

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 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.

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.

MECHANISM 6.5

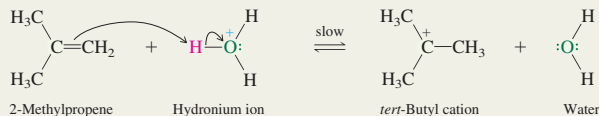
Acid-Catalyzed Hydration of 2-Methylpropene

The overall reaction:

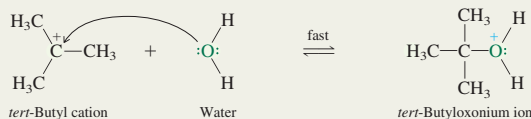


The mechanism:

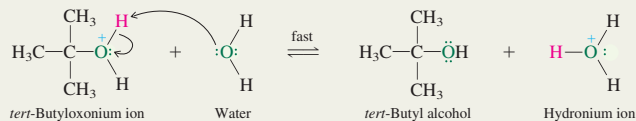
STEP 1: Protonation of the carbon–carbon double bond in the direction that leads to more stable carbocation:



STEP 2: Water acts as a nucleophile to capture *tert*-butyl cation:



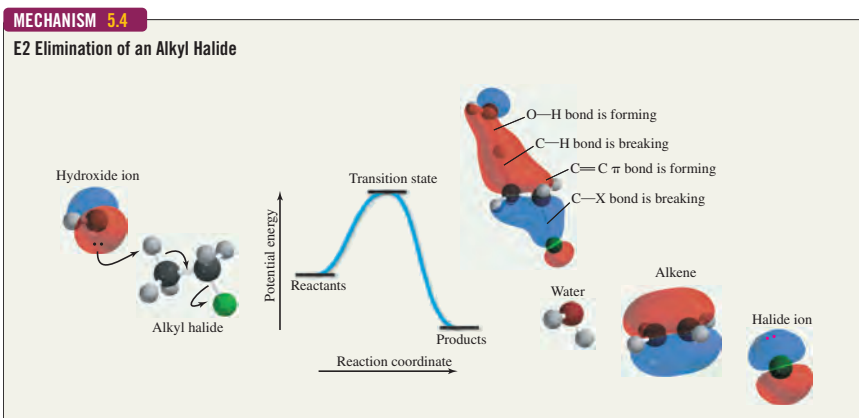
STEP 3: Deprotonation of *tert*-butyloxonium ion. Water acts as a Brønsted base:



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.

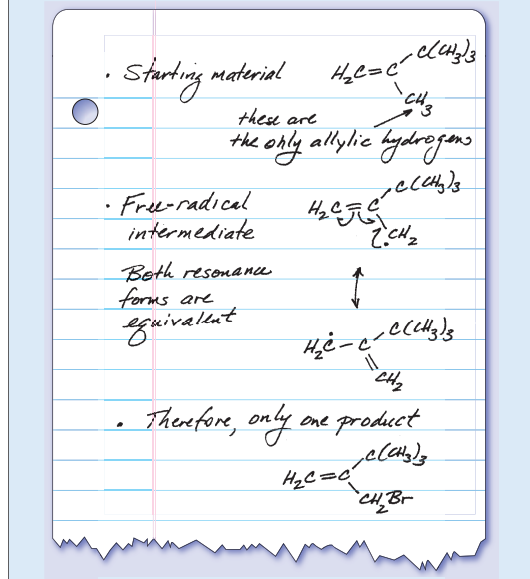


Problems

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.

PROBLEM 10.6

Evaluate 2,3,3-trimethyl-1-butene as a candidate for free-radical bromination. How many allylic bromides would you expect to result from its treatment with *N*-bromosuccinimide?



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 $\text{S}_{\text{N}}2$ Mechanism*

Alkyl bromide	Structure	Class	Relative rate [†]
Methyl bromide	CH_3Br	Unsubstituted	221,000
Ethyl bromide	$\text{CH}_3\text{CH}_2\text{Br}$	Primary	1,350
Isopropyl bromide	$(\text{CH}_3)_2\text{CHBr}$	Secondary	1
<i>tert</i> -Butyl bromide	$(\text{CH}_3)_3\text{CBr}$	Tertiary	Too small to measure

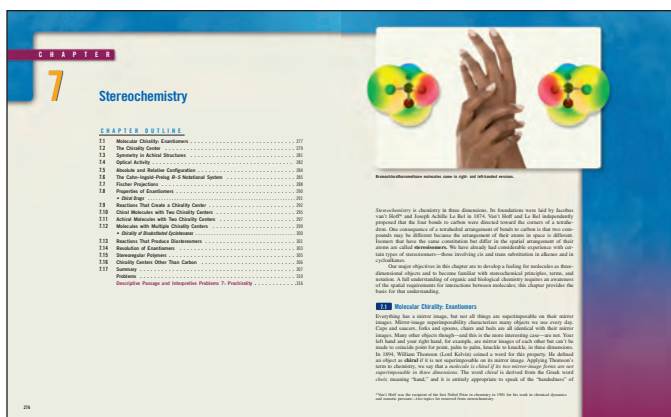
*Substitution of bromide by lithium iodide in acetone.

[†]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 Interpretive 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.



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.

12.19 SUMMARY

Section 12.1 On reaction with electrophilic reagents, compounds that contain a benzene ring undergo **electrophilic aromatic substitution**. Table 12.1 in Section 12.1 and Table 12.3 in this summary give examples.

Section 12.2 The mechanism of electrophilic aromatic substitution involves two stages: bonding of the electrophile by the π electrons of the ring (slow, rate-determining), followed by rapid loss of a proton to restore the aromaticity of the ring.

Benzene	Electrophilic reagent	Cyclohexadienyl cation intermediate	Product of electrophilic aromatic substitution	
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Sections 12.3–12.5 See Table 12.3

Sections 12.6–12.7 See Tables 12.3 and 12.4.

Section 12.8 Friedel–Crafts acylation, followed by Clemmensen or Wolff–Kishner reduction is a standard sequence used to introduce a primary alkyl group onto an aromatic ring.



