$$\frac{1}{9}\sqrt[3]{\frac{T_o}{d_c}} = \frac{1}{K_3\sqrt[3]{\epsilon_{TA_3}}}\left[\frac{1}{3A_o}\right] + \frac{1}{\sqrt[3]{\epsilon_{TA_3}}}$$

where $d_c = d_T - T_o\epsilon_T - A_o\epsilon_A$ and d_T is the total measured optical density in an absorption cell having a 1-cm. light path. To test this equation, we plot $\frac{1}{9}\sqrt[3]{\frac{T_o}{d_c}}$ *vs.* $\frac{1}{3A_o}$. The points should fall on a straight line with the slope equal to $\frac{1}{K_3\sqrt[3]{\epsilon_{TA_3}}}$ and the intercept equal to $\frac{1}{\sqrt[3]{\epsilon_{TA_3}}}$. Such a plot, using the data reported by Foster, Hammick, and Wardley,[1] is shown in Figure 1. As can be seen from the figure, the fit is all that can be expected and lends some support to our structural hypothesis.

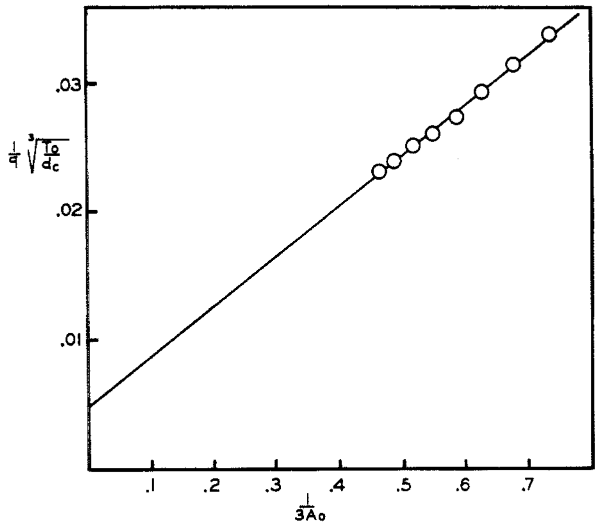

FIG. 1.—A PLOT OF $1/9\sqrt[3]{\frac{T_o}{d_c}}$ *vs.* $\frac{1}{3A_o}$ WHICH TESTS THE FIT OF THE DATA TO THE PROPOSED HYPOTHESIS OF 3:1 COMPLEXING CO-EXISTING WITH 1:1 AND 2:1 COMPLEXING.

In a similar way and making similar assumptions, it is possible to derive an expression for the case where the complexes present are 2:1 and 1:1.[3] However, when the data are plotted for this case a curve rather than a straight line is obtained. The possibility of simple 1:1 complexing has been adequately eliminated by Foster, Hammick, and Wardley.[1] We have not considered the possibility of a 4:1 complex coexisting with the 1:1, 2:1, and 3:1 complexes, since our structural hypothesis cannot accommodate the fourth amine molecule.

Finally, a dioxane solution which is 0.101 *M* in 1,3,5-trinitrobenzene and 0.043 *M* in dimethylamine shows appreciable color formation at 25° (d_c's of about 0.06 from 390 to 440 mμ). At the same temperature, a solution which was 0.021 *M* in trinitromesitylene and 0.043 *M* in dimethylamine showed no additional color formation (d_c's = 0). Similar observations have been reported by Lewis and Seaborg[2] for solutions in petroleum ether. We consider this to be evidence for the proposed hypothesis, since the anticipated effect of the methyl groups in trinitromesitylene is to inhibit resonance of the nitro groups with the ring and prevent formation of the postulated complexes.

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[3] The final equation for this case is

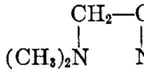
$$\sqrt{\frac{T_o}{d_o}} = \frac{1}{K_2\sqrt{\epsilon_{TA_2}}}\frac{1}{2A_o} + \frac{1}{\sqrt{\epsilon_{TA_2}}}$$

Amines. I. N,N,N′,N′-Tetramethyl-1,2-propanediamine and Its Characterization

ROSS W. MOSHIER AND LEONARD SPIALTER

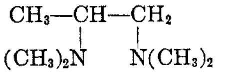
Received April 16, 1956

The methylation of ethylenediamine to the N,N,N′,N′-tetramethyl derivative, I, was first reported by Eschweiler[1] to result from the action of excess formaldehyde on the primary diamine. Subsequently, the Clarke modification, where formic acid is used as the reductant, was introduced[2] in the methylation of 1,4-butanediamine and certain monoamines. Wide application of this method of N-methylation to the synthesis of poly-tertiary amines has been hindered by the unavailability of the starting polyamines. It was, therefore, surprising to find that N,N,N′,N′-tetramethyl-1,2-propanediamine (II) had not been previously reported although 1,2-propanediamine is a common commercial chemical,[3] as is also 1,2-dichloropropane,[3] an intermediate for the alternative preparative route *via* condensation with dimethylamine. This latter reaction has been used for the synthesis from 1,3-dichloropropane of the isomeric N,N,N′,N′-tetramethyl-1,3-propanediamine (III) and for the preparation of compound I.[4]



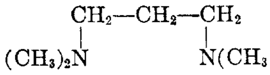
$(CH_3)_2N{-}CH_2{-}CH_2{-}N(CH_3)_2$

I



$CH_3{-}CH(N(CH_3)_2){-}CH_2{-}N(CH_3)_2$

II



$(CH_3)_2N{-}CH_2{-}CH_2{-}CH_2{-}N(CH_3)_2$

III

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(1) W. Eschweiler, *Ber.*, **38**, 880 (1905).

(2) H. T. Clarke, H. B. Gillespie, and S. Z. Weisshaus, *J. Am. Chem. Soc.*, **55**, 4571 (1933).

(3) This compound, ethylenediamine and various polyethylenepolyamines are prepared and marketed by Carbide and Carbon Chemicals Corporation, 30 E. 42nd Street, New York 17, N. Y.

(4) (a) L. Knorr and P. Roth, *Ber.*, **39**, 1420 (1906); (b) M. Freund and H. Michaels, *Ber.*, **30**, 1374 (1897); (c) G. F. Grail, L. E. Tenenbaum, A. V. Tolstoouhov, C. J. Duca, J. F. Reinhard, F. E. Anderson, and J. V. Scudi, *J. Am. Chem. Soc.*, **74**, 1313 (1952); (d) I. G. Farbenindustrie A-G, French Patent 802,105 (1936).

The present note describes the synthesis, physical properties, and standard derivatives, which characterize the diamine molecule II.

EXPERIMENTAL[5]

N,N,N',N'-Tetramethyl-1,2-propanediamine (II). To 4060 ml. of 90% formic acid in a 12-l. 3-neck round-bottom flask fitted with a condenser, stirrer, and dropping-funnel was slowly added 1334 g. (17.3 moles) of 1,2-propanediamine[6] with thorough mixing. Then somewhat more rapidly was introduced 5960 ml. of a 37% formalin solution. The uniform evolution of bubbles of carbon dioxide from the body of the solution indicated the progress of the reaction. After the early rapid gas liberation had subsided, the flask was heated at a gentle refluxing temperature for 48 hours. While still boiling, the reaction mixture was carefully treated with 1.0 l. of concentrated sulfuric acid to bind the amine as a salt. The excess formaldehyde, formic acid, and water then were distilled off.

When the still pot residue began to froth badly (after 5600 ml. of distillate had been collected), 900 g. of sodium hydroxide (as a warm 50% aqueous solution) was added. About one liter of amine product distilled over. More was obtained by salting it out from the residue with concentrated aqueous potassium hydroxide. The combined amine fractions were dried over potassium hydroxide pellets and distilled from sodium. The yield of N,N,N',N'-tetramethyl-1,2-propanediamine, b.p. 138–139° at 745 mm. was 1692 g. (76%) of clear colorless liquid with a very strong amine odor. The product was completely miscible with water and organic solvents. It remained a mobile fluid even at $-100°$. Cooling below this temperature in a liquid nitrogen bath led to a rapid increase in viscosity with ready supercooling to a hard brittle glass. It was not found possible to crystallize this amine.

Other physical properties found include n_D^{25} 1.4230 (Abbe-type refractometer); d_4^{25} 0.7900 (pycnometer); and dielectric constant 2.4 (determined with dielectric constant meter made by Yellow Springs Instrument Co., Yellow Springs, Ohio).

Anal. Calc'd for $C_7H_{18}N_2$: C, 64.56; H, 13.93; N, 21.51; Neut. equiv., 65.1; MR_D, 42.00.[7] Found: C, 64.47; H, 13.75; N, 21.42; Neut. equiv., 65.0; MR_D, 41.98.

II·Dihydrochloride. This compound was obtained by adding dropwise from a hypodermic syringe 5 ml. of diamine II to 15 g. of concentrated hydrochloric acid in a 50-ml. Erlenmeyer flask with shaking and cooling in an ice-bath to remove the high heat of neutralization. The reaction mixture then was concentrated by heating to remove almost all of the water. There resulted a clear colorless viscous resin which set to a glass on cooling to room temperature. Slow crystallization took place over a period of days. A portion of the crystals, removed and washed with a small amount of absolute ethanol, had m.p. 177–179°. Potentiometric titration with base proved the diprotic nature of this compound.

II·Monopicrate.[8] To 10 ml. of a saturated solution of picric acid in anhydrous ethanol was added 1.0 ml. of diamine II. The solution was refluxed for one minute and allowed to cool slowly overnight. The yellow crystalline salt was filtered off and washed well with ethanol. Yield was 0.80 g., m.p. 112–114°.

Anal. Calc'd for $C_{13}H_{21}N_5O_7$: C, 43.45; H, 5.89; N, 19.49. Found: C, 43.75; H, 5.95; N, 19.40.

II·Di(methiodide). To 2.0 ml. of methyl iodide in 10 ml. of methanol in a 25-ml. Erlenmeyer flask cooled in an ice-bath was added dropwise from a hypodermic syringe 1.0 ml. of diamine II. Constant shaking and cooling were required to dissipate the heat of reaction. After addition was complete, the solution was heated to boiling and allowed to cool slowly overnight. Crystallization occurred. The product was filtered off and washed thoroughly with cold methanol. Yield was 2.0 g. (80%), m.p. 222–224° with decomposition and gas evolution. Recrystallization from methanol gave crystals, m.p. 223–225° with decomposition.

Anal. Calc'd for $C_9H_{24}I_2N_2$: C, 26.10; H, 5.84. Found: C, 26.20; H, 5.80.

II·Di(methyl-p-toluenesulfonate). This derivative was prepared by a procedure identical with that described above for the dimethiodide except for the use of 2.0 ml. of methyl *p*-toluenesulfonate instead of the iodide. The yield was 2.4 g. (80%) of the di(methotosylate), m.p. 225–228°. Recrystallization from methanol gave m.p. 228–229° with a little decomposition since the fused material, after crystallization, had m.p. 223–225°.

Anal. Calc'd for $C_{23}H_{38}N_2O_6S_2$: C, 54.95; H, 7.62. Found: C, 55.11; H, 7.45.

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(5) Analyses were performed by Oakwold Laboratories, Alexandria, Virginia. Melting points were corrected values taken on a Kofler micro hot-stage.

(6) The diamine was the Matheson, Coleman, and Bell technical grade propylenediamine. A representative sample subjected to analysis by fractional distillation indicated 96% purity, b.p. 119–120°. The 1,2-propanediamine forms no azeotrope with water, according to ***Synthetic Organic Chemicals Catalog***, Carbide and Carbon Chemicals Corporation, New York, N. Y., 1945, 12th ed., p. 75.

(7) Values for atomic refractivities (sodium D-line) were those of A. I. Vogel, *A Textbook of Practical Organic Chemistry*, Longmans, Green and Co., Inc., New York, N. Y., 1948, p. 898.

(8) One of the referees called our attention to a paper by E. Rothstein, *J. Chem. Soc.*, 1560 (1940), which reports in a small footnote the isolation of a compound presumed to be the bis-quaternary ammonium picrate of the diamine described in the present note. This purported "N,N,N,-N',N',N'-hexamethylpropylenediammonium picrate" was obtained by extended heating of trimethyl-β-chloropropylammonium chloride with potassium hydroxide and then adding picrate ions. The nature of the reaction conditions, lack of structure proof, and the reported m.p. 315–316° make us feel that Rothstein's compound may be tetramethylammonium picrate which fits the analytical data better and has been described as melting at 312–313°, W. Lossen, *Ann.*, **181**, 364 (1876); 318–320°, M. Kohn and F. Grauer, *Monatsh.*, **34**, 1751 (1913); 313°, P. Walden, H. Uhlich, and G. Busch, *Z. physik. Chem.*, **A123**, 429 (1926).

Amines. II.[1] The Preparation and Reduction of Benzo[*c*]cinnoline

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AND JEROME HOLLANDER[1a]

Received May 7, 1956

An unreported preparation and catalytic reduction product of benzo[*c*]cinnoline have been found. Benzo[*c*]cinnoline (I) also referred to in the literature as 2,2'-azodiphenyl, dibenzopyridazine, phen-

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(1) For previous paper in this series, see R. W. Moshier and L. Spialter, *J Org. Chem.*, **21**, 1050 (1956).

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