N-(2-Nitro-4-methylphenyl)-*dl*-α-alanine.—A mixture of 7.6 g. (0.05 mole) of 3-nitro-4-aminotoluene[5] and 3.83 g. (0.021 mole) of α-bromopropionic acid[9] was heated for 8 hours on a steam-bath. The cooled melt was extracted with 20 ml. of 15% ammonium hydroxide. The ammonium hydroxide solution was treated with charcoal, then acidified with 10% hydrochloric acid to give 2.1 g. of red crystals, m.p. 142–144°. Repetition of the above purification gave 1.8 g. (38% yield) of N-(2-nitro-4-methylphenyl)-*dl*-α-alanine, m.p. 149.5–150°. Hinsberg[4] prepared this compound by a different process, reporting a melting point of 148°.

2-Hydroxy-3,7-dimethylquinoxaline.—A solution of 2.65 g. (0.012 mole) of N-(2-nitro-4-methylphenyl)-*dl*-α-alanine in 40 ml. of ethanol was reduced over palladium–charcoal at 30° and two atmospheres of hydrogen until the theoretical quantity of hydrogen had been absorbed. Catalyst and solvent were removed, and the tan residue was dissolved in 35 ml. of 10% sodium hydroxide solution and oxidized by drawing air through the solution for 18 hours at 70–80°. The solution was cooled and clarified by filtration; the filtrate was brought to *p*H 4 with acetic acid, precipitating 2-hydroxy-3,7-dimethylquinoxaline. The precipitate was sublimed at 150° (1 mm.) to give 0.9 g. (43% yield) of white sublimate, m.p. 240–241°. The material was crystallized from ethanol–water to constant melting point with no appreciable loss of product, m.p. 243–244°. The melting point previously reported[4] was 237°.

Anal. Calcd. for $C_{12}H_{10}N_2O$: N, 16.1. Found: N, 16.1.

Absorption Spectra.—The ultraviolet absorption spectra in Fig. 2 were obtained on a Beckman model DU quartz spectrophotometer. All curves were run on analytical material at concentrations of 10 mg./l. of solvent; width of quartz sample cell was 1.003 cm.

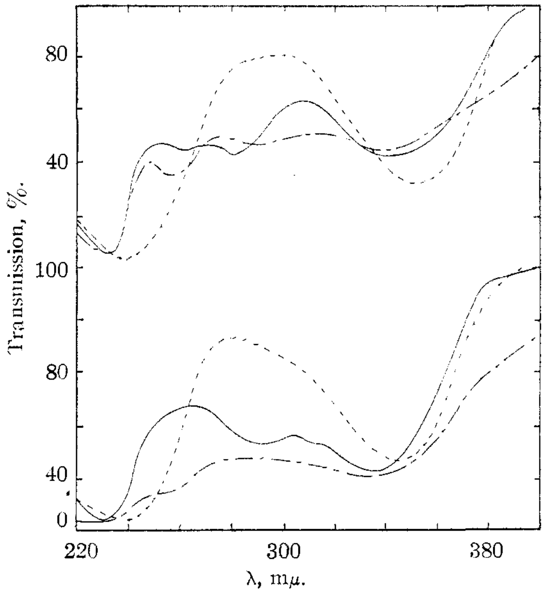

Fig. 2.—Ultraviolet absorption spectra of 2-hydroxy-3,6-dimethylquinoxaline, upper: 2-hydroxy-3,7-dimethylquinoxaline, lower; —, 95% ethanol; – – – – – –, 0.1 *N* sodium hydroxide; —·—·— 0.1 *N* hydrochloric acid.

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(9) Eastman Kodak Company White Label material.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MIAMI
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The Preparation of N-Alkylethylenediamines

BY RUSSELL C. O'GEE AND HENRY M. WOODBURN[1]

N-Alkylethylenediamines are desirable intermediates for certain types of organic synthesis but their preparation has been unsatisfactory because of poor yields, complicated procedures, or methods limited to a specific type of substituent.

The situation has been reviewed by Aspinall[2] and by Coleman and Callen[3] both of whom proposed methods of their own. The first requires preliminary preparation of monoacetylethylenediamine and its N-benzenesulfonyl derivative and gives over-all yields of 10–33%. The second employs the catalytic addition of primary and secondary amines to ethylenimine, the reaction being favored by elevated temperatures. Actually, the only primary amines described are aniline and benzylamine.

The recent offering of 2-bromoethylamine hydrobromide in commercial quantities[4] suggested investigation of the reaction

$$\mathrm{RNH_2 + BrCH_2CH_2NH_2{\cdot}HBr \longrightarrow RNHCH_2CH_2NH_2 + 2HBr}$$

as a source of N-alkylethylenediamines. The reaction proved to be straightforward and easily carried out. Yields from both normal and branched-chain aliphatic primary amines are quite acceptable and the reaction has the double advantage of simplicity and the use of easily available reagents. Results of the investigation are summarized in Table I.

TABLE I

N-ALKYLETHYLENEDIAMINES ($\mathrm{RNHCH_2CH_2NH_2}$)

R	Yield, %	B.p.,[a] observed °C.	Mm.	Ref.	Derivatives: Dihydrochloride m.p., °C. Obsd.	Ref.	Dipicrate m.p., °C. Obsd.	Ref.
CH_3	41	113–115	748	(2)	131	(5)	222–223	(5)
C_2H_5	40	125–127	743	(2)	168		193–194	(2)
n-C_3H_7	38	153–154	749	(6)	204–205		167–168[b]	(6)
i-C_3H_7	35	137–138	752	(7)	122–123		192–193	
n-C_4H_9	52	76–78	25	(6)	230	(5)	177	

[a] B.p.'s and m.p.'s uncorrected. [b] King and McMillan[6] report 224°. Our figure is supported by the following analysis: Calcd. for $C_5H_{14}N_2{\cdot}2C_6H_3N_3O_7$: C, 36.4; H, 3.6. Found: C, 36.6; H, 3.7.

Experimental

A solution of 102.5 g. (0.5 mole) of 2-bromoethylamine hydrobromide in 100 ml. of water was added to a 25% aqueous solution containing 2.5 moles of alkylamine. The resulting mixture was refluxed gently for 12 hours. It was then cooled and treated with solid sodium hydroxide until the base no longer dissolved. The solution separated into two layers as it became alkaline. The upper layer was taken off and the lower layer extracted with ether. The combined upper layer and extracts were dried over anhydrous potassium carbonate and fractionated through a 12″ column packed with glass helices.

The dihydrochlorides and dipicrates were made as an additional check on the identity of the diamines. The hydrochlorides not previously reported were analyzed for chlorine by the Mohr method. New picrates were analyzed for carbon and hydrogen by semi-micro carbon combustion technique.

N-Ethylethylenediamine dihydrochloride: Calcd. for $C_4H_{12}N_2{\cdot}2HCl$: Cl, 44.1. Found: Cl, 44.3.

N-Propylethylenediamine dihydrochloride: Calcd. for $C_5H_{14}N_2{\cdot}2HCl$: Cl, 40.6. Found: Cl, 40.7.

N-Isopropylethylenediamine dihydrochloride: Calcd. for $C_5H_{14}N_2{\cdot}2HCl$: Cl, 40.6. Found: Cl, 40.6.

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[1] To whom inquiries regarding this article should be sent.

(2) Aspinall, THIS JOURNAL, **63**, 852 (1941).

(3) Coleman and Callen, *ibid.*, **68**, 2006 (1946).

(4) Dow Chemical Co., Midland, Michigan.

(5) Johnson and Bailey, THIS JOURNAL, **38**, 2135 (1916).

(6) King and McMillan, *ibid.*, **68**, 1774 (1946).

(7) Pearson, Jones and Cope, *ibid.*, **68**, 1225 (1946).

N-Isopropylethylenediamine dipicrate: Calcd. for $C_5H_{14}N_2 \cdot 2C_6H_3N_3O_7$: C, 36.4; H, 3.6. Found: C, 36.7; H, 4.1.

N-Butylethylenediamine dipicrate: Calcd. for $C_6H_{16}N_2 \cdot 2C_6H_3N_3O_7$: C, 37.6; H, 3.8. Found: C, 37.3; H, 4.0.

Grateful acknowledgment is made to the Dow Chemical Co. which furnished a sample of 2-bromoethylamine hydrobromide, and to Sharples Chemicals, Inc., which furnished the *n*-propylamine.

DEPARTMENT OF CHEMISTRY
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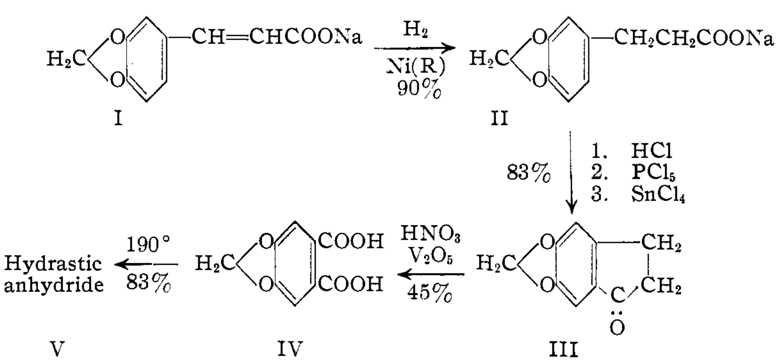
The Synthesis of Hydrastic Acid

BY WILKINS REEVE AND HERBERT MYERS

Of the methods available for the preparation of hydrastic acid[1,2,3] (IV), the four step scheme of Perkin and Robinson appears to be the most promising even though the over-all yield from piperonal is only 2 to 3%. In the present work, these steps have been carried out by different means with the result that hydrastic acid can be obtained in an over-all yield of 25–27%, and hydrastic anhydride in an over-all yield of 20–23%. The greatest improvement has been realized in the oxidation step III → IV which was effected in 45% yield in contrast with less than 5% by the old method.



Melting points ranging from 172 to 188°[1,4] have been reported for hydrastic acid. We have found its melting point to be approximately 225° by a procedure which corrects for the lowering of the observed melting point occurring, due to decomposition, during the time the melting point sample is heated. The time necessary for the sample to melt when placed in a bath at a given temperature is plotted against the temperature as shown in Fig. 1. The straight line AB represents the time required for the heat to flow through the capillary tube and the sample; the temperature of immediate melting is where the lines meet. This procedure may prove useful with other thermally unstable materials.

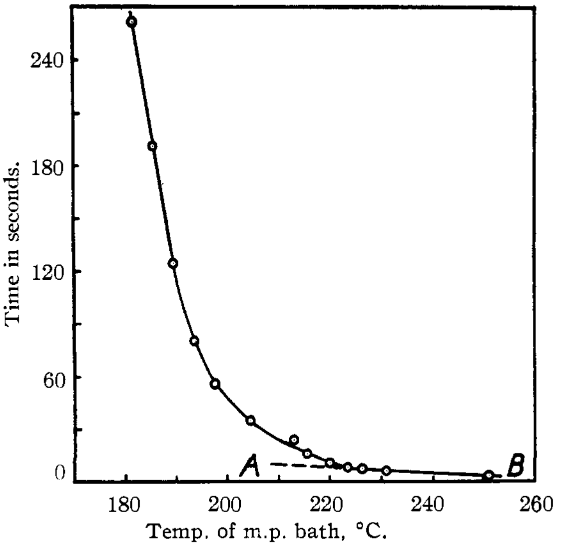


Fig. 1.—Relationship between m.p. of pure hydrastic acid and time sample is in the m.p. bath.

In view of the unsuitability of the melting point as a measure of purity, the solubility temperature[5] was determined, and found to be 86.5° at a 12:1 ratio of water to hydrastic acid. The solubility temperatures at other ratios were also determined over the temperature range of 34 to 87°, and from these data a solubility equation was calculated.

$$\text{Log } S = 0.2879 + 0.01384t + 5.82 \times 10^{-5} t^2$$

S = solubility in g./l. water; t = temp. in °C.

The maximum deviation between the observed and the calculated solubility data using the above equation is 2%. Some values for the calculated solubility are: at 20° (3.9 g./l.), 40° (8.6), 60° (21.3), 80° (57), 100° (180). By differentiation of the above equation, it can be calculated that the solubility temperature at a 12:1 ratio is lowered 0.18° for each per cent. of soluble impurity.

Experimental

All melting points are corrected. Analyses are by Mrs. Mary Aldridge and Mr. Byron Baer of this Laboratory.

3,4-Methylenedioxydihydrocinnamic acid was prepared by hydrogenating a slurry of the sodium salt of 3,4-methylenedioxycinnamic acid[6] (from 380 g. (1.98 moles) of the acid and 80 g. of sodium hydroxide) in 1300 ml. of distilled water under 3000 lb. (200 atm.) pressure at 110–130° over 50 g. of Raney nickel for 2 hours. The reaction mixture was filtered to remove the catalyst and acidified with concentrated hydrochloric acid to congo red. Water was added as necessary to thin the thick slurry of the insoluble acid which precipitated. After filtering and air drying, 345 g. (90%) was obtained, m.p. 83–84°; reported m.p. 87–88°.[1] This light tan colored material was satisfactory for the next step. A pure white product, m.p. 87–88°, was obtained after two recrystallizations from water, using 2 g. of acid and 0.4 g. of activated carbon (Darco G-60) per 100 ml. of water. The yield after two recrystallizations was 1.4 g.

5,6-Methylenedioxyhydrindone-1.—The acid chloride of the dihydrocinnamic acid was prepared by adding 208 g. (1 mole) of phosphorus pentachloride to a chilled solution of 194 g. (1 mole) of the crude 3,4-methylenedioxydihydrocinnamic acid, dissolved in 1500 ml. of dry, thiophene-free benzene, and stirring for 1.5 hours at room temperature. An excess of the phosphorus pentachloride attacks the methylenedioxy bridge and lowers the yield.

The cyclization was carried out by the dropwise addition

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(4) M. Freund, *Ann.*, **271**, 370, 381 (1892).

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