FUNDAMENTALS OF ORGANIC CHEMISTRY

A.N. NESMEYANOV, N.A. NESMEYANOV

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Volume I

А. Н. Несмеянов, Н. А. Несмеянов

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A. N. NESMEYANOV and N. A. NESMEYANOV

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Brief Contents
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Preface

The present course of organic chemistry is intended for chemical departments at universities and higher schools of chemistry. It has evolved from the lectures read by one of the authors to students of chemistry at Moscow State University and includes the elements of theoretical foundations of organic chemistry—the subject matter of the course taught at Moscow State University by Academician O. A. Reutov and the co-author of this book. This accounts for the order of presentation of the material, which is more classical and departs somewhat from that adopted in many modern textbooks, chiefly those written by Nenitzescu, Roberts and Caserio, Cram and Hammond. This traditional approach consists in presenting first an introduction (with a brief historical outline of organic chemistry and of development of the fundamental concepts, methods of characterization of organic compounds, analysis, determination of molecular formulas, structural theory), followed by a systematic exposition of the material in the sequence: the aliphatic series, alicyclic compounds, the aromatic series, heterocyclic compounds. These topics constitute the subject matter of Part I (volumes I, II, and III).

The theoretical material—elements of the theory of chemical reactions, the chemical-bond theory, classical and dynamic stereochemistry, conformations—will be found incorporated, as separate sections, in the appropriate places in the text, after the adequate factual material has accumulated for assimilation of the theory introduced. The same applies to the physical methods of investigation of organic compounds. From our own experience, we know that this approach makes it possible to pass gradually to the most advanced topics of organic chemistry.

Part I, which consists of three volumes, is intended for close study. Part II (volume IV) is written in a more condensed form and is therefore difficult for understanding. The material introduced in Part II partly generalizes and extends the concepts associated with reaction mechanisms, which are treated at a more elementary level in Part I.

It contains chapters dealing with carbanions, free radicals, carbenes, carbonium ions, rearrangements, elimination reactions, the transition state. Furthermore, Part II includes more sophisticated material of organic chemistry, such as organoelement compounds, nonbenzoid aromatics, isoprenoids (including terpenes and steroids), alkaloids, proteins, enzymes, nucleic acids. Preliminary information on organoelement compounds, isoprenoids, alkaloids, and proteins is given in Part I.

We think that all the topics covered by Part II must be read attentively in order to get a general picture; chemistry students need not study them. Teaching experience shows that the mastering of this material is a rather formidable task in a general course. Chemistry majors will be able to master this material in the later years of their study.

Thus, the amount of material that the student is strongly urged to work through in detail is not too large, the more so that we allowed for some repetitions (each time in a more extended form), which will undoubtedly facilitate the study.

Both authors have equally contributed to all the principal sections of all the four volumes. This book could not have been written without the help of our friends and colleagues, to whom we express our deep gratitude for the various contributions to the text. We very much appreciate the contributions made by Professor D. A. Bochvar, who has written the section devoted to the modern theory of the chemical bond, and by Professor A. I. Kitaigorodsky who has written the section on diffraction methods of structural analysis.

The authors are greatly indebted to Academicians M. I. Kabachnik, V. A. Engelgardt, and A. E. Braunshtein, Associate Member of the USSR Academy of Sciences N. K. Kochetkov, Professors M. M. Botvinnik and Z. A. Shabarova, Doctors V. T. Aleksanyan and E. I. Fedin for the perusal of separate sections of the manuscript and for their valuable corrections and many critical comments and suggestions for its improvement.

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We extend our heartfelt thanks to M. A. Vinogradova, E. I. Kan and V. A. Ventskovskaya for the indispensable assistance in preparing the manuscript for publication.

We will be grateful for any constructive criticism of this book.

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PART ONE

Chapter 1

Introduction

1.1. The Subject of Organic Chemistry. The Historical Background

Chemistry is concerned mainly with study of chemical entities—chemical compounds—and their transformations. An independent branch of the chemical science—*organic chemistry*—deals with compounds formed by carbon with other elements. Carbon forms an especially large number of compounds with elements called **organogenetic elements** or **organogens**: hydrogen (H), oxygen (O), nitrogen (N), sulphur (S), phosphorus (P), and the halogens. These compounds are widespread in nature and have mostly been investigated and produced artificially through synthesis.

Some organic compounds have been known to man in a more or less pure form since times immemorial (for example, vinegar—an aqueous solution of acetic acid, and many organic dyes). A number of organic compounds, such as urea and ethyl ether (sulphuric ether), were produced by alchemists. A great many compounds, especially organic acids (oxalic, citric, lactic, and others) and organic bases (alkaloids), were isolated from plant and animal sources in the second half of the eighteenth and at the beginning of the nineteenth century. This period should be regarded as the birth of scientific organic chemistry corresponding to the two branches of the former chemistry which was separated into mineral chemistry and the chemistry of plants and animals (the name "organic chemistry" originated later).

In the eighteenth century and in the first quarter of the nineteenth century there reigned the belief that the chemistry of living matter was fundamentally different from the chemistry of inanimate matter (mineral chemistry) and that living organisms built their substances under the influence of a special **vital force** or vital energy (*the doctrine of vitalism*), without which compounds of this type could not be produced artificially in the laboratory. Since from the beginning of the nineteenth century an ever increasing number of substances common to the world of animals and plants were detected (beginning with acids, such as oxalic and formic, up to fats and proteins), the borderline between the chemistry of plants and that of animals gradually disappeared. When it became clear that the chemistry of plants and the chemistry of living organisms must be integrated into a single science, the new branch of chemical science was named *organic chemistry*. The credit for this goes to the notorious Swedish chemist J. J. Berzelius (1779-1848). Following A. L. Lavoisier (1743-1794), he made extensive use of quantitative analysis in his studies, discovered a number of new elements, established the atomic weights of many elements, discovered the phenomenon of isomerism and worked out the dualistic electrochemical theory.

Organic chemistry was considered to include not only substances isolated directly from plant and animal sources (which could not be obtained by synthesis according to the views of that time) but also the products of their chemical transformations. In 1824, the German chemist Friedrich Wöhler (1800-1882) produced oxalic acid, an organic compound, through the hydrolysis of cyanogen, of recognized mineral origin. An important discovery was that of Wöhler who in 1828 found that urea, a typical organic substance that derives its name from urine, in which it is found, could be prepared from the "inorganic" compound ammonium cyanate:

$$NH_4CNO \longrightarrow NH_2{-}CO{-}NH_2$$

It is this discovery that made a break in the wall of prejudices that separated organic chemistry from the chemistry of compounds of inanimate origins, and led the chemists of the time to believe that organic substances could also be produced artificially, without the intervention of a hypothetical vital force. Wöhler's discovery, however, did not immediately demolish vitalism. How firmly these erroneous views still persisted follows from the words of the French chemist Charles Gerhardt who developed certain fundamental concepts of organic chemistry (for example, the concept of homology) and was one of the authors of the Avogadro-Gerhardt law. In 1842, when many simple organic substances had already been obtained in the laboratory, Gerhardt held the view that the synthesis of such a complex compound as sugar could never be accomplished. This sceptical prediction was discredited in 1861 when A. M. Butlerov first obtained synthetically sugar substances from formalin. This was paralleled by the rapid growth of the number of individual carbon-containing compounds that did not occur in nature. Thus, in 1825, Faraday prepared benzene; ethylene, ethylene bromide, and a number of derivatives of benzene had become known still earlier. In 1842, Zinin obtained aniline from nitrobenzene, and in the fifties of the same century the first aniline dyes—mauveine (Perkin's mauve) and fuchsin—were synthesized from aniline.