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 $C_{13}H_{17}O_8N_5$: 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).

CHEMISTRY DEPARTMENT
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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

TABLE I

Carbonyl compound, ketone	Physical appearance of 2,4-dinitrophenylhydrazone	Ultraviolet absorption, maxima	M.p., °C.	Dumas Nitrogen, % Calcd.	Dumas Nitrogen, % Obsd.
n-Hexyl phenyl	Red monoclinic prisms showing all pinacoid views	378	135.0	15.13	15.07
	Orange monoclinic plates	378	135.0	15.13	14.63
n-Heptyl phenyl	Orange monoclinic plates lying on 010; very thin	379	103.0–103.5	14.58	14.38
n-Tridecyl phenyl	Orange plates; very thin; either monoclinic or triclinic	382	100.0–100.1	11.96	11.90
n-Pentadecyl phenyl	Orange monoclinic plates lying on 010	375	98.0–99.0	11.28	11.10
n-Heptadecyl phenyl	Orange monoclinic tablets lying on 100 and 010	380	98.0–99.0	10.68	10.79

more than seven carbon atoms result in the formation of oils and solid solutions. In order to learn more about the effect of large alkyl side chains on the formation of 2,4-dinitrophenylhydrazones, derivatives of several alkyl phenyl ketones were prepared by Brady's[1] method. None of the above mentioned difficulties was observed. It is believed that the two forms of hexyl phenyl ketone 2,4-dinitrophenylhydrazone are polymorphs. Both exhibit the same melting point and the same ultraviolet absorption maxima. There is no resultant melting point depression when the two are mixed. The results of the work are summarized in Table I.

The *n*-hexyl phenyl ketone 2,4-dinitrophenylhydrazone was previously reported as one form melting at 135.0°[2]; the *n*-tridecyl phenyl ketone derivative was reported as melting at 98.0 to 98.5°.[2]

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[1] O. L. Brady, *J. Chem. Soc.*, 756 (1931).

[2] T. Y. Ju, G. Shen and C. E. Wood, *J. Inst. Petroleum*, **26**, 514 (1940).

DEPARTMENT OF CHEMISTRY
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The Heat of Solution of Lithium in Ammonia at −33°

BY LOWELL V. COULTER AND LOUIS MONCHICK

A common heat of reduction of ammonium ion in liquid ammonia by dilute solutions of sodium, potassium and cesium[1] has indicated an identical state for the reducing agent, "the solvated electron," in moderately dilute solutions of these metals. For this reaction represented by the equation

$$^1/_2e_2^-(\mathrm{am}) + \mathrm{NH_4}^+(\mathrm{am}) = \mathrm{NH_3}(\mathrm{l}) + {^1/_2}\mathrm{H_2}(\mathrm{g}) \quad (1)$$

$\Delta H = -40.4 \pm 1$ kcal. per equivalent which has been calculated from the experimentally measured heats of solution of these metals in pure ammonia[2] and the heats of reaction of the solid metals with ammonium ion in liquid ammonia.[1] For this reaction in lithium solutions, however, $\Delta H = -42.5$ kcal. based, in part, on 8.0 kcal.[2] for the exothermic heat of solution of lithium in pure ammonia. Indication of typical alkali metal behavior has been obtained for lithium solutions, however, by Coulter and Maybury[1] who have obtained $\Delta H = -40.9$ kcal. for equation 1 based on a single redetermination of the heat of solution of lithium in pure ammonia.

In view of the significance of this thermochemical value for the proper understanding of lithium metal solutions relative to the other alkali metals we have remeasured the heat of solution of lithium in liquid ammonia over the concentration range 150 to 600 moles of ammonia per gram atom of metal.

The calorimetric procedure employed in this research has already been described.[1] To ensure the complete elimination of water from the calorimeter solvent, anhydrous ammonia was distilled directly into the calorimeter from an ammonia solution of sodium metal.

The lithium used for the measurements was obtained from the Metalloy Corporation and was specified to have a low sodium content as indicated by the following typical analysis furnished by the supplier: Na, 0.005%; K, 0.005%; Ca, 0.02%; N, 0.06%. Analysis, in this research, by the collection of evolved gas upon solution in water indicated 101.2% lithium. Titration for total alkalinity gave a purity of 99.6%. Samples were prepared by cutting cylinders of the metal from ingots under oil followed by anhydrous benzene rinses and storage of the samples in evacuated fragile sample bulbs.

The results of the measurements are presented in Table I.

TABLE I

Sample wt., g.	Moles NH_3/Li	Obsd. heat effect, cal.	$-\Delta H$, kcal.
0.3038	154	425.0	9.71
.1811	277	251.6	9.64
.1059	461	148.2	9.71
.1001	525	136.0	9.43
.0782	599	110.3	9.78
Mean			9.65 ± 0.2

For the concentration range 150 to 600 moles of ammonia per gram atom of lithium the mean value, 9.65 kcal., is in good agreement with the single value, 9.55 kcal., at a dilution ratio of 99 previously reported from this Laboratory.[1]

As a consequence, the earlier tentative value for the ΔH of equation 1 remains essentially unchanged at −40.8 kcal. for lithium solutions thereby confirming the earlier conclusion that lithium forms a typical alkali metal solution with ammonia in the moderately dilute region.

Experiments now in progress indicate that an energy absorption process, presumably the uncoupling of electron spins, is associated with the dilution of potassium solutions having a concentration ratio of ~100 moles NH_3/K. In accordance with

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[1] L. V. Coulter and R. H. Maybury, THIS JOURNAL, **71**, 3394 (1949).

[2] C. A. Kraus and F. C. Schmidt, *ibid.*, **56**, 2298 (1934), and F. C. Schmidt, F. J. Studer and J. Sottysiak, *ibid.*, **60**, 2780 (1938).