

The physical constants of the three amines as well as some derivatives are listed below.

TABLE I  
PHYSICAL CONSTANTS OF THE CARVACRYLAMINES AND THEIR DERIVATIVES

	Carvacryl-amine	N-Methyl-	N,N-Dimethyl-
B. p., °C.	242	236	84 (5 mm.)
$n_D^{22}$	1.5402	1.5363	1.5131
$d_4^{22}$	0.9463 <sup>a</sup>	0.9325	0.9028
Oxalate			
M. p., °C.	149-150 <sup>b</sup>	114-115 <sup>c</sup>	132-133
Phenylthiourea			
M. p., °C.	117	95-96	.....

<sup>a</sup> F. W. Semmler, *Ber.*, **25**, 3352 (1892), reported 0.9442 but this was recorded in Beilstein as 0.9942. <sup>b</sup> R. G. Cooke and A. K. Macbeth, *J. Chem. Soc.*, 1593 (1937) reported m. p. of 150°. <sup>c</sup> Apparently an acid salt, unstable on standing. May also be dehydrated.

*Anal.* Calcd. for N-methyl carvacrylamine acid oxalate hydrate, C<sub>10</sub>H<sub>13</sub>NHCH<sub>3</sub>·C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O: C, 57.53; H, 7.80; N, 5.17. Found: C, 57.72; H, 7.55; N, 5.12, 5.38.

*Anal.* Calcd. for N,N-dimethyl carvacrylamine oxalate, (C<sub>10</sub>H<sub>13</sub>N<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>·C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O: subs. 0.2652 g., 0.1340 g.; 0.09661 N KOH, 20.35 ml., 10.34 ml. Found: 20.48 ml., 10.34 ml.

*Anal.* Calcd. for carvacrylamine, C<sub>10</sub>N<sub>15</sub>N: N, 9.39. Found: N, 9.16.

*Anal.* Calcd. for N-methylcarvacrylamine, C<sub>11</sub>H<sub>17</sub>N: N, 8.59. Found: N, 8.65, 8.70.

*Anal.* Calcd. for N,N-dimethylcarvacrylamine, C<sub>12</sub>H<sub>19</sub>N: N, 7.91. Found: N, 7.78, 7.82.

*Anal.* Calcd. for carvacrylamine phenylthiourea, C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>S: C, 71.78; H, 7.09. Found: C, 71.75; H, 7.00.

*Anal.* Calcd. for N-methylcarvacrylamine phenylthiourea, C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>S: C, 72.45; H, 7.43. Found: C, 72.36; H, 7.04.

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### Carbalkoxythiophanones

BY EDMOND E. MOORE AND MARJORIE B. MOORE

Several reports on the direction of the ring closure of dialkyl esters of  $\beta$ -carboxyethylthioglycolic acid have appeared in the recent literature.<sup>1,2,3,4</sup>

Using sodium in benzene Karrer and Schmid<sup>1</sup> and Buchman and Cohen<sup>2</sup> reported that the main product formed was 4-carbalkoxythiophan-3-one. Woodward and Eastman<sup>3</sup> using sodium methoxide in ether reported that at low temperatures the main product was 2-carbalkoxythiophan-3-one while at high temperatures (110°) sodium methoxide in toluene gave mostly 4-carbalkoxythiophan-3-one. Avison, *et al.*,<sup>4</sup> reported that sodium in benzene gave 2-carbalkoxythiophan-3-one.

During the course of some work on ring closures of this type, we investigated the use of methyl

and ethyl alcohols as solvents in order to eliminate the necessity of preparing powdered sodium, sodamide or alcohol-free sodium ethylate. We found that reactions could be carried out more quickly, the yields were good, and the direction of ring closure not affected.

Ethyl- $\beta$ -carbomethoxyethylthioglycolate was cyclized at 0° in four ways, the ureides prepared and their melting points compared with those of known ureides.<sup>4</sup>

(A) Sodium methylate in ether: The major product was 2-carbomethoxythiophan-3-one (oil, b. p. -102.5-105° [5-6 mm.]). *Anal.* calcd. for C<sub>6</sub>H<sub>8</sub>O<sub>3</sub>S; C, 44.99; H, 5.03. Found: C, 45.76; H, 5.15. Ureide, m. p. 221-222°.

(B) Sodium methylate in methyl alcohol gave the same product as (A). *Anal.* Found: C, 45.08; H, 5.16. Ureide, m. p. 222°.

(C) Sodium ethylate in ether gave 2-carbomethoxythiophan-3-one (oil, b. p. 98-101° [3-4 mm.]). *Anal.* calcd. for C<sub>7</sub>H<sub>10</sub>O<sub>3</sub>S; C, 48.26; H, 5.79; Found: C, 48.09; H, 5.68. Ureide, m. p. 171-172°.

(D) Sodium ethylate in ethyl alcohol gave the same product as (C). Found: C, 48.00; H, 5.80. Ureide, m. p. 172°.

In all cases the 2-carbalkoxythiophan-3-one was the main product formed.

Methyl and ethyl alcohols are suitable solvents for this ring closure if one keeps in mind the possibility of ester exchange such as occurred to a large extent in (A) and completely in (B).

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### 6-Methoxy-8-amino-1,2,3,4-tetrahydroquinoline<sup>1</sup>

BY CHARLES C. PRICE<sup>2</sup> AND HARRY F. HERBRANDSON

Although Balaban<sup>3</sup> has reported the successful reduction of 5-amino-6-methoxyquinoline and 5-amino-8-methoxyquinoline to the tetrahydro analogs by the action of tin and hydrochloric acid, 6-methoxy-8-aminoquinoline was reported to form an intensely purple solution from which the tetrahydroquinoline was not isolated.

We have experienced no difficulty in isolating the product in good yield, either from tin and hydrochloric acid reduction or catalytic hydrogenation. The product is easily oxidizable and discolors on exposure to air. It was characterized as the picrate and by conversion to the imidazole.

**8-Amino-6-methoxy-1,2,3,4-tetrahydroquinoline Hydrochloride.**—To 3.5 g. (0.02 mole) of distilled 8-amino-6-

(1) The work reported in this note was carried out under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and the University of Illinois.

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(3) Balaban, *J. Chem. Soc.*, 2624 (1932).

(1) Karrer and Schmid, *Helv. Chim. Acta*, **27**, 124 (1944).

(2) Buchman and Cohen, *This Journal*, **66**, 847 (1944).

(3) Woodward and Eastman, *ibid.*, **66**, 849 (1944).

(4) Avison, Bergel, Cohen and Haworth, *Nature*, **154**, 459 (1944).