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The Essence of Organic Chemistry

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Chemistry

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Preface

No authors write a new textbook of elementary organic chemistry without the belief that they can improve on the many already available. We are no exception. Our major challenge in developing this book was to encompass the main themes of organic chemistry in the space of 500 pages. A second challenge was to develop a text which was as little dependent on the teacher and on ancillary material as possible. A third challenge has been to introduce enough biological chemistry to illustrate the analogies and dissimilarities between the compounds and reactions found in the laboratory and in the cell. Although the students to whom this book is addressed have different career objectives, enough of them are oriented toward the life sciences to justify our stress of those features of organic chemistry most relevant to life processes.

The enormous correlative power of the structural theory of organic chemistry finds its expression in the classes of organic compounds on the one hand, and the classes of organic reactions on the other. The organization of the text at the chapter level follows the traditional pattern in which compound classes are taken up in order of their increasing complexity. The first four chapters deal largely with the nature of the chemical bond as applied to the structures, reactions, and physical properties of hydrocarbons. In these chapters, the other classes of compounds are introduced as derivatives of the hydrocarbons and of simple inorganic compounds already familiar to the student. Chapter 5 treats alcohols, phenols, and ethers, which are the simple organic derivatives of water. Chapter 6 introduces the alkyl halides, sulfates, phosphates, thiols, and sulfides, which are organic derivatives of the simple inorganic acids. The compound classes treated through Chapter 6 can be interconverted largely through simple substitution, addition, and elimination reactions. Thus the reaction classes with their similar general mechanistic features are used to integrate otherwise individual reactions into families of reactions.

By the time Chapter 7 is reached, enough compounds and reactions have been discussed to allow a thorough treatment of chirality and of dynamic stereochemistry. Once developed, the stereochemical themes appear again and again in the subsequent discussions. Chapters 8 and 9 deal with carboxylic acids and their near relatives, the acid chlorides, esters, and fats. These compounds and their interconvertibility provide analogies for the amines, amides, and proteins of Chapter 10. In Chapter 11 on aldehydes and ketones, oxidation, reduction, and condensation reactions relate these compounds to those compound classes discussed previously. These middle chapters provide opportunities for comparing and contrasting the structures and reactions of organic and biochemistry. While the facts and theories of organic chemistry build on one another as the book progresses, the biochemical sections depend directly on the preceding organic sections rather than on preceding biochemical sections.

Chapters 12 through 15 in turn take up aromatic substitution, carbohydrates, carbon chain-building reactions, and organic spectroscopy. The unique character of each of these subjects and the absence of their interdependence allows them to be studied in any order.

In our attempt to make this book as self-contained as possible, subjects are not mentioned unless they are treated in depth. Problems are interspersed with the text so the students can test their knowledge section by section. The problems at the end of each chapter depend more on the chapter taken as a whole and on material found in previous chapters. The problems become progressively more difficult as the end of the problem section is approached. So that the students can learn whether they have been successful in answering our problems, *the answers to all problems are found at the end of the book.* The important topics and reactions summarized at the end of each chapter provide the students with an overview of the subject.

A separate Study Guide for Students has been written to help them learn the material in this text. The text and the Study Guide play reciprocal roles, not unlike those of participants in a dialogue. Thus the Study Guide poses a series of questions to which the continuity of the text provides the series of answers. Conversely, the Study Guide reveals the thought patterns required for solutions of the more difficult problems in the text. The questions of the Study Guide are Socratic in character and anticipate the development of the subject matter in the text. The questions of the text are designed to allow the students to measure their progress and to self-test their development.

We are indebted to Professor J. John Uebel of the University of New Hampshire and to Professor Kenneth G. Hancock of the University of California at Davis, who read the entire manuscript, for their many constructive comments and suggestions. The comments of a number of reviewers helped to shape the book in its early stages. It has been a pleasure to work with Miss Laura Rich, the editor, whose consistent

interest helped to move the book through to completion. Lastly, we wish to acknowledge the impatience and lack of cooperation between the coauthors, without which this book would never have been completed.

Los Angeles, California J. M. C

September 1977 D. J. C.

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Chapter 11 Aldehydes and Ketones

CHAPTER 1

The Ingredients of Organic Compounds: Atoms, Orbitals, and Bonds

Human beings are curious; otherwise the questions that organic chemistry answers would never have been asked. These questions originally centered around attempts to understand life processes and the operations of "organs," hence the term **organic chemistry**. Since compounds of carbon and hydrogen were always encountered in organs, organic chemistry became associated with the study of compounds of carbon and hydrogen. As the science developed, many compounds of carbon and hydrogen were synthesized in the laboratory which were identical to those isolated from "organic" sources. Many others were prepared that were unrelated to the *natural* compounds. Some of the syntheses involved inorganic starting materials, but most were transformations of one compound of carbon and hydrogen into a second, a third, etc. Since the properties of the compounds were found to be independent of their "natural" or "unnatural" origins, the term organic chemistry became more general, and now refers to the **chemistry of compounds that contain carbon and hydrogen**.

The intimate relationship between laboratory and cellular chemistry continues, and the term "organic" appropriately refers to that relationship. The evolutionary compounds of carbon produced in cells and those compounds prepared in the laboratory are governed by the same chemical rules. This book, then, describes the compounds of carbon and hydrogen and the rules that govern their transformations.

1.1 PERSPECTIVE

Matter exhibits different organizational characteristics at different temperatures. Above about 100,000°K, the electrons and nuclei that compose plasma are stable and associate to form atoms only below that temperature. Atoms, in turn, associate to form molecules only at temperatures below a few thousand degrees. The common chemical bonds of organic compounds are those between carbon and carbon, carbon and hydrogen, carbon and oxygen, carbon and nitrogen, carbon and sulfur, and carbon and the halogens. These bonds are stable only in the range between absolute zero and about 1000°K. Evolutionary organic compounds, those associated with living systems, are produced and used at temperatures that vary between about 260°K and 373°K, and are often unstable at higher temperatures. "Unnatural" organic compounds have been designed and synthesized which are stable to about 773°K, but these are noteworthy exceptions, since most organic compounds decompose at much lower temperatures.

What are the sizes of organic compounds? One of the smallest molecules is methane (the main component in natural gas), which is about 0.00000003 cm in diameter. One of the largest is polyethylene, which can be as long as 0.00009 cm. A small enzyme molecule—one of the machines of life—is about 0.0000003 cm in diameter. The size of objects in the world we perceive with the unaided eye ranges from 10^{-2} to 10^{10} cm (0.01 to 10 billion cm). Even with the help of the electron microscope, our sight can barely detect only the largest organic compounds,