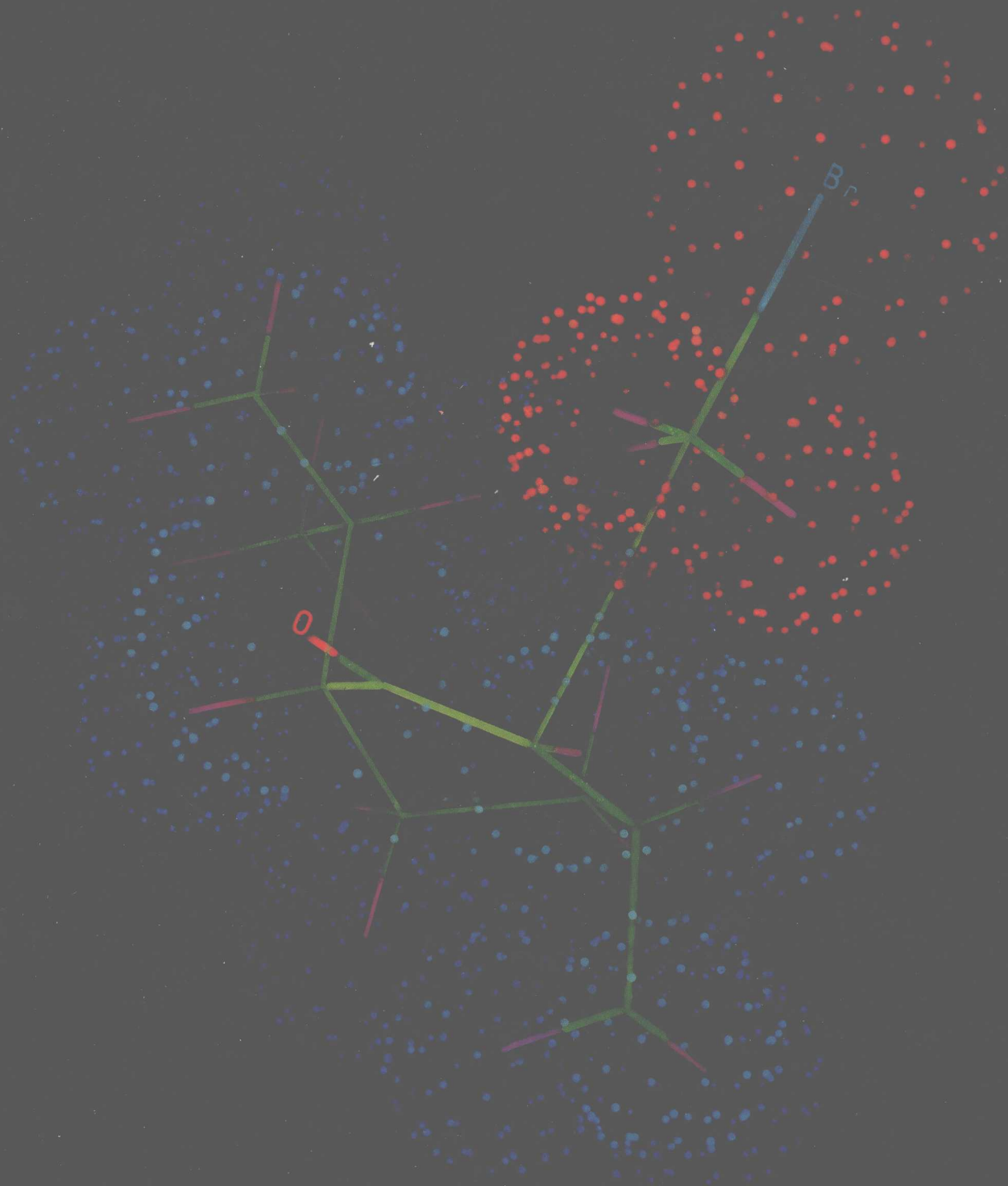


ORGANIC CHEMISTRY



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Courtesy of Columbia
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A Note to the Instructor

Organic chemistry is a rapidly changing field. In the past ten years, exciting technical and intellectual advances have been made in the development of synthetic methodology, mechanistic tools, and spectroscopic instrumentation. My conviction in writing this book is that such advances should be incorporated in the teaching of introductory organic chemistry even as basic rules and concepts are emphasized. I am fortunate that I have had the opportunity to teach a great variety of students at both undergraduate and graduate levels. Invariably, the beginning students arrive with diverse amounts of preparation, as well as different reasons for studying chemistry. Out of this teaching and my ongoing desire to communicate the excitement of research in organic chemistry to students, this book was born. My goal is to present the richness of modern organic chemistry in a simple and readily understandable manner. The effort has taken almost eight years and three drafts; I hope that you, my fellow teachers, will judge that effort to have been worthwhile.

Following the Functional-Group Approach

The unifying theme of this book is one that has proved to be instructionally most successful in the past: organic chemistry is best comprehended when divided into the chemistry of its functional groups. Thus, after a fairly comprehensive review of first-year chemistry (which in my experience most students have forgotten), the presentation follows a logical sequence starting with the alkanes (which have no functional group) and progressing to more and more highly functionalized classes of molecules. The physical properties of simple organic compounds are introduced early, as are such basic physical concepts as kinetics and thermodynamics. Within the functional-group approach, chemical reactions are routinely juxtaposed to the mechanisms by which they proceed. The point is made that, in this respect, organic chemistry is much like a language—the

reactions are the vocabulary, the mechanistic descriptions the grammar. Finally, at strategic points throughout the book, the important spectroscopic techniques in organic chemistry are introduced.

Pedagogical Features

Several pedagogical features of this book distinguish it from others.

Learning Simplified by the Use of Color

One of the most important innovative features of this text is the way in which color is used. Color is used not only in marking centers of reactivity, as it is in many textbooks, but also in a functional sense. For example, the application of several colors is very effective in demonstrating how to name a functional molecule: the stem, the ancillary substituents, and the functional group of the structure can be differentiated by color, as can the corresponding components of the name itself. Whenever possible, *s* orbitals are shown in red, *2p* orbitals in blue, and *3p* orbitals in green. In the chapter on stereoisomerism (Chapter 5), the order of diminishing priority of substituents is indicated by the sequence red-blue-green-black. Most importantly, color is used to specify the type of reactivity of transforming centers in reactions and mechanisms. For example, all radicals, which are introduced in Chapter 3, are shown in green. In the mechanistic description of polar reactions, all nucleophiles are red, electrophiles are blue, and leaving groups are green. The various applications of color are explained to the student wherever necessary.

Illustrations

The thoughtful rendering of illustrations is essential in an organic chemistry textbook, because the massive scope of the subject dictates that all possible visual assistance be available to students. Color-coded airbrushed drawings throughout this book illustrate the three-dimensionality of orbitals and related spheres. The use of color in these drawings and in diagrams serves to reinforce key physical and chemical principles. A particularly nice example is found in *sp*³ hybrids whose composition of *s* (red) and *p* (blue) orbitals is indicated by violet.

Nomenclature

A never-ending problem in teaching is that the naming of organic compounds, particularly the highly functionalized molecules, can be extremely confusing to students: this is because of the abundance of common names. This book introduces rigorous IUPAC nomenclature for the alkanes and then builds on this system for the naming of compounds having functional groups: the alkanols, alkanals, alkanones, alkanolic acids, alkanenitriles, and so forth. If a common name is firmly entrenched in the literature, it is given in parentheses following the systematic name. For example, the smallest ketone, propanone, is followed by (acetone). Common names are given in this way with particular frequency in the chapters on aromatic compounds and heterocycles.

Spectral Data

Almost all ¹H NMR and IR spectra presented in this book have been recorded on state-of-the-art equipment. Most of the ¹H NMR spectra were measured at

90 MHz (on a Varian Associates EM390 instrument), a frequency that is becoming the standard for routine use. IR spectra were recorded on a Perkin-Elmer 681 Spectrometer equipped with a 580B data station. The application of color in these spectra affords a unique opportunity to highlight spectral assignments.

Authenticity of Reactions

With the help of a generous grant from my publisher, all reactions in this book have been checked in the literature by undergraduate students to verify yields and conditions. Some of the reactions for which such data were unavailable were rerun in the laboratory.

Up-to-dateness of the Material

To the extent that they enhance the teaching value of the material presented and enable the student to perceive that organic chemistry is an advancing science, new developments at the forefront of organic research have been incorporated. These developments encompass natural products, medicinal compounds, coal chemistry, synthetic methodology, biochemical mechanisms, the mode of action of carcinogenic compounds, and energy-related matters.

Synthetic Strategy

The concepts of retrosynthetic analysis are introduced early so that the student can work backward in a synthetic scheme to unravel a target structure. These concepts are continually reinforced and reviewed.

Biological and Industrial Processes

Reactions and mechanisms pertinent to biochemistry and industrial chemistry are introduced to demonstrate the application of concepts developed throughout the text. Their incorporation serves to illustrate the relevance of organic chemistry to the life sciences, to our everyday lives, and to the economy.

End-of-Chapter Summaries

The text of each chapter ends with a summary of the important new concepts presented therein. Most chapters also include a summary of new reactions.

Cross-references

The book is extensively cross-referenced, to call the student's attention to the relation of a new concept or reaction to material covered in earlier chapters or to material that is to come. Basic principles are presented repeatedly within the framework of new reaction chemistry to insure that the student has an intellectual grasp of them and to emphasize their generality.

Exercises and Problems

The in-text exercises and the end-of-chapter problems are included not only for practice in the application of synthetic methodology, mechanisms, and new concepts, but also for the introduction of new material, whenever it is readily derived from the chemistry described in the text. Many of the exercises and problems have as their bases biochemical reactions, with a strong emphasis on the chemical aspects of these processes. Answers to all of the exercises can be found at the end of the book; those to the end-of-chapter problems are in a separate solutions manual.

Boxes

Many textbooks introduce ancillary or more-advanced material in the form of special topics, addenda, or appendices. In my experience, a two-semester course does not allow enough time to cover these topics. It is my belief that a discussion of this type of material, particularly if it concerns advanced concepts, should be left to advanced textbooks. In this book, such topics are presented briefly in boxes to inform the student not only of their existence, but also of the richness of organic chemistry beyond the introductory level. They are meant to stimulate the interested student, by adding depth or breadth to the subject at hand.

Ancillary Materials

The study guide and solutions manual was written by my colleague at the University of California at Davis, Professor Neil Schore, who presents the subject matter in a lively and easily understandable fashion. In this guide, Professor Schore summarizes the contents of each chapter again, but from a different perspective. Sample problems are worked out and the solutions to the end-of-chapter problems given. Finally, many hints to the student point out some of the pitfalls of applying faulty logic and help those who find it hard to visualize the steps and sequences that comprise solutions to various exercises.

A set of four-color overhead transparencies is available from the publisher. This selection of illustrations from the text includes reproductions of spectra, orbital pictures, diagrams, and mechanisms. It is designed to assist the instructor in presenting information in lectures.

K. Peter C. Vollhardt

January 1987

A Note to the Student

Organic chemistry is sometimes perceived by students as being a formidable subject, with an overwhelming number of facts to be memorized and with many seemingly difficult concepts. It does have a fairly rigid structure, with each new topic building on the preceding one. However, there is nothing inherently difficult about the subject, although it may be quite different from others that you have studied. Having spent much of my life in the study and teaching of organic chemistry, I have several bits of advice to offer that may be of help to you. Avoid falling behind. Make sure that your schedule allows you to set aside a short period every day for reading the book, for working the problems, for reviewing material presented in class, and for practicing the “vocabulary and grammar” of organic chemistry—that is, for learning the reactions and understanding their mechanisms. Make regular use of the office hours of your instructors and teaching assistants. They have specifically arranged their schedules so that they can help you deal with difficult material, instruct you on how to solve exercises, and inspire you to *think* organic chemistry. If you are not under pressure because of falling behind, you will enjoy organic chemistry as a learning experience that gives you a stimulating and different view of the chemical world that surrounds you.

To help you organize your thoughts and to provide you with an easy review, each chapter has a short introductory paragraph and an extensive summary section. The order of presentation of topics is the same in most chapters: you will learn, first, how to name the compounds to be covered; then, what their physical properties, in particular spectral characteristics, are; subsequently, the methods used to make these compounds; and, finally, how they react. The many transformations that you will encounter are reported in a consistent fashion: first, by an outline of the reagents, substrates, and reaction conditions; and, second, by the mechanistic details of the reaction. All topics are extensively reviewed in the study guide and solutions manual that accompanies this book.

The guide also summarizes new reactions and concepts, reminds you of material covered earlier, presents you with alternative explanations, and helps you to solve problems.

I urge you to acquire a molecular model-making kit (such as the Maruzen Molecular Structure Model set). It is an *invaluable* tool for dealing with stereochemistry, the shape of molecules, intra- and intermolecular interactions, and molecular mobility. Its utility is not limited to this course; it can also be used in other courses dealing with organic molecules.

Perhaps one of the strongest features of this book and one that most distinctively sets it apart from others is the use of color as a teaching tool. Color is employed not only as a "marker" to indicate the fate of individual atoms or molecular units in the course of a particular transformation, but also as a "highlighter" to show the relation of the names of organic molecules to their structures and the association of spectral features with certain molecular units. Most importantly, it is used in a functional sense: all electron-rich, nucleophilic moieties are in red, all electron-deficient, electrophilic parts blue, and all radicals and leaving groups green. The movement of electrons in a particular molecular transformation is indicated by red arrows. In descriptions of the mechanisms of organic reactions, the color reveals the reactivity of the functional groups. Because such reactivity may change from step to step, the color of such units may change as the overall reaction progresses. Do not be confused by these changes; they should allow you to visualize the metamorphosis of reactive centers as they transform starting materials into products. Although an attempt has been made to use color consistently within a section, you will note that its application may change from section to section (and chapter to chapter) because of emphasis on the material under discussion or the particular concept being highlighted. Frequently, color is applied only sparingly, and dropped when it serves no purpose. You will quickly grasp the basic idea behind the functional use of color, and you should be able to exploit it to your advantage. After you have done so, you should be able to apply what you have learned without the use of color. For this reason, the summary sections, as well as almost all exercises and all end-of-chapter problems, are presented without color, just as they would be in a test.

Enjoy organic chemistry and good luck!

K. Peter C. Vollhardt

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