国外名校名著

有机化学

Organic Chemistry

（原著第十三版）

[美] David J. Hart
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陆 阳 杨丽敏 等改编

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·北 京·

本书以尽量简短的篇幅向大家介绍有机化学的全貌，并注意有机化学与医药学等专业的紧密联系。本书的章节组织符合认知规律，在第1章介绍化学键、异构体和有机化合物分类的基础上，顺势引出了饱和、不饱和及芳香族碳氢化合物等三章内容。反应机理的概念引入较早，以便在后面各章反复加强。立体异构现象在第2章和第3章作了简单介绍，然后在第5章进行了专门探讨。第6章含卤有机化合物的介绍作为理解取代反应、消除反应和立体化学动力学的工具。第7～10章按碳的氧化态升高的顺序介绍含氧官能团化合物——醇和酚、醚和环氧化合物、醛和酮、羧酸及其衍生物，它们的含硫类似物也都简单提及。第11章介绍胺类化合物。第2～11章为本书的核心。第12章为波谱学基础，重点介绍核磁共振及其应用。第13、14章介绍了杂环化合物和高聚物。最后四章为脂类，糖类，氨基酸、肽和蛋白质，核酸等重要生物物质的介绍。

本书可作为医学、药学、护理学、生物学、营养学、农学、林学等专业的教材，对化学及相关专业亦有很好的参考作用。

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前 言

《Organic Chemistry：A Brief Course》是供临床医学、生物学、药学等学科相关专业使用的有机化学本科英语教材，其内容表述规范，可读性强。该教材与我国供基础、临床、预防、口腔医学等专业使用的卫生部“十二五”规划教材《有机化学》的知识体系及教学内容接近，符合我国医学学科相关专业有机化学教学的基本要求，可用于我国高等学校医学相关专业有机化学的双语教学。

为了使本教材更适合我国医学学科相关专业的有机化学教学，化学工业出版社组织国内五所高等院校10位富有有机化学教学经验的教师，以该教材的第13版为蓝本，在尊重原教材版权的基础上，对该教材进行了改编。改编版本既充分体现原书特点，又更适用于我国的读者。改编重点为：第3章、第7~10章增加了若干知识点，第14章删减了部分内容。为使教材更加精炼紧凑，改编教材还删除了原书的静电势能图、部分球棍模型图、“A Word About…”小短文以及索引等内容。全书调整了部分内容的陈述顺序、章节标题，添加了专业术语的中文译注，增删了部分习题。改编后，教材内容具有更好的系统性、完整性和可读性。该教材改编后，除了可用作相关专业有机化学双语教学的教材外，也可供非双语教学的师生及其他科技工作者用作学习有机化学的参考书。

该教材的改编由上海交通大学医学院的陆阳、杨丽敏负责统稿。参加改编的教师有上海交通大学医学院陆阳、杨丽敏、林琦，山东大学郭今心，中南大学罗一鸣，大连医科大学贺欣、徐乃进，南华大学邓健、孙允凯、聂长明。由于水平有限，该教材的改编难免有不妥之处，敬请广大师生及其他读者批评指正。

编　者

2013年6月25日于上海

Preface

Purpose

Over fifty years have passed since the first edition of this text was published. Although the content and appearance of the book have changed over time, our purpose in writing *Organic Chemistry: A Brief Course* remains constant: to present a brief introduction to modern organic chemistry in a clear and engaging manner.

This book was written for students who, for the most part, will not major in chemistry, but whose main interest requires some knowledge of organic chemistry, such as agriculture, biology, human or veterinary medicine, pharmacy, nursing, medical technology, health sciences, engineering, nutrition, and forestry. To encourage these students to enjoy the subject as we do, we have made a special effort to relate the practical applications of organic chemistry to biological processes and everyday life. The success of this approach is demonstrated by the widespread use of this textbook by hundreds of thousands of students in the United States and around the world, via its numerous translations.

Organic Chemistry: A Brief Course is designed for a one-semester introductory course, but it can be readily adapted to other course types. Often, it is used in a one- or two-quarter course. In some countries (France and Japan, for example), it serves as an introductory text for chemistry majors, followed by a longer and more detailed full-year text. It has even been used in the United States for a one-year science majors course (with suitable supplementation by the instructor). In many high schools, it is used as the text for a second-year course, following the usual introductory general chemistry course.

New to the 13th Edition

The text was critically revised to clarify difficult content and to improve the presentation. In addition to many small changes, major changes to this edition have focused on improving graphics throughout the text in a pedagogically useful manner. For example, (1) some new ball-and-stick structures have been added to help students visualize molecules in three dimensions; (2) many additional problems have been written, and many of these problems require students to develop their three-dimensional visualization skills; (3) in some locations, new graphics and some electrostatic potential maps have been added in order to help in discussions of acid–base chemistry; and (4) several energy diagrams are used to illustrate the structural changes that occur as reactions proceed from reactants to products. Other changes include increased use of the arrow-pushing formalism to facilitate teaching and understanding of reaction mechanisms.

We are very conscious of the need to keep the book to a manageable size for the one-semester course. Outdated information has been deleted and, in some cases, replaced with new material. In the end, users will find this edition practically identical in length to the previous one.

Organization

The organization is fairly classical, with some exceptions. After an introductory chapter on bonding, isomerism, and an overview of the subject (Chapter 1), the next three chapters treat saturated, unsaturated, and aromatic hydrocarbons in sequence. The concept of reaction mechanism is presented early, and examples are included in vir-

tually all subsequent chapters. Stereoisomerism is also introduced early, briefly in Chapters 2 and 3, and then given separate attention in a full chapter (Chapter 5). Halogenated compounds are used in Chapter 6 as a vehicle for introducing aliphatic substitution and elimination mechanisms and dynamic stereochemistry.

Chapters 7 through 10 cover oxygen functionality in order of the increasing oxidation state of carbon—alcohols and phenols, ethers and epoxides, aldehydes and ketones, and acids and their derivatives. Brief mention of sulfur analogs is made in these chapters. Chapter 11 deals with amines. Chapters 2 through 11 treat every main functional group and constitute the heart of the course. Chapter 12 then takes up spectroscopy, with an emphasis on nuclear magnetic resonance (NMR) and applications to structure determination. This chapter handles the student's question: How do you know that those molecules really have the structures you say they have?

Next come two chapters on topics not always treated in introductory texts but that are especially important in practical organic chemistry—Chapter 13 on heterocyclic compounds and Chapter 14 on polymers. The book ends with four chapters on biologically important substances—lipids; carbohydrates; amino acids, peptides, and proteins; and nucleic acids.

Examples and Problems

Problem solving is essential to learning organic chemistry. Examples (worked-out problems) appear at appropriate places within each chapter to help students develop these skills. These examples and their solutions are clearly marked. Unsolved problems that provide immediate learning reinforcement are included in each chapter and are supplemented with an abundance of end-of-chapter problems. The combined number of examples and problems is over 1,000—an average of almost 60 per chapter.

OWL

OWL for Organic Chemistry

By Steve Hixson and Peter Lillya of the University of Massachusetts, Amherst, and William Vining of the State University of New York at Oneonta. End-of chapter questions by David W. Brown, Florida Gulf Coast University. **OWL** Online Web Learning offers more assignable, gradable content and more reliability and flexibility than any other system. OWL's powerful course management tools allow instructors to control due dates, number of attempts, and whether students see answers or receive feedback on how to solve problems. OWL includes the **YouBook**, a Flash-based eBook that is interactive and customizable. It features a text edit tool that allows instructors to modify the textbook narrative as needed. With YouBook, instructors can quickly re-order entire sections and chapters or hide any content they don't teach to create an eBook that perfectly matches their syllabus. Instructors can further customize the YouBook by publishing web links. The YouBook also includes animated figures, video clips, highlighting, notes, and more.

Developed by chemistry instructors for teaching chemistry, OWL is the only system specifically designed to support **mastery learning**, where students work as long as they need to master each chemical concept and skill. OWL has already helped hundreds of thousands of students master chemistry through a wide range of assignment types, including tutorials, interactive simulations, and algorithmically generated homework questions that provide instant, answer-specific feedback.

OWL is continually enhanced with online learning tools to address the various learning styles of today's students such as:

- **Quick Prep** review courses that help students learn essential skills to succeed in General and Organic Chemistry
- **Jmol** molecular visualization program for rotating molecules and measuring bond distances and angles

In addition, when you become an OWL user, you can expect service that goes far beyond the ordinary. For more information or to see a demo, please contact your Cengage Learning representative or visit us at **www.cengage.com/owl.**

Student Ancillaries

Study Guide and Solutions Manual Written by the authors of the main text, this guide contains chapter summaries and learning objectives, reaction summaries, mechanism summaries, answers to all text problems, and sample test questions.

Laboratory Manual Written by Leslie Craine and T. K. Vinod, this manual contains thirty experiments that have been tested with thousands of students. Most of the preparative experiments contain procedures on both macroscale and microscale, thus adding considerable flexibility for the instructor and the opportunity for both types of laboratory experience for the student. Experiments involving molecular modeling now contain computer-modeling activities in addition to activities based on traditional modeling kits. The experiments, capable of being completed in a two- or three-hour lab period, are a good mix of techniques, preparations, tests, and applications. Hazardous chemicals on the OSHA list have been avoided, care has been taken to minimize contact with solvents, and updated caution notes and waste disposal instructions are included. ISBN-10: 1-111-42584-1, ISBN-13: 978-1-111-42584-8

Student Companion Website The Student Companion Website includes a glossary, flashcards, and an interactive periodic table, which are accessible from **www.cengagebrain.com.**

CengageBrain.com App Now, students can prepare for class anytime and anywhere using the CengageBrain.com application developed specifically for the Apple iPhone® and iPod touch®, which allows students to access free study materials—book-specific quizzes, flash cards, related Cengage Learning materials and more—so they can study the way they want, when they want to . . . even on the go. For more information about this complimentary application, please visit **www.cengagebrain.com.**

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Instructor Ancillaries

A complete suite of customizable teaching tools accompanies *Organic Chemistry: A Brief Course.* These integrated resources are designed to save you time and help make class preparation, presentation, assessment, and course management more efficient and effective.

Instructor Resource Website

This is a one-stop digital library and presentation tool that includes:

- Prepared **Microsoft® PowerPoint® Lecture Slides** that cover all key points from the text in a convenient format that you can enhance with your own materials or with the supplied interactive video and animations for personalized, media-enhanced lectures.
- Image libraries in PowerPoint and JPEG formats that contain **digital files for all text art, all**

photographs, and all numbered tables in the text. These files can be used to create your own transparencies or PowerPoint lectures.

- ***Instructor's Resource Manual*** written by Christopher M. Hadad that offers a transition guide, tables suggesting the approximate number of lectures to devote to each chapter, summaries of the worked examples and problems, a chapter-by-chapter outline listing those sections that are most important, and answers to the review problems on synthesis that are featured in the Study Guide and Solutions Manual.
- ***Instructor's Resource Guide* for the *Laboratory Manual*** written by Christopher M. Hadad of The Ohio State University, that contains detailed discussions of experiments and answers to all of the prelab exercise questions and most of the questions in the report sheets contained in the Laboratory Manual.
- **ExamView Computerized Testing** that enables you to create customized tests of up to 250 items in print or online using more than 700 questions carefully matched to the corresponding text sections. Tests can be taken electronically or printed for class distribution.

Acknowledgments

We would like to thank the following reviewers for diligently contributing their insights to this edition of *Organic Chemistry:*

Scott W. Cowley, *Colorado School of Mines*; Sarah A. Cummings, *University of Nevada, Reno*; J. Brent Friesen, *Dominican University*; Michael Harmata,*University of Missouri-Columbia*; Marjorie J. Hummel, *Governors State University*; and Barbara Oviedo Mejia, *California State University, Chico.*

We have incorporated many of their recommendations, and the book is much improved as a result.

One pleasure of authorship is receiving letters from students (and their teachers) who have benefited from the book. We thank all who have written to us, from all parts of the world, since the last edition; many of the suggestions have been incorporated into this revision. We are happy to hear from users and nonusers, faculty and students, who have suggestions for further improvement.

David J. Hart
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Harold Hart
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Natural and synthetic organic compounds are everywhere in the environment and in our material culture.

To the Student

In this introduction, we will briefly discuss organic chemistry and its importance in a technological society. We will also explain how this course is organized and give you a few hints that may help you to study more effectively.

What Is Organic Chemistry About?

The term *organic* suggests that this branch of chemistry has something to do with *organisms,* or living things. Originally, organic chemistry did deal only with substances obtained from living matter. Years ago, chemists spent much of their time extracting, purifying, and analyzing substances from animals and plants. They were motivated by a natural curiosity about living matter and also by the desire to obtain from nature ingredients for medicines, dyes, and other useful products.

It gradually became clear that most compounds in plants and animals differ in several respects from those that occur in nonliving matter, such as minerals. In particular, most compounds in living matter are made up of the same few elements: carbon, hydrogen, oxygen, nitrogen, and sometimes sulfur, phosphorus, and a few others. Carbon is virtually always present. This fact led to our present definition: **Organic chemistry** is the chemistry of carbon compounds. This definition broadens the scope of the subject to include not only compounds from nature but also synthetic compounds—compounds invented by organic chemists and prepared in their laboratories.

Organic chemistry is the chemistry of carbon compounds.

Synthetic Organic Compounds

Scientists used to believe that compounds occurring in living matter were different from other substances and that they contained some sort of intangible vital force that imbued them with life. This idea discouraged chemists from trying to make organic compounds in the laboratory. But in 1828, the German chemist Friedrich Wöhler, then 28 years old, accidentally prepared urea, a well-known constituent of urine, by heating the inorganic (or mineral) substance ammonium cyanate. He was quite excited about this result, and in a letter to his former teacher, the Swedish chemist Jöns Jacob Berzelius, he wrote, "I can make urea without the necessity of a kidney, or even of an animal, whether man or dog." This experiment and others like it gradually discredited the vital-force theory and opened the way for modern synthetic organic chemistry.

Synthesis consists of piecing together small simple molecules to make larger, more complex molecules.

Synthesis usually consists of piecing together small, relatively simple molecules to make larger, more complex ones. To make a molecule that contains many atoms from molecules that contain fewer atoms, one must know how to link atoms to each other—that is, how to make and break chemical bonds. Wöhler's preparation of urea was accidental, but synthesis is much more effective when it is carried out in a controlled and rational way so that when all the atoms are assembled, they will be connected to one another in the correct manner to give the desired product.

Chemical bonds are made or broken during chemical reactions. In this course, you will learn about quite a few reactions that can be used to make new bonds and that are therefore useful in the synthesis of pharmaceuticals and industrial chemicals.

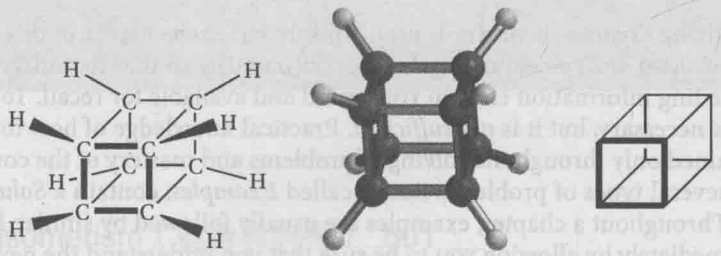
Why Synthesis?

At present, the number of organic compounds that have been synthesized in research laboratories is far greater than the number isolated from nature. Why is it important to know how to synthesize molecules? There are several reasons. For one, it might be important to synthesize a natural product in the laboratory to make the substance more widely available at lower cost than it would be if the compound had to be extracted from its natural source. Some examples of compounds first isolated from nature but now produced synthetically for commercial use are vitamins, amino acids, dyes for clothing, fragrances, and the moth-repellent camphor. Although the term *synthetic* is sometimes frowned upon as implying something artificial or unnatural, these synthetic natural products are in fact identical to the same compounds extracted from nature.

Another reason for synthesis is to create new substances that may have new and useful properties. Synthetic fibers such as nylon and Orlon, for example, have properties that make them superior for some uses to natural fibers such as silk, cotton, and hemp. Most pharmaceutical drugs used in medicine are synthetic (including aspirin, ether, Novocain, and ibuprofen). The list of synthetic products that we take for granted is long indeed—plastics, detergents, insecticides, and oral contraceptives are just a few. All of these are compounds of carbon; all are organic compounds.

Finally, organic chemists sometimes synthesize new compounds to test chemical theories—and sometimes they synthesize compounds just for the fun of it. Certain geometric structures, for example, are aesthetically pleasing, and it can be a challenge to make a molecule in which the carbon atoms are arranged in some regular way. One example is the hydrocarbon cubane, C_8H_8. First synthesized in 1964, its molecules have eight carbons at the corners of a cube, each carbon with one hydrogen and three other carbons connected to it. Cubane is more than just aesthetically pleasing. The bond angles in cubane are distorted from normal because of its geometry. Studying the chemistry of cubane therefore gives chemists information about how the distortion of carbon–carbon and carbon–hydrogen bonds affects their chemical behavior.

Although initially of only theoretical interest, the special properties of cubane may eventually lead to its practical use in medicine and in explosives.



cubane, C_8H_8
mp 130–131°C
P. E. Eaton (U. of Chicago), 1964

Organic Chemistry in Everyday Life

Organic chemistry touches our daily lives. We are made of and surrounded by organic compounds. Almost all of the reactions in living matter involve organic compounds, and it is impossible to understand life, at least from the physical point of view, without knowing some organic chemistry. The major constituents of living matter—proteins, carbohydrates, lipids (fats), nucleic acids (DNA and RNA), cell membranes, enzymes, hormones—are organic, and later in the book, we will describe their chemical structures. These structures are quite complex. To understand them, we will first have to discuss simpler molecules.

Other organic substances include the gasoline, oil, and tires for our cars; the clothing we wear; the wood for our furniture; the paper for our books; the medicines we take; and plastic containers, camera film, perfume, carpeting, and fabrics. Name it, and the chances are good that it is organic. Daily, in the paper, on the Internet, or on television, we encounter references to polyethylene, epoxys, Styrofoam, nicotine, polyunsaturated fats, and cholesterol. All of these terms refer to organic substances; we will study them and many more like them in this book.

In short, organic chemistry is more than just a branch of science for the professional chemist or for the student preparing to become a physician, dentist, veterinarian, pharmacist, nurse, or agriculturist. It is part of our technological culture.

Organization

Organic chemistry is a vast subject. Some molecules and reactions are simple; others are quite complex. We will proceed from the simple to the complex by beginning with a chapter on bonding, with special emphasis on bonds to carbon. Next, there are three chapters on organic compounds containing only two elements: carbon and hydrogen (called hydrocarbons). The second of these chapters (Chapter 3) contains an introduction to organic reaction mechanisms and a discussion of reaction equilibria and rates. These are followed by a chapter that deals with the three-dimensionality of organic compounds. Next, we add other elements to the carbon and hydrogen framework, halogens in Chapter 6, oxygen and sulfur in Chapters 7 through 10, and nitrogen in Chapter 11. At that point, we will have completed an introduction to all the main classes of organic compounds.

Spectroscopy is a valuable tool for determining organic structures—that is, the details of how atoms and groups are arranged in organic molecules. We take up this topic in Chapter 12. Next comes a chapter on heterocyclic compounds, many of which are important in medicine and in natural products. It is followed by a chapter on polymers, which highlights one of the most important industrial uses of organic chemistry. The last four chapters deal with the organic chemistry of four major classes of biologically important molecules: the lipids, carbohydrates, proteins, and nucleic acids. Because the structures of these molecules of nature are rather complex, we leave them for last. But with the background knowledge of simpler molecules that you will have acquired by then, these compounds and their chemistry will be clearer and more understandable.

To help you organize and review new material, we have placed a *Reaction Summary* and a *Mechanism Summary* at the end of each chapter in which new reactions and new reaction mechanisms are introduced.

The Importance of Problem Solving

One key to success in studying organic chemistry is problem solving. Each chapter in this book contains numerous facts that must be digested. Also, the subject matter builds continuously so that to understand each new topic, it is essential to have the preceding information clear in your mind and available for recall. To learn all these materials, careful study of the text is necessary, but it is *not sufficient.* Practical knowledge of how to use the facts is required, and such skill can be obtained only through the solving of problems and mastery of the concepts.

This book contains several types of problems. Some, called *Examples*, contain a *Solution*, so you can see how to work such problems. Throughout a chapter, examples are usually followed by similar *Problems*, designed to reinforce your learning immediately by allowing you to be sure that you understand the new material just presented. These *Problems* will be of most value if you work them when you come across them as you read the book. At the end of each chapter, *Additional Problems* enable you to practice your problem-solving skills and evaluate your retention of material. The end-of-chapter problems are grouped by topics. In general, problems that simply test your knowledge come first and more challenging problems follow.

Try to work as many problems as you can. If you have trouble, two sources of help we suggest are your instructor and the *Study Guide and Solutions Manual* that accompanies this text. If you visit your instructors with your questions, you are likely to find that they are thrilled to be asked to help, and they may provide you with the insight you need to better understand a concept or problem. The study guide provides answers to the problems and explains how to solve them. It also provides you with review materials and additional problems that do not appear in the textbook. Problem solving is time-consuming, but it will pay off in an understanding of the subject.

And now, let us begin.

Brief Contents

Contents