



are based on the stereostructure III and its mirror image.

Dihydrohaemanthamine³ (V, R = OH), was treated with thionyl chloride for one hour at 78°. The excess reagent was removed and the residue was refluxed with an excess of lithium aluminum hydride in tetrahydrofuran for 5 hours. The reaction product, desoxydihydrohaemanthamine, isolated in 52% yield, was identical in melting point (95–97°) and infrared spectrum (KBr) with dihydrobuphanisine (V, R = H).⁵ A mixture

(5) H. M. Fales and W. C. Wildman, *THIS JOURNAL*, **80**, 4395 (1958).

melting point determination was depressed below 70°. The optical rotatory dispersion curves (330–700 m μ) in chloroform of the product ($[\alpha]^{25}_D +28^\circ$) and dihydrobuphanisine ($[\alpha]^{25}_D -28^\circ$) revealed that the two substances were optical antipodes.

This transformation identifies the alkaloids hydroxylated in the 5-membered D ring (haemanthamine, haemanthidine, crinamine³ and haemultine⁶) with the (+)-crinane nucleus (III) while the alkaloids not hydroxylated in this position, crinine, powelline, buphanidrine, buphanisine, undulatine, and buphanamine, have been shown to contain the enantiomorphic (–)-crinane nucleus.^{5,7,8,9} Finally, it seems likely that pharmacological differences between the alkaloids of this nucleus stem from the absolute configurations of the bases rather than the stereochemical differences associated with the fusion of the octahydroindole ring.

(6) H.-G. Boit and W. Döpke, *Chem. Ber.*, **91**, 1965 (1958).

(7) E. W. Warnhoff and W. C. Wildman, *Chemistry & Industry*, 1293 (1958).

(8) W. C. Wildman, *THIS JOURNAL*, **80**, 2567 (1958).

(9) These observations should not be interpreted as a general rule, since the occurrence of vittatine, the optical antipode of crinine, has been reported.¹⁰

(10) H.-G. Boit and H. Ehmke, *Chem. Ber.*, **90**, 369 (1957).

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BOOK REVIEWS

Biochemical Preparations. Volume 5. DAVID SHEMIN, Editor-in-Chief. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1957. ix + 115 pp. 15.5 × 23.5 cm. Price, \$4.75.

This volume, the fifth in the series, gives comprehensive procedures for the synthesis or isolation of over thirty substances of special interest to biochemists. The excellent style and format, resembling the "Organic Syntheses" series established in previous volumes, are maintained. The utility of the volume is increased by the inclusion of a cumulative subject index, a reference list of compounds of biochemical interest which have appeared in "Organic Syntheses" (through volume 37), a section on the properties and purity of each product and cross references given in the description of each preparation. The reliability and feasibility of each procedure submitted has been checked by an independent expert, whose comments appear as separate notes. The fifth volume of the series is another notable achievement of the objectives of the series as stated in the preface of the first volume: "to provide authoritative, thoroughly checked preparations for substances used in biochemical research and to provide preparations illustrating manipulative techniques and methods that may be useful both to research workers and to students."

A list of the contents of volume five follows: dibenzyl phosphorochloridate, phosphatidyl ethanolamine, sodium phosphocreatine, aldolase, crystalline condensing enzyme, S-succinyl coenzyme A, cytochrome c (addendum) and reduced cytochrome c, separations of nucleotides of ribonucleic acid, separation of 5'-deoxyribonucleotides, nicotinamide mononucleotide (NMN), S-adenosylmethionine (AMe), adenine-8-C¹⁴, D-glyceric acid 2-phosphate (trisodium salt), 2-deoxy-D-ribose, L-glutamine and D-glutamine, S-benzyl-DL-

homocysteine, S-benzyl-L-homocysteine, and S-benzyl-D-homocysteine, homocystine and homocysteine, cyanomethylimidazole and imidazoleacetic acid hydrochloride, formiminoglycine, formimino-L-aspartic acid, formimino-L-glutamic acid.

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Encyclopedia of Chemical Reactions. Volume VII. Strontium, Sulfur, Tantalum, Technetium, Tellurium, Terbium, Thallium, Thorium, Thulium, Tin and Titanium. Compiled by C. A. JACOBSON, Late Professor of Chemistry, West Virginia University. Edited by CLIFFORD A. HAMPEL, Manager, Chemical Equipment Division, Fansteel Metallurgical Corporation, Editor, "Rare Metals Handbook." Reinhold Publishing Corporation, 430 Park Avenue, New York 22, N. Y. 1958. 479 pp. 16 × 23.5 cm. Price, \$12.75.

This seventh volume of the "Encyclopedia of Chemical Reactions" retains essentially the features of its predecessors. The early literature on a large variety of reactions is well covered; the indexes are remarkably complete; the book is printed and bound in a readable and attractive style. That some effort has been made to counter criticisms of earlier volumes is evidenced by the appearance of references as recent as 1957.

A number of the elements included in this volume have been studied intensively during the past fifteen years, and it is unfortunate that more of this new chemistry has not been included. Hydride reactions are omitted almost com-

pletely; recent halide chemistry (particularly of the fluorides) warrants review and inclusion in an encyclopedia; various interesting and important compounds such as the tellurides, phosphides, arsenides, etc., are not mentioned.

The editor, in his preface, notes the incomplete coverage. However, with the aid of "Chemical Abstracts" and "Nuclear Science Abstracts" it should be possible and worth while to make a broader coverage of even moderately current literature than has been done. The principal value of this volume thus remains as a guide to the early literature.

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The book of pH . A simple and complete description of the theory and practice of the measurement of pH as applied to science and industry. BY R. B. WEBBER, M. A. (Cantab.), Lecturer in Physics, Cambridgeshire Technical College. The Macmillan Company, 60 Fifth Avenue, New York 11, N. Y. 1958. 111 pp. 19 × 25.5 cm. Price, \$6.00.

Following a brief introduction on what is meant by pH , ten pages give examples of the importance of pH determinations in the home, research, and industry. The next twenty pages are devoted to essential pH theory as interpreted in terms of aqueous solutions of Arrhenius acids and bases.

Two short sections summarize the principles of pH measurement. The first covers colorimetric methods, with special emphasis on the use of Lovibond glasses as standards. The second covers electrometric methods, including commonly used electrodes and measuring instruments.

Two brief sections deal with hydrogen ion activity, including the British and United States pH scales, and with acidity in non-aqueous solutions. A glossary of terms follows.

This is a very elementary presentation, written presumably for those having little chemical training. Compared to works such as those by H. T. S. Britton, J. E. Ricci and R. G. Bates, it is hardly *the* book of pH .

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Advances in Enzymology and Related Subjects of Biochemistry. Volume XIX. Edited by F. F. NORD, Fordham University, New York, N. Y. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1957. v + 457 pp. 16 × 23.5 cm. Price, \$9.85.

This volume, in keeping with the tradition of other volumes, has continued to emphasize authoritative reviews by distinguished workers in the field. The topics on which advances are reported include Enzymatic Aspects of Photosynthesis, by Vishniac, Horecker and Ochoa; Mechanisms of Oxygen Metabolism, by Mason; Activation of Amino Acids, by T. Wieland and Pfeleiderer; The Properties of Papain, by Kimmel and E. L. Smith; Principal Pathways of Assimilation and Dissimilation of Nitrogen in Animals, by Braunstein.

In the first review, three of the outstanding workers in the field have joined together to give a most comprehensive summary of current views on the experimental data on carbohydrate metabolism, carbon dioxide fixation and light-dependent reactions in photosynthesis. The treatment of topics in this field is objective and is focused upon the experiments themselves rather than the many hypotheses with which this field is studded. The review was written on the basis of the experimental evidence that led to the general acceptance of the ribulose diphosphate pathway and does not take into consideration current thinking on the importance of other intermediates. The discussion of the role of chlorophyll in carbon dioxide fixation is of great interest in evaluating the recent hypothesis of stoichiometric relationships between carbon dioxide and chlorophyll. This review will stand as an authoritative presentation of the current status of enzymatic aspects of photosynthesis for some time to come.

In a review of exceptional length (133 pages, 842 references) H. S. Mason again puts forward his reasons for a new nomenclature and classification of a number of enzymes that would otherwise be termed oxidases, peroxidases, and in some cases dehydrogenases. As evidence for the lack of unanimity on enzyme nomenclature and classification, it is noteworthy that Dixon and Webb, in their recent text, classify as hydrogen transfer enzymes those that Mason terms oxygen transferases. The use of the words "oxygen metabolism" in the title is somewhat deceptive, for only one of the 133 pages of the article is devoted to the principal pathway of oxygen metabolism of the cell. Mason's review is extraordinarily complete in its description of the substrate specificities and organic chemistry of oxidation reactions (a 29-page table is included). There are many diagrams and tables on intermediates in the transformations of substrates involved in these reactions. Perhaps as a consequence of the ambitious scope of this review, uncertain reaction schemes are included without a full discussion of contrary evidence. In addition, an extraordinary number of typographical errors appear in the tables where substituents are lacking or are improper. In the text as well some slips have occurred: homogentisic acid is indicated a substrate and 2,5-dihydroxyphenylacetic acid is indicated to be "not attacked" by the same enzyme. It is therefore necessary to refer to the original literature for authoritative information and a complete discussion on some of the reaction schemes described.

A considerable portion of the detailed reaction mechanism for the action of peroxidase in "oxygen transferase" action requires the postulation of a ferropoxidase-oxygen intermediate which in some schemes is identified with peroxidase complex III. While this affords an interesting hypothesis, its serious consideration requires direct experimental answers to certain questions: whether complex III can be converted directly in ferropoxidase-CO, and whether the light sensitivity of the CO-inhibition of the dihydroxyfumarate oxidase activity corresponds to the spectrum of ferropoxidase-CO. Currently available evidence on the first point is contrary to the proposed hypothesis.

T. Wieland and Pfeleiderer have given an authoritative and concise report on the activation of amino acids. Their chapter covers detection of activated amino acids, their synthesis and their reactions. The role of ATP in the biological activation of amino acids is also discussed. The report ends with a summary of the newer aspects of the biological reactions of activated amino acids. The contribution is of special interest because it contains reports on syntheses and other data that come largely from the authors' unpublished work.

The essay on papain by Kimmel and E. L. Smith is a model of a complete and authoritative study of an enzyme. The details on the purification of the physical properties of papain and the criteria for homogeneity, together with the progress made on the amino acid sequences in this catalyst, are indeed striking. Furthermore, studies on specificity and reaction kinetics give considerable insight on the mechanism of action of this enzyme.

The volume is concluded with a competent and imaginative review of the principal pathways of assimilation and dissimilation of nitrogen in animals by Braunstein. This review is of interest since it gives, in addition to the purely biochemical aspects, an interpretation of the results on the basis of comparative biochemistry.

In summary, this volume continues in most respects the tradition of excellence of the "Advances in Enzymology." A suggestion of the reviewer, however, is that a stronger editorial policy might lead to more concise and thus more effective presentations.

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BRITTON CHANCE

Chemistry of Carbon Compounds. Volume IV, Part A. Heterocyclic Compounds. Edited by E. H. RODD, D. I. C., D.Sc., F.C.G.I., F.R.I.C. D. Van Nostrand Company, Inc., 126 Alexander Street, Princeton, N. J. 1957. xxvi + 808 pp. 15.5 × 23 cm. Price, \$28.00.

This volume, the first of three dealing with heterocyclic substances, continues the monumental treatise on organic chemistry being prepared under the editorship of E. H.