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
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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.

(B-1) Concentrated hydrochloric acid (10 ml.) was added to the aqueous filtrate, which had been heated to 55°. Benzaldehyde (20 ml.) was then added and the solution shaken for 10 minutes. The orange colored oil which separated became semi-solid after overnight chilling at 0°. The supernatant liquid was decanted (0.7 g. of benzalazine, m.p. 90–91°, was recovered from this solution) and the solid triturated with 40 ml. of cold water, which was also decanted and discarded. The yield of soft solid, after vacuum drying, was 37.3 g. When this crude product was dissolved in 200 ml. of boiling absolute methanol and the solution cooled to 25°, there was recovered 4.8 g. of material melting at 176°. One recrystallization from 86% ethanol (70 ml. per gram) yielded flat needles; m.p. 176–177° with decomposition.

Anal. Calcd. for the benzalhydrazone of 1-methyl-2-amino-3-nitroguanidine, $C_9H_{11}O_2N_5$: C, 48.86; H, 5.01; N, 31.66. Found: C, 48.68; H, 5.05; N, 31.60; 31.83.

(B-2) Evaporation of the methanol solution from B-1 to 100 ml. and cooling gave 1.9 g. of small round clusters and aggregates melting at 170–173°. (The mother liquors were retained for C.) Recrystallization from 100 ml. of 95% ethanol yielded very pale yellow spherulites, m.p. 178–179°; a mixed melting point with the preceding hydrazone was 167–170°. The compound was analyzed but not identified. This compound did not form a picrate. It gave a salt with benzalaminoguanidine, crystallizing from absolute methanol as yellow platelets, m.p. 182–182.5° (dec.).

Anal. Found: C, 53.17, 53.28, 53.23; H, 5.38, 4.92; N, 29.93, 29.60, 29.49.

(C) The final methanolic mother liquors from B-2 were diluted to 120 ml. with 95% ethanol, heated to boiling, and treated with 23.4 g. of picric acid dissolved in 120 ml. of hot ethanol. A yellow crystalline precipitate formed immediately; after the solution had cooled to 25°, the solid was removed by filtration and dried. The yield was 23 g.; m.p. 175–180°. When this crude product was extracted with one 600-ml. portion and one 400-ml. portion of boiling 95% ethanol, there was left 9.6 g. of very sparingly soluble material, decomposing at 239–240°. A mixed melting point with dibenzaldiaminoguanidine picrate was 240–241°. The yield of this picrate corresponded to a 9.7% conversion of the nitroaminoguanidine to diaminoguanidine.

From the alcoholic extraction liquors there crystallized upon cooling, 8.6 g. of material melting at 208–209°. A second recrystallization from 95% ethanol gave two materials. The more soluble material melted at 185–186°, resolidified, then remelted with decomposition at 210°. The less soluble material melted at 210–211° with decomposition. A mixed m.p. of the two materials was 210°. Mixed melting points of either material with an authentic sample of benzal 1-methyl-3-aminoguanidine picrate (see below) was 213°. The low melting compound is a meta-stable form. The yield of picrate recovered corresponds to a 10.7% conversion of nitroaminoguanidine to 1-methyl-3-aminoguanidine; because of losses due to the solubility of the low melting form of the picrate, the actual conversion is probably considerably higher.

Benzalmethylaminoguanidine Picrate.—1-Methyl-3-nitroguanidine (11.8 g., 0.1 mole) was reduced according to the procedure of Davis.[5] When the reduction was completed, the solution was filtered from unreacted zinc, treated with 10 ml. of concd. nitric acid, heated to 60°, and shaken for 10 minutes with 10 ml. of benzaldehyde. Only an oil separated when the solution was cooled to 0°. The aqueous layer was decanted, the oil dissolved in 50 ml. of boiling 95% ethanol, and treated with a solution of 20 g. of picric acid in 150 ml. of hot 95% ethanol. The bright yellow picrate was removed from the cooled solution by filtration and dried. The yield was 20.0 g. (49.4% of theory); m.p. 206–210° with decomposition. One gram was recrystallized from 100 ml. of 95% ethanol; spherulites of fine needles, m.p. 215–216° (dec.).

Anal. Calcd. for $C_{15}H_{15}O_7N_7$: C, 44.45; H, 3.73; N, 24.20. Found: C, 44.46, 44.49; H, 3.49, 3.74; N, 24.19, 24.32.

1,3-Dimethyl-2-aminoguanidine Iodide.—A solution of 24.5 g. of N,N',S-trimethylisothiourea iodide (0.1 mole) and 5.8 g. of 86% hydrazine hydrate (0.1 mole) in 65 ml. of water was allowed to stand at room temperature. There was a steady evolution of methyl mercaptan and the gradual crystallization of a white solid. After 4 hours the solution was heated to boiling to complete the reaction; the solid dissolved but recrystallized as long, white needles when the solution was cooled. The product was removed by filtration and the mother liquor evaporated to dryness. The yield of product melting at 265–270° was essentially quantitative. Two recrystallizations from 95% ethanol raised the melting point to 290–295°.

Anal. Calcd. for $C_3H_{11}N_4I$: N, 24.36; hydrazino nitrogen, 12.18; I, 55.17. Found: N, 24.36; hydrazino nitrogen, 12.33; I, 55.64, 55.88.

The picrate melted at 180–181° after recrystallization from water.

Anal. Calcd. for $C_9H_{13}O_7N_7$: N, 29.60. Found: N, 29.65.

The iodide of the benzalhydrazone melted at 75–76° after recrystallization from 95% ethanol.

Anal. Calcd. for $C_{10}H_{15}N_4I$: C, 37.75; H, 4.75. Found: C, 37.14; H, 4.78.

The picrate of the benzalhydrazone, crystallizing from 95% ethanol as fine needles, decomposed at 206–207°.

Anal. Calcd. for $C_{16}H_{17}N_7O_7$: N, 23.38. Found: N, 23.19.

The free **benzalhydrazone** crystallized from aqueous ethanol as pale yellow, flat needles; m.p. 86.5–87.5°.

1-Methyl-1-amino-3-nitroguanidine.—A solution of methylhydrazine, prepared by dissolving 3.2 g. of the sulfate and 2.3 g. of anhydrous sodium carbonate in 10 ml. of water, was added during 20 minutes with shaking to a cold slurry of 2.94 g. of methylnitrosonitroguanidine in 10 ml. of water. After the solution stood overnight at 25°, it was chilled to 0° and the solid removed by filtration. The dried product, melting about 161°, was a mixture of sodium sulfate and methylaminonitroguanidine. By extraction with one 100-ml. portion and one 50-ml. portion of boiling 95% ethanol there was recovered 1.8 g. of compound (68% of theory), melting at 170–171°. Recrystallization from ethanol gave rosettes of flat needles with unchanged melting point.

Anal. Calcd. for $C_2H_7O_2N_5$: C, 18.04; H, 5.30. Found: C, 18.26; H, 5.31.

Several attempts to detect or isolate 1-(methylamino)-3-nitroguanidine, $CH_3NHNHC(NH)NHNO_2$, in the original aqueous mother liquors or in the alcoholic recrystallization liquors were unsuccessful; only further amounts of 1-methyl-1-amino-3-nitroguanidine or its benzalhydrazone were isolated. This would indicate that under these conditions of reaction the nucleophilic center of methylhydrazine is on the nitrogen adjacent to the methyl group and that addition occurs exclusively at that point.

The benzalhydrazone melted with decomposition at 193–193.5° after recrystallization from 95% ethanol.

Anal. Calcd. for $C_9H_{11}O_2N_5$: N, 31.66. Found: N, 31.65.

INORGANIC CHEMISTRY BRANCH
CHEMISTRY DIVISION
U. S. NAVAL ORDNANCE TEST STATION
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The Synthesis of Some Amino Alcohols

BY R. E. HOLMEN AND D. D. CARROLL

The reduction of amic or anilic acids with lithium aluminum hydride offers a fairly convenient synthesis of a wide variety of amino alcohols, some of which are not readily obtained otherwise. In view of the recent application of this method to the modification of anti-tubercular compounds,[1] we wish to record some syntheses of new amino alcohols used by us prior to that disclosure. Included also is another new compound, 2-*t*-butylaminoethanol, prepared by an adaptation of a

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[5] T. L. Davis, "Chemistry of Powder and Explosives," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 383.

[1] V. C. Barry, J. G. Belton, R. M. Kelly and D. Twomey, *Nature*, **166**, 303 (1950).