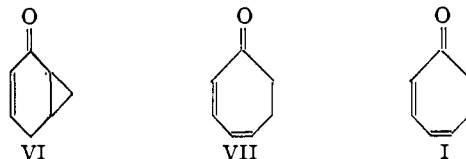


**SYNTHESIS OF TROPONE VIA A NORCARENONE →
CYCLOHEPTADIENONE REARRANGEMENT**

Sir:

In view of the widespread interest in the field of tropones and tropolones, certain value should be attached to any selective synthetic route which shows promise of generality and versatility. Such a route is illustrated below by a new preparation of tropone (I) itself.¹ From the available 3,5-dihydroxybenzoic acid² we have obtained, by Raney nickel catalyzed hydrogenation in aqueous sodium hydroxide, 3,5-diketohexahydrobenzoic acid (II), m.p. 178.5–180° (Calcd. for C₇H₈O₄: C, 53.86; H, 5.16. Found: C, 53.60; H, 5.33). Treatment of the acid under esterification conditions with ethanol afforded the ethyl enol ether ethyl ester (III) of II, b.p. 125–126° at 0.4 mm., *n*_D²⁵ 1.4923 (Calcd. for C₁₁H₁₆O₄: C, 62.25, H, 7.61. Found: C, 61.76, H, 7.36). Reduction of III with lithium aluminum hydride followed by mild acid hydrolysis³ gave 5-hydroxymethyl-cyclohexen-2-one (IV), λ_{max} 226mμ, which was isolated and purified as the 2,4-dinitrophenylhydrazone, m.p. 147.0–148.5°, λ_{max} 252 mμ, ε 15,800; 374 mμ, ε 26,600 (Calcd. for C₁₃H₁₄N₄O₆: C, 50.97, H, 4.61. Found: C, 50.94, H, 4.90). The *p*-toluenesulfonate, m.p. 75–75.7° (V), of IV (Calcd. for C₁₄H₁₆O₄S: C, 59.98, H, 5.75. Found: C, 60.21, H, 5.54), on being stirred with dilute aqueous sodium hydroxide, readily yielded, *via* norcaren-3-one (VI),⁴ the rearrange-



ment product, cycloheptadien-2,4-one (VII), λ_{max} 292 mμ, ε 5400 (characterized by catalytic hydrogenation to cycloheptanone). The ketone VII, without isolation, was converted by selenium dioxide dehydrogenation to *tropone*, which was identified by the complete agreement of its characteristic ultraviolet absorption spectrum with that already reported,¹ as well as by the preparation of two salts, the monopicrate, m.p. 99.0–100.3° (Calcd. for C₁₃H₉N₃O₈: C, 46.65, H, 2.84, N, 12.54. Found: C, 46.45, H, 2.98, N, 12.88) and the picrylsulfonate, m.p. 268–270°. The melting points reported for these salts are 99–100°^{1a} and 266–267°^{1b} respectively. In practice one need isolate only three intermediates, II, III and V, each of which can be obtained in a yield of 60% or better.

In view of Doering's reported transformation⁵ of tropone to 2-aminotropone (VIII) by means of hydrazine or hydroxylamine, the above approach would thus appear to embrace tropolones as well, since the parent of this class may be obtained by hydrolysis of VIII.⁶ The application of this overall scheme to the synthesis of natural products containing the tropolone ring is in progress in this Laboratory.

(5) W. von E. Doering, Abstracts of American Chemical Society Symposium, June, 1953, p. 3.

(6) W. von E. Doering and L. H. Knox, THIS JOURNAL, **73**, 837 (1951).

(1) Two syntheses of tropone have been reported: (a) W. von E. Doering and F. L. Detert, THIS JOURNAL, **73**, 877 (1951); (b) H. J. Dauben, Jr., and H. J. Ringold, *ibid.*, **73**, 876 (1951).

(2) A. W. Weston and C. M. Suter, "Organic Syntheses," Vol. 21, John Wiley and Sons, Inc., New York, N.Y., 1941, p. 27.

(3) J. P. Blanchard and H. L. Goering, THIS JOURNAL, **73**, 5863 (1951).

(4) The mechanism of this rearrangement (*cf.* R. W. L. Clarke and A. Lapworth, *J. Chem. Soc.*, **97**, 11 (1910)) will constitute the subject of a separate publication.

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BOOK REVIEWS

La Chimica Delle Fermentazioni. Microbiologia—Enzimologia Chimica E Tecnica Delle Fermentazioni. Second Edition. By VIRGILIO BOLCATO, Incaricato Nell' Università di Pavia. Nicola Zanichelli, Editore, Bologna, Italy. 1952. xxi + 665 pp. 18 × 25.5 cm. Price, Lire 5000 Nette.

This book is intended to bring up-to-date the first edition written in 1944–1945, which suffered from the unavailability of foreign literature. The book is written in simple Italian, so that it can be read by anyone familiar with one of the romance languages. The subject matter is presented at the level of the biochemistry graduate student. It is divided into four parts, including elements of general microbiology (89 pages), enzymology (161 pages), the chemistry of fermentations (173 pages) and the technical aspects of industrial fermentations (190 pages).

Certain sections of the book dealing with biological oxidations and chemistry of fermentations are well covered. Historical development of various major lines of work, associating names with particular contributions has also been

treated well. However, the author has endeavored to cover such a very wide range of subject matter that it is inevitable that some of the material suffers from incomplete treatment. For example, the coverage of more recent literature and patents since 1945 could be better. Discussion of microbiological production of antibiotics, vitamin B₁₂, riboflavin and steroids is neglected. The book does not contain a substantial treatment of the vitamin and growth factor requirements of microorganisms, nor of the use of microorganisms for vitamin and amino acid assays. Some of the industrial fermentations described by the author might still be in use in Europe but are obsolete in this country.

The author, an authority in his field, is to be commended for having assembled such a tremendous amount of closely related material in rapidly growing fields. We believe that the book should prove of value to both the academic and technical workers in Italy, even when the subject matter is available in several fine books in the English language.

JULIUS BERGER
JOHN T. PLATI