analysis, titration characteristics and melting point.[11] Thus it is concluded that this primary excretion product of Orinase (I) is 1-butyl-3-*p*-carboxyphenylsulfonyl-urea (II).

ADDED IN PROOF.—After submission of this paper, T. Dorfmueller, *Deut. med. Wochschr.*, **81**, 888 (1956), appeared, indicating the same finding on the structure of the Orinase excretion product.

(11) The authors wish to thank Susan Theal for the potentiometric titrations, James E. Stafford for the ultraviolet spectral studies, and Albert Lallinger for technical assistance.

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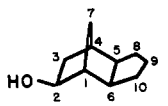
RECEIVED SEPTEMBER 4, 1956

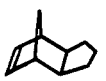
THE DEHYDRATION PRODUCT OF *exo*-TRIMETHYLENE-2-*exo*-NORBORNANOL[1]

Sir:

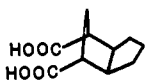
In 1948, Bruson and Riener[2] reported the phosphoric acid catalyzed dehydration of *exo*-trimethylene-2-*exo*-norbornanol (I). The olefinic product was assigned structure II, but no evidence was presented to support this assumption. Very recently, Wilder and Youngblood[3] examined the bromination of the dehydration product, again formulated as II, as well as studying several reactions of the resultant dibromide. It is significant that the permanganate oxidation of the olefin was reported to give a dicarboxylic acid of m.p. 162–163° (uncor.), a value quite different from that of the diacid, m.p. 182–184°, to which the structure III can be reliably assigned.[4,5]



I

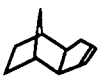


II

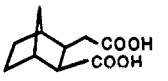


III

We wish to report evidence that the dehydration product (b.p. 760 mm.) 180.1°, $n^{25}D$ 1.4985, when purified by distillation through an efficient column) has been incorrectly formulated as II, and in fact was *exo*-trimethylene-8-norbornene (IV). The infrared spectrum of the olefin in question was identical in all respects with that of an authentic sample of IV, b.p. 760 180.1°, $n^{25}D$ 2.4985, whose structure can be considered to have been established rigorously.[5] Neither spectrum showed a band at 6.35 μ, possessed by all bicyclo[2.2.1]-2-heptene derivatives,[6] but rather absorbed at 6.18 μ, a value characteristic of the presence of a carbon–carbon double bond in an unstrained five membered ring. Permanganate oxidation of both samples of IV, produced by the two methods, gave the same diacid V, m.p.'s and mixed m.p. 165.1–165.6° (cor.). The dehydration product did not react with phenyl azide at room temperature indicating that it did not possess the norbornene structure.[7]



IV



V

Authentic *exo*-trimethylene-2-norbornene (II), b.p. (760 mm.) 176.0°, $n^{25}D$ 1.4927, could be prepared easily by sodium ethoxide dehydrohalogenation of *exo*-trimethylene-2-*exo*-norbornyl iodide.[8] The spectrum of this hydrocarbon was completely different from that of IV and possessed the expected band at 6.35 μ. The phenyl azide adduct, which formed unusually rapidly, had m.p. 144.6–145.1. *Anal.* Calcd. for $C_{16}H_{19}N_3$: C, 75.85; H, 7.56; N, 16.59. Found: C, 76.09; H, 7.66; N, 16.84. Oxidation gave diacid III, m.p. 182.9–183.2°; the mixed m.p. with an authentic sample[4] of m.p. 182.8–183.2° was 183.0–183.3°.

Distillation of hydrocarbon II from phosphoric acid resulted in almost complete conversion into IV. Dehydration of other stereoisomers of alcohol I gave also the same product. Possible mechanistic interpretations of the above rearrangements as well as a discussion of some further reactions of hydrocarbons II and IV will be presented in future publications.

(1) It is suggested that the semi-trivial name "trimethylenenorbornane," numbered as in I, be utilized for the nomenclature of this series in a similar manner to that suggested for "bornane" and "norbornane," in the naming of other bicyclo[2.2.1]heptane derivatives ("Nomenclature for Terpene Hydrocarbons," No. 14, Advances in Chemistry Series, Am. Chem. Soc., Washington, D. C., 1955).

(2) H. A. Bruson and T. W. Riener, THIS JOURNAL, **70**, 2809 (1948).

(3) P. Wilder, Jr., and G. T. Youngblood, *ibid.*, **78**, 3795 (1956).

(4) H. A. Bruson and T. W. Riener, *ibid.*, **67**, 723 (1945).

(5) P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946).

(6) Unpublished observations: *cf.*, P. R. Schleyer, paper presented at the 130th ACS Meeting, Atlantic City, N. J., Sept., 1956.

(7) K. Alder, G. Stein and W. Friedrichsen, *Ann.*, **501**, 1 (1933).

(8) The method used was analogous to that employed for the preparation of *exo*-dicyclopentadiene (P. D. Bartlett, and I. S. Goldstein, THIS JOURNAL, **67**, 2553 (1947)).

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FORMIMINO-TETRAHYDROFOLIC ACID AND METHENYLTETRAHYDROFOLIC ACID AS INTERMEDIATES IN THE FORMATION OF N^{10}-FORMYLTETRAHYDROFOLIC ACID

Sir:

In a previous communication[1] evidence was presented for the formation of 10-formyl-THF[2] from FIG and THF by purified extracts of *Clostridium cylindrosporum*, as shown by reaction (1)

$$\text{FIG} + \text{THF} \longrightarrow \text{10-formyl-THF} + \text{glycine} + NH_3 \quad (1)$$

This over-all reaction has now been shown to be the sum of the three reactions, given by the equations.[3]

Enzymes I and II, acting together, are responsible for the formation of an intermediate in reaction (1) having an absorption maximum at 356 mμ and other spectral characteristics of 5,10-methenyl-THF. Evidence for the enzymatic formation of

(1) J. C. Rabinowitz and W. E. Pricer, Jr., THIS JOURNAL, **78**, 4176 (1956).

(2) Abbreviations used are: FIG, formiminoglycine; THF, tetrahydrofolic acid; 10-formyl-THF, N^{10}-formyltetrahydrofolic acid; 5-formyl-THF, N^5-formyltetrahydrofolic acid (leucovorin or citrovorum factor); 5-formimino-THF, N^5-formiminotetrahydrofolic acid; 5,10-methenyl-THF, the cyclic N^5-N^{10}-imidazolinium derivative of 5-formyl-THF, previously abbreviated as 5,10-formyl-THF[1] (anhydroleucovorin or anhydrocitrovorum factor); EDTA, ethylenediaminetetraacetic acid.

(3) R = benzoyl-L-glutamic acid.