

isothiocyanate and 2.2 equivalents of aluminum chloride with *ca.* ten parts of carbon disulfide for four days gave a 45% yield of 2a-thio-3-methylphthalimide, m.p. 192°. Alkaline hydrolysis gave 80% of 3-methylphthalic acid, m.p. 157–158° (lit.⁶ 157°), and sublimation gave 62% of 3-methylphthalic anhydride, m.p. 117–118° (lit.⁷ 117–118°); 3-methylphthalimide, m.p. 188–189° (lit.⁸ 189–190°). Treating 3,5-dimethylbenzoyl chloride with lead thiocyanate gave 63% of the isothiocyanate, b.p. 99° (1.5 mm.). Treatment with aluminum chloride gave 65% of 3,5-dimethyl-2a-thiophthalimide, m.p. 209–210°; hydrolysis gave 3,5-dimethylphthalic acid, m.p. 185° dec. (lit.⁹ 185–186° dec.) (neutr. equiv., calcd. 97; found, 97 ± 1). Phenylacetyl chloride gave 72% of isothiocyanate, b.p. 86° (0.5 mm.); N-phenylacetyl-N'-phenylthiourea, m.p. 107–108°. Cyclization gave 2a-thiohomophthalimide (52%), m.p. 221–222°, hydrolysis of which gave homophthalic acid, m.p. 178° (lit.¹⁰ 181°) (neutr. equiv. calcd., 90; found, 91), and reduction with excess lithium

(6) F. Mayer and O. Stark, *Ber.*, **64**, 2006 (1931).

(7) F. Mayer and H. Günthe, *ibid.*, **63**, 1459 (1930).

(8) S. Gabriel and A. Thieme, *ibid.*, **52**, 1083 (1919).

(9) W. H. Perkin and R. A. B. Tapley, *J. Chem. Soc.*, **125**, 2436 (1924).

(10) W. Davies and H. G. Poole, *ibid.*, 1616 (1928).

aluminum hydride gave tetrahydroisoquinoline, 47% as its picrate, m.p. 196° (lit.¹¹ 195–196°). β -Naphthoyl chloride gave 44% of isothiocyanate, m.p. 74°; N- β -naphthoyl-N'-phenylthiourea, m.p. 148–149°. Cyclization gave 25% of 1a-thio-1,2-naphthalimide, m.p. 248–249°, which was hydrolyzed to naphthalene-1,2-dicarboxylic acid, m.p. 175° dec. (lit.¹² 175° dec.). β -Phenylethyl isothiocyanate¹³ gave 40% of 1-thiodihydroisocarbostyryl, m.p. 98–99°, which was hydrolyzed to o-(2-aminoethyl)-benzoic acid hydrochloride, m.p. 197–198° (lit.¹⁴ 199–200°), and reduced by lithium aluminum hydride to tetrahydroisoquinoline, picrate m.p. 196°. α -Naphthylacetyl chloride gave 72% of isothiocyanate (N- α -naphthylacetyl-N'-phenylthiourea, m.p. 125°), which was cyclized in 41% yield to 8a-thio-1-homonaphthalimide, m.p. 254–255°. Hydrolysis gave homonaphthalic acid, m.p. 214–215° (lit.¹⁵ 213–214°).

(11) E. F. Bradbrook and R. P. Linstead, *ibid.*, 1739 (1936).

(12) J. von Braun and H. Deutsch, *Ber.*, **45**, 2188 (1912).

(13) E. Bamberger and W. Dieckmann, *ibid.*, **26**, 1217 (1893).

(14) A. Pictet and T. Spengler, *ibid.*, **44**, 2034 (1911).

(15) H. G. Rule and H. M. Turner, *J. Chem. Soc.*, 317 (1935).

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BOOK REVIEWS

The Alkaloids, Chemistry and Physiology. Volume VI. Supplement to Volumes I and II. Edited by R. H. F. MANSKE, Dominion Rubber Research Laboratory, Guelph, Ontario. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1960. xii + 442 pp. 16 × 23.5 cm. Price, \$14.00.

The appearance of this supplement is a very welcome addition to the alkaloid literature. It is not strictly a supplement to Vols. I and II since there is no further treatment of the indole, acridine or *Erythrina* alkaloids which were reviewed in Vol. II. The publishers have been extremely tardy in bringing this book to the public. Many of the chapters were written in 1957 and I would like to add my small voice to that of Carl Djerassi (*cf.* THIS JOURNAL, **81**, 6092 (1959)) and protest at this inexcusable delay in publishing. In this review I will attempt to bring the prospective buyer up to date and mention recent important developments.

Chapter 1. Alkaloids in the plant, by K. Mothes: Having read this chapter one comes to the conclusion that the only thing which is common to all alkaloids is the presence of nitrogen in their structures. The large number of references attest considerable activity in this field and rapid progress is being made in elucidating the biosynthesis, metabolism and translocation of alkaloids in plants, especially by utilizing tracers (*cf.* also *Symposium Soc. Expt. Biol.* No. 13, 258 (1959)). The structure of echinulin, p. 3, has been modified (*Tetrahedron Letters*, No. 16, 1 (1959)).

Chapter 2. The pyrrolidine alkaloids, by L. Marion: This is a short chapter indicating that there has been little activity in this field in the last ten years. *In vivo* studies on stachydrine indicate that the elucidation of the biogenesis of even a simple alkaloid can involve considerable effort

(*Can. J. Chem.*, **37**, 1197 (1959); **38**, 396 (1960)). Repetition of Hess's hygrine synthesis led to a tetrahydrooxazine (*Coll. Czech. Chem. Comm.*, **24**, 2433 (1959)). Betonicine has been isolated from *Achillea millefolium* (*Monatsh.*, **90**, 396 (1959)).

Chapter 3. Senecio alkaloids, by N. J. Leonard: This is an excellent review of the pyrrolizidine alkaloids and the author has been able to mention work published in 1958 (!) in an addendum. Since then viridifloric acid has been shown to be the (-)-*erythro* isomer (*Austral. J. Chem.*, **12**, 694 (1959)). The amide of heliotricinic acid has been synthesized (*ibid.*, **12**, 706 (1959)) and has the *threo* configuration. Mikanicic acid is an artifact produced by the dehydration and dimerization of sarracenic acid (*Chemistry & Industry*, 366 (1959)). The structure of seneciphylic acid has been modified (*ibid.*, 21 (1959)). The correct structures of jaconecic acid, jaconine, jacobine and related compounds have finally been elucidated (*Austral. J. Chem.*, **12**, 247 (1959); THIS JOURNAL, **81**, 5201 (1959)). The absolute configuration at C-8 in retronecine has been determined (*ibid.*, **81**, 5803 (1959)). It is interesting to learn that 1-methylenepyrrolizidine is the major alkaloid in a *Crotalaria* sps. (*Austral. J. Chem.*, **12**, 255 (1959)). The Robinson-Schöpf scheme for the biosynthesis of the pyrrolizidine nucleus has been realized in the laboratory (*Chem. Zvesti.*, **13**, 163 (1959); THIS JOURNAL, **82**, 503 (1960)).

Chapter 4. The pyridine alkaloids, by L. Marion: The pelletierine myth seems to be finally buried and a re-examination of the rearrangement of isopelletierine oxime (*ibid.*, **81**, 4664 (1959)) has added nails to the coffin. Isopelletierine has been isolated from *Duboisia* sps. (*J. Chem. Soc.*, 3967 (1957); *Austral. J. Chem.*, **11**, 82 (1958)). The efficiency of modern methods for the separation of alkaloids has been demonstrated in a study of the bases of

Lobelia inflata in which thirty minor alkaloids were detected (*Ann.*, 608, 88 (1957)). New alkaloids, sedinine and sedinone, have been isolated from *Sedum acre* (*Ber.*, 91, 2803 (1958); 92, 1001 (1959)). The absolute configuration of sedamine has been deduced (*Ann.*, 626, 134 (1959)). It is difficult to reconcile recent work on ricinine biogenesis (*J. Chem. Soc.*, 2921 (1959)) with earlier studies. The absolute configuration of conhydrine and its pseudo isomer has attracted much attention (*Tetrahedron*, 6, 103 (1959), and ref. cited therein). The biosynthesis of the hemlock alkaloids has been investigated (*Z. naturforsch.*, 13b, 691 (1958); *Biochem. J.*, 64, 259 (1956); 73, 556 (1959)). New precursors of the pyrrolidine and piperidine rings of nicotine and anabasine have been discovered (*THIS JOURNAL*, 80, 2162, 4393 (1958); *J. Biol. Chem.*, 233, 939 (1958)) and work is progressing on the origin of the pyridine ring (*Chemistry & Industry*, 1270 (1957), 1477 (1958); *Science*, 129, 1485 (1959); *J. Biol. Chem.*, 235, 800 (1960)) although the final story is not yet told. Smokers should read *Chem. Revs.*, 59, 885 (1959), and feel humble when they learn of the large number of compounds with which they pollute our air. New alkaloids which contain the pyridine ring are anibine (*THIS JOURNAL*, 79, 4507 (1957); 80, 2263 (1958); *Monatsh.*, 89, 391 (1958)), α -picoline (*Nature*, 181, 636 (1958)), actinidine (*Bull. Chem. Soc. (Japan)*, 32, 315, 1155 (1959)), muscopyridine (*THIS JOURNAL*, 79, 5558 (1957)), and homostachydrine (*Can. J. Chem.*, 36, 339 (1958)).

Chapter 5. The tropane alkaloids, by G. Fodor: Since the author is one of the most active workers in this field he has been able to present an up to date account of these alkaloids. Details of the synthesis of scopolamine (*J. Chem. Soc.*, 3461 (1959)) and tropinone (*ibid.*, 2433 (1959)) have now been published. The absolute configuration of tropic acid (*Tetrahedron Letters*, No. 7, 16 (1959) and its biogenesis (*THIS JOURNAL*, 82, 612 (1960)) have been elucidated. Structure LXXVIIb for dioscorine has been confirmed (*ibid.*, 80, 6146 (1958); *J. Chem. Soc.*, 615 (1959)). New tropane alkaloids have been isolated (*ibid.*, 1406 (1959), *Naturwissenschaften*, 46, 492 (1959)). N.m.r. has been used to investigate the configuration of the N-methyl group of the tropane bases (*THIS JOURNAL*, 81, 5456 (1959)). The conversion of scopinium bromide to *m*-hydroxybenzaldehyde has been investigated (*ibid.*, 81, 5800 (1959)).

Chapter 6. The Strychnos alkaloids, by J. B. Hendrickson: This is a lucid and entertaining account of the recent chemistry of strychnine, vomicine and their derivatives, culminating in Woodward's brilliant synthesis. Since this chapter was written there has been much clarification of the alkaloids of the S. American *Strychnos* species. There is insufficient space here to list all the significant references; however, the dedicated reader can start with part 41 of a series of papers by Karrer's group (*Helv. Chim. Acta*, 43, 141 (1960)) and trace his way back through this fascinating story. Key references to other workers in this field are *J. Chem. Soc.*, 736 (1960), and *THIS JOURNAL*, 81, 2256 (1959). A recent review has also appeared (*Prog. Chem. Nat. Prod.*, 17, 183 (1959)). It is extremely interesting to note that caracurine VII is identical with the Wieland-Gumlich aldehyde (formula CCXXIII, p. 188). The structure of gelsemine finally has been established (*Tetrahedron Letters*, No. 4, 1, 6 (1959)).

Chapter 7. The morphine alkaloids, by G. Stork: Recent work on the stereochemistry and synthesis of morphine, codeine and thebaine has been admirably described and the excellent structural formulas make it easy to understand the many rearrangements and displacements which occur with these alkaloids. Pseudomorphine has been shown to be 2,2'-bimorphine (*J. Chem. Soc.*, 2574 (1959)). Robinson's biogenetic scheme for morphine has been confirmed by the use of tracers (*THIS JOURNAL*, 81, 3948 (1959); *Chemistry & Industry*, 364, 977 (1958); *Z. naturforschung*, 14b, 52 (1959)).

Chapter 8. Colchicine and related compounds, by W. C. Wildman: Many of the perplexing reactions of colchicine have now been clarified and several minor alkaloids have been isolated and their structures determined. The structures of the lumicolchicines are remarkable and an analogous photochemical transformation has been realized with a γ -tropolone (*THIS JOURNAL*, 80, 6685 (1958)). The total synthesis of colchicine has been achieved (*ibid.*, 81, 6341 (1959); *Angew. Chem.* 71, 637 (1959)). Recent results obtained by the reviewer (unpublished) have shown that

Belleau's hypothesis for the biogenesis of colchicine is untenable.

Chapter 9. Alkaloids of the amaryllidaceae, by W. C. Wildman: This is the longest chapter of the book (124 pp.) and its length is indicative of the intense activity in this field. In six years more than 55 new alkaloids have been isolated from this family and the structures of many of them have been elucidated by the author. As a result, a very authoritative chapter has been written containing material obtained by personal communication with other workers in this area. Structures have since been deduced for amaryllidine, parkamine (*Ber.*, 92, 2578 (1959)), criwelline (*Chemistry & Industry*, 1415 (1959)), powellamine (*Naturwissenschaften*, 46, 475 (1959)), montanine and coccinine (Abstracts of the 136th Meeting of the Amer. Chem. Soc., Sept., 1959, p. 48-P). The stereochemistry of lycorine, lycorine and related compounds has been elucidated (*J. Chem. Soc.*, 3736 (1959)).

The subject index is inadequate, taking up only seven pages. Furthermore many of the entries such as β -picoline, puberulic acid and *Nicotiana* serve no useful purpose. On the other hand, important entries have been omitted. There is considerable discussion of the biogenesis of hyoscyamine in chapters 1 and 5, but the reader will find no clue to this in the index. I was amazed to discover the single page reference to morphine—a page apparently picked at random.

In spite of these deficiencies this is a book which all chemists working with natural products will wish to possess. The structural formulas are consistently well drawn throughout the book which is remarkably free of typographical errors (one was detected!—ajmaline (p. 210) lacks a methyl group). My order for Volume VII of "The Alkaloids" is already placed with the publishers.

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Statistische Theorie der Materie. Band I. Allgemeine Grundlagen und Anwendungen auf Gase. By Dr. KLAUS SCHÄFER, ord. Professor für physikalische Chemie an der Universität Heidelberg. Vanderhoeck und Ruprecht, Postfach 77 (20b) Göttingen, Germany. 1960. xi + 282 pp. 16 × 23.5 cm. Price, DM. 38.00.

The Preface to this book explains that it originates in a course of lectures. It is obviously intended as a textbook for physical chemistry students at what we would call a moderately advanced level, seniors or first year graduate students. In addition to this usefulness, however, it contains a large number of equations and tables that are a handy reference for the advanced worker.

Since the main interest in America is likely to be the latter, only some short comments about the nature of the book as a text are called for in this review. Opinions about the ideal method of teaching statistical mechanics to students are a little like opinions about religion. Every specialist in the field has his own ideas, and there is little scientific basis for judgment on the values.

This book presents a comprehensive outline of the methods of obtaining the thermodynamic functions of gases from the "atomistic" structure of the molecules. It does so without reference to the more general (Gibbs) treatment of systems of interacting molecules, which is necessary in the treatment of liquids and solids. However, it does not limit itself to perfect gases without interaction between molecules. There is a chapter (chapter IV), on the treatment of temperature-dependent quantum states, which can only occur with interacting molecules. A section of this chapter treats ionic solutes in a solution. Similarly the last chapter includes two sections on virial coefficients which again imply interaction.

This reviewer would prefer, in a textbook, or a course, to defer these subjects until after the more general treatment of statistical mechanics had been presented. In addition this reviewer would choose to present the Boltzmann with the Bose-Einstein and Fermi-Dirac systems, rather than to isolate the Boltzmann "statistics" as the initial subject of introduction.

Quite obviously, since the treatment of this volume is limited to gases, that is to an approximation in which the molecules are treated as independent except in so far as they