



would be expected to occur in partially reduced phenylalanyl peptides.

A number of model compounds containing phenylalanine were synthesized in order to study the proposed method of cleavage (table). In all cases the amino group of the phenylalanine was blocked by an acetyl residue. Benzoyl or carbobenzyloxy substituents were not used because these aromatic groups also would be subject to reduction.

TABLE I

## REDUCTION AND CLEAVAGE OF PHENYLALANYL PEPTIDES

Peptide <sup>a</sup>	M.p., °C.	Yield of reduced peptide, %	Extent of cleavage of the reduced peptide, %
Phenylpropionyl-L-valine	173	75	70
Acetyl-DL-phenylalanyl-glycine	180	52	65
Acetyl-DL-phenylalanyl-DL-valine	178	54	65

<sup>a</sup> The peptides were synthesized by dicyclohexylcarbodiimide method.

For the reduction 1 g. of each model peptide was dissolved in 25 ml. of methylamine and 5-6 equiv. of metallic lithium was added. The reaction mixture was kept at  $-70$  to  $80^\circ$  (acetone/ $\text{CO}_2$  bath) for 2-3 hours, and a small amount of ethanol or

ammonium chloride then was added to discharge the blue color of the mixture. After 10 min., the solvent was drawn off *in vacuo* at room temperature. The reduced derivative was dissolved in water, acidified with HCl and purified by recrystallization from ethyl acetate/petroleum ether. The yields averaged 50%. Elemental analysis of the reduced peptides, and quantitative catalytic hydrogenation over Pt indicated the presence of a mixture of cyclohexene and cyclohexadiene derivatives.

The reduced products were dissolved in 50% aqueous acetic acid and treated with bromine or N-bromosuccinimide. Paper chromatography of the reaction mixtures showed the presence of free valine or glycine, respectively, in yields averaging 65-70%.

In a second series of experiments, designed to show that the method is applicable to milligram quantities, 2-mg. portions of the model peptides were reduced and cleaved successively without isolation of intermediates. Again paper chromatography of the reaction mixture showed the liberated amino acids in yields averaging 70%.

Thus, phenylalanyl peptides, after reduction with lithium in methylamine, can be cleaved with either N-bromosuccinimide or bromine. The application of this procedure to sequence analysis of proteins is now being studied.

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## BOOK REVIEWS

**Advances in Comparative Physiology and Biochemistry Volume 1.** Edited by O. LOWENSTEIN, Department of Zoology and Comparative Physiology, University of Birmingham, England. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1962 15.5 × 23.5 cm. Price, \$12.00.

This volume initiates a new series of "Advances" added to the many parallel series currently issued by this publisher. Volume 1 consists of six extensive monographs by seven authors, all of whom reside in Great Britain. Each attempts to show how a "theme and variations" of animal function serves to accomplish different tasks for different species.

"Digestive enzymes" (E. J. W. Barrington) especially emphasizes cellulases. A review of the occurrence of cellulases in various phyla of animals describes the properties and regulations that effect the utilization of normal and experimental diets. In turn, the properties of the enzymes secreted differ appreciably in accordance with the food available. Unsuspected specificities of enzyme action have been revealed by use of purified substrates and of newer methods of chromatography, viscosimetry, turbidimetry and others.

"Amine oxidases of mammalian blood plasma" (H. Blaschko) illustrates the variation of substrate specificities in a single kind of enzyme. The variations reside in the

enzyme protein, and probably in its amino acid composition. Differences in immune reactions aid in their comparison among species. Further, these differences bear upon the taxonomic relationships among mammals. Since study of these extracellular enzymes is a relatively new development in biochemistry, the review includes tables of species examined, enzyme differences and substrates tested. Physiological significances are discussed; for instance, spermine oxidase is especially abundant in plasmas of herbivorous animals with large absorbing surfaces in the stomach and caecum. However, absence of this enzyme in other herbivora has not been accounted for.

"Temperature receptors" (R. W. Murray) presents the difficulties of identification of organs specifically sensitive to heat and to temperature change. Very likely, many animals avoid harmfully hot environments without use of particular receptors. Four stages of investigation are indicated: (a) behavioral responses, particularly in a gradient of temperatures; (b) effects of blocking or amputation of parts; (c) impulse codes revealed by electrophysiological recordings; and (d) the analysis of receptors-transducers. The latter analysis includes a new hypothesis of transducer action, based on the exploration of membrane potentials in sensitive cells. The main problem is: how specific are temperature receptors? The present answer is that all degrees of specificity can be found, and often within a single species.

"Neuromuscular physiology" (G. Hoyle) raises the question: can one hypothesis of how muscle contracts fill the requirements for all species of muscles that have been studied? The Huxleys' hypothesis that two kinds of filaments slide over one another in contraction meets great difficulties, some muscles shortening only 5%, others 90%. Electron microscopy furnishes at present the most critical evidence, but has not proved decisive. Membrane potentials measured by intracellular electrodes do not all agree with the hypothesis that sodium moves inward and potassium outward during excitation. Thus, certain insect muscles contract in a medium of high magnesium and zero sodium. Again, pharmacological actions upon impulse-transmission are of considerable variety, as shown by actions of picrotoxin, glutamate and aminobutyrate. Other studies of control of nerve-muscle relations reveal that two kinds of motor axones serve a single muscle fiber; and also that different fibers respond differently to impulses within the same axone. A wealth of detail is brought to bear to show the special advantages of comparative physiological studies.

"Animal luminescence" (J. A. C. Nicol) dwells upon the biochemical reactions concerned in production of light. The reactants differ in bacteria, crustacea and fireflies; and the catalysts concerned in energy transfer also differ. Regulation of the flashes and intensities of luminescence differs widely throughout the animal kingdom. Some species secrete substances that reset extracellularly, again at characteristic rates and spectra. What good does the production of light do in various species? No single answer can be given; some serve as signals, others are lures; some aid vision, others have display patterns.

"Respiratory mechanisms in fish" (G. M. Hughes and G. Shelton) constitutes a definitive monograph in itself. Special structures, co-ordinated, rhythmically pump water that aerates the gills. The pressures and volume flows are phasic, for valves are concerned in the flow of water over the gill filaments. Gas exchanges with the blood depend upon volume flows, solubilities and surfaces. Variations of the main arrangements are illustrated in different species, and particularly are related to the oxygen availability in the water in which each lives. The sensory and nervous activities employed in respiratory control are clearly related to oxygen and carbon dioxide pressures, and the role of blood flow is part of the same functional system. Major consideration is given to the arrangements for rhythmical alternation of each pumping movement.

All the six reviews are carefully organized under subheadings. Evidently the general editor suggested some features common to the plans. The "coverage" tends to be exhaustive, so that numerous items are included without much relation to those general principles that are being put forward. Each chapter has a set of observations arranged according to phyla, an arrangement that did not generate much enthusiasm in some authors.

Of the several chapters, the one that illustrates best the power of comparative physiology is the one on neuromuscular physiology. The dangers of reliance upon studies of a single type of excitable tissue are clearly shown. At the same time, a single type of excitation and a single scheme of contraction seem to have been utilized in at least a dozen types of cellular performances. Certainly "important new generalizations have emerged from the extension of studies."

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Methoden der Organischen Chemie (Houben-Weyl). Vierte, Völlig Neu Gestaltete Auflage. Band V/3. Halogenverbindungen. Fluorverbindungen. Herstellung, Reaktivität und Umwandlung. Chlorverbindungen. Herstellung. Edited by EUGEN MÜLLER, Tübingen. With O. BAYER, Leverkusen, H. MEERWEIN, Marburg, and K. ZIEGLER, Mülheim. Georg Thieme Verlag, Herdweg 63, Stuttgart, Germany. 1962. lxiv + 1217 pp. 18.5 × 26 cm. Price, DM. 262.-; Subskriptionspreis, DM. 235.80.

Volume V/3 completes the treatment of halogen compounds in the new "Houben-Weyl." About one-half of the page space is devoted to the preparation and reactions of organic fluorine compounds. Newcomers to this field, which has undergone virtually exponential expansion,

will welcome the brief discussion of the peculiarities of the nomenclature of organic fluorides. The preparative methods are presented in two large groups, the first describing procedures to introduce fluorine into organic molecules by a variety of reagents, and the second detailing modifications of compounds that already contain fluorine. The reactivity and transformations of fluorine compounds occupy the concluding portion.

The remainder of the volume is occupied by procedures for the preparation of organic chlorides. As the editors point out prefatorily, classification according to type of chlorinating agent has again been adhered to in contrast to the system adopted for the two heavier halogens, because the surpassing importance of elementary chlorine made desirable a presentation of the action of this reagent upon all types of compounds. To evaluate the possibilities of obtaining a specific chloro compound, the reader may avail himself of the unique tabulation at the end of the volume; here all compound types referred to in the text are arranged systematically, and the reagent employed for their preparations as well as the type of reaction and the page reference are included. The reactivity of the organic chloro compounds, as noted earlier, has been treated in volume V/4.

The selection of examples has again been made with wisdom and circumspection; the increasing shelf footage required as more and more volumes of the new "Houben-Weyl" appear engenders a feeling of gratitude toward the editors and colleagues, who have made readily available to the practicing organic chemist a large segment of the less and less manageable literature.

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Catalysis by Metals. By G. C. BOND, Department of Chemistry, The University, Hull. Academic Press Inc., (London), Ltd., Wing 1, 7th Floor, Berkeley Square House, Berkeley Square, London, W. 1, England. 1962. ix + 519 pp. 16 × 23.5 cm. Price, \$15.50.

This book which covers a major division of a difficult inter-disciplinary science is noteworthy among treatises in being written by a single author. Professor Bond has a perspective in presentation and a uniformity of treatment impossible to the team of selected specialists. The integration of the text with the Periodic Classification and in general with the electronic structure of the elements is one important factor in the author's success. This should prove useful in rational catalyst design. The excellent organization of the book highlights gaps and inconsistencies in the literature and, as the author states, these are useful in providing projects for future research.

The chapter titles describe the emphases of the book well: Introduction to Catalysis by Metals; Physics and Chemistry of Metals; Preparation and Study of Metal Surfaces; Adsorption at Metal Surfaces; Chemistry and Energetics of Adsorption; Kinetics of Adsorption and Desorption; Kinetics of Surface Reactions; Reactions of Hydrogen at Metal Surfaces; Exchange Reactions of Saturated Hydrocarbons with Deuterium; Exchange Reactions of Other Molecules with Deuterium; Hydrogenation of Monoolefins and Alicyclic Molecules; Hydrogenation of Acetylenic Compounds and Diolefins; Hydrogenation of Aromatic and Heterocyclic Compounds; Hydrogenation of Other Unsaturated Groups; Hydrogenation of the Oxides of Carbon and the Fischer-Tropsch Synthesis; Catalytic Synthesis and Decomposition of Ammonia and Related Reactions; Catalytic Hydrogenolysis; Catalytic Dehydrogenation; Catalytic Reforming; Catalytic Oxidation; Catalysis and Chemistry.

At least nine of the twenty-one chapters deal with ancillary aspects of the mechanism of catalysis, such as chemisorption and surface kinetics. The other chapters deal with specific catalytic reactions, such as hydrogen exchange, hydrogenation, ammonia synthesis, hydrogenolysis, dehydrogenation, reforming, and oxidation. The text is discriminating in its use of data and topics. Details of experimental techniques and details of commercial processes are skipped over in order to emphasize the unifying concepts of catalysis. Each chapter is accompanied by an excellent list of selected references which can serve as an introduction to a deeper study.