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.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TORONTO
TORONTO, ONTARIO

RECEIVED OCTOBER 13, 1951

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.

NEPERA CHEMICAL CO., INC.
NEPERA PARK
YONKERS, N. Y., AND THE
DEPARTMENT OF CHEMISTRY
POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN, NEW YORK

RECEIVED NOVEMBER 23, 1951

---

(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.