

Essential Organic Chemistry

THIRD EDITION

Paula Yurkanis Bruice

ALWAYS LEARNING

PEARSON

TO THE STUDENT

Welcome to the fascinating world of organic chemistry. You are about to embark on an exciting journey. This book has been written with students like you in mind—those who are encountering the subject for the first time. The book's central goal is to make this journey through organic chemistry both stimulating and enjoyable by helping you understand central principles and asking you to apply them as you progress through the pages. You will be reminded about these principles at frequent intervals in references back to sections you have already mastered.

You should start by familiarizing yourself with the book. Inside the front and back covers is information you may want to refer to often during the course. The list of Some Important Things to Remember and the Reaction Summary at each chapter's end provide helpful checklists of the concepts you should understand after studying the chapter. The Glossary at the end of the book can also be a useful study aid. The molecular models and electrostatic potential maps that you will find throughout the book are provided to give you an appreciation of what molecules look like in three dimensions and to show how charge is distributed within a molecule. Think of the margin notes as the author's opportunity to inject personal reminders of ideas and facts that are important to remember. Be sure to read them.

Work all the problems *within* each chapter. These are drill problems that you will find at the end of each section that allow you to check whether you have mastered the skills and concepts the particular section is teaching before you go on to the next section. Some of these problems are solved for you in the text. Short answers to some of the others—those marked with a diamond—are provided at the end of the book. Do not overlook the "Problem-Solving Strategies" that are also sprinkled throughout the text; they provide practical suggestions on the best way to approach important types of problems.

In addition to the *within-chapter* problems, work as many *end-of-chapter* problems as you can. The more problems you work, the more comfortable you will be with the subject matter and the better prepared you will be for the material in subsequent chapters. Do not let any problem frustrate you. If you cannot figure out the answer in a reasonable amount of time, turn to the *Study Guide and Solutions Manual* to learn how you should have approached the problem. Later on, go back and try to work the problem on your own again. Be sure to visit www.MasteringChemistry.com, where you can explore study tools, including Exercise Sets, an Interactive Molecular Gallery, and Biographical Sketches of historically important chemists, and where you can access content on many important topics.

The most important advice to remember (and follow) in studying organic chemistry is DO NOT FALL BEHIND! The individual steps to learning organic chemistry are quite simple; each by itself is relatively easy to master. But they are numerous, and the subject can quickly become overwhelming if you do not keep up.

Before many of the theories and mechanisms were figured out, organic chemistry was a discipline that could be mastered only through memorization. Fortunately, that is no longer true. You will find many unifying ideas that allow you to use what you have learned in one situation to predict what will happen in other situations. So, as you read the book and study your notes, always make sure that you understand *why* each chemical event or behavior happens. For example, when the reasons behind reactivity are understood, most reactions can be predicted. Approaching the course with the misconception that to succeed you must memorize hundreds of unrelated reactions could be your downfall. There is simply too much material to memorize. Understanding and reasoning, not memorization, provide the necessary foundation on which to lay subsequent learning. Nevertheless, from time to time some memorization will be required: some fundamental rules will have to be memorized, and you will need to learn the common names of a number of organic compounds. But that should not be a problem; after all, your friends have common names that you have been able to learn and remember.

Students who study organic chemistry to gain entrance into professional schools sometimes wonder why these schools pay so much attention to this topic. The importance of organic chemistry is not in the subject matter alone. Mastering organic chemistry requires a thorough understanding of certain fundamental principles and the ability to use those fundamentals to analyze, classify, and predict. Many professions make similar demands.

Good luck in your study. I hope you will enjoy studying organic chemistry and learn to appreciate the logic of this fascinating discipline. If you have any comments about the book or any suggestions for improving it, I would love to hear from you. Remember, positive comments are the most fun, but negative comments are the most useful.

> Paula Yurkanis Bruice pybruice@chem.ucsb.edu

Common Functional Groups



Approximate pK_a Values





Common Symbols and Abbreviations

| | 1 | | | 1 | |
|-----------------------|-----------------------------------|-------------------|-----------------------------|-----------------|---|
| [α] | specific rotation | $E_{\rm a}$ | energy of activation | pH | measure of the acidity of |
| α | observed rotation | Et | ethyl | | a solution $(= -\log [H^+])$ |
| Ad | adenosyl | Et ₂ O | diethyl ether | pI | isoelectric point |
| ATP | adenosine triphosphate | FAD | flavin adenine dinucleotide | pK _a | measure of the strength |
| B_0 | applied magnetic field | H_2CrO_4 | chromic acid | | of an acid $(= -\log K_a)$ |
| Bu | butyl | HOCI | hypochlorous acid | PLP | pyridoxal phosphate |
| D | Debye: a measure of dipole | IR | infrared | ppm | parts per million |
| D | moment | k | rate constant | | (of the applied field) |
| δ | partial or chemical shift | $K_{\rm a}$ | acid dissociation constant | R | alkyl group; group derived |
| Δ | heat | $K_{\rm eq}$ | equilibrium constant | | from a hydrocarbon |
| ΔG^{\ddagger} | free energy of activation | $LiAlH_4$ | lithium aluminum hydride | R,S | configuration about an |
| ΔG° | Gibbs standard free energy change | MS | mass spectroscopy | | asymmetric center |
| ΔH° | change in enthalpy | μ | dipole moment | THF | tetrahydrofuran or tetrahydrofolate |
| ٨So | change in entrony | $NaBH_4$ | sodium borohydride | TMS | tetramethylsilane, (CH ₃) ₄ Si |
| | | NAD^+ | nicotinamide adenine | TPP | thiamine pyrophosphate |
| DMF | dimethylformamide | | dinucleotide | UV/Vis | ultraviolet/visible |
| DMSO | dimethyl sulfoxide | NaOCl | sodium hypochlorite | X | halogen atom |
| Ε | entgegen (opposite sides in | nm | nanometers | Z | zusammen (same side in |
| | E,Z nomenclature) | NMR | nuclear magnetic resonance | | <i>E</i> , <i>Z</i> nomenclature) |
| | | | | | |

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Essential Organic Chemistry

THIRD EDITION GLOBAL EDITION

Paula Yurkanis Bruice

UNIVERSITY OF CALIFORNIA SANTA BARBARA



Editor-in-Chief: Jeanne Zalesky Marketing Manager: Will Moore Program Managers: Coleen Morrison / Sarah Shefveland Team Lead, Project Management Biology, Chemistry, Environmental Science, and Geo Science: David Zielonka Project Manager: Beth Sweeten Publishing Administrator and Business Analyst, Global Edition: Shokhi Shah Khandelwal Assistant Acquisitions Editor, Global Edition: Murchana Borthakur

Pearson Education Limited Edinburgh Gate Harlow Essex CM20 2JE England

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Authorized adaptation from the United States edition, entitled Essential Organic Chemistry, 3rd edition, ISBN 978-0-321-93771-1, by Paula Yurkanis Bruice, published by Pearson Education © 2016.

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ISBN 10: 1-292-08903-2 ISBN 13: 978-1-292-08903-4

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

10 9 8 7 6 5 4 3 2 1 14 13 12 11 10

Typeset in Times LT Std 10.5/12 by Lumina Datamatics, Inc.

Printed and bound in Malaysia.

Assitant Project Editor, Global Edition: *Sinjita Basu* Senior Manufacturing Controller, Production, Global Edition: *Trudy Kimber* Operations Specialist: *Maura Zaldivar-Garcia* Text Permissions Manager: *William Opaluch* Compositor: *Lumina Datamatics, Inc.* Cover Designer: *Lumina Datamatics, Inc.* Cover Photo Source: *Shutterstock* Cover Printer: *Printpack*

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New chapter on Acid/ **Base Chemistry reinforces** fundamental concepts and foundational skills needed for future topics in organic chemistry.

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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 electronegative 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 276, 360, 508) 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 435, 443, 474, 478).

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 147. 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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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.

> Paula Yurkanis Bruice University of California, Santa Barbara pybruice@chem.ucsb.edu

Pearson wishes to thank and acknowledge the following reviewers for their work on the Global Edition:

Dharam Vir Singh Jain, Department of Chemistry, Punjab University Rajarshi Banerjee, PhD Scholar, Delhi

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.

H*

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.** CH₃OH **b.** CH₃ŇH₃ **c.** CH₃NH₂ **d.** H₃O^{*} **e.** H₂O

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.



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.

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^+ .)

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

a. H<sub>2</sub>O b. HO<sup>-</sup> c. CH<sub>3</sub>OH d. NH<sub>3</sub> c. Cl<sup>-</sup>
```

Acid–Base Reactions

TUTORIAL

MasteringChemistry*

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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 CH₃COOH and H₂O 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 CH₃COOH and 15.7 for H₂O. 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 acts as base (it will gain a proton).

$$\begin{array}{c} 0 \\ CH_{3}^{-}C \\ \rho K_{a} = 4.8 \end{array} + H_{2}O \rightleftharpoons CH_{3}^{-}C \\ CH_{3}^{-}C \\ O^{-} \end{array} + H_{3}O^{+}$$

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

 a. $CH_3\dot{N}H_3$ + H_2O **c.** $CH_3\dot{N}H_3$ + HO^-
b. HBr + CH_3OH **d.** CH_3NH_2 + CH_3OH

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 CH₃OH₂ is a stronger acid than CH₄COOH.



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 $S_N 2$ Reaction Causes a Severe Clinical Disorder, and Electron Delocalization Affects the Three-Dimensional Shape of Proteins.



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

| Name of Supplement | Available Online | Instructor or Student Resource | Description |
|---|---------------------|-----------------------------------|--|
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Remembering General Chemistry: Electronic Structure and Bonding



To stay alive, early humans must have been able to distinguish between the different kinds of materials in their world. "You can live on roots and berries," they might have said, "but you can't eat dirt. You can stay warm by burning tree branches, but you can't burn rocks."

By the early eighteenth century, scientists thought they had grasped the nature of that difference, and in 1807 Jöns Jakob Berzelius gave names to the two kinds of materials. Compounds derived from living organisms were believed to contain an immeasurable vital force—the essence of life. These he called "organic." Compounds derived from minerals—those lacking the vital force—were "inorganic."

Because chemists could not create life in the laboratory, they assumed they could not create compounds that had a vital force. Since this was their mind-set, you can imagine how surprised chemists were in 1828 when Friedrich Wöhler produced urea a compound known to be excreted by mammals—by heating ammonium cyanate, an inorganic mineral.



For the first time, an "organic" compound had been obtained from something other than a living organism and certainly without the aid of any kind of vital force. Chemists, therefore, needed a new definition for "organic compounds." **Organic compounds** are now defined as *compounds that contain carbon*.

Why is an entire branch of chemistry devoted to the study of carbon-containing compounds? We study organic chemistry because just about all of the molecules that make life possible and that make us who we are—proteins, enzymes, vitamins, lipids, carbohydrates, DNA, RNA—are organic compounds. Thus, the chemical reactions that take

Organic compounds are compounds that contain carbon.

place in living systems, including our own bodies, are reactions of organic compounds. Most of the compounds found in nature—those that we rely on for all of our food, for some of our clothing (cotton, wool, silk), and for energy (natural gas, petroleum)—are organic as well.

Organic compounds are not limited, however, to those found in nature. Chemists have learned how to synthesize millions of organic compounds never found in nature, including synthetic fabrics, plastics, synthetic rubber, and even things like compact discs and Super Glue. And most importantly, almost all of our commonly prescribed drugs are synthetic organic compounds.

Some synthetic organic compounds prevent shortages of naturally occurring products. For example, it has been estimated that if synthetic materials—nylon, polyester, Lycra were not available for clothing, then all of the arable land in the United States would have to be used for the production of cotton and wool just to provide enough material to clothe us. Other synthetic organic compounds provide us with materials we would not have—Teflon, Plexiglas, Kevlar—if we had only naturally occurring organic compounds. Currently, there are about 16 million known organic compounds, and many more are possible that we cannot even imagine today.

What makes carbon so special? Why are there so many carbon-containing compounds? The answer lies in carbon's position in the periodic table. Carbon is in the center of the second row of elements. We will see that the atoms to the left of carbon have a tendency to give up electrons, whereas the atoms to the right have a tendency to accept electrons (Section 1.3).



the second row of the periodic table

Because carbon is in the middle, it neither readily gives up nor readily accepts electrons. Instead, it shares electrons. Carbon can share electrons with several different kinds of atoms, and it can share electrons with other carbon atoms. Consequently, carbon is able to form millions of stable compounds with a wide range of chemical properties simply by sharing electrons.

Natural Organic Compounds Versus Synthetic Organic Compounds

It is a popular belief that natural substances—those made in nature—are superior to synthetic ones—those made in the laboratory. Yet when a chemist synthesizes a compound, such as penicillin or morphine, the compound is exactly the same in all respects as the compound synthesized in nature. Sometimes chemists can even improve on nature. For example, chemists have synthesized analogues of penicillin that do not produce the allergic responses that a significant fraction of the population experiences from naturally produced penicillin, or that do not have the bacterial resistance of the naturally produced antibiotic (Section 16.15). Chemists have also synthesized analogues of morphine—compounds with structures similar to but not identical to that of morphine—that have the same pain-killing effects but, unlike morphine, are not habit forming.



