ω-Amino-3,6-dimethoxy-2-nitroacetophenone Hydrochloride.—To a stirred suspension of 21 g. of hexamethylene tetramine in 150 ml. of chlorobenzene at room temperature was added in one portion 45.6 g. of ω-bromo-3,6-dimethoxy-2-nitroacetophenone. The mixture was stirred at 60–70° for 4.5 hours, then chilled in an ice-bath and filtered. The dried, yellow powder, which weighed 62 g., was stirred at room temperature for 18 hours with 140 ml. of 95% ethanol and 70 ml. of concentrated hydrochloric acid. The yellow solid was recovered by filtration and stirred for 20 minutes with 70 ml. of water. The suspension was chilled and filtered. The yellow product weighed 31.5 g. (71%). A small sample was recrystallized with high recovery from 10% hydrochloric acid as long yellow needles, m.p. 222–223° (dec.).

Anal. Calcd. for $C_{10}H_{13}O_5N_2Cl$: C, 43.4; H, 4.71; N, 10.12. Found: C, 43.1; H, 4.73; N, 10.18.

ω-Acetamido-3,6-dimethoxy-2-nitroacetophenone.—Twenty-seven and one-half grams of ω-amino-3,6-dimethoxy-2-nitroacetophenone hydrochloride was acetylated by the procedure of Long and Troutman[3] with 19.2 ml. of acetic anhydride and 27.6 g. of sodium acetate trihydrate, followed by 60 ml. of concentrated hydrochloric acid. The dried product weighed 25 g. (87%). A small portion was recrystallized with high recovery from ethyl acetate. The short, thick yellow needles melted with reddening and partial sublimation at 170–173°.

Anal. Calcd. for $C_{12}H_{14}O_6N_2$: C, 51.1; H, 5.00; N, 9.92; $-OCH_3$, 22.0. Found: C, 51.4; H, 5.24; N, 9.93; $-OCH_3$, 21.9.

1-(3,6-Dimethoxy-2-nitrophenyl)-2-acetamidoethanol.—Twenty-four grams of ω-acetamido-3,6-dimethoxy-2-nitroacetophenone was reduced with a solution of 24.2 g. of aluminum isopropoxide in 205 ml. of isopropyl alcohol by the procedure of Long, *et al.*[3,4] The reaction mixture was hydrolyzed with 25 ml. of water and the product extracted out with hot 80% isopropyl alcohol. Light tan crystals weighing 17.5 g. (73%), m.p. 168° (dec.), were obtained by chilling, then concentrating the extracts. A small sample was recrystallized from hot water as thick, tan crystals, m.p. 169° (dec.).

Anal. Calcd. for $C_{12}H_{16}O_6N_2$: C, 50.7; H, 5.68; N, 9.85; $-OCH_3$, 21.9. Found: C, 50.4; H, 5.88; N, 9.83; $-OCH_3$, 21.7.

1-(3,6-Dimethoxy-2-nitrophenyl)-2-aminoethanol.—A mixture of 17.5 g. of 1-(3,6-dimethoxy-2-nitrophenyl)-2-acetamidoethanol and 200 ml. of 5% hydrochloric acid was stirred at 100° for six hours. The resulting solution was filtered and made basic with 25% sodium hydroxide while still hot. Twelve and one-half grams (84%) of light tan crystals was obtained on cooling. A small sample was recrystallized twice from hot water (Norite). The light tan, shining platelets melted at 171° (dec.) using the technique of Cortese and Bauman.[11]

Anal. Calcd. for $C_{10}H_{14}O_5N_2$: C, 49.6; H, 5.83; N, 11.56. Found: C, 49.4; H, 6.00; N, 11.41.

1-(3,6-Dimethoxy-2-nitrophenyl)-2-dichloroacetamidoethanol.—A mixture of 12.5 g. of 1-(3,6-dimethoxy-2-nitrophenyl)-2-aminoethanol and 75 ml. of methyl dichloroacetate was warmed at 75° for two hours with occasional swirling. The dark solution was filtered and the filtrate evaporated to dryness on a steam-bath under reduced pressure (30 mm.). The residue was washed with two small portions of chloroform. The yellow powder which remained weighed 10.5 g. and was recrystallized from 2.1 liters of 33% ethanol. The long yellow needles weighed 8.1 g. (46%), m.p. 163–165°. A second recrystallization raised the melting point to 164–166°.

Anal. Calcd. for $C_{12}H_{14}O_6N_2Cl_2$: C, 40.8; H, 4.00; N, 7.93; Cl, 20.1. Found: C, 41.1; H, 4.14; N, 7.85; Cl, 19.6.

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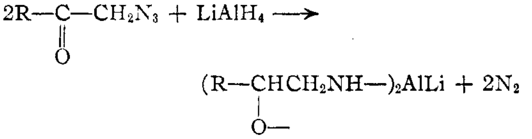
[11] F. Cortese and L. Bauman, THIS JOURNAL, **57**, 1394 (1935).

Reduction of Organic Azides to Primary Amines with Lithium Aluminum Hydride

BY J. H. BOYER

The reduction of aliphatic and aromatic azides to primary amines with lithium aluminum hydride has been realized (1). The reaction provides a new procedure for the preparation of α-aminocarbinols from α-azidoketones (2). Stoichiometrically the reactions may proceed according to the following equations, although in the preliminary experiments shown here a two- to five-fold excess of lithium aluminum hydride was used to assure a positive reaction.

$$4R{-}N_3 + LiAlH_4 \longrightarrow (R{-}NH{-})_4AlLi + 4N_2 \qquad (1)$$



$$2R{-}\underset{\overset{\|}{O}}{C}{-}CH_2N_3 + LiAlH_4 \longrightarrow (R{-}\underset{\overset{|}{O-}}{C}HCH_2NH{-})_2AlLi + 2N_2 \qquad (2)$$

Experimental[1]

Reduction of the azides was carried out under the general conditions for lithium aluminum hydride reduction described by Nystrom and Brown.[2] In each case a suspension of the hydride in dry ether was treated with an ethereal solution of the azide at such a rate that reflux was maintained. Following addition of the azide the mixture was kept at reflux temperature for two hours. Moist ether was then added to destroy the excess lithium aluminum hydride, followed by distilled water to break up the complex. The inorganic salts were removed by filtration and the amines were isolated from the ethereal layer of the filtrate. Modifications found useful for the isolation of the aminoalcohols from the filtrates obtained at this stage in the reduction of the azidoketones are described below.

α-Naphthylamine.—From 1.7 g. (0.01 mole) of α-naphthyl azide[3] in 100 ml. of anhydrous ether and 0.60 g. (0.015 mole) of lithium aluminum hydride in 200 ml. of anhydrous ether there was obtained 1.13 g. (79% based on the azide) of α-naphthylamine, m.p. 50°, alone and when mixed with an authentic sample of α-naphthylamine. The picrate derivative was prepared in ether and recrystallized from aqueous ethanol, m.p. 183–185°, alone and when mixed with an authentic sample.

β-Phenylethylamine.—From 3.0 g. (0.02 mole) of β-phenylethyl azide[4] in 100 ml. of anhydrous ether and 1.0 g. (0.025 mole) of lithium aluminum hydride in 250 ml. of anhydrous ether there was obtained 2.15 g. (89% based on the azide) of β-phenylethylamine (absorbs carbon dioxide), b.p. 190–192°,[5] carbonate, m.p. 105–106°,[6] picrate m.p. 169–170°,[5] and hydrochloride, m.p. 217°.[5]

α-Phenyl-β-aminoethanol.—From 4.6 g. (0.029 mole of phenacyl azide,[7] m.p. 17°, in 250 ml. of anhydrous ether and 1.5 g. (0.04 mole) of lithium aluminum hydride in 300 ml. of anhydrous ether was obtained 1.94 g. of the light yellow α-phenyl-β-aminoethanol, b.p. 135–137° (1 mm.), m.p. 43–45°[8] (49.5% based on the azide). Appreciable solubility in both water and ether accounted for the isolation of this product in roughly equal quantities from the aqueous and ethereal layers of the filtrate obtained from the filtration of the inorganic salts. A picrate derivative was prepared in benzene and recrystallized from a mixture of chloroform and alcohol, m.p. 154–155°.[9]

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[1] Microanalyses by the Clark Microanalytical Laboratory, Urbana, Illinois. Melting and boiling points are uncorrected.

[2] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947).

[3] M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **91**, 1942 (1907).

[4] Generously submitted by Dr. P. A. S. Smith.

[5] A. Wohl and E. Berthold, *Ber.*, **43**, 2183 (1910).

[6] E. Erlenmeyer and A. Lipp, *Ann.*, **219**, 179 (1883).

[7] M. O. Forster and R. Müller, *J. Chem. Soc.*, **97**, 126 (1910).

[8] C. Mannich and E. Thiele, *Arch. Pharm.*, **253**, 181 (1915).

[9] German Patent 193,634, *cf.*, *Chem. Centr.*, **79**, I, 430 (1908).

α-Methyl-β-aminoethanol.—A solution of 5.65 g. (0.056 mole) of triazoacetone,[10] b.p. 54–56° (1 mm.) in 250 ml. of anhydrous ether was slowly added to a suspension of 2.90 g. (0.04 mole) of lithium aluminum hydride in 400 ml. of anhydrous ether. Since the product, α-methyl-β-aminoethanol, is much more soluble in water than it is in ether, it was found convenient to acidify the aqueous layer of the filtrate obtained from the filtration of the inorganic salts with hydrochloric acid and isolate the amine hydrochloride by evaporation of the solvent in an air stream. Purification of the black tarry residue from a boiling mixture of absolute ethanol–ethyl acetate gave colorless hygroscopic prisms only after five to seven days in the refrigerator, wt. 2.25 g. (36.2% yield based on the azide), m.p. 70–73° (lit.[11] m.p. 72.5–74°).

From the ethereal layer of the filtrate 0.50 g. (11.9% based on the azide) of the free aminoalcohol, b.p. 150–160°, was obtained. The total yield of the reaction was 48.1%. A picrate derivative was prepared in ether and recrystallized from a mixture of chloroform and ethanol, m.p. 144–145° (lit.[12] m.p. 142°). A picrolonate was prepared in ether and recrystallized to a constant m.p. 224–225° (decomposition) from a benzene–alcohol mixture.

Anal. Calcd. for $C_{13}H_{17}O_6N_5$: C, 46.01; H, 5.05; N, 20.64. Found: C, 46.20; H, 4.87; N, 20.45.

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[10] M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **93**, 72 (1908).

[11] S. Gabriel and H. Ohle, *Ber.*, **50**, 804 (1917).

[12] E. Peeters, *Rec. trav. chim.*, **20**, 259 (1901).

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The Preparation of Anhydrous Hydrazine and Deutero-hydrazine from Hydrazine Dihydrochloride[1]

BY E. L. BULGOZDY AND E. L. WAGNER

In the course of an investigation to determine the molecular spectra of anhydrous hydrazine and deutero-hydrazine a method for obtaining the anhydrous material was desired which could readily be adapted to preparing the deutero compound on utilizing the appropriate deuterium substituted starting materials. Since the reported methods[2] of synthesizing hydrazine in a practical way are generally carried out in aqueous solution or in other hydrogen-rich media, and the principal methods of concentrating the anhydrous substance utilize hydrazine hydrate as a starting material,[3] a new procedure was sought which, when adapted to the preparation of deutero-hydrazine, would be more parsimonious in its use of deuterium. The method ultimately employed involves the removal of hydrogen chloride from solid hydrazine dihydrochloride by low temperature fusion with the stronger base sodium hydroxide. Sufficient solid sodium hydroxide is required to neutralize the hydrogen chloride plus that necessary to tie up the water formed in the neutralization as sodium hydroxide monohydrate. The fusion was carried out above the melting point of the monohydrate so that after neutralization had taken place the reaction mixture was a relatively homogeneous liquid. Anhydrous hydrazine was removed from this resulting mixture by distillation under reduced pressure using the optimum conditions of Penneman and Audrieth.[3]

In utilizing this procedure for the preparation of anhydrous deuterohydrazine, the hydrochloride salt was first deuterated by two or three successive exchanges with sufficient quantities of deuterium oxide to readily dissolve the salt at the boiling point of the solution. After each exchange the exchange water was evaporated off and the salt residue dried at room temperature under reduced pressure in the usual manner. Subsequent steps in the procedure were conducted so as to prevent re-exchange of the deuterium atoms in the chloride salt with hydrogen atoms in atmospheric moisture or in the reagents. The anhydrous deuterohydrazine produced by this procedure contained less than 0.5% deuterium oxide. From analysis of the infrared and Raman spectra, it was estimated that the resulting compound was more than 90% deuterated.

Experimental Procedure.—Seventy grams of crushed sodium hydroxide was added on top of 40 g. of recrystallized Eastman hydrazine dihydrochloride in a 150-ml. round-bottom flask. This flask was connected by means of a standard taper joint to a short (10 cm.) coarse packed fractionating column which in turn was connected to a water-cooled condenser and receiver. This all glass system could be maintained at any desired reduced pressure by allowing dry nitrogen to leak in through a controllable bleeder valve while the system was being evacuated. After thoroughly flushing with dry nitrogen the system was evacuated and maintained at a pressure of 200–250 mm. while the flask and its contents were being heated on an oil-bath. Reaction at the interface between the two solids usually commenced when the bath temperature reached about 100°. The resulting reaction proceeded vigorously and was completed in 20–40 minutes. This is the crucial step in the process as well as the most dangerous and care must be exercised to prevent the reaction from becoming too violent. In general, immediate removal of the oil-bath at the inception of the reaction was a sufficient control. After completion of the initial neutralization reaction the temperature of the reaction mixture was lowered to 65° (bath 75–80°) and the pressure reduced to 100–110 mm. Under these conditions a cut of 6–7 of the possible 12 ml. of anhydrous hydrazine was distilled over in two hours.

Analyses.—The direct iodate titration method using carbon tetrachloride[2] to extract the iodine was used to analyze the products of this procedure for purity. The accompanying table lists the results of several different preparations.

Sample weight, g.	0.025 *M* KIO_3, ml.	N_2H_4, %
0.0432	53.61	99.8
.0436	55.98	99.4
.0438	54.01	98.6
.0437	54.40	99.6
.0625	77.56	99.3
.0623	77.54	99.5

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[1] Taken from a thesis submitted by Eugene L. Bulgozdy in partial fulfillment of the requirements for the degree of Master of Science at the State College of Washington.

[2] L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951.

[3] R. A. Penneman and L. F. Audrieth, THIS JOURNAL, **71**, 1644 (1949).

The 2,4-Dinitrophenylhydrazones of the Alkyl Phenyl Ketones

BY L. I. BRADDOCK AND MARY L. WILLARD

Attempts to prepare the 2,4-dinitrophenylhydrazones of the symmetrical, aliphatic ketones with