

stants relative to cyclohexanecarboxylic acid are given in Table I.

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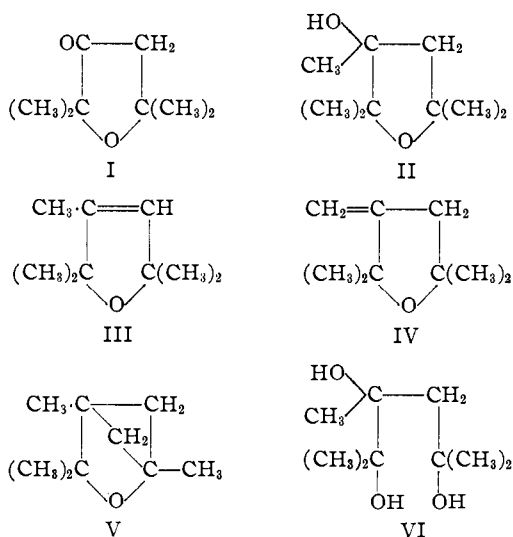
### The Dehydration of 4-Hydroxy-2,2,4,5,5-pentamethyltetrahydrofuran (Acetylene Studies, Part VI)<sup>1</sup>

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When II, the product of the reaction between 4-keto-2,2,5,5-tetramethyltetrahydrofuran (I) and methylmagnesium iodide, is dehydrated, a compound of the expected composition  $C_9H_{16}O$  is obtained. Apart from the normal formulas, III, IV, the structure V is possible for this compound. Indeed, V has been proposed by Bouveault and Locquin,<sup>2</sup> as the same substance is also formed by acid dehydration of 2,3,5-trimethylhexane-2,3,5-triol (VI).

The infrared spectrum of the dehydration product is compatible only with formula V. Whilst it does not show any sign of double bond absorption in the 1620–1700  $cm^{-1}$  region, the following bands were observed: 980  $cm^{-1}$  (optical density  $d = 0.6$ ) cyclobutane<sup>3</sup>; 1099  $cm^{-1}$  ( $d = 0.3$ ) isopropyl; 1175  $cm^{-1}$  ( $d = 0.8$ ) superposition of the isopropyl and the tetrahydrofuran absorption.<sup>4</sup> The chemical properties of the compound  $C_9H_{16}O$  are in accord with formula V. It could not be hydrogenated catalytically to 2,2,4,5,5-pentamethyltetrahydrofuran at ordinary temperature and pressure, and did not decolorize bromine in carbon tetrachloride.



#### Experimental

I was prepared in quantitative yield from 1,1,4,4-tetra-

(1) Part I: THIS JOURNAL, **73**, 4013 (1951); Part II–V, *J. Applied Chem.*, **3**, 39, 42, 97, 145 (1953).

(2) L. Bouveault and R. Locquin, *Ann. chim.*, [8] **21**, 414 (1910).

(3) L. W. Marrison, *J. Chem. Soc.*, 1614 (1951).

(4) H. Tschamler and H. Voetter, *Monatsh.*, **83**, 302 (1952). See also G. M. Barrow and S. Searles, THIS JOURNAL, **76**, 1175 (1953).

methyl-2-butyne-1,4-diol and aqueous mercuric sulfate,<sup>5–7</sup> b.p. 150° (760 mm.).

4-Hydroxy-2,2,4,5,5-pentamethyltetrahydrofuran (II).—The reaction of I with 2 moles of methylmagnesium iodide<sup>8</sup> gave II in 63% yield; from diisopropyl ether, m.p. 77°.<sup>8</sup>

Dehydration to V.—The mixture of 80 g. of II and 100 g. of freshly fused and finely ground potassium hydrogen sulfate was heated for six hours at 120°. The liquid product was distilled directly, dried and fractionated; b.p. 132°, yield 68 g. (96%),  $d_{25}^{25}$ , 0.820 (literature 0.826).

Anal. Calcd. for  $C_9H_{16}O$ : C, 77.1; H, 11.4. Found: C, 77.0; H, 11.5.

The infrared spectrum was measured in the 950–1200  $cm^{-1}$  region in carbon disulfide solution (0.015 g. plus 1 cc. of solvent), in the 1600–1700  $cm^{-1}$  region in carbon tetrachloride (0.016 g. plus 1 cc. of solvent); cell thickness 0.5 mm.<sup>9</sup>

(5) G. Dupont, *Compt. rend.*, **152**, 1486 (1911).

(6) G. Dupont, *Ann. chim.*, [8] **30**, 536 (1913).

(7) H. Richet, *ibid.*, [12] **3**, 317 (1948).

(8) G. Dupont, *Compt. rend.*, **154**, 601 (1912).

(9) We are greatly indebted to Dr. S. Pinchas, Optics Department, Weizmann Institute of Science, Rehovoth, for the determination of the spectrum.

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### *cis*- and *trans*-Tropine (Tropanol)<sup>1</sup>

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Recent papers establish the stereochemical structure of the tropine (tropanol) isomers,<sup>4–6</sup> namely, that in tropine the hydroxyl group and N-methyl bridge are *trans* and that in  $\psi$ -tropine they are *cis*. We now submit additional experimental evidence confirming these conclusions.

A study of models suggested that the structure with the  $-OH$  and  $\setminus NCH_3$  groups in close proximity might be expected, owing perhaps to hydrogen bonding, to exhibit greater  $pK$  values in aqueous solution and less change in  $pH$  upon titration. Our results, obtained from the titration of 20.00-ml. portions of 0.050 *N* solutions of the isomeric tropines (purified by sublimation *in vacuo*) with 0.0613 *N* hydrochloric acid, are summarized in Fig. 1. The  $pK$  values at 25°, as estimated from the half neutralization points, are 2.98 for tropine and 3.67 for  $\psi$ -tropine. The greater value for  $\psi$ -tropine is suggestive of intramolecular hydrogen bonding and therefore a configuration of the  $-OH$  *cis* to the  $\setminus NCH_3$  group.

Tropine, refluxed for ten minutes with benzoyl chloride in a 1:8 molar ratio, yielded 84.5% of tropine benzoate hydrochloride.  $\psi$ -Tropine, identically treated, yielded 79.2% of  $\psi$ -tropine benzoate hydrochloride. Regrettably limited amounts of materials did not permit further study of the reactivity of the  $-OH$  groups in the isomeric alcohols.

(1) Experimental work performed at the University of Maryland.

(2) Rutgers University, Newark, N. J.

(3) University of North Carolina, Chapel Hill, N. C.

(4) G. Fodor and K. Nador, *Nature*, **160**, 462 (1952).

(5) B. L. Zenitz, C. M. Martini, M. Priznar and F. C. Nachod, THIS JOURNAL, **74**, 5564 (1952).

(6) A. Nickon and L. F. Fieser, *ibid.*, **74**, 5566 (1952).