Reaction of Cyanogen Bromide with Some Alkyl Hydrazines

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During the course of an investigation of the lower alkyl hydrazines in this Laboratory it became of interest to study their reaction with cyanogen bromide. Pellizzari and co-workers[1] found that hydrazine and cyanogen bromide reacted to form aminoguanazol, $H_2NNC(NH)NH$-$NHCNH$, and diaminoguanidine depending upon the mole ratio of the reactants. Phenylhydrazine reacting in aqueous solution with cyanogen bromide gave 1-cyano-1-phenylhydrazine as well as phenylsemicarbazide and diphenyldiaminoguanidine hydrobromide.[2]

In the present investigation the first compound studied was trimethylhydrazine. This compound was chosen because it had only one position open for substitution and would be unlikely to undergo side reactions. The reaction of trimethylhydrazine with cyanogen bromide in ether gave 1-cyano-1,2,2-trimethylhydrazine. Similar reactions of cyanogen bromide with 1,1-dimethylhydrazine and 1,1-diethylhydrazine gave 1-cyano-2,2-dimethylhydrazine and 1-cyano-2,2-diethylhydrazine, respectively. All three cyanohydrazines exhibited a strong cyano group absorption at 4.5–4.55μ in their infrared spectra. Addition of a solution of anhydrous oxalic acid in ether to an ether solution of 1-cyano-1,2,2-trimethylhydrazine did not result in the formation of a crystalline oxalate as usually occurs with other hydrazines which have been studied previously. Under the same conditions, crystalline oxalates were formed by the two other cyanohydrazines which were prepared. The behavior of the 1-cyano-1,2,2-trimethylhydrazine might be attributed to the strongly electron withdrawing action of the cyano group which decreases the basicity of the nitrogen atoms. This difference in salt-forming ability seems to be in accord with the findings of Hinman[3] whose work indicates that substitution of alkyl groups for hydrogens in the hydrazine molecule is accompanied by a decrease in basicity. None of the three cyanohydrazines would reduce potassium iodate in $6N$ hydrochloric acid solution.[4] Again, it appears possible that the cyano group had reduced the availability of the electrons on the nitrogen atoms to such a degree that oxidation by acidic iodate solutions did not take place.

EXPERIMENTAL

Starting Materials. Trimethylhydrazine was prepared by the method of Class, Aston, and Oakwood.[5] Commercial 1,1-dimethylhydrazine (Westvaco) was used without further purification. The 1,1-diethylhydrazine was a special sample prepared for this laboratory by Commercial Solvents Corp. and was also used without further purification. Cyanogen bromide was obtained from Eastman Kodak Co. It had no trace of color and dissolved in ether to give a clear solution.

Reaction of trimethylhydrazine with cyanogen bromide. A solution of 31.2 g. (0.30 mole) of cyanogen bromide in 200 ml. of ether was slowly added to 44.4 g. (0.60 mole) of trimethylhydrazine in 150 ml. of ether. The temperature was held at 0° during the addition which required 1 hr. As addition progressed the solution became cloudy and white solid trimethylhydrazine hydrobromide precipitated. After completion of the reaction, the mixture was stirred and refluxed for 0.5 hr. longer and then allowed to stand for 16 hr. The ether solution was removed from the solid by decantation and the solid washed three times with small portions of ether. The ether solution and washings were combined, dried over calcium sulfate, and the ether removed by flash distillation. The crude product was purified by vacuum distillation through a small Vigreux column. From this distillation was obtained 23.5 g. (79.2%) of 1-cyano-1,2,2-trimethylhydrazine boiling at 66.3–67.8°/30–32 mm.; n_D^{25} 1.4222. Cryoscopic determination of the molecular weight in nitrobenzene solvent gave a value of 99.0 (theor., 99.1).

Anal. Calcd. for $C_4H_9N_3$: C, 48.46; H, 9.15; N, 42.29. Found: C, 48.28; H, 8.94; N, 42.39.

Reaction of 1,1-dimethylhydrazine with cyanogen bromide. A solution containing 24 g. (0.40 mole) of 1,1-dimethylhydrazine in 100 ml. of ether was slowly added to 21.2 g. (0.20 mole) of cyanogen bromide in 100 ml. of ether over a period of 25 min. The temperature was maintained at −10° to −20° during the addition. When addition was complete the solution was stirred for 10 min. longer and then decanted from the solid 1,1-dimethylhydrazine hydrobromide (31.6 g.) which had precipitated. The precipitate was washed with two small portions of ether and the washings and solution were combined. After drying over calcium sulfate, the solution was filtered and the ether removed by distillation under slightly reduced pressure. The residual liquid crystallized in the flask. The yield of crude product was 10 g. (59%). The product was soluble in water, acetone, ethyl acetate, alcohol, tetrahydrofuran, benzene, and ethylene dichloride. Ethyl acetate proved the most satisfactory solvent for recrystallization of the product. The recrystallized 1-cyano-2,2-dimethylhydrazine melted at 128–129.5° with decomposition.

Anal. Calcd. for $C_3H_7N_3$: C, 42.33; H, 8.29; N, 49.38. Found: C, 42.24; H, 8.16; N, 49.14.

An oxalate salt was also prepared from the ether solution of the product and recrystallized from a mixture of ethyl alcohol and ethyl acetate. This salt melted at 154.5–155° and had the composition $2(C_3H_7N_3).H_2C_2O_4$ as indicated by analysis.

Anal. Calcd. for $C_8H_{16}N_6O_4$: C, 36.92; H, 6.20; N, 32.20. Found: C. 36.95; H, 6.04; N, 32.13.

Reaction of 1,1-diethylhydrazine with cyanogen bromide. The reaction was carried out in a manner similar to that for 1,1-dimethylhydrazine and cyanogen bromide. A solution containing 35.2 g. (0.40 mole) of 1,1-diethylhydrazine in ether was treated with 21.2 g. (0.20 mole) of cyanogen

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(1) (a) G. Pellizzari and C. Cantoni, *Ber.*, **38**, 283 (1905). (b) G. Pellizzari and C. Cantoni, *Gazz. chim. ital.*, **35**, 291 (1905). (c) G. Pellizzari and A. Repetto, *Gazz. chim. ital.*, **37**, 317 (1907).

(2) G. Pellizzari, *Gazz. chim. ital.*, **37**, 611 (1907).

(3) R. L. Hinman, *J. Org. Chem.*, **23**, 1587 (1958).

(4) R. A. Penneman and L. F. Audrieth, *Anal. Chem.*, **20**, 1058 (1949).

(5) J. B. Class, J. G. Aston, and T. S. Oakwood, *J. Am. Chem. Soc.*, **75**, 2938 (1953).

bromide in ether. From this reaction was obtained 11.6 g. (51.3%) of crude 1-cyano-2,2-diethylhydrazine. After several recrystallizations from ethyl acetate using Norite A decolorizing carbon the product melted at 115.5–116.8°.

Anal. Calcd. for $C_5H_{11}N_3$: C, 53.07; H, 9.80; N. 37.14. Found: C, 53.35; H, 10.00; N, 37.11.

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Preparation and Reduction of Methylvinylnitrosamine

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As a part of the investigation of hydrazines and related compounds in this laboratory, attempts were made to prepare 1-methyl-1-vinylhydrazine. One route to the synthesis of this compound appeared to lie through the reduction of methylvinylnitrosamine. This nitrosamine was selected because it has been found that the nitroso group in diallylnitrosamine can be reduced to give the corresponding hydrazine leaving the carbon-carbon bonds intact.[1] Methylvinylnitrosamine was synthesized in 51.7% yield from β-hydroxyethylmethylamine through nitrosation, chlorination, and dehydrohalogenation. It was later found that Workman[2] had prepared methylvinylnitrosamine in a similar manner during the course of a study undertaken to determine the products resulting from the thermal decomposition of β-chloroethylmethylnitrosamine.

Reduction of methylvinylnitrosamine was attempted with a number of reducing agents. The first reactions were carried out with lithium aluminum hydride in ether. Because the desired compound was not obtained, several variations of the hydride reduction were investigated. These included reverse addition of the hydride solution to the nitrosamine solution, change in solvent to tetrahydrofuran, and variation of the amount of hydride. None of these methods gave 1-methyl-1-vinylhydrazine. From the crude reaction mixtures only methylhydrazine and 1-ethyl-1-methylhydrazine were isolated and identified. Other fractions were separated from the reaction mixture but were too small and impure to identify. Reduction with sodium borohydride was also attempted after first verifying that dimethylnitrosamine could be reduced to 1,1-dimethylhydrazine by the borohydride. Small yields were obtained when the reaction was carried out in water at 70° for eight hours. Similar treatment of methylvinylnitrosamine, however, gave no reaction and the compound was recovered unchanged.

Other reducing agents included sodium hydrosulfite in basic solution. Reaction of this reagent with methylvinylnitrosamine gave a 63.5% yield of methylamine which was identified as its oxalate. Traces of ammonia also were produced. Reduction with sodium in liquid ammonia of methylvinylnitrosamine did not give an isolable product. Only a brown solid residue was obtained from this reaction. Catalytic hydrogenation of methylvinylnitrosamine also was attempted a number of times because it seemed to offer an easy method for isolation of the product. Catalysts employed were freshly activated palladium on charcoal, palladium on gum arabic, and platinum oxide. The reductions were run in ethyl alcohol either with a trace of hydrochloric acid or a trace of acetic acid. The solutions from these reductions had the power to reduce potassium iodate but the concentration of the products was such that no volatile products could be isolated. Hydrogenation in ethyl alcohol without acid using platinum oxide catalyst gave a 53.4% yield of ethylmethylnitrosamine.

In the course of an alternative procedure for the preparation of 1-methyl-1-vinylhydrazine, an effort was made to prepare 1-β-chloroethyl-1-methylhydrazine as an intermediate which could be dehydrohalogenated. Reduction of β-chloroethylmethylnitrosamine with lithium aluminum hydride in ether, however, gave a 54.2% yield of crude 1-ethyl-1-methylhydrazine. Similar results were obtained by Wawzonek and Culbertson[3] in the lithium aluminum hydride reduction of *n*-butyl-4-chlor-*n*-butylnitrosamine. The reduction produced mainly 1,1-di-*n*-butylhydrazine and di-*n*-butylnitrosamine.

EXPERIMENTAL

β-Hydroxyethylmethylnitrosamine. To 751.1 g. (10.0 moles) of β-methylaminoethanol (Eastman Kodak Co.) was added approximately 200 ml. of water. While cooling the flask in an ice bath the amine solution was made just acid to litmus with 835 ml. of concd. hydrochloric acid. The solution was then heated to 70–75°, and 793 g. (11.5 moles) of sodium nitrite dissolved in 1 l. of water was added slowly through a dropping funnel. Addition required 2 hr. during which time the reaction mixture was held at the above temperature. Additional small quantities of concentrated hydrochloric acid were added from time to time to keep the solution acidic. After completion of the sodium nitrite addition, the mixture was held at reaction temperature and stirred for an hour longer. It was then cooled to room temperature and the precipitated inorganic salts removed by filtration. Most of the water and ethyl alcohol were removed from the product by means of a rotating vacuum evaporator. Final purification was accomplished by distillation at reduced pressure. The yield of bright yellow β-hydroxyethylmethylnitrosamine was 1019.5 g. (97.9%) boiling at 110.5–111.5°/1.0 mm., n_D^{25} 1.4778.

β-Chloroethylmethylnitrosamine. A solution of 312.3 g. (2.5 moles) of β-hydroxyethylmethylnitrosamine in 600 ml. of dry thiophene-free benzene was prepared and cooled to

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(1) Unpublished results.

(2) W. R. Workman, *Dissertation Abstr.*, **15**, 1733 (1955).

(3) S. Wawzonek and T. P. Culbertson, *J. Am. Chem. Soc.*, **81**, 3367 (1959).