(B-1) Concentrated hydrochloric acid (10 ml.) was added to the aqueous filtrate, which had been heated to 55°. Benzaldehyde (20 ml.) was then added and the solution shaken for 10 minutes. The orange colored oil which separated became semi-solid after overnight chilling at 0°. The supernatant liquid was decanted (0.7 g. of benzalazine, m.p. 90–91°, was recovered from this solution) and the solid triturated with 40 ml. of cold water, which was also decanted and discarded. The yield of soft solid, after vacuum drying, was 37.3 g. When this crude product was dissolved in 200 ml. of boiling absolute methanol and the solution cooled to 25°, there was recovered 4.8 g. of material melting at 176°. One recrystallization from 86% ethanol (70 ml. per gram) yielded flat needles; m.p. 176–177° with decomposition.

Anal. Calcd. for the benzalhydrazone of 1-methyl-2-amino-3-nitroguanidine, $C_9H_{11}O_2N_5$: C, 48.86; H, 5.01; N, 31.66. Found: C, 48.68; H, 5.05; N, 31.60; 31.83.

(B-2) Evaporation of the methanol solution from B-1 to 100 ml. and cooling gave 1.9 g. of small round clusters and aggregates melting at 170–173°. (The mother liquors were retained for C.) Recrystallization from 100 ml. of 95% ethanol yielded very pale yellow spherulites, m.p. 178–179°; a mixed melting point with the preceding hydrazone was 167–170°. The compound was analyzed but not identified. This compound did not form a picrate. It gave a salt with benzalaminoguanidine, crystallizing from absolute methanol as yellow platelets, m.p. 182–182.5° (dec.).

Anal. Found: C, 53.17, 53.28, 53.23; H, 5.38, 4.92; N, 29.93, 29.60, 29.49.

(C) The final methanolic mother liquors from B-2 were diluted to 120 ml. with 95% ethanol, heated to boiling, and treated with 23.4 g. of picric acid dissolved in 120 ml. of hot ethanol. A yellow crystalline precipitate formed immediately; after the solution had cooled to 25°, the solid was removed by filtration and dried. The yield was 23 g.; m.p. 175–180°. When this crude product was extracted with one 600-ml. portion and one 400-ml. portion of boiling 95% ethanol, there was left 9.6 g. of very sparingly soluble material, decomposing at 239–240°. A mixed melting point with dibenzaldiaminoguanidine picrate was 240–241°. The yield of this picrate corresponded to a 9.7% conversion of the nitroaminoguanidine to diaminoguanidine.

From the alcoholic extraction liquors there crystallized upon cooling, 8.6 g. of material melting at 208–209°. A second recrystallization from 95% ethanol gave two materials. The more soluble material melted at 185–186°, resolidified, then remelted with decomposition at 210°. The less soluble material melted at 210–211° with decomposition. A mixed m.p. of the two materials was 210°. Mixed melting points of either material with an authentic sample of benzal 1-methyl-3-aminoguanidine picrate (see below) was 213°. The low melting compound is a meta-stable form. The yield of picrate recovered corresponds to a 10.7% conversion of nitroaminoguanidine to 1-methyl-3-aminoguanidine; because of losses due to the solubility of the low melting form of the picrate, the actual conversion is probably considerably higher.

Benzalmethylaminoguanidine Picrate.—1-Methyl-3-nitroguanidine (11.8 g., 0.1 mole) was reduced according to the procedure of Davis.[5] When the reduction was completed, the solution was filtered from unreacted zinc, treated with 10 ml. of concd. nitric acid, heated to 60°, and shaken for 10 minutes with 10 ml. of benzaldehyde. Only an oil separated when the solution was cooled to 0°. The aqueous layer was decanted, the oil dissolved in 50 ml. of boiling 95% ethanol, and treated with a solution of 20 g. of picric acid in 150 ml. of hot 95% ethanol. The bright yellow picrate was removed from the cooled solution by filtration and dried. The yield was 20.0 g. (49.4% of theory); m.p. 206–210° with decomposition. One gram was recrystallized from 100 ml. of 95% ethanol; spherulites of fine needles, m.p. 215–216° (dec.).

Anal. Calcd. for $C_{15}H_{15}O_7N_7$: C, 44.45; H, 3.73; N, 24.20. Found: C, 44.46, 44.49; H, 3.49, 3.74; N, 24.19, 24.32.

1,3-Dimethyl-2-aminoguanidine Iodide.—A solution of 24.5 g. of N,N′,S-trimethylisothiourea iodide (0.1 mole) and 5.8 g. of 86% hydrazine hydrate (0.1 mole) in 65 ml. of water was allowed to stand at room temperature. There was a steady evolution of methyl mercaptan and the gradual crystallization of a white solid. After 4 hours the solution was heated to boiling to complete the reaction; the solid dissolved but recrystallized as long, white needles when the solution was cooled. The product was removed by filtration and the mother liquor evaporated to dryness. The yield of product melting at 265–270° was essentially quantitative. Two recrystallizations from 95% ethanol raised the melting point to 290–295°.

Anal. Calcd. for $C_3H_{11}N_4I$: N, 24.36; hydrazino nitrogen, 12.18; I, 55.17. Found: N, 24.36; hydrazino nitrogen, 12.33; I, 55.64, 55.88.

The picrate melted at 180–181° after recrystallization from water.

Anal. Calcd. for $C_9H_{13}O_7N_7$: N, 29.60. Found: N, 29.65.

The iodide of the benzalhydrazone melted at 75–76° after recrystallization from 95% ethanol.

Anal. Calcd. for $C_{10}H_{15}N_4I$: C, 37.75; H, 4.75. Found: C, 37.14; H, 4.78.

The picrate of the benzalhydrazone, crystallizing from 95% ethanol as fine needles, decomposed at 206–207°.

Anal. Calcd. for $C_{16}H_{17}N_7O_7$: N, 23.38. Found: N, 23.19.

The free **benzalhydrazone** crystallized from aqueous ethanol as pale yellow, flat needles; m.p. 86.5–87.5°.

1-Methyl-1-amino-3-nitroguanidine.—A solution of methylhydrazine, prepared by dissolving 3.2 g. of the sulfate and 2.3 g. of anhydrous sodium carbonate in 10 ml. of water, was added during 20 minutes with shaking to a cold slurry of 2.94 g. of methylnitrosonitroguanidine in 10 ml. of water. After the solution stood overnight at 25°, it was chilled to 0° and the solid removed by filtration. The dried product, melting about 161°, was a mixture of sodium sulfate and methylaminonitroguanidine. By extraction with one 100-ml. portion and one 50-ml. portion of boiling 95% ethanol there was recovered 1.8 g. of compound (68% of theory), melting at 170–171°. Recrystallization from ethanol gave rosettes of flat needles with unchanged melting point.

Anal. Calcd. for $C_2H_7O_2N_5$: C, 18.04; H, 5.30. Found: C, 18.26; H, 5.31.

Several attempts to detect or isolate 1-(methylamino)-3-nitroguanidine, $CH_3NHNHC(NH)NHNO_2$, in the original aqueous mother liquors or in the alcoholic recrystallization liquors were unsuccessful; only further amounts of 1-methyl-1-amino-3-nitroguanidine or its benzalhydrazone were isolated. This would indicate that under these conditions of reaction the nucleophilic center of methylhydrazine is on the nitrogen adjacent to the methyl group and that addition occurs exclusively at that point.

The benzalhydrazone melted with decomposition at 193–193.5° after recrystallization from 95% ethanol.

Anal. Calcd. for $C_9H_{11}O_2N_5$: N, 31.66. Found: N, 31.65.

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[5] T. L. Davis, "Chemistry of Powder and Explosives," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 383.

The Synthesis of Some Amino Alcohols

By R. E. Holmen and D. D. Carroll

The reduction of amic or anilic acids with lithium aluminum hydride offers a fairly convenient synthesis of a wide variety of amino alcohols, some of which are not readily obtained otherwise. In view of the recent application of this method to the modification of anti-tubercular compounds,[1] we wish to record some syntheses of new amino alcohols used by us prior to that disclosure. Included also is another new compound, 2-*t*-butylaminoethanol, prepared by an adaptation of a

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[1] V. C. Barry, J. G. Belton, R. M. Kelly and D. Twomey, *Nature*, 166, 303 (1950).

known method[2] for the synthesis of aminoethanols.

Experimental

10-Anilino-1-decanol.—A 1-l. three-necked flask was equipped with a reflux condenser, nitrogen inlet, dropping funnel and a sparkless motor-driven stirrer. The apparatus was protected with calcium chloride tubes. Dry nitrogen was passed (1.5–2 cu. ft./hr.) through the flask during all subsequent operations until final decomposition of the reaction mixture. Dry ether (*ca.* 300 ml.) and powdered lithium aluminum hydride (14.3 g., 0.375 mole) were placed in the flask and stirred for a period of two hours prior to portionwise addition of a suspension of ω-carbomethoxypelargonanilide (36.4 g., 0.125 mole) in dry ether (250 ml.) over a 75-minute period. An insoluble product precipitated. Stirring and gentle refluxing were continued for 2.5 hours more, after which the reaction mixture was allowed to stand overnight under a slow stream of nitrogen (0.2 cu. ft./hr.).

Decomposition of the excess lithium aluminum hydride and the reaction complex was effected by the *cautious* addition first of water (60 ml.) from a dropping funnel and later of a 20% solution of sodium hydroxide (300 ml.). Even the great excess of alkali failed to dissolve the inorganic precipitate; hence, the mass was extracted several times with ether before being subjected to filtration under reduced pressure. The combined ethereal extracts were concentrated in a current of air to give a residue of 25.2 g. This was redissolved in ether and stirred with a slight excess of 5% hydrochloric acid. The precipitate of the amine hydrochloride was filtered after separation of the ethereal layer. From the aqueous filtrate a quantity of the desired free amino alcohol was liberated by the addition of 10% sodium hydroxide. The yield comprised 19.1 g. of the **hydrochloride of 10-anilino-1-decanol**, m.p. 101–104°, and 3 g. of 10-anilino-1-decanol, m.p. 42.5–43.7°, for a total of 63% of theoretical. Recrystallization of the hydrochloride twice from benzene–ethanol–ethyl acetate gave a sample of m.p. 104–105°.

Anal. Calcd. for $C_{16}H_{28}ClNO$: Cl, 12.4; N, 4.9; neut. equiv., 285.8. Found: Cl, 12.3; N, 4.9; neut. equiv., 286.

Two recrystallizations of the amino alcohol from aqueous methanol, then from ether–petroleum ether, gave a sample of m.p. 43–44°.

Anal. Calcd. for $C_{16}H_{27}NO$: C, 77.1; H, 10.9; N, 5.6. Found: C, 77.1; H, 10.7; N, 5.7.

4-Anilino-1-butanol (a) From Tetramethylene Chlorohydrin.—Aniline (93 g., 1 mole), tetramethylene chlorohydrin (54.25 g., 0.5 mole) and benzene (100 ml.) were refluxed for 26 hours in a 500-ml. round-bottom flask equipped with a suitable condenser. At the end of this time the supernatant liquid was decanted from the precipitate of aniline hydrochloride and combined with a little benzene used to rinse this precipitate. After distillation of the benzene at atmospheric pressure and the excess aniline at 3 mm. pressure, there was obtained 20 g. of nearly colorless product; b.p. 139–140° (3 mm.); $n^{20}D$ 1.565; yield 24%. In some runs an intermediate fraction, b.p. 85–100° (3 mm.), possibly N-phenylpyrrolidine, was obtained.

(b) **From Succinanilic Acid.**—Following the procedure described for 10-anilino-1-decanol a 42% yield of crude 4-anilino-1-butanol, distilling between 127–137° (*ca.* 2 mm.), was obtained by the reduction of succinanilic acid, using the following reagents: lithium aluminum hydride (5.9 g., 0.154 mole) in dry ether (100 ml.), and succinanilic acid (9.1 g., 0.047 mole) suspended in dry ether (150 ml.). Decomposition of the reaction mixture was effected as before. An analytical sample of the product distilled at 133° (*ca.* 1 mm.); $n^{20}D$ 1.563.

Anal. Calcd. for $C_{10}H_{15}NO$: N, 8.5. Found: N, 8.3.

4-Anilino-1-butanol formed a bright yellow, granular picrate (crystals pptd. from ether), m.p. 98–99°.

Anal. Calcd. for $C_{16}H_{18}N_4O_8$: C, 48.75; H, 4.6; N, 14.2; neut, equiv. 394.3. Found: C, 48.7; H, 4.6; N, 14.4; neut. equiv. 394.

2-*t*-Butylaminoethanol.—In a 500-ml. three-necked flask equipped with a reflux condenser, stirrer, dropping funnel and thermometer were placed 68.7 g. (0.94 mole) of *t*-butylamine, 200 ml. of water and 110 g. (1.04 moles) of sodium carbonate. By means of an ice-bath the temperature was held at 25–30° while 135 g. (0.945 mole) of β-chloroethylchloroformate was dropped slowly into the stirred reaction mixture (*ca.* one hour). Stirring was continued for about two hours, after which the contents of the flask were allowed to stand at room temperature overnight before the accumulated precipitate of the crude carbamate was collected on a filter and washed with ether. The aqueous filtrate was extracted with ether and the combined ethereal extracts evaporated in a stream of air to give a small additional amount of product.

The crude β-chloroethyl-N-*t*-butylcarbamate (150 g., 90% yield) was then placed in a 2-l. flask, cyclized, hydrolyzed and decarboxylated in one operation by the cautious addition of potassium hydroxide (224 g., 4 moles) in methanol (900 ml.). This step was somewhat exothermic. Refluxing for two hours completed the reaction after which the inorganic precipitate was filtered. Excess dry potassium carbonate was added to the filtrate, allowed to remain for two hours, then filtered. The alcohol was then evaporated and the product was distilled under reduced pressure into a receiver attached directly to the large-bore arm of a Claisen type head. The 2-*t*-butylaminoethanol was collected as long, hygroscopic white needles; over-all yield: 48.7 g., 44%, b.p. 72° (14 mm.) and 84° (20 mm.), m.p. 43–45°.

Anal. Calcd. for $C_6H_{15}NO$: N, 11.9; neut. equiv., 117.2. Found: N, 12.2; neut. equiv., 117.

This compound gave a bright yellow picrate; crystals from methanol, m.p. 156–157°.

Anal. Calcd. for $C_{12}H_{18}N_4O_8$: C, 41.7; H, 5.2; N, 16.2. Found: C, 41.7; H, 5.2; N, 16.0.

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[2] Roger Adams and J. B. Segur, THIS JOURNAL, 45, 785 (1923); J. B. Pierce with Roger Adams, *ibid.*, 45, 790 (1923).

On the Melting Point, Oxidation, and Vapor Pressure of Lead Bromide

BY J. L. HYDE

Disagreement in the literature regarding the m.p. of lead bromide, as recently reviewed by Knowles,[1] clearly indicates some difficulty in the preparation of the pure compound. The present investigation reports some factors affecting the purity of $PbBr_2$, which is now known to melt at 370°,[1,2] and indicates errors in most of the available thermodynamic data, arising from the use of impure samples reported to melt at 488°.

In this work, Mallinckrodt lead bromide (No. 0469) was used as a starting material. It gave lead and bromine analyses corresponding to less than 2 mole % of a basic bromide (calculated as $PbO_{1/2}Br$). It also gave an X-ray powder pattern closely corresponding to that obtained for $PbBr_2$ by Calingaert, Lamb and Meyer,[2] but differing considerably from the earlier pattern given by Hanawalt, Rinn and Frevel.[3]

Attempted recrystallization from distilled water gave a solution of approximately *p*H 3 and an undissolved residue due to hydrolysis. Analysis of a typical residue corresponded to about 78 mole % $PbO_{1/2}Br$.

Recrystallization of the Mallinckrodt lead bromide was successfully carried out in 0.001 *N* hydro-

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[1] Knowles, THIS JOURNAL, 72, 4817 (1950).

[2] Calingaert, Lamb and Meyer, *ibid.*, 71, 3709 (1949).

[3] Hanawalt, Rinn and Frevel, *Ind. Eng. Chem., Anal. Ed.*, 10, 457 (1938).