Organic Chemistry

G. MARC LOUDON

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Purdue University

ADDISON-WESLEY PUBLISHING COMPANY
Reading, Massachusetts • Menlo Park, California • London
Amsterdam • Don Mills, Ontario • Sydney

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Library of Congress Cataloging in Publication Data

Loudon, G. Marc.
Organic chemistry.

Includes index.
1. Chemistry, Organic. I. Title.
QD251.2.L68 1983 547 83-7073
ISBN 0-201-14438-7

ABCDEFGHIJ-RN-8987654

Preface

This book was written because I have for several years felt the need for a text that corresponds more closely to the course I teach than the existing texts do. Although it is organized along tried-and-true functional group lines, the book contains some unique features that have served me well in both my teaching and learning of organic chemistry. In the hope that others will find some of my ideas useful, I offer yet another organic chemistry text.

Although the "curved-arrow" formalism is a standard mechanistic tool in the repertoire of most practicing organic chemists, this useful device has received surprisingly little emphasis in fundamental texts. In this book the two-electron curved-arrow formalism is introduced in Sections 1.3 and 1.4 with two of chemistry's most fundamental reactions. The Lewis acid–base reaction illustrates the formalism used in the addition reaction, and the Brønsted acid–base reaction illustrates that used in the displacement. All other polar reactions, no matter how complex, can be written essentially as combinations of these simple processes. Students are systematically shown how to use this formalism and are tested on their understanding before embarking on their study of organic chemistry.

Organic chemistry can be taught using several different reactions as the "mechanistic centerpiece"—the reaction that is used to introduce mechanistic concepts. Most authors use free-radical halogenation of alkanes to develop mechanistic principles. I have found that polar or heterolytic reactions make more attractive mechanistic vehicles because so many more of the reactions that the student encounters in a first course are of this type. One or two authors with a similar point of view have used S_N1 and S_N2 displacements as the mechanistic point of departure. I have found such an approach difficult because it inevitably requires analysis of relative rate data for reactions of different starting materials involving different intermediates with energies that cannot be rigorously compared. (Of course, most of us at one time or another have compared the energies of nonisomeric secondary and tertiary carbonium ions, but beginning students are not in a position to appreciate the approximations and assumptions inherent in such a comparison.) The approach taken here is completely different, using polar additions to alkenes as the mechanistic centerpiece (Chapter 4). *Addition to an unsymmetrical alkene such as isobutylene provides a built-in competition between two reaction pathways from a common starting material through isomeric intermediates with energies that can be directly and meaningfully compared.* Carbonium ion chemistry can be introduced immediately, and the consequences of relative carbonium ion stability are immediately obvious in the outcome of the reaction, as codified in the Markovnikov rule. The two-electron arrow formalism is used consistently throughout this discussion.

Although I find the use of heterolytic reactions to be the best introductory mechanistic vehicle, free-radical processes are not ignored. They are not introduced, however, until the student has had a chance to master the rudiments of the two-electron formalism throughout Chapter 4. After an interlude in Chapter 5 dealing with rates and equilibria (which uses examples from the alkene chemistry of Chapter 4), homolytic processes make their appearance in Chapter 6, where the student is taught the one-electron ("fishhook") formalism. Here free-radical addition to alkenes is used as the mechanistic vehicle. Additions to alkenes are used as examples again in the discussion of the role of stereochemistry in chemical reactions (Chapter 8).

Within its functional group framework the text places strong emphasis on mechanisms, particularly in the relationship of the mechanisms of different reactions to each other. Many elementary organic reactions find analogy in simple acid-base chemistry, and I have not hesitated to drive this point home repeatedly. A mechanistic emphasis is important so that students take away from a first course in organic chemistry an understanding of why molecules react as they do, as well as some rudimentary ability to predict the outcome of organic reactions. The mechanistic approach has served my students well in subsequent courses such as biochemistry that build on an organic background, and it discourages the tendency of some students to memorize their way through the first course.

Structure and bonding are introduced in Chapter 1 using Lewis concepts only. The student is required to master the rudiments of Lewis structures before elementary quantum-mechanical concepts are introduced in Chapter 3. After all, most organic reactions can be adequately discussed with Lewis structures. As fundamental as Lewis structures are, many students have difficulties with organic chemistry that are attributable in good measure to a shaky foundation with Lewis structures; therefore, this topic receives heavy emphasis in the first chapter. Resonance is also introduced in Chapter 1, and students are taught there that the arrow formalism can also be used to draw resonance structures. However, in this first discussion resonance is used only as a device for describing molecules that are inadequately portrayed by a single Lewis structure. The energetic ramifications of resonance arguments are deferred until Chapter 14.

Despite the mechanistic emphasis of the book, chemical synthesis is not given short shrift, but it is developed in a somewhat unique way. In most cases a synthesis is not discussed until the student has had the mechanistic basis for understanding the reaction. For example, the student learns no alkene syntheses in Chapter 4 or 6 because the mechanistic foundations for discussing the E2 elimination or the Wittig reaction have not been laid. However, the student does learn syntheses that start with alkenes, such as hydroboration. Nowhere in my text will the student find a table listing twenty-five ways to make alkenes; but when an alkene synthesis is discussed farther down the line, the student has the tools to use the reaction intelligently with proper attention to its mechanism and, if appropriate, its stereochemistry. There is plenty of practice in chemical synthesis within the early chapters, but the emphasis on synthesis grows throughout the text until its culmination in the overview of organic synthesis in Section 25.4. This section logically follows the chapters on the carbonyl-containing functional groups since carbonyl chemistry is the linchpin of modern organic synthesis.

Also in Chapter 25 is an introduction to the chemical literature, which, if not immediately useful in the first course, should prove to be of archival value to any student moving into undergraduate research.

The treatment of nomenclature in this text reflects my belief that a student should, after completing a first course, be able to construct a systematic name for most common types of organic compounds—not just for alkanes. The number of supplementary texts available that deal solely with nomenclature suggests to me that others seem to share this view and are dissatisfied with the typical treatment of nomenclature. This text gives somewhat more attention to nomenclature than most, emphasizing the logical and straightforward IUPAC concept of the principal group and principal chain in the construction of systematic names. Common nomenclature is also covered.

Aromatic chemistry is fully introduced in Chapter 15, about half-way through the text, and is integrated into subsequent chapters. However, the notion that there is something special about aromatic chemistry and aryl groups is presented much earlier, in Section 2.9; and in a somewhat unique treatment in Section 4.13, benzene is described as a "puzzling alkene." Thus the student obtains an early appreciation of the lack of reactivity of the phenyl ring, and compounds containing unreactive aromatic rings are used in examples throughout the text prior to Chapter 15.

Some of the most important research in recent years has concerned the role of solvent in chemical reactions. In Section 19.4 the student learns to classify solvents and discovers some of the factors that govern solubility and the effect of solvent on reaction rate. In other parts of the text I have also discussed briefly gas-phase acidity and its relationship to solution acidity.

Some experimental aspects of organic chemistry are presented here and there, not as verbatim procedures, but as asides about reagents and conditions and their role in the success of a reaction. For example, I have noted how Le Chatelier's principle plays a crucial role in certain reactions and how chemical properties, including acidity and basicity, are important in the design of some chemical separations. Actual literature yields are given for most reactions. I have in a few places discussed experiments that have led to key conclusions. In some problems the student is asked to formulate a theory from data in a table before the theory is discussed in the text. I have tried to drive home repeatedly the point that organic chemistry is an experimental science and that theories are born of, and tested by, experiment.

The chapters on spectroscopy are oriented toward determination of structure and contain only a modest amount of theory. Chapter 11 (NMR), in particular, contains a step-by-step guide to interpreting spectra that utilizes a prodigious number of actual spectra with gradually increasing complexity. The length of the spectroscopy chapters is attributable largely to this step-by-step approach; these chapters do not really contain an unusually large amount of material. The NMR chapter does, however, contain a discussion of certain topics that might be considered optional, such as group equivalence and nonequivalence and dynamic NMR.

The text contains more than 1550 original problems, many of them class-tested. A substantial number are based on actual cases in the chemical literature. The in-text problems are largely of the drill type, and the ones following each chapter, although containing some drill material, largely serve to integrate the material of the foregoing chapters. Among these problems are some that can be worked easily by the student of modest abilities as well as some that will challenge the brightest students.

Within the text cross-referencing is unusually extensive so that the student should have little difficulty locating discussion of a seminal topic. I have also not hesitated to use mundane analogies that help the student relate possibly unfamiliar principles to common experience. Several different techniques have been used to improve problem-solving skills: in-text solutions to in-text problems; advice on how to solve particular types of problems; and several examples of retrosynthetic analysis. There are a number of brief historical essays, most of an anecdotal flavor, intended to emphasize to the student that chemistry is a human endeavor and that the road to knowledge is paved with frustration, serendipity, and humor. The process of discovery is seldom as cut-and-dried as textbooks might make it seem.

The text contains many examples from biology, not set apart in separate chapters but included in special sections that occur near the chemistry to which they relate and that stress the chemical principles involved. There are also examples of industrial or societal relevance designed to show the importance of chemistry in today's economy and the crucial dependence of industrial chemistry on petroleum.

A strong emphasis is placed on stereochemistry in this text, beginning with the prediction of chemical structure in Section 1.6. The concept of stereoisomers is introduced in Section 4.2. This section also introduces the Cahn–Ingold–Prelog system as part of the *E-Z* designation, even though it is not applied to chiral carbon until Chapter 7, where chirality and the essentials of stereochemical terminology are developed. Conformational analysis and the role of stereochemistry in chemical reactions follow in Chapter 8. Stereochemistry is strongly reinforced thereafter; most chapters contain some discussion and several problems with a stereochemical component, and there are particularly heavy doses of stereochemistry in Chapter 20 (Epoxides and Glycols) as well as in Chapters 28 and 29, which deal with biomolecules. I debated whether to include a section on group equivalence and nonequivalence; my decision to do so arises from the fact that most modern biochemistry courses address this issue and take for granted some student experience with the appropriate concepts! Thus the notion of diastereotopic groups appears in Section 11.9 of the NMR chapter since many of the best nonenzymatic examples of this phenomenon occur in NMR spectra.

During the writing of this book I have always tried to anticipate the questions of a student studying organic chemistry for the first time. At the same time, I have not hesitated to try to challenge the student to think about the subject rather than just memorizing it. My hope is that students using this text will see some of the considerable intellectual beauty of organic chemistry and that a few who were not previously inclined might want to move into a research career.

It would be presumptuous to say that this book is free of factual errors, but I have tried to make it as nearly so as possible by thoroughly researching each topic back to the literature. The text has also benefited from several test-teaching programs in addition to my own at Purdue. I shall greatly appreciate suggestions from users about how it might be improved. I can only conclude by expressing my wish that others will enjoy using this text as much as I have enjoyed writing it.

Many people contributed to the successful completion of this project. I am indebted to my dean, Professor Varro E. Tyler, and to my chairman, Professor John Cassady, for their encouragement and for providing an environment in which writing could proceed in a timely manner, including a semester's leave of absence. I am particularly grateful to Professor John Pinzelik, Chemistry Librarian at Purdue, to Professor Theodora Andrews, Pharmacy Librarian, and to their staffs for constant assistance throughout this project. Several reviewers read the text at various stages and offered constructive and useful criticism, especially Professor Mel Schiavelli of the College of William and Mary; Professor Cary Morrow of the University of New Mexico; Professor Leroy G. Wade of Colorado State University; Professor Guilford Jones II of Boston University; and Professor Mary Hickey of Henry Ford Community College. I am particularly pleased to acknowledge the constant advice, encouragement, and good humor of Professor Ronald Magid of the University of Tennessee, who reviewed the first draft of the manuscript and critically read the second. I am grateful to Professors Cassady, Schiavelli, and Hickey, as well as my Purdue colleague Professor Mark Cushman for conducting test-teaching projects using the text at various stages of its development. In addition I am indebted to the many students who used the trial version of the text and offered constructive advice that was incorporated into the final manuscript.

The relationship between author and publisher has been particularly gratifying, and for this I would especially like to acknowledge Laura Rich Finney, who twisted my arm originally, and Bob Rogers, editor and friend, who helped, goaded, cajoled, and, most importantly, encouraged me to complete this project. Sue Michener, Art Coordinator, and Margaret Pinette, Production Editor, are due special thanks for their work on the text. I am also grateful to Caroline Eastman, who copyedited the final text with exceptional skill and provided much useful advice above and beyond the call of duty.

Thanks are due to Sadtler Research, Inc., Varian Associates, The Aldrich Chemical Company, and the U.S. Government Office of Standard Reference Data (David R. Lide, Chief) for permission to reproduce spectra. I also appreciate greatly the permission of the other publishers and authors, acknowledged in credits at the back of the book, who gave permission to reproduce material in the figures.

Most importantly, I acknowledge the love, encouragement, and forbearance of my family, to whom this book is dedicated.

G. M. L.

West Lafayette, Indiana
October 1983

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