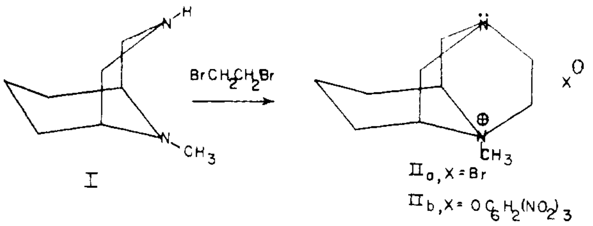
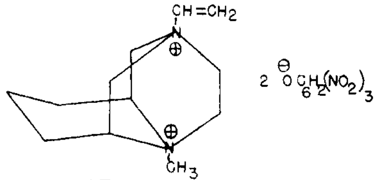


sulting from establishment of ethylene bridges between the nitrogen atoms of two molecules of I.

The 9-vinyl structure is eliminated because the infrared curve for IIb shows no absorption at 2.9–3.2 μ (N–H band). The 3-vinyl structure is also eliminated since this would be a di-tertiary amine containing no quaternary nitrogen atom.

The observation by Mann and Mukherjee[2] that only traces of a dimeric substance were formed in the reaction of N,N′-dimethylpiperazine with ethylene bromide strongly suggests that II is monomeric. As these authors point out, the dimeric compound demands effectively planar piperazine rings in order to preserve the normal intervalency angle of tri- or tetracovalent nitrogen (*ca.* 110°). Even less dimer might be expected from I since favored configurations of this bicyclic system require a puckered piperazine ring.

When the reaction was run with an excess of ethylene bromide at 130° the sole product isolated upon addition of lithium picrate was a neutral quaternary ammonium picrate whose analysis agreed with the values calculated for compound III.



III

This substance could have resulted from the reaction of IIa with additional ethylene bromide followed by elimination of hydrogen bromide. Compound III exhibited two peaks (6.12, 6.20 μ) in the infrared region assigned to double bonds while compound IIb showed only one peak at 6.08 μ.

Experimental[3]

9-Methyl-3,9-diazabicyclo[3.3.1]nonane (I).—This compound, isolated previously as a dihydrochloride, was obtained as the free base by adding strong alkali to a concentrated aqueous solution of the hydrochloride followed by rapid extraction with ether. Evaporation of the dried solvent left a volatile semi-crystalline mass having a typical amine odor. The compound rapidly absorbed carbon dioxide and water from the air forming a solid carbonate, m.p. 69–70° dec.

The free amine was repeatedly sublimed at 70° (15 mm.) finally forming short prisms, m.p. 62–65° (sealed, evacuated capillary). Recrystallization was impossible since the compound was very soluble in ice-water, alcohols and even cold petroleum ether.

Anal. Calcd. for $C_8H_{16}N_2$: N, 19.98. Found: N, 19.24 (by $HClO_4$ titration in glacial acetic acid).

The dihydriodide after recrystallization from water did not decompose up to 280°.

Anal. Calcd. for $C_8H_{18}N_2I_2$: C, 24.26; H, 4.58. Found: C, 24.18; H, 4.62.

The presence of a secondary amine was demonstrated by the preparation of an N-picryl picrate. A small sample of the free amine was treated with an excess of picryl chloride in ethanol. After the solution had been allowed to stand overnight, a concentrated solution of lithium picrate was added and the N-picryl picrate precipitated. After three recrystallizations from dimethylformamide–ethanol mixtures the product melted at 263–266° dec.

Anal. Calcd. for $C_{20}N_8O_{13}$: C, 41.38; H, 3.47. Found: C, 41.84; H, 3.52.

9-Methyl-3,9-diazatricyclo[3.3.1.2^{3,9}]undecane Picrate (IIb).—The carbonate of I (0.53 g.) was heated in 10 ml. of toluene to drive off water and carbon dioxide. Ethylene bromide (0.75 g.) was added to the cooled solution which was then allowed to stand at 40° for several days. After removing the toluene and excess ethylene bromide on the aspirator a basic solution of lithium picrate was added and the precipitated salt collected and washed with ether. The dried product (0.44 g., *ca.* 64%) was recrystallized from either formamide–isobutyl alcohol or dimethylformamide–ethanol mixtures and formed long brown needles. Successive recrystallizations caused the picrate to become bright yellow, m.p. 275–280° (dec. without evolving gas).

Anal. Calcd. for $C_{16}H_{21}N_5O_7$: C, 48.60; H, 5.35. Found: C, 48.42, 48.56; H, 5.62, 5.40.

The corresponding bromide (IIa) was obtained through quaternization as above followed by evaporation of solvents and addition of 98% ethanol. This precipitated the dihydrobromide salt of unchanged starting material. Evaporation of the mother liquors from this precipitate left a crystalline product which was crystallized from alcohol–ethyl acetate or moist isobutyl alcohol. The product apparently retained water of crystallization even when dried at 100° (0.005 mm.); m.p. 243–247°.

Anal. Calcd. for $C_{10}H_{19}N_2Br \cdot H_2O$: C, 45.29; H, 7.98; N, 10.57. Found: C, 45.65; H, 7.96; N, 10.47.

A sample of the bromide was treated with aqueous lithium picrate and the resulting precipitate recrystallized from dimethylformamide–ethanol. The resulting light-yellow needles decomposed at 275–280°. For substances of this type the mixture melting point technique is unreliable, therefore X-ray diffraction photographs were taken both of the picrate from the above bromide and that obtained directly. Their powder diagrams were identical.

Both of the above picrates formed salts with additional picric acid. After recrystallization from dimethylformamide–ethanol the salts both decomposed at 225–230° and evolved picric acid.

Compound III, suspected to have the structure shown, was obtained by suspending a sample of the carbonate (1.44 g.) of I in a large excess of ethylene bromide (4.0 g.) and refluxing the solution for 20 minutes. Evaporation of the ethylene bromide and addition of basic lithium picrate precipitated a light-yellow solid (0.925 g.). After several recrystallizations from dimethylformamide–isobutyl alcohol mixtures the silky yellow needles decomposed at 272–280°. This compound did not combine with additional picric acid.

Anal. Calcd. for $C_{24}H_{26}N_8O_{14}$: C, 44.31; H, 4.03; N, 17.23. Found: C, 44.70; H, 4.31; N, 17.29.

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[2] F. G. Mann and Deb. P. Mukherjee, *J. Chem. Soc.*, 2298 (1949).

[3] Microanalyses by W. Manser, Zurich, Switzerland, and J. F. Alicino, Metuchen, N. J. All melting points were observed on a Köfler hot-stage.

Triazines. VII. The Reaction of Cyanuric Chloride with Lithium Aluminum Hydride[1]

BY CHRISTOPH GRUNDMANN AND ELFRIEDE BEYER

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Recently Burger and Hornbaker[2] described the reduction of cyanuric chloride with lithium aluminum hydride which leads to formation of 2-dimeth-

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[1] Paper VI, C. Grundmann and A. Kreutzberger, THIS JOURNAL, **76**, 632 (1954).

[2] A. Burger and E. D. Hornbaker, *ibid.*, **75**, 4579 (1953).

ylamino-4,6-dichloro-1,3,5-triazine instead of the desired monochlorotriazine. In the course of numerous attempts to prepare 1,3,5-triazine from known triazine derivatives[3] we also studied this reaction some time ago.

An excess of lithium aluminum hydride in ethereal solution at room temperature converts cyanuric chloride almost completely into a mixture of inorganic compounds insoluble in ether, consisting mainly of lithium chloride, aluminum chloride and lithium aluminum cyanide, $LiAl(CN)_4$. The ether contains only traces of organic material. During the reaction hydrogen is evolved. Since these experiments have been carried out, we have discovered that 1,3,5-triazine is identical with the long known compound erroneously described as the dimer of hydrocyanic acid,[1] and we feel therefore now able to give a possible explanation of the path of this reaction

$$3LiAlH_4 + 4C_3N_3Cl_3 \longrightarrow 3LiCl + 3AlCl_3 + 4C_3H_3N_3 \quad (A)$$

The so-formed triazine is then catalytically depolymerized by the aluminum chloride[4]

$$4C_3H_3N_3 \longrightarrow 12HCN \quad (B)$$

Hydrocyanic acid reacts with lithium aluminum hydride according to Wittig and Bille[5]

$$3LiAlH_4 + 12HCN \longrightarrow 3LiAl(CN)_4 + 12H_2 \quad (C)$$

As it is impossible to isolate either triazine or hydrocyanic acid even when working with the stoichiometrical amount of the reducing agent, reactions B and C must occur with a higher rate than A. However, adding an insufficient amount of lithium aluminum hydride to a large excess of cyanuric chloride in ethereal solution at −10° enabled us to separate by fractional sublimation from the unreacted starting material 2,4-dichloro-1,3,5-triazine, in small yield, obviously the first intermediate in the reduction of cyanuric chloride according to A. From the less volatile parts of the reaction mixture we obtained as a further by-product 2-dimethylamino-4,6-dichloro-1,3,5-triazine indicating that part of the triazine formed according to equation A undergoes further hydrogenolysis to dimethylamine which then reacts with unchanged cyanuric chloride.[2] Even under these conditions the main reaction product is a mixture of ether-insoluble salts as mentioned above.

2,4-Dichloro-1,3,5-triazine is a volatile crystalline compound, m.p. 50–52°, with a pungent odor similar to cyanuric chloride but much more irritating. It is identical with the product obtained by mixed polymerization of hydrocyanuric acid and cyanogen chloride[6] following the general method described some time ago.[7] Water hydrolyzes it at least as easily as cyanuric chloride, and concentrated aqueous ammonia converts it into 2,4-diamino-1,3,5-triazine (formoguanamine).

Experimental

To a well-stirred solution of 9.2 g. of cyanuric chloride in 200 ml. of dry ether cooled by an ice–salt-bath to −10° was added 1.9 g. of lithium aluminum hydride in small portions during 15 minutes in an atmosphere of nitrogen with exclusion of moisture. During the reaction the temperature rose to −6°. After 30 minutes the cooling bath was removed and the reaction mixture allowed to warm to room temperature during one hour. The white precipitate was removed by filtration and washed with ether (7.8 g.). The ethereal filtrate yielded on evaporation a crystalline residue soaked with oil (3.5 g.) which was dried on a porous clay plate and then sublimed at 10 mm. (bath temperature 80 to 130°). The first portion of the sublimate (0.5 g.) yielded after resublimation at 80° (10 mm.) 0.2 g. of 2,4-dichloro-1,3,5-triazine, colorless prisms, m.p. 50–52°. The analysis indicates that the material is not completely free of cyanuric chloride.

Anal. Calcd. for $C_3HN_3Cl_2$: N, 28.02; Cl, 47.22. Found: N, 26.77; Cl, 48.25

The residue from the sublimation which was essentially free of cyanuric chloride was extracted with ether; from the extract 1.6 g. of crude 2-dimethylamino-4,6-dichloro-1,3,5-triazine was isolated, m.p. after repeated recrystallization from petroleum ether 122–124°. It showed no depression in m.p. when mixed with an authentic sample.[8] Finely powdered 2,4-dichloro-1,3,5-triazine (0.15 g.) was suspended in 10 ml. of 28% aqueous ammonia, kept overnight at room temperature and then held for one hour at 80°. After evaporation of the water in an open dish on the steam-bath, the residue was recrystallized from 5 cc. of boiling water with the addition of a few drops of 40% sodium hydroxide. 2,4-Diamino-1,3,5-triazine (0.1 g.) was obtained in thin long needles melting at 316° identified by mixed melting point with an authentic sample.

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[3] C. Grundmann, H. Ulrich and A. Kreutzberger, *Chem. Ber.*, **86**, 181 (1953).

[4] L. E. Hinkel, E. E. Ayling and J. H. Beynon, *J. Chem. Soc.*, 674 (1935).

[5] G. Wittig and H. Bille, *Z. Naturforsch.*, **6B**, 226 (1951).

[6] D. W. Kaiser and F. C. Schaefer (to American Cyanamid Co.), U. S. Patent 2,653,934 (September 29, 1953).

[7] C. Grundmann, G. Weisse and S. Seide, *Ann.*, **577**, 77 (1952).

[8] W. M. Pearlman and C. K. Banks, THIS JOURNAL, **70**, 3726 (1948).

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Reaction of Azide Ion with N-Methyl-N-nitroso-N-nitroguanidine and N-Nitro-S-methylisothiourea

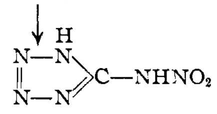
BY RONALD A. HENRY AND ROBERT H. BOSCHAN

RECEIVED NOVEMBER 4, 1953

McKay and Wright[1] demonstrated that primary alkyl or aryl amines and N-methyl-N-nitroso-N′-nitroguanidine react with the elimination of the methylnitrosamino group and the formation of substituted nitroguanidines. More recently, Fishbein and Gallaghan[2] found that these same nucleophilic reagents would eliminate methyl mercaptan from N-nitro-S-methylisothiourea with the formation of similar nitroguanidine derivatives. These reactions have now been extended to another nucleophilic reagent, namely, the azide ion. Thus, sodium azide and either N-methyl-N-nitroso-N′-nitroguanidine or N-nitro-S-methylisothiourea react to form 5-nitroaminotetrazole, which is conveniently isolated as its sparingly soluble guanidinium salt in 50 to 60% yield. The intermediate nitroguanylazide, which results from the elimina-

$$RC(NH)NHNO_2 + N_3^- \longrightarrow R^- + N_3C(NH)NHNO_2$$

$R = CH_3N(NO)$
or CH_3S



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[1] A. F. McKay and G. F. Wright, THIS JOURNAL, **69**, 3028 (1947); A. F. McKay, *ibid.*, **71**, 1968 (1949).

[2] L. Fishbein and J. A. Gallaghan, *ibid.*, **76**, 1877 (1954).