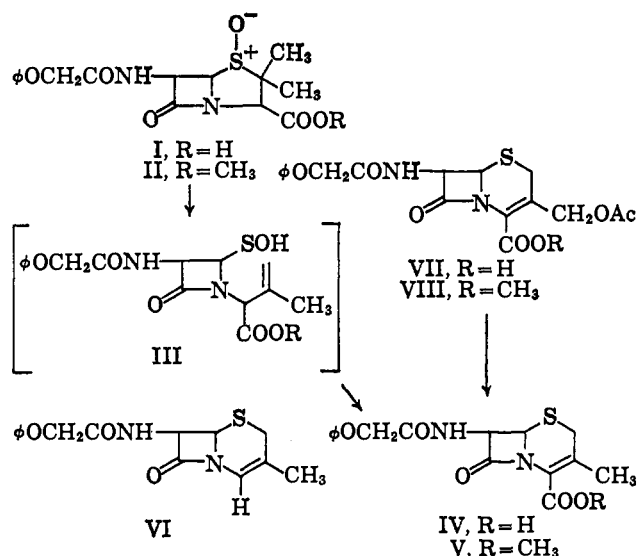


tion and the size of the sulfur-containing ring. We now report the chemical conversion of penicillin to cephalosporin-type compounds.

Treatment of phenoxymethylpenicillin sulfoxide methyl ester (II), m.p. 121.5–122.5°,  $[\alpha]_D^{20} +200^\circ$  (periodate oxidation of phenoxymethyl penicillin<sup>2</sup> and esterification with diazomethane) with a trace of *p*-toluenesulfonic acid in xylene at reflux temperature gave a 15% yield of a less polar compound, m.p. 141–142°,  $[\alpha]_D^{20} +94^\circ$ ,  $\lambda_{\max}^{\text{EtOH}}$  268 m $\mu$ ,  $\epsilon$  7600,  $\lambda_{\max}^{\text{CHCl}_3}$  5.62, 5.82, 5.92 and 6.12  $\mu$ , to which we have assigned structure V.<sup>3</sup> The survival of the  $\beta$ -lactam is indicated by the infrared band at 5.62  $\mu$  and the presence in the n.m.r. spectrum of a one proton quartet at 4.14  $\tau$  and a one proton doublet at 4.95  $\tau$ , characteristic of the two



hydrogen atoms on the four-membered ring in cephalosporins and certain penicillin derivatives. Also, the n.m.r. spectrum shows a single methyl group attached

(2) We wish to thank Dr. E. H. Flynn of these Laboratories for this procedure.

(3) Rotations were determined in dioxane, n.m.r. spectra were recorded on Varian HR-60 in CDCl<sub>3</sub> with tetramethylsilane as internal standard and all compounds for which melting points are reported have given satisfactory elemental analyses.

to carbon (7.84  $\tau$ ) and non-equivalent methylene signals (6.73 and 6.44  $\tau$ ,  $J = 18$  c.p.s.) which can be assigned to the hydrogens attached to the carbon adjacent to sulfur. The presence of the double bond is indicated by the infrared band at 6.12  $\mu$  and the ultraviolet absorption spectrum which is similar to that of the corresponding cephalosporin derivative (VIII). A plausible pathway for the formation of V is *via* a sulfoxide elimination<sup>4</sup> to the intermediate (III), subsequent addition of the sulfenic acid to the double bond with the sulfur becoming attached to the primary carbon<sup>5</sup> and the loss of a proton to yield V.

Thermal treatment of phenoxymethylpenicillin sulfoxide (I)<sup>2,6</sup> with and without added mineral acid yielded not the desired product (IV) but a neutral substance (VI), m.p. 173.5–174.5°,  $[\alpha]_D^{20} -35.3^\circ$ ,  $\lambda_{\max}^{\text{EtOH}}$  256 m $\mu$ ,  $\epsilon$  9150,  $\lambda_{\max}^{\text{CHCl}_3}$  5.65, 5.92 and 6.03  $\mu$  (sh) which possessed an olefinic proton as shown by a peak at 3.52  $\tau$  in the n.m.r. spectrum. High pressure catalytic (Pd-C) hydrogenolysis of VII<sup>1b</sup> provided an acid assigned structure IV since its methyl ester, also obtained by reduction of VIII, m.p. 149–150°,  $[\alpha]_D^{20} +53^\circ$ , was identical with V made by the sulfoxide rearrangement.

The isolation of the same derivative (V) from both a cephalosporin and a penicillin provides a direct chemical correlation of the two types of compounds. The sulfoxide rearrangement involved in this correlation is not peculiar to penicillin sulfoxide but can be applied to simpler cyclic sulfoxides.<sup>7</sup>

(4) This initial step is analogous to the thermal *cis*-elimination of 1,2-diphenyl-1-propyl-phenyl sulfoxides to  $\alpha$ -methylstilbenes: C. A. Kingsbury and D. J. Cram, *J. Am. Chem. Soc.*, **82**, 1810 (1960). In our case a trace quantity of acid was necessary to cause a reaction.

(5) The compound arising from addition of the sulfenic acid to the double bond in the opposite sense apparently is unstable in the described experiment. Under other conditions this is the predominant product isolated. Details will be reported in future publications.

(6) A. W. Chow, N. M. Hall and J. R. E. Hoover, *J. Org. Chem.*, **27**, 1381 (1962).

(7) R. A. Mueller and R. B. Morin, unpublished results from these Laboratories.

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## BOOK REVIEWS

### Gas Chromatography. Principles, Techniques and Applications.

By A. B. LITTLEWOOD, King's College, University of Durham, Newcastle upon Tyne 1, England. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1962. xi + 514 pp. 16 × 23.5 cm. Price, \$15.00.

Dr. Littlewood's book represents an excellent addition to the suddenly proliferating number of general texts on the theory and practice of gas chromatography. The text is highly recommended for graduate level and as an introductory work for research people. No previous familiarity with gas chromatography is required. The first chapter supplies the reader with an introduction to the mechanism, apparatus, history and applicability of the gas chromatography technique in a notably clear exposition distinguished by the author's ability to avoid the obscuring use of chromatographic jargon and equations. Succeeding chapters deal with theory of chromatographic separations, column performance and, finally, the practical selection and preparation of column construction materials. The author treats difficult theoretical discussions in a pedagogical progression, proceeding from the simple to the complex and even giving illustrative calculations where necessary. Chapters are also devoted to theory, construc-

tion and operation of most of the detectors used in gas chromatography, injection systems, quantitative analysis principles and techniques, and temperature programming. Finally, a major portion of the text (pp. 372–471) is devoted to a discussion of the important applications of gas chromatography. The organization of this chapter is based on the chemical type of sample material; *i.e.*, permanent gases, aromatic hydrocarbons, nitrogen compounds. The book makes excellent use of diagrams and includes many prints of applications, illustrations. Here the author faces what must be a common problem. The illustrations chosen are generally chromatograms taken from the "original" publication on a particular subject. While this is of historical value and gives proper credit to the scientist who first performed the separation, the results shown are often primitive compared to what may be obtainable in current practice. It might be more appropriate in a text which features applications guidance to obtain more representative illustration from current rather than "classical" sources.

The nomenclature used generally follows IUPAC recommendations, but occasionally employs unique symbols where they aid in the orderly development of a theoretical principle. Adequate references are cited, including publications as recent as 1961.

In considering the book as a guide to laboratory practice, the unwillingness of the author to editorialize might hamper a practitioner of gas chromatography in selecting equipment or techniques. For example, Dr. Littlewood clearly describes eight ionization detectors, but prefaces the discussion with only a mild statement that the argon and flame ionization detectors are receiving much more attention than the others. In the United States, at least, the flame detector essentially monopolizes the field today, electron capture detectors are of increasing interest, and argon detectors are rapidly disappearing from use. Such information might be of more value to the reader looking to the text for guidance in practice. An analogous situation exists in the chapter on catharometry in which it implied that ion gages are equivalent to catharometers for low sensitivity work, are superior for high sensitivity work, and are gradually replacing them. Again, in the United States, at least 80% of all work is still performed on catharometer-equipped chromatographs, and their lower cost and operating convenience will probably perpetuate this situation.

Some minor errors were noted in the text. For example, in the coating of capillary columns (p. 208), methyl chloride is not a practical choice as a solvent; methylene chloride was probably used. Further, the oven evaporation system described as one technique is never used in practice. The author also states rather dogmatically (p. 209) that capillary columns coated with polar stationary phases are far less efficient than those coated with non-polar phases. While early results tended to show this distinction, the difference has been shown to be a result of failure to produce equivalently thin coating films with polar liquids. Where the coating procedure is modified to yield suitably thin coatings, polar columns of very high efficiency have been produced.

In summary, Dr. Littlewood's book is highly recommended for clarity and completeness and should serve as an excellent general text in gas chromatography.

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NATHANIEL BRENNER

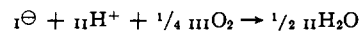
**Thermodynamische Elektrochemie.** Von Dr.-Ing. ERICH LANGE, ordentlicher Professor für Physikalische Chemie, Vorstand des Instituts für Physikalische Chemie der Universität Erlangen-Nürnberg, in Gemeinschaft mit Dr. Phil Nat. HERMANN GÖHR, Assistent am Institute für Physikalische Chemie der Universität Erlangen-Nürnberg. Dr. Alfred Hüthig Verlag G.m.b.H., Postfach 727, Heidelberg, Germany. 1962. 429 pp. 16.5 × 23.5 cm. Price, DM. 39.

The outstanding characteristic of this book is that it presents electrochemistry in a series of brief chapters arranged in order of increasing complexity with respect to the thermodynamic phases under consideration. Beginning with a single phase in the absence of current, it proceeds to discuss a single phase with current passing (conductance, transference, diffusion), transport processes in a non-isothermal single phase, a simple electrode at equilibrium, the Volta potential of a two-phase electrochemical system, the electrochemical double layer, phase transformations with flow of current at simple electrodes, Peltier heat at simple electrodes, some electrochemical three-phase systems at equilibrium, the ideal galvanic cell at equilibrium, the real galvanic cell, the galvanic thermocell, a general thermodynamic-kinetic view of polarized electrodes, a general thermodynamic-kinetic view of polarized galvanic cells, the twofold electrode, the surface-layer equilibrium electrode, the surface-layer mixed electrode, the corrosion surface-layer electrode, the double surface-layer electrode and abrasion effects at electrodes.

This approach will undoubtedly appeal more to the electrochemical pragmatist than to the thermodynamic purist. As appealing as the idea is to proceed gradually from simplicity to complexity, an inevitable result is that single ion activities are introduced before mean activities of strong electrolytes (p. 66).

An exceptionally clear distinction is made between Volta and galvanic potentials, and the treatment in general is orderly, sys-

tematic and logical. The notation unfortunately becomes cumbersome, and the reader finds himself making frequent reference to the five-page list of symbols at the front of the book. Even simple equations become loaded down, as for example the equation for the oxygen electrode reaction in acid solution (p. 70)



where the subscripts I, II and III refer to the metal, solution and gas phases, respectively.

A more serious criticism though, is that the kinetics which is allowed to permeate a "thermodynamic" book is at best a treatment of the steady state, and the variables that affect the steady state are not adequately handled nor is the rate of attainment of steady state considered. Thus the Nernst diffusion layer concept (p. 196) is used to describe limiting currents, but the inadequacy of this treatment is not pointed out, nor are transient currents upon sudden polarization considered. It is true that an adequate discussion of transient and steady state processes would have lengthened the book considerably, but an incomplete and out-of-date treatment can hardly be defended in the light of the emphasis on transient phenomena in modern electrochemical research.

On p. 198, in considering the effect of supporting electrolyte on limiting currents, the charge-types but not the individual ion mobilities are taken into account.

The book is relatively free from typographical errors, and the quality of paper, printing and binding are adequate. The German is easily understood even by a reader whose native language is English. Nevertheless, it is difficult to find sufficient advantage in this treatment over material available in English to justify purchase by the average American electrochemist.

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**Magnetische Kernresonanz und Chemische Struktur—Fort-schritte der Physikalischen Chemie, Band 7.** By H. STREHLOW, Max-Planck-Institut für physikalische Chemie, Göttingen. Dr. Dietrich Steinkopff Verlag, Darmstadt, Germany. 1962. xii + 179 pp. 15.5 × 23 cm. Price, DM. 36.

The author states in the preface that this book is intended as an introduction to nuclear magnetic resonance (n.m.r.) for chemists and students of chemistry, and should enable the reader to evaluate possible applications of n.m.r. in his own research. This statement characterizes the scope of the book well. It is not a reference book, and neither does it present any original approaches in theoretical development or in chemical applications. It does provide a clear exposition of those aspects of n.m.r. which are of interest to the chemist, at a level which presupposes only average knowledge of mathematics or physics.

The book is divided into two about equal parts. The first, "physical principles," contains an introduction to relaxation and line width theory, a discussion of the Bloch equations and their solution, the principles of high resolution spectrum interpretation in terms of chemical shift and spin-spin coupling constants, and a short section on experimental methods. In the second part, "chemical applications," the use of n.m.r. in structural analysis is illustrated by a number of examples, both from organic and inorganic chemistry. The effect of hydrogen bonding and complexing on the n.m.r. spectrum is discussed, and the use of n.m.r. in fast chemical kinetics is treated in some detail. A short section on n.m.r. in solids follows.

The book is well written, and very few errors in printing or in fact have been noted by this reviewer (the statement on page 19 that for liquids  $T_1 \approx T_2'$  is one of the few). As a short introduction to a large and rapidly growing field, it should prove very useful.

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