

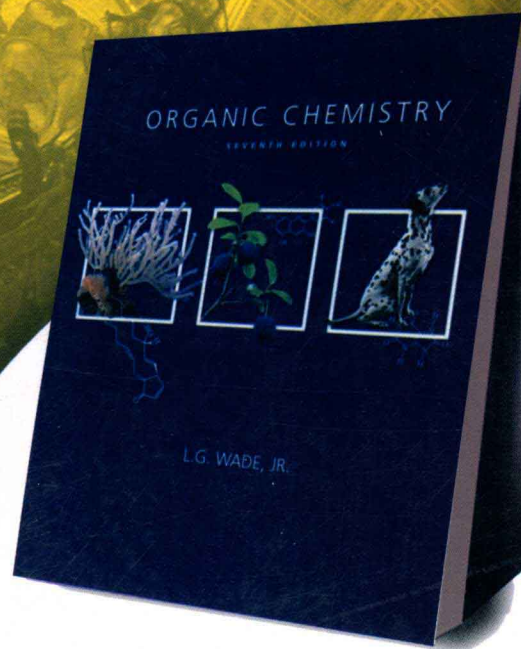
时代教育·国外高校优秀教材精选

有机化学

(英文版·原书第7版)

ORGANIC CHEMISTRY, 7E

(美) L. G. Wade, Jr. 著



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机械工业出版社

本书内容包括有机分子, 烷烃, 化学反应的研究, 立体化学, 卤代烷, 烯烃, 炔烃, 醇, 红外光谱与质谱, 核磁共振谱, 醚、环氧与硫醚, 共轭体系、轨道体系与紫外光谱, 芳香族化合物, 酮类和醛类, 胺, 羧酸, 羧酸衍生物, 羰基化合物的缩合与 α -取代反应, 碳水化合物和核酸, 氨基酸、肽和蛋白质, 类脂, 合成聚合物。可供化学、化工类专业用作双语教材, 也可供医药等相关专业师生参考。

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出版说明

随着我国加入 WTO，国际间的竞争越来越激烈，而国际间的竞争实际上也就是人才的竞争、教育的竞争。为了加快培养具有国际竞争力的高水平技术人才，加快我国教育改革的步伐，国家教育部近来出台了一系列倡导高校开展双语教学、引进原版教材的政策。以此为契机，机械工业出版社陆续推出了一系列国外影印版教材，其内容涉及高等学校公共基础课，以及机、电、信息、化工等领域的专业基础课和专业课。

引进国外优秀原版教材，在有条件的学校推动开展英语授课或双语教学，自然也引进了先进的教学思想和教学方法，这对提高我国自编教材的水平，加强学生的英语实际应用能力，使我国的高等教育尽快与国际接轨，必将起到积极的推动作用。

为了做好教材的引进工作，机械工业出版社特别成立了由著名专家组成的国外高校优秀教材审定委员会。这些专家对实施双语教学作了深入细致的调查研究，对引进原版教材提出了许多建设性意见，并慎重地对每一本将要引进的原版教材一审再审，精选再精选，确认教材本身的质量水平，以及权威性和先进性，以期所引进的原版教材能适应我国学生的外语水平和学习特点。在引进工作中，审定委员会还结合我国高校教学课程体系的设置和要求，对原版教材的教学思想和方法的先进性、科学性严格把关，同时尽量考虑原版教材的系统性和经济性。

这套教材出版后，我们将根据各高校的双语教学计划，举办原版教材的教师培训，及时地将其推荐给各高校选用。希望高校师生在使用教材后及时反馈意见和建议，使我们更好地为教学改革服务。

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影印版序

该书从 1987 年面世至 2010 年出版第 7 版, 已历经 23 年教、学两方面的检阅和锤炼。先后有几十位美国教授参与审稿。因其对教学规律, 对知识的深度、广度、难度和新知识等方面协调把握得当而成为一本深受欢迎的有机化学教材, 被许多名校, 包括麻省理工学院、Emory 大学等, 选用作为教材。

该书以现代性和适度性为编写目标, 从而在教学理念、教学内容和教学形式等方面体现了该教材的先进性。

在内容上, 除了传统的有机反应外, 该书注重吸纳、介绍现代化学中近年获得广泛应用的技术和反应、新进展、新知识, 从近年获得诺贝尔化学奖的成果(新反应)到化学用词等方面都能得到反映。例如, Noyori 不对称氢化, Sharpless 不对称氧化, Grubbs 烯烃复分解反应及其机理。在书中较早引入分子轨道理论用于解释电子效应、周环反应和紫外光谱; 引入核磁共振碳谱和 DEPT 技术。全书注重有机合成, 把它作为有机化学的重点目标, 并引入逆合成分析法。书中把光谱作为有机化学家最重要的工具之一加以介绍, 除了重点叙述常用的“四谱”外, 其他光谱, 如拉曼光谱等也有介绍。

在编排形式上, 注重研究、采用先进的教学理念和最富有成效的教学方式, 形成了贴近学生, 以学生的学习理解和解决问题为导向的编排特色。不但把反应机理和关键反应机理列入目录, 在目录栏后汇总了反应机理和关键反应机理, 还在各章把反应机理和关键反应机理以蓝框强调。

该书特别重视小结、总结, 用蓝框提示要点。每章设立官能团性质和反应小结栏目, 章末均配有词汇表, 对该章的新概念、专业词进行小结; 以绿色表格式小结进行解题示范; 还设有解题策略示范、解题技巧等栏目。除归纳出 20 个关键反应机理外, 对核磁共振和红外光谱, 以表格式总结出 12 个特征核磁共振区和 12 个红外吸收区。使得学生可很快掌握用波谱手段解析有机分子的结构。

在辅助教学手段上, 有多种与之相配套的多媒体和在线教学资源等教学辅助手段。

在内容体上, 该书按照现代性和适读性的编写目标, 在编排上体现了以结构为基础, 以官能团为主线、以反应及其机理为核心的教学思路。

在介绍结构与反应时讲究知识的衔接性, 注重结构与反应性的关联, 使新概念的引入有水到渠成之效; 在介绍立体化学概念时, 注重对比; 在讲解官能团时, 采用循序渐进、归纳对比的方式, 每次集中介绍一种官能团, 并与其他官能团进行结构和反应性差异对比。

对反应的强调始于第 1 章的 Lewis 酸碱反应, 接着在第 4 章介绍反应的热力学和动力学, 而立体化学则贯穿于大多数重要的取代加成和消除反应, 并用有空间感的示意图加以直观地阐述。红外、质谱和核磁共振技术的基本原理在第 12、13 章介绍, 以便可以在第一学期讲授。而其应用则分述于随后章节。

该书十分重视对反应机理的完整讨论, 包括范围和细节。全书共介绍了一百多个反应机理。通过对反应机理的梳理, 归纳了 20 个关键反应机理, 并用框加以强调, 使学生能够通过最少量的理解记忆, 领会最重要的概念, 从而把握许多反应的本质。

对于官能团性质, 注重比对分析, 提供性质、反应的归纳、总结, 解题帮助及独特的解题策略和提示。

对教师而言该书具有灵活性。为适应不同教师教学方法上的差异, 该书对所有基础性的专题作了详尽的介绍, 教师可以根据其判断进行取舍。这样的专题包括核磁共振碳谱、紫外光谱、轨道对称守恒、氨基酸、核酸、类脂和合成聚合物等专题性的章节。另一个可以灵活选用的是作业题。每章后附有大量从各个角度提出的问题, 师生可根据不同的课程安排选取部分作为作业。

这是一本以大学理科本科生为主要对象, 按两学期课程安排的教材, 适于国内化学、化工类专业用作双语教材, 也可供医药等相关专业师生参考。

厦门大学化学与化工学院
黄培强

PREFACE

To the Student

As you begin your study of organic chemistry, you might feel overwhelmed by the number of compounds, names, reactions, and mechanisms that confront you. You might even wonder whether you can learn all this material in a single year. The most important function of a textbook is to organize the material to show that most of organic chemistry consists of a few basic principles and many extensions and applications of these principles. Relatively little memorization is required if you grasp the major concepts and develop flexibility in applying those concepts. Frankly, I have a poor memory, and I hate memorizing lists of information. I don't remember the specifics of most of the reactions and mechanisms in this book, but I can work them out by remembering a few basic principles, such as "alcohol dehydrations usually go by E1 mechanisms."

Still, you'll have to learn some facts and fundamental principles to serve as the working "vocabulary" of each chapter. As a student, I learned this the hard way when I made a D on my second organic chemistry exam. I thought organic would be like general chemistry, where I could memorize a couple of equations and fake my way through the exams. For example, in the ideal gas chapter, I would memorize $PV = nRT$, and I was good to go. When I tried the same approach in organic, I got a D. We learn by making mistakes, and I learned a lot in organic chemistry.

In writing this book, I've tried to point out a small number of important facts and principles that should be learned to prepare for solving problems. For example, of the hundreds of reaction mechanisms shown in this book, about 20 are the fundamental mechanistic steps that combine into the longer, more complicated mechanisms. I've highlighted these fundamental mechanisms in *Key Mechanism* boxes to alert you to their importance. Spectroscopy is another area where a student might feel pressured to memorize hundreds of facts, such as NMR chemical shifts and infrared vibration frequencies. I couldn't do that, so I've always gotten by with knowing about a dozen NMR chemical shifts and about a dozen IR vibration frequencies, and knowing how they are affected by other influences. I've listed those important infrared frequencies in Table 12-2 and the important NMR chemical shifts in Table 13-3.

Don't try to memorize your way through this course. It doesn't work; you have to know what's going on so you can apply the material. Also, don't think (like I did) that you can get by without memorizing *anything*. Read the chapter, listen carefully to the lectures, and *work the problems*. The problems will tell you whether or not you know the material. If you can do the problems, you should do well on the exams. If you can't do the problems, you probably won't be able to do the exams, either. If you keep having to look up an item to do the problems, that item is a good one to learn.

Here are some hints I give my students at the beginning of the course:

1. Read the material in the book before the lecture (expect 13–15 pages per lecture). Knowing what to expect and what is in the book, you can take fewer notes and spend more time listening and understanding the lecture.
2. After the lecture, review your notes and the book, and do the in-chapter problems. Also, read the material for the next lecture.
3. If you are confused about something, visit your instructor during office hours immediately, before you fall behind. Bring your attempted solutions to problems with you to show the instructor where you are having trouble.
4. To study for an exam, begin by reviewing each chapter and your notes, then concentrate on the end-of-chapter problems. Also use old exams for practice, if available.

Remember the two “golden rules” of organic chemistry.

1. **Don't Get Behind!** The course moves too fast, and it's hard to catch up.
2. **Work Lots of Problems.** Everyone needs the practice, and the problems show where you need more work.

I am always interested to hear from students using this book. If you have any suggestions about how the book might be made better, or if you've found an error, please let me know (L. G. Wade, Whitman College, Walla Walla, WA 99362: E-mail wadelg@whitman.edu). I take students' suggestions seriously, and hundreds of them now appear in this book. For example, Whitman student Brian Lian suggested Figure 21-9, and University of Minnesota student (and race-car driver) Jim Coleman gave me the facts on the use of methanol at Indianapolis.

Good luck with your study of organic chemistry. I'm certain you will enjoy this course, especially if you let yourself relax and develop an interest in how organic compounds influence our lives. My goal in writing this book has been to make the process a little easier: to build the concepts logically on top of each other, so they flow naturally from one to the next. The hints and suggestions for problem solving have helped my students in the past, and I hope some of them will help you to learn and use the material. Even if your memory is worse than mine (highly unlikely), you should be able to do well in organic chemistry. I hope this will be a good learning experience for all of us.

L. G. Wade, Jr.
Walla Walla, Washington
wadelg@whitman.edu

To the Instructor

In writing the first edition of this text, my goal was to produce a modern, readable text that uses the most effective techniques of presentation and review. Subsequent editions extended and refined that goal, with substantial rewriting and reorganization and with the addition of several new features. This seventh edition incorporates even more refinements than the sixth, with revisions in the organization, writing, and graphics. Some of the modifications made in the most recent editions are:

1. **Mechanism Boxes.** About 100 of the most important mechanisms have been organized into mechanism boxes, with large blue headings for easy review. In this seventh edition, these boxes have been refined to make the individual steps clearer to students. I've tried to choose most of the standard mechanisms that nearly everyone teaches; yet, in some cases, it seems that other mechanisms would be good candidates. If there are additional mechanisms that should be boxed, or some that should not be boxed, please let me know what you think.

In choosing the Key Mechanisms, I've used two major criteria. If the mechanism is one of the fundamental mechanisms that make up the longer, more complex mechanisms, then it must be a Key Mechanism. Examples are S_N1 , S_N2 , E1, E2, nucleophilic acyl substitution, electrophilic aromatic substitution, nucleophilic addition to carbonyls, and so on. The other criterion is more subjective. If the mechanism is one of the ones I routinely expect students to do on exams, then it is a Key Mechanism. Examples are formation of imines and acetals, aldol and Claisen condensations, and so on. If you feel I have left one out or included one that should not be a Key Mechanism, please let me know.

2. **Updated Coverage.** In the sixth and seventh editions, I've updated several terms to those that have gradually received acceptance among organic chemists. Examples are *bond-dissociation enthalpy* to replace the more ambiguous *bond-dissociation energy* and the newer transliteration *Zaitsev* to replace the older *Saytzeff*.

I've continued the gradual transition to the newer IUPAC names with the revised locations of numbers, such as in hexa-1,3-diene instead of 1,3-hexadiene. I've also completed the transition from kcal to kJ as the primary energy units, since kJ units are used in all general chemistry texts at this time.

I've added several sections to recent editions to cover new material or material of current interest.

Chapter 4: A section on free-radical inhibitors was added to show students how some of the common inhibitors break the free-radical chain reaction, and their importance in chemistry and biochemistry.

Chapter 5: Using the Mislow and Siegel definition (*J. Am. Chem. Soc.* **1984**, *106*, 3319), I introduce the popular (but often incorrectly defined) term *stereocenter* and explain the differences between this term and the IUPAC terms *chirality center* and *asymmetric carbon atom* (or *chiral carbon atom*). The term *stereocenter* is much broader than the more precise term *asymmetric carbon atom*, and it assumes that one already knows the stereochemical properties of the molecule (to know which bonds will give rise to stereoisomers upon their interchange). The casual use of the broad term *stereocenter* where a more precise term is required often results in logical fallacies (*J. Chem. Educ.* **2006**, *83*, 1793). Therefore, I have continued to encourage students to identify the (immediately apparent) asymmetric carbon atoms to use as tools in examining a molecule to determine its stereochemistry.

Chapter 8: The Nobel Prize-winning asymmetric reduction work by Noyori and Knowles is discussed, together with its implications for enantioselective drug synthesis. Another new section has been added covering the mechanism and synthetic uses of olefin metathesis, highlighting the work by Chauvin, Grubbs, and Schrock that recently won the Nobel Prize.

Chapter 12: Fourier-transform IR spectroscopy is discussed, together with the reasons why this technique gives improved sensitivity and resolution over the dispersive method.

Chapter 13: The NMR spectra have been converted to high-field (300 MHz) spectra from the excellent Aldrich collection. The expansion boxes have been refined and clarified to make sure that the individual splittings are visible. The DEPT technique has been expanded and used in more of the problems.

Chapter 14: The Nobel Prize-winning Sharpless asymmetric epoxidation is discussed, together with the factors that selectively enhance the formation of one enantiomer of the product.

Chapter 16: A section has been added that discusses the aromaticity of Fullerenes and their relationship to other allotropes of carbon.

Chapter 24: A section has been added that discusses *prions*: proteins which are thought to be infectious because of misfolding, resulting in clumping and formation of plaques. This topic relates the topic at hand (protein conformations) directly to the ongoing concern about mad cow disease.

3. Electrostatic Potential Maps. Electrostatic potential maps are used in cases where they might help students to visualize the charge distribution of a species in a way that helps to explain the electrophilic or nucleophilic nature of a compound. In introducing EPMs, I've emphasized their qualitative nature without stressing their mathematical derivation. As a result, I've explained and used EPMs much like they are introduced in the general chemistry textbooks. Several new EPMs have been added in the seventh edition.

The entire book has been edited, with many sections reorganized and rewritten to enhance clarity. As in the first edition, each new topic is introduced carefully and explained thoroughly. Many introductory sections have been rewritten to update them and make them more approachable for students. Whenever possible, illustrations have been added or modified to help students visualize the physical concepts.

The emphasis continues to be on *chemical reactivity*. Chemical reactions are introduced as soon as possible, and each functional group is considered in view of its reactivity toward electrophiles, nucleophiles, oxidants, reductants, and other reagents. “Electron-pushing” mechanisms are stressed throughout as a means of explaining and predicting this reactivity. Structural concepts such as stereochemistry and spectroscopy are thoroughly treated as useful techniques that enhance the fundamental study of chemical reactivity.

Organization

This book maintains the traditional organization that concentrates on one functional group at a time while comparing and contrasting the reactivity of different functional groups. Reactions are emphasized, beginning with Lewis acid–base reactions in Chapter 1, continuing with thermodynamics and kinetics in Chapter 4, and covering most of the important substitution, addition, and elimination reactions in the three chapters following stereochemistry.

Spectroscopic techniques (IR, MS, and NMR) are covered in Chapters 12 and 13, so that they can be included in the first semester if desired. This early coverage is needed to allow effective use of spectroscopy in the laboratory. Still, a large amount of organic chemistry has been covered before this digression into structure determination. The principles of spectroscopy are practiced and reinforced in later chapters, where the characteristic spectral features of each functional group are summarized and reinforced by practice problems.

Key Features

FLEXIBILITY OF COVERAGE

No two instructors teach organic chemistry exactly the same way. This book covers all the fundamental topics in detail, building each new concept on those that come before. Many topics may be given more or less emphasis at the discretion of the instructor. Examples of these topics are ^{13}C NMR spectroscopy, ultraviolet spectroscopy, conservation of orbital symmetry, amino acids and proteins, nucleic acids, and the special topics chapters, lipids and synthetic polymers.

Another area of flexibility is in the problems. The wide-ranging problem sets review the material from several viewpoints, and more study problems are provided than most students are able to complete. This large variety allows the instructor to select the most appropriate problems for the individual course.

UP-TO-DATE TREATMENT

In addition to the classical reactions, this book covers many techniques and reactions that have more recently gained wide use among practicing chemists. Molecular-orbital theory is introduced early and used to explain electronic effects in conjugated and aromatic systems, pericyclic reactions, and ultraviolet spectroscopy. Carbon-13 NMR spectroscopy is treated as the routine tool it has become in most research laboratories, and the DEPT technique is introduced in this edition. Many of the newer synthetic techniques are also included, such as asymmetric hydrogenation and epoxidation, use of sodium triacetoxyborohydride, Birch reduction, Swern oxidations, alkylation of 1,3-dithianes, olefin metathesis, and oxidations using pyridinium chlorochromate.

REACTION MECHANISMS

Reaction mechanisms are important in all areas of organic chemistry, but they are difficult for many students. Students fall into the trap of memorizing a mechanism while not understanding why it proceeds as it does. This book stresses the principles used to predict mechanisms. Problem-solving sections develop basic techniques for approaching

mechanism problems, and they work to minimize rote memorization. These techniques emphasize deciding whether the reaction is acidic, basic, or free radical in nature, then breaking it down into Lewis acid–base interactions and using “electron pushing arrows” to illustrate these individual steps. Important mechanisms are highlighted by placing them in the *Mechanism* and *Key Mechanism* boxes.

INTRODUCTION TO MECHANISMS USING FREE-RADICAL HALOGENATION

The advantages and disadvantages of using free-radical halogenation to introduce reaction mechanisms have been debated for many years. The principal objection to free-radical halogenation is that it is not a useful synthetic reaction. But useful reactions such as nucleophilic substitution and additions to alkenes are complicated by participation of the solvent and other effects. Gas-phase free-radical halogenation allows a clearer treatment of kinetics and thermodynamics, as long as its disadvantages as a synthetic reaction are discussed and students are aware of the limitations.

ORGANIC SYNTHESIS

Organic synthesis is stressed throughout this book, with progressive discussions of the process involved in developing a synthesis. *Retrosynthetic analysis* is emphasized, and the student learns to work backward from the target compound and forward from the starting materials to find a common intermediate.

Typical yields have been provided for many synthetic reactions, although I hope students will not misuse these numbers. Too often students consider the yield of a reaction to be a fixed characteristic just as the melting point of a compound is fixed. In practice, many factors affect product yields, and literature values for apparently similar reactions often differ by a factor of 2 or more. The yields given in this book are *typical* yields that a good student with excellent technique might obtain.

SPECTROSCOPY

Spectroscopy is one of the most important tools of the organic chemist. This book develops the theory for each type of spectroscopy and then discusses the characteristic spectral features. The most useful and dependable characteristics are summarized into a small number of rules of thumb that allow the student to interpret most spectra without looking up or memorizing large tables of data. For reference use, extensive tables of NMR and IR data and a more complete version of the Woodward–Fieser rules for UV are provided as appendices.

This approach is particularly effective with IR and NMR spectroscopy, and with mass spectrometry. Practical rules are given to help students see what information is available in the spectrum and what spectral characteristics usually correspond to what structural features. Sample problems show how the information from various spectra is combined to propose a structure. The emphasis is on helping students develop an intuitive feel for using spectroscopy to solve structural problems.

NOMENCLATURE

IUPAC nomenclature is stressed throughout the book, but common nomenclature is also discussed and used to develop students' familiarity. Teaching only the IUPAC nomenclature might be justifiable in theory, but such an approach would handicap students in their further study and use of the literature. Much of the literature of chemistry, biology, and medicine uses common names such as methyl ethyl ketone, isovaleric acid, methyl *tert*-butyl ether, γ -aminobutyric acid, and ϵ -caprolactam. This book emphasizes why systematic nomenclature is often preferred, yet it encourages familiarity with common names as well.

I've enjoyed working on this new edition, and I hope that it is an improved fine-tuning of the sixth edition. I've tried to make this book as error-free as possible, but I'm sure some errors have slipped by. If you find errors, or have suggestions about how the book might be made better, please let me know (L. G. Wade, Whitman College,

Walla Walla, WA 99362; e-mail: wadelg@whitman.edu). Errors can be fixed quickly in the next printing. I've already started a file of possible changes and improvements for the eighth edition, and I hope many of the current users will contribute suggestions to this file. I hope this book makes your job easier and helps more of your students to succeed. That's the most important reason why I wrote it.

Acknowledgments

I am pleased to thank the many talented people who helped with this revision. More than anyone else, Jan Simek, author of the *Solutions Manual*, has consistently provided me with excellent advice and sound judgment through several editions of this book. In this edition, Jan provided input on all of the chapter revisions, and helped with the writing of the new section on olefin metathesis. He also co-authored most of the new problems and all of the Answers to Selected Problems. Particular thanks are also due to John Murdzek and Ray Mullaney, who both made thousands of useful suggestions throughout the writing and revision process, and who helped to shape this new edition.

I would like to thank the reviewers for their valuable insight and commentary. Although I did not adopt all their suggestions, most of them were helpful and contributed to the quality of the final product.

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- 3 烷烃的结构和立体化学
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- 5 立体化学
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- 11 醇的反应
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