BASIC PRINCIPLES OF ORGANIC CHEMISTRY

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PREFACE

PROGRESS IN organic chemistry is like that of a forest fire—fastest when fanned by the winds of new ideas; brightest when passing through heavily wooded virgin areas. Although organic chemistry is more than 150 years old, its fire rages faster and brighter than ever, as the result of a veritable hurricane of new theoretical concepts and experimental techniques from other areas of science. The new ideas are leading to a new kind of organic chemist, one who is versed in all the disciplines of chemistry from chemical physics to chemical biology and who may be called an organic chemist solely because he happens to work on the chemistry of carbon compounds.

The gradual recognition that physical chemical principles are vital to the understanding and improvement of synthetic reactions has helped more than anything else to broaden the outlook of organic chemists. One of the pioneers in this respect was Professor Howard J. Lucas of the California Institute of Technology—whose text, *Organic Chemistry,* published in 1935, made the first real attempt to suffuse thermodynamics and quantum mechanics into the teaching of elementary organic chemistry. This textbook was very much ahead of its time—so much so that no other book published in the intervening years has gone quite so far, particularly in the application of thermodynamics to organic chemistry.

The present text owes much to Professor Lucas, because it was originally conceived as a revision of the second edition of his *Organic Chemistry* and follows a somewhat similar order of presentation, as well as placing a similar emphasis on thermochemistry as an aid to the understanding of organic reactions. This emphasis should be of general value in undergraduate education because the gradual shift of teaching in elementary physical chemistry toward quantum mechanics and statistical mechanics has tended to displace the study of many applications of thermodynamics from the undergraduate chemistry curriculum.

Much has been said and written about possible orders of presentation of topics in elementary organic chemistry texts. Whether or not to mix aliphatic and aromatic chemistry, whether or not to go heavily into organic structural theory before discussing reactions—these and similar questions

have been subjected to serious debate without any clear decision (if one is indeed possible). The approach in this book has been an intermediate one which takes cognizance of the fact that it is difficult, if not impossible, to teach everything at once and that a certain degree of repetition is helpful to the learning process. Thus, we cover electronic theory of organic chemistry lightly in Chapter 1 (Lewis structures), extensively in Chapter 5 (atomic orbital models), extensively again in Chapter 9 (the resonance method and rudiments of molecular orbital theory), somewhat in Chapter 28 (molecular orbital theory) and finally lightly in Chapter 31 (bonding between carbon and elements such as silicon, boron, and phosphorus).

At each juncture, the intention has been to introduce only as many new ideas as important for the subject at hand. As a result, Chapters 6 and 7 cover the basic physical and chemical properties of alkenes, yet do not cover the methods by which alkenes are prepared simply because the reactions involved could not be properly understood at this juncture. A reaction index is provided, however, to enable the student to refer quickly to the various reactions by which types of compounds are synthesized.

We cannot claim that there is much that is revolutionary or original about the format or arrangement of our book and yet we believe there is an element of newness about the way we have approached the subject, with unceasing effort to test both traditional and current concepts to see if they really ring true when hit hard. Sometimes, a sort of schizophrenia has resulted, because we have not been able to decide which of two different theoretical treatments is more useful. Usually, we have not made clearcut decisions to accept or reject, but have presented the alternatives. This may be unsettling for elementary students expecting, for example, a consistent treatment of bond angles, in terms of either hybridization or electron repulsion (Chapter 5); or of unsaturated compounds, in terms of either the resonance method or molecular orbital theory (Chapters 9 and 28). We regret this, but the fact is we couldn't make up our own minds on how best to handle these subjects.

The present book is a large one—not so much because of the amount of factual material covered, but perhaps more because of the detail in which many basic ideas are discussed. In some cases, such as with hemiacetal and acetal formation (Chapter 14), the discussion is considerably longer than the synthetic importance of reactions themselves would warrant; however, such discussions have been given in detail because they illustrate principles of broad importance—in the case cited, of the factors governing acid- and base-catalyzed additions to carbonyl groups. Still, the number of topics is large and an instructor with limited time for presentation of an elementary organic course may well find himself in the position of having a small appetite at a sumptuous buffet supper. This is not a problem unique to our book. At least, we have made an attempt to solve it by following the suggestion of Dr. Christian E. Kaslow, that each important topic be assigned a section

number, so that an instructor pressed for time, or wishing to ignore some of our alternative treatments, can quickly and easily plan and assign an appropriate table d'hôte menu for his students.

Two features of the book seem to call for special comment. First, the exercises, of which there are many—not only at the ends of the chapters but also integrated into the text. None of these exercises is of the "Write twelve reactions of aldehydes" type. Such questions may well provide useful review but our concept of the purpose of exercises was different. We hoped to make the students think, make them scour the text for clues, and, in many cases, lead them into areas rather beyond those explicitly covered in the text. Some of the exercises may be exasperating to instructor and student alike because they do not have well-defined, precise answers. However, such exercises often have the advantage of helping to stimulate classroom discussions. There are many more exercises than a student could be expected to work in a year course, but here, again, the idea has been to provide the instructor with a wide range of possible choices. The tables of synthetic reactions contained in many of the chapters and the special reaction-type index should be useful aids to solving the exercises pertaining to organic syntheses.

The other feature of the book which seems to merit separate discussion is the emphasis on applications of the various forms of spectroscopy to problems in organic chemistry. Chapter 2 is particularly controversial in this respect—some reviewers liked it, some thought it belonged in an appendix, and some believed it had no place at all in an elementary text. The importance of spectroscopic methods to structural analysis of organic compounds cannot be questioned. Despite the qualms of the older generation in this respect, it really is the proper thing to take spectra before determining the melting point of a new compound—vastly more information can be obtained thereby. However, this does not mean that instruction in spectroscopic methods is necessary or even desirable in elementary organic courses. There is always a limit to how much material can be covered and an argument can be made for possible pedagogical disadvantages to teaching subjects which may be of no very immediate value to the student.

The material on spectroscopy is available in Chapter 2 and in parts of later chapters—to be used or not at the discretion of the instructor. We see no important difficulties with omitting all of it, if the instructor so desires, except possibly in the latter part of Chapter 28 (which covers some of the recent developments in organic photochemistry). If spectroscopy is covered, the student should be given to understand that it is not necessary for him to grasp all the material in Chapter 2 at once. Rather, he should expect to enhance his ability to comprehend and use spectroscopic methods by returning to this chapter for study and reference material as new applications are encountered with the different classes of compounds. The extensive use we have made of nuclear magnetic resonance spectroscopy may seem to reflect

too much of our own research interests. Nonetheless, we feel this requires no apology because, for qualitative analysis, n.m.r. spectroscopy is usually quite superior to infrared spectroscopy and has the further advantage of being much easier to understand.

This book is not only designed as an introductory text for the student of organic chemistry; it aims also to reach the chemistry major, graduate student, and research man alike—to whom we intend it to serve as a useful reference text. It is the sixth revision and extension of a handful of mimeographed lecture supplements compiled in 1954. Many of our colleagues and friends have contributed to its improvement over the ensuing ten years. At the early stages, Dr. Verner Schomaker was particularly helpful in guiding the presentation of thermochemistry (Chapter 3) and of the resonance method (Chapter 9). At a later stage, Professor Christian E. Kaslow made a very large number of valuable suggestions as the result of using the fifth edition in a summer course at the University of Indiana. Very detailed and helpful reviews of the whole manuscript were provided by Professor Douglas E. Applequist, Henry E. Baumgarten, and William K. Noyce. Many helpful suggestions with respect to particular chapters were also made by Drs. E. R. Buchman and L. H. Klee and Professors Virgil Boekelheide, Kenneth N. Harmon, Carl Niemann, and John H. Richards.

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We shall be grateful for suggestions for improvements on matters of fact, interpretation, or presentation.

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