ment through path b should lead to retention of configuration (IIa, starred atom). Accordingly, pyrolyses of Feist's ester (IIa), $[\alpha]^{25}\text{D}$ −119°,[3] were carried to roughly 25 and 50% completion. The chromatographically separated products were Ia,[4] $[\alpha]^{25}\text{D}$ +28°, +10°[5]; Ib[4], $[\alpha]^{25}\text{D}$ +18°, +6°; and IIa, $[\alpha]^{25}\text{D}$ −93°, −34°, respectively. No *cis*-Feist's ester (IIb) was detected.

The isolation of active product provides convincing evidence for the "valence-tautomerization" pathway (b), but the observed racemization of starting material requires additional comment. Two racemization mechanisms not involving the "zwitterion" III appear possible. (1) The *trans*-ester (IIa) might equilibrate rapidly with product which has partially racemized either by equilibration with the internally-compensated *cis*-ester (IIb) or by some other unspecified route. (2) The *trans*-ester might equilibrate directly with its *cis*-isomer.

The first alternative is untenable because the experimental conditions effectively inhibit reconversion of product to IIa or IIb by virtue of the demonstrably favorable equilibria between the product and these esters.[6] The second was tested by partial pyrolysis of the *cis*-ester[7] (IIb) using conditions under which the *trans*-isomer was substantially unaffected.[3] The resulting mixture was shown by n.m.r. to be pyrolysis product (I), *trans*-ester (IIa) and *cis*-ester (IIb) in the approximate ratios 75:10:15. Thus the *cis*-ester (IIb) rearranges about 7.5 times faster than it isomerizes to the *trans*-ester (IIa) and, contrary to fact, racemization of IIa *via* IIb could occur only less than 1/7.5 times the rate of product appearance.

It is thus concluded that racemization must occur by reversible equilibration of *trans*-ester with the "zwitterion" IIIa (and/or IIIb) and that rearrangement proceeds competitively by both mechanisms a and b.

The author thanks W. von E. Doering and A. S. Kende for helpful suggestions and J. E. Lancaster for the n.m.r. spectra.

[3] Pyrolyses were carried out in 2% benzene solutions in a bomb partially immersed in a 210° bath for intervals of 30 and 45 minutes for IIa and 23 minutes for IIb.

[4] Stereochemistry not implied.

[5] The +10° sample was contaminated with Ib.

[6] An equilibrium ratio of IIa:IIb:I was found by n.m.r. analysis to be 6:<0.5:94 (*cf.* ref. 1).

[7] *Cf.* M. G. Ettlinger and F. Kennedy, *Chemistry & Industry*, 891 (1957).

ORGANIC CHEMICAL RESEARCH SECTION
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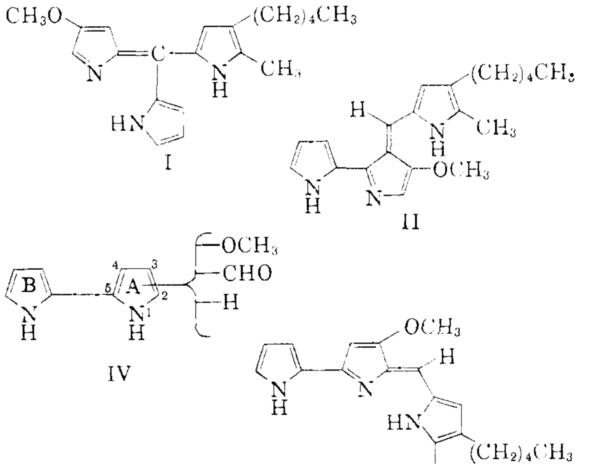
RECEIVED DECEMBER 3, 1959

PRODIGIOSIN. STRUCTURE AND PARTIAL SYNTHESIS[1]

Sir:

Prodigiosin, the blood-red pigment[2] of *Serratia marcescens*, assigned the tripyrrylmethene structure I by Wrede,[3] has attracted recent interest because of the possible relationship of I to the tripyrrylmethane type of intermediate in the biosynthesis of porphyrin.[4] We now present new evidence which makes I untenable, and which shows that prodigiosin is II, or III.



Wrede isolated 2-methyl-3-amylpyrrole, $C_{10}H_{17}N$, (A) from prodigiosin,[3] while Santer and Vogel[5] showed recently that a mutant strain (9–3–3) of *Serratia* accumulated a $C_{10}H_{10}O_2N_2$ precursor (B) which could be converted to prodigiosin by another mutant (W-1).[6] In a formal way, the condensation of these two C-10 fragments leads to prodigiosin, $C_{10}H_{17}N + C_{10}H_{10}O_2N_2 \rightarrow C_{20}H_{25}ON_3 + H_2O$. We have now, in fact, shown that pure A and B react readily under conditions of dipyrrylmethene synthesis to form prodigiosin, indistinguishable (infrared spectra of zinc salt and hydrochloride) from the natural material.

The n.m.r. spectrum of B (60 m.c. in dimethyl sulfoxide) contains two broad peaks at $\tau = -1.35$ and -1.52 (two pyrrolic NH protons) and a sharp singlet at $\tau = 0.57$ (aldehyde hydrogen). The α,α'-linkage of the pyrrole rings is shown by the isolation of pyrrolecarboxamide from the alkaline-peroxide oxidation of both B and prodigiosin.

The above evidence, and other properties of B[5] (one OCH_3, ultraviolet absorption at $\lambda_{\max}^{\text{CHCl}_3}$ 254 mμ, ε 13000; 363 mμ, ε 35000), now can be accommodated by expression IV. This can be refined further: (i) the strong ultraviolet absorption requires conjugation of both pyrrole rings with the formyl group and excludes any structure with −CHO at C-3. (ii) In view of the isolation of methoxymaleimide from prodigiosin[7] the methoxyl must be at C-3 or C-4. (iii) In the n.m.r. spectrum of B, the doublet at $\tau = 3.69$, which changes to a singlet in base, corresponds to the lone C–H proton on ring A (IV). Were this proton located at C-3, adjacent to CHO at C-2, it would be expected to show resonance closer to $\tau = 2.7$–2.9, as in 2-pyrrolealdehyde. B thus contains OCH_3 at C-3, and CHO

[1] This investigation was supported by Grants P-64 and P-64A from the American Cancer Society.

[2] E. N. Morgan and E. M. Tanner, *J. Chem. Soc.*, 3305 (1955).

[3] F. Wrede and A. Rothhaas, *Z. physiol. Chem.*, **226**, 95 (1934).

[4] D. Shemin, C. S. Russel and T. Abramsky, *J. Biol. Chem.*, **215**, 613 (1955).

[5] U. V. Santer and H. J. Vogel, *Biochim. Biophys. Acta*, **19**, 578 (1956).

[6] M. T. M. Rizki, *Proc. Natl. Acad. Sci.*, **40**, 1057 (1954).

[7] F. Wrede and A. Rothhaas, *Z. physiol. Chem.*, **215**, 67 (1933).

at C-2 or C-4. While we are attempting to distinguish rigorously between the two possibilities for B, we consider the α,α'-dipyrrylmethene III, formed from A + B, to accommodate the properties of prodigiosin better than the α,β'-alternative II.

We thank Drs. M. Bunting, D. Bonner, U. Santer, H. Vogel, and the Lederle Laboratories of the American Cyanamid Co. for generous assistance in the microbiological phases of this work.

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RECEIVED OCTOBER 26, 1959

BOOK REVIEWS

Elasticity, Plasticity and Structure of Matter. Second Edition. By R. HOUWINK. Dover Publications. Inc., 920 Broadway, New York 10, N. Y. 1958. xviii + 368 pp. 13.5 × 20.5 cm. Price, $2.45.

This book, which had been received with acclaim when first published in 1937, may now be considered a classic. It represented a rather successful attempt to present a physical outlook on diverse chemical and rheological observations of such systems as clays and doughs, synthetic and natural polymers and crystals.

Although the theories advanced two decades ago may appear inadequate today to describe "structure," the work provides a good survey of the phenomena of elasticity and plasticity. The revisions incorporated into the second edition (1952) still kept the point of view of 1937, although a section on the statistical theory of rubber elasticity was added.

In spite of its age, the book presents the field of rheology in a manner worth reading today. A reissue is thus amply justified. This economical, paperbound reproduction of the second edition should find itself in the libraries of rheologists who will find in it valuable history and of others who will discover a readable account of an important field.

RESEARCH SERVICE DEPARTMENT
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DONALD L. SWANSON

Organic Sequestering Agents. A Discussion of the Chemical Behavior and Applications of Metal Chelate Compounds in Aqueous Systems. By STANLEY CHABEREK, The Dow Chemical Co., and ARTHUR E. MARTELL, Clark University. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1959. xv + 616 pp. 16 × 23.5 cm. Price, $25.00.

In this book the authors have accomplished their stated aim admirably, namely, "to employ the principles required for an understanding of the behavior of aqueous metal chelates as a basis for understanding the varied functions and uses of chelating agents and metal chelate compounds." The book is definitely not a mere revision of "The Chemistry of the Metal Compounds" by Martell and Calvin.

The first third of the book, Chapters 1-4, may be considered as a presentation of fundamental principles involved in the stoichiometry, structure and stability of metal chelates and the methods used in determining these properties. There is no discussion of the theories of the coordinate bond, this subject being considered by the authors as beyond the scope of the book. There are excellent discussions of hydrolysis of metal chelates.

Chapter 5 is a good treatment of "metal buffer" systems, in which chelating agents regulate metal ion concentrations.

The remaining three chapters, comprising over half of the text, is devoted to the role of chelating agents in analytical chemistry, in industry, and in biological systems. The subject is discussed from both theoretical and practical points of view.

In the appendix the authors have tabulated about 2000 reported stability constants.

The book is profusely documented, although the reviewer found no satisfaction in being referred on page 39 to "unpublished results" for the demonstration of the olated cyclic trimer, (Cr(tren)(OH))$_3$.

Every book contains some unavoidable errors, but a few in this book leave the reviewer puzzled. For instance, on page 34 a structural formula is given for a (biscitratodioxouranate(VI))$^{-6}$ ion, although there is long-standing evidence in the literature that citrate does not chelate the uranyl ion in greater than a 1:1 citrate/uranium ratio even in eight-fold excess citrate. Also, on page 308 the weaker chelation tendency of tartrate ion relative to that of the citrate ion is explained on the basis of tridentate chelation by two alcoholic OH groups and one carboxyl group in the case of the tartrate ion in preference to chelation by one ethanolic group and two carboxyl groups as depicted for the citrate ion. There is no evidence in the literature for the type of tridentate chelation attributed to the tartrate ion. On the contrary, the literature shows that tridentate chelation by tartrate is similar in type to that by malate and citrate, *i.e.*, involving two carboxyls and one alcoholic hydroxyl, as is shown on page 448 for ferric citrate. In fact, the authors abandon their own arguments of page 308 in citing on page 448, as a possible structure for the magnesium citrate chelate, formula IX.

This book should be of greatest value to the beginner in the field of metal chelates and to those primarily interested in applications. Even the tyro should find it to be smooth reading and easily understandable, although he may in a few cases have difficulty in distinguishing between proven explanations and unsupported speculations.

The book is quite free of typographical errors. The quality of the binding and paper is good, but the price of the book seems inflationary.

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ISAAC FELDMAN

Anleitungen für die Chemische Laboratoriumspraxis. Band X. Gaschromatographie. By ERNST BAYER, Privatdozent an der Technischen Hochschule Karlsruhe, Institut für Organische Chemie. Edited by H. Mayer-Kaupp. Springer-Verlag, Heildelberger Platz 3, Berlin-Wilmersdorf, Germany. 1959. viii + 163 pp. 16 × 23.5 ch. Price, DM 39.60.

This little monograph describes the correlation of an obviously extensive literature survey. It is divided into four chapters and two lengthy appendices.

The book is designed to deal with the practical aspects of the analytical applications of gas chromatography. This point is exemplified by the length, 12 pages, of the chapters devoted to introductory material and to the theoretical foundations of the technique. The principles of linear, ideal chromatography are clearly enunciated and equations given for the calculation of the number of theoretical plates, etc. Linear, non-ideal chromatography receives passing mention by quoting the van Deemter equation. Although the implications of this equation are not discussed in detail, a copious selection of references to the bibliography is given. An interesting anecdote is the revelation, page 6, that a form of gas chromatography was reported in the year 1512.