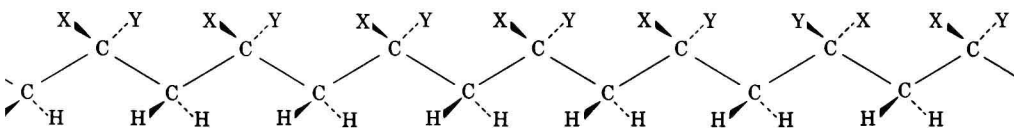


**ORGANIC  
CHEMISTRY**

**SHIRLEY**

*University of Tennessee*

# CHEMISTRY



*New York, Chicago, San Francisco, Toronto, London*

***This book is dedicated,  
as in the last analysis all  
textbooks must be dedicated,  
to the serious student.***

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July, 1966

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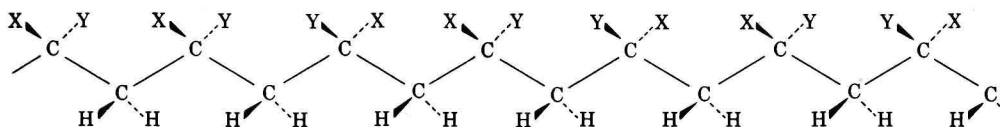
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# **ORGANIC CHEMISTRY**

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DAVID A. SHIRLEY

# ORGANIC



*Holt, Rinehart and Winston*



## **PREFACE**

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The organic chemist of today is surrounded by powerful new laboratory tools and much new information of fundamental importance to the understanding of his subject. This combination allows a penetrating insight into the fascinating problems of molecular structure and of the pathways of molecular interactions. The exciting new research results that are coming from the laboratory are rapidly moving from the research journals to advanced organic courses in the universities and thence to the beginning undergraduate courses. It is proper that this stream of man's new knowledge should flow rapidly into the undergraduate arena; but at the same time it is required that the teacher and the textbook author answer difficult and challenging new questions of what to present to the student and how best to present it. In addition it is certainly required that we do our utmost to serve our ever-present and demanding masters, namely, rigor of subject matter and lucidity of presentation. This textbook is addressed to these requirements.

This text is designed for the one-year undergraduate course in elementary organic chemistry, which is a customary presentation to a diverse group of students including chemistry majors, chemical engineering students, premedical students, and a number of allied groups. The teacher of this course is well aware of the rapid changes in subject matter emphasis that have occurred during the past decade and that continue to occur at a seemingly accelerated pace. The properties of organic molecules may be presented increasingly in terms of such unifying concepts as transition state theory, electron delocalization, conformational analysis, kinetic and equilibrium control of reactions, solvent effects, and a host of others. Consideration of the mechanism of organic reactions allows the perceptive student an effective opportunity to correlate, and therefore better to understand and to learn, the basic principles of the science. While it has become quite feasible to classify

the chemical properties of organic molecules by mechanistic type, it appears to the writer that the best organizational approach for the elementary student remains the long-used classification by functional groups. This division of subject matter allows a sufficient opportunity for presentation of mechanistic correlations, and serious effort has been made in this text to utilize these opportunities. In accord with this objective, many theoretical concepts and principles have been introduced at relatively early points in the text. The point selected corresponds to the utilization of a principle or concept in the description of a particular experimental result. For example, resonance is introduced with the structure of the nitro group under nitration of alkanes in Chapter 3 and free radical initiated chain processes under chlorination of alkanes, also in Chapter 3. It is felt that early introduction of many such concepts allows an effective subsequent interweaving of theory, functional group properties, and industrial practices.

This text falls into the category of a separate treatment of aliphatic and aromatic chemistry. However the structure of benzene is treated along with alkenes and cycloalkenes in Chapter 4. Thereafter reference to benzene chemistry is made occasionally as needed until a more detailed treatment of aromatic compounds is provided in Chapters 22 through 30.

The author would like to call attention to two chapters in this text that represent a perhaps significant degree of innovation over other elementary organic texts. Chapter 8 attempts to develop, in an essentially descriptive manner, some concepts of physical chemistry that are vital to an understanding of subsequent material. This chapter presents the fundamental ideas of rate and equilibrium, the transition state, and the thermodynamic quantities that govern passage of reactants to products. Chapter 31 deals with the absorption of radiant energy by organic molecules. The great importance of electronic, vibrational, and NMR spectra to modern organic chemistry requires treatment of these techniques in an elementary text.

The increasing emphasis in modern texts on theoretical principles of organic chemistry has tended to restrict presentation of many interesting and important areas such as dyes, alkaloids, medicinal products, terpenes, etc. Other similar areas have held their own in this struggle for space because of significant recent developments. In this latter category may be mentioned polymers, nucleic acids, and steroids. The author of this text has tried to do justice to most special interest areas even at the risk of bringing forth that oft-repeated but seldom heeded criticism—a too lengthy book. In common with most other organic texts, special chapters have been provided on petroleum and coal, proteins, carbohydrates, fats, and heterocyclic compounds. Subjects such as steroids, porphyrins, anthocyanins, and terpenes have been incorporated at appropriate single places in chapters dealing predominantly with other subject matter. The material on certain other subjects (for example, dyes, medicinals, polymers, and alkaloids) will be found incorporated at several different points in the text. No attempt has been made to include an examination of the enzymatically controlled reactions of living systems. It is

felt that the elementary organic chemistry course best limits its coverage to the structures and gross chemical properties of the compounds that make up living systems, while to biochemistry texts is properly left the specific interactions of these compounds in the processes of life.

The author would like to acknowledge the cooperation of the editors and publishers of the numerous journals and books noted throughout the text in granting permission to utilize published materials.

The author would like to express his appreciation to Prof. Jerome E. Eastham of The University of Tennessee, Prof. Cheves Walling of Columbia University, and Prof. William E. Truce of Purdue University who read the entire manuscript and who offered many valuable constructive comments. The help of Dean H. A. Smith and Prof. C. A. Buehler of The University of Tennessee with portions of the manuscript is gratefully acknowledged. The author is particularly appreciative for the help of Mrs. Georgia Troglen in manuscript typing. Her cheerful and efficient work greatly eased that not inconsiderable burden of authorship involved in the conversion of semilegible manuscript to near perfect typescript.

D.A.S.

Knoxville, Tennessee  
October 1963



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In the latter part of the sixteenth and early part of the seventeenth centuries, the Spanish conquerors of Peru observed the natives using the powdered bark of a certain tree for the treatment of malaria. It is alleged that the bark was used successfully in the treatment of the wife of the vicéroy to Peru, Countess de Cinchon. About 1640 this material was introduced into Europe, largely through the efforts of Jesuit priests, and for many years it was known as "Jesuit bark."

The French chemists Pelletier and Caventou in 1820 investigated the nature of this bark of the cinchona tree, as it had come to be called, and they succeeded in isolating a pure crystalline compound. They called this substance *quinine*, and it was demonstrated that the pure substance possessed the medicinal properties of the crude bark. Quinine was shown to consist of carbon, hydrogen, nitrogen, and oxygen, and in 1831 the German chemist Justus Liebig carried out a quantitative analysis of the compound and some of its salts. This showed quinine to have the formula  $C_{20}H_{24}N_2O_2$ .

It required many years of intensive effort by various workers before knowledge was obtained of *arrangement* of these 48 atoms of the quinine molecule. Around 1900 the German chemist Rabe was able to postulate a satisfactory structure or arrangement of the atoms. This postulate remained without proof until 1944, when the Americans Woodward and Doering announced the *synthesis*, or building-up, from simple materials of an arrangement of atoms corresponding to the Rabe structure. The identity of the synthetic product with natural quinine confirmed the correctness of the Rabe postulate and therefore proved the structure of quinine.

The synthesis of quinine, however, is too difficult, and therefore expensive, for economical preparation of the compound in the quantities needed for medicinal