

Essential Organic Chemistry

THIRD EDITION

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New Feature—Organizing What We Know About Organic Chemistry lets students see how families of organic compounds react in similar ways.

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Preface

In deciding what constitutes “essential” organic chemistry, I asked myself the following question: What do students need to know if they are not planning to be synthetic organic chemists? In other words, what do they need to know for their careers in medicine, dentistry, applied health professions, nutrition, or engineering?

Based on the answers to that question, I made content and organizational choices with the following goals in mind:

- Students should understand how and why organic compounds react the way they do.
- Students should understand that the reactions they learn in the first part of the course are the same as the reactions that occur in biological systems (that is, that occur in cells).
- Students should appreciate the fun and challenge of designing simple syntheses. (This is also a good way to check if they truly understand reactivity.)
- Students should understand how organic chemistry is integral to biology, to medicine, and to their daily lives.
- In order to achieve the above goals, students need to work as many problems as possible.

To counter the impression that the study of organic chemistry consists primarily of memorizing a diverse collection of molecules and reactions, this book is organized around shared features and unifying concepts, emphasizing principles that can be applied again and again. I want students to learn how to apply what they have learned to new settings, reasoning their way to a solution rather than memorizing a multitude of facts.

A new feature, “**Organizing What We Know about the Reactions of Organic Compounds**,” lets students see where they have been and where they are going as they proceed through the course, encouraging them to keep in mind the fundamental reason behind the reactions of all organic compounds: *electrophiles react with nucleophiles*.

When students see the first reaction of an organic compound (other than an acid–base reaction), they are told that all organic compounds can be divided into families and all members of a family react in the same way. To make things even easier, each family can be put into one of four groups and all the families in a group react in similar ways.

The book then proceeds with each of the four groups (Group I: compounds with carbon–carbon double and triple bonds; Group II: benzene; Group III: compounds with an electro-negative group attached to an sp^3 carbon; and Group IV: carbonyl compounds). When the chemistry of all the members of a particular group has been covered, students see a summary of the characteristic reactions of that group (see pages 248, 332, 480) that they can compare with the summary of the characteristic reactions of the group(s) studied previously.

The **margin notes** throughout the book encapsulate key points that students should remember. (For example, “when an acid is added to a reaction, it protonates the most basic atom in the reactant”; “with bases of the same type, the weaker the base, the better it is as a leaving group”; and stable bases are weak bases”.) To simplify mechanistic understanding, common features are pointed out in margin notes (see pages 407, 415, 446, 450).

There are about 140 **application boxes** sprinkled throughout the book. These are designed to show the students the relevance of organic chemistry to medicine (dissolving sutures, mad cow disease, artificial blood, cholesterol and heart disease), to agriculture (acid rain, resisting herbicides, pesticides: natural and synthetic), to nutrition (trans fats, basal metabolic rate, lactose intolerance, omega fatty acids), and to our shared life on this planet (fossil fuels, biodegradable polymers, whales and echolocation).

Success in organic chemistry requires students to work as many problems as possible. Therefore, the book is structured to encourage problem solving. The answers (and explanations, when needed) to all the problems are in the accompanying *Study Guide and Solutions Manual*, which I authored to ensure consistency in language with the text.

New **Tutorials** following relevant chapters give students extra practice so that they can better master important topics: Acids and Bases, Drawing Curved Arrows: Pushing Electrons, and Drawing Resonance Contributors.

The problems within each chapter are primarily drill problems. They appear at the end of each section, so they allow students to test themselves on the material they have just read to see if they are ready to move on to the next section. Selected problems in each chapter are accompanied by worked-out solutions to provide insight into problem-solving techniques. Short answers are provided at the back of the book for problems marked with a diamond to give students immediate feedback concerning their mastery of a skill or concept.

The many **Problem-Solving Strategies** in the book teach students how to approach various kinds of problems. Each Problem-Solving Strategy is followed by an exercise to give the student an opportunity to use the strategy just learned.

The **end-of-chapter problems** vary in difficulty. They begin with drill problems that integrate material from the entire chapter, requiring students to think in terms of all the material in the chapter rather than focusing on individual sections. The problems become more challenging as the student proceeds. The net result for the student is a progressive building of both problem-solving ability and confidence. (I have chosen not to label problems as particularly challenging so as not to intimidate the students before they try to solve the problem.)

Many of the end-of-chapter problems can also be found in MasteringChemistry. Students can master concepts through traditional homework assignments in Mastering that provide hints and answer-specific feedback. Students learn chemistry by practicing chemistry.

Additionally, tutorials in MasteringChemistry, featuring specific wrong-answer feedback, hints, and a wide variety of educationally effective content, guide your students through the course. The hallmark Hints and Feedback offer scaffolded instruction similar to what students would experience in an office hour, allowing them to learn from their mistakes without being given the answer. Organic Chemistry Tutorials in MasteringChemistry pinpoint errors by assessing the logic and accuracy of the student's answers. Individual evaluators written and linked to each problem by organic chemists look at the validity of the student's entry and generate error-specific feedback based on information received from a JChem database.

The book contains **two new chapters**: "Radicals" and "Synthetic Polymers." There is no longer a chapter on the "Organic Chemistry of Drugs." Much of the material that was in that chapter is now in application boxes, so students have the opportunity to learn about that material who may have not had that opportunity if that last chapter were not covered in their course.

Similarly, some of the information on the chemistry of living systems has been integrated into earlier chapters. As examples, noncovalent interactions in biological systems has been added to Chapter 3, the discussion of catalysis in Chapter 5 now includes a discussion of enzymatic catalysis, and acetal formation by glucose has been added to Chapter 12.

The six chapters (Chapters 16–21) that focus primarily on the organic chemistry of living systems have been rewritten to emphasize the connection between the organic reactions that occur in the laboratory and those that occur in cells. Each organic reaction that occurs in a cell is explicitly compared to the organic reaction with which the student is already familiar. Chapter 18 can be found on the Instructor Resource Center.

The chapter on spectroscopy is modular, so it can be covered at any time during the course—at the very beginning, at the very end, somewhere in between, or not covered at all. When I wrote that chapter, I did not want students to be overwhelmed by a topic they may never revisit in their lives, but I did want them to enjoy being able to interpret relatively simple spectra. In addition to the spectroscopy problems in the text, there are over forty new spectroscopy problems in the *Study Guide and Solutions Manual* with worked-out answers. The answers come after the problems, so students have the opportunity to try to solve them on their own first.

New **modern design**, **streamlined narrative**, and **bulleted summaries** at the end of each chapter allow students to navigate through the content and study more efficiently with the next.

ACKNOWLEDGMENTS

It gives me great pleasure to acknowledge the dedicated efforts of Jordan Fantini and Malcolm Forbes, who checked every inch of the book for accuracy; David Yerzley, M.D., for his assistance with the section on MRI; Warren Hehre of Wavefunction, Inc., and Alan Shusterman of Reed College for their advice on the electrostatic potential maps that appear in the book; and Jeremy Davis, who created the art that appears on page 119. I am also very grateful to my students, who pointed out sections that needed clarification, worked the problems and suggested new ones, and searched for errors.

The following reviewers have played an enormously important role in the development of this book.

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Malcolm Forbes, *University of North Carolina*

I am deeply grateful to my editor, Jeanne Zalesky, whose talents guided this book and caused it to be as good as it could be, and to Coleen Morrison, whose gentle prodding and attention to detail made the book actually happen. I also want to thank the other talented and dedicated people at Pearson whose contributions made this book a reality. And thank you to Lauren Layn, the creative brains behind the technology that accompanies the book.

I particularly want to thank the many wonderful and talented students I have had over the years, who taught me how to be a teacher. And I want to thank my children, from whom I may have learned the most.

To make this textbook as user friendly as possible, I would appreciate any comments that will help me achieve this goal in future editions. If you find sections that could be clarified or expanded, or examples that could be added, please let me know. Finally, this edition has been painstakingly combed for typographical errors. Any that remain are my responsibility; if you find any, please send me a quick e-mail so that they can be corrected in future printings of this edition.

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About the Author



Paula Bruice with Zeus, Bacchus, and Abigail

Paula Yurkanis Bruice was raised primarily in Massachusetts. After graduating from the Girls' Latin School in Boston, she earned an A.B. from Mount Holyoke College and a Ph.D. in chemistry from the University of Virginia. She then received an NIH postdoctoral fellowship for study in the Department of Biochemistry at the University of Virginia Medical School and held a postdoctoral appointment in the Department of Pharmacology at the Yale School of Medicine.

Paula has been a member of the faculty at the University of California, Santa Barbara since 1972, where she has received the Associated Students Teacher of the Year Award, the Academic Senate Distinguished Teaching Award, two Mortar Board Professor of the Year Awards, and the UCSB Alumni Association Teaching Award. Her research interests center on the mechanism and catalysis of organic reactions, particularly those of biological significance. Paula has a daughter and a son who are physicians and a son who is a lawyer. Her main hobbies are reading suspense novels, any biographies, and enjoying her pets (three dogs, two cats, and two parrots).



Essential Skills for Organic Chemistry

New features and major revisions to this third edition focus on developing students' problem solving and analytical reasoning skills. Organized around mechanistic similarities, Bruice encourages students to be mindful of the fundamental reasoning behind the reactions of all organic compounds: electrophiles react with nucleophiles.

New Tutorials Skill Builders following select chapters deepen student understanding of key topics while developing their problem solving skills. Tutorials include acid-base chemistry, building molecular models, and drawing curved arrows and are paired with assignable MasteringChemistry® tutorials with wrong answer-specific feedback and coaching.

ACIDS AND BASES

This tutorial is designed to give you practice solving problems based on some of the concepts you learned in Chapter 2. Most of the concepts are given here without explanation because full explanations can be found in Chapter 2.

An Acid and Its Conjugate Base

An acid is a species that can lose a proton (the Brønsted–Lowry definition). When an acid loses a proton (H^+), it forms its conjugate base. When the proton comes off the acid, the conjugate base retains the electron pair that attached the proton to the acid.



Often, the lone pairs and bonding electrons are not shown.



Notice that a neutral acid forms a negatively charged conjugate base, whereas a positively charged acid forms a neutral conjugate base. (In each case, the charge *decreases* by one because the acid *loses* H^+ .)

PROBLEM 1 Draw the conjugate base of each of the following acids:

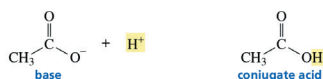
- a. CH_3OH b. CH_3NH_3^+ c. CH_3NH_2 d. H_3O^+ e. H_2O

A Base and Its Conjugate Acid

A base is a species that can gain a proton (the Brønsted–Lowry definition). When a base gains a proton (H^+), it forms its conjugate acid. In order to gain a proton, a base must have a lone pair that it can use to form a new bond with the proton.



Often, the lone pairs and bonding electrons are not shown.



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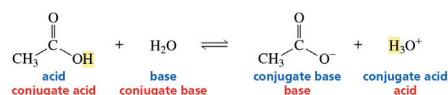
Notice that a negatively charged base forms a neutral conjugate acid, whereas a neutral base forms a positively charged conjugate acid. (In each case, the charge *increases* by one because the compound *gains* H^+ .)

PROBLEM 2 Draw the conjugate acid of each of the following bases:

- a. H_2O b. HO^- c. CH_3OH d. NH_3 e. Cl^-

Acid–Base Reactions

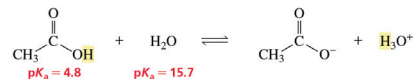
An acid cannot lose a proton unless a base is present to accept the proton. Therefore, an acid always reacts with a base. The reaction of an acid with a base is called an acid–base reaction or a proton transfer reaction. Acid–base reactions are reversible reactions.



Notice that an acid reacts with a base in the forward direction (blue labels) and an acid reacts with a base in the reverse direction (red labels).

The Products of an Acid–Base Reaction

Both CH_3COOH and H_2O in the preceding reaction have protons that can be lost (that is, both can act as acids), and both have lone pairs that can form a bond with a proton (that is, both can act as bases). How do we know which reactant will lose a proton and which will gain a proton? We can determine this by comparing the pK_a values of the two reactants; these values are 4.8 for CH_3COOH and 15.7 for H_2O . The stronger acid (the one with the lower pK_a value) will be the one that acts as an acid (it will lose a proton). The other reactant will act as a base (it will gain a proton).

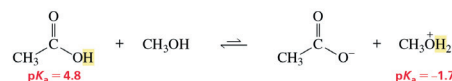


PROBLEM 3 Draw the products of the following acid–base reactions:

- a. $\text{CH}_3\text{NH}_3^+ + \text{H}_2\text{O}$ c. $\text{CH}_3\text{NH}_3^+ + \text{HO}^-$
b. $\text{HBr} + \text{CH}_3\text{OH}$ d. $\text{CH}_3\text{NH}_2 + \text{CH}_3\text{OH}$

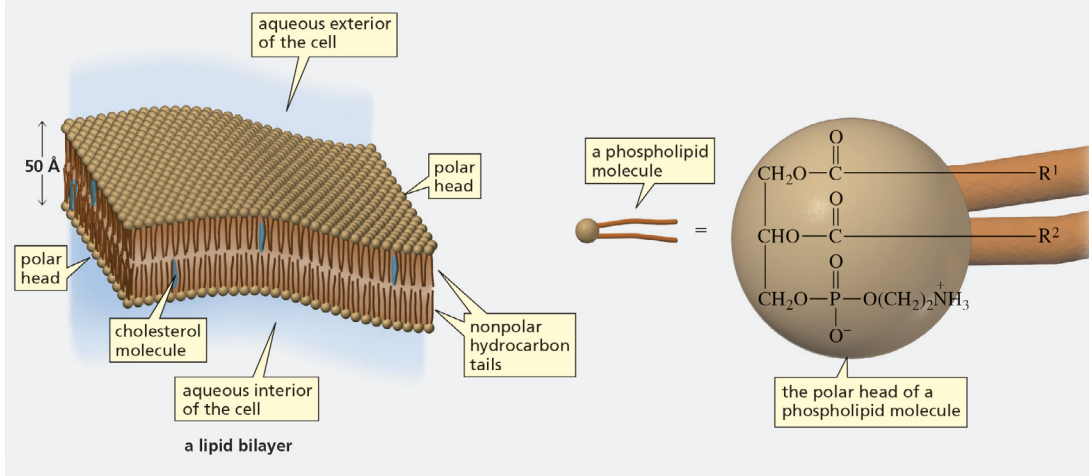
The Position of Equilibrium

Whether an acid–base reaction favors formation of the products or formation of the reactants can be determined by comparing the pK_a value of the acid that loses a proton in the forward direction with the pK_a value of the acid that loses a proton in the reverse direction. The equilibrium will favor the reaction of the stronger acid to form the weaker acid. The following reaction favors formation of the reactants, because CH_3OH_2^+ is a stronger acid than CH_3COOH .



Cell Membranes

Cell membranes demonstrate how nonpolar molecules are attracted to other nonpolar molecules, whereas polar molecules are attracted to other polar molecules. All cells are enclosed by a membrane that prevents the aqueous (polar) contents of the cell from pouring out into the aqueous fluid that surrounds the cell. The membrane consists of two layers of phospholipid molecules—called a lipid bilayer. A phospholipid molecule has a polar head and two long nonpolar hydrocarbon tails. The phospholipids are arranged so that the nonpolar tails meet in the center of the membrane. The polar heads are on both the outside surface and the inside surface, where they face the polar solutions on the outside and inside of the cell. Nonpolar cholesterol molecules are found between the tails in order to keep the nonpolar tails from moving around too much. The structure of cholesterol is shown and discussed in Section 3.14.



New Applications Boxes Throughout!

Numerous new interest boxes throughout each chapter connect chemistry to students' lives and often provide any needed additional explanation on the organic chemistry occurring. New applications include: *Using Genetic Engineering to Treat Ebola, Diseases Caused by a Misfolded Protein, The Inability to Perform an S_N2 Reaction Causes a Severe Clinical Disorder*, and *Electron Delocalization Affects the Three-Dimensional Shape of Proteins*.

10. Elimination Reactions of Alkyl Ha... Substitution and Elimination Reactions

Item Type: Tutorial | Difficulty: 3 | Time: 16m | Learning Outcomes | Contact the Publisher

Part B

2-Bromobutane is treated with sodium methoxide in methanol at 323 K. Draw the major product of the reaction. Make sure to consider the stereochemistry of the reaction.

$$\begin{array}{c} \text{H} \\ | \\ \text{CH}_3-\text{C}-\text{CH}_2\text{CH}_3 \\ | \\ \text{Br} \end{array} + \text{CH}_3\text{O}^-\text{Na}^+ \xrightarrow[323 \text{ K}]{\text{CH}_3\text{OH}}$$

Draw the molecule on the canvas by choosing buttons from the Tools (for bonds), Atoms, and Advanced Template toolbars. The single bond is active by default.

Hint 1. How to approach the problem

First, identify the substrate (alkyl halide) undergoing the reaction as primary (1°), secondary (2°), or tertiary (3°). Then, identify the nature of the reagent (attacking species) in the reaction. Correlate this with the conditions of substitution or elimination.

Note that for an elimination reaction, both the β -hydrogen atom and the leaving group need to be coplanar and anti to each other. The negatively charged base and the leaving group will be farthest from each other, whereas the leaving group and the abstracted β -hydrogen atom are anti to each other.

Hint 2. Identify the substrate (alkyl halide) as primary, secondary, or tertiary (click to open)

Hint 3. Identify the nature of the reagent (click to open)

Hint 4.

This hint will be shown after you complete previous hint(s).

Student Tutorials

MasteringChemistry® provides instant feedback specific to the structure or mechanism each student has drawn. Rather than simply providing feedback of the “right/wrong/try again” variety, Mastering recognizes the individual student error by applying evaluators to each problem that analyze chemical accuracy, employing data gathered from all student entries in Mastering, and providing wrong answer-specific feedback that helps students overcome misconceptions. An updated, mobile compatible drawing tool (java-free), provides wrong-answer feedback and guidance on every mechanism problem.



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Before Class

Reading Quizzes

Mobile-friendly Reading Quizzes give instructors the opportunity to assign reading and test students on their comprehension of chapter content. Wrong answer-specific feedback directs students to the explanation within the eBook while hints support student problem-solving skills.

4. Isomers: The Arrangement of Atoms ... Chapter 4 Reading Question 6

Item Type: Reading Questions | Difficulty: 2 | Time: 2m | [Learning Outcomes](#) | [Contact the Publisher](#) | Manage this Item: Standard View

Part A
Which of the following has/have the R configuration?

I: CC[C@H](Cl)C

II: CC[C@@H](Br)C

III: CC[C@@H](O)C(=O)O

only I
 I, II, and III
 only II
 I and II
 I and III

Submit Hints My Answers Give Up Review Part

Incorrect; Try Again
II is indeed R, but it isn't the only one. See Section 4.6. ([page 154](#))

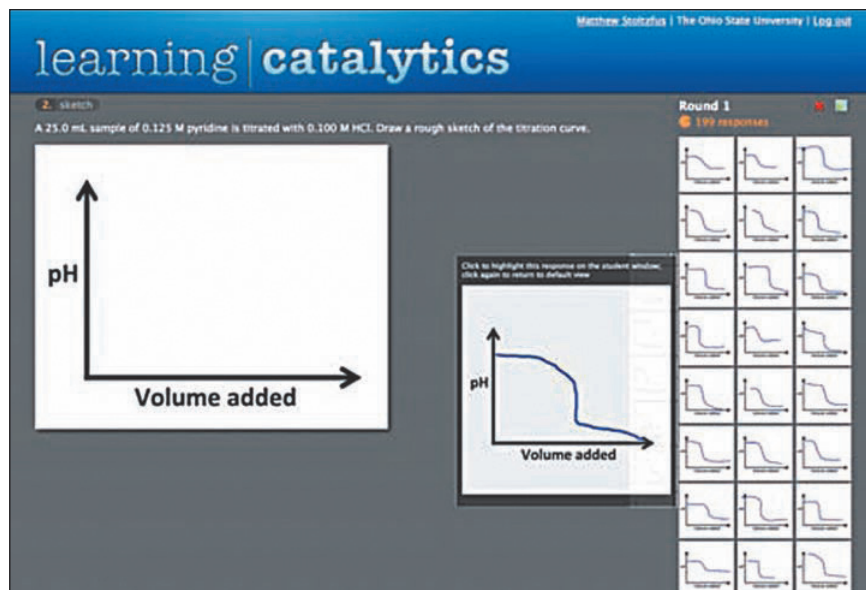
« Previous Item | Item 5 of 9 | Next Item »

During Class

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After Class

Students learn chemistry by practicing chemistry.

Tutorials, featuring wrong answer-specific feedback, hints, and a wide variety of educationally effective content, guide your students through the toughest topics in chemistry. The hallmark Hints and Feedback offer instruction similar to what students would experience in an office hour, allowing them to learn from their mistakes without being given the answer.

Digital and Print Resources

Essential Organic Chemistry provides an integrated teaching and learning package of support material for both students and professors.

Name of Supplement	Available in Print	Available Online	Instructor or Student Resource	Description
Study Guide and Solutions Manual ISBN: 0133867250	✓		Student	This manual for students, written by Paula Bruice, contains complete and detailed explanations of the solutions to the problems in the text, and definitions of all key terms used in each chapter. In addition, you will find more than 40 new spectroscopy problems, a special topics section on pH, pK_a , and buffers, and 21 practice tests.
MasteringChemistry® www.masteringchemistry.com ISBN: 0133867218		✓	Students & Instructors	MasteringChemistry® from Pearson is the leading online teaching and learning system designed to improve results by engaging students before, during, and after class with powerful content.
Pearson eText ISBN: 0133866890 within Mastering Chemistry® ISBN: 0133858499		✓	Student	<i>Essential Organic Chemistry</i> features a Pearson eText within MasteringChemistry®. The Pearson eText offers students the power to create notes, highlight text in different colors, create bookmarks, zoom, and view single or multiple pages.
TestGen Test Bank ISBN: 0133867234		✓	Instructor	Prepared by Ethan Tsai, this resource includes more than 1200 questions in multiple-choice, matching, true/false, and short answer format. Available for download on the Pearson catalog page for <i>Essential Organic Chemistry</i> at www.pearsonhighered.com
Instructor Resource Materials ISBN: 0133867242		✓	Instructor	Includes all the art, photos, and tables from the book in JPEG format for use in classroom projection or when creating study materials and tests. Available for download on the Pearson catalog page for <i>Essential Organic Chemistry</i> at www.pearsonhighered.com