

BASIC  
PRINCIPLES OF  
ORGANIC  
CHEMISTRY  
SECOND EDITION



# BASIC PRINCIPLES OF ORGANIC CHEMISTRY

SECOND EDITION

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John D. Roberts

*Institute Professor of Chemistry*  
California Institute of Technology

Marjorie C. Caserio

Professor of Chemistry  
University of California, Irvine



**W. A. Benjamin, Inc.**

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SECOND EDITION

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# PREFACE

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No period in the history of organic chemistry has been as dynamic and productive of research accomplishment as the twelve years between the completion of the first and present editions of this textbook. New reagents, new reactions, and extraordinary syntheses have been manifold. New techniques and new instruments for analysis and determination of structures, improved methods for theoretical calculations, as well as new junctures with physical, inorganic, and biochemistry, have made organic chemistry an enormously vital discipline.

But along with this “best of times,” there is a “worst of times” coming from the recognition that many widely used organic compounds are more toxic than previously suspected. Some are carcinogenic; some may be destroying the ozone layer in the upper atmosphere, which protects all life from the sun’s strong ultraviolet radiation; others are concentrated and persist in living tissue to as yet unknown effect. Nonetheless, our society has come to depend on synthetic organic chemicals, and we may ponder the fact that in just a few years the petroleum that makes so many useful organic compounds easily available will be in very short supply throughout the world.

It has been a real challenge for us to try to cover the elements of modern organic chemistry with sufficient breadth to anticipate the interests and needs of the future chemists, biologists, physicians, medical scientists, and engineers, who constitute the majority of those who study the subject, and, at the same time, give a balanced view of both its current accomplishments and difficulties. Our attempt has resulted in a large book that may appear unwieldy. Between editions, we often received suggestions from professors to write a book “covering just the material I need in my course,” but no two ever seemed to agree on what “the” material should be. Perhaps the discipline has now progressed in breadth and complexity that no simple short text can suffice, any more than the old-fashioned grocery store can compete with the supermarket to supply the diverse needs of a modern community.

To a degree, our book has a parallel to a supermarket because not only do we cover many subjects, we cover the important ones in detail. There is no intention on our part to supply just the right amount of material for some particular course of study. Instead, we intend to provide a broad enough range of topics to accommodate almost any desired emphasis or approach to the subject. More on our objectives with regard to different possible approaches to the study of organic chemistry is given in the latter part of Section 1-5 (p. 24).

This book makes a substantial break with tradition in the matter of organic nomenclature. It was difficult to decide to do this because changes in this area are very hard to achieve, perhaps for the reason that they threaten the viability of what already is published and, indeed, even our customary forms of verbal communication. One of the authors remembers vividly the protests of his thesis supervisor to the idea of acquiescing to the admonition of a manuscript reviewer who felt that "crotyl chloride" and "methylvinylcarbinyl chloride" represented just too much of a mixing of nomenclature systems for isomeric compounds. "But we've used those names in nineteen earlier papers!" Nonetheless, organic chemists and organic chemistry will surely be better off to name these same compounds systematically as 1-chloro-2-butene and 3-chloro-1-butene.

Use of systematic nomenclature is a bit like energy conservation—we all recognize it is necessary, but we would just as soon the start be made after we are dead. The phenomenal growth of organic chemistry during the past decade and the switch by the indexes of *Chemical Abstracts* to use much more systematic nomenclature suggests that the right time is now. The approach we will take in this book to the nomenclature problem is described in more detail in Chapter 3 (pp. 49–51).

As in the earlier edition, considerable attention is given to the application of the principles of thermodynamics, quantum mechanics, kinetics, and spectroscopy to understanding and correlating the myriad of seemingly unrelated facts of organic chemistry. Much of this material could be appropriately categorized as belonging to a "Department of Fuller Explanation," and rightly so because it represents a real attempt to achieve a genuine understanding of difficult points of fact and theory. Examples include rather detailed discussions of the properties of solvents, the differences between resonance and molecular-orbital treatments of valence, ionization strengths of acids, the origin of spin-spin splitting and kinetic effects in nuclear magnetic resonance spectra, reaction mechanisms, photosynthesis, carbohydrate metabolism, peptide-sequence determinations and peptide syntheses, enzyme action, and reactions of transition-metal compounds. It will not be possible to cover many of these topics in the usual one-year course, but many options are possible, as well as opportunities for individual studies.

Many individuals contributed to the progress and content of this edition. Special thanks are due for the suggestions of the reviewers, in particular to Professor George E. Hall of Mount Holyoke College, who read and commented not only on the whole of the first draft but also a much-revised second draft. Helpful suggestions also were received from Professors Robert E. Ireland, Robert G. Bergman, W. A. Goddard III, and John H. Richards of the California Institute of Technology, Jerome Berson of Yale University, Ernst Berliner of Bryn Mawr College, Emil T. Kaiser of the University of Chicago, J. E. Guillet of the University of Toronto, and Dr. John Thirtle of Eastman Kodak. The students at both Caltech and the Univer-

sity of California at Irvine participated in class-testing the first draft and contributed significantly to the final draft. We owe them much for their patience and helpful suggestions.

Over the years, many teachers and students have taken time to send us their comments regarding the first edition, and many of these suggestions have been very helpful in preparing the second edition. Also, we are indebted to our respective colleagues for providing the encouragement that makes an endeavor of this kind possible. The revised drafts were prepared in part while one of us was on leave at Stanford University and the other at the University of Hawaii. We are very appreciative of the substantial assistance and hospitality provided by these universities.

The manuscript and its interminable revisions were typed with skill and patience by Ms. Rose Meldrum. Our thanks also go to Ms. Margaret Swingle. It was a pleasure to work with Mr. Georg Klatt who did the final artwork, and Ms. Mary Forkner who was the production supervisor. The index was prepared with a HP9830 calculator system, and it would never have been possible to alphabetize and edit the 7500 entries without the help of equipment loaned by Mr. Stanley Kurzet of Infotek Systems.

Special thanks are due to Drs. James L. Hall and Jean D. Lassila (as well as Ms. Patricia Sullivan) for their seemingly tireless efforts and continual contributions through the various stages of editing and proofreading. Finally, the patience of our families during the several years that it has taken to write and produce this book is worthy of very particular mention and appreciation.

As before, we will be pleased to receive corrections and suggestions from our readers for further improvement of later editions.

John D. Roberts  
Marjorie C. Caserio

May 15, 1977





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