AN INTRODUCTION TO ORGANIC CHEMISTRY

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PREFACE

IN CHOOSING an organic chemistry text from the assortment of introductory books now available, teachers of this subject must evaluate the relative importance of the many features—some common, some unique—that each book offers their instructional program. This is by no means a trivial task, and I hope my comments here will prove helpful to those facing such a decision. In the long run, of course, it will be the student users of a text who will determine its instructional value.

My purpose in writing this book has been to provide a thorough but concise introduction to the most important and fundamental principles of organic chemistry. In this effort I have tried wherever possible to show the importance of the experimental evidence on which these principles are founded. Innovations in presentation have been made where a clear improvement in understanding results. However, traditional approaches of proven effectiveness have been retained, and no changes were made just for the sake of being different. I believe that careful inspection—or better yet, use—of this text will disclose a freshness of approach, a clarity of exposition, and a variety of content which make it unique. In the following paragraphs I have outlined some important features that make this book an ideal text for a beginning course in organic chemistry.

By a judicious selection of topics, this book has been kept to a reasonable size for use in a one-year course serving both chemistry majors and nonmajors. To this end, I have tried to emphasize those aspects of organic chemistry that are truly central and necessary if understanding is to be achieved, and in cutting topics I have chosen to sacrifice breadth rather than depth of coverage. As a consequence of this decision, instructors may find some old friends missing (the benzoin condensation) or treated only in the supplemental problems (the haloform reaction). I apologize if I have ruffled any feathers with these omissions, but I firmly believe that it is unrealistic to ask beginning students to familiarize themselves with all important reactions and mechanisms in one year.

I designed and wrote this book to serve as a teaching text, and not as an encyclopedia. Since it is good pedagogy to develop complex subjects gradually, this results in some important topics being discussed progressively in different sections of the book. For example, Brønsted acid-base concepts are first treated in conjunction with *E*2 elimination reactions (Chapter 3), placed in a quantitative framework during the development of aromaticity (Chapter 9), and then reviewed and further refined in Chapters 12 and 14. A similar sequential development is used for spectroscopy, bonding, and electrophilic aromatic substitution. My guideline here has been to carry the exposition of a subject only to that stage actually used in accompanying discussions. If a later topic requires a more sophisticated treatment, the necessary elaboration is provided at that time.

I have chosen a functional-group organization for the first fourteen chapters of the text. The effectiveness of this approach has been established many times, and within this context particular emphasis is placed on the structure and reactivity of common classes of organic substances. The order of presentation is arranged so that the characteristic reactions of one functional group illustrate preparations of subsequently discussed groups. Most commonly used organic compounds come from petroleum or coal; the book therefore begins with a discussion of alkane and cycloalkane chemistry (mainly combustion and halogenation), followed immediately by a chapter on alkyl halides. This allows a very early treatment of substitution and elimination reactions, which in turn lead naturally to chapters on alkenes, alkynes, and alcohols.

The characteristic reactions of each functional-group class are organized according to reaction types and simple mechanistic concepts. In this way key similarities and differences between functional classes are underlined, making it easier for students to manage the large number of reactions they are encountering for the first time.

The importance of chemical reactions in effecting specific molecular transformations (that is, as tools for synthesis) is clearly described, and a summary of key reactions, organized according to use, is given in a separate section following the last chapter. However, the degree to which synthesis should be emphasized has been left up to the instructor, since in my opinion nonmajors need not be well versed in this skill. For those wishing to stress synthesis, brief reviews of important preparation methods are given in turn for alkenes, alkynes, alcohols, amines, and carbonyl compounds. Furthermore, the ability to devise two- or three-step reaction sequences leading to specific compounds is gradually nurtured by carefully chosen problems, and more complex synthesis pathways are discussed in the chapters on carbonyl compounds and carboxylic acid derivatives. Finally, a comprehensive treatment of the strategy and methodology of synthesis is provided in Chapter 19. The chemistry major should find this a stimulating and useful review of the entire subject.

A clear distinction between fact and theory is maintained throughout. Reaction mechanisms are useful in correlating, organizing, and remembering experimental observations. However, if mechanisms are presented in a manner that overemphasizes their importance, we risk establishing a situation in which students memorize mechanisms rather than reactions, often with a minimum of understanding. In accordance with this

principle, I have also chosen to discuss theoretical bonding models at several different points, increasing the sophistication of the model as required by the case under consideration. A simple covalent electron-pair model is used in the introductory chapters; then a σ,π bonding model is presented for use with alkenes and alkynes. This model is subsequently elaborated for aromatic systems, a subject which also lends itself to a comparison of resonance and molecular-orbital models. Orbital-symmetry considerations are treated in still a later chapter (16).

In accordance with my effort to show the experimental foundation of organic chemistry, important spectroscopic tools (notable pmr and infrared spectroscopy) are introduced in the first chapter and are used over and over again in subsequent chapters. In my opinion pmr spectroscopy is particularly suitable for beginning students because the chemical-shift concept serves to illustrate and reinforce the recognition of structurally equivalent groups of atoms, a facet of organic chemistry that is often troublesome for the novice. Furthermore, pmr is easier to understand and yields more immediately useful information than infrared spectroscopy. The treatment of pmr in Chapter 1 is very elementary and dwells only on the chemical-shift concept. The student is made aware of spin-spin splitting effects, but a full exposition of this aspect of nmr spectra is deferred to Chapter 8.

Naturally occurring compounds representative of each functional group are presented and discussed in turn in each chapter. An artificial distinction between synthetic compounds and natural products is thus avoided. This incorporation of biologically related substances and topics begins in Chapter 1 with the subject of isomerism (progesterone and tetrahydrocannabinol are isomers) and continues in later chapters with topics as diverse as insect pheromones, nerve-signal transmission, transformations of vitamin-D precursors, and biosynthetic pathways. Because I consider proteins and carbohydrates to be special cases, involving relatively subtle variations on given structural themes, I have chosen to develop these topics separately, in Chapters 17 and 18.

Within the limitations implied by an arrangement of topics according to functional groups, this book is organized in a way that allows for flexibility of use to meet a variety of instructional needs. Each important topic and subtopic is identified by a heading, so that the instructor can easily rearrange or select material for reading assignments. In teaching chemistry majors, for example, many instructors may wish to consolidate the aromatic-substitution discussion in Section 15.2 with that in Chapter 10. For a short nonmajors course, the treatment in Chapter 9 (and 10) is adequate.

Elaboration of the fundamental facts and principles developed in the first fourteen chapters may proceed in any of several directions with the final group of special-topic chapters. One of these, Chapter 15, provides a unique review of earlier material in the context of interacting functional groups. Another, Chapter 16, discusses two important classes of nonionic reactions. Chapters dealing with carbohydrates, proteins, and the strategy of organic synthesis complete this group. Although these special chapters may be taken up in any order, the chapter on synthesis is more effective if it is preceded by the material on interacting functional groups.

As an aid to the beginning student, important terms and concepts are summarized at the end of each functional-group chapter. In addition, problems designed to probe the reader's understanding of important topics and to extend a particular line of reasoning are inserted throughout the text. Complete answers to all these problems are provided at the end of the book. These text problems are buttressed by additional problem sets at the end of each chapter. Answers to the latter problem sets are given in a separate study guide and solutions manual, prepared by Prof. Ronald Starkey of the University of Wisconsin, Green Bay. Students undertaking a self-instruction program in organic chemistry will find this study guide especially helpful.

Many people have helped produce this book, and any success it may enjoy is due in part to their efforts. Professors Peter Yates and Frank Lambert provided helpful commentary as the manuscript was being written. This "feedback" helped avoid a major rewriting of the first draft. Other valuable reviews of part or all of the text were conducted by

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Ronald Starkey not only assembled the problem sets at the end of each chapter, but also read the entire manuscript and offered many constructive suggestions. His study guide and solutions manual reflects both his years of teaching experience and his intimate association with this book. The artwork which enhances and clarifies many technical discussions was prepared by Basil Wood; Rosetta Reusch did most of the indexing.

Finally, special thanks are due two persons. Nancy Clark guided the manuscript and its author through the labyrinth of events leading to a published book. Her professionalism and attention to detail are evident throughout this text. Fred Murphy, President of Holden-Day, demonstrated unflagging enthusiasm and patience during the long years I spent writing this book. His role in encouraging me to undertake the project and in assembling a superb production team is deeply appreciated.

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William H. Reusch

TO THE STUDENT

WHETHER you approach the study of organic chemistry enthusiastically or with reluctance and trepidation, you may find the following guidelines helpful in achieving mastery of the subject.

First, the study of organic chemistry is in many respects similar to the study of a foreign language. There is, for example, a new vocabulary of terms and symbols. Indeed, reaction equations are essentially sentences describing the consequences of certain experimental operations. As with a language, most of what you learn will be used constantly thereafter. You must therefore try to acquire a firm foundation of fact and principle through a regular program of study and practice (problem solving).

Second, the mastery of organic chemistry will require a significant memorization effort on your part. Some students tend to regard memorizing as an inferior alternative to understanding; however, these two important qualities are so complexly intertwined they cannot be artificially separated in this fashion. One of the best methods of learning organic chemistry is to organize its multitude of facts according to certain well-established principles of structure and reactivity. In this way understanding and memorization can be achieved together. The major difficulty you may encounter in this approach is that many interesting and thought-provoking questions of "how" and "why" are not easily answered. Ironically, a beginning student's desire for full and straightforward explanations sometimes exceeds the professional chemist's knowledge and ability to provide answers. For this reason organic chemistry is still a lively and exciting subject.

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