

BOOK REVIEWS

J. ENGLISH and H. G. CASSIDY: **Principles of Organic Chemistry** (second edition). McGraw-Hill, New York, 1956. 473 pp. 49s.

THIS text book of 473 pages has been written to cover a first-year course in organic chemistry in such a way as to stress the fundamental principles of the subject. The reviewer believes that the authors have largely succeeded in their intentions. There are twenty-four chapters divided into sections, which are well indexed, so that it has been possible to use cross-references. The first chapter, or introduction, deals with the geometry of the carbon atom and the types of bond which it forms. Ions, radicals, formulae, and the various electronic effects are also defined. The hydrocarbons, acyclic and aromatic, are next described, followed by the chemistry of alcohols and phenols (described together), halogen compounds, ethers, carbonyl compounds, amines and derivatives, sulphur compounds, substituted acids including hydroxy, keto, and amino acids, brief reference to colour and chemical constitution, stereoisomerism, carbohydrates, macromolecules, and a chapter devoted to heterocyclic chemistry.

Each chapter ends with historical notes and a very useful summary; useful that is, if employed wisely. It is, unfortunately, only too common for students to try to exist on predigested information. A wide variety of exercises are also provided chapter by chapter and some answers are given.

In this book, organic chemistry has been approached from the underlying theory of reaction mechanism, treated qualitatively. Although there is a wide difference of opinion on the wisdom of this method of treatment, the reviewer is decidedly of the opinion that in a first-year course in organic chemistry the minimum of mathematics should be introduced; there are always many students who do not wish to pursue chemistry beyond one or two years.

There are a number of minor points in the treatment of the course of study which might be raised. Thus, whilst the authors quite rightly indicate how in a Friedel and Crafts reaction a carbonium ion is produced as the reacting entity, they omit to show how in, say, nitration the NO_2^+ ion is produced. The student could be left with the impression that sulphuric acid is employed merely for removal of water. Again, whilst it is shown that, in general, hydrolysis of carboxylic esters takes place by breakage of acyl-oxygen bond, it is not shown that alkyl esters of sulphonic acids undergo breakage of the oxygen-alkyl bond, a fact which is so important in alkylation reactions. There are other topics where a chance to impress a difference in behaviour of two somewhat similar series of compounds has been missed. But these are not serious criticisms.

The printing and the layout of the text is very good. There are a number of mistakes in formulae which will have to be corrected in a second edition.

The reviewer enjoyed reading this book and can commend it to students; he wonders whether the average student will pay 49s. for a text which will serve him for only one year.

W. COCKER

Organic Syntheses, Vol. 36. Editor in chief, N. J. Leonard. John Wiley & Sons, Inc., New York; Chapman & Hall, Ltd., London, 1956. 120 pp.

It seems almost superfluous to be asked to review any volume of *Organic Syntheses*. These volumes, first published in 1921, and made into Collective volumes at ten-yearly intervals, are necessary literature of any chemical laboratory. The present volume (36; 1956) maintains the high standard of printing and general layout which is associated with this publication.

For convenience the compounds synthesised are arranged alphabetically although in the present volume this brings *cyclodecanediol* and *cyclodecanone* together early in the book and their precursor *sebacoin* or *sebacil* quite late. This review would be too lengthy if reference were made to all the compounds for which preparations are given, but it might not be out of place to mention that two methods for the preparation of ferrocene are given.

W. COCKER

S. T. YOFFE and A. N. NESMEYANOV: *A Handbook of Magnesium-Organic Compounds*, Pergamon Press, 1956. Vol. I, pp. 744; Vol. II, pp. 664; Vol. III, pp. 644. £24.

THIS ambitious work, by two distinguished Academicians, is a compilation of reactions involving the formation and the use of Grignard reagents and other organo-magnesium compounds. The first two volumes contain a list of 13395 reactions of substances—arranged in the order used in *Chemical Abstracts* indexes—with various Grignard reagents. This list (Section I) gives the products of the reactions and numerical references (5375, beginning with references to Russian authors in Cyrillic script and finishing with other references in Latin script). The third volume is essentially for cross-reference purposes and contains not only the literature references but also a formula index of end-products (Section II) of the reactions listed in the first two volumes, and a formula index of the Grignard reagents (Section III), excluding the simplest such as those derived from methyl, ethyl, phenyl, and tolyl halides. These formula indexes refer the reader to the number of the appropriate reaction to be found in the main list in the first two volumes. The three volumes are thus intended to be used together.

The *Handbook*, with the exception of a few title pages, is a photo-lithographic reproduction of the Russian volumes. Since, however, the main list of reactions (Section I, the subject of the first two volumes) is described by means of conventional formulae in Latin script, its use does not require a knowledge of Russian. The extensive (330 page) index of end-products, which begins Volume III, is arranged in order of empirical formulae. This is also true of the 33 page index of Grignard reagents. Many compounds may be listed under one such formula, and these are described by Russian names. Even this index could be used without a knowledge of Russian since the numbers set against each name refer to the main list of reactions in which structural formulae are given in Latin script. However, a great deal of effort can be saved merely by transliteration of the Russian names into Latin script; this is very easily done and the transliterated names are usually recognisable without difficulty. The translator's preface, by Dr. A. L. Mackay, thoughtfully provides not only a table for the transliteration of Russian letters into their Latin equivalents, but also a glossary of some Russian chemical words whose meaning is not obvious after transliteration, and a few general hints on the use of the book for those who do not know Russian.

With the main volumes is provided a 31 page booklet comprising a Foreword by Professor W. Wardlaw, and translations of the Russian Preface and Introduction. The last contains the essential instructions on the use of the book and illustrations of the nomenclature adopted, including the linear representation of cyclic formulae. The Preface is mainly concerned with the contributions of Russian chemists to the study of Grignard reactions. Though there is reference to Barbier and Grignard, there is none to Gilman, or to Frankland, although organo-zinc compounds are discussed; however, the latter omission is rectified in the Foreword. Similarly, though the authors refer to Runge's excellent monograph, they do not mention the extremely useful recent (1954) and detailed 1384-page book by Kharasch and Reinmuth, *Grignard Reactions of Nonmetallic Substances*. It is probable that both works were prepared more or less at the same time, and they will certainly be compared. Kharasch and Reinmuth's book has the advantage of later literature coverage, up to *Chemical Abstracts* of June 1950, in spite of earlier publication, since the *Handbook* under review contains references published in abstract up to 1 January 1948; it has also the very great advantage of being a critical textbook in which yields are nearly always given, as well as a compilation of reactions. The *Handbook*, by contrast, has the advantage of including reactions of Grignard reagents with metallic as well as nonmetallic substances, and also the reactions of compounds in which magnesium is not directly linked to carbon. Both works aim to provide answers to similar kinds of enquiry about Grignard reagents and their use; Kharasch and Reinmuth's book differs essentially in being a critical text covering a narrower though still a remarkably wide range, and it must be pointed out that the *Handbook* costs over three and a half times as much.

Supplements are planned to keep the *Handbook* up to date. The organic compounds of magnesium will thus become one of the best documented of chemical topics. It is also most satisfactory to note the publication of the *Annotated Bibliography on the use of Organolithium Compounds in Organic Synthesis with Supplements*.

The reviewer has not read the *Handbook* page by page—not many chemists will—and has noticed no errors. A work of this kind is worth its high price only if the reader has confidence in its completeness. The *Handbook* is to be recommended, and nearly all chemical libraries should have a copy of this valuable contribution to an important subject.

G. E. COATES

R. P. LINSTEAD* and B. C. L. WEEDON:† **A Guide to Qualitative Organic Chemical Analysis**. Butterworths, London, and Academic Press, New York, 1956. xi + 169 pp. 21s. \$4.50.

THE approach of the present text to the subject is slightly different from that commonly employed in most American universities. Instead of using the solubility of the compound as a starting point, the present authors turn instead to the type of procedure originally used by Mulliken and Huntress, in which the compound is initially classified according to its elemental analysis. The new system is otherwise rather different from the one of Mulliken and Huntress, however, as to the order in which functional groups are tested for.

The authors imply their general procedure is superior to others available, and state that it is sufficiently different to justify publication. That their procedure is different is apparent. The reviewer, however, while admitting to not actually having used their system in the laboratory, is not convinced that it is superior to the more commonly used ones as typified by those of Shriner and Fuson or McElvain. It would rather seem a matter of personal preference as to exactly how the various tests are conducted and their results interpreted.

The very small size of the book is a result of both rather fine printing, and of complete omission of any description of the techniques and apparatus used in manipulating small amounts of material. In regards to the latter, the authors comment that no printed directions can adequately replace practical demonstration.

The chemical tests used, besides the conventional ones, are good and up-to-date. The coverage of the less common compounds (e.g. azo, azoxy, nitroso, sulphonamides, thiomides, sulphonyl halides, etc.) is more detailed than usual while, as customary, highly specialized compounds (e.g. alkaloids, peptides, phosphorus derivatives, etc.) are not considered. Leading references are generally given where desirable.

The separation and identification of mixtures is exceedingly brief (four pages).

The use of spectra in deducing structure is not considered, and the reviewer regards this as unfortunate, since although it may tend to encourage an understanding of chemical methods of identification, it actually widens the gap between the subject as used in research and as taught in the course.

NORMAN L. ALLINGER

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Essays in Biochemistry. Edited by SAMUEL GRAFF, John Wiley and Sons, Inc., New York; Chapman and Hall Ltd., London, 1956. x + 345 pp. 52s.

IN this collection there are twenty-five essays written in honour of Hans Thacher Clarke on his retirement as Professor and Chairman of the Department of Biochemistry, College of Physicians and Surgeons, Columbia University, New York. The authors, all former students or academic associates of Professor Clarke, were given a completely free hand by the editor, both in regard to the subject and to the style of their contribution. This absence of editorial restraint, so seldom allowed to scientific authors, has resulted in a number of most interesting essays, several of which are excitingly speculative.

For those whose interest is in the chemistry of natural products there are the essays on "Some Metabolic Products of Basidiomycetes" by Dr. Marjorie Anchel and on "The Veratrum Alkalines" by Dr. Oskar Wintersteiner. Dr. William H. Stein gives an excellent account of the work on the determination of the amino-acid sequence in the protein ribonuclease, to which he and his colleagues at the Rockefeller Institute for Medical Research have made such a great contribution. The elucidation of the exact chemical structure of proteins, by methods which were exploited so brilliantly by Sanger with insulin, may lead a wider group of organic chemists to interest themselves in these macromolecules which, up to now, may have appeared to be rather too indeterminate and "messy" for serious consideration.

For the theoretical organic chemist there are the essays on "Tetrazoles as Carboxylic Acid Analogs" by Professor Robert M. Herbst and "The Structural Basis for the Differentiation of Identical Groups in Asymmetric Reactions" by Dr. Hans Hirschmann. In this last essay the author proposes a new criterion to decide whether, in a given case, two identical groups in a reactant can or cannot be differentiated from each other in any reaction. The author's ideas, and those of others, are discussed in detail and are illustrated by a number of examples.

Professor Erwin Chargaff in his provocative essay entitled "The Very Big and the Very Small: Remarks on Conjugated Proteins" enjoins future generations of investigators to continue to be astonished by the complexities of living organisms, to continue their probing to attain a deeper understanding of the chemical processes of cells and to beware of the too facile model experiment. Professor David Rittenberg, writing "On the Bigness of Enzymes" puts forward an hypothesis for the mechanism of action of oxidoreduction and hydrolytic enzymes. This hypothesis uses an analogy between enzymes and metal catalysts of the transition groups with vacant *d* orbitals which may be used for chemisorption. It is postulated that the electrons of the enzyme protein molecule could move in a periodic field arising from the regular linear arrangement of the peptide bonds of the polypeptide chain. The electrons in this excited state would be distributed in a number of discrete levels forming an energy band, the lower edge of which approaches closely to the ground state. Should a peptide substrate, say, approach the enzyme two of the π electrons of the carbonyl group might be transferred to a low level of the excited state energy band of the enzyme. The approach of a water molecule or an hydroxyl ion to the now positively charged substrate carbon atom is thus facilitated. The presence of divalent metal ions, which is often required for such enzyme reactions, would provide a set of energy levels which would facilitate the transfer of electrons to the enzyme.

There are other essays dealing with the biosynthesis of branched-chain compounds (Konrad Bloch), the biosynthesis of porphyrins (David Shemin), glycogen turnover (De Witt and Marjorie Stetten) and the biochemistry of the steroid hormones (L. L. Engel). Dr. Sarah Ratner gives a stimulating account of nitrogen transfer in biosynthetic mechanisms, in which the energy relations of the synthesis of urea are discussed. There are some thoughtful contributions on the more peripheral fields of biochemistry: lysogeny (Ernest Borek), unbalanced growth and death (S. S. Cohen), bacterial viruses (E. A. Evans), and the nature of cancer (Samuel Graff).

It is only natural that such a collection of essays should not all be of the same high level as some of those mentioned above, nor would one expect many to read straight through this book. There is no doubt, however, that every biochemist will find a great deal to interest him here, as will most organic chemists.

S. P. DATTA

BOOKS RECEIVED

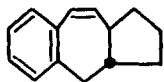
MIGRDICHIAN, VARTCES: *Organic Synthesis Vols. I and II*. 1882 pages (Reinhold Publishing Corporation, New York; Chapman and Hall Ltd., London, 1957) £14

KELLEY, L: *Organic Chemistry* (second edition) 757 pages. (McGraw-Hill Book Co. Ltd., 1957) \$7.50 (56s. 6d.)

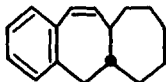
ERRATUM

Tetrahedron 1/2, 9 (1957): Alicyclic studies—XI.
Attempted syntheses of 5:6-benzazulene and
benzheptalenes.

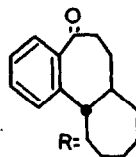
The formula on p. 11 should read as follows:



XI



XII



XIII (a) R = H₂
(b) R = O