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

	Carvacrylamine	N-Methyl-	N,N-Dimethyl-
B. p., °C.	242	236	84 (5 mm.)
n^{22}_D	1.5402	1.5363	1.5131
d^{22}_4	0.9463[a]	0.9325	0.9028
Oxalate			
M. p., °C.	149–150[b]	114–115[c]	132–133
Phenylthiourea			
M. p., °C.	117	95–96	.....

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

Anal. Calcd. for N-methyl carvacrylamine acid oxalate hydrate, $C_{10}H_{13}NHCH_3 \cdot C_2H_2O_4 \cdot H_2O$: C, 57.53; H, 7.80; N, 517. Found: C, 57.72; H, 7.55; N, 5.12, 5.38.

Anal. Calcd. for N,N-dimethyl carvacrylamine oxalate, $(C_{10}H_{13}NC_2H_6)_2 \cdot C_2H_2O_4 \cdot H_2O$: 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, $C_{10}N_{15}N$: N, 9.39. Found: N, 9.16.

Anal. Calcd. for N-methylcarvacrylamine, $C_{11}H_{17}N$: N, 8.59. Found: N, 8.65, 8.70.

Anal. Calcd. for N,N-dimethylcarvacrylamine, $C_{12}H_{19}N$: N, 7.91. Found: N, 7.78, 7.82.

Anal. Calcd. for carvacrylamine phenylthiourea, $C_{17}H_{20}N_2S$: C, 71.78; H, 7.09. Found: C, 71.75; H, 7.00.

Anal. Calcd. for N-methylcarvacrylamine phenylthiourea, $C_{18}H_{22}N_2S$: 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 β-carboxyethylthioglycolic acid have appeared in the recent literature.[1,2,3,4]

Using sodium in benzene Karrer and Schmid[1] and Buchman and Cohen[2] reported that the main product formed was 4-carbalkoxythiophan-3-one. Woodward and Eastman[3] 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.*,[4] 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-β-carbomethoxyethylthioglycolate was cyclized at 0° in four ways, the ureides prepared and their melting points compared with those of known ureides.[4]

(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 $C_6H_8O_3S$; 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-carbethoxythiophan-3-one (oil, b. p. 98–101° [3–4 mm.]). *Anal.* calcd. for $C_7H_{10}O_3S$; 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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(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).

6-Methoxy-8-amino-1,2,3,4-tetrahydroquinoline[1]

BY CHARLES C. PRICE[2] AND HARRY F. HERBRANDSON

Although Balaban[3] 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-

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(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.

(2) Present address: Department of Chemistry, University of Notre Dame, Notre Dame, Indiana.

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

methoxyquinoline and 100 ml. of concentrated hydrochloric acid, 30 g. (0.25 mole) of mossy tin was added and the whole was refluxed for two and one-half hours. The clear solution was then evaporated to 50 ml., cooled and made strongly alkaline with sodium hydroxide. The amine was extracted with three portions of benzene, the benzene dried by distillation and the hydrochloride precipitated with dry hydrogen chloride. Distillation of a small portion of the benzene dried the salt, which was then filtered. The yield was 3.1 g., or 62%, calculated as dihydrochloride. The salt crystallized from water as very light, cream-colored plates which lost water when heated to 100° and then melted at 205–207°. The water of hydration was lost when the hydrochloride was dried over anhydrous calcium chloride. The salt was oxidized readily when it was exposed to moist air. Treatment of an aqueous solution of the salt with dilute ammonium hydroxide liberated a white solid which immediately darkened.

The reduction was also carried out catalytically using copper–chromium oxide as the catalyst. The reactants, 22.0 g. (0.126 mole) of 8-amino-6-methoxyquinoline and 2.0 g. of copper–chromium oxide, were heated to 200° at 2000 pounds pressure of hydrogen for three hours. The amine was dissolved in dry benzene and 24.8 g. (78%, calculated as the dihydrochloride) of the salt was precipitated with hydrogen chloride gas. The compound was identified by means of the picrate and the imidazole.

The **monopicrate** crystallized from 95% ethanol as yellow needles; m. p. 151.5–152° (dec.).

Anal. Calcd. for $C_{16}H_{17}N_5O_8$: C, 47.17; H, 4.21; N, 17.20. Found: C, 47.35; H, 4.34; N, 17.08.

2-Methyl-8-methoxy-5,6-dihydro-4-imidazo[ij]quinoline.—A solution of 2 g. of 8-amino-6-methoxy-1,2,3,4-tetrahydroquinoline hydrochloride, 5 ml. of acetic acid, 0.5 ml. of acetic anhydride and 3 g. of anhydrous sodium acetate was refluxed for two hours. Thirty ml. of water was added and the solution was made alkaline with ammonium hydroxide. An oil separated which was removed from the aqueous layer by three extractions with ether. The ethereal solution was dried with magnesium sulfate and then evaporated. The residue, which solidified when cooled, crystallized from benzene–petroleum ether (b. p. 30–60°) as white needles. The analytical sample, m. p. 119–119.5°, was recrystallized from petroleum ether (b. p. 90–110°).

Anal. Calcd. for $C_{12}H_{14}N_2O$: C, 71.26; H, 6.98; N, 13.85. Found: C, 71.47; H, 7.04; N, 13.95.

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A Convenient Small Osmometer

BY B. H. ZIMM AND I. MYERSON

In connection with some work on the solution thermodynamics of high polymers, it has been found necessary to have a rapid and accurate osmometer requiring no more than 5 cc. of solution. The design which was evolved has in addition the following advantages: (1) it may be easily constructed by any glassblower and requires no expensive machine work; (2) there are no joints or valves to leak, other than those around the membrane; (3) it may be emptied, rinsed, filled, and the level adjusted without disassembly; (4) it employs the easily prepared flat membranes. The only disadvantage it suffers when compared with larger osmometers (*e. g.*, that of Fuoss and Mead[1]) is in the speed of attainment of equilibrium; even so, a static reading may be obtained within an hour or two with fast membranes and solvents of low viscosity.

Construction.—The osmometer (Fig. 1) consists of an open-end cylindrical cell A made from heavy-walled glass tubing, into whose side are sealed two capillary tubes, one a 0.5 mm. i. d. measuring capillary B, and the other a 2-mm. i. d. filling tube C flared into a funnel at the top. The open ends of the cylindrical portion, which are to come into contact with the membrane, are ground flat and finished with #1000 Corundum. Two membranes M are held in place over the open ends by perforated metal plates P which are drawn together with three machine screws and wing nuts. The membranes thereby serve as their own gaskets.

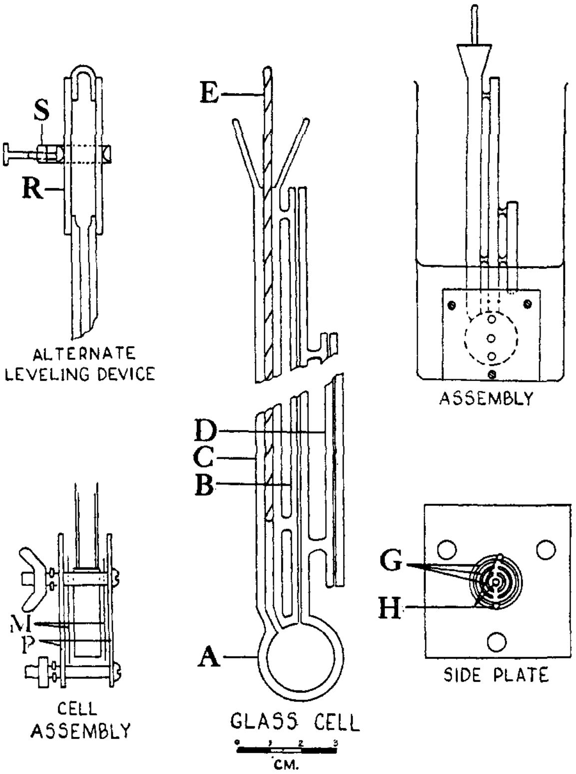

Fig. 1.

The end plates are made of brass or stainless steel. Several holes H are drilled through the plates and circular grooves G machined into their inner faces to permit the solvent free access to the membranes.

The cell is filled with solution through the wide tube. A metal rod E, whose diameter is as close as possible (within 0.1 mm.) to the internal diameter of the filling tube, is inserted. The rod is not expected to close completely the filling tube, but it must fit tightly enough for the capillary rise between the rod and the walls to keep the meniscus at the top of the tube. Since this meniscus is stationary, the tube is effectively sealed. Steel

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[1] R. Fuoss and D. Mead, *J. Phys. Chem.*, **47**, 59 (1943).