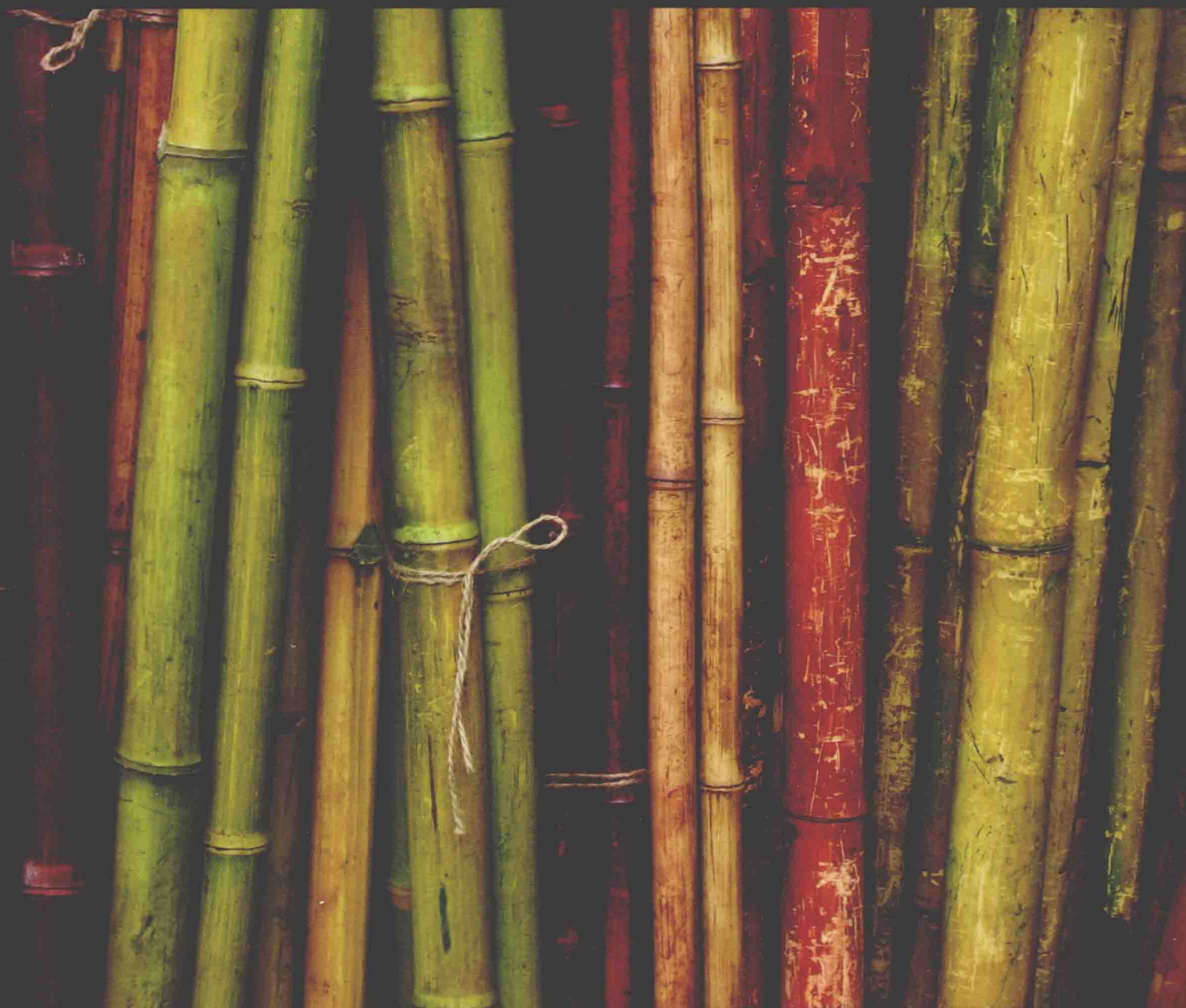


TENTH EDITION

# Organic Chemistry

T.W. Graham Solomons | Craig B. Fryhle



**International Student Version**

TENTH EDITION

# Organic Chemistry

International Student Version

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*In memory of my beloved son, John Allen Solomons, TWGS  
To Deanna, in the year of our 25th anniversary. CBF*

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**TABLE 3.1** Relative Strength of Selected Acids and Their Conjugate Bases

	Acid	Approximate $pK_a$	Conjugate Base	
Strongest acid	$\text{HSbF}_6$	$< -12$	$\text{SbF}_6^-$	Weakest base
	$\text{HI}$	$-10$	$\text{I}^-$	
	$\text{H}_2\text{SO}_4$	$-9$	$\text{HSO}_4^-$	
	$\text{HBr}$	$-9$	$\text{Br}^-$	
	$\text{HCl}$	$-7$	$\text{Cl}^-$	
	$\text{C}_6\text{H}_5\text{SO}_3\text{H}$	$-6.5$	$\text{C}_6\text{H}_5\text{SO}_3^-$	
	$(\text{CH}_3)_2\text{OH}^+$	$-3.8$	$(\text{CH}_3)_2\text{O}$	
	$(\text{CH}_3)_2\text{C}=\text{OH}^+$	$-2.9$	$(\text{CH}_3)_2\text{C}=\text{O}$	
	$\text{CH}_3\text{OH}_2^+$	$-2.5$	$\text{CH}_3\text{OH}$	
	$\text{H}_3\text{O}^+$	$-1.74$	$\text{H}_2\text{O}$	
	$\text{HNO}_3$	$-1.4$	$\text{NO}_3^-$	
	$\text{CF}_3\text{CO}_2\text{H}$	$0.18$	$\text{CF}_3\text{CO}_2^-$	
	$\text{HF}$	$3.2$	$\text{F}^-$	
	$\text{C}_6\text{H}_5\text{CO}_2\text{H}$	$4.21$	$\text{C}_6\text{H}_5\text{CO}_2^-$	
	$\text{C}_6\text{H}_5\text{NH}_3^+$	$4.63$	$\text{C}_6\text{H}_5\text{NH}_2$	
	$\text{CH}_3\text{CO}_2\text{H}$	$4.75$	$\text{CH}_3\text{CO}_2^-$	
	$\text{H}_2\text{CO}_3$	$6.35$	$\text{HCO}_3^-$	
	$\text{CH}_3\text{COCH}_2\text{COCH}_3$	$9.0$	$\text{CH}_3\text{COHCOCH}_3$	
	$\text{NH}_4^+$	$9.2$	$\text{NH}_3$	
	$\text{C}_6\text{H}_5\text{OH}$	$9.9$	$\text{C}_6\text{H}_5\text{O}^-$	
	$\text{HCO}_3^-$	$10.2$	$\text{CO}_3^{2-}$	
	$\text{CH}_3\text{NH}_3^+$	$10.6$	$\text{CH}_3\text{NH}_2$	
	$\text{H}_2\text{O}$	$15.7$	$\text{OH}^-$	
	$\text{CH}_3\text{CH}_2\text{OH}$	$16$	$\text{CH}_3\text{CH}_2\text{O}^-$	
	$(\text{CH}_3)_3\text{COH}$	$18$	$(\text{CH}_3)_3\text{CO}^-$	
	$\text{CH}_3\text{COCH}_3$	$19.2$	$^-\text{CH}_2\text{COCH}_3$	
	$\text{HC}\equiv\text{CH}$	$25$	$\text{HC}\equiv\text{C}^-$	
	$\text{H}_2$	$35$	$\text{H}^-$	
	$\text{NH}_3$	$38$	$\text{NH}_2^-$	
	$\text{CH}_2=\text{CH}_2$	$44$	$\text{CH}_2=\text{CH}^-$	
Weakest acid	$\text{CH}_3\text{CH}_3$	$50$	$\text{CH}_3\text{CH}_2^-$	Strongest base

Increasing acid strength

Increasing base strength



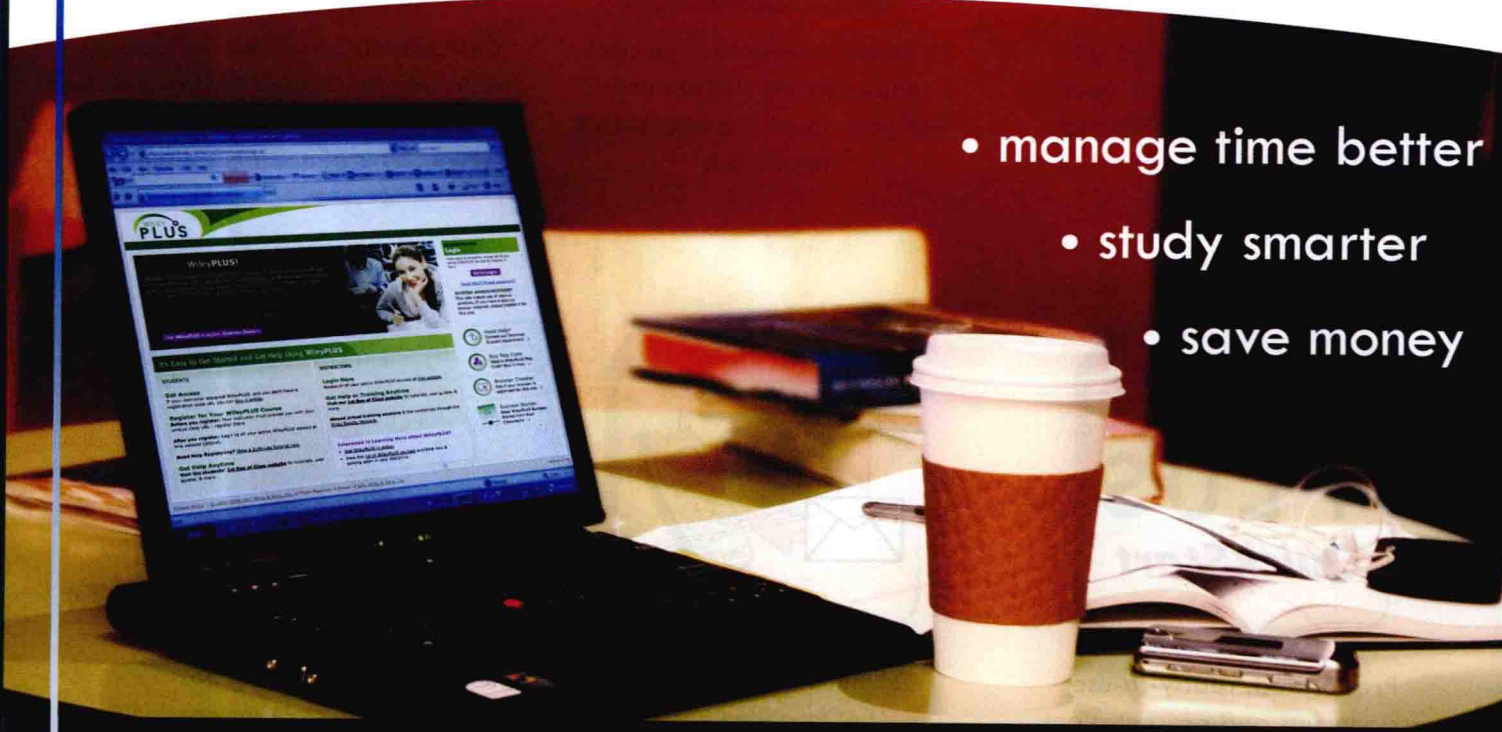
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TENTH EDITION

# Organic Chemistry

International Student Version



## "Capturing the Powerful and Exciting Subject of Organic Chemistry"

We want our students to learn organic chemistry as well and as easily as possible. We also want students to enjoy this exciting subject and to learn about the relevance of organic chemistry to their lives. At the same time, we want to help students develop the skills of critical thinking, problem solving, and analysis that are so important in today's world, no matter what career paths they choose. The richness of organic chemistry lends itself to solutions for our time, from the fields of health care, to energy, sustainability, and the environment.

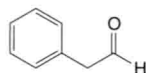
Guided by these goals, and by wanting to make our book even more **accessible to students** than it has ever been before, we have brought many changes to this edition.

## New To This Edition

- **Solved Problems.** We have greatly increased the number of Solved Problems. Now over 150 **Solved Problems** guide students in their strategies for problem solving. Solved Problems are **usually paired with a related Review Problem**.
- **Review Problems.** In-text **Review Problems**, over 10% of them new, provide students with opportunities to check their progress as they study. If they can work the review problem, they should move on. If not, they should review the preceding presentation.

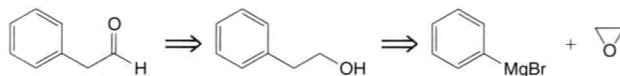
### Solved Problem 12.6

**ILLUSTRATING A MULTISTEP SYNTHESIS** Starting with bromobenzene and any other needed reagents, outline a synthesis of the following aldehyde:

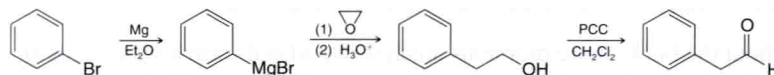


**ANSWER** Working backward, we remember that we can synthesize the aldehyde from the corresponding alcohol by oxidation with PCC (Section 12.4A). The alcohol can be made by treating phenylmagnesium bromide with oxirane. [Adding oxirane to a Grignard reagent is a very useful method for adding a  $-\text{CH}_2\text{CH}_2\text{OH}$  unit to an organic group (Section 12.7B).] Phenylmagnesium bromide can be made in the usual way, by treating bromobenzene with magnesium in an ether solvent.

#### Retrosynthetic Analysis

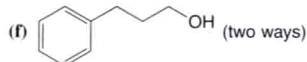
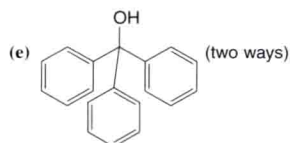
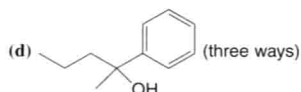
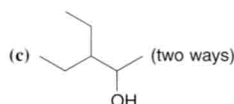
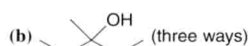
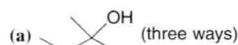


#### Synthesis



Provide retrosynthetic analyses and syntheses for each of the following alcohols, starting with appropriate alkyl or aryl halides.

#### Review Problem 12.8







- **End-of-Chapter Problems.** Over 15% of the end-of-chapter problems are new, and others have been revised.



- End-of-chapter problems have been grouped and labeled by topic. Students and instructors can more easily select problems for specific purposes.

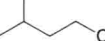

**RELATIVE RATES OF NUCLEOPHILIC SUBSTITUTION**



**6.20** Which alkyl halide would you expect to react more rapidly by an  $S_N2$  mechanism? Explain your answer.

(a)  Br or  Br


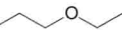

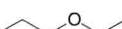
(b)  Cl or  I

(c)  Cl or  Cl

(d)  Cl or  Cl


(e)  Br or  Cl

**6.21** Which  $S_N2$  reaction of each pair would you expect to take place more rapidly in a protic solvent?

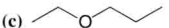
(a) (1)  Cl + EtO<sup>-</sup> →  + Cl<sup>-</sup>  
or  
(2)  Cl + EtOH →  + HCl

**SYNTHESIS**

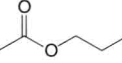
**6.23** Show how you might use a nucleophilic substitution reaction of 1-bromopropane to synthesize each of the following compounds. (You may use any other compounds that are necessary.)


(a)  OH

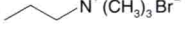
(b) 1-Iodopropane


(c)  O


(d) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-S-CH<sub>3</sub>

(e)  O

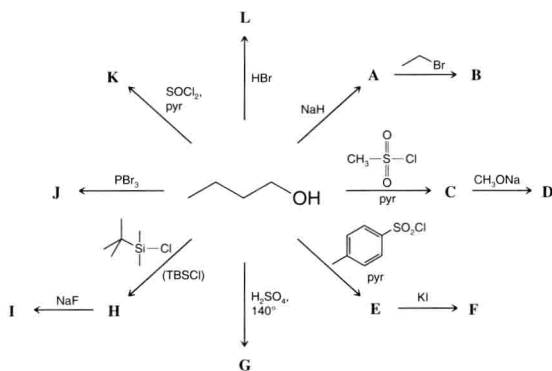
(f)  N<sub>3</sub>

(g)  N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>Br<sup>-</sup>

(h)  N

(i)  SH

- 11.34** Considering **A–L** to represent the major products formed in each of the following reactions, provide a structure for each of **A** through **L**. If more than one product can reasonably be conceived from a given reaction, include those as well.



- Throughout the book, more problems are cast in a visual format using structures, equations, and schemes. In addition, we still provide **Challenge Problems** and **Learning Group Problems** to serve additional teaching goals.
- Key ideas in every section have been rewritten and emphasized as **bullet points** to help students focus on the most essential topics.

### 3.2A Brønsted–Lowry Acids and Bases

Two classes of acid–base reactions are fundamental in organic chemistry: Brønsted–Lowry and Lewis acid–base reactions. We start our discussion with Brønsted–Lowry acid–base reactions.

- Brønsted–Lowry acid–base reactions involve the transfer of protons.
- A **Brønsted–Lowry acid** is a substance that can donate (or lose) a proton.
- A **Brønsted–Lowry base** is a substance that can accept (or remove) a proton.

- “How to” Sections give step-by-step instructions to guide students in performing important tasks, such as using curved arrows, drawing chair conformations, planning a Grignard synthesis, determining formal charges, writing Lewis structures, and using  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra to determine structure.

### 3.5 How to Use Curved Arrows in Illustrating Reactions

Up to this point we have not indicated how bonding changes occur in the reactions we have presented, but this can easily be done using curved-arrow notation.

#### Curved arrows

- show the direction of electron flow in a reaction mechanism.
- point from the source of an electron pair to the atom receiving the pair. (Curved arrows can also show the movement of single electrons. We shall discuss reactions of this type in a later chapter.)
- always show the flow of electrons from a site of higher electron density to a site of lower electron density.
- **never** show the movement of atoms. Atoms are assumed to follow the flow of the electrons.

- New and updated **chapter-opening vignettes** and **The Chemistry of . . .** boxes bring organic chemistry home to everyday life experiences. **More photos are included** to help students relate organic chemistry to the world around them.

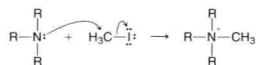


## Ionic Reactions

### Nucleophilic Substitution and Elimination Reactions of Alkyl Halides



Organic syntheses, whether they take place in the glassware of the laboratory or in the cells of living organisms, often involve fairly simple processes, such as the installation of a methyl group on the nitrogen atom of a tertiary amine. For example, we may want to install a methyl group on the nitrogen atom of a tertiary amine. This is an important counterpart in biochemistry. To do this we often employ a reaction called nucleophilic substitution.



If we wanted to describe this reaction to an organic chemist we would describe it as a nucleophilic substitution reaction, a kind of reaction we describe in detail in this chapter.

On the other hand, if we wanted to describe this reaction to a biochemist we would describe it as a methylation reaction. Biochemists have described many similar reactions this way, for example, the methylation of S-adenosylmethionine (SAM) to a tertiary amine to make choline. Choline is incorporated into the phospholipids of our cell membranes, and it is the hydrolysis product of acetylcholine, an important neurotransmitter. (Crystals of acetylcholine are shown in the polarized light microscopy image above.)

Now, the biological reaction may seem more complicated, but its essence is similar to many nucleophilic substitution reactions we shall study in this chapter. First we consider alkyl halides, one of the most important types of reactants in nucleophilic substitution reactions.



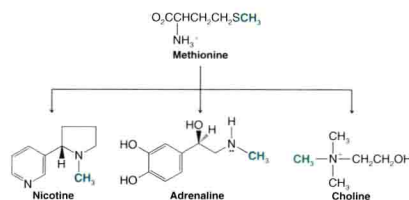
#### THE CHEMISTRY OF . . .

##### Biological Methylation: A Biological Nucleophilic Substitution Reaction

The cells of living organisms synthesize many of the compounds they need from smaller molecules. Often these biosyntheses resemble the syntheses organic chemists carry out in their laboratories. Let us examine one example now.

Many reactions taking place in the cells of plants and animals involve the transfer of a methyl group from an amino acid called methionine to some other compound. That this

transfer takes place can be demonstrated experimentally by feeding a plant or animal methionine containing an isotopically labeled carbon atom (e.g.,  $^{13}\text{C}$  or  $^{14}\text{C}$ ) in its methyl group. Later, other compounds containing the “labeled” methyl group can be isolated from the organism. Some of the compounds that get their methyl groups from methionine are the following. The isotopically labeled carbon atom is shown in green.





- **Bond-line formulas** replace almost all dash and condensed structural formulas after Chapter One where they are introduced and explained. Bond-line formulas are cleaner, simpler, and faster for students to interpret, and they are the format most often used by chemists to depict organic molecules.

**Hydroboration**

3-methylcyclopentene  $\xrightarrow{\text{BH}_3 \cdot \text{THF}}$  3-(2-methylcyclopentyl)borane + enantiomer  
 Anti-Markovnikov and syn addition  
 $\text{R} = 2\text{-methylcyclopentyl}$

**Oxidation**

3-(2-methylcyclopentyl)borane  $\xrightarrow{\text{H}_2\text{O}_2, \text{HO}^-}$  3-methylcyclopentanol  
 —OH replaces boron with retention of configuration

**A MECHANISM FOR THE REACTION**

Mechanism for the  $\text{S}_{\text{N}}1$  Reaction

**REACTION**

$$\text{CH}_3\text{C}(\text{CH}_3)_2\text{Cl} + 2 \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{C}(\text{CH}_3)_2\text{OH} + \text{H}_3\text{O}^+ + \text{Cl}^-$$

**MECHANISM**

*Step 1*

Aided by the polar solvent, a chlorine departs with the electron pair that bonded it to the carbon.

This slow step produces the 3° carbocation intermediate and a chloride ion. Although not shown here, the ions are solvated (and stabilized) by water molecules.

*Step 2*

A water molecule acting as

The product is a *tert*-

*Step 3*

accepts a proton from the *tert*-butyloxonium ion.

**Free Energy Diagrams:**

Free energy vs. Reaction coordinate

Step 1:  $\Delta G^{\ddagger}(1)$  is much larger than  $\Delta G^{\ddagger}(2)$  or  $\Delta G^{\ddagger}(3)$ , hence this is the slowest step.

Step 2:  $\Delta G^{\ddagger}(2)$

Step 3:  $\Delta G^{\ddagger}(3)$

**Summary of  $\text{S}_{\text{N}}1$  versus  $\text{S}_{\text{N}}2$  Reactions**

$\text{S}_{\text{N}}1$ : The Following Conditions Favor an  $\text{S}_{\text{N}}1$  Reaction:

1. A substrate that can form a relatively stable carbocation (such as a substrate with a leaving group at a tertiary position)
2. A relatively weak nucleophile
3. A polar, protic solvent

*Helpful Hint*

$\text{S}_{\text{N}}1$  versus  $\text{S}_{\text{N}}2$

- This edition also offers students many visually oriented tools to accommodate diverse learning styles. These include **Synthetic Connections, Concept Maps, Thematic Mechanism Review Summaries**, and the detailed **Mechanism for the Reaction Boxes** already mentioned. We also offer **Helpful Hints** and richly annotated illustrations.

- Chapters on **carbonyl chemistry** have been reorganized to emphasize mechanistic themes of nucleophilic addition, acyl substitution, and reactivity at the  $\alpha$ -carbon.
- The important modern synthetic methods of the **Grubbs, Heck, Sonogashira, Stille, and Suzuki** transition metal catalyzed carbon-carbon bond-forming reactions are presented in a practical and student-oriented way that includes review problems and mechanistic context (Special Topic G).
- Throughout the book, we have **streamlined or reduced content** to match the modern practice of organic chemistry, and we have provided new coverage of current reactions. We have made our book more accessible to students than ever before. While maintaining our commitment to an appropriate level and breadth of coverage.

## Organization - An Emphasis on the Fundamentals

So much of organic chemistry makes sense and can be generalized if students master and apply a few fundamental concepts. Therein lays the beauty of organic chemistry. If students learn the essential principles, they will see that memorization is not needed to succeed in organic chemistry.

Most important is for students to have a solid understanding of structure—of hybridization and geometry, steric hindrance, electronegativity, polarity, formal charges, and resonance — so that they can make intuitive sense of mechanisms. It is with these topics that we begin in Chapter 1. In Chapter 2 we introduce the families of functional groups – so that students have a platform on which to apply these concepts. We also introduce intermolecular forces, and infrared (IR) spectroscopy – a key tool for identifying functional groups. Throughout the book we include calculated models of molecular orbitals, electron density surfaces, and maps of electrostatic potential. These models enhance students' appreciation for the role of structure in properties and reactivity.

We begin our study of mechanisms in the context of acid-base chemistry in Chapter 3. Acid-base reactions are fundamental to organic reactions, and they lend themselves to introducing several important topics that students need early in the course: (1) curved arrow notation for illustrating mechanisms, (2) the relationship between free-energy changes and equilibrium constants, and (3) the importance of inductive and resonance effects and of solvent effects.

In Chapter 3 we present the first of many “Mechanism for the Reaction” boxes, using an example that embodies both Bronsted-Lowry and Lewis acid-base principles. All throughout the book, we use boxes like these to show the details of key reaction mechanisms. All of the Mechanism for the Reaction boxes are listed in the Table of Contents so that students can easily refer to them when desired.

A central theme of our approach is to emphasize the *relationship between structure and reactivity*. This is why we choose an organization that combines the most useful features of a functional group approach with one based on reaction mechanisms. Our philosophy is to emphasize mechanisms and fundamental principles, while giving students the anchor points of functional groups to apply their mechanistic knowledge and intuition. The structural aspects of our approach show students **what organic chemistry is**. Mechanistic aspects of our approach show students **how it works**. And wherever an opportunity arises, we show them **what it does** in living systems and the physical world around us.

In summary, our work on the 10<sup>th</sup> edition reflects the commitment we have as teachers to do the best we can to help students learn organic chemistry and to see how they can apply their knowledge to improve our world. The enduring features of our book have proven over the years to help students learn organic chemistry. The changes in our 10th edition make organic chemistry even more accessible and relevant. Students who use the in-text learning aids, work the problems, and take advantage of the resources and practice available in *WileyPLUS* (our online teaching and learning solution) will be assured of success in organic chemistry.



This online teaching and learning environment integrates the **entire digital textbook** with the most effective instructor and student resources to fit every learning style. With *WileyPLUS* ([www.wileyplus.com](http://www.wileyplus.com)):

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- Instructors personalize and manage their course more effectively with assessment, assignments, grade tracking, and more.

*WileyPLUS* can complement your current textbook or replace the printed text altogether. The problem types and resources in *WileyPLUS* are designed to enable and support problem-solving skill development and conceptual understanding. **Three unique repositories of assessment are offered which provides breadth, depth and flexibility:**

1. **End of chapter exercises**, many of which are algorithmic, feature structure drawing/assessment functionality using MarvinSketch, and provide immediate answer feedback. A subset of these end of chapter questions are linked to **Guided Online Tutorials** which are stepped-out problem-solving tutorials that walk the student

through the problem, offering individualized feedback at each step.

2. **Test Bank questions** consisting of over 3,000 questions.

3. **Prebuilt concept mastery assignments**, organized by topic and concept, featuring robust answer feedback.

2-butanol

CCC(O)C  $\xrightarrow[\text{heat}]{\text{H}_2\text{SO}_4}$  ?

Click on the drawing box above to activate the MarvinSketch drawing tool and then draw your answer to this question. If there is no reaction, then check the "no reaction" box below.

no reaction

✓ Your answer is correct!

C1=CC=C(C=C1)/C=C/C2=CC=CC=C2  $\xrightarrow[2) \text{NaHSO}_3, \text{H}_2\text{O}]{1) \text{OsO}_4}$  ?

O[C@H](c1ccccc1)[C@@H](O)c2ccccc2

Click on the drawing box above to activate the MarvinSketch drawing tool and then draw your answer to this question. If there is no reaction, then check the "no reaction" box below.

no reaction

Show Answer

### WileyPLUS For Students

Different learning styles, different levels of proficiency, different levels of preparation—each of your students is unique. *WileyPLUS* offers a myriad of rich multimedia resources for students to facilitate learning. These include:

- **Office Hour Videos:** The solved problems from the book are presented by an organic chemistry professor, using audio and a whiteboard. It emulates the experience that a student would get if she or he were to attend office hours and ask for assistance in working a problem. The goal is to illustrate good problem solving strategies.



**NUCLEOPHILES AND ELECTROPHILES**

**Skill Building Exercise**

- MO Bases of nucleophiles and electrophiles
  - Problem 1
  - Problem 2
  - Problem 3
  - Problem 4
  - Problem 5
  - Problem 6

**Nucleophiles and Electrophiles: Problem #2**

Click on all of the nucleophilic centers in the following compound, and then hit the submit button:

CC1=CCCC(S)C1

- **SkillBuilding Exercises:** Animated exercises, with instant feedback, reinforce the key skills required to succeed in organic chemistry.
- **Core Concept Animations:** Concepts are thoroughly explained using audio and whiteboard.

### WileyPLUS For Instructors

WileyPLUS empowers you with the tools and resources you need to make your teaching even more effective:

- You can customize your classroom presentation with a wealth of resources and functionality from PowerPoint slides to a database of rich visuals. You can even add your own materials to your *WileyPLUS* course.
- *WileyPLUS* allows you to help students who might fall behind, by tracking their progress and offering assistance easily, even before they come to office hours.
- *WileyPLUS* simplifies and automates such tasks as student performance assessment, creating assignments, scoring student work, keeping grades, and more.

## Supplements

### Study Guide and Solutions Manual

The Study Guide and Solutions Manual for *Organic Chemistry, Tenth Edition*, authored by Robert Johnson, of Xavier University, Craig Fryhle, Graham Solomons, with contributions from Christopher Callam, of The Ohio State University, **contains explained solutions to all of the problems in the text.** The Study Guide also contains:

- An introductory essay “Solving the Puzzle—or—Structure is Everything” that serves as a bridge from general to organic chemistry
- Summary tables of reactions by mechanistic type and functional group
- A review quiz for each chapter
- A set of hands-on molecular model exercises
- Solutions to the problems in the Special Topics sections (many of the Special Topics are only available within *WileyPLUS*)



## Organic Chemistry as a Second Language™, Volumes I & II By David Klein (Johns Hopkins University)

David Klein's series of course companions has been an enormous success with students and instructors (Organic Chemistry as a Second Language, Part I, ISBN: 978-0-470-12929-6; Organic Chemistry as a Second Language, Part II, ISBN: 978-0-471-73808-5). Presenting fundamental principles, problem-solving strategies, and skill-building exercise in relaxed, student-friendly language, these books have been cited by many students as integral to their success in organic chemistry.

### Molecular Visions™ Model Kits

We believe that the tactile experience of manipulating physical models is key to students' understanding that organic molecules have shape and occupy space. To support our pedagogy, we have arranged with the Darling Company to bundle a special ensemble of Molecular Visions™ model kits with our book (for those who choose that option). We use Helpful Hint icons and margin notes to frequently encourage students to use hand-held models to investigate the three-dimensional shape of molecules we are discussing in the book.

### Instructor Resources

All Instructor Resources are available within *WileyPLUS* or they can be accessed by contacting your local Wiley Sales Representative.

**Test Bank.** Authored by Robert Rossi, of Gloucester County College, Justin Wyatt, of the College of Charleston, and Maged Henary, of Georgia State University, the Test Bank for this edition has been completely revised and updated to include over 3,000 short answer, multiple choice, and essay/drawing questions. It is available in both a printed and computerized version.

**PowerPoint Lecture slides.** A set of PowerPoint Lecture Slides have been prepared by Professor William Tam, of the University of Guelph and his wife, Dr. Phillis Chang. This new set of PowerPoint slides includes additional examples, illustrations, and presentations that help reinforce and test students' grasp of organic chemistry concepts. An additional set of PowerPoint slides features the illustrations, figures, and tables from the text. All PowerPoint slide presentations are customizable to fit your course.

**Personal Response System (“Clicker”) Questions.** A bank of questions is available for anyone using personal response system technology in their classroom. The clicker questions are also available in a separate set of PowerPoint slides.

**Digital Image Library.** Images from the text are available online in JPEG format. Instructors may use these to customize their presentations and to provide additional visual support for quizzes and exams.