benzene and was isolated by fractional condensation of the mixture on a vacuum line. The benzyl alcohol weighed 1.03 g., 91% of the quantity expected from the equation

$$4C_6H_5CHO + LiBH_4 \longrightarrow LiB(OCH_2C_6H_5)_4$$

The benzyl alcohol was analyzed by combustion, and the ion current of hydrogen obtained from the water of combustion was determined.

Found: C, 77.29; H, 7.46; microcuries tritium per millimole hydrogen, 3.12. Expected: C, 77.74; H, 7.46; microcuries tritium per millimole hydrogen, 3.11.

Hydrolysis of Sodium Borohydride.—The sodium borohydride from Run 13, Table I, was freed from possible decomposition products by dissolution in isopropylamine. The clarified solution was evaporated and the residue was hydrolyzed, in an evacuated vessel, by addition of dilute hydrochloric acid. The generated hydrogen was freed from water vapor, measured manometrically, and assayed for tritium. The yield of hydrogen was 13.70 millimoles with a specific activity of 0.621 microcurie per millimole; the values expected from the equation

$$NaBH_4 + 3H_2O + HCl \longrightarrow H_3BO_3 + 4H_2 + NaCl$$

were 14.44 millimoles and 0.63 microcurie per millimole.

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Polymerization of Tris-β-nitroxyethylamine

BY G. E. DUNN, R. H. MEEN AND GEORGE F WRIGHT

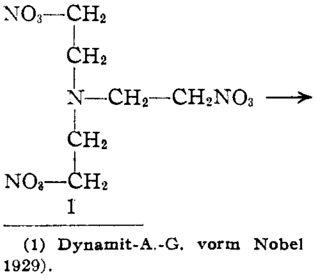
The preparation of tris-β-nitroxyethylamine has been described briefly.[1,2] We have obtained the compound by another method and confirmed the report[1] that it is unstable.

The nitrate salt of I can be prepared in 77% yield by esterification of tris-β-hydroxyethylamine in nitric acid and acetic anhydride. A new polymorph, m.p. 65° is obtained occasionally instead of the usual form,[2] m.p. 75°. This salt is reasonably stable although it would be unsuitable as an explosive since it decomposes violently after five minutes at 65° and immediately with explosion at 100°.

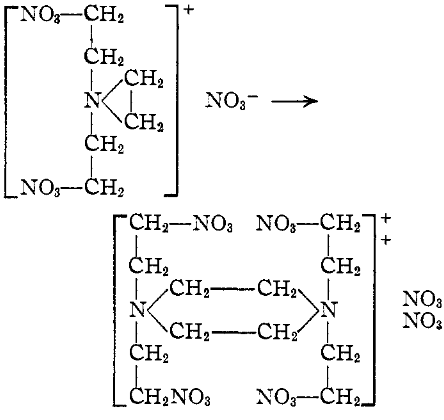
We confirmed the previous report[2] that the free base was unstable. Several days after the amine had been freed from a water solution of its salt by addition of alkali, it set to a gum from which a crystalline solid melting at 216° could be separated.

This solid is a nitrate salt since its aqueous solution will precipitate nitron nitrate. It is probably tetra-β-nitroxyethylpiperazinium dinitrate (II) analogous with the piperazinium di-salt reported by Crane and Rydon[3] from a corresponding decomposition of tris-β-chloroethylamine.

Although the dinitrate, II, was more stable than I or its nitrate salt the melting (decomposition) point of this quaternary salt decreased about 20° after storage for eight years.



I



II

Experimental[4]

Tris-β-nitroxyethylammonium Nitrate.—A stirred flask containing 580 g. (5.68 moles) of acetic anhydride was maintained at −5 to −10° while 156 g. (1.00 mole) of 95% tris-β-hydroxyethylamine and 284 g. (4.51 moles) of 99% nitric acid were added proportionately from burets. After a five-hour addition period the mixture was stirred for 90 minutes longer and then poured into sufficient ice and water to give a final volume of 3 liters. The heavy oil that separated soon crystallized. It was filtered off and vacuum-dried to weigh 266 g. (77%), m.p. 72–73°.

The salt may be crystallized from methanol or it may be precipitated from an acetic acid solution by addition of water. It melts at 74.5–75°. X-Ray diffraction with CuKα gave powder spacings (Å.) with intensities [I/I_0]: [10] 4.06; [9] 5.69; [8] 4.63; [7] 7.79; [5] 3.00; [4] 3.90, 2.46; [3] 4.90, 3.68, 3.44, 3.29, 2.91, 2.34; [2] 4.28, 4.18, 3.19, 2.83, 2.58; [1] 5.35, 4.44, 2.74, 2.28.

Anal. Calcd. for $C_6H_{13}N_5O_{12}$: C, 20.7; H, 3.77; N, 20.2. Found: C, 21.1; H, 3.73; N, 19.7.

When this salt is decomposed in concentrated sulfuric acid no acetic acid is released. The salt is slightly soluble in water and its aqueous solution gives positive brucine and nitron tests for nitrate ion.

Occasionally the salt was obtained in another polymorphic form, m.p. 64–65°. X-Ray diffraction with CuKα gave principal powder spacings (Å) with intensities [I/I_0]: [10] 3.70; [8] 3.28; [6] 5.12; [4] 4.62; [2] 3.02; [1] 3.15. The higher melting polymorph was obtained on seeding methanol solutions of the lower melting form.

Tris-β-nitroxyethylamine (I).—To a solution of 0.17 g. (0.0043 mole) of sodium hydroxide in water at 0° was added 1.5 g. (0.0043 mole) of the nitrate salt. The oil which formed after agitation was separated, washed twice with water, twice with cold methanol and again with water and was dried quickly over anhydrous sodium sulfate. The 0.5 g. thus obtained was analyzed immediately since it would not withstand distillation. Analysis indicated that it was not pure.

Anal. Calcd. for $C_6H_{12}N_4O_9$: C, 25.4; H, 4.26; N, 19.7. Found: C, 25.8; H, 4.07; N, 19.0.

Tetra-β-nitroxyethylpiperazinium Dinitrate (II).—When 7 g. of the dry amine was allowed to stand at 25° for 2 days, it set to a gummy mass. When this gum, after a total time of 16 days, was shaken with 20 cc. of acetone a suspension was produced. The brown solid was filtered off, washed with water and dried under vacuum to weigh 1.27 g. (18%), m.p. 199°. After periods of 3, 5 and 10 days the crude yields were 0.8, 1.6 and 9%, respectively. The same compound was also precipitated in about the same yields when the polymerization was carried out in 2 volumes of methanol. Treatment of the crude product with Nuchar followed by three crystallizations from boiling water (60 cc. per g.) gave a 60% recovery of crystals, m.p. 216° (dec.). The compound was soluble in hot water, slightly soluble in dimethylformamide and insoluble in anhydrous acetone, methanol, ethanol, ether, benzene, nitromethane and acetic acid. It was stable in hot water, and it dissolved in lime-

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(1) Dynamit-A.-G. vorm Nobel & Co. Brit. 350,293 (Nov. 22, 1929).

(2) J. Barbiere, *Bull. soc. chim.*, [5] 11, 470 (1944).

(3) C. W. Crane and H. N. Rydon, *J. Chem. Soc.*, 527 (1947).

(4) All melting points were corrected against reliable standards.

water without cloudiness. The aqueous solution gave a positive brucine test for nitrate ion and with nitron gave 95% of the theoretical amount of nitron nitrate. No reaction occurred with bromine water. X-Ray diffraction with CuKα gave powder spacings (Å.) at relative intensities [I/I_0]: [10] 3.50; [9] 3.89; [8] 4.51, 2.76; [6] 6.20, 4.82, 2.88; [5] 7.56, 5.14; [4] 3.23; [3] 3.07, 2.49; [2] 5.30; [1] 6.43, 3.71, 2.17, 2.07.

Anal. Calcd. for $C_6H_{12}N_4O_9$: C, 25.4; H, 4.26; N, 19.7. Found: C, 24.9; H, 4.17; N, 19.5.

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Preparation and Thermal Decomposition of Pyrazinoic Benzenesulfonhydrazide[1]

BY T. I. FAND AND P.E. SPOERRI

Niemann, Lewis and Hays[2] successfully applied the method of McFadyen and Stevens[3] in preparing the 2- and 3-pyridylaldehydes from the corresponding pyridinemonocarboxylic acids. The general equation for this reaction may be represented as

$$\mathrm{RCONHNHSO_2Ar + OH^- \longrightarrow RCHO + ArSO_2^- + N_2 + H_2O}$$

The reaction proceeds as above except when the aromatic or heterocyclic radical, R, contains a strongly meta directing group ortho or para to the hydrazide side chain. On the basis of the thermal decomposition of benzenesulfonyl-*p*-nitrobenzhydrazide to benzoic acid, Niemann and Hayes[4] proposed the alternative mechanism

$$\mathrm{2RCONHNHSO_2Ar + 2OH^- \longrightarrow RCONHNHCOR + 2ArSO_2^- + N_2 + H_2O}$$

$$\mathrm{RCONHNHCOR + 2OH^- \longrightarrow 2RCOO^- + NH_2NH_2}$$

As one of the reaction products, they obtained a high melting substance which appeared to be the intermediate *sym*-dihydrazide.

In an attempt to prepare pyrazinealdehyde by the method of McFadyen and Stevens,[3] the following series of reactions was carried out: pyrazinoic acid→methyl pyrazinoate hydrochloride→pyrazinoic hydrazide→pyrazinoic benzenesulfonhydrazide. Repeated attempts to obtain pyrazine aldehyde by the thermal decomposition of pyrazinoic benzenesulfonhydrazide were unsuccessful. However, we were able to isolate N,N′-dipyrazinoylhydrazine as the main product, indicating that this reaction followed the course of the alternative mechanism proposed by Niemann and Hays.[4] We were also able to isolate and identify diphenyl disulfide, pyrazinoic acid and pyrazinoic acid amide as additional products of this reaction.

Experimental

Methyl Pyrazinoate Hydrochloride.—Anhydrous HCl gas was bubbled into a suspension of 7 g. of pyrazinoic acid in 95 ml. of anhydrous methanol. When the solid dissolved, the solution was further refluxed on the steam-bath for 2 hr. while passing in HCl gas. After cooling in the refrigerator overnight, 6.9 g. or 70% yield of tan crystals was collected which when recrystallized from ether–methanol gave tan crystals, m.p. 140–141°.

Anal. Calcd. for $C_6H_4N_2O_2\cdot HCl$: neut. equiv., 174.5. Found: neut. equiv., 173.

A small amount of methyl pyrazinoate hydrochloride was dissolved in water, neutralized with $NaHCO_3$ and extracted with ether. After drying and evaporating the ether extract, a crystalline residue was obtained which gave white, silky needles, from petroleum ether, m.p. 61–62°. The melting point of methyl pyrazinoate is reported[5] as 62°.

Pyrazinoic Acid Hydrazide.—Ten ml. of hydrazine hydrate (85%) was added dropwise to a suspension of 6 g. of methyl pyrazinoate hydrochloride in 15 ml. of methanol. Soon after the hydrochloride dissolved, a heavy precipitate reappeared. The reaction was completed by refluxing for 2 hr., cooling and filtering; 4.3 g. of light tan crystals was obtained (90% yield), m.p. 167–169°. The melting point of pyrazinoic acid hydrazide is reported[5] as 168°.

Pyrazinoic Benzenesulfonhydrazide.—21.1 grams of pyrazinoic acid hydrazide and 135 ml. of anhydrous pyridine were mixed in a 200-ml. flask. Thirty grams of benzene sulfonyl chloride was added dropwise with stirring while maintaining the temperature at 15–20°. After stirring the mixture overnight, the pyridine was removed *in vacuo* and the residue treated with ice-water. The precipitate was filtered, washed with water and alcohol; 40.6 g. or 96% yield was obtained. Recrystallization from ethanol gave white crystals, m.p. 175.5–176°.

Anal. Calcd. for $C_{11}H_{10}N_4O_3S$: C, 47.5; H, 3.62; N, 20.1; S, 11.5. Found: C, 47.6; H, 3.92; N, 19.8; S, 11.4.

Decomposition of Pyrazinoic Benzenesulfonhydrazide.—The decomposition of 25 g. of pyrazinoic benzenesulfonhydrazide was carried out according to the method of Buchman and Richardson.[6] Three grams of golden-yellow crystals was filtered from the reaction mixture. Analysis of this material indicated the presence of sodium. Therefore, 2.8 g. of the yellow precipitate was suspended in 25 ml. of water and a slight excess of hydrochloric acid was added until the color of the precipitate changed from yellow to white. The white precipitate was recrystallized from methanol to give 2.3 g. of white, cottony needles which melted at 245–246°.

Anal. Calcd. for $C_{10}H_8N_6O_2$: C, 49.3; H, 3.28; N, 34.3. Found: C, 49.7; H, 3.26; N, 34.3.

Alkaline hydrolysis of the white precipitate yielded pyrazinoic acid, identified by neutral equivalent and mixed melting point with an authentic sample. In addition, hydrazine was obtained and identified as dibenzalhydrazine, m.p. 93–94°, which showed no depression when mixed with an authentic sample of dibenzalhydrazine. From the above analytical data, it appeared that the compound might be N,N′-dipyrazinoylhydrazine. This compound was then synthesized by interacting pyrazinoyl chloride and pyrazinoic acid hydrazide in pyridine in the usual manner. White, cottony needles were obtained from methanol, m.p. 246–247°.

The product we obtained from the thermal decomposition of pyrazinoic benzenesulfonhydrazide gave no depression in melting point when mixed with the sample of N,N′-dipyrazinoylhydrazine prepared synthetically.

We also isolated and identified diphenyl disulfide,[7] pyrazinoic acid, and pyrazinoic acid amide as by-products in the above thermal decomposition.

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(1) Presented at the Meeting-in-Miniature, A.C.S., New York Section, New York, N. Y., February 8, 1952.

(2) C. Niemann, R. N. Lewis and J. T. Hays, THIS JOURNAL, **64**, 1678 (1942).

(3) J. S. McFadyen and T. S. Stevens. *J. Chem. Soc.*, 584 (1936).

(4) C. Niemann and J. T. Hays, THIS JOURNAL, **65**, 482 (1943).

(5) O. Dalmer and E. Walter, U. S. Patent 2,149,279 (March 7, 1939).

(6) E. R. Buchman and E. M. Richardson, THIS JOURNAL, **61**, 891 (1939).

(7) Reported by A. Dornow and W. Schacht, *Ber.*, **80**, 505 (1947), as by-products in the thermal decomposition of nicotinic benzenesulfonhydrazide.