T. W. GRAHAM SOLOMONS CRAIG B. FRYHLE | ORGANIC CHEMISTRY | 10e

Periodic Table of the Elements

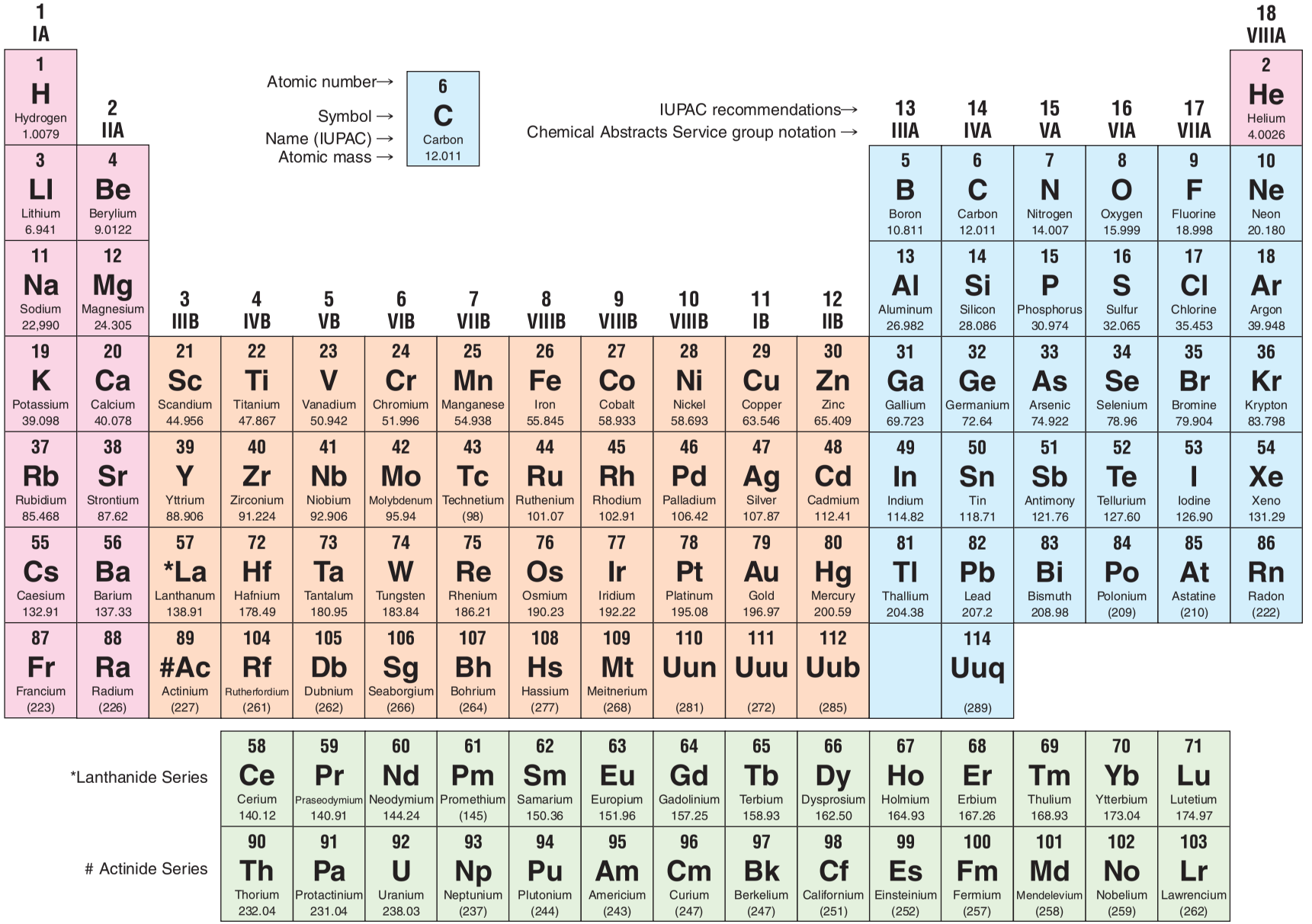


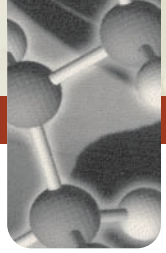
TABLE 3.1 Relative Strength of Selected Acids and Their Conjugate Bases

	Acid	Approximate pK_a	Conjugate Base	
Strongest acid	$HSbF_6$	<-12	SbF_6^-	Weakest base
	HI	-10	I^-	
	H_2SO_4	-9	HSO_4^-	
	HBr	-9	Br^-	
	HCl	-7	Cl^-	
	$C_6H_5SO_3H$	-6.5	$C_6H_5SO_3^-$	
	$(CH_3)_2\overset{+}{O}H$	-3.8	$(CH_3)_2O$	
	$(CH_3)_2C{=}\overset{+}{O}H$	-2.9	$(CH_3)_2C{=}O$	
	$CH_3\overset{+}{O}H_2$	-2.5	CH_3OH	
	H_3O^+	-1.74	H_2O	
	HNO_3	-1.4	NO_3^-	
	CF_3CO_2H	0.18	$CF_3CO_2^-$	
	HF	3.2	F^-	
	$C_6H_5CO_2H$	4.21	$C_6H_5CO_2^-$	
	$C_6H_5NH_3^+$	4.63	$C_6H_5NH_2$	
	CH_3CO_2H	4.75	$CH_3CO_2^-$	
	H_2CO_3	6.35	HCO_3^-	
	$CH_3COCH_2COCH_3$	9.0	$CH_3COHCOCH_3$	
	NH_4^+	9.2	NH_3	
	C_6H_5OH	9.9	$C_6H_5O^-$	
	HCO_3^-	10.2	CO_3^{2-}	
	$CH_3NH_3^+$	10.6	CH_3NH_2	
	H_2O	15.7	OH^-	
	CH_3CH_2OH	16	$CH_3CH_2O^-$	
	$(CH_3)_3COH$	18	$(CH_3)_3CO^-$	
	CH_3COCH_3	19.2	$^-CH_2COCH_3$	
	$HC{\equiv}CH$	25	$HC{\equiv}C^-$	
	H_2	35	H^-	
	NH_3	38	NH_2^-	
	$CH_2{=}CH_2$	44	$CH_2{=}CH^-$	
Weakest acid	CH_3CH_3	50	$CH_3CH_2^-$	Strongest base

Increasing acid strength

Increasing base strength

TENTH EDITION



Organic Chemistry

TENTH EDITION

Organic Chemistry

T.W. GRAHAM SOLOMONS

University of South Florida

CRAIG B. FRYHLE

Pacific Lutheran University

WILEY

JOHN WILEY & SONS, INC.

In memory of my beloved son, John Allen Solomons, TWGS

To Deanna, in the year of our 25th anniversary. CBF

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This book was set in 10/12 Times Roman by Preparé and printed and bound by Courier Kendallville. The cover was printed by Courier Kendallville.

This book is printed on acid-free paper.

Library of Congress Cataloging-in-Publication Data
Solomons, T. W. Graham.
Organic chemistry/T.W. Graham Solomons.—10th ed./Craig B. Fryhle.
p. cm.
Includes index.
ISBN 978-0-470-40141-5 (cloth)
Binder-ready version ISBN 978-0-470-55659-7

1. Chemistry, Organic—Textbooks. I. Fryhle, Craig B. II. Title.

QD253.2.S65 2011
547—dc22

2009032800

Printed in the United States of America
10 9 8 7 6 5 4 3 2 1

A MECHANISM FOR THE REACTION *BOXES*

THE CHEMISTRY OF . . . *BOXES*

"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.

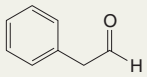
Guided by these goals, and by wanting to make our book even more **accessible to students** than it has ever been before, we have brought many changes to this edition.

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.

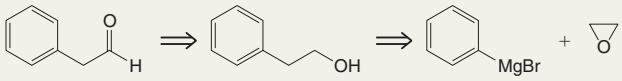
Solved Problem 12.6

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

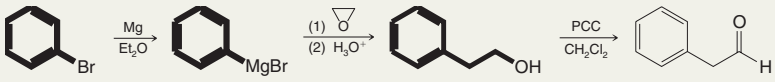


ANSWER Working backward, we remember that we can synthesize the aldehyde from the corresponding alcohol by oxidation with PCC (Section 12.4A). The alcohol can be made by treating phenylmagnesium bromide with oxirane. [Adding oxirane to a Grignard reagent is a very useful method for adding a $—CH_2CH_2OH$ 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

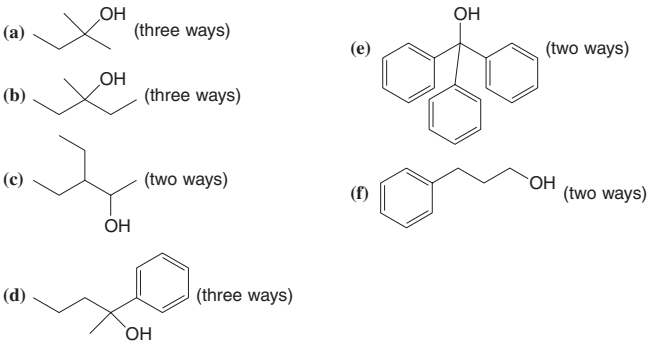


Synthesis



Review Problem 12.8

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

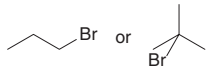


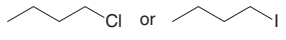
- **End-of-Chapter Problems.** Over 15% of the end-of-chapter problems are new, and others have been revised.

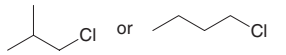
- End-of-chapter problems have been grouped and labeled by topic. Students and instructors can more easily select problems for specific purposes.

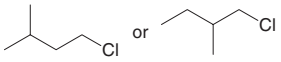
RELATIVE RATES OF NUCLEOPHILIC SUBSTITUTION

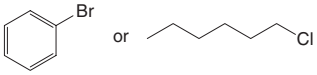
6.20 Which alkyl halide would you expect to react more rapidly by an S_N2 mechanism? Explain your answer.

(a) 

(b) 

(c) 

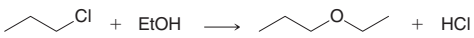
(d) 

(e) 

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

(a) (1) 

or

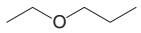
(2) 

SYNTHESIS

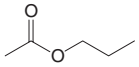
6.23 Show how you might use a nucleophilic substitution reaction of 1-bromopropane to synthesize each of the following compounds. (You may use any other compounds that are necessary.)

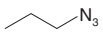
(a) 

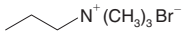
(b) 1-Iodopropane

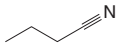
(c) 

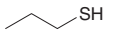
(d) $CH_3CH_2CH_2—S—CH_3$

(e) 

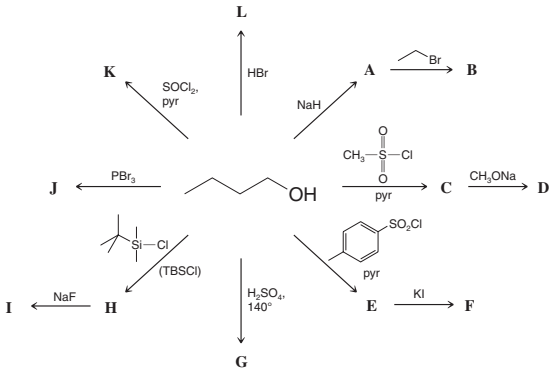
(f) 

(g) 

(h) 

(i) 

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}C and ^{1}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.

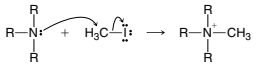
- New and updated **chapter-opening vignettes** and **The Chemistry of . . .** boxes bring organic chemistry home to everyday life experiences. **More photos are included** to help students relate organic chemistry to the world around them.

6

Ionic Reactions

Nucleophilic Substitution and Elimination Reactions of Alkyl Halides

Organic syntheses, whether they take place in the glassware of the laboratory
ism, often involve fairly simple processes, such as the installation of a methyl
example, we may want to install a methyl group on the nitrogen atom of a te
an important counterpart in biochemistry. To do this we often employ a reacti



If we wanted to describe this reaction to an organic chemist we would descri
tion 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
fer reaction. Biochemists have described many similar reactions this way, for e
transfers a methyl group from *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.

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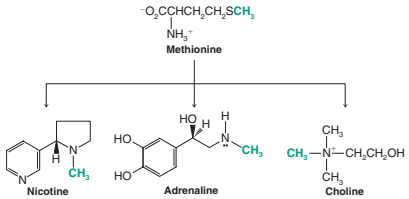
THE CHEMISTRY OF . . .

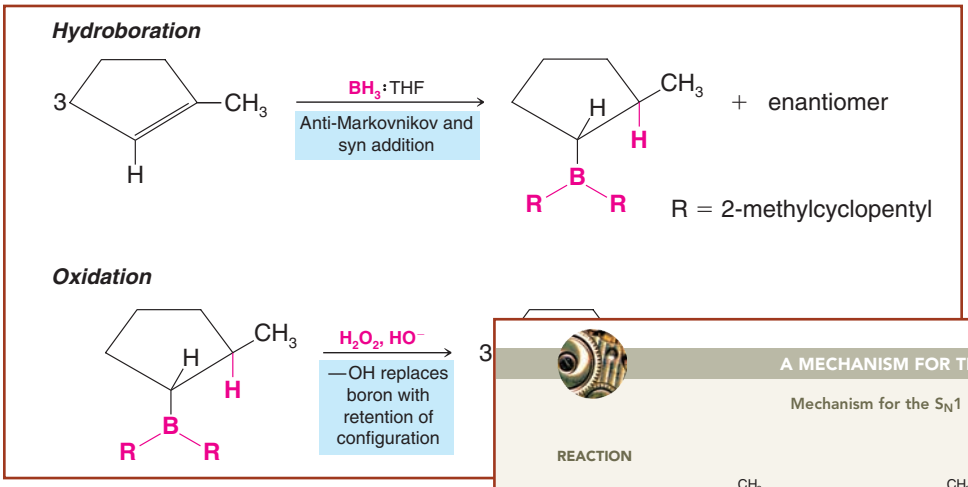
Biological Methylation: A Biological Nucleophilic Substitution Reaction

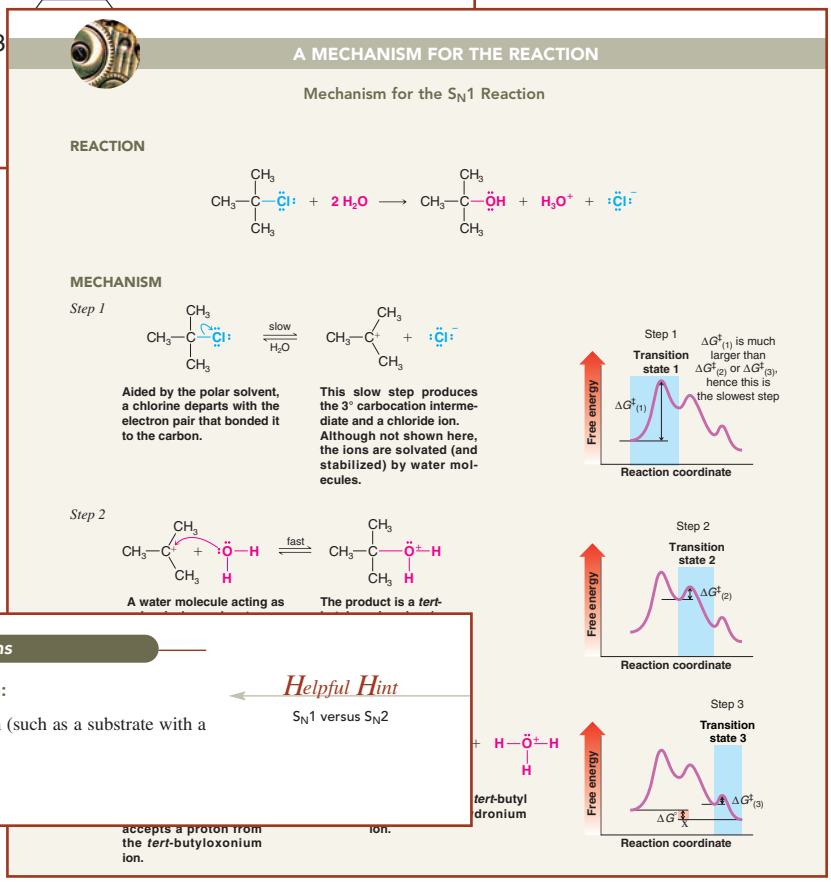
The cells of living organisms synthesize many of the compounds they need from smaller molecules. Often these biosyntheses resemble the syntheses organic chemists carry out in their laboratories. Let us examine one example now.

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}C or ^{14}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.

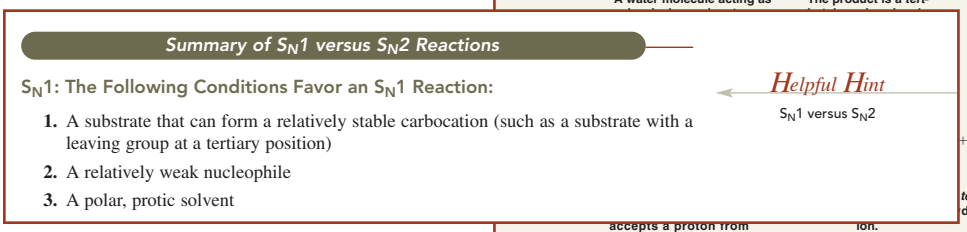


- **Bond-line formulas** replace almost all dash and condensed structural formulas after Chapter One where they are introduced and explained. Bond-line formulas are cleaner, simpler, and faster for students to interpret, and they are the format most often used by chemists to depict organic molecules.





- 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 α-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 10th 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.

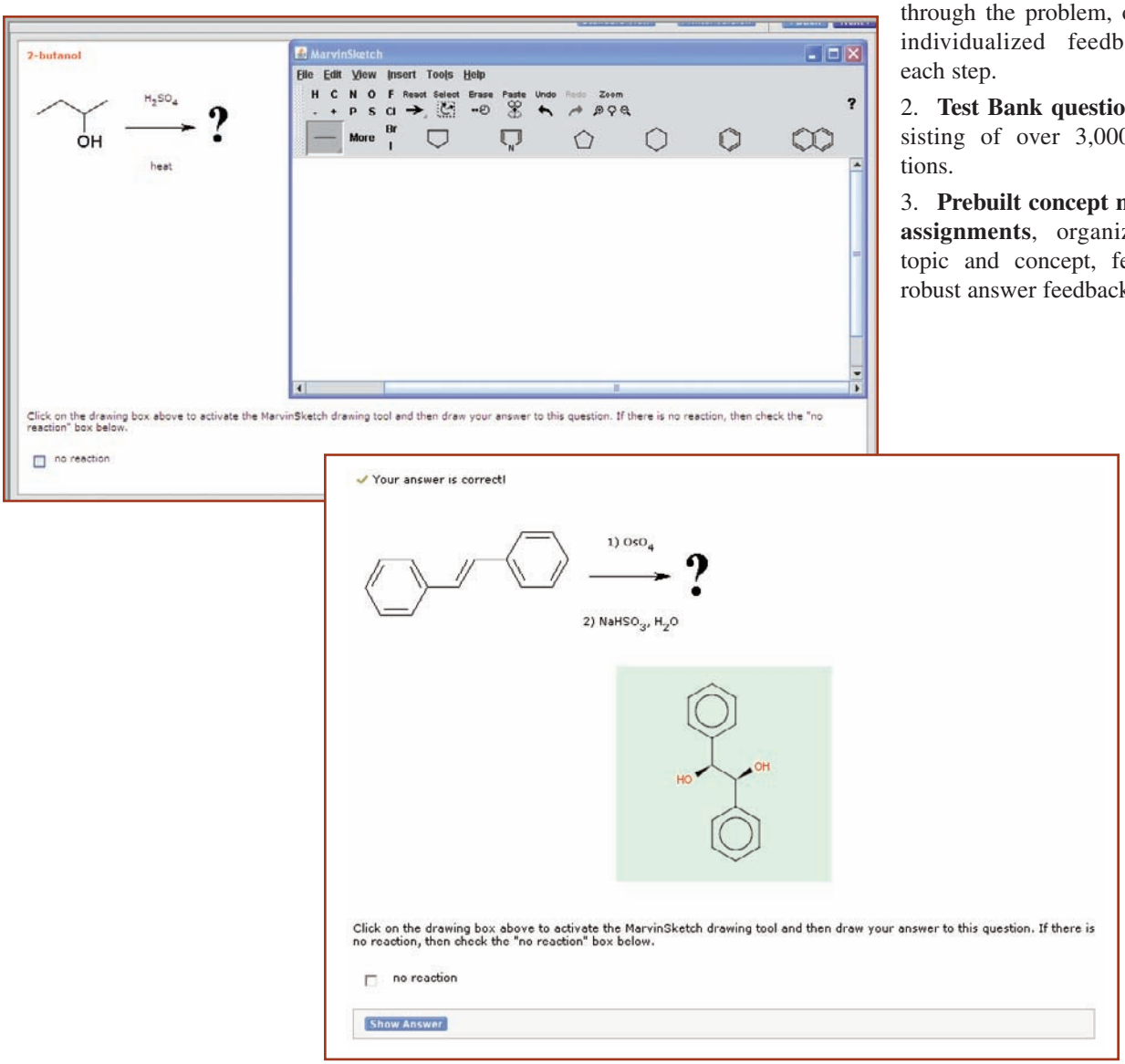
WileyPLUS for Organic Chemistry – *A Powerful Teaching and Learning Solution*

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):

- Students achieve concept mastery in a rich, structured environment that's available 24/7
- 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**:

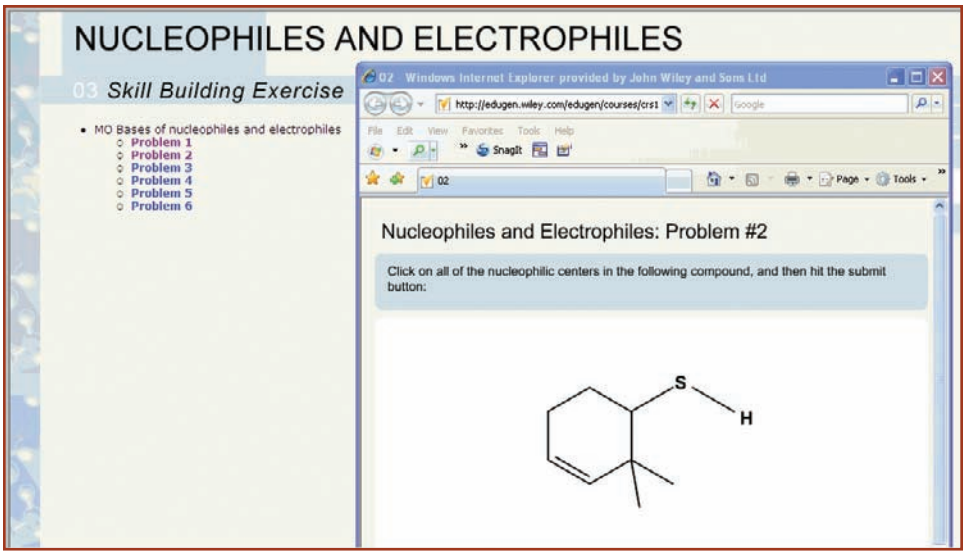
1. **End of chapter exercises**, many of which are algorithmic, feature structure drawing/assessment functionality using MarvinSketch, and provide immediate answer feedback. A subset of these end of chapter questions are linked to **Guided Online Tutorials** which are stepped-out problem-solving tutorials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



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.



- **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.
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- *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 (ISBN 978-0-470-47839-4)

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)

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Acknowledgments

We are especially grateful to the following people who provided detailed reviews that helped us prepare this new edition of Organic Chemistry.

Angela J. Allen, *University of Michigan-Dearborn*

Karen Aubrecht, *State University of New York, Stonybrook*

Jovica Badjic, *Ohio State University*

Ed Biehl, *SMU*

Kaiguo Chang, *University of Arkansas at Fort Smith*

Christopher Callam, *Ohio State University*

Arthur Cammers, *University of Kentucky*

Jeremy Cody, *Rochester Institute of Technology*

Arlene R. Courtney, *Western Oregon University*

Shadi Dalili, *University of Toronto*

D. Scott Davis, *Mercer University*

Peter deLijser, *California State University Fullerton*

Clarke W. Earley, *Kent State University*

James Ellern, *University of Southern California*

Ihsan Erden, *San Francisco State University*

Bill Fowler, *State University of New York, Stonybrook*

Andreas Franz, *University of the Pacific*

Sandro Gambarotta, *University of Ottawa*

Tiffany Gierasch, *University of Maryland-Baltimore County*

David Harpp, *McGill University*

Nina E. Heard, *University of North Carolina-Greensboro*

Frederick J. Heldrich, *College of Charleston*

James W. Hershberger, *Miami University-Oxford*

Sean Hickey, *University of New Orleans*

Ian Hunt, *University of Calgary*

Shouquan Huo, *East Carolina University*

Ekaterina N. Kadnikova, *University of Missouri*

Mohammad R. Karim, *Tennessee State University*

Adam I. Keller, *Columbus State Community College*

Jennifer Koviach-Cote, *Bates College*

Michael S. Leonard, *Washington and Jefferson College*

Jesse More, *Loyola College*

Ed O'Connell, *Fairfield University*

Cathrine Reck, *Indiana University-Bloomington*

Joel Ressner, *West Chester University*

Harold R. Rogers, *California State University-Fullerton*

Robert Stolow, *Tufts University*

Neal Tonks, *College of Charleston*

Janelle Torres y Torres, *Muscatine Community College*

Leyte L. Winfield, *Spelman College*

Justin Wyatt, *College of Charleston*

Linfeng Xie, *University of Wisconsin, Oshkosh*

Aleksey Vasiliev, *East Tennessee State University*

Kirk William Voska, *Rogers State University*

Regina Zibuck, *Wayne State University*

We are also grateful to the many people who provided reviews that guided preparation of the earlier editions of our book

Chris Abelt, *College of William and Mary*; James Ames, *University of Michigan, Flint*; Merritt B. Andrus, *Brigham Young University*; W. Lawrence Armstrong. *SUNY College at Oneonta*; Steven Bachrach. *Trinity University*; Winfield M. Baldwin, *University of Georgia*; David Ball, *California State University*, Bill J. Baker. *University of South Florida; Chico*; George Bandik, *University of Pittsburgh*; Paul A. Barks, *North Hennepin State Junior College*; Kevin Bartlett. *Seattle Pacific University*; Ronald Baumgarten, *University of Illinois at Chicago*; Harold Bell, *Virginia Polytechnic Institute and State University*; Kenneth Berlin, *Oklahoma State University*; Stuart R. Berryhill, *California State University, Long Beach*; Edward V. Blackburn, *University of Alberta*; Brian M. Bocknack, *University of Texas, Austin*; Eric Bosch, *Southwest Missouri StateUniversity*; Newell S. Bowman, *The University of Tennessee*; Bruce Branchaud, *University of Oregon*; Wayne Brouillette, *University of Alabama*; Ed Brusch, *Tufts University*; Christine Brzezowski, *University of Alberta*; Edward M. Burgess, *Georgia Institute of Technology*; Bruce S. Burnham, *Rider University*; Robert Carlson, *University of Minnesota*; Todd A. Carlson, *Grand Valley State University*; Lyle W. Castle, *Idaho State University*; Jeff Charonnat, *California State University, Northridge*; George Clemans, *Bowling Green State University*; William D. Closson, *State University of New York at Albany*; Sidney Cohen, *Buffalo State College*; Randolph Coleman, *College of William & Mary*; David Collard, *Georgia Institute of Technology*; David M. Collard, *Georgia Institute of Technology*; Brian Coppola, *University of Michigan*; Phillip Crews, *University of California, Santa Cruz*; James Damewood, *University of Delaware*; D. Scott Davis, *Mercer University*; Roman Dembinski, *Oakland University*; O. C. Dermer, *Oklahoma StateUniversity*; Phillip DeShong, *University of Maryland*; John DiCesare, *University of Tulsa*; Trudy Dickneider, *University of Scranton*; Marion T. Doig III, *College of Charleston*; Paul Dowd, *University of Pittsburgh*; Robert C. Duty, *Illinois State University*; Eric Edstrom, *Utah State University*; James Ellern, *University of Southern California*; Stuart

Fenton, *University of Minnesota*; George Fisher, *Barry University*; Gideon Fraenkel, *The Ohio State University*; Jeremiah P. Freeman, *University of Notre Dame*; Mark Forman, *Saint Joseph's University*; Peter Gaspar, *Washington University, St. Louis*; Cristina H.Geiger, *SUNY Geneseo*; M. K. Gleicher, *Oregon State University*; Brad Glorvigen, *University of St. Thomas*; Felix Goodson, *West Chester University*; Ray A. Goss Jr., *Prince George's Community College*; Roy Gratz, *Mary Washington College*; Wayne Guida, *Eckerd College*; Frank Guziec, *New Mexico State University*; Christopher M. Hadad, *Ohio State University*; Dennis Hall, *University of Alberta*; Philip L. Hall, *Virginia Polytechnic Institute and State University*; Steven A. Hardinger, *University of California at Los Angeles*; Lee Harris, *University of Arizona*; Kenneth Hartman, *Geneva College*; Bruce A. Hathaway, *Southeast Missouri State University*; David C. Hawkinson, *University of South Dakota*; Michael Hearn, *Wellesley College*; Rick Heldrich, *College of Charleston*; John Helling, *University of Florida*; William H. Hersh, *Queens College*; Paul Higgs, *Barry University*; Jerry A. Hirsch, *Seton Hall University*; Carl A. Hoeger, *University of California, San Diego*; John Hogg, *Texas A & M University*; John Holum, *Augsburg College*; John L. Isidor, *Montclair State University*; John Jewett, *University of Vermont*; A. William Johnson, *University of North Dakota*; Robert G. Johnson, *Xavier University*; Stanley N. Johnson, *Orange Coast College*; Jeffrey P. Jones, *Washington State University, Pullman*; John F. Keana, *University of Oregon*; John W. Keller, *University of Alaska, Fairbanks*; Colleen Kelley, *Pima Community College*; David H. Kenny, *Michigan Technological University*; Robert C. Kerber, *State University of New York at Stony Brook*; Karl R. Kopecky, *The University of Alberta*; Paul J. Kropp, *University of North Carolina at Chapel Hill*; Michael Kzell, *Orange Coast College*; Cynthia M. Lamberty, *Nicholls State University*; John A. Landgrebe, *University of Kansas*; Paul Langford, *David Lipscomb University*; Julie E. Larson, *Bemidji State University*; Allan K. Lazarus, *Trenton State College*; Thomas Lectka, *Johns Hopkins University*; James Leighton, *Columbia University*; Philip W. LeQuesne, *Northeastern University*; Robert Levine, *University of Pittsburgh*; Samuel G. Levine, *North Carolina State University*; James W. Long, *University of Oregon*; Eugene Losey, *Elmhurst College*; Patricia Lutz, *Wagner College*; Frederick A. Luzzio, *University of Louisville*; Javier Macossay, *The University of Texas, Pan American*; Ronald M. 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Paul, *Pittsburg State University, KS*; James W. Pavlik, *Worcester Polytechnic Institute*; Robert Pavlis, *Pittsburg State University*; John H. Penn, *West Virginia University*; Christine A. Pruis, *Arizona State University*; William A. Pryor, *Louisiana StateUniversity*; Shon Pulley, *University of Missouri, Columbia*; Eric Remy, *Virginia Polytechnic Institute*; Joel M. Ressner, *West Chester University*; Michael Richmond, *University of North Texas*; Thomas R. Riggs, *University of Michigan*; Frank Robinson, *University of Victoria, British Columbia*; Stephen Rodemeyer, *California State University, Fresno*; Alan Rosan, *Drew University*; Christine Russell, *College of DuPage*; Ralph Salvatore, *University of Massachusetts, Boston*; Vyacheslav V. Samoshin, *University of the Pacific*; Tomikazu Sasaki, *University of Washington*; Yousry Sayed, *University of North Carolina at Wilmington*; Adrian L. Schwan, *University of Guelph*; Jonathan Sessler, *University of Texas at Austin*; John Sevenair, *Xavier University of Louisiana*; Warren Sherman, *Chicago State University*; Don Slavin, *Community College of Philadelphia*; Chase Smith, *Ohio Northern University*; Doug Smith, *University of Toledo*; John Sowa, *Seton Hall University*; Jean Stanley, *Wellesley College*; Ronald Starkey, *University of Wisconsin—Green Bay*; Richard Steiner, *University of Utah*; Robert Stolow, *Tufts University*; Frank Switzer, *Xavier University*; Richard Tarkka, *George Washington University*; James G. Traynham, *Louisiana State University*; Daniel Trifan, *Fairleigh Dickinson University*; Jennifer A. Tripp, *University of Scranton*; Joseph J. Tufariello, *State University of New York, Buffalo*; Kay Turner, *Rochester Institute of Technology*; Rik R. Tykwinski, *University of Alberta*; James Van Verth, *Canisius College*; Heidi Vollmer-Snarr, *Brigham Young University*; George Wahl, *North Carolina State University*; Rueben Walter, *Tarleton State University*; Darrell Watson, *GMI Engineering and Management Institure*; Arthur Watterson, *University of Massachusetts-Lowell*; Donald Wedegaertner, *University of the Pacific*; Carolyn Kraebel Weinreb, *Saint Anselm College*; Mark Welker, *Wake Forest University*; Michael Wells, *Campbell University*; Desmond M. S. Wheeler, *University of Nebraska*; Kraig Wheeler, *Delaware State University*; James K. Whitesell, *The University of Texas at Austin*; David Wiedenfeld, *University of North Texas*; John Williams, *Temple University*; Carlton Willson, *University of Texas at Austin*; Joseph Wolinski, *Purdue University*; Anne M. Wilson, *Butler University*; Darrell J. Woodman, *University of Washington*; Stephen A. Woski, *University of Alabama*; Linfeng Xie, *University of Wisconsin, Oshkosh*; Viktor V. Zhdankin, *University of Minnesota, Duluth*; Regina Zibuck, *Wayne State University*; Herman E. Zieger, *Brooklyn College*.

Many people have helped with this edition, and we owe a great deal of thanks to each one of them. We would especially like to thank Robert G. Johnson (Professor Emeritus, Xavier University) for his meticulous assistance with the 10th edition Study Guide and Solutions Manual. Bob also had an uncanny ability to spot the minutest inconsistency or error in the main text, and his proofreading has always been valuable. We are thankful to Christopher Callam (The Ohio State University) for many new problems contributed to the 10th edition and for his assistance with the Solutions Manual. We thank Sean Hickey (University of New Orleans) and Justin Wyatt (College of Charleston) for their reviews of the manuscript and problems. We thank Neal Tonks (College of Charleston) for his review of the problems. We also thank James Ellern (University of Southern California) for helpful comments. We are grateful to Alan Shusterman (Reed College) and Warren Hehre (Wavefunction, Inc.) for assistance in prior editions regarding explanations of electrostatic potential maps and other calculated molecular models. We would also like to thank those scientists who allowed us to use or adapt figures from their research as illustrations for a number of the topics in our book.

A book of this scope could not be produced without the excellent support we have had from many people at John Wiley and Sons, Inc. Photo Editor Lisa Gee helped obtain photographs that illustrate some examples in our book. Joan Kalkut gave valuable assistance following up with and tracking down sources and attributions. Copy Editor Connie Parks helped to ensure consistency throughout the text and made many helpful suggestions at a highly detailed level. Jennifer Yee ensured coordination and cohesion among many aspects of this project. Madelyn Lesure created the captivating new design of the 10th edition, further enhanced by Carole Anson's creative work on the cover. Illustration Editor Sandra Rigby ensured that the art program met the high technical standards required for illustrations in a book of this sort. Associate Publisher Petra Recter helped steer the project from the outset and provided careful oversight and encouragement through all stages of work on this revision. Production Editor Elizabeth Swain oversaw production and printing of the 10th edition with her characteristic and amazing skill, efficiency, and attention to detail. Tom Kulesa and Marc Wezdecki supported development of WileyPlus resources for the book. Kristine Ruff enthusiastically and effectively helped tell the 'story' of our book to the many people we hope will consider using it. We are thankful to all of these people and others behind the scenes at Wiley for the skills and dedication that they provided to bring this book to fruition.

CBF would like to thank his colleagues, students, and mentors for what they have taught him over the years. Most of all, he would like to thank his wife Deanna for the support and patience she gives to make this work possible.

TWGS would like to thank his wife Judith for her support over ten editions of this book. She joins me in dedicating this edition to the memory of our beloved son, Allen.

T. W. Graham Solomons

Craig B. Fryhle

About the Authors

T. W. Graham Solomons

T. W. Graham Solomons did his undergraduate work at The Citadel and received his doctorate in organic chemistry in 1959 from Duke University where he worked with C. K. Bradsher. Following this he was a Sloan Foundation Postdoctoral Fellow at the University of Rochester where he worked with V. Boekelheide. In 1960 he became a charter member of the faculty of the University of South Florida and became Professor of Chemistry in 1973. In 1992 he was made Professor Emeritus. In 1994 he was a visiting professor with the Faculté des Sciences Pharmaceutiques et Biologiques, Université René Descartes (Paris V). He is a member of Sigma Xi, Phi Lambda Upsilon, and Sigma Pi Sigma. He has received research grants from the Research Corporation and the American Chemical Society Petroleum Research Fund. For several years he was director of an NSF-sponsored Undergraduate Research Participation Program at USF. His research interests have been in the areas of heterocyclic chemistry and unusual aromatic compounds. He has published papers in the *Journal of the American Chemical Society*, the *Journal of Organic Chemistry*, and the *Journal of Heterocyclic Chemistry*. He has received several awards for distinguished teaching. His organic chemistry textbooks have been widely used for 30 years and have been translated into French, Japanese, Chinese, Korean, Malaysian, Arabic, Portuguese, Spanish, Turkish, and Italian. He and his wife Judith have a daughter who is a building conservator and a son who is a research biochemist.

Craig Barton Fryhle

Craig Barton Fryhle is Chair and Professor of Chemistry at Pacific Lutheran University. He earned his B.A. degree from Gettysburg College and Ph.D. from Brown University. His experiences at these institutions shaped his dedication to mentoring undergraduate students in chemistry and the liberal arts, which is a passion that burns strongly for him. His research interests have been in areas relating to the shikimic acid pathway, including molecular modeling and NMR spectrometry of substrates and analogues, as well as structure and reactivity studies of shikimate pathway enzymes using isotopic labeling and mass spectrometry. He has mentored many students in undergraduate research, a number of whom have later earned their Ph.D. degrees and gone on to academic or industrial positions. He has participated in workshops on fostering undergraduate participation in research, and has been an invited participant in efforts by the National Science Foundation to enhance undergraduate research in chemistry. He has received research and instrumentation grants from the National Science Foundation, the M J. Murdock Charitable Trust, and other private foundations. His work in chemical education, in addition to textbook coauthorship, involves incorporation of student-led teaching in the classroom and technology-based strategies in organic chemistry. He has also developed experiments for undergraduate students in organic laboratory and instrumental analysis courses. He has been a volunteer with the hands-on science program in Seattle public schools, and Chair of the Puget Sound Section of the American Chemical Society. He lives in Seattle with his wife and two daughters.

Contrary to what you may have heard, organic chemisty does not have to be a difficult course. It will be a rigorous course, and it will offer a challenge. But you will learn more in it than in almost any course you will take—and what you learn will have a special relevance to life and the world around you. However, because organic chemistry can be approached in a logical and systematic way, you will find that with the right study habits, mastering organic chemistry can be a deeply satisfying experience. Here, then, are some suggestions about how to study:

1. Keep up with your work from day to day—never let yourself get behind. Organic chemistry is a course in which one idea almost always builds on another that has gone before. It is essential, therefore, that you keep up with, or better yet, be a little ahead of your instructor. Ideally, you should try to stay one day ahead of your instructor's lectures in your own class preparations. The lecture, then, will be much more helpful because you will already have some understanding of the assigned material. Your time in class will clarify and expand ideas that are already familiar ones.

2. Study material in small units, and be sure that you understand each new section before you go on to the next. Again, because of the cumulative nature of organic chemistry, your studying will be much more effective if you take each new idea as it comes and try to understand it completely before you move on to the next concept.

3. Work all of the in-chapter and assigned problems. One way to check your progress is to work each of the in-chapter problems when you come to it. These problems have been written just for this purpose and are designed to help you decide whether or not you understand the material that has just been explained. You should also carefully study the Solved Problems. If you understand a Solved Problem and can work the related in-chapter problem, then you should go on; if you cannot, then you should go back and study the preceding material again. Work all of the problems assigned by your instructor from the end of the chapter, as well. Do all of your problems in a notebook and bring this book with you when you go to see your instructor for extra help.

4. Write when you study. Write the reactions, mechanisms, structures, and so on, over and over again. Organic chemistry is best assimilated through the fingertips by writing, and not through the eyes by simply looking, or by highlighting material in the text, or by referring to flash cards. There is a good reason for this. Organic structures, mechanisms, and reactions are complex. If you simply examine them, you may think you understand them thoroughly, but that will be a misperception. The reaction mechanism may make sense to you in a certain way, but you need a deeper understanding than this. You need to know the material so thoroughly that you can explain it to someone else. This level of understanding comes to most of us (those of us without photographic memories) through writing. Only by writing the reaction mechanisms do we pay sufficient attention to their details, such as which atoms are connected to which atoms, which bonds break in a reaction and which bonds form, and the three-dimensional aspects of the structures. When we write reactions and mechanisms, connections are made in our brains that provide the long-term memory needed for success in organic chemistry. We virtually guarantee that your grade in the course will be directly proportional to the number of pages of paper that your fill with your own writing in studying during the term.

5. Learn by teaching and explaining. Study with your student peers and practice explaining concepts and mechanisms to each other. Use the *Learning Group Problems* and other exercises your instructor may assign as vehicles for teaching and learning interactively with your peers.

6. Use the answers to the problems in the *Study Guide* in the proper way. Refer to the answers only in two circumstances: (1) When you have finished a problem, use the Study Guide to check your answer. (2) When, after making a real effort to solve the problem, you find that you are completely stuck, then look at the answer for a clue and go back to work out the problem on your own. The value of a problem is in solving it. If you simply read the problem and look up the answer, you will deprive yourself of an important way to learn.

7. Use molecular models when you study. Because of the three-dimensional nature of most organic molecules, molecular models can be an invaluable aid to your understanding of them. When you need to see the three-dimensional aspect of a particular topic, use the Molecular Visions™ model set that may have been packaged with your textbook, or buy a set of models separately. An appendix to the *Study Guide* that accompanies this text provides a set of highly useful molecular model exercises.

8. Make use of the rich online teaching resources in *WileyPLUS* and do any online exercises that may be assigned by your instructor.