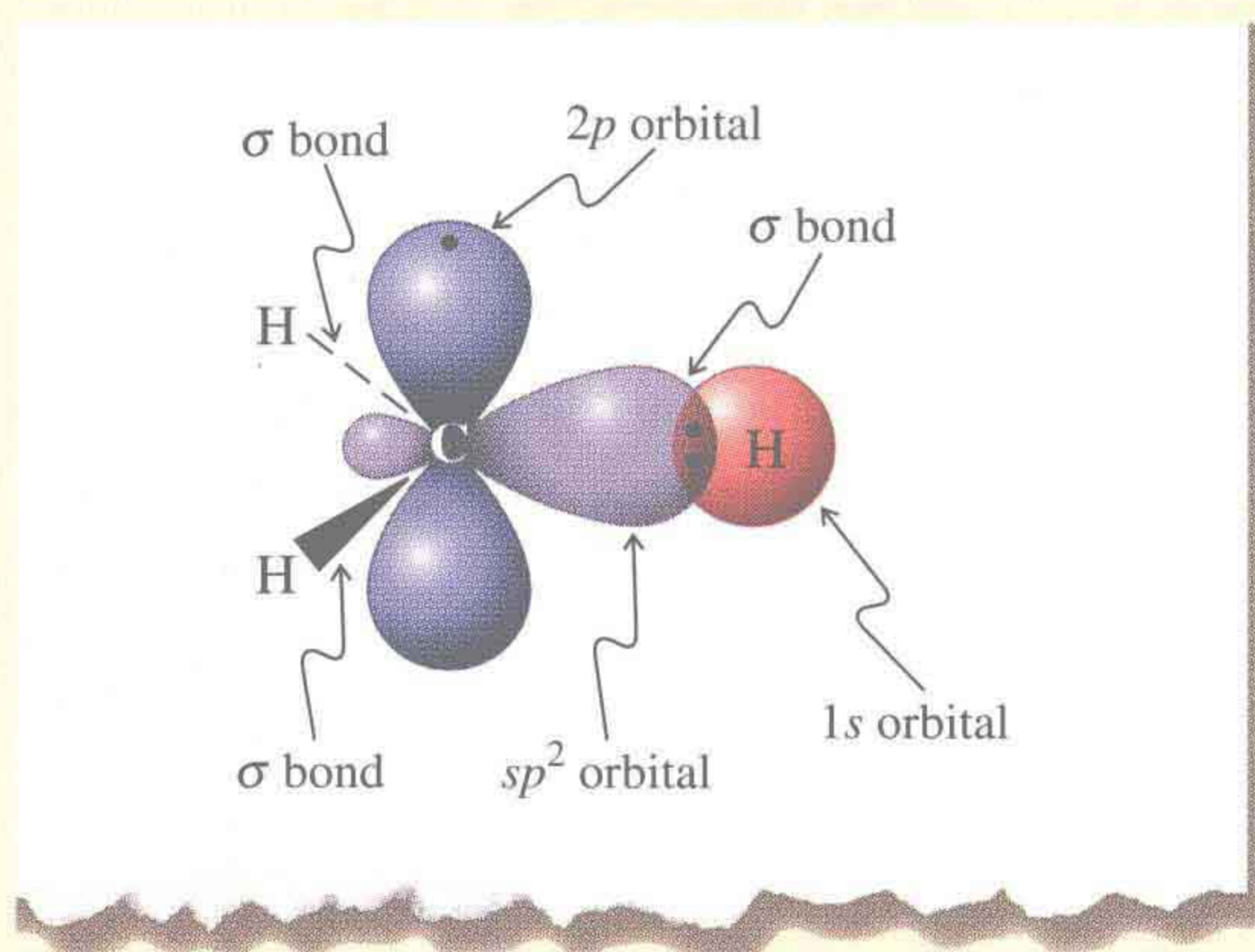
- *The Test Bank*, by Charles M. Garner and Kevin G. Pinney of Baylor University, is new to this edition. With the Windows and Macintosh software of the computerized versions, instructors can easily change and add questions as well as import their own electronic drawings.

- *The Maruzen Molecular Structure Model Set* and *Space-Filling Model Set* are also available for student purchase. These essential tools can be used to present orbitals; single, double, and triple bonds; and locations of atoms.

- *Experimental Organic Chemistry: Macroscale and Microscale*. With these texts by Jerry R. Mohrig, Christina Noring Hammond, Terence C. Morrill, and Douglas C. Neckers, the laboratory becomes a place of discovery and critical thinking. Instead of simply following directions, students immerse themselves in the experimental process. Instructors will appreciate the versatility of the manuals' balanced approach, with enough experiments to use macroscale glassware, microscale glassware, or a combination of both. Innovative discovery-based experiments and multiweek projects encourage students in scientific investigation. A CD-ROM of techniques accompanies both texts.

A KEY TO THE FUNCTIONAL USE OF COLOR

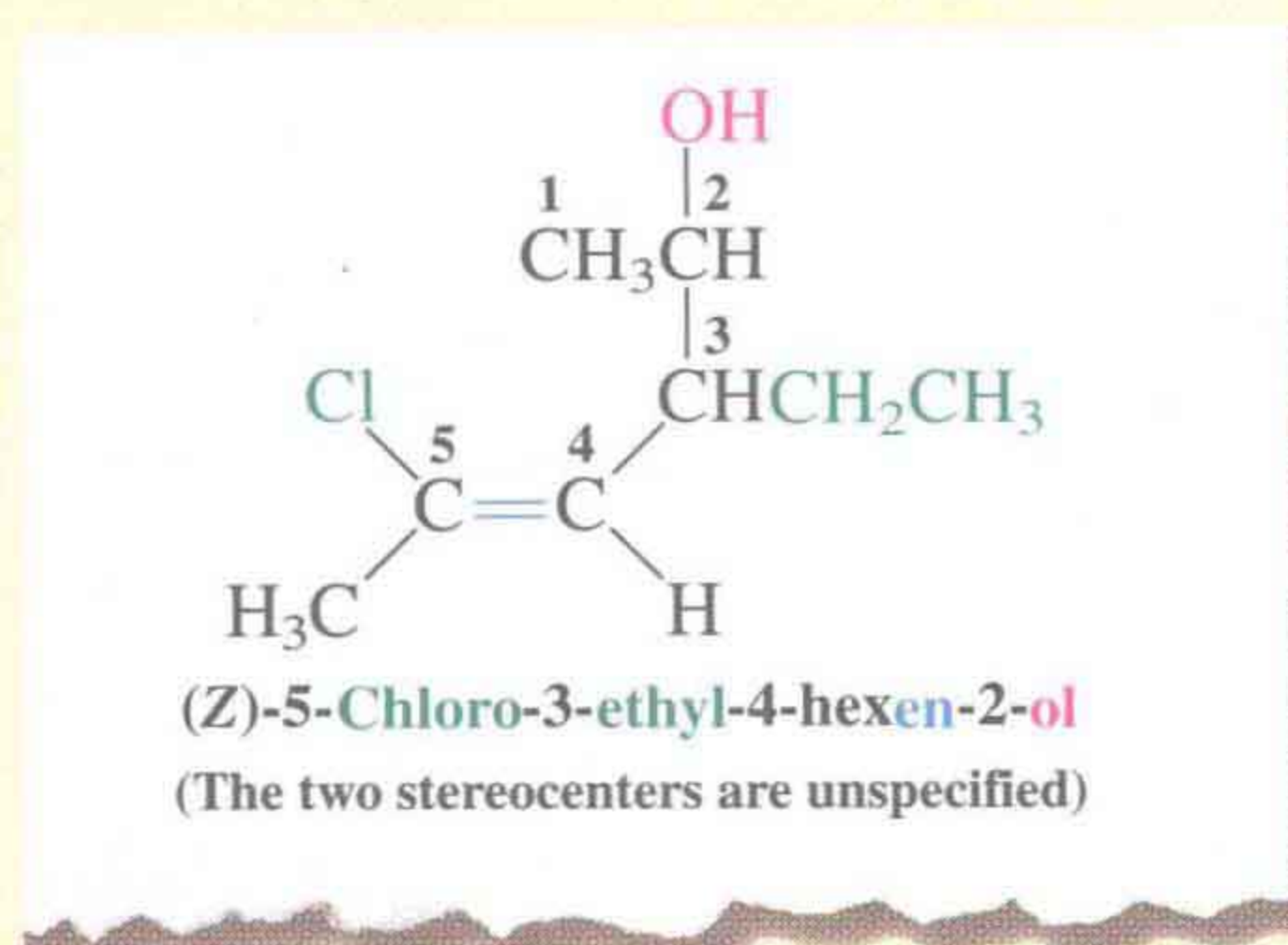
We use color consistently and functionally to help students master basic principles, including nomenclature, orbitals, sequence rules in stereochemistry, the relation of spectral lines to functional groups, topological changes in molecular transformations, and the reactivity of functional groups. Color is suspended in exercises, chapter reviews, and problems, however, because it is important to learn how not to rely on it. In this edition, we have carefully reevaluated the application of color in reaction schemes and simplified its use.



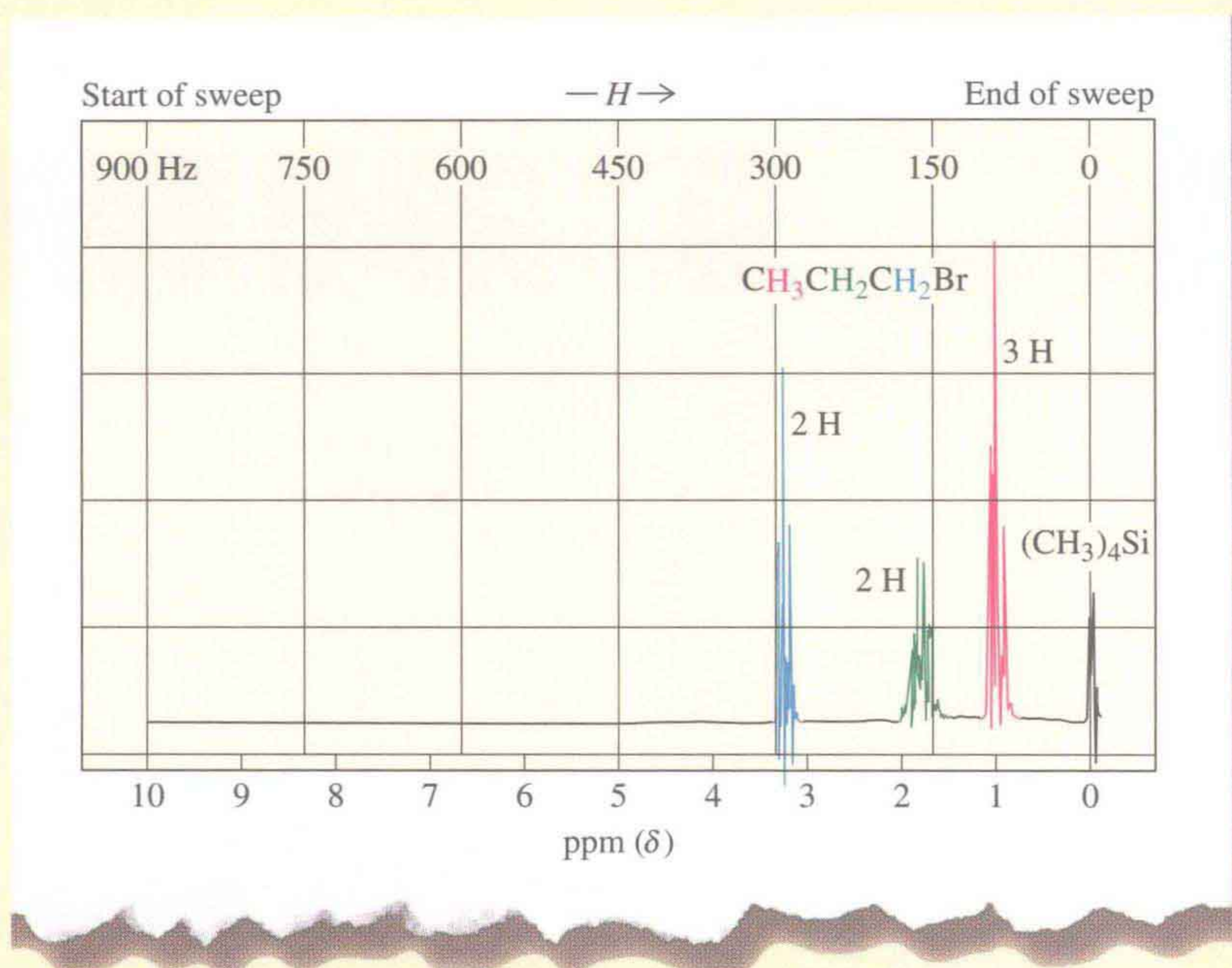
For example, wherever possible, *s* orbitals are shown in red, *2p* orbitals in blue, *spⁿ* hybrids in purple, and *3p* orbitals in green.

Color shows the relation of the names of organic molecules to their structures. In the illustration shown at the top of the next page, which is from Chapter 11, the func-

tional group that gives the molecule its unique chemical behavior and other substituents are clearly differentiated from the stem.

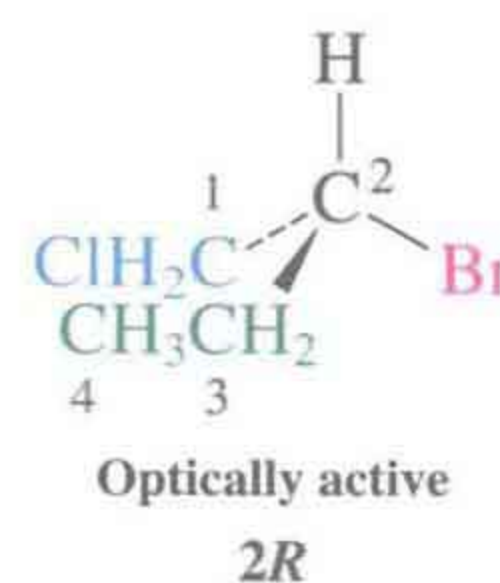


Color is used to associate spectral features with certain molecular units. For example, in the adjoining spectrum, the three colors show how the three non-equivalent hydrogens give rise to three distinct “peaks”—an observation that will help the students identify a molecule when they know its spectrum.

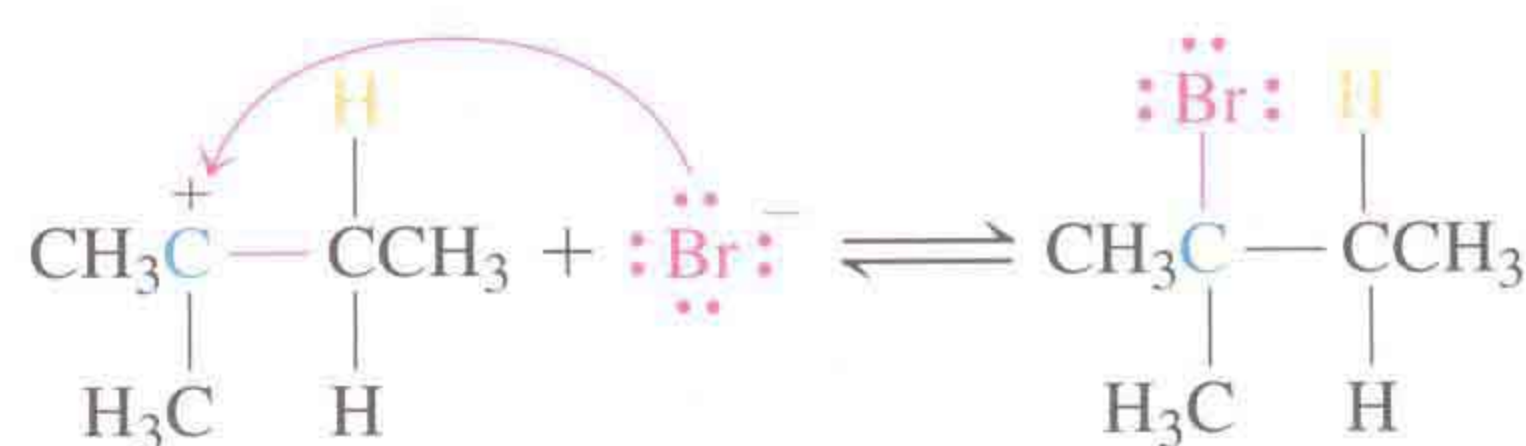


Color offers clues to a molecule’s stereochemistry, or the arrangement of its atoms in space. The student will see in Chapter 5 that substituents in three dimensions can be assigned a priority according to certain “sequence rules,” and this assignment has been indicated, in diminishing order of priority, by red, blue, green, and black.

Remember the use of color to denote group priorities:
Highest—red
Second highest—blue
Third highest—green
Lowest—black



STEP 4. Trapping by bromide



Most important, color frequently shows how the functional groups transform in the reaction mechanism. Electron-rich, or “nucleophilic,” parts are shown in red; electron-deficient, or “electrophilic,” fragments are blue; and radicals and leaving groups are green. Red arrows in these transformations indicate the movements of electrons.

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ABOUT THE AUTHORS

K. PETER C. VOLLHARDT was born in Madrid in 1946, raised in Buenos Aires and Munich, studied at the University of Munich, received his Ph.D. with Professor Peter Garratt at the University College, London, and was a postdoctoral fellow with Professor Bob Bergman (then) at the California Institute of Technology. He moved to Berkeley in 1974, when he began his efforts toward the development of organocobalt reagents in organic synthesis, the preparation of theoretically interesting hydrocarbons, the assembly of novel transition metal arrays with potential in catalysis, and the discovery of a parking space. Among other pleasant experiences, he was a Studienstiftler, Adolf Windaus medalist,

Humboldt Senior Scientist, ACS Organometallic Awardee, Otto Bayer Prize Awardee, and A. C. Cope Scholar. He is the current Chief Editor of SYNLETT. Among his more than 240 publications, he especially treasures this textbook in organic chemistry, translated into seven languages. Peter is married to Marie-José Sat, a French artist, and they have two children, Paloma (b. 1994), whose picture you can admire in Chapter 5, and Julien (b. 1997), who refused to pose.



NEIL SCHORE was born in Newark, New Jersey, in 1948. His education took him through the public schools of the Bronx, New York, and Ridgefield, New Jersey, after which he completed a B.A. with honors in chemistry at the University of Pennsylvania in 1969. Moving back to New York, he worked with Professor Nicholas Turro at Columbia University, studying photochemical and photophysical processes of organic compounds for his Ph.D. thesis. He first met Peter Vollhardt when he and Peter were doing postdoctoral work in Professor Robert Bergman's laboratory at Cal Tech in the 1970s. Since joining the U. C. Davis faculty in 1976, he has taught organic chemistry to over 10,000 nonchemistry majors, winning three teaching awards, and published over 70 papers in various areas related to organic synthesis. Neil is married to Carrie Erickson, a microbiologist at the U. C. Davis School of Veterinary Medicine. They have two children, Michael (b. 1981) and Stefanie (b. 1983), both of whom carried out experiments for this book.

ORGANIC CHEMISTRY

Structure and Function

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