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.

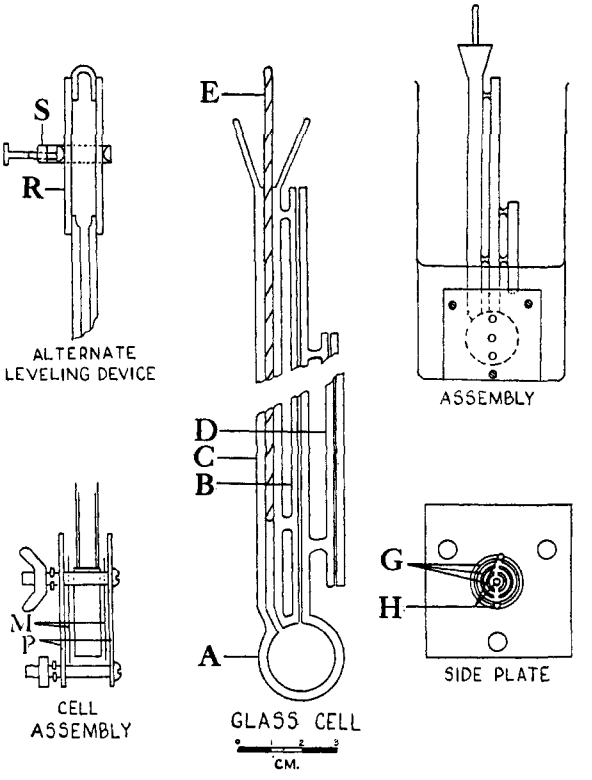

Fig. 1.

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

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

drill rod, which is available in a wide range of diameters, has been found satisfactory for most organic solvents. The meniscus in the measuring capillary may be adjusted to any desired position by raising or lowering the metal rod. This permits the use of the osmometer as a dynamic instrument by the method of Fuoss and Mead[1] or as a static instrument in which the level may be set at the expected equilibrium position with consequent saving of time.

As an alternative level changing device, the rod may be omitted and a blind piece of rubber tubing R slipped over the filling tube instead. A screw clamp S on the rubber tube is then used to adjust the level. This has been found satisfactory with aqueous solutions where corrosion of the steel rod presents difficulties.

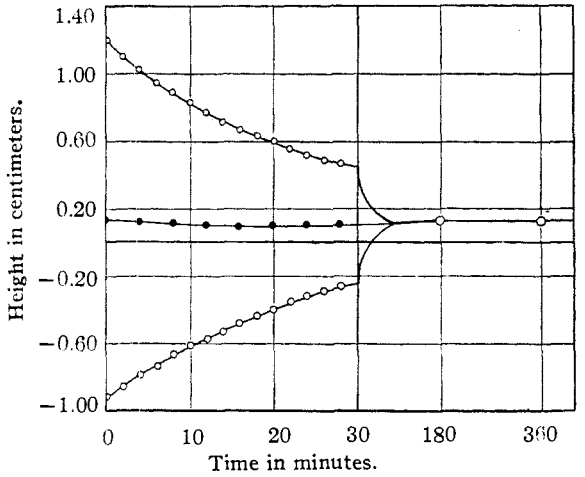

Fig. 2.—Meniscus height *versus* time, polystyrene–toluene: O, experimental points; ●, half sum values.

The osmometer filled with the solution is placed in a glass cylinder containing the solvent. A short length of capillary tubing D, of the same internal diameter as the measuring capillary, is immersed in the solvent for the purpose of correcting for capillary rise. When equilibrium has been established, the difference in level of the menisci in the measuring and reference capillaries (determined with a cathetometer) is the osmotic head. It is desirable to place the apparatus in a glass-walled thermostat held constant to within 0.01° to avoid variations due to thermal expansion of the solution in the osmometer.

When volatile solvents are being used a drop of mercury may be placed in the funnel to prevent evaporation around the rod. As so constructed the capacity of the osmometer cell is about 3 ml. Because of the absence of narrow channels, the interior may be adequately rinsed with not more than 2 ml. of solution.

Operation.—The general procedure of measuring osmotic pressure has been described previously, *e. g.*, Flory,[2] Fuoss and Mead,[1] and Wagner,[3,4] from which no essential changes have been made by us. The glass construction of the cell simplifies the elimination of bubbles in filling.

It has been found that aqueous solutions tend to stick in the fine capillary. In such cases the use of an immiscible liquid, *e. g.*, hexane or toluene, as a pressure indicator is desirable. The cell is filled about seven-eighths full with the aqueous solution and the remaining portion of the cell and capillaries filled with the manometric liquid. In such cases, the correction for capillary rise (of the manometric liquid) is determined separately.

The approach of the meniscus to equilibrium is shown in Fig. 2. These data were obtained on a solution of polystyrene in toluene using a denitrated collodion membrane. The equilibrium value, which was attained within three hours in this case, was reproducible on subsequent resettings within 0.02 cm. This is the order of reproducibility that is generally attained even when the total rise is greater.

(2) P. J. Flory, THIS JOURNAL, **65**, 372 (1943).

(3) H. Wagner, *Ind. Eng. Chem., Anal. Ed.*, **16**, 520 (1944).

(4) H. Wagner, "Physical Methods of Organic Chemistry," Vol. I, Chap. VIII, Weissberger, editor, Interscience Publishers, Inc., New York, N. Y., 1945.

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Convenient Syntheses of Thymine and 5-Methylisocytosine

BY HENRY W. SCHERP

Davidson and Baudisch[1] found that uracil could be synthesized conveniently by heating a solution of malic acid and urea in concentrated sulfuric acid. By substituting guanidine hydrochloride for urea, Caldwell and Kime[2] utilized this reaction for the synthesis of isocytosine. The present communication concerns the preparation of thymine and 5-methylisocytosine (2-amino-5-methyl-4(3)-pyrimidone) by the reaction between β-methylmalic acid and urea or guanidine, respectively. Thymine was synthesized also by the reaction between diethyl β-methylmalate and urea. This alternative procedure eliminated one step in the synthesis, but the yield was about one-sixth less.

β-Methylmalic acid was prepared by the hydrolysis of diethyl β-methylmalate, which was in turn prepared by the reduction of ethyl ethoxalylpropionate by catalytic hydrogenation at low pressures. This method of reduction was found to be superior to other methods used previously.[3]

Experimental

Ethyl Ethoxalylpropionate.—This substance was synthesized by the Claisen condensation of diethyl oxalate and ethyl propionate.[4] Decomposition of the sodium salt

(1) Davidson and Baudisch, THIS JOURNAL, **48**, 2379 (1926).

(2) Caldwell and Kime, *ibid.*, **62**, 2365 (1940).

(3) (a) Wislicenus, *Ber.*, **25**, 196 (1892); (b) Abbott and McKenzie, *ibid.*, **71B**, 1214 (1938); (c) Wojcik and Adkins, THIS JOURNAL, **55**, 4939 (1933).

(4) "Organic Syntheses," Coll. Vol. II, 1943, p. 272.