

symmetry $P\bar{6}2m$) with the following approximate positions: Oxygen: $0,0p$; $0,0,-p$; $1/3, 2/3,q$; $2/3, 1/3,q$; $2/3, 1/3,-q$; Sodium: $r,0,1/2$; $0,r,1/2$; $-r,-r, 1/2$; $s,0,0$; $0,s,0$; $-s,-s,0$; where $p = 0.167$, $q = 0.333$, $r = 0.724$, $s = 0.366$. Intensities calculated from these parameters are consistent with estimated powder and rotation intensities.

This structure has been deduced independently by Klemm and Foppl.²

In this structure, the peroxide ions lie parallel to the c -direction, one at the corner and two within the unit cell. Each peroxide ion is in contact with nine sodium ions, three about the middle and three about each end. A sodium ion of 0.98 Å. radius, and a peroxide ion regarded as a cylinder of radius 1.29 Å. and length 1.49 Å. with caps of radius 1.29 Å. are consistent with this structure and with other crystallographic data.^{3,4}

There appears to be no direct correlation between this hexagonal unit cell and the tetragonal unit cell reported by Feher¹ with dimensions $a = 6.65$ Å., $c = 9.91$ Å., and $Z = 8$. The fact that the ASTM Index lists for Na_2O_2 at least 15 powder lines (of the 29 listed) either not observed or of significantly greater intensity than observed for pure Na_2O_2 is readily explained as due to the presence of impurities, principally NaOH, in the material which gave the ASTM pattern.

We wish to acknowledge the support of a du Pont Summer Fellowship (R.L.T.) and of funds from the Wisconsin Alumni Research Foundation in this work.

(2) W. Klemm, private communication, 1957.

(3) S. C. Abrahams and J. Kalnajs, *Acta Cryst.*, **7**, 838 (1954).

(4) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 140.

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ACETOLACTATE, AN EARLY INTERMEDIATE IN VALINE BIOSYNTHESIS¹

Sir:

Strassman, *et al.*,^{2,3} and Adelberg⁴ have proposed schemes for the conversion of pyruvate to L-valine and of α -ketobutyrate to L-isoleucine. Each scheme involved a condensation of acetaldehyde and the appropriate keto acid followed by a pinacol rearrangement to account for the distribution of C¹⁴ in tracer studies. As pointed out by Adelberg,⁴ the first step in L-valine biosynthesis might be a ketol (as first proposed by Strassman, *et al.*)² or an aldol condensation, since either reaction would be consistent with the data. Evidence that

(1) Supported by Grant RG-4015 of the United States Public Health Service and by funds from the Eugene Higgins Trust.

(2) M. Strassman, A. J. Thomas and S. Weinhouse, *THIS JOURNAL*, **75**, 5135 (1953).

(3) M. Strassman, A. J. Thomas, L. A. Locke and S. Weinhouse, *ibid.*, **76**, 424 (1954).

(4) E. A. Adelberg, *ibid.*, **76**, 4241 (1954).

the initial step is acetolactate formation (ketol condensation) is presented here.

A valineless mutant of *Escherichia coli*, strain M4862,⁵ accumulates α -acetolactic acid when grown in media supplemented with limiting amounts of L-valine. Extracts prepared by sonic oscillation of cells of this mutant, harvested when acetolactate accumulation was marked, were observed to produce at least ten times as much α -acetolactate from pyruvate as did an extract of the parent *E. coli* strain W (Table I, Expt. 1). The formation of acetolactate was inhibited by L-valine.

A similar valine sensitive system was also formed by a wild type *Aerobacter aerogenes*, strain 1033, when grown in minimal medium containing L-histidine as the sole carbon source (chosen so as to assure absence of the classical carboligase⁶ system). The same strain grown in nutrient broth with 1% glucose exhibits virtually no carboligase activity at pH 8 but is extremely active when tested at pH 6 (Table I, Expt. 2). L-Valine does not inhibit this enzyme.

TABLE I

ACETOLACTATE FORMATION BY BACTERIAL EXTRACTS

| Expt. | Extract | Moles/10 min. | | | |
|-------|------------------------------------|--------------------------|----------------------------|--------------------------|----------------------------|
| | | Without L-valine Acetoin | With L-valine Acetolactate | Without L-valine Acetoin | With L-valine Acetolactate |
| 1 | <i>E. coli</i> Strain W pH 8.0 | 0.04 | 0.14 | .. | .. |
| | <i>E. coli</i> Strain M4862 pH 8.0 | .05 | 1.74 | 0.01 | 0.28 |
| 2 | <i>A. aerogenes</i> 1033 pH 8.0 | <0.01 | <0.01 | <0.01 | <0.01 |
| | (Broth grown) pH 6.0 | 1.47 | <0.01 | 1.52 | <0.01 |
| | <i>A. aerogenes</i> 1033 pH 8.0 | <0.01 | .06 | <0.01 | <0.01 |
| | (Histidine grown) pH 6.0 | <0.01 | <0.01 | <0.01 | <0.01 |

Assay system contained 10^{-2} M pyruvate, 20 μ g. co-carboxylase, 2×10^{-3} M Mg^{++} and cell-free extract equivalent to 25 mg. wet weight of cells in one ml. 0.1 M phosphate buffer. Ten minutes incubation at 37° in air. Reaction stopped with $Zn(OH)_2$. Acetoin and acetolactate determined by method of Westerfeld⁷ before and after decarboxylation⁸ of β -ketoacids with 1.8 N H_2SO_4 . In a separate experiment the acetolactate was isolated and converted to the bis-phenylhydrazone of diacetyl. The melting point was 258–259° (uncorrected) and there was no depression upon mixing with the same derivative prepared from synthetic α -acetolactic acid.

If acetolactate is an intermediate in L-valine biosynthesis, the inhibition of its formation by L-valine could be the feedback loop by which L-valine controls its own biosynthesis.⁸ That acetolactate is very likely on the pathway in question is indicated by the following observations: (1) acetolactate labeled in the β -methyl position was incorporated into L-valine and L-leucine of *E. coli* pro-

(5) H. E. Umbarger and E. A. Adelberg, *J. Biol. Chem.*, **192**, 88; (1951).

(6) E. Juni, *ibid.*, **195**, 715 (1952).

(7) W. W. Westerfeld, *J. Biol. Chem.*, **161**, 495 (1945).

(8) E. A. Adelberg and H. E. Umbarger, *ibid.*, **205**, 475 (1953).

tein. (2) It was converted to an L-valine precursor, α,β -dihydroxyisovaleric acid, by an appropriately blocked mutant^b in the presence of L-valine (which blocks the accumulation of this precursor if glucose or pyruvate only are supplied). (3) Like other 5-carbon precursors of L-valine, it inhibited the growth of *E. coli* strain K-12 but not of valine-resistant mutants and (4) the inhibition

was non-competitively reversed by L-isoleucine. Further studies on the importance of this enzyme system in biosynthesis are in progress.

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BOOK REVIEWS

Chemistry of Carbon Compounds. Volume III, Part B. Aromatic Compounds. Edited by E. H. Rodd, D.Sc., F.C.G.I., F.R.I.C., D. Van Nostrand Company, Inc., 126 Alexander Street, Princeton, New Jersey. 1956. xx + pp. 687-1670. 16.5 × 23 cm. Price, \$25.00.

This volume continues the excellent treatise on organic chemistry which began appearing in 1951, and which seems destined to be the standard reference on the subject for the next decade or two.

It completes the treatment of aromatic compounds begun in Volume IIIA and is largely devoted to polyfunctional benzene derivatives (some of which were treated in Volume IIIA) and polycyclic aromatic substances. A major share of the preparation of this volume has fallen to W. J. Hickinbottom who has prepared six of the twelve chapters. Other contributors are Z. E. Jolles, R. F. Garwood, M. F. Ansell, S. H. Harper, G. L. Buchanan, R. A. Raphael, E. H. Rodd, J. van Alphen, S. Coffey, G. M. Badger and J. W. Cook. It is highly recommended.

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MARSHALL GATES

Perspectives in Organic Chemistry. A volume dedicated to Sir Robert Robinson, prepared by friends, colleagues and former pupils under the editorship of SIR ALEXANDER TODD. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1956. x + 527 pp. 16 x 23.5 cm. Price, \$7.50.

Sir Robert Robinson has been one of the giants of the art and science of organic chemistry, and it is altogether fitting that a distinguished group of leaders in the practice of this art and science have been banded together under the leadership of Sir Alexander Todd to honor Sir Robert on his 70th birthday by the publication of this series of essays.

One of the most pleasant characteristics of the book is the frankly speculative nature of some of the chapters. Others are masterful syntheses of the state of knowledge in particular fields. These characteristics seem peculiarly appropriate in a book dedicated to Robinson, who has always been at his best and most forceful when advancing inspired speculation and when assembling and interpreting the widely divergent and often conflicting evidence applicable to problems falling within his interest. Likewise, the very breadth of the fields covered reflect Robinson's own catholic tastes.

Chapters have been contributed by Linus Pauling, Paul D. Bartlett, Wilson Baker, D. H. R. Barton, V. Prelog, A. J. Birch, R. B. Woodward, Karl Ziegler, E. L. Hirst, Sir Alexander Todd, L. Ruzicka, C. W. Shoppee, E. Schlittler, J. W. Cornforth, Karl Folkers, James Walker, Holger Erdtman and A. Butenandt.

The book is stimulating and entertaining.

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MARSHALL GATES

Photoconductivity Conference. Held at Atlantic City November 4-6, 1954. Editorial Committee: R. G. BRECKENRIDGE, Chairman, B. R. RUSSELL and the late E. E. HAHN. Sponsored by University of Pennsylvania, Radio Corporation of America, Office of Naval Research. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1956. xiii + 653 pp. 16 × 23 cm. Price, \$13.50.

This large volume is a compilation of thirty papers which were presented at a conference in Atlantic City a little more than two years ago. As stated in the forward, "The purpose of this conference was to advance the science of photoconductivity through plenary discussion among the leading workers in the field. . . . Sensing keenly a gap in the literature, the sponsors considered it particularly desirable to publish the papers presented, together with pertinent discussions, as a comprehensive treatise on photoconductivity." There can be little doubt that the papers in this book span the science of photoconductivity no matter what definition of this field one chooses to use, and that there is at present no other source which can give one such a complete view of all of the avenues of research leading to an understanding of this complex phenomenon. However, it would be nearly miraculous if any collection of separately conceived papers in a new and controversial field could be arranged in such a manner as to give the reader a systematic exposition of all of the facts and principles involved, *i.e.*, a treatise. This is not the sort of book one starts at the front cover and finishes at the back cover. Any worker in this field will find some papers of immediate interest, other papers useful in gaining perspective for his own field, and still others of rather negligible interest. In many cases, the table of contents is not a sufficiently reliable guide to the selection of those papers in which one is most interested. Fortunately, almost all of the papers are concluded with brief summary paragraphs, and many of them have introductory paragraphs which are nearly abstracts.

The book has been divided into five sections: I. Phenomenological Theory of Photoconductivity (2 papers); II. Photon Absorption Process (6 papers); III. Electron Processes (6 papers); IV. Photoconducting Materials (7 papers); and V. Current Topics (9 papers). The first paper in Section I, by Rose, comes about as close as anything in the book to being a general introduction to photoconductive phenomena, and also gives sufficient warning that the subject is one of great complexity. The second paper in this section, by Petritz, is considerably more specialized, treating signal-to-noise problems in the use of photoconductors as signal detectors. The second section is the domain of the solid-state theoretical physicist, being an account of the quantum-mechanics of the interaction of photons with semiconductors and insulators and their imperfections (including phonons). The first article, by Herring, is fairly readable for the non-theoretician and gives one at least a feeling for theories of centers. Section III is largely concerned with the application of transistor physics to photoconduction and is of primary interest to the experimentalist. There does not appear to be much of a division between the subject matters of the last two sections,