

A TEXT-BOOK OF  
**PRACTICAL ORGANIC  
CHEMISTRY**

INCLUDING  
QUALITATIVE ORGANIC ANALYSIS

By  
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*With diagrams and 8 photographs*

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## PREFACE TO THIRD EDITION

THE favourable reception accorded to previous editions by reviewers, students and practising organic chemists has encouraged the author to undertake an exhaustive revision of the entire text in the light of the numerous developments in practical organic chemistry since the book was first written (1945-46). The net result has been an increase in the length of the volume by some 150 pages, a figure which gives some indication of the new matter incorporated in the present edition.

It is impossible within the limitations of a short preface to give a detailed list of the numerous changes and additions. Some of the more important new preparations include :

1. *Chapter III.* 1-Heptene (III,10); alkyl iodides (KI-H<sub>3</sub>PO<sub>4</sub> method) (III,38); alkyl fluorides (KF-ethylene glycol method) (III,41); keten (nichrome wire method) (III,90); ion exchange resin catalyst method for esters (III,102); acetamide (urea method) (III,107); ethyl  $\alpha$ -bromopropionate (III,126); acetoacetic ester condensation using sodium triphenylmethide (III,151).

2. *Chapter IV.*  $\alpha$ -Chloromethylnaphthalene (IV,23); benzylamine (Gabriel synthesis) (IV,39); *NN*-dialkylanilines (from amines and trialkyl orthophosphates) (IV,42);  $\alpha$ -naphthaldehyde (Sommelet reaction) (IV,120);  $\alpha$ -phenylcinnamic acid (Perkin reaction using triethylamine) (IV,124);  $\beta$ -nitrostyrene (IV,129);  $\beta$ -bromonaphthalene and  $\beta$ -naphthoic acid (from 2-naphthylamine-1-sulphonic acid) (IV,62 and IV,164); diphenic acid (from phenanthrene) (IV,165).

3. *Chapter V.* Quinaldine (V,2); 2-methyl-, 2:5-dimethyl- and 2-acetylthiophene (V,8-V,10); 2:5-dimethyl- and 2:4-dimethyl-dicarbethoxy-pyrrole (V,12-V,13); 2-amino- and 2:4-dimethyl-thiazole (V,15-V,16); 3:5-dimethylpyrazole (V,17); 4-ethylpyridine (from pyridine) (V,19); *n*-amyl-pyridines from picolines (V,28); picolinic, nicotinic and isonicotinic acid (V,21-V,22); ethyl nicotinate and  $\beta$ -cyanopyridine (V,23-V,24); uramil (V,25); 4-methylcoumarin (V,28); 2-hydroxylepidine (V,29).

4. *Chapter VI.* Reductions with potassium borohydride (VI,11); Oppenauer oxidation (VI,13); epoxidation and hydroxylation of ethylenic compounds (VI,15); Arndt-Eistert reaction (VI,17); Darzens glycidic ester condensation (VI,18); Erlenmeyer azlactone reaction (VI,19); Mannich reaction (VI,20); Michael reaction (VI,21); Schmidt reaction (VI,23); Stobbe condensation (VI,24); Willgerodt reaction (VI,25); unsymmetrical diaryls (VI,27); syntheses with organolithium compounds (VI,28); syntheses with organosodium compounds (VI,29); syntheses with organocadmium compounds (VI,30); some electrolytic syntheses (VI,31); chromatographic adsorption (VI,33); ring enlargement with diazomethane (VI,34).

5. *Chapters VII-IX.* Diazomethane (*p*-tolylsulphonylmethylnitrosamide method) (VII,20); Girard's reagents "T" and "P" (VII,25); pseudo-saccharin chloride (VII,26); 2:2'-dipyridyl (VIII,13); ninhydrin (VIII,14); 3-indoleacetic acid (IX,14).

A new feature is the account of the electronic mechanisms (in outline) of the numerous reactions described in the text. Although some of these mechanisms may be modified in the near future, it is hoped that the brief treatment scattered throughout the volume will stimulate the student's interest in this important branch of organic chemistry. It will be noted that many reactions are designated by name; this may be undesirable on pedagogical grounds but, in most cases, established usage and the example set by the various volumes of *Organic Reactions* (J. Wiley) may be put forward in justification.

Chapter XII is concerned with Semimicro Technique. There can be little doubt that preparations on a smaller scale than has hitherto been customary have many advantages; particular reference may be made to cost, time and bench space, all of which are important factors in teaching laboratories and also in training for research. Once the student has mastered the special technique, no difficulty should be experienced in adapting most of the preparations described in the book to the semi-micro scale. A few examples of small-scale preparations are included together with a suggested list of experiments for an elementary course.

Section A,7, "Applications of infrared and ultraviolet absorption spectra to organic chemistry," should provide a brief introduction to the subject.

It is regretted that the size of the volume has rendered the insertion of literature references impossible: the Selected Bibliography (A,5) may partly compensate for this omission. Section numbers are now included in the headings of the pages—a feature introduced in response to requests by many readers. The volume comprises virtually at least three books under one cover, *viz.*, experimental technique, preparations, and qualitative organic analysis. It should therefore continue to be of value as a one-volume reference work in the laboratory. Students at all levels will find their requirements for laboratory work (excluding quantitative organic analysis) adequately provided for and, furthermore, the writer hopes that the book will be used as a source of information to supplement their theoretical studies.

The author wishes to thank Dr. G. H. Jeffery, C. T. Cresswell, B.Sc., C. M. Ellis, M.Sc., Dr. J. Leicester and C. Kyte, B.Sc., for assistance with the proof reading and for helpful suggestions; Dr. G. H. Jeffery for invaluable assistance in numerous ways; and C. Kyte, B.Sc., and R. Grezskowiak, B.Sc., for a number of original preparations and also for checking and improving many of the new experimental procedures.

Criticisms and also suggestions for improving the book are welcomed.

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*September 1955.*

## PREFACE TO FIRST EDITION

THE present volume is an attempt to give to students of practical organic chemistry the benefit of some twenty years' experience in research and teaching of the subject. The real foundations of the author's knowledge of the subject were laid in 1925–1929 when, as a research student at the Imperial College under the late Professor J. F. Thorpe, F.R.S., he was introduced to the methods and experimental technique employed in a large and flourishing school of research in organic chemistry. Since that period the author and his students have been engaged *inter alia* in researches on *Physical Properties and Chemical Constitution* (published in the *Journal of the Chemical Society*) and this has involved the preparation of over a thousand pure compounds of very varied type. Many of

the new procedures and much of the specialised technique developed and employed in these researches are incorporated in this book. Furthermore, new experiments for the elementary student have emanated from these researches; these have been tried out with large classes of undergraduate students over several sessions with gratifying success and have now been included in the present text-book.

In compiling this book, the author has drawn freely from all sources of information available to him—research notes, original memoirs in scientific journals, reference works on organic chemistry, the numerous text-books on practical organic chemistry, and pamphlets of manufacturers of specialised apparatus. Whilst individual acknowledgement cannot obviously be made—in many cases the original source has been lost track of—it is a duty and a pleasure to place on record the debt the writer owes to all these sources. Mention must, however, be made of *Organic Syntheses*, to which the reader is referred for further details of many of the preparations described in the text.

The book opens with a chapter on the theory underlying the technique of the chief operations of practical organic chemistry: it is considered that a proper understanding of these operations cannot be achieved without a knowledge of the appropriate theoretical principles. Chapter II is devoted to a detailed discussion of experimental technique; the inclusion of this subject in one chapter leads to economy of space, particularly in the description of advanced preparations. It is not expected that the student will employ even the major proportion of the operations described, but a knowledge of their existence is thought desirable for the advanced student so that he may apply them when occasion demands.

Chapters III and IV are confined to the preparation and properties of Aliphatic Compounds and Aromatic Compounds respectively. This division, although perhaps artificial, falls into line with the treatment in many of the existing theoretical text-books and also with the author's own lecture courses. A short theoretical introduction precedes the detailed preparations of the various classes of organic compounds: it is recommended that these be read concurrently with the student's lecture course and, it is hoped, that with such reading the subject will become alive and possess real meaning. The partition of the chapters in this manner provides the opportunity of introducing the reactions and the methods of characterisation of the various classes of organic compounds: the foundations of qualitative organic analysis are thus laid gradually, but many teachers may prefer to postpone the study of this subject until a representative number of elementary preparations has been carried out by the student. The division into sections will facilitate the introduction of any scheme of instruction which the teacher considers desirable.

Chapters V–X deal respectively with Heterocyclic and Alicyclic Compounds; Miscellaneous Reactions; Organic Reagents in Inorganic and Organic Chemistry; Dyestuffs, Indicators and Related Compounds; Some Physiologically-Active Compounds; and Synthetic Polymers. Many of these preparations are of course intended for advanced students, but a mere perusal of the experimental details of selected preparations by those whose time for experimental work is limited may assist to impress them on the memory. Attention is particularly directed to the chapter

upon Organic Reagents in Inorganic and Organic Chemistry. It is always a good plan to set advanced students or adequately-trained laboratory assistants on the preparation of those compounds which are required in the laboratory for organic and inorganic analysis; the resulting cost is comparatively low (for *o*-phenanthroline, for example, it is less than one-tenth of the commercial price) and will serve to promote the use of these, otherwise relatively expensive, organic reagents in the laboratory.

Chapter XI is devoted to Qualitative Organic Analysis. The subject is discussed in moderate detail and this, coupled with the various Sections and Tables of Physical Constants of Organic Compounds and their Derivatives in Chapters III and IV, will provide a satisfactory course of study in this important branch of chemistry. No attempt has been made to deal with Quantitative Organic Analysis in this volume.

The text-book is intended to meet the requirements of the student of chemistry throughout the whole of his training. Considerable detail is given in those sections of particular interest to the elementary student; in the author's opinion it is the duty of a writer of a practical text-book to lay a secure foundation of sound experimental technique for the beginner. The subject matter of the book is sufficiently comprehensive to permit the teacher to cover any reasonable course of instruction. It will be observed that the scale of the preparations varies considerably; the instructor can easily adapt the preparation to a smaller scale when such a step is necessary from considerations of cost and time or for other reasons. Quantities of liquid reagents are generally expressed as weights and volumes: the latter refer to a temperature of 20°. The book will be suitable for students preparing for the Pass and Honours (General and Special) B.Sc. of the Universities, the A.R.I.C. and the F.R.I.C. (Organic Chemistry). It will also provide an introduction to research methods in organic chemistry and, it is hoped, may serve as an intermediate reference book for practising organic chemists.

Attention is directed to the numerous references, particularly in Chapter II on Experimental Technique, to firms supplying specialised apparatus. The author has usually had first-hand experience with this apparatus and he feels that some readers may wish to know the present source of supply and also from whom to obtain additional information. It must be mentioned that most of the specialised apparatus has been introduced to the market for the first time by the respective firms after much development research and exhaustive tests in their laboratories. A reference to such a firm is, in the writer's opinion, equivalent to an original literature reference or to a book. During the last decade or two much development work has been carried out in the laboratories of the manufacturers of chemical apparatus (and also of industrial chemicals) and some acknowledgement of the great help rendered to practical organic chemists by these industrial organisations is long overdue; it is certainly no exaggeration to state that they have materially assisted the advancement of the science. A short list of the various firms is given on the next page.

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Woolwich Polytechnic, London, S.E. 18.  
December 1946.

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