

国外化学经典教材系列（影印版）

2

有机反应机理的 书写艺术

**The Art of Writing Reasonable Organic
Reaction Mechanisms**
(2nd Edition)

Robert B. Grossman

原著第2版

 科学出版社

有机反应机理的书写艺术 (原著第2版)

每一个满怀抱负的有机化学家都尝试写出合理的有机反应机理，然而市面上的有关机理正确书写的手册却寥寥无几。本书将帮助学生和科研人员提高这一重要技能。本书的突出特点体现在：正确的书写形式，“常见错误提示”，配以大量的难度适宜的问题。其另一个特色是包含过渡金属参与或催化的反应章节。相对新的课题，例如，烯烃复分解反应、芳香环化反应等在本书中均有所涉及。

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— Jens Hartung, *Angewandte Chemie International Edition*

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— Amy Howell, *Synthesis*

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by Robert B. Grossman

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Preface to the Student

The purpose of this book is to help you learn how to draw reasonable mechanisms for organic reactions. A *mechanism* is a story that we tell to explain how compound **A** is transformed into compound **B** under given reaction conditions. Imagine being asked to describe how you travelled from New York to Los Angeles (an overall reaction). You might tell how you traveled through New Jersey to Pennsylvania, across to St. Louis, over to Denver, then through the Southwest to the West Coast (the mechanism). You might include details about the mode of transportation you used (reaction conditions), cities where you stopped for a few days (intermediates), detours you took (side reactions), and your speed at various points along the route (rates). To carry the analogy further, there is more than one way to get from New York to Los Angeles; at the same time, not every story about how you traveled from New York to Los Angeles is believable. Likewise, more than one reasonable mechanism can often be drawn for a reaction, and one of the purposes of this book is to teach you how to distinguish a reasonable mechanism from a whopper.

It is important to learn how to draw reasonable mechanisms for organic reactions because mechanisms are the framework that makes organic chemistry make sense. Understanding and remembering the bewildering array of reactions known to organic chemists would be completely impossible were it not possible to organize them into just a few basic mechanistic types. The ability to formulate mechanistic hypotheses about how organic reactions proceed is also required for the discovery and optimization of new reactions.

The general approach of this book is to familiarize you with the classes and types of reaction mechanisms that are known and to give you the tools to learn how to draw mechanisms for reactions that you have never seen before. The body of each chapter discusses the more common mechanistic pathways and suggests practical tips for drawing them. The discussion of each type of mechanism contains both worked and unworked problems. You are urged to work the unsolved problems yourself. **Common error alerts** are scattered throughout the text to warn you about common pitfalls and misconceptions that bedevil students. Pay attention to these alerts, as failure to observe their strictures has caused many, many exam points to be lost over the years.

Occasionally, you will see indented, tightly spaced paragraphs such as this one. The information in these paragraphs is usually of a parenthetical nature, either because it deals with formalisms, minor points, or exceptions to general rules, or because it deals with topics that extend beyond the scope of the textbook.

Extensive problem sets are found at the end of all chapters. The *only way* you will learn to draw reaction mechanisms is to *work the problems!* If you do not work problems, you will not learn the material. The problems vary in difficulty from relatively easy to very difficult. Many of the reactions covered in the problem sets are classical organic reactions, including many “name reactions.” All examples are taken from the literature. Additional problems may be found in other textbooks. Ask your librarian, or consult some of the books discussed below.

Detailed answer keys are provided in a separate volume that is available for download from the Springer-Verlag web site (<http://www.springer-ny.com/detail.tpl?isbn=0387985409>) at no additional cost. The answer keys are formatted in PDF. You can view or print the document on any platform with Adobe's Acrobat Reader®, a program that is available for free from Adobe's web site (<http://www.adobe.com>). It is important for you to be able to work the problems *without* looking at the answers. Understanding what makes *Pride and Prejudice* a great novel is not the same as being able to write a great novel yourself. The same can be said of mechanisms. If you find you have to look at the answer to solve a problem, be sure that you work the problem again a few days later. Remember, you will have to work problems like these on exams. If you can't solve them at home without looking at the answers, how do you expect to solve them on exams when the answers are no longer available?

This book assumes you have studied (and retained) the material covered in two semesters of introductory organic chemistry. You should have a working familiarity with hybridization, stereochemistry, and ways of representing organic structures. You do not need to remember specific reactions from introductory organic chemistry, although it will certainly help. If you find that you are weak in certain aspects of introductory organic chemistry or that you don't remember some important concepts, you should go back and review that material. There is no shame in needing to refresh your memory occasionally. Pine's *Organic Chemistry*, 5th ed. (McGraw-Hill, 1987) and Scudder's *Electron Flow in Organic Chemistry* (John Wiley & Sons, 1992) provide basic information supplemental to the topics covered in this book.

This book definitely does not attempt to teach specific synthetic procedures, reactions, or strategies. Only rarely will you be asked to *predict* the products of a particular reaction. This book also does not attempt to teach physical organic chemistry (i.e., how mechanisms are proven or disproven in the laboratory). Before you can learn how to determine reaction mechanisms experimentally, you must learn what qualifies as a reasonable mechanism in the first place. Isotope effects, Hammett plots, kinetic analysis, and the like are all left to be learned from other textbooks.

Errors occasionally creep into any textbook, and this one is no exception. I have posted a page of errata at this book's Web site (<http://www.chem.uky.edu/research/grossman/textbook.html>). If you find an error that is not listed there, please contact me (rbgros1@uky.edu). In gratitude and as a reward, you will be immortalized on the Web page as an alert and critical reader.

Graduate students and advanced undergraduates in organic, biological, and medicinal chemistry will find the knowledge gained from a study of this book invaluable for both their graduate careers, especially cumulative exams, and their professional work. Chemists at the bachelor's or master's level who are working in industry will also find this book very useful.

Lexington, Kentucky
January 2002

Robert B. Grossman

Preface to the Instructor

Intermediate organic chemistry textbooks generally fall into two categories. Some textbooks survey organic chemistry rather broadly, providing some information on synthesis, some on drawing mechanisms, some on physical organic chemistry, and some on the literature. Other textbooks cover either physical organic chemistry or organic synthesis in great detail. There are many excellent textbooks in both of these categories, but as far as I am aware, there are only a handful of textbooks that teach students how to write a reasonable mechanism for an organic reaction. Carey and Sundberg, *Advanced Organic Chemistry, Part A*, 4th ed. (New York: Kluwer Academic/Plenum Publishers, 2000), Lowry and Richardson's *Mechanism and Theory in Organic Chemistry*, 3rd ed. (New York: Addison Wesley, 1987), and Carroll's *Perspectives on Structure and Mechanism in Organic Chemistry* (Monterey CA: Brooks/Cole Publishing Co., 1998), are all physical organic chemistry textbooks. They teach students the experimental basis for elucidating reaction mechanisms, not how to draw reasonable ones in the first place. Smith and March, *March's Advanced Organic Chemistry*, 5th ed. (John Wiley & Sons, 2001) provides a great deal of information on mechanism, but its emphasis is synthesis, and it is more a reference book than a textbook. Scudder's *Electron Flow in Organic Chemistry* (John Wiley & Sons, 1992) is an excellent textbook on mechanism, but it is suited more for introductory organic chemistry than for an intermediate course. Edenborough's *Writing Organic Reaction Mechanisms: A Practical Guide*, 2nd ed. (Bristol, PA: Taylor & Francis, 1997) is a good self-help book, but it does not lend itself to use in an American context. Miller and Solomon's *Writing Reaction Mechanisms in Organic Chemistry*, 2nd ed. (New York: Academic Press, 1999) is the textbook most closely allied in purpose and method to the present one. This book provides an alternative to Miller & Solomon and to Edenborough.

Existing textbooks usually fail to show how common mechanistic steps link seemingly disparate reactions, or how seemingly similar transformations often have wildly disparate mechanisms. For example, substitutions at carbonyls and nucleophilic aromatic substitutions are usually dealt with in separate chapters in other textbooks, despite the fact that the mechanisms are essentially identical. This textbook, by contrast, is organized according to mechanistic types, not ac-

ording to overall transformations. This rather unusual organizational structure, borrowed from Miller and Solomon, is better suited to teaching students how to draw reasonable mechanisms than the more traditional structures, perhaps because the all-important first steps of mechanisms are usually more closely related to the conditions under which the reaction is executed than they are to the overall transformation. The first chapter of the book provides general information on such basic concepts as Lewis structures, resonance structures, aromaticity, hybridization, and acidity. It also shows how nucleophiles, electrophiles, and leaving groups can be recognized, and it provides practical techniques for determining the general mechanistic type of a reaction and the specific chemical transformations that need to be explained. The following five chapters examine polar mechanisms taking place under basic conditions, polar mechanisms taking place under acidic conditions, pericyclic reactions, free-radical reactions, and transition-metal-mediated and -catalyzed reactions, giving typical examples and general mechanistic patterns for each class of reaction along with practical advice for solving mechanism problems.

This textbook is *not* a physical organic chemistry textbook! The sole purpose of this textbook is to teach students how to come up with reasonable mechanisms for reactions that they have never seen before. As most chemists know, it is usually possible to draw more than one reasonable mechanism for any given reaction. For example, both an S_N2 and a single electron transfer mechanism can be drawn for many substitution reactions, and either a one-step concerted or a two-step radical mechanism can be drawn for [2 + 2] photocycloadditions. In cases like these, my philosophy is that the student should develop a good command of simple and generally sufficient reaction mechanisms before learning the modifications that are necessitated by detailed mechanistic analysis. I try to teach students how to draw reasonable mechanisms by *themselves*, not to teach them the "right" mechanisms for various reactions.

Another important difference between this textbook and others is the inclusion of a chapter on the mechanisms of transition-metal-mediated and -catalyzed reactions. Organometallic chemistry has pervaded organic chemistry in recent years, and a working knowledge of the mechanisms of such reactions as metal-catalyzed hydrogenation, the Stille and Suzuki couplings, and olefin metathesis is absolutely indispensable to any self-respecting organic chemist. Many organometallic chemistry textbooks discuss the mechanisms of these reactions, but the average organic chemistry student may not take a course on organometallic chemistry until fairly late in his or her studies, if at all. This textbook is the first on organic mechanisms to discuss these very important topics.

In all of the chapters, I have made a great effort to show the forest for the trees and to demonstrate how just a few concepts can unify disparate reactions. This philosophy has led to some unusual pedagogical decisions. For example, in the chapter on polar reactions under acidic conditions, protonated carbonyl compounds are depicted as carbocations in order to show how they undergo the same three fundamental reactions (addition of a nucleophile, fragmentation, and re-

arrangement) that other carbocations undergo. Radical anions are also drawn in an unusual manner to emphasize their reactivity in $S_{RN}1$ substitution reactions.

This philosophy has led to some unusual organizational decisions, too. $S_{RN}1$ reactions and carbene reactions are treated in the chapter on polar reactions under basic conditions. Most books on mechanism discuss $S_{RN}1$ reactions at the same time as other free-radical reactions, and carbenes are usually discussed at the same time as carbocations, to which they bear some similarities. I decided to locate these reactions in the chapter on polar reactions under basic conditions because of the book's emphasis on teaching practical methods for drawing reaction mechanisms. Students cannot be expected to look at a reaction and know immediately that its mechanism involves an electron-deficient intermediate. Rather, the mechanism should flow naturally from the starting materials and the reaction conditions. $S_{RN}1$ reactions usually proceed under strongly basic conditions, as do most reactions involving carbenes, so these classes of reactions are treated in the chapter on polar reactions under basic conditions. However, Favorskii rearrangements are treated in the chapter on pericyclic reactions, despite the basic conditions under which these reactions occur, to emphasize the pericyclic nature of the key ring contraction step.

Stereochemistry is not discussed in great detail, except in the context of the Woodward–Hoffmann rules. Molecular orbital theory is also given generally short shrift, again except in the context of the Woodward–Hoffmann rules. I have found that students must master the basic principles of drawing mechanisms before additional considerations such as stereochemistry and MO theory are loaded onto the edifice. Individual instructors might wish to put more emphasis on stereoelectronic effects and the like as their tastes and their students' abilities dictate.

I agonized a good deal over which basic topics should be covered in the first chapter. I finally decided to review a few important topics from introductory organic chemistry in a cursory fashion, reserving detailed discussions for common misconceptions. A basic familiarity with Lewis structures and electron-pushing is assumed. I rely on Weeks's excellent workbook, *Pushing Electrons: A Guide for Students of Organic Chemistry*, 3rd ed. (Saunders College Publishing, 1998), to refresh students' electron-pushing abilities. If Weeks fails to bring students up to speed, an introductory organic chemistry textbook such as Joseph M. Hornback's *Organic Chemistry* (Brooks/Cole, 1998) should probably be consulted.

I have written the book in a very informal style. The second person is used pervasively, and an occasional first-person pronoun creeps in, too. Atoms and molecules are anthropomorphized constantly. The style of the book is due partly to its evolution from a series of lecture notes, but I also feel strongly that anthropomorphization and exhortations addressed directly to the student aid greatly in pushing students to think for themselves. I vividly remember my graduate physical organic chemistry instructor asking, "What would you do if *you* were an electron?", and I remember also how much easier mechanisms were to solve after he asked that question. The third person and the passive tense certainly have

their place in scientific writing, but if we want to encourage students to take intellectual control of the material themselves, then maybe we should stop talking about our theories and explanations as if they were phenomena that happened only “out there” and instead talk about them as what they are: our best attempts at rationalizing the bewildering array of phenomena that Nature presents to us.

I have not included references in this textbook for several reasons. The primary literature is full of reactions, but the mechanisms of these reactions are rarely drawn, and even when they are, it is usually in a cursory fashion, with crucial details omitted. Moreover, as stated previously, the purpose of this book is not to teach students the “correct” mechanisms, it is to teach them how to draw *reasonable* mechanisms using their own knowledge and some basic principles and mechanistic types. In my opinion, references in this textbook would serve little or no useful pedagogical purpose. However, some general guidance as to where to look for mechanistic information is provided at the end of the book.

All of the chapters in this book except for the one on transition-metal-mediated and -catalyzed reactions can be covered in a one-semester course.

The present second edition of this book corrects two major errors (the mechanisms of substitution of arenediazonium ions and why Wittig reactions proceed) and some minor ones in the first edition. Free-radical reactions in Chapter 5 are reorganized into chain and nonchain processes. The separate treatment of transition-metal-mediated and -catalyzed reactions in Chapter 6 is eliminated, and more in-text problems are added. Some material has been added to various chapters. Finally, the use of italics, especially in Common Error Alerts, has been curtailed.

I would like to thank my colleagues and students here at the University of Kentucky and at companies and universities across the country and around the world for their enthusiastic embrace of the first edition of this book. Their response was unexpected and overwhelming. I hope they find this new edition equally satisfactory.

Lexington, Kentucky
January 2002

Robert B. Grossman

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