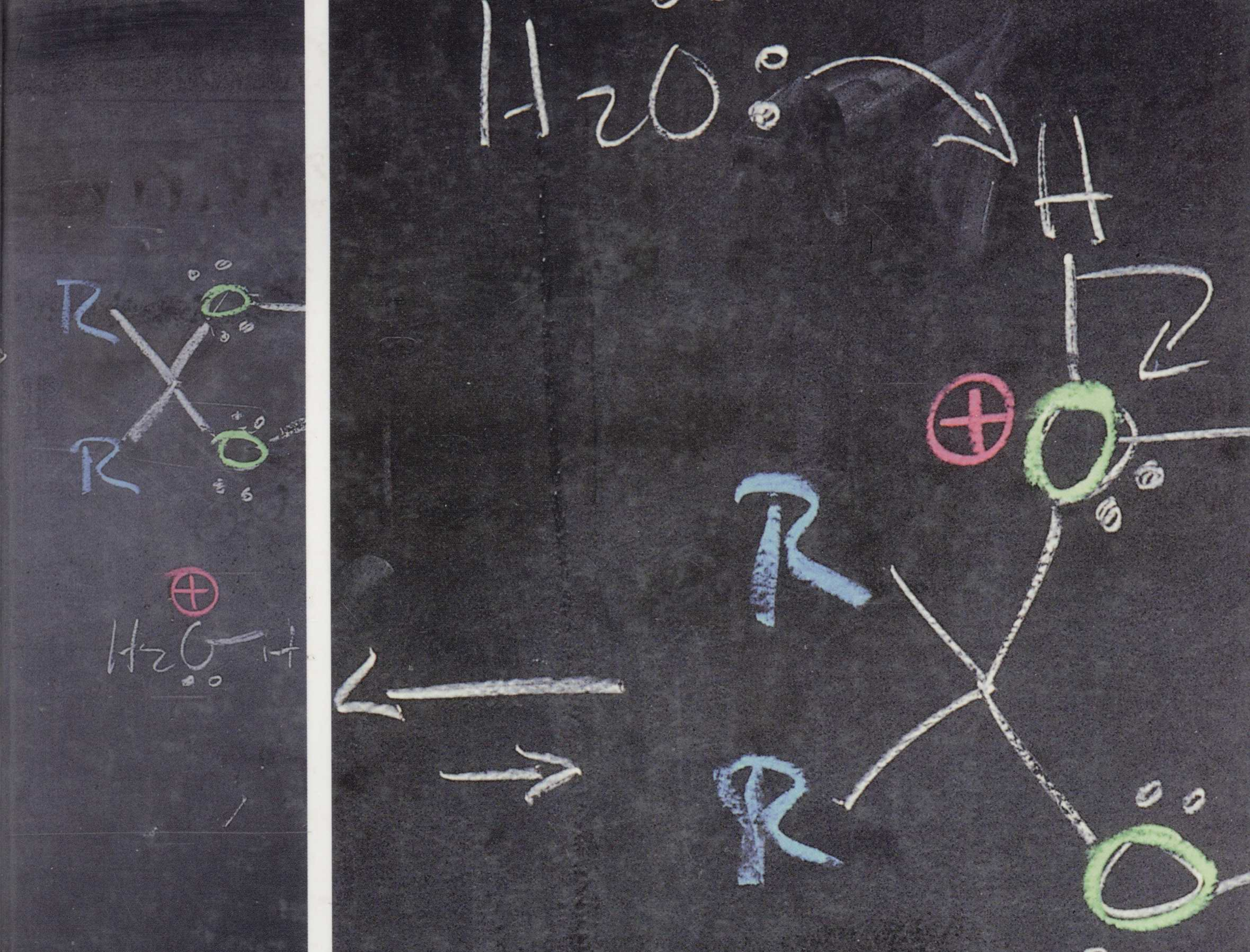

Organic Chemistry

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W · W · NORTON & COMPANY · NEW YORK · LONDON

PRINTED IN THE UNITED STATES OF AMERICA
Composition by TSI Graphics
Manufacturing by R.R. Donnelley & Sons Company
Book design: Jack Meserole
Illustrations: J/B Woolsey Associates
Cover photographs: Nat Clymer
Cover design: Maitland Jones, III, and Susan Hockaday

Library of Congress Cataloging-in-Publication Data
Jones, Maitland, 1937–
Organic chemistry / Maitland Jones, Jr.
p. cm.
Includes index.
ISBN 0-393-97079-5
1. Chemistry, Organic. I. Title.
QD253.J65 1997 96.52944
547—dc21

W.W. Norton & Company, Inc., 500 Fifth Avenue, New York, N.Y. 10110
W.W. Norton & Company, Ltd., 10 Coptic Street, London, WC1A 1PU

2 3 4 5 6 7 8 9 0

Preface

Organic chemistry has long been recognized as an essential ingredient in the education of scientists in a wide range of fields, particularly in the life sciences. Indeed, as more and more disciplines come into contact with organic chemistry, new connections are constantly being forged. By extension, a career in medicine—an applied life science—is also becoming more and more dependent on organic chemistry, and not just because medical schools these days take special notice of the grade in organic! The practice of medicine nowadays increasingly requires a knowledge of the behavior of molecules. The molecular basis of pathogen action and of therapeutic agents are two obvious examples. These are developing areas at the moment, but there can be no doubt that the physician of tomorrow will have to be even more of a scientist—an organic chemist, among other things—than his or her predecessors.

Accordingly, this book is written not just for the chemistry major, but is aimed instead at the person who wants a broad, yet modern introduction to the subject. General principles are stressed, because it is impossible to memorize all the details of this vast subject these days. One can, however, learn to make connections and to apply widely a set of organizing general principles, and that helps to render the prolific detail more manageable.

A Brief Tour of the Book

To understand molecules we must first understand atoms and, especially, the volumes of space occupied by the electrons that orbit the atomic nuclei. Thus, Chapter 1 begins with atoms and electrons. To think sensibly about electrons we need to understand a bit of what quantum mechanics tells us. That does *not* mean that we will all have to become mathematicians, far from it. We only have to understand qualitatively what the mathematicians have to say to us. We also need mathematics because of a problem of scale. We live in a world of certain sizes, and our intuitions are honed by everyday experience. We know how baseballs and basketballs behave. Unfortunately, our experience in the world of such objects poorly equips us to anticipate matters in the large-scale universe—pulsars, quasars, black holes, and other bizarre inhabitants of the macro-universe. What is generally less well appreciated by students is that we operate intuitively just as poorly on the micro scale—the world of atoms and electrons.

Atoms and molecules are really quite strange things; they are not really like the objects that populate our daily experience. For one thing, molecular events take place on a time scale we cannot easily appreciate. Under typical conditions in the gas phase a single molecule undergoes 10^{10}–10^{11} collisions per second. Let's call one of those collisions an ordinary event in a molecule's "life," analogous to an ordinary event in a human life—taking a breath, for example. If you breathe 60 times a minute, you will take over 2.5 billion (2.5×10^9) breaths over an 80-year lifespan. So, in one second, a molecule undergoes more ordinary events than you will take breaths in your entire life. We do not appreciate such differences easily!

The language that makes both the macro scale and the micro scale accessible to us is mathematics. Although we need not do the mathematical operations ourselves, we do need to appreciate some of the things that quantum mechanics has to say to us. Chapter 1 also focuses strongly on Lewis structures—pictorial representations of atoms and ions. Much of this chapter may be review, and if so, this material can be skipped or covered very lightly. However, the ability to write good Lewis structures easily and to determine the locations of charges in molecules with ease is an essential skill. This skill is part of the language of chemistry and will be as important in Chapter 26 as it is in Chapter 1.

Chapter 2 moves on to molecules, and to the regions of space occupied by electrons in molecules: molecular orbitals. Qualitative molecular orbital theory is not too complicated a subject for students, and requires no mathematics. Yet, this simple theory is amazingly powerful in its ability to rationalize and, especially, to predict structure and reactivity. The tutorial in Chapter 2 on qualitative applications of molecular orbital theory is likely to be new to students. This material is very important, as it enables us to emphasize explanations throughout the rest of the book. Not only are traditional subjects such as aromaticity and conjugation (Chapters 12–14) more accessible with the background of Chapter 2, but explanations for the essential, building-block reactions of organic chemistry (Chapters 7 and 9, for example) become possible.

After the two introductory chapters comes a sequence of four chapters on aspects of structure (3–6). Here, some fundamental structural types—some functional groups—are introduced, and stereochemistry is dealt with in depth. This platform allows us to launch a discussion of several archetypal reactions of organic chemistry, and more functional groups, in Chapter 7. Chapter 7 is one of the key chapters, and the reactions of this chapter serve as reference points throughout the book; they are fundamental reactions to which we return over and over again in the later chapters in order to make analogies.

Once we have these basic, reference reactions under control, a general discussion of the role of energetics—kinetics and thermodynamics—becomes appropriate (Chapter 8). Chapters 9 and 10 introduce other building-block reactions, and other functional groups, in the context of a discussion of addition reactions. These provide a foundation for the chemistry of carbonyl compounds, the subject of a series of chapters in the second half of the book (16 and 18–20). Chapter 17 is devoted to a summary of the chemistry of alcohols. As alcohols are exemplars of many of the properties of organic molecules, and are the starting materials or products of many of the reactions of organic chemistry, one may legitimately wonder why we wait so long to bring them up. The answer is that we don't! Chapter 17 appears here as a summary of what has gone before: a collection of all the alcohol chemistry we have discussed in the previous 16 chapters. Alcohol chemistry is scattered throughout the early chapters of the book and is summarized here as a review, and as a prelude to the further chemistry of alcohols that will come in later chapters.

To make an analogy to the study of a language, in the first sequence of reaction chapters (7, 9, and 10) we write sentences constructed from the vocabulary and grammar developed in the early, structural chapters. We will go on in later chapters in the book to more complicated mechanisms and molecules, and to write whole paragraphs and even short essays in organic chemistry. Some of those essays are contained in the "special topics" chapters toward the end of the book (22–26) in which biological chemistry and physical-organic chemistry are further explored with the material of the early chapters as a foundation.

Special Features of This Book

Voice. This book talks directly to the reader, not only about the material at hand, but also about the "how and why" of organic chemistry. It tries to do so in a voice that is personal, not distant. I think it is much easier to enjoy, and learn, organic chemistry if a strong focus on "Where are we and why are we here?" and "What is the best way to do this?" is maintained. Of course, the main arena for such talk must be the lecture, and no book can hope to substitute for the direction and inspiration given by the lecturer. At the same time, it is important for students to hear different voices, to see the path we are all on in different ways. This approach provides at least two views of the material, two different routes to understanding. The sum of these perspectives is likely to be greater than either of them alone.

Flexibility. There is no consensus on the precise order in which to take up many subjects in organic chemistry. This book makes different decisions possible. For example, the spectroscopy chapter is largely free-standing. Traditionally, it comes where it is here, roughly at the midpoint of the book. But cogent arguments can be made that spectroscopy should be introduced earlier, and that is possible, if one is willing to pay the price of delaying the introduction of chemical reactions one more chapter. As in all organic texts, the last few chapters constitute a series of special topics. No one really hopes to finish everything in an organic textbook in one year, and this book provides a number of choices. One might emphasize biological aspects of our science, for example, and Chapters 24–26 provide an opportunity to do this. Alternatively, a more physical approach would see the exciting chemistry of Chapters 22 and 23 as more appropriate.

Extensive Use of Figures and Constructive Use of Color. Organic chemistry is a highly visual subject. Chemists think by constructing mental pictures of molecules, and we talk to each other by drawing pictures. This book favors series of figures over long discussions in the text. The text serves to point out the changes in successive figures. Color is used to highlight change, and track the fates of atoms and groups in reactions. The use of color is judicious, however. There are times when "more is less," and the use of color in organic textbooks can easily fall into this trap. Color is for emphasis. Too much color leads to visual clutter, in which case the emphasis intended by color can be lost.

Cross-Referencing. There is extensive cross-referencing in this book, which is facilitated by the early use of prototypal reaction examples to which analogy is repeatedly made. The reader is consistently reminded that the current material is "not really new—you have seen something like it before, and it's on page xxx." The hope is to supply a unifying treatment in which seemingly different topics are brought together. In turn, this reduces the need to memorize.

Problems. This book incorporates problems in two ways. First, there are many unsolved problems scattered throughout the text, and more, of all degrees of difficulty, are found at the end of each chapter. These range from drill exercises and simple examples designed to emphasize important skills and illustrate techniques, to sophisticated, challenging problems. In the latter cases, we are careful to provide hints and references to material useful for the solution. Answers to all problems of this type can be found in the Study Guide. The Study Guide tries to help students learn how to approach problems, and gives much more than bare-bones answers to most problems. Second, and most critical, is the use of problems as an integral part of the discussion in the text. There are times when a skill must be mastered or a point well understood before further discussion can take place effectively. Rather than simply emphasizing this point in the discussion, a solved, illustrative problem is almost always provided. It is important that these problems be worked. The answer is not there just to be read. These problems are vital to effective progress through the text and must be "read with a pencil."

Molecules in Boxes. Each chapter contains a boxed story of a molecule, which connects the material of the chapter to some aspect of the world around us. Organic chemistry is not a subject confined to the lecture room, or even to the laboratory. It is alive and well all around us. There should be no real surprise about this—after all, we and most of the rest of the biological world are made largely of carbon, and carbon-based creatures and materials affect us greatly. These boxes try to provide some connective tissue between our study of this subject and the rest of the world.

Important Details

Authenticity and Reaction Descriptions. Reactions have been pursued back to the original literature in most cases, and at least to the review literature in all cases. When reactions are discussed, both the general case and at least one specific example are shown. Generality is emphasized, but the particular is not ignored.

Convention Alerts. One factor that can make organic chemistry difficult is that a language must be learned. Organic chemists talk to each other using many different conventions, and at least some of that language must be learned or communication is impossible. In a real sense, this is analogous to learning the vocabulary and grammar of a language. In addition to general treatments of nomenclature at the beginnings of many chapters, we have incorporated numerous "Convention Alerts" in which aspects of the language chemists use are highlighted.

Chapter Summaries. Each chapter ends with a summary of the important concepts, reaction mechanisms, and synthetic procedures discussed therein. These recapitulate and reinforce the material of the chapter. These summaries are further extended with problems and detailed solutions in the Study Guide. In each summary, there is also a section on common errors. What kinds of traps can one easily fall into? How can they be avoided?

Key Terms. Each chapter also contains a glossary of the important terms introduced in the chapter. The Study Guide collects these chapter glossaries into an overall glossary for the book.

"Something More" Sections. Most chapters end with a section in which the material of the chapter is concluded with a special topic. These typically consist of an especially interesting extension or an unusual practical or chemical application of the material in the chapter.

Biological Examples. Throughout the book, reference is made to the connection between organic chemistry and the world of biology. Although many biological reactions are given, these are framed as examples and do not preempt discussions of simple, prototypal reactions. We all have to walk before we can run.

In-Chapter Summary Sections. There are many moments in any course on organic chemistry when it is important to take stock of where we are. What have we done, why did we do it, and where are we going? The introductions to each chapter do some of this, but there are many points in the book where we pause to take stock and summarize. Sometimes these are whole sections, sometimes just a sentence or two. There is even a whole chapter (Chapter 17) that is largely devoted to a summary of the chemistry of alcohols that has permeated the earlier chapters. These sections allow us to focus and keep the direction in which we are going straight in our heads.

Acknowledgments. When I was 13, desperate to spend a summer or two on the tennis circuit, my parents had the wit to see that I was no future Laver or McEnroe, and to insist, over my strenuous objections, that I get a job. That "job" as a volunteer bottle washer and gopher began my lifelong association with William Doering. I went on as an undergraduate to learn organic chemistry from Professor Doering in what was the most exciting (and demanding) course I ever took, and I remained at Yale to do my graduate work with him. I remain his student today, and there is no easy way to acknowledge adequately my debt to him. I can only hope that this book helps others to get off to a similar start, and that they will encounter someone of Doering's intellectual honesty and power along their way.

After serving my sentence as a bottle washer for Doering I began real laboratory work, and was lucky enough to fall under the influence of two masters, Lawrence H. Knox and Gunther Laber. Much of the pleasure of organic chemistry comes from the design and execution of a well-done experiment. From these two patient teachers I learned the great pleasure in carrying out the manipulations of organic chemistry: preparing the exquisite glassware, setting up the apparatus, and finally handling the wonderful liquids and powders that were to be combined to make something new.

I have been lucky enough to have studied with some wonderful teachers both before and after my days as a university student. Stanley Feret and Margaret Frankel taught me in elementary school, and were surely greatly responsible for setting me on my way. Arthur B. Darling, who taught me American History in high school, was particularly inspiring. One could ask for no better example of how to communicate a love for a subject than his. And thirty years ago I spent a postdoctoral year with Jerome Berson, a man who wrote complex papers on carbonium ions that I couldn't yet read sensibly. I learned to read those papers during my year with Jerry, but more important, I discovered an intellectual atmosphere that affected me forever.

Chemists have families, too. Some even have lives. If I have had one during the construction of this book, it is largely the result of the efforts of my family. Adequate thanks to all of them would be far too long to fit here, but their names should be mentioned, and they should know that I understand some of what they put up with. So, thanks to Stephanie and Matt for cheerful, if often crazed chatter by e-mail; to Mait and Perla for delightful dinners in Brooklyn and for introducing me to Tom Waits; and to Hilary for being so splendidly all-Galaxy. My parents really did extract me from the tennis court and get me into a lab for the first time. They had the intelligence to see that a kid who was devoted to picking up frogs might find science a passion. I'm sorry that my father never got to see this book, but he surely had a lot to do with it. I'm glad that my mother has seen it, and I hope she thinks it was worthwhile driving that 13-year-old to and from the lab all those years ago. My wife Susan bore much of the brunt of the writing of this book. Too many absences, too much preoccupation, all coped with. Love and great thanks to her.

Paul Valery said that a poem is never finished, only abandoned. I have found, somewhat to my dismay, that the same is true of textbooks on organic chemistry. Nonetheless, it is surely past time to abandon the writing of this one. But I must point out first that books don't get written by setting an author on his or her way and then waiting for the manuscript to appear. There is a great deal of work to be done; misguided authors need to be straightened out, bribes and threats need to be administered, and commas inserted and deleted. In general, it is an editor's job to make it possible for the author to do the best of which he is capable. Don Fusting and Joe Wisnovsky at W. W. Norton were exemplary in their execution of this role, and my thanks go to them. Jeannette Stiefel, my copy editor, and Rachel Warren at Norton straightened out my prose on many an occasion and were helpful in many other ways. Joel Dubin and the rest of the crew at J/B Woolsey Associates did a great job of producing the art, and coped with great skill and reasonable cheer with my many corrections.

This book also profited vastly from the comments and advice of an army of reviewers, and I am very much in their debt. Their names and affiliations follow: William F. Bailey, University of Connecticut; Ronald J. Baumgarten, University of Illinois at Chicago; John I. Brauman, Stanford University; Donald B. Denney, Rutgers University; John C. Gilbert, University of Texas at Austin; Henry L. Gingrich, Princeton University; Richard K. Hill, University of Georgia; A. William Johnson, University of Massachusetts; Guilford Jones, II, Boston University; Joseph B. Lambert, Northwestern University; Steven V. Ley, Imperial College of Science, Technology and Medicine; Ronald M. Magid, University of Tennessee-Knoxville; Eugene A. Mash, Jr., University of Arizona; Robert J. McMahon, University of Wisconsin-Madison; Andrew F. Montana, California State University-Fullerton; Roger K. Murray, Jr., University of Delaware; Thomas W. Nalli, State University of New York at Purchase; Patrick Perlmutter, Monash University; R. M. Paton, University of Edinburgh; Matthew S. Platz, Ohio State University; Lawrence M. Principe, Johns Hopkins University; Charles B. Rose, University of Nevada-Reno; John F. Sebastian, Miami University; Carl H. Schiesser, Deakin University; Martin A. Schwartz, Florida State University; Jonathan L. Sessler, University of Texas at Austin; Robert S. Sheridan, University of Nevada-Reno; Philip B. Shevlin, Auburn University; Harry H. Wasserman, Yale University; Craig Wilcox, University of Pittsburgh; David R. Williams, Indiana University.

At the risk of slighting some, and delaying unduly the abandonment of this work, I must take a moment to single out two special reviewers, Henry L. Gingrich of Princeton and Ronald M. Magid of the University of Tennessee. These gentlemen read the work line by line, word by word, comma by missing comma. Their comments, pungent at times, but helpful always, were all too accurate in uncovering both the gross errors and lurking oversimplifications in the early versions of this work. The book is much improved by their efforts.

Ron Magid, Peter Gaspar, and Bob Willcott remain steadfast friends from our days together at Yale, many years ago, and are still people with whom I can talk and learn about obscure chemical (and other) subjects. Many other colleagues over the years have also been especially helpful to me; Bob Moss at Rutgers and Matt Platz at Ohio State, as well as Jeff Schwartz and Bob Pascal at Princeton are prime examples.

Despite all the efforts of editors and reviewers, errors will persist. These are my fault only. When you find them, let me know.

Princeton, November, 1996

Contents in Brief

Contents