

aqueous thiocyanic acid. Ostwald's<sup>2</sup> earlier conductivity experiments indicated that this acid is almost as strong as hydrochloric, but more recently Latimer<sup>3</sup> estimated from thermodynamic calculations that it is a weak acid with an ionization constant of approximately  $1 \times 10^{-4}$ . The experiments summarized in Table I prove that thiocyanic acid is a strong acid. The third column gives the *pH* calculated from the relation,  $pH = -\log(H^+)$ , where  $(H^+)$  is the concentration of the hydrogen ion in moles per liter for complete dissociation of the acids. In a private communication Latimer has informed us that soon after he published his book he realized that thiocyanic acid is a strong acid.

**Experimental.**—Solutions of thiocyanic acid were prepared by mixing equivalent amounts of perchloric acid and potassium thiocyanate solutions. The *pH* of each thiocyanic acid solution was measured with a commercial model, glass electrode at intervals over a period of thirty minutes. As a check, several solutions of pure perchloric acid having the same concentration as some of the thiocyanic acid solutions were tested likewise. All readings were constant to within 0.02–0.03 *pH* unit. The temperature was 25°.

TABLE I

Concentration of acid, moles/liter		<i>pH</i> calcd.	HCNS <i>pH</i> obs.	HClO <sub>4</sub> <i>pH</i> obs.
HCNS	HClO <sub>4</sub>			
0.2506		0.60	0.63	
.1244	0.1244	.91	.94	0.93
.04958		1.30	1.33	
.02513	.02513	1.60	1.63	1.62
.01256	.01256	1.90	1.92	1.91
.00764		2.12	2.15	
.00509		2.29	2.32	
.00188	.00188	2.72	2.72	2.73

(2) W. Ostwald, *J. prakt. Chem.*, **32**, 305 (1885).

(3) W. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 128.

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## A Synthesis of 6-Methoxytetralin

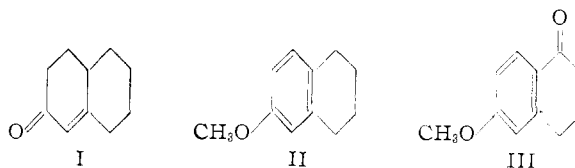
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Concurrently with other studies which have resulted in a satisfactory method<sup>1</sup> for the production of 6-methoxytetralone-1 (III) in relatively large amounts, a synthesis of this compound from cyclohexanone was developed.

In the procedure of Thomas and Nathan,<sup>1</sup> the ultimate step involves the oxidation of 6-methoxytetralin (II) to the ketone (III). The new method described herein for the preparation of (II) was investigated as an alternative to that used,<sup>1</sup> but was abandoned in view of the unfavorable yields.

Since aromatization of  $\alpha,\beta$ -cyclohexenones to phenols is an established but comparatively little used reaction,<sup>2</sup> it was of considerable interest to

ascertain whether partial aromatization could be applied to an  $\alpha,\beta$ -unsaturated bicyclic ketone such as I.



2-Keto-2,3,4,5,6,7,8,10-octahydronaphthalene (I) was prepared from cyclohexanone through 2-carbethoxycyclohexanone<sup>3</sup> according to the procedure of Du Feu, McQuillin and Robinson.<sup>4</sup> Extension of the classical method<sup>5</sup> of bromination and subsequent dehydrobromination to the keto-perhydronaphthalene (I) was unpromising; however, selective dehydrogenation with sulfur<sup>6</sup> or palladinized charcoal<sup>7</sup> according to procedures which have been used for aromatization of monocyclic unsaturated ketones yielded a phenolic product. Methylation of this crude product gave 6-methoxytetralin (II)<sup>8</sup> in approximately 30% yield.

Oxidation of II with chromic anhydride according to the method of Burnop, Elliot and Linstead<sup>9</sup> yielded 6-methoxytetralone-1 (III), identified by mixed melting point with an authentic specimen.<sup>1</sup>

### Experimental<sup>10</sup>

**6-Methoxytetralin.**—A mixture of 7.5 g. (0.05 mole) of 2-keto-2,3,4,5,6,7,8,10-octahydronaphthalene<sup>4</sup> and 1.5 g. (0.05 mole) of sublimed sulfur was heated under reflux for one hour at a bath temperature up to 220°; during the early stages of heating brisk boiling occurred and hydrogen sulfide was evolved. The mixture was cooled and transferred to a small Claisen flask. Distillation gave 6.0 g. of yellowish oil, b. p. 130–160° at 11 mm. The distillate was dissolved in ether, extracted twice with dilute sodium hydroxide solution, and once with water. Carbon dioxide was bubbled into the alkaline fraction until precipitation of the oily phenolic material was complete. The oil was extracted with ether, dried over magnesium sulfate and the solvent removed; yield, 3.87 g.

The crude phenol was dissolved in 35 ml. of 10% sodium hydroxide solution, and 6 ml. of dimethyl sulfate added dropwise with mechanical stirring. After stirring for one and one-half hours, the product was extracted with ether, the ethereal extract washed with water, dried over magnesium sulfate and the solvent removed. Distillation of the residue gave 2.69 g. (33%) of 6-methoxytetralin boiling at 127–129° at 11 mm.

*Anal.* Calcd. for C<sub>11</sub>H<sub>14</sub>O: C, 81.44; H, 8.70. Found: C, 81.04; H, 8.67.

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(3) Kotz and Michels, *Ann.*, **350**, 210 (1906).

(4) Du Feu, McQuillin and Robinson, *J. Chem. Soc.*, 53 (1937).

(5) Knoevenagel, *Ann.*, **281**, 98 (1894); *Ber.*, **26**, 1951 (1893); *Ann.*, **288**, 339, 346 (1895).

(6) Horning, *This Journal*, **67**, 1421 (1945).

(7) Smith and Rouault, *ibid.*, **65**, 631 (1943).

(8) Schroeter, *Ann.*, **426**, 83 (1922).

(9) Burnop, Elliot and Linstead, *J. Chem. Soc.*, 727 (1940).

(10) Details for the preparation of 6-methoxytetralin (II) only are described since adequate directions for all other compounds involved are recorded in the literature.

(1) Thomas and Nathan, in press.

(2) Horning, *Chem. Rev.*, **33**, 89 (1943).