

**SECOND  
EDITION**

# **Writing Reaction Mechanisms in Organic Chemistry**

**描述有机化学反应机理  
(第2版)**

**Audrey Miller · Philippa H. Solomon**

ADVANCED ORGANIC CHEMISTRY SERIES



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ADVANCED ORGANIC CHEMISTRY SERIES

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## P R E F A C E   T O   T H E   S E C O N D   E D I T I O N

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In revising this text for the second edition, a major goal was to make the book more user-friendly for both graduate and undergraduate students. Introductory material has been fleshed out. Headings have been added to make it easier to locate topics. The structures have been redrawn throughout, with added emphasis on the stereochemical aspects of reaction mechanisms. Coverage of some topics such as solvent effects and neighboring group effects has been expanded, and Chapter 6 has been completely reorganized and extensively rewritten.

As in the previous edition, the focus of this book is on the *how* of writing organic mechanisms. For this reason and to keep the book compact and portable, the number of additional examples and problems has been minimized, and no attempt has been made to cover additional topics such as oxidation-reduction and organotransition metal reactions. The skills developed while working through the material in this book should equip the reader to deal with reactions whose mechanisms have been explored less thoroughly.

I am most grateful to the reviewers, who gave so generously of their time and experience in making suggestions for improving this book. Particular thanks go to series editor Jim Whitesell, who cast his eagle eye over the numerous structures and contributed to many stimulating discussions. Thanks also to John DiCesare and Hilton Weiss, and to John Murdzek, who meticulously annotated the entire manuscript both before and after revisions. Any comments regarding errors or suggestions for improvements in future editions will be most welcome.

Finally, my warmest thanks go to my husband, Dan, and to my children, Michael, Sarah, and Jeremy. Their loyal support, unflagging patience, and bizarre sense of humor bolster my spirits daily and shortened the long hours involved in preparing the manuscript.

*Philippa Solomon*

## P R E F A C E   T O   T H E   F I R S T   E D I T I O N

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The ability to write feasible reaction mechanisms in organic chemistry depends on the extent of the individual's preparation. This book assumes the knowledge obtained in a one-year undergraduate course. A course based on this book is suitable for advanced undergraduates or beginning graduate students in chemistry. It can also be used as a supplementary text for a first-year course in organic chemistry.

Because detailed answers are given to all problems, the book also can be used as a tutorial and a review of many important organic reaction mechanisms and concepts. The answers are located conveniently at the end of each chapter. Examples of unlikely mechanistic steps have been drawn from my experience in teaching a course for beginning graduate students. As a result, the book clears up many aspects that are confusing to students. The most benefit will be obtained from the book if an intense effort is made to solve the problem before looking at the answer. It is often helpful to work on a problem in several different blocks of time.

The first chapter, a review of fundamental principles, reflects some of the deficiencies in knowledge often noted in students with the background cited above. The second chapter discusses some helpful techniques that can be utilized in considering possible mechanisms for reactions that may be found in the literature or during the course of laboratory research. The remaining chapters describe several of the common types of organic reactions and their mechanisms and propose mechanisms for a variety of reactions reported in the literature. The book does not cover all types of reactions. Nonetheless,



anyone who works all the problems will gain insights that should facilitate the writing of reasonable mechanisms for many organic reactions.

Literature sources for most of the problems are provided. The papers cited do not always supply an answer to the problem but put the problem into a larger context. The answers to problems and examples often consider more than one possible mechanism. Pros and cons for each mechanism are provided. In order to emphasize the fact that frequently more than one reasonable pathway to a product may be written, in some cases experimental evidence supporting a particular mechanism is introduced only at the end of consideration of the problem. It is hoped that this approach will encourage users of this book to consider more than one mechanistic pathway.

I acknowledge with deep gratitude the help of all the students who have taken the course upon which this book is based. Special thanks to Drs. David Kronenthal, Tae-Woo Kwon, and John Freilich and Professor Hilton Weiss for reading the manuscript and making extremely helpful suggestions. Many thanks to Dr. James Holden for his editing of the entire manuscript and to my editor, Nancy Olsen, for her constant encouragement.

*Audrey Miller*

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# I

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# Introduction—Molecular Structure and Reactivity

Reaction mechanisms offer us insights into how molecules react, enable us to manipulate the course of known reactions, aid us in predicting the course of known reactions using new substrates, and help us to develop new reactions and reagents. In order to understand and write reaction mechanisms, it is essential to have a detailed knowledge of the structures of the molecules involved and to be able to notate these structures unambiguously. In this chapter, we present a review of fundamental principles relating to molecular structure and of ways to convey structural information. A crucial aspect of structure from the mechanistic viewpoint is the distribution of electrons, so this chapter outlines how to analyze and notate electron distributions. Mastering the material in this chapter will provide you with the tools you need to propose reasonable mechanisms and to convey these mechanisms clearly to others.

## I. HOW TO WRITE LEWIS STRUCTURES AND CALCULATE FORMAL CHARGES

The ability to construct Lewis structures is fundamental to writing or understanding organic reaction mechanisms. It is particularly important because lone pairs of electrons frequently are crucial to the mechanism but often are omitted from structures appearing in the chemical literature.

There are two methods commonly used to show Lewis structures. One shows all electrons as dots. The other shows all bonds (two shared electrons) as lines and all unshared electrons as dots.

### A. Determining the Number of Bonds

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**Hint 1.1**

To facilitate the drawing of Lewis structures, estimate the number of bonds.

For a stable structure with an even number of electrons, the number of bonds is given by the equation:

$$(\text{Electron Demand} - \text{Electron Supply}) / 2 = \text{Number of Bonds}$$

The electron demand is two for each hydrogen and eight for all other atoms usually considered in organic chemistry. (The tendency of most atoms to acquire eight valence electrons is known as the octet rule.) For elements in group IIIA (e.g., B, Al, Ga), the electron demand is six. Other exceptions are noted, as they arise, in examples and problems.

For neutral molecules, the contribution of each atom to the electron supply is the number of valence electrons of the neutral atom. (This is the same as the group number of the element when the periodic table is divided into eight groups.) For ions, the electron supply is decreased by one for each positive charge of a cation and is increased by one for each negative charge of an anion.

Use the estimated number of bonds to draw that number of two-electron bonds in your structure. This may involve drawing a number of double and triple bonds (see the following section).

### B. Determining the Number of Rings and / or $\pi$ Bonds (Degree of Unsaturation)

The total number of rings and/or  $\pi$  bonds can be calculated from the molecular formula, bearing in mind that in an acyclic saturated hydrocarbon the number of hydrogens is  $2n + 2$ , where  $n$  is the number of carbon atoms.

Each time a ring or  $\pi$  bond is formed, there will be two fewer hydrogens needed to complete the structure.

On the basis of the molecular formula, the degree of unsaturation for a hydrocarbon is calculated as  $(2m + 2 - n) / 2$ , where  $m$  is the number of carbons and  $n$  is the number of hydrogens. The number calculated is the number of rings and / or  $\pi$  bonds. For molecules containing heteroatoms, the degree of unsaturation can be calculated as follows:

**Hint 1.2**

*Nitrogen:* For each nitrogen atom, subtract 1 from  $n$ .

*Halogens:* For each halogen atom, add 1 to  $n$ .

*Oxygen:* Use the formula for hydrocarbons.

This method cannot be used for molecules in which there are atoms like sulfur and phosphorus whose valence shell can expand beyond eight.

**Example 1.1.** Calculate the number of rings and/or  $\pi$  bonds corresponding to each of the following molecular formulas.

a.  $\text{C}_2\text{H}_2\text{Cl}_2\text{Br}_2$

There are a total of four halogen atoms. Using the formula  $(2m + 2 - n) / 2$ , we calculate the degree of unsaturation to be  $[2(2) + 2 - (2 + 4)] / 2 = 0$ .

b.  $\text{C}_2\text{H}_3\text{N}$

There is one nitrogen atom, so the degree of unsaturation is  $[2(2) + 2 - (3 - 1)] = 2$ .

### C. Drawing the Lewis Structure

Start by drawing the skeleton of the molecule, using the correct number of rings or  $\pi$  bonds, then attach hydrogen atoms to satisfy the remaining valences. For organic molecules, the carbon skeleton frequently is given in an abbreviated form.

Once the atoms and bonds have been placed, add lone pairs of electrons to give each atom a total of eight valence electrons. When this process is complete, there should be two electrons for hydrogen, six for B, Al, or Ga, and eight for all other atoms. The total number of valence electrons for each element in the final representation of a molecule is obtained by counting each electron around the element as one electron, even if the electron is shared with another atom. (This should not be confused with counting electrons for charges or formal charges; see Section 1.D.) The number of valence electrons around each atom equals the electron demand. Thus, when