metabolite, 4-aminodedimethylaminoanhydrodemethylchlortetracycline[7] (**2**). This mutant of a 6-demethylchlortetracycline (DMCT) producing parental strain was observed to accumulate very little antibiotic (less than 2 μg/ml as DMCT). In mixed fermentations of 1E1407 with several other point-blocked mutants of *S. aureofaciens*, significant quantities of tetracycline antibiotics were produced by cosynthesis,[8] suggesting that 1E1407 was also point blocked in the biosynthetic pathway to the tetracyclines. The nature of the antibiotic accumulated in each instance was indicative of the relative locations of the blocks in 1E1407 and its cosynthesizing partner, as we have observed that a cosynthetic response is usually due to transfer of a partially finished tetracycline molecule from a donor to an acceptor cell. Thus a positive result usually has been observed only in transfer of an intermediate from the mutant having the later block to the one having the earlier block.[9] The positive results in these experiments led to testing a killed preparation of 1E1407 mash by addition to living cultures of other mutants, and now evidence of accumulation of a stable precursor (or precursors) by 1E1407 was found. In this situation, antibiotic is produced only when the precursor is a stable substance and occupies a place in the biosynthetic chain which is later than the point at which the test culture is blocked.

Absorption spectra of an acidic aqueous extract of 1E1407 fermented mash suggested the presence of an anhydrotetracycline-like substance, and this, together with the biological conversion data mentioned above, strongly suggested that the active precursor might be **2**.

Isolation of the precursor was accomplished by an adaptation of the method of Miller, *et al.*,[5] in which ethyl acetate extraction of the perchloric acid acidified whole mash was followed by simple partition of the crude material between chloroform and 0.1 *N* hydrochloric acid. The aqueous phase from the partition was evaporated to dryness to yield a partly crystalline crude product which was about 60% pure. Recrystallization was accomplished by dissolving the crude product in ten parts of 2 *N* hydrochloric acid in methoxyethanol and precipitating with toluene to give the pure product in good yield; absorption spectrum, λ_{max} mμ (ϵ): 424 (8600), 329 (3520), 314 sh (3720), 302 sh (5470), 269 (53,400), 223 (35,000); R_f 0.39 in butanol–0.1 *M* EDTA, pH 4.9, and 0.13 in butanol–0.1 *M* EDTA, pH 6.0. *Anal.* Found for $C_{19}H_{15}N_2O_7Cl_2 \cdot H_2O$: C, 48.45; H, 3.50; N, 5.85; H_2O, 4.06.

Biological conversion of **2** to DMCT was demonstrated in the usual way[2] utilizing *S. aureofaciens* mutant V828. A 34% conversion was found based on microbiological assay; the product, DMCT, was identified by paper chromatographic comparison with authentic material in two chromatographic systems. The pure substance, **2**, was shown by direct spectrophotometric and paper chromatographic comparison to be identical with the principal component in the partially purified material[10] reported by Miller, *et al.*[5]

This isolation of an anhydrotetracycline derivative from a mutant of *S. aureofaciens* affirms the earlier presumed role of the anhydrotetracyclines as intermediates in the biosynthetic pathway to the tetracyclines and reenforces the conclusions of Miller, *et al.*,[5] that the anhydrotetracyclines themselves arise by way of N-methylation of their amino analogs.[11]

(7) This compound has been previously described in terms of its chromatographic behavior and some chemical and biochemical properties.[5]

(8) J. R. D. McCormick, U. Hirsch, N. O. Sjolander, and A. P. Doerschuk, *J. Am. Chem. Soc.*, **82**, 5006 (1960).

(9) CF-1, a transferable hydrogenation cofactor, is the one exception to this. See P. A. Miller, N. O. Sjolander, S. Nalesnyk, N. Arnold, S. Johnson, A. P. Doerschuk, and J. R. D. McCormick, *ibid.*, **82**, 5002 (1960).

(10) A comparison sample of this material was kindly supplied by Dr. L. A. Mitscher of these laboratories.

(11) The earlier conclusion of one of us (J. R. D. M.) that N-methylation preceded reduction at C-4 has since been found to have been based on an isolation artifact at a key point. (See J. R. D. McCormick in "Antibiotics, Vol. 2, Biogenesis," D. Gottlieb and P. D. Shaw, Ed., Springer-Verlag, Berlin-Heidelberg, 1967.)

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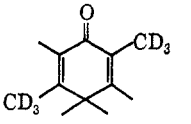
Additions and Corrections

Divinyl Sulfide: Copolymerization and Spectra [*J. Am. Chem. Soc.*, **81**, 2672 (1959)]. By CHARLES E. SCOTT and CHARLES C. PRICE, Chemistry Departments, University of Notre Dame, Notre Dame, Indiana, and University of Pennsylvania, Philadelphia, Pennsylvania.

In Table IV, change the values for ϵ_{max} for divinyl sulfide from 41,800 and 38,000 to 8350 and 7600.

Intermediates in the Photochemical Rearrangements of Bicyclo[3.1.0]hexenones [*J. Am. Chem. Soc.*, **89**, 1874 (1967)]. By HAROLD HART and DAVID W. SWATTON, Department of Chemistry, Michigan State University, East Lansing, Michigan 48823.

On page 1876, formula **11** should be



Acylation of Cyclooctatetraene Dianion and the Chemistry of Its Products [*J. Am. Chem. Soc.*, **89**, 5868 (1967)]. By THOMAS S. CANTRELL and HAROLD SHECHTER, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

On page 5872, the figure in the last line of column 1 should be XV instead of XIV. On page 5875 in the last paragraph heading in column 1 "Benzyl Chloride" should read "Benzoyl Chloride."

Magnetic Resonance Studies of Copper(II)–Triglycylglycine Complexes [*J. Am. Chem. Soc.*, **89**, 6071 (1967)]. By K.-E. FALK, H. C. FREEMAN, T. JANSSON, B. G. MALMSTROM, and T. VÄNNGÅRD, Departments of Physical Chemistry and Biochemistry, University of Goteborg, Göteborg, Sweden.

Dr. F. J. C. Rossotti, Oxford, has pointed out to us that the volume ratios on page 6076 are a factor of 4 too high. Consequently the reported Cu–O distances should be reduced by 25%. This leads to axial Cu–O distances considerably shorter than one has found for similar complexes, probably reflecting the approximate nature of the analysis. On the other hand, our conclusion that one or two water molecules are coordinated in solution seems even better supported.

A Mass Spectrometric Investigation of the Low-Pressure Pyrolysis of Diphosphine-4 [*J. Am. Chem. Soc.*, **89**, 6477 (1967)]. By T. P. FEHLNER, Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556.

The ordinate of Figure 7 should read $(P_2H_4)_0 - (P_2H_4) \times 2 \times 10^4$ torr and $(PH_3) \times 2 \times 10^4$ torr.

The Crystal and Molecular Structure of 14c-Hydro-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene-5,10-dione ($C_{30}H_{18}O_2$) [*J. Am. Chem. Soc.*, **90**, 291 (1968)]. By A. L. BEDNOWITZ, W. C. HAMILTON, R. BROWN, L. G. DONARUMA, P. L. SOUTHWICK, R. KROPF, and R. A. STANFIELD, Departments of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, Clarkson College of Technology, Potsdam, New York 13676, and Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213.

On page 291, column 2, line 6 should read "of the hexacyclic product."

Unambiguous Specification of Stereoisomerism about a Double Bond [*J. Am. Chem. Soc.*, **90**, 509 (1968)]. By J. E. BLACKWOOD, C. L. GLADYS, K. L. LOENING, A. E. PETRARCA, and J. E. RUSH, Chemical Abstracts Service, The Ohio State University, Columbus, Ohio 43210.

In references 3 and 14, the journal citations should read *J. Chem. Doc.* rather than *J. Chem. Soc.*

Book Reviews

Organic Semiconductors. By FELIX GUTMANN, University of New South Wales, Sydney, Australia, and LAWRENCE E. LYONS, University of Queensland, Brisbane, Australia. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1967. xvii + 858 pp. 16.5 × 23.5 cm. $27.95.

This book is the first comprehensive literature survey to be made in the field concerned with the study of the electrical and associated optical properties of organic semiconductors. It includes data up to early 1966. The materials classified as organic semiconductors include molecular crystals, complex metal compounds, charge-transfer complexes, free radicals and their salts, polymers, dyes, and compounds of biological interest.

It is instructive to compare the size of this book with that of a review of this field that appeared in 1959 consisting of 39 pages of text and 112 references. The present review has 41 pages devoted merely to an index and contains more than 1500 references. Thus, in a span of about 7 years, activity has increased more than tenfold.

Aside from the normal curiosity of researchers in university laboratories, considerable impetus has been given to these studies with the expectation that breakthroughs might be found, connecting this field with biology or with the phenomena characteristic of the more glamorous inorganic solid-state semiconductors. This expectation has not yet been realized; the authors devote a chapter to the present and speculative future applications of these materials.

This book satisfies an urgent need for all research workers in this field. The authors have done a monumental and laudable job of collecting and describing the wide variety of experiments, experimental techniques, and theories characteristic of this rapidly developing field. Since it was not the aim of this book to provide critical evaluation, there are many experimental results and theories that with present knowledge can be discounted. Thus, unless the reader is familiar with this field, he is likely to become confused.

The first chapter, dealing with basic solid-state physics, should definitely be skipped by the beginner. It is unclear or misleading in spots and it contains numerous typographical errors in the equations used. The second chapter deals with the types of measurements that have been made. It is somewhat marred by its failure to remind the reader at the very outset that Ohm's law is frequently not obeyed, in which case the conductivity measurements do not give a constant of the material (this precaution is voiced later on). There is also a confusion of units in an equation defining the carrier mobility in the space-charge limited current mode.

The third chapter dealing with purification starts with a discussion of the role of impurities that I found somewhat confusing. If the reader has his own opinions on the requirements for purification, the rest of the chapter will be valuable as source material.

The rest of the book contains in the main, a discussion of band theory, excited states of molecular crystals, ionized states (dark and photogenerated), and space charge effects. These discussions start at the level of the original articles and are not designed to provide anything but a minimum of background material.

This book will be most useful to those familiar with the field. It is, however, an absolute requirement for anyone entering the field because it will save him vast amounts of time. The reference tables and indexes are excellent and easy to use. I expect that this book will be the definitive reference book for many years to come.

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BOOKS RECEIVED, *February 1968*

MARGARET H. BACK and KEITH J. LAIDLER. "Selected Readings in Chemical Kinetics." Pergamon Press, Inc., 44-01 21st St., Long Island City, N. Y. 1967. 175 pp. $5.50.

RAYMOND F. BADDOUR and ROBERT S. TIMMINS, Editors. "The Application of Plasmas to Chemical Processing." The MIT Press, 50 Ames St., Cambridge, Mass. 1967. 206 pp. $12.50.