

gave penicillin G in 77% isolated yield as the crystalline *N*-ethylpiperidine salt,⁹ m.p. 153–155° (dec.). Penicillin V, prepared in 79% yield by phenoxyacetylation of compound V, was isolated as the potassium salt. Identity of these synthetic samples with the corresponding penicillin salts obtained directly by fermentation was established rigorously by infrared spectra (KBr), m.p. and mixed m.p., optical rotation and microbiological assay. Treatment of V with benzyldisulfonyl chloride led to 6-benzylsulfonamidopenicillanic acid.¹⁰ These acylation experiments demonstrate the generality of these synthetic routes for the preparation of both "natural" and "unnatural" penicillins.

We are indebted to Bristol Laboratories of Syracuse, N. Y., for financial support, for bioassays, and for a sample of natural 6-aminopenicillanic acid, and to Mr. Edward J. Hessler for technical assistance.

(9) J. C. Sheehan, W. J. Mader and D. J. Cram, *THIS JOURNAL*, **68**, 2407 (1946).

(10) J. C. Sheehan and D. R. Hoff, *ibid.*, **79**, 237 (1957).

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FREE-RADICAL-INITIATED *CIS-TRANS*
ISOMERIZATION OF DECAHYDRONAPHTHALENE
Sir:

We wish to report *cis-trans* isomerization of decahydronaphthalene (I) by a free radical chain reaction. Di-*tert*-butyl peroxide (0.002 mole) was added over a period of one hour to pure *cis*-I (0.131 mole) refluxing at 195°. After one hour the *trans*-I content had increased from 0.1 to 7.8%,

based on total I. Assuming the generation of two free radicals by each peroxide molecule, 2.6 moles of *trans*-I were formed per mole of free radical, clearly demonstrating that the isomerization proceeds by a free radical chain process. No isomerization took place at 195° in the absence of initiator.

We wish to suggest a mechanism for this free radical chain isomerization. The weakest bonds in I, those on the 9 or 10 carbon atoms, are preferentially attacked by a free radical, removing a hydrogen atom from one of those carbon atoms. The resulting free radical, 9-decahydronaphthyl (II), is assumed to have a planar arrangement of C-C bonds around the 9 carbon atom. *cis-trans* Isomerization then occurs by hydrogen atom exchange between I and II, since the hydrogen atom would add to II with equal probability at either side of the plane referred to, producing either *cis*- or *trans*-I. A chain reaction, II + I → I + II, proceeds until radical II is removed by reaction with another free radical.

cis-trans Isomerization of I also was found to occur thermally in the gas phase in the temperature range 440 to 460°, at a rate increasing with pressure. Thus, with one hour time of reaction at 450°, and initial *cis*-I concentrations of 0.0117, 1.53, and 2.66 moles/liter, the I in the product contained 0.9, 31.5, and 43.5% *trans*-I, respectively.¹ It appears not unlikely that the thermal isomerization and the peroxide-initiated isomerization proceed by the same free radical chain mechanism.

(1) Calculations by T. Miyakawa and K. S. Pitzer, *THIS JOURNAL*, **80**, 61 (1958), give 86.6% *trans*-I, 13.4% *cis*-I at equilibrium at 450°.

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RECEIVED APRIL 4, 1959

BOOK REVIEWS

The Determination of Molecular Structure. By P. J. WHEATLEY. Oxford University Press, 417 Fifth Avenue, New York 16, N. Y. 1959. vi + 263 pp. 14.5 × 22 cm. Price, \$5.60.

Since all of chemistry ultimately depends on the details of the structure of molecules and atoms, it behooves every chemist to know something of the methods by which molecular structure may be determined. This book should provide a reasonably complete introduction to this broad field. It is written strictly for the non-specialist and contains neither extensive details of experimental techniques nor elaborate mathematical discussions. To quote the author, "... the emphasis throughout has been placed on the scope and limitations of the various methods."

Following a lucid introduction to molecular symmetry, the book is divided into three main sections: I. Spectroscopic Methods, II. Diffraction Methods, and III. Miscellaneous Methods, the latter including such topics as stereochemistry, electric and magnetic moments, and nuclear magnetic resonance. Each section contains a general description of the method as well as several real examples from the literature illustrating the way in which molecular *size* and *shape* may be determined from the experimental data. Chemical behavior, of course, also depends inti-

imately on the detailed *electronic* structures of molecules, and an amplification of the few references to this aspect of structural chemistry would have greatly increased the usefulness of the book.

Active workers in the fields discussed will find both omissions and statements with which they are not in complete sympathy, but this should not detract seriously from the usefulness of the book to the general reader.

The section on x-ray diffraction, the author's specialty, is perhaps the best written, although it is somewhat surprising that no mention is made of the least squares method, which is in at least as common use as are Fourier methods in the final stages of a structure refinement. Furthermore, the estimate of six man-years as the time required to determine molecular parameters to an accuracy of 0.015 Å. for a ten atom problem is unduly pessimistic, particularly in the light of modern computing methods. An error of fact appears on p. 121; the structure of NaCl is *not* uniquely determined by the observations that it is face-centered cubic and that there are four formulae units per unit cell.

The section on electron diffraction in its emphasis on the radial distribution method and on the positions of diffraction maxima and minima seems to reflect a certain unfamiliarity with some of the better work in the field. In addition,

the discussion of errors and limitations of the method is somewhat inadequate.

The treatment of normal coordinates in the section on spectroscopy seems unnecessarily brief; for example, there are a number of points in the discussion of the structure of monodeuterioacetylene which will probably be unclear to the general reader because of this deficiency.

In view of the author's professed desire to give a clear idea of the limitations of the various methods, this reviewer feels that the discussion of experimental error for some of the methods is far from adequate. Also there are surprisingly many quotations of molecular parameters without any indication of the associated estimates of error.

If the reader is aware that the brevity of the discussions results in certain inadequacies of presentation, and if he makes full use of the references at the end of each chapter for further details of a technique in which he may be particularly interested, the objections which a specialist has to parts of the book may be regarded as minor.

The book should prove to be most useful as a supplementary text in an undergraduate physical chemistry course and may also be recommended to any chemist who wishes to have a somewhat better understanding of what is behind the occasional interatomic distance which he quotes.

CHEMISTRY DEPARTMENT
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Radioactivity Measuring Instruments. A Guide to their Construction and Use. By M. C. NOKES. Philosophical Library, Inc., 15 East 40th Street, New York 16, N. Y. 1958. viii + 75 pp. 14.5 × 22 cm. Price, \$4.75.

According to the author "this book is an attempt to show how instruments of fair accuracy can be made with the minimum of expense and without the consumption of too much time." Chief emphasis is on radioactivity measuring instruments employing halogen filled G-M tubes which can be used to illustrate elementary experiments in radioactivity. The book is addressed to science students and their teachers. In 5 pages of the first chapter the author explains the properties of the various radiations, defines the units of source strength and dose, and discusses the health hazards of handling radioactive substances.

Chapters 2 and 3 discuss the operation of G-M tubes and the statistics of counting random events.

The remaining 6 chapters are devoted to descriptions of trigger circuits, power supplies, scalers and ratemeters. Components and prices are listed, but this information will be of little use to most U. S. readers because the components are almost entirely of European manufacture.

The book is useful as a guide to "do-it-yourself" science teachers who have a limited budget for radioactivity demonstration equipment.

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Organic Syntheses. Volume 38. JOHN C. SHEEHAN, Editor-in-chief. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1958. vii + 120 pp. 15 × 23.5 cm. Price, \$4.00.

The current volume of this worthwhile series continues the high standards previously maintained. The thirty-one syntheses listed offer a variety of organic compounds and general reactions which should be useful to organic chemists in diverse areas of research. Some of the more general procedures include the synthesis of 2-benzylaminopyridine, N-ethyl-*p*-chloroaniline, hendecanedioic acid, 1-nitroöctane and 1-methyl-isoquinoline. The use of cupric acetate as an improved catalyst for the cyanoethylation of *o*-chloroaniline is reported. A procedure involving the use of commercially available peracetic acid for epoxidation of carbon double bonds is also a useful addition to this volume. Several interesting heterocyclic syntheses are described, including the preparation of 2-amino-4-anilino-6-(chloromethyl)-*s*-triazine and 2-vinylthiophene. Among the compounds which offer promise as intermediates in other syntheses are diethyl methylenemalonate, β -methylglutaric anhydride, monovinylacetylene and 1,4-pentadiene.

In addition to the variety of syntheses, Volume 38 also contains the cumulative index of material from Volumes 30-38, thereby increasing its usefulness to the practicing organic chemist.

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Curare and Curare-like Agents. Edited by D. BOVET, F. BOVET-NITTI and G. B. MARINI-BETTOLO, Instituto Superiore di Sanita, Roma. D. Van Nostrand Co., Inc., 120 Alexander St., Princeton, New Jersey. 1959. xi + 478 pp. 17 × 24.5 cm. Price, \$15.75.

This beautifully printed and richly illustrated volume is comprised of the papers delivered at the International Symposium on Curare and Curare-like Agents in Rio de Janeiro, August 5-12, 1957. It is divided into five sections dealing with the ethnographic problems, the botanical aspects, chemistry, pharmacology and clinical application of curare and related compounds. The standard of most of the communications is high and their total represents an up to date picture of the rapidly changing concepts of the chemistry, physiology and pharmacology of neuromuscular blocking agents. The editors did a splendid job of welding into a uniform structure the various communications presented in English or French. This book will serve as a valuable source of reference for those engaged in research in the field of neuromuscular blocking agents. It should be especially useful for the chemist interested in the isolation of natural alkaloids and the synthesis of compounds active at the neuromuscular junction.

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BOOKS RECEIVED

September 10, 1959–October 10, 1959

H. EYRING, Editor, C. J. CHRISTENSEN, Associate Editor, AND H. S. JOHNSTON, Associate Editor. "Annual Reviews of Physical Chemistry." Volume 10. Annual Reviews, Inc., Grant Avenue, Palo Alto, California. 1959. 537 pp. \$7.00 (U.S.A.); \$7.50 (elsewhere).

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A. I. M. KEULEMANS. C. G. VERVER, Edited by. "Gas Chromatography." Second Edition. Reinhold Publishing Corporation, 430 Park Avenue, New York 22, N. Y. 1959. 234 pp. \$7.50.

K. LARK-HOROVITZ AND VIVIAN A. JOHNSON, Edited by. "Methods of Experimental Physics." Volume 6. "Solid State Physics." Part A. "Preparation, Structure, Mechanical and Thermal Properties." Academic Press, Inc., 111 Fifth Avenue, New York 3, N. Y. 1959. 466 pp. \$11.80.

K. MENDELSSOHN, Editor. "Progress in Cryogenics." Volume 1. Academic Press, Inc., 111 Fifth Avenue, New York 3, N. Y. 1959. 259 pp. \$11.00.

HANS NETTER. "Theoretische Biochemie. Physikalisch-Chemische Grundlagen der Lebensvorgänge." Springer-Verlag, Heidelberger Platz 3, Berlin-Wilmersdorf, Germany. 1959. 816 pp. DM. 88.--.

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FREDERICK SEITZ AND DAVID TURNBULL, Editors. "Solid State Physics. Advances in Research and Applications." Volume 9. Academic Press, Inc., 111 Fifth Avenue, New York 3, N. Y. 1959. 548 pp. \$14.50.