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

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

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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