

acetic anhydride and three equivalents of potassium acetate. Hydrogenation of I in the presence of 10% palladium-charcoal and 3.1 equivalents of sodium hydroxide (1% aqueous solution) at 80° resulted in absorption of two moles of hydrogen and gave, after acidification, 92% of II, m.p. 146–147° (Found: C, 66.03; H, 6.31; $\lambda_{\max}^{\text{chf.}}$ 5.78 and 5.85 μ). Unlike I, compound II gave positive tests with ferric chloride and 2,4-dinitrophenylhydrazine. Treatment of II with polyphosphoric acid at 100° for an hour gave 95% of a mixture of two isomers of III, separated by fractional crystallization (methanol) into colorless crystals, m.p. 183–186° (resolidified, remelted 207–211° dec.) (Found: C, 70.8; H, 5.99; $\lambda_{\max}^{\text{chf.}}$ 5.86 and 6.02–6.07 μ), and yellow, chloroform-insoluble crystals, m.p. 218–219° dec. (Found: C, 70.4; H, 5.89). Esterification of either isomer of III with methanol (sulfuric acid) gave the same methyl ester, m.p. 119–121° (Found: C, 71.3; H, 6.33; $\lambda_{\max}^{\text{chf.}}$ 5.80 and 6.02–6.07 μ ; $\lambda_{\max}^{\text{EtOH}}$ 242 and 326 m μ with log ϵ 4.05 and 4.39, respectively). The red 2,4-dinitrophenylhydrazone of this ketoester had m.p. 246–247° dec. (Found: C, 59.3; H, 4.82). Decarboxylation of III (quinoline) gave ketone IV, m.p. 114–115.5°³ ($\lambda_{\max}^{\text{chf.}}$ 6.02–6.07 μ ; $\lambda_{\max}^{\text{EtOH}}$ 241 and 328 m μ , with log ϵ 4.02 and 4.40, respectively), further identified as the 2,4-dinitrophenylhydrazone, deep red crystals, m.p. 219–220° dec. (Found: C, 61.6; H, 5.13). Aromatization and decarboxylation of III (palladium-charcoal in *p*-cymene) followed by acetylation gave 2-methoxy-6-acetoxyphenanthrene, m.p. 114–115° (Found: C, 76.57; H, 5.53); $\lambda_{\max}^{\text{EtOH}}$ 221, 255, 278, 291, 319, 334 and 350 m μ (log ϵ 4.38, 4.84,

(3) G. T. Tatevosyan, P. A. Zagorets and A. G. Vardanyan, *J. Gen. Chem., U.S.S.R.*, **23**, 979 (1953) report m.p. 114–115° and 219–220° for this ketone and its 2,4-dinitrophenylhydrazone, respectively, prepared by a more circuitous method (*cf. Chem. Abstracts*, **48**, 7593 (1954), **49**, 4604 (1955)).

4.27, 4.17, 2.76, 2.91 and 2.83, respectively).⁴ Aromatization and decarboxylation of the sodium borohydride reduction product from III gave 2-methoxyphenanthrene,⁵ m.p. 93–95°, $\lambda_{\max}^{\text{EtOH}}$ 221, 229, 254, 277, 289, 319, 334 and 350 m μ (log ϵ 4.36, 4.24, 4.89, 4.27, 4.19, 2.85, 3.02 and 3.00, respectively); *picrate*, m.p. 122–123°.

The same series of reactions, starting with homoveratric acid instead of 3-methoxyphenylacetic acid, gave a mixture of isomers of 1,2,3,9,10,10a-hexahydro-3-keto-6,7-dimethoxy-9-carboxyphenanthrene. The higher-melting isomer of this compound has m.p. 229–231° dec. (Found: C, 67.43; H, 5.97; $\lambda_{\max}^{\text{EtOH}}$ 226, 242 and 341 m μ , with log ϵ 4.02, 4.06 and 4.30, respectively); the lower-melting isomer has not yet been obtained completely pure. The 2,4-dinitrophenylhydrazone of the corresponding ethyl ester has m.p. 245–246° dec. (Found: C, 58.93; H, 5.28).

The concepts involved in this work eventually may prove to be applicable in preparation, reduction, and homocyclization of compounds other than coumarins (I), and future studies are aimed at finding such related processes. Aside from the fact that the work outlined above represents a long-sought, fundamental development in the chemistry of hydrophenanthrenes, the synthesis, which now makes III and similar ketoacids readily available, very likely will provide some new compounds of potential pharmacological interest.

(4) See R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, curve 373.

(5) R. Pschorr and C. Seydel, *Ber.*, **34**, 3998 (1902).

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BOOK REVIEWS

Elements of X-Ray Diffraction. By B. D. CULLITY, Associate Professor of Metallurgy, University of Notre Dame. Addison-Wesley Publishing Company, Inc., Reading, Massachusetts. 1956. xiv + 514 pp. 16 X 23.5 cm. Price, \$10.00.

Elements of X-Ray Diffraction is published as one in a series of reference books primarily designed for metallurgists. The treatment is introductory, intended for the reader who has had little or no previous experience with the theory or application of X-rays to structure problems. Problems of particular concern in the study of metals and alloys are emphasized. The book does not attempt to provide adequate background for the complete elucidation of the structures of complex crystals. It primarily presents the apparatus and theory of methods for study of crystalline powders and of the Laue method. It is written in terms of Bragg's law; reciprocal lattice theory is described only briefly in an appendix. Space group theory is also only briefly mentioned as the

subject of crystal structure is approached through the concept of the point lattice.

Although the scope of the book is limited, it is written lucidly and will be found valuable as an introductory text by chemists as well as metallurgists. The author discusses basic concepts in considerable detail. Introductory chapters on properties of X-rays and the geometry of crystals are followed by a discussion of the positions of the diffracted beams and of the intensity-structure factor problem. Methods for determining structures from powder data are described and examples given. A chapter on diffractometer measurements, giving a description of instruments currently available for the measurement of the intensity of diffracted beams, is included.

Effects associated with crystal size, imperfections, twinning, solid solutions, order-disorder phenomenon, and problems of phase diagram determination, particularly as they occur in metal-metal alloy systems, are discussed.

Chapters are included on application of diffraction, fluorescence and absorption for purposes of chemical analysis. Information to be gained in the study of deformation and stress measurement is described.

The book is well illustrated and well written. It will be found very useful by students of X-ray diffraction.

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Advances in Catalysis and Related Subjects, Volume VIII. Edited by W. S. FRANKENBURG, Lancaster, Pennsylvania; V. I. KOMAREWSKY, Chicago, Illinois; and E. K. RIDEAL, London, England. Academic Press, Inc., Publishers, 111 Fifth Avenue, New York 3, N. Y., 1956. viii + 353 pp. 16 × 23 cm. Price \$10.00.

This book is another distinguished volume in a series already known for its reliability and usefulness. Recognized authorities have written each of the seven chapters: 1. "Current Problems of Heterogeneous Catalysis," by J. Arvid Hedvall, contains a survey of the fields in catalysis which at present show promise of yielding important new developments. Attention is directed to defect structures, ferromagnetic and ferroelectric Curie points, crystalline transitions in catalyst phases, photoadsorption, etc. 2. "Adsorption Phenomena," by J. H. DeBoer, comprises 133 pages and is the major chapter of the present volume. The article, indicating that there is no clear line of demarcation between physical and chemical adsorption, covers the theory of both, in as quantitative a manner as present knowledge will permit. A bibliography of 407 entries provides an excellent introduction to the periodical literature. 3. "Activation of Molecular Hydrogen by Homogeneous Catalysts," by S. W. Weller and S. A. Mills, is a detailed critical analysis of the mechanisms by which hydrogen dissociates and becomes available for reaction in systems of (a) cuprous salts in quinoline, (b) cuprous and silver salts in pyridine and dodecylamine, (c) cupric and mercuric salts in aqueous solution, (d) ethylene-platinous chloride, (e) cobalt carbonyl, (f) certain bases of miscellaneous composition. This study is directed toward the elucidation of the mechanism of activation of hydrogen as it proceeds on heterogeneous catalysts. 4. "Catalytic Synthesis of Ketones," by V. I. Komarewsky and J. R. Coley, emphasizes the aldol and Tishchenko ester condensations as methods of synthesizing ketones in contrast to the better known and more widely used dehydrogenation of secondary alcohols and decarboxylation condensations. 5. "Polymerization of Olefins from Cracked Gases," by Edwin K. Jones, is a summary of modern industrial practice in catalytic polymerization of olefins. It covers such subjects as process variables, catalysts, catalyst poisons, feed stocks and products. 6. "Coal-Hydrogenation Vapor-Phase Catalysts," by E. E. Donath, describes the development of catalysts based on molybdenum, tungsten and nickel in Germany and elsewhere for the hydrogenation of tars, heavy oil, and middle oil produced by the action of hydrogen on coal. 7. "The Kinetics of the Cracking of Cumene by Silica-Alumina Catalysts," by Charles D. Prater and Rudolph M. Lago, is a detailed analysis of published kinetic data on the cracking of cumene, combined with additional experimental data and a determination of the true kinetics at the active sites.

Catalytic chemistry is a broad and yet poorly understood field of science. Contributions to this field come from such widely different fields as chemical kinetics, thermodynamics, photochemistry, magnetism, crystallography, solid state physics, chemical engineering, aerodynamics, hydrodynamics, atomic physics, quantum mechanics, various types of spectroscopy, organic chemistry, tracer chemistry and surface chemistry. Recent theoretical and experimental developments in these sciences have stimulated the science of catalysis to rapid growth. The present volume of "Advances in Catalysis" together with its predecessors provides an indispensable focus where new developments and techniques as they apply to catalysis are summarized and critically evaluated. The twelve pages of subject and author index aid in making this book a useful reference work. Scientists working in the field of catalysis should

have ready access to this and the earlier volumes of "Advances in Catalysis."

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Progress in Nuclear Energy. Series III. Volume I. Process Chemistry. BY F. R. BRUCE, Oak Ridge National Laboratory, J. M. FLETCHER, A.E.R.E., Harwell, H. H. HYMAN, and J. J. KATZ, Argonne National Laboratory, Editors. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 36, N. Y. 1956. xii + 407 pp. 16 × 23.5 cm. Price, \$12.00.

Chemists and chemical engineers should find this volume an extremely informative account of the accomplishments in chemical technology attained by various individuals and laboratories working in the atomic energy field.

To date, both professional people and the public have been treated to numerous popularized accounts of reactor designs and applications, while the equally fascinating aspects of chemical reprocessing have been dealt with only occasionally. It is understandable that this situation should prevail, since the focal point for any reactor power cycle is the "reactor." When reactors are employed to produce fissionable materials, chemical processing is a required step in the process. The future role of reprocessing in a power generation cycle is not at all clear at the moment, since metallurgists, physicists and reactor engineers will set their sights on a degree of fuel burnout that will allow ashes to be "shoveled out" of the reactor periodically without the need for reprocessing. Many reactor engineers will agree that vastly improved chemical reprocessing techniques could influence the choice of the best power reactor cycle. For many applications, a cheap and effective chemical process could obviate the need for expensive high-integrity fuel or costly reactor design features required to assure prolonged operation without refueling. As reactor engineers, physicists and metallurgists gain knowledge on the problems of high burn-up reactor operation, and chemists and engineers continue their advance toward more economical reprocessing methods, we may well see a more effective integration of the reactor and separations technologies in future reactor power cycles.

Process Chemistry should provide an excellent educational review and background for those who simply want to keep abreast of developments and for those who now may be actively involved in power reactor engineering and economics. The volume is neither a textbook nor a handbook. It is a blend of both chemistry and engineering as applied to chemical processing of irradiated fissionable materials. The scope of treatment includes laboratory, pilot-plant, and full-scale activities for both research- and development-type experimentation. The volume contains 22 papers presented by English and American scientists and specialists at the August, 1953, International Conference for the Peaceful Uses of Atomic Energy at Geneva. Many of these have been updated and appropriately modified. In addition, 14 papers have been added by the editors to provide a balanced treatment of the subject and to include some of the more advanced concepts that were not included at the "Geneva" meeting. Thirteen of the papers are by English authors and the volume is a result of joint editorship of U.S. and U.K. scientists together with an editorial advisory board that is composed of specialists from many other countries involved in the peacetime applications of atomic energy.

Broadly, the volume describes chemical processes for the purification of uranium and thorium ores, the separation of the fissionable materials following irradiation of uranium and thorium fuel elements, and the disposal and/or recovery of the waste fission products. The papers leave no doubt that at present, solvent extraction is a well-demonstrated unit operation for separating and decontaminating the key products of irradiation. Readers should be impressed by the versatility and flexibility of this technique and will probably conclude that additional applications should be possible in areas of activity other than those in the nuclear field. It would be reasonable to expect that many of the chemical principles and unit operations discussed might be applied effectively to isolate and produce extremely pure materials for specialty use. The solvent extraction processes presented are indeed designed to achieve sharp separation and