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ORGANIC CHEMISTRY

Sixth Edition



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SIXTH EDITION Organic Chemistry

Robert Thornton Morrison Robert Neilson Boyd

New York University



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Preface

In preparing this third edition, we have done just about all the things that one can do to revise a textbook: added new material, deleted old, corrected mistakes, rewritten, and reorganized. To increase the book's value as a teaching aid, we have made two major, related changes: a change in organization, and a change in content. Our aim was to bring the book up-to-date—not just in the chemistry of each topic, but in the *selection* of topics, so that it would reflect, to the extent that a beginning textbook can, the directions that organic chemistry is taking today.

We have divided the book into three parts, and thus have explicitly recognized what has always been our practice and that of most other teachers: to assign for study the first twenty-odd chapters of our book and then, of the last ten or twelve chapters, to pick three or four or five.

In the twenty-four chapters of Part I, the student is introduced to the fundamentals of organic chemistry. As before, these chapters are tightly woven together; although certain sections—or even chapters—can be omitted, or their sequence altered, the organization is necessarily a fairly rigid one.

In Parts II and III the student reinforces his understanding of the fundamentals by applying them to more complicated systems. It is not really so important just which of these later chapters are chosen—although each of us may consider one or another of these topics absolutely essential—as that *some* of them are studied. What is learned at the beginning of the course can evaporate pretty rapidly if the lid is not screwed down at the end.

The new edition is about as long as the previous one, and contains the same number of chapters. But, through deletion and transfer of material, about 100 pages have been cut from the early part of the book. Using these pages, and rearranging some old material, we have written seven quite new chapters: Carbanions I, Carbanions II, Macromolecules, Rearrangements and Neighboring Group Effects, Molecular Orbitals and Orbital Symmetry, Fats, and Biochemical Processes and Molecular Biology.

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The teacher will most probably assign all or most of Part I. From Part II he may then select topics to take the student more deeply into "straight" organic chemistry: use of carbanions in organic synthesis; conjugate addition; polynuclear and heterocyclic compounds; rearrangements and neighboring group effects; the application of the orbital symmetry concept to concerted reactions of various kinds. In Part III, he may have the student learn something of the organic chemistry of biomolecules; fats, carbohydrates, proteins, and nucleic acids. And, as before, the brighter or more ambitious student may dip into chemistry not studied by the rest of the class.

There are other changes in organization. Glycols are introduced with alcohols, epoxides with ethers, and dicarboxylic acids with monocarboxylic acids. The aldol and Claisen condensations and the Wittig and Reformatsky reactions appear in Chapter 21, just after aldehydes and ketones and esters. These changes do not, we have found, place an undue burden on the student, but they do stimulate him and keep him busy in the middle part of the course: after the onslaught of new ideas in the beginning and before the complexities of the later topics. The student is *ready* for polyfunctional compounds at this time. He certainly finds epoxides more exciting than ordinary ethers, and can do more with phthalic and succinic anhydrides than with acetic anhydride. With carbanion chemistry in Chapter 21, he has opened to him the really important routes to carbon-carbon bond formation.

As before, we use problems as the best way to help the student to *learn* what he has been exposed to, and to let him broaden his acquaintance with organic chemistry beyond the bounds of the text. We have extended the practice—introduced in our first edition—of inserting problems within the chapter as checkpoints on the student's progress; nearly half of the more than 1300 problems are thus used to provide a kind of programmed instruction.

Spectroscopic analysis, chiefly nmr and infrared, is again introduced in Chapter 13, and in subsequent chapters the spectral characteristics of each class of compound is outlined. Emphasis is on the study of spectra themselves—there are 97 nmr and infrared spectra to be analyzed in problems—or of spectral data.

There is much that is entirely new: new reactions, like thallation, solvomercuration, Corey-House hydrocarbon synthesis, organoborane synthesis of acids and ketones; the use of enamines, 2-oxazolines, tetrahydropyranyl esters; and, of course, electrocyclic reactions, cycloaddition, and sigmatropic shifts. In one of the new chapters, rearrangements and neighboring group effects are discussed as related, often indistinguishable, kinds of intramolecular nucleophilic attack. In another, the concept of orbital symmetry is applied to concerted reactions; the treatment is based on the roles played by the highest occupied and lowest unoccupied molecular orbitals, and the student learns the enormous power of the simple Woodward-Hoffmann rules by applying them to dozens of examples: in the text, and in problems of graded difficulty.

In teaching today, one must recognize that many organic chemists will end up working in biological fields, and even those calling themselves biologists must know much organic chemistry. It seems clear, then, that we must do an even better job of teaching the fundamentals of organic chemistry to all students, whatever their ultimate goal. At the same time, the student should be made aware of the role of organic chemistry in biology, and it is with this in mind that we approach the study of biomolecules. Emphasis is on their structure and their chemistry in

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the test tube—the foundation for any further study. In addition, we have tried to give the student some idea of the ways in which their properties as organic molecules underlie their functions in biological systems, and how all this ultimately goes back to our fundamental ideas of structure. Biology, on the molecular level, *is* organic chemistry, and we try to let the student see this.

No changes have been made just for the sake of change. In our rewriting and in the selection of new topics, we have stuck to the principle we have always held: these are beginning students, and they need all the help they can get. Discussion of neighboring group effects or the Woodward-Hoffmann rules is pitched at the same level as the chlorination of methane in Chapter 2. New material is introduced at the rate at which we have found students can absorb it. Once presented, a principle is used and re-used. In a beginning course, we cannot hope to cover more than a tiny fraction of this enormous field; but what we can hope for is to make a good job of what we do teach.

> ROBERT THORNTON MORRISON ROBERT NEILSON BOYD

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