Reaction of the Diamine with Orthoesters.—2,3-Diaminoquinoxaline was suspended in five equivalents of ethyl orthoformate. The mixture was heated in an oil-bath maintained at 140–145° for six hours, with stirring. At this temperature a slow distillation of ethyl orthoformate took place. The volume was kept constant by a dropwise addition of fresh orthoformate. At the end of the reaction period the excess of ethyl orthoformate was removed under reduced pressure and the residue worked up in the manner described above for the formic acid method.

2-Methylimidazo(b)quinoxaline was prepared in a similar way using ethyl orthoacetate in place of ethyl orthoformate.

Reaction of the Diamine with Acyl Halides.—The following example illustrates the general method. Three grams of acetyl chloride was added to 25 ml. of cold pyridine. Then 5 g. of 2,3-diaminoquinoxaline was added with stirring and the mixture slowly heated on a steam-bath until most of the solid had gone into solution. The reaction mixture was heated at 100° for three hours and the excess solvent then removed under reduced pressure. The residues were worked up according to the directions given under "Reaction of the Diamine with Formic Acid."

Minor modifications were made in the above method for certain acyl halides. Where methoxyacetyl chloride was used, a trace of concentrated sulfuric acid was added to the reaction mixture. With phenylacetyl and furoyl chlorides, xylene proved to be a better solvent than pyridine.

With aromatic acyl chlorides, products were obtained which were consistently high in carbon. This problem has not been resolved successfully up to now.

Reaction of the Diamine with Acid Anhydrides.—2,3-Diaminoquinoxaline was refluxed for one hour with six equivalents of acetic anhydride. Crude 1-acetyl-2-methylimidazo(b)quinoxaline separated on standing overnight. It was recrystallized from dry ethanol using Darco as the decolorizing agent; yield 72%, m.p. 158–159°.

Anal. Calcd. for $C_{11}H_8ON_4$: C, 63.70; H, 4.45; N, 24.77. Found: C, 63.54; H, 4.28; N, 24.88.

The 1-acetyl derivative is converted to 2-methylimidazo(b)quinoxaline by boiling for a few minutes with dilute sodium hydroxide solution.

The reaction of the diamine with succinic anhydride was carried out in pyridine solution as described for the acyl chlorides. The crude 2-β-imidazo(b)quinoxaline propionic acid so obtained was recrystallized from 70% ethanol.

Fusion of the Diamine with Urea.—A mixture of 2,3-diaminoquinoxaline with two moles of urea was heated at 180° until no more ammonia evolved. The residue was broken up and washed with alcohol. The product was then dissolved in hot concentrated ammonium hydroxide, decolorized with Darco and filtered. Neutralization of the filtrate with acetic acid precipitated the imidazolone.

Preparation of 4-Methylisoimidazoquinoxaline.—1-Methyl-2-imino-3-amino-1,2-dihydroquinoxaline was heated with ethyl orthoformate as previously described for 2,3-diaminoquinoxaline. After removal of the ethyl orthoformate, the residue was dissolved in a minimum amount of butanol-2, decolorized with Darco and filtered. The filtrate was diluted with an equal volume of dry ether and kept at 0° for 24 hours; yield 66%, m.p. 210–213° dec.

Anal. Calcd. for $C_{10}H_8O_4$: C, 65.20; H, 4.38; N, 30.43. Found: C, 65.33; H, 4.09; N, 30.20.

Preparation of 2-Hydroxy-4-methylisoimidazoquinoxaline.—1-Methyl-2-imino-3-amino-1,2-dihydroquinoxaline was fused with urea by the procedure previously described. The fusion temperature was 150–155°; yield 61%, m.p. 355°.

Anal. Calcd. for $C_{10}H_8ON_4$: C, 59.99; H, 4.03; N, 27.99. Found: C, 60.06; H, 4.16; N, 27.74.

Hydrolysis of Imidazo(b)quinoxaline. Acid Hydrolysis.—One gram of imidazo(b)quinoxaline was refluxed for five minutes with 20 ml. of 2.5 *N* hydrochloric acid. Neutralization of the solution with ammonium hydroxide precipitated an almost quantitative yield of 2-hydroxy-3-aminoquinoxaline. It proved to be identical with an authentic sample.[15]

Anal. Calcd. for $C_8H_7ON_3$: C, 59.58; H, 4.37; N, 26.08. Found: C, 59.69; H, 4.26; N, 25.99.

Basic Hydrolysis.—One gram of imidazo(b)quinoxaline was refluxed for one hour with 100 ml. of 1 *N* sodium hydroxide. After cooling a 65% yield of 2,3-diaminoquinoxaline was obtained.

Oxidation of 2-β-Phenylvinylimidazo(b)quinoxaline.—Two grams of 2-β-phenylvinylimidazo(b)quinoxaline was dissolved in 200 ml. of pyridine. With stirring, 612 ml. of 0.5% potassium permanganate was added gradually with stirring. The mixture was allowed to stand overnight and filtered. The filtrate was heated to boiling and again filtered. Neutralization of the filtrate with acetic acid precipitated imidazo(b)quinoxaline, yield 35%.

Condensation of 2-Methylimidazo(b)quinoxaline with Benzaldehyde.—One gram of 2-methylimidazo(b)quinoxaline was refluxed with 5 ml. of benzaldehyde and 0.5 ml. of piperidine for two hours. The product obtained on cooling was washed with ether, then dissolved in hot dilute sodium hydroxide and reprecipitated by neutralizing with acetic acid; yield of 2-β-phenylvinylimidazo(b)quinoxaline, 83%.

(15) J. R. Stevens, K. Pfister and J. Wolf, THIS JOURNAL, **68**, 1035 (1946).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Reactions of N-Monoalkylhydroxylamines with Sulfur Dioxide, Sulfur Trioxide and Phthalic Anhydride [1]

BY AUGUST I. RYER[2] AND G. B. L. SMITH[3]

The crystalline N-monoalkylhydroxylamines (hydroxaminoalkanes), N-isopropylhydroxylamine (2-hydroxaminopropane), N-(*n*-propyl)-hydroxylamine (1-hydroxaminopropane) and N-ethylhydroxylamine (hydroxaminoethane) have been isolated in crystalline form and the oxalates of the first two have been prepared. These alkylhydroxylamines yield alkylsulfamic acids with sulfur dioxide and N-alkylhydroxaminosulfonic acids (N-alkyl-N-hydroxysulfamic acids) with sulfur trioxide. The N-monoalkylhydroxylamines with phthalic anhydride give N-alkyl-N-hydroxyphthalamic anhydrides rather than the N-alkyl-N-hydroxyphthalamic acids although the copper salts of the latter were isolated as dihydrates.

Introduction

Although N-monoalkylhydroxylamines have been known for over 50 years, few reactions of these compounds have been studied. Early investigators[4] prepared the N-monoalkylhydroxylamines by the reduction of the corresponding nitroparaffins.

The electrochemical reduction of the commercial nitroparaffins was studied by Leeds and Smith[5] who developed a simple process for the preparation of the N-alkylhydroxylamines. They did not,

(1) From the doctoral dissertation of August I. Ryer submitted to the Faculty of the Graduate School of Polytechnic Institute of Brooklyn, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in June, 1946.

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(3) Chemistry Division, U. S. Naval Ordnance Test Station, Inyokern, Post Office, China Lake, California.

(4) E. Hoffman and Victor Meyer, *Ber.*, **24**, 3528 (1891); A. Kirpal, *ibid.*, **25**, 1714 (1892); E. Bamberger, *ibid.*, **27**, 1347 (1894); P. Pierron, *Bull. soc. chim.*, **21**, 780 (1899).

(5) M. W. Leeds and G. B. L. Smith, *J. Electrochem. Soc.*, **98**, 129 (1951).

however, isolate the N-alkylhydroxylamines or their salts in a pure form; instead, the reduction mixtures were concentrated to a thick sirup in which the hydroxylamines were present as the primary sulfates, together with small amounts of the corresponding ammonium sulfates and other by-products. The Kjellin[6] method was unsuitable for treating these electrolytic reduction residues. This investigation was undertaken to develop procedures for the isolation of the N-alkylhydroxylamines in crystalline form from the crude reduction concentrates of Leeds and Smith, and to study their reactions with some acid anhydrides.

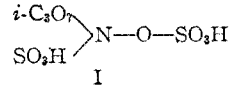
Discussion

A satisfactory procedure for isolating N-isopropylhydroxylamine and N-(*n*-propyl)-hydroxylamine was found by treating the electrochemical reduction concentrates with solid sodium carbonate until the mixtures were distinctly alkaline and extracting the resulting pasty mass with hot ligroin or petroleum ether. On chilling the extracts, the free bases came down in crystalline form. This procedure was not suitable for N-ethylhydroxylamine owing to its low solubility in these solvents. N-Ethylhydroxylamine was isolated by dissolving the alkaline paste in a minimum of water and extracting with ethyl ether. The N-alkylhydroxylamines although quite unstable at room temperature remain unchanged for months when stored below $-10°$.

The reaction of the N-alkylhydroxylamines with sulfur dioxide gave the corresponding alkylsulfamic acids. The reaction with sulfur trioxide yielded the N-alkylhydroxaminosulfonic acids.

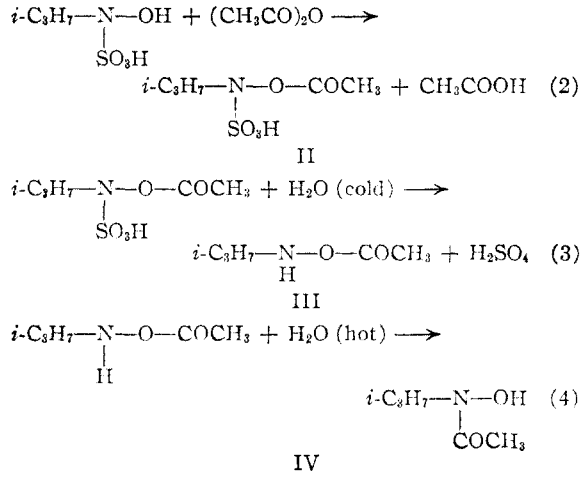
$$RNHOH + SO_3 \longrightarrow RN(OH)SO_3H \qquad (1)$$

These products are the N-alkyl derivatives of hydroxaminosulfonic acid known only in the form of its alkali salts.[7] The possibility that these acids might be alkyl derivatives of aminoöxysulfonic acid[8] was precluded by the fact that they did not possess the oxidizing properties of these derivatives of Caro's acid. An attempt was made to prepare the N-isopropyl derivative of hydroxaminodisulfonic acid (I) by treating N-isopropylhydroxylamine with two moles of sulfur trioxide. Only the N-isopropylhydroxaminosulfonic acid was isolated. Hence the nitrogen hydroxyl group is not attacked by sulfur trioxide under the conditions of this reaction.



I

N-Isopropylhydroxaminosulfonic acid reacted with acetic anhydride to give a product which could not be purified. On dissolving this product in cold water, sulfate ion was found to be present in abundance and the solution gave no color reaction with ferric chloride. On heating the aqueous solution for several minutes, the presence of a hydroxamic acid could be demonstrated by the characteristic color reaction with ferric chloride and green precipitate with copper acetate. These observations indicate that the following reactions probably occurred



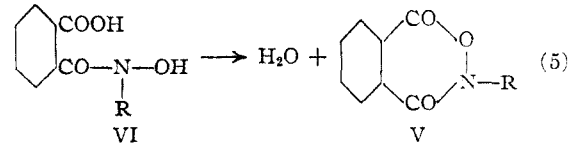
II

III

IV

N-Isopropylhydroxaminosulfonic acid with acetic anhydride formed the corresponding acetyl derivative (II). This on treatment with cold water gave sulfuric acid and O-acetyl-N-isopropylhydroxylamine (III). This is not a hydroxamic acid and therefore does not give a color reaction with ferric chloride. On heating the solution, (III) rearranged to give the N-isopropyl acethydroxamic acid (IV). Only two examples of O-monoacylhydroxylamines have been reported: O-acetyl-4-hydroxylaminobenzenesulfonamide[9] and O-(2-aminobenzoyl)-hydroxylamine.[10] The latter readily isomerized to the corresponding hydroxamic acid.

The reaction of methylhydroxylamine with phthalic anhydride has been reported to give N-methylphthaloxime.[11] The reaction of the N-alkylhydroxylamines with phthalic anhydride was examined under a variety of conditions in an attempt to prepare the N-alkyl-N-hydroxyphthalamic acids. The products which were isolated did not give a color test with ferric chloride, nor form insoluble copper salts, and were found to be N-alkyl-N-hydroxyphthalamic anhydrides (V). They are mixed anhydrides derived from the N-alkyl-N-hydroxyphthalamic acids (VI) by the loss of water. On heating with water (V) is slowly and partially hydrolyzed to give (VI). When N-*isopropylhydroxylamine* and N-(*n*-propyl)-hydroxylamine were allowed to react with phthalic anhydride in a small volume of methanol, the N-alkyl-N-hydroxyphthalamic acids were obtained as sticky solids. The products could not be purified, the solids spontaneously losing water to give



VI V

(6) C. Kjellin, *Ber.*, **26**, 2377 (1893); *ibid.*, **30**, 1891 (1897).

(7) F. Raschig, "Schwefel u. Stickstoff-Studien," Verlag Chemie, 1924, pp. 128–162.

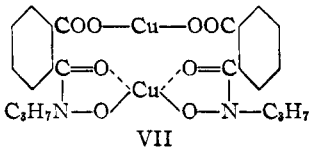
(8) F. Sommer, O. F. Schulz and M. Nassau, *Z. anorg. allgem. Chem.*, **147**, 142 (1925).

(9) H. Bauer and S. M. Rosenthal, THIS JOURNAL, **66**, 611 (1944).

(10) A. W. Scott and B. L. Wood, Jr., *J. Org. Chem.*, **7**, 508 (1942).

(11) O. L. Brady, L. C. Baker, R. F. Goldstein and S. Harris, *J. Chem. Soc.*, 529 (1928). This may well be an anhydride related to V.

the N-alkyl-N-hydroxyphthalamic anhydrides. By adding copper acetate to the reaction mixture, copper salts of the N-alkyl-N-hydroxyphthalamic acids were isolated. The analyses best fitted dihydrates of structure VII.



VII

The water of crystallization was held firmly but could be removed by drying *in vacuo* at 110° over phosphorus pentoxide.

Experimental

N-Isopropylhydroxylamine.—To 150 g. of a concentrated solution of crude N-isopropylhydroxammonium sulfate was added 50 ml. of water and 800 ml. of ligroin (b.p. 70–90°). Sodium carbonate was added gradually to the well agitated mixture until it was basic to litmus. The mixture was boiled and stirred for 5–10 minutes on a steam-bath. The ligroin was decanted from the pasty residue and filtered while hot through a fluted funnel. The residue was then treated in a similar manner twice with 300-ml. portions of hot ligroin. The combined filtrates were chilled in an ice-bath. The N-isopropylhydroxylamine crystallized as fine, silky needles, which were filtered and air-dried on filter paper; yield 20.3 g. (40%), m.p. 85°. One recrystallization from ligroin raised the m.p. to 86–87°.

This N-alkylhydroxylamine is not stable at room temperature but will keep for several weeks if stored in a closed bottle below −10°. N-Isopropylhydroxylamine is volatile and will slowly sublime even at room temperature; at 40–50° it sublimes quite rapidly. It is very soluble in petroleum ether or ligroin.

Anal. Calcd. for C_3H_9NO: N, 18.65. Found: N, 18.43.

N-Isopropylhydroxammonium Oxalate.—To 6.20 g. (0.083 mole) of N-isopropylhydroxylamine in 60 ml. of ethyl acetate was added a solution of 3.60 g. of anhydrous oxalic acid (0.040 mole) in 60 ml. of ethyl acetate. The precipitated solid was filtered under reduced pressure, washed with ethyl acetate and dried; yield 6.15 g. (63%), m.p. 155–157°. The oxalate, which was insoluble in acetone, but moderately soluble in methanol and water, crystallized from methanol as needles, m.p. 159–160°. The oxalate was analyzed by suspending in water and titrating with standard alkali using phenolphthalein as indicator.

Anal. Calcd. for $(C_3H_7NHOH)_2H_2C_2O_4$: oxalic acid, 37.48. Found: oxalic acid, 37.30.

N-(*n*-Propyl)-hydroxylamine was prepared by the procedure described for N-isopropylhydroxylamine except that petroleum ether (b.p. 35–60°) was used as the solvent and the extracts were chilled to −40° in a methanol–Dry Ice-bath. The N-(*n*-propyl)-hydroxylamine crystallized as a felted mass of needles. These were filtered and the funnel containing the moist crystals placed in a desiccator over calcium chloride until they had reached room temperature. The crystals were quickly air dried; yield 18.6 g. (44%), m.p. 45.5–46° (in agreement with the literature[6]). The filtrate was used to re-extract the pasty residue. On chilling this filtrate to −40°, additional crystals of 3.6 g. (6%) were obtained.

N-(*n*-Propyl)-hydroxylammonium oxalate was prepared in the same way as the N-isopropylhydroxylammonium salt, m.p. 154–155°.

Anal. Calcd. for $(C_3H_7NHOH)_2H_2C_2O_4$: oxalic acid, 37.48. Found: oxalic acid, 37.33.

N-Ethylhydroxylamine.—The procedure used for the preparation of N-isopropyl- and N-(*n*-propyl)-hydroxylamine gave a poor yield of N-ethylhydroxylamine. The following procedure which utilized a liquid–liquid extraction with ethyl ether gave better results. To 100 g. of crude N-ethylhydroxammonium sulfate concentrate was added 200 ml. of water and the mixture neutralized with sodium carbonate. The aqueous solution was saturated with calcium chloride and extracted six times with 300-ml. portions of ethyl ether. The extracts were combined and the solvent removed on a steam-bath leaving a light yellow oil. Petroleum ether (5 ml.) was stirred into the oil and the mixture chilled until it had solidified. The product was pressed on a porous tile and air-dried; yield 11.2 g. (43%), waxy plates, m.p. 55–56°. (Kjellin[6] reports m.p. 59–60°.)

Isopropylsulfamic Acid.—Sulfur dioxide was passed into a solution of 2.0 g. of N-isopropylhydroxylamine in 15 ml. of chloroform for a few minutes at a rapid rate. The solution boiled and set to a solid mass. The reaction mixture was cooled and filtered under reduced pressure, the precipitate washed with chloroform and dried; yield 2.2 g. (60%), m.p. 167–168°. The acid crystallized from ethyl acetate as needles, m.p. 177°. The product is very soluble in methanol and water, sparingly soluble in benzene and chloroform and insoluble in ligroin. The acid was titrated potentiometrically against sodium hydroxide giving the strong acid–strong base curve of a monobasic acid.

Anal. Calcd. for $C_3H_9NO_3S$: C, 25.89; H, 6.52; neut. equiv., 139.2. Found: C, 25.84; H, 6.85; neut. equiv., 138.8.

***n*-Propylsulfamic acid** was prepared in the same manner as isopropylsulfamic acid; yield 55%, m.p. 182–184°. The crude product was crystallized from acetone giving soft, waxy plates, m.p. 186.5–187.0.[12]

Anal. Calcd. for $C_3H_9NO_3S$: C, 25.89; H, 6.52; N, 10.07; neut. equiv., 139.2. Found: C, 26.16; H, 6.67; N, 9.45; neut. equiv., 139.8.

Ethylsulfamic acid was prepared in the same manner as isopropylsulfamic acid; yield 52%, m.p. 177–178°.[12] The product, crystallized from a mixture of ethyl acetate and methanol, melts at 183–184° and is very soluble in water, methanol, slightly soluble in acetone, and only sparingly soluble in chloroform and ethyl acetate.

Anal. Calcd. for $C_2H_7NO_3S$: C, 19.19; H, 5.64; neut. equiv., 125.1. Found: C, 19.76; H, 6.03; neut. equiv., 125.1.

The alkylsulfamic acids are strong acids which give typical strong acid curves when titrated potentiometrically. The *p*H of 0.02 *M* solutions of the sulfamic acids prepared have been measured with the following results: sulfamic acid, 1.99; ethylsulfamic acid, 2.13; *n*-propylsulfamic acid, 2.08; isopropylsulfamic acid, 2.18.

N-Isopropylhydroxaminosulfonic Acid. Method A.—Solid sulfur trioxide (8.67 g.)[13] was covered with 50 ml. of dry chloroform and to this suspension was added slowly a solution of 9.0 g. of N-isopropylhydroxylamine in 50 ml. of dry chloroform in a dry, ground joint glass apparatus assembled without grease and protected from moisture. The apparatus was shaken occasionally and the reaction flask cooled. The thick paste was diluted with 50 ml. of dry chloroform, shaken, filtered through a fritted glass büchner funnel and washed with chloroform without permitting the filter cake to dry. The moist cake was dissolved in 10 ml. of dry methanol, filtered, and poured slowly with stirring into 300 ml. of anhydrous ethyl ether. The white precipitate which formed was filtered under reduced pressure through a fritted funnel, washed with anhydrous ether and dried in a vacuum desiccator; yield 5.8 g. (32%), m.p. 137°.

The product is very soluble in water and methanol, sparingly soluble in chloroform and insoluble in ethyl ether. Its aqueous solution is acid to congo red paper and does not reduce ammoniacal silver nor give a precipitate with barium chloride. On slowly evaporating a solution in methanol, the product can be obtained in the form of rosettes of feathery needles. The hygroscopic acid must be carefully protected from moisture. A boiled aqueous solution of the acid will reduce Tollens reagent and form a precipitate with barium chloride. The dry acid decomposes rapidly in a desiccator to regenerate the hydroxylamine as the following data indicate:

(12) W. Traube and E. Brehmer, *Ber.*, **52**, 1284 (1919), report the following m.p.: *n*-propylsulfamic acid, 172–173°; ethylsulfamic acid, 167–168°.

(13) Prepared by heating 20% fuming sulfuric acid between 170–220° in an all glass apparatus protected from moisture and condensing the sulfur trioxide as a solid in a tared receiver immersed in ice. The receiver flask was closed with a glass stopper and stored in a refrigerator until ready for use.

Acid: freshly prepared	m.p. 137°
Acid: 2 days after preparation	119°
Acid: 3 days after preparation	111° (reduces Tollens reagent and gives a precipitate with barium chloride)
Acid: 5 days after preparation	oily solid

The freshly prepared acid titrates as a monobasic acid with phenolphthalein as indicator.

Anal. Calcd. for $C_3H_9NO_4S$: S, 20.66; neut. equiv., 155.2. Found: S, 20.56; neut. equiv., 154.4.

Method B.—By running the reaction in more dilute solution, it was possible to get a higher melting product but in lower yield. A solution of 0.93 g. of N-isopropylhydroxylamine in 15 ml. of dry chloroform was added to 0.93 g. of sulfur trioxide suspended in 20 ml. of dry chloroform, observing the precautions outlined under Method A. The clear reaction mixture was placed in a refrigerator for two days. The crystals which formed were filtered, washed with dry chloroform and dried; yield 0.35 g., m.p. 143°.

N-(*n*-Propyl)-hydroxaminosulfonic acid was prepared in the same manner as N-isopropylhydroxaminosulfonic acid; yield 29%, m.p. 152–153°. On slowly evaporating a methanolic solution, the acid deposits as fine needles. The product titrates as a monobasic acid with phenolphthalein as indicator.

Anal. Calcd. for $C_3H_9NO_4S$: S, 20.66; neut. equiv., 155.2. Found: S, 20.29; neut. equiv., 154.7.

N-Ethylhydroxaminosulfonic acid was prepared in the same way as the isopropyl analog. However, the product on addition of ethyl ether to its methanolic solution formed as an oil. The solvent was decanted, the oil stirred with 30 ml. of dry chloroform in which it was partly soluble and an excess of ether added. The product changed to a fluffy solid which was filtered under reduced pressure and dried *in vacuo;* yield 0.9 g. (21%); softened at 70° and was completely melted at 135°. The hygroscopic acid rapidly changed to a sticky solid when exposed to the atmosphere. Its solution in water gave a slight precipitate with barium chloride and a weak test with ammoniacal silver, indicating that it was not completely pure. The product was titrated using phenolphthalein as indicator.

Anal. Calcd. for $C_2H_5NOH\text{-}SO_3H$: neut. equiv., 141.4. Found: neut. equiv., 140.0.

Reaction of N-Isopropylhydroxaminosulfonic Acid with Acetic Anhydride.—N-Isopropylhydroxaminosulfonic acid (2.5 g.) was covered with 3.0 g. of acetic anhydride in a stoppered flask. The acid slowly dissolved with only a slight heat of reaction; solution was complete in one hour leaving a viscous, light brown oil. The product could not be crystallized from any of the common solvents or mixtures of solvents. The product was chilled and dissolved in 25 ml. of cold water. The solution gave no color with ferric chloride, no precipitate with copper acetate and did not reduce ammoniacal silver, but gave heavy precipitates with barium chloride, silver nitrate and lead acetate which were found to be the corresponding sulfates of the heavy metals. When the solution was heated for several minutes on a steam-bath, it gave a deep violet color with ferric chloride and a green precipitate with copper acetate.

N-Isopropyl-N-hydroxyphthalamic Anhydride. Method A.—To a solution of 3.75 g. of N-isopropylhydroxylamine in 40 ml. of water was added with stirring 7.0 g. of powdered phthalic anhydride. The anhydride rapidly went into solution with only a little remaining undissolved. In about 10 minutes, a precipitate started to form. The mixture was stirred for one hour at room temperature, filtered using suction, washed with water and dried in an oven at 60°, yield 5.1 g. The crude product was extracted with hot petroleum ether. The combined extracts were concentrated to 100 ml., cooled and 1.1 g. of white needles melting at 86° were obtained. The filtrate on further concentration and cooling gave an additional yield of 1.4 g. of needles melting at 84–87°. The product, recrystallized from petroleum ether, m.p. 92°, gave a positive test for nitrogen but did not give a color test with ferric chloride nor did it form an insoluble copper salt.

Anal. Calcd. for $C_{11}H_{11}O_3N$: C, 64.38; H, 5.40. Found: C, 64.79; H, 5.57.

The aqueous liquor from which the N-isopropyl-N-hydroxyphthalamic anhydride had been filtered was allowed to stand in a refrigerator for several days, and an additional 0.2 g. of anhydride (needles, m.p. 88°) was obtained. From the filtrate N-isopropylhydroxylammonium acid phthalate was isolated (see below).

Method B.—A mixture of 1.30 g. of phthalic anhydride, 0.75 g. of N-isopropylhydroxylamine and 100 ml. of petroleum ether (b.p. 35–60°) was refluxed for 1.5 hours during which time the anhydride went into solution. The petroleum ether was decanted from a small amount of yellow oil and filtered from some unreacted anhydride. The solvent on evaporation on a steam-bath left an oily residue which solidified on cooling; yield 1.15 g. (59%), m.p. 90–91°. The product recrystallized from petroleum ether, gave fluffy needles, m.p. 92°.

N-Isopropylhydroxylammonium Acid Phthalate.—The filtrate from Procedure A, which reduced Tollens solution and gave a red color with ferric chloride, slowly evaporated on standing to give a mass of oily crystals. The residue was extracted several times with boiling toluene, the combined extracts treated with Norite and cooled. An oil formed which slowly crystallized; yield 0.2 g., m.p. 98–99°. The product was recrystallized from ethyl acetate; m.p. 100–101°. Its aqueous solution was acid to litmus, reduced Tollens reagent and Fehling solution, but did not give a color with ferric chloride. The product was suspended in water and titrated using phenolphthalein as indicator. Calcd. for $C_3H_7NHOH\cdot C_6H_4(COOH)_2$: phthalic acid, 68.87. Found: phthalic acid, 68.3.

Anal. Calcd. for $C_{11}H_{15}O_5N$: C, 54.76; H, 6.27. Found: C, 54.62; H, 6.29.

N-(*n*-Propyl)-N-hydroxyphthalamic anhydride was prepared by Procedures A and B, for the isopropyl analog. The product was an oil which solidified on standing for several days in a refrigerator. The crude product was dissolved in warm petroleum ether in a tube which was placed inside a stoppered dewar flask in a refrigerator. On standing for several days, the product came down as clusters of needles, m.p. 30–33°.

Anal. Calcd. for $C_{11}H_{11}O_3N$: C, 64.38; H, 5.40. Found: C, 64.00; H, 5.41.

N-Ethyl-N-hydroxyphthalamic anhydride was prepared by Procedures A and B, for the isopropyl analog, m.p. 87–103°. The crude product crystallized from methanol as needles, m.p. 120.5–121°.

Anal. Calcd. for $C_{10}H_9O_3N$: C, 62.82; H, 4.75. Found: C, 62.73; H, 4.86.

N-Isopropyl-N-hydroxyphthalamic Acid, Copper Salt.—N-Isopropylhydroxylamine (0.75 g.) was covered with 3.5 ml. of methanol and 1.48 g. of powdered phthalic anhydride added with stirring. The anhydride quickly dissolved with only slight heat of reaction, solution being completed in 5 minutes. The oily liquid which gave a deep red color with ferric chloride could not be crystallized. When the oil was dried in a vacuum desiccator at room temperature for several days, it changed to a solid which gave no color with ferric chloride and was identified as N-isopropyl-N-hydroxyphthalamic anhydride.

The experiment was repeated except that 10 ml. of methanol was used as the solvent. As soon as all the phthalic anhydride had dissolved, a solution of 2.0 g. of copper acetate in 30 ml. of water was added. The grass-green precipitate was filtered under reduced pressure, washed with water and dried; yield 1.75 g. The copper salt could not be crystallized; it was insoluble in all the usual solvents. A portion of the product dried in an oven at 115° for 15 hours showed no change in weight. The product was analyzed without further purification.

Anal. Calcd. for $C_{22}H_{22}O_8N_2Cu_2\cdot 2H_2O$: C, 43.63; H, 4.33; Cu, 20.99. Found: C, 42.62; H, 4.57; Cu, 20.1.

A sample was heated in a vacuum oven at 110° over phosphorus pentoxide; after seven hours there was no further loss in weight. Calcd.: H_2O, 5.95. Found: H_2O, 4.32.

N-(*n*-Propyl)-N-hydroxyphthalamic acid, copper salt was prepared in the same manner as the isopropyl analog.

Anal. Calcd. for $C_{22}H_{22}O_8N_2Cu_2\cdot 2H_2O$: Cu, 20.99. Found: Cu, 20.5.

A sample was heated in a vacuum oven at 110° over phosphorus pentoxide until constant weight was attained. Calcd.: H_2O, 5.95. Found: H_2O, 6.34.

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