Preface

What Sets This Book Apart?

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.

The goal of this text, as it has been through six previous editions, is to provide students with the conceptual tools to understand and apply the relationship between the structures of organic compounds and their properties. Both the organization of the text and the presentation of individual topics were designed with this objective in mind.

A Functional Group Organization

The text is organized according to functional groups—structural units within a molecule that are most closely identified with characteristic properties. This organization offers two major advantages over alternative organizations based on mechanisms or reaction types.

- 1. The information content of individual chapters is more manageable when organized according to functional groups.
- **2.** Patterns of reactivity are reinforced when a reaction used to prepare a particular functional group reappears as a characteristic reaction of a different functional group.

A Mechanistic Emphasis and Its Presentation

The text emphasizes mechanisms and encourages students to see similarities in mechanisms among different functional groups. Mechanisms are developed from observations; thus, reactions are normally

presented first, followed by their mechanism.

To maintain consistency with what our students have already learned, this text presents multistep mechanisms in the same way as do most general chemistry textbooks that is, as a series of *elementary steps*. Additionally, we provide a brief comment about how each step contributes to the overall mechanism.

Section 1.11, "Curved Arrows and Chemical Reactions," introduces students to the notational system employed in all of the mechanistic discussions in the text.

Numerous reaction mechanisms are accompanied by potential energy diagrams. Section 4.9, "Potential Energy Diagrams for Multistep Reactions: The S_N1 Mechanism," shows how the potential energy diagrams for three elementary steps are combined to give the diagram for the overall reaction.



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Enhanced Graphics

The teaching of organic chemistry has especially benefited as powerful modeling and graphics software have become routinely available. For example, computer-generated molecular models and electrostatic potential maps were integrated into the third edition of



this text, and their number has increased with each succeeding edition. Also seeing increasing use are graphically correct representations of orbitals and the role of orbital interactions in chemical reactivity. The E2 mechanism of elimination, which involves a single elementary step, is supplemented by showing the orbital interactions that occur during that step.

Problems

Problem-solving strategies and skills are emphasized throughout. Understanding is progressively reinforced by problems that appear within topic sections. For many problems, sample solutions are given, including an increased number of examples of handwritten solutions from the author.



Generous and Effective Use of Tables

The relative reactivity of different compounds is pertinent to both the theory and practice of organic chemistry. While it is helpful—and even important—to know that one compound is more reactive than another, it is even better to know by how much. Our text provides more experimental information of this type than is customary. Chapter 8, "Nucleophilic Substitution," for example, contains seven tables of *quantitative* relative rate data, of which the following is but one example.

Annotated summary tables have been a staple of *Organic Chemistry* since the first edition. Some tables review reactions from earlier chapters, others review reactions or concepts of a current chapter, and still others walk the reader step-by-step through skill

TABLE 8.2	Reactivity of Some Alkyl Bromides Toward Substitution by the S_N2 Mechanism*			
Alkyl bromide		Structure	Class	Relative rate [†]
Methyl bromide Ethyl bromide Isopropyl bromide <i>tert</i> -Butyl bromide		CH_3Br CH_3CH_2Br $(CH_3)_2CHBr$ $(CH_3)_3CBr$	Unsubstituted Primary Secondary Tertiary	221,000 1,350 1 Too small to measure

*Substitution of bromide by lithium iodide in acetone.

[†]Ratio of second-order rate constant k for indicated alkyl bromide to k for isopropyl bromide at 25°C

builders and concepts unique to organic chemistry. Well received by students and faculty alike, these summary tables remain one of the text's strengths.

Pedagogy

- A list of mechanisms, tables, boxed essays and Descriptive Passages and Interpretive Problems is included in the front matter (page xix) as a quick reference to these important learning tools in each chapter.
- Each chapter opens with a list of section headings, boxed essays, reaction mechanisms, and Descriptive Passages and Inter-

pretive Problems along with their corresponding page numbers.

- 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.



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Audience

Organic Chemistry is 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 about our intended audience. Is the topic appropriate for them with respect to 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?

Even the art that opens each chapter in this edition has been designed with the audience in mind. The electrostatic potential maps that have opened the chapters through several editions have been joined by a graphic of a familiar object that connects the map to the chapter's content. Chapter 8, for example, opens by illustrating the umbrella-in-a-windstorm analogy used by virtually everyone who has ever taught nucleophilic substitution.



What's New?

Descriptive Passages and Interpretive Problems

New to this edition is an original feature that adds breadth, flexibility, and timeliness to our coverage. Because so many organic chemistry students later take standardized pre-professional examinations composed of problems derived from a descriptive passage, we decided to include comparable passages and problems in our text to familiarize students with this testing style. We soon discovered that descriptive passages accompanied by interpretive problems can serve the even greater purpose of enhancing this text's content.

The passages focus on a wide range of topics—from structure, synthesis, mechanism, and natural products to using the Internet to calculate ¹³C chemical shifts. They provide instructors with numerous opportunities to customize their own organic chemistry course while giving students practice in combining new information with what they have already learned.



Boxed Essays: Revised and New

- What's in a Name? Organic Nomenclature describes the evolution of organic nomenclature and compares the 1979, 1993, and 2004 IUPAC recommendations for naming organic compounds.
- β-Lactam Antibiotics expands the familiar penicillin story beyond its discovery to include its large-scale development as a lifesaving drug during World War II and its mode of action.
- Peptide Mapping and MALDI Mass Spectrometry illustrates the application of a cuttingedge mass spectrometric technique to peptide sequencing.

New Topics

- Section 10.4: "S_N2 Reactions of Allylic Halides"
- Section 10.7: "Allylic Anions"
- Section 11.14: "S_N1 Reactions of Benzylic Halides"
- Section 11.15: "S_N2 Reactions of Benzylic Halides"

Major Revisions

- Sections 13.20–13.22 are a complete rewrite of infrared (IR) spectroscopy. All of the IR spectra displayed in the text are new and were recorded by Thomas Gallaher of James Madison University using the attenuated total reflectance (ATR) method.
- Section 25.8 "Mutarotation and the Anomeric Effect" revises the previous discussion of mutarotation to include the now-generally accepted molecular orbital explanation for the anomeric effect.



Nucleophilic substitution is one of a variety of mechanisms by which living systems detoxify halogenated organic compounds introduced into the environment. Enzymes that catalyze these reactions are known as haloalkane dehalogenases. The hydrolysis of 1,2-dichloroethane to 2-chloroethanol, for example, is a biological nucleophilic substitution catalyzed by the dehalogenase shown in Figure 8.4.

$$\begin{array}{rcl} & \underset{enzyme}{\overset{dehalogenase}{\overset{enzyme}{\overset{enzyme}{\overset{enzyme}{\overset{}}{\overset{}}}}} \\ 1,2\text{-Dichloroethane} & Water \\ & CICH_2CH_2OH & + & H_3O^+ & + & CI^- \\ 2\text{-Chloroethanol} & Hydronium ion & Chloride \\ \end{array}$$

This haloalkane dehalogenase is believed to act by using one of its side-chain carboxylates to displace chloride by an $S_{N}2$ mechanism. (Recall the reaction of carboxylate ions with alkyl halides from Table 8.1.)



The product of nucleophilic substitution then reacts with water, restoring the enzyme to its original state and giving the observed products of the reaction.

This stage of the reaction proceeds by a mechanism that will be discussed in Chapter 20. Both stages are faster than the reaction of 1,2-dichloroethane with water in the absence of the enzyme. Enzyme-catalyzed hydrolysis of racemic 2-chloropropanoic acid is a key step in the large-scale preparation of (S)-2-chloropropanoic acid used for the preparation of agricultural chemicals.



In this enzymatic resolution (Section 7.14), the dehalogenase enzyme catalyzes the hydrolysis of the *R*-enantiomer of 2-chloropropanoic acid to (S)-lactic acid. The desired (S)-2chloropropanoic acid is unaffected and recovered in a nearly enantiomerically pure state.

Some of the most common biological S_N2 reactions involve attack at methyl groups, especially a methyl group of S-adenosylmethionine. Examples of these will be given in Chapter 16.



A ribbon diagram of the dehalogenase enzyme that catalyzes the hydrolysis of 1,2-dichloroethane. The progression of amino acids along the chain is indicated by a color change. The nucleophilic carboxylate group is near the center of the diagram.