and the corresponding acid being obtained even when the reaction and isolation were carried out without the addition of water at any stage.

Experimental

The benzenesulfonyl fluorides were prepared by the slow addition during the course of one hour of 0.30 mole of sodium nitrite to a solution of 0.25 mole of the benzene sulfonamide in 5.5 moles of anhydrous hydrogen fluoride contained in a monel metal flask at a temperature slightly above 0°. The mixture was stirred for an additional hour in an ice-bath and then decomposed with steam at about 80°, until evolution of gas had ceased. The contents were poured into a stainless steel beaker containing 200 g. of ice. The resulting oily layer was separated and taken up in 200 ml. of ether. The ether solution was washed with water, dried over anhydrous magnesium sulfate, the ether removed by distillation, and the residue distilled at a pressure of 2 mm.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

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The Preparation of β-Nitropropanoic Acid

BY H. B. HASS,[1] H. FEUER AND S. M. PIER

In a recent patent[2] "Preparation of Substituted Acids From Lactones," it is stated that "the reaction of β-propiolactone with sodium nitrite produces principally β-nitropropanoic acid, some of the nitrate also probably being formed." However, no conditions for this reaction are given.

We have obtained a 35% yield of β-nitropropanoic acid when β-propiolactone was added slowly to an aqueous solution of sodium nitrite. Variations in the molar ratios of lactone and salt did not effect the yield. No nitrite or nitrate was isolated from the reaction mixture. The reaction of the lactone with nitrogen tetroxide under anhydrous conditions resulted only in a partial polymerization of the lactone.

Experimental

One-fourth mole (18 g.) of β-propiolactone was added dropwise during 15 minutes to 25 g. (0.35 mole) of sodium nitrite dissolved in 50 ml. of water in a three-neck flask equipped with stirrer, thermometer and dropping funnel. The reaction mixture was kept at 15–20° by use of a cold water-bath. Stirring was continued 4 hours after the addition was completed. The resulting clear, red solution was cooled to −5°, in an erlenmeyer flask, ether was added and 85% phosphoric acid dropped in until the solution was acid to litmus. During the acidification step the ether was frequently decanted and fresh ether added. The combined ether extracts were dried with Drierite and the ether evaporated. The orange-red oil remaining was frozen and allowed to thaw on a suction filter and a white solid remained behind. Repetition of the crystallization gave a total of 9.5 g. (35%) of white solid. Recrystallization from benzene or chloroform yielded white needles, m.p. 66°; lit. value 66°.[3,4]

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[1] General Aniline and Film Corp., New York, N. Y.

[2] T. L. Gresham, U. S. Patent 2,449,987 (1948).

[3] I. M. Heilbron, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1943, Vol. III, p. 238.

[4] Financial Support of this research was supplied by the United States Office of Naval Research.

DEPARTMENT OF CHEMISTRY AND
PURDUE RESEARCH FOUNDATION
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

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The Reaction of Methylamine with Nitroaminoguanidine

BY RONALD A. HENRY AND G. B. L. SMITH

The dearrangement of nitroaminoguanidine in a solution of ammonium carbonate was shown previously[1] to yield hydrazine, guanidine, nitroguanidine, aminoguanidine and diaminoguanidine. The hydrazinolysis of nitroaminoguanidine also gives diaminoguanidine.[2] The reaction of methylamine with nitroaminoguanidine in aqueous solution has now been studied and is analogous to these other reactions. The principal products isolated and identified were 1-methyl-3-nitroguanidine, 1-methyl-3-aminoguanidine, 1,3-diaminoguanidine and 1-methyl-2-amino-3-nitroguanidine. Minor amounts of triaminoguanidine and other unidentified compounds were also isolated as derivatives. Although 1,3-dimethyl-2-aminoguanidine and 1,3-dimethylguanidine could also theoretically be formed, they were not among the products; the former compound has been prepared by the hydrazinolysis of N,N′,S-trimethylisothiourea iodide.

1-Methyl-1-amino-3-nitroguanidine has been prepared by the reaction of methylhydrazine and 1-methyl-1-nitroso-3-nitroguanidine, using a method developed by McKay and Wright.[3]

Experimental[4]

Methylamine with Nitroaminoguanidine.—To a solution of 23.8 g. (0.2 mole) of nitroaminoguanidine and 24.0 g. of potassium hydroxide in 60 ml. of water at 30° was added, all at once, 27.0 g. (0.4 mole) of methylamine hydrochloride. While the resulting viscous solution was stirred, the temperature was raised to 60° during 5 minutes and maintained there for 25 minutes. The reaction mixture was then cooled to 0°, neutralized with concentrated hydrochloric acid, and stored for 4 days at 0°. The solid material (5.6 g.), which separated, was removed by filtration, washed with 10 ml. of cold water and dried (A); the mother liquors were retained (B).

(A) When the solid material was extracted with one 25-ml. and two 10-ml. portions of hot absolute ethanol, about 4.5 g. of potassium chloride was left. From the alcoholic extract there was recovered 0.02 g. of unreacted nitroaminoguanidine (dec. 182–183°) and 0.5 g. of 1-methyl-3-nitroguanidine (2.2%), melting at 159° after one recrystallization from 3 ml. of ethanol. A mixed melting point with an authentic specimen of methylnitroguanidine was 160°.

By treating the final alcoholic mother liquors with benzaldehyde and picric acid there was occasionally obtained a small quantity of very fine yellow needles, decomposing at 230–231° (depends on the rate of heating). A mixed melting point with a sample of tribenzaltriaminoguanidine picrate (m.p. 227°) was 227° (dec.). An X-ray powder pattern was also the same as that for tribenzaltriaminoguanidine picrate.

Anal. Calcd. for $C_{28}H_{23}N_9O_7$: C, 56.28; H, 3.88; N, 21.10. Found: C, 56.20; H, 3.83; N, 21.33.

In one experiment in which the original reaction mixture was evaporated to a small volume before cooling, there was isolated, in addition to the above compounds, about 0.3 g. of a compound which decomposed at 191–193° after recrystallization from water. This compound in an acid solution reduced potassium iodate very slowly indicating a protected hydrazino group. It was analyzed but not identified.

Anal. Found: C, 15.10, 15.05; H, 3.66, 3.41; N, 53.69.

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[1] R. A. Henry and G. B. L. Smith, THIS JOURNAL, **71**, 1872 (1949).

[2] R. A. Henry, H. D. Lewis and G. B. L. Smith, *ibid.*, **72**, 2015 (1950).

[3] A. F. McKay and G. F. Wright, *ibid.*, **69**, 3028 (1947); A. F. McKay, *ibid.*, **71**, 1968 (1948).

[4] All melting points have been corrected against known standards.