

completely prevent the chlorination of cyclopentane, 2,3-dimethylbutane, toluene, and ethylbenzene.

These results strongly suggest some sort of interaction or complex formation between the alkoxy radical and olefin,⁸ leading to a species which decomposes rather than attacking usually reactive substrates. Why the phenomenon is particularly marked for this alkoxy radical is obscure, but may be related to the relatively large resonance stabilization of the benzyl radical produced in the decomposition.⁹ We are investigating these reactions

(8) Small solvent effects in alkoxy radical reactions have been reported previously, cf. ref. 6, also G. L. Russell, *J. Org. Chem.*, **24**, 300 (1959). However, they have been much smaller than that reported here.

(9) Association of a radical with solvent (since it must involve some

further, but, in the meantime our results indicate not only a striking "solvent effect" in a radical reaction, but also the need for caution in interpreting the results of competitions between reactions 1-3 in studying radical processes.

stabilization of the system) would be expected to favor those subsequent reactions of the radical having the lowest activation energy. Decomposition of *t*-butoxy radicals has an activation energy several kcal. larger than typical hydrogen abstraction. Here, resonance stabilization of the benzyl radical should greatly reduce (or even reverse) this difference.

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BOOK REVIEWS

Recent Developments in the Chemistry of Natural Phenolic Compounds. Proceedings of the Plant Phenolics Group Symposium. Edited by W. D. OLLIS, Department of Organic Chemistry, University of Bristol. Pergamon Press, Ltd., Headington Hill Hall, Oxford, England. 1961. viii + 237 pp. 16 × 23.5 cm. Price, \$12.00

As the title suggests, this volume is the record of a symposium, in this case the Plant Phenolics Group Symposium held in England in April, 1960. It deserves, however, to be considered as a more basic monograph than this implies, partly since no other basic work covering this field of natural products exists and partly since the contributions here have been expanded with the apparent intent of filling this lacuna. It has only been in recent years, with the rising acceptance of their common biogenetic origin from acetate, that the plant phenolics have been considered as a unit, and the Plant Phenolics Group, which offers this symposium, was organized only five years ago. The present volume should go far toward focusing recognition on this large and important field of natural products, previously dealt with only in isolated fragments, and it is accordingly commendable that this symposium represents many of the foremost authorities in the field.

The book is roughly divided into two parts, dealing with biosynthesis and structure determination, respectively. Of the chapters on biosynthesis, those by Grisebach on isoflavone biosynthesis and Hassall and Scott on oxidative coupling and its laboratory simulation represent excellent, thorough coverages of these fields by their most active practitioners, while the editor has provided an exhaustive and lucid survey, generously larded with formulas, of the origin of isoprenoid units attached to phenolic skeletons. The chapters by Rickards on the work of the Manchester school confirming acetate biosynthesis by tracers and by Whalley on biogenetic relationships deduced from structures are, however, unfortunately both cursory and fragmentary; the material of these two chapters deserves to be considered together, as it is complementary, and to be covered with a thoroughness commensurate with its importance since it has several times previously been treated in this same cavalier fashion.

Of three chapters on the structures of tannin compounds, two (by Haworth and Haslam) are only brief summaries of the corresponding lectures with the explanation that the work is awaiting publication; the reader may well question whether they might not reasonably have been included here in full nonetheless.

The remaining chapters deal with recent structure work which reveals several new families of natural compounds. These areas are covered in detail with clarity, although the

chapters (on biflavonyls and the "mycinone" antibiotics) by the editor and his Bristol colleagues occasionally suggest more involvement with establishment of priority than facts. Hörhammer and Wagner have surveyed well the interesting new area of C-glycosides while Dreiding has presented an account of the betacyanins, a complex and still but dimly understood class of plant pigments on which surprisingly little chemical work has apparently been done.

On the whole the book is free of error and the format and formulas are clear and readable. Despite the several cavils above, this volume is a very valuable addition to the book shelf of any natural products chemist.

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Solid State Physics. Advances in Research and Applications. Volume 12. Editors, FREDERICK SEITZ, Department of Physics, University of Illinois, Urbana, Illinois, and DAVID TURNBULL, General Electric Research Laboratory, Schenectady, New York. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1961. xv + 459 pp. 16 × 23.5 cm. Price, \$16.00.

This is the twelfth volume of a very distinguished series which features key review articles written by top-experts on a wide variety of topics involved in solid state physics. The present issue contains five articles:

I. Group Theory and Crystal Field Theory by C. M. Herzfeld and P. H. Meijer. This article is exceptionally well written. It contains a concise presentation of group theory liberally laced with interesting applications. It will be especially helpful to chemists interested in ligand field theory.

II. Electrical Conductivity of Organic Semiconductors by H. Inokuchi and H. Akamatsu. This article summarizes all the information, both theory and experiment, which is not listed as "company secret" on a topic of great interest to both industrial and university chemists. Indeed, there is considerable speculation that semiconductor properties of organic molecules may also play an important role in biochemistry.

III. Hydrothermal Crystal Growth by R. A. Laudise and J. W. Nielsen. The term "hydrothermal" is used to describe reactions taking place at high temperatures and high pressures in the presence of water. Thus, Laudise and Nielsen describe how geophysicists are performing experiments in the laboratory that mother nature carried on in the earth's crust. The unravelling of complicated thermody-

namic phase diagrams is necessary in order to predict the proper conditions required to produce a particular type of crystal.

IV. Thermal Conductivity of Metals at Low Temperatures by K. Mendelssohn and H. M. Rosenberg. At very low temperatures the thermal conductivity of metals behaves in an anomalous manner. However, when the metal becomes electrically superconducting, the thermal conductivity decreases. Heat conductivity is explained by the manner in which the two carriers of heat, the electrons and the phonons, are scattered in their passage through the material. Considerable attention is given to the effect of crystal defects.

V. Theory of Anharmonic Effects in Crystals by G. Leibfried and W. Ludwig. This chapter is concerned with the secondary effects which become all-important as one tends to exceed Hooke's law, or as the crystal is heated to near the melting point. The mathematical treatment is necessarily very complicated. However, the authors are to be complimented on making their treatment clear and concise.

This book is especially valuable since each of its articles is self-contained and pitched at a level which is not too tough for a good research chemist. The twelve volumes of this series which have already been published constitute a liberal education in solid-state physics. Already, 34 additional articles are listed as under preparation for future volumes. All solid-state chemists will want to keep abreast of these new developments in solid-state physics. Thus, this series is a "must" for most chemical libraries.

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Pyrazolone und Dioxypyrazolidine. By DR. WALTER KROHS and DR. OTTO HENSEL. Editio Cantor, Aulendorf i. Wurtt., Germany. 1961. xx + 488 pp. 17 × 24.5 cm. Price, DM. 98.--.

This book is the eleventh of a series published in German by Editio Cantor on progress in the chemistry of medicinal compounds. It is a welcome addition to the scant body of collected literature on pyrazolones and diketopyrazolidines. The pyrazolones, especially, are important to several industries, providing numerous dyes, pigments and medicinals. Both classes are important to medicine. This fact has prompted the writing of the book. Further justification is found in the editor's charge to the authors, "to prepare a monograph on pyrazolones which should be the most outstanding in this interesting field."

The book is divided into several sections. At the outset Ludwig Knorr is hailed as the father of pyrazolone chemistry in a two-page biography reprinted from a 1927 issue of *Berichte der Deutschen Chemischen Gesellschaft*. There follow twelve pages of generalities, one hundred and ten pages of chemistry on medicinal compounds, two hundred and thirty-seven pages of tabulated structural formulas and references, thirty-five pages of empirical formulas, and seventy-five pages about pyrazolone dyes, chiefly structural formulas. The general and medicinal sections were written by Walter Krohs, that on pyrazolones by Otto Hensel. The tables were apparently compiled jointly.

Importance of these heterocyclic classes in medicine is emphasized repeatedly. Their utility is discussed at length with extensive references to physiological and pharmacological sources. The single compound antipyridine, 1-phenyl-2,3-dimethyl-5-pyrazolone, furnishes a base on which much of the knowledge of pyrazolones has been constructed. In consequence, a seemingly unwarranted bulk of the book describes 1,2,3-substituted-5-pyrazolones.

Readability of this book is enhanced by numerous techniques. The table of contents is organized conscientiously. It leads to the interesting result that as many as four entries may be used to describe the content of a single page or that a single entry describes the content of sixteen pages. Structural formulas are numerous and uncrowded. A more vigorous adherence to the conventions for orienting the given heterocycles would have been a slight but real improvement. Possibly the habits of the two authors are reflected by noting that the medical pyrazolones are oriented with the number 1 nitrogen at the top of the page whereas the dye pyrazolones are oriented just the opposite.

The method of presenting the chemistry contributes to the readability if not to the depth of understanding. All the chemistry is descriptive without any attempt to rationalize reaction mechanisms. Apparently the authors were motivated more strongly to make their compilations as complete as possible rather than by any desire to make critical comment. For example, on page 103 Conrad and Zahrdt's version of the reaction between ethyl cyanoacetate and phenylhydrazine is reported to give 1-phenyl-3-keto-5-iminopyrazolidine. No acknowledgment is made of the Porter and Weissberger study of this reaction from which came a correction of the chemistry and the important color photographic chemical, 1-phenyl-3-amino-5-pyrazolone.

The literature is covered to the end of 1958.

Someone has combed the text for typographical errors. They are noted on page X, directly after the table of contents. Errors noted by your reviewer were trivial. On page XII B.I.O.S. is recorded as B.J.O.S. At the top of page 90 either the covalency count is wrong or a charged structure should be shown; the same is true with structures on pages 94 and 95. The type structural formula on page 357 needs correction. The misspelled Eastman on page 419 seemed unnecessary.

In conclusion, your reviewer wishes to emphasize again the timeliness and usefulness of this book to anyone interested in this area of heterocyclic chemistry. The literature gap since Cohn's "Die Pyrazolofarbstoffe" published in 1910 or Henecka's "Chemie der β -Dicarbonyl Verbindungen" published in 1950 is no longer glaring.

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Chemical Kinetics for General Students of Chemistry.

By B. STEVENS, M.A., D. Phil., Lecturer in Chemistry, Sheffield University. Chapman and Hall, Ltd., 37 Essex Street, London, W. C. 2, England. 1961. viii + 107 pp. 13 × 19 cm. Price, 12s. 6d.

This slim book is the first of a series of six Physical Chemistry texts, the others to include: Atomic Structure and Valency, Chemical Thermodynamics, Molecular Structure, Electrochemistry and The States of Matter. They are intended "primarily for the degree student who is reading chemistry as a secondary subject." By North American standards, judging from the first volume, the level is approximately that of undergraduate work by chemistry majors. In this respect, the series represents an interesting publishing venture—the production of the equivalent of a standard physical chemistry textbook as a set of small flexible units. If this method were adopted more widely, the selection of references for particular courses could be greatly simplified, but the total cost would exceed that of most one-volume texts. However, since all six of these books will be written by but two authors, rather than by experts in each area, the principal advantage of the system has been lost.

After an introductory section there follow conventional chapters on the rate of reaction and its integrated forms, on the concentration and temperature dependence, all summed up by a very brief theoretical outline covering unimolecular, collision and absolute rate theories. Both homogeneous and heterogeneous catalysis receive extensive coverage which includes a short discussion of autocatalysis and inhibition. Two unaccountably brief chapters on photo and radiation chemistry and on atom and free radical chemistry conclude the text. References by author and date identify experimental data, but no general references to more advanced monographs have been made. A set of 25 problems covers most aspects of experimental kinetics dealt with in the book.

A strong feature of the book concerns the emphasis given to experimental data. Almost every subject is neatly illustrated with well drawn diagrams. Its main weakness is to be found in the last chapter, on atom and free radical chemistry. The introductory part of this chapter will erroneously imply to the unwary student that in a bond dissociation reaction the energy " kT " only must be supplied, and that "hot" radicals do not exist. The now defunct treatment (chain *versus* molecular reaction) of the inhibition of hydrocarbon decompositions by nitric oxide should not have been included. "Chemical Kinetics" thus does not