

given by Schroeter³ it would appear advisable to use the oxime acetate for the Semmler aromatization. Further, it would appear that the aromatization is achieved by saturating a solution of the oxime acetate in acetic acid-acetic anhydride with hydrogen chloride and heating. It is not necessary to use the oxime acetate;⁴ the oxime may be used itself. Also, it is necessary to keep the acetic acid-acetic anhydride solution saturated with hydrogen chloride while heating;⁵ if this is not done the yield of amine is lowered considerably.

The 7-nitro-1-naphthylamine obtained from our work was diazotized and coupled by the general method of Cohen and Oesper.⁶ The 7,7'-dinitro-1,1'-azonaphthalene, m.p. 311–312°, was obtained in 37.6% yield. This compound does not appear to have been reported hitherto.

EXPERIMENTAL

7-Nitro- α -tetralone oxime. Thirty grams of 7-nitro- α -tetralone was dissolved in 400 ml. of hot 95% ethanol. To this was added a solution of 75 g. of hydroxylamine hydrochloride and 75 g. of sodium acetate in 150 ml. of water. A further 350 ml. of ethanol was added and the mixture was heated until all solid dissolved. After standing overnight 1800 ml. of water was added. The finely crystalline precipitate was filtered, washed with water, and dried under vacuum. The yield was 31.9 g. (98.5%), m.p. 169–170.5°.

7-Nitro- α -tetralone oxime acetate. Two grams of the oxime was dissolved in 10 ml. of pyridine and 10 ml. of cold acetic anhydride was added. The solution was refrigerated for 3 hr. Chipped ice was added followed by water. The suspension thus formed turned pink. Filtration gave a pink solid. This was dissolved in ethanol and the solution was acidified with 5 ml. of 10% hydrochloric acid. Dilution with water gave a white flocculent precipitate. Filtration, washing with water, and drying under vacuum were carried out in subdued light, giving 2.29 g. (95%) of a fluffy white solid, sintering at 103°, melting sharply at 114.5–115.5°. The solidified melt remelted sharply at 114.5–115.5°.

7-Nitro-1-naphthylamine. In separate tubes containing 6 ml. of acetic acid and 0.2 ml. of acetic anhydride protected by calcium chloride were placed 0.5 g. of oxime acetate and 0.5 g. of oxime. The tubes were heated in boiling water for 30 min. while anhydrous hydrogen chloride was passed through the solution. After cooling and filtering the solid obtained in each case was triturated with sodium acetate solution, washed and dried to yield 0.15 g. (35.6%), and 0.18 g. (40%), respectively. The amine in each case was purified by dissolving in warm aqueous ethanol containing ammonia. Crystallization gave red needles, m.p. 130–131°.

7,7'-Dinitro-1,1'-azonaphthylamine. By using the general procedure⁶ 3.66 g. amine gave 4 g. of tan solid. This was extracted in a Soxhlet apparatus with 95% ethanol for 7 hr.; the ethanol solution was discarded. The insoluble material was then similarly extracted with chloroform for 6 hr. On standing the chloroform solution deposited purple needles, 1.36 g. (37.6%). Recrystallization from 1200 ml. of boiling benzene gave 1.25 g. fine lustrous needles, m.p. 311–312°.

(4) This was first brought to our notice by Dr. E. R. Ward.

(5) After making this observation we were notified by Dr. Ward that the same was found in his laboratory.

(6) S. Cohen and R. E. Oesper, *Ind. Eng. Chem., Anal. Ed.*, **8**, 306 (1936).

Anal. Calcd. for C₂₀H₁₂N₄O₄: C, 64.51; H, 3.25; N, 15.04. Found: C, 64.47; H, 3.28; N, 14.63.

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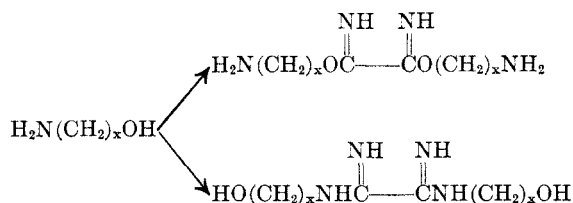
(7) Analysis by Schwarzkopf Microanalytical Laboratories, Woodside 77, N. Y.

The Chemistry of Oxamidines. II. Reaction with Hydrogen Sulfide¹

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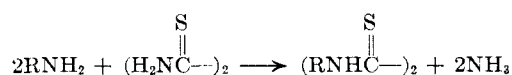
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In a study of the reaction of cyanogen with alkanolamines, Graminski² had the problem of deciding under what conditions the product was an oxaldiimidate and when it was an oxamidine:



A possible method of differentiation resulted from the discovery that *N,N'*-bis(2-hydroxyethyl)dithiooxamide, a compound whose properties and structure were known,³ could be made from one of the products originating in ethanolamine but not from the other.

Inspection of the reaction equations, whereby the dithiooxamide would be formed from either the oxaldiimidate or the oxamidine, argues for its formation from the oxamidine. Experimentally, this was confirmed by the treatment of oxamidines of known structure with hydrogen sulfide to yield dithiooxamides which were identified by independent synthesis using the Wallach method:⁴



(1) Mainly from the thesis submitted by Walter Platek in partial fulfillment of the requirements for the B.A. degree, University of Buffalo, June 1957. Paper I, *J. Org. Chem.*, **23**, 263 (1958).

(2) E. L. Graminski, Doctoral Dissertation, University of Buffalo, June 1956.

(3) Private communication, James Venerable, Mallinckrodt Chemical Works.

(4) O. Wallach, *Ann.*, **262**, 354 (1891).

sym - Bis(2 - methylaminoethyl)oxaldiimidate, $(\text{CH}_3\text{NHC}_2\text{H}_4\text{OC}-\text{NH})_2$ gave no such reaction with hydrogen sulfide.

The hydrogen sulfide reaction resembles the partial hydrolysis of oxamidines which can be accomplished by allowing a cold aqueous solution to stand in the presence of amine.⁵



EXPERIMENTAL

Oxamidines were prepared by the reaction of cyanogen with amines.⁶ Dithiooxamide was a gift from the Malinkrodt Chemical Works.

N,N'-Di-*n*-butyldithiooxamide. (a) A cold solution of *sym*-di-*n*-butyloxamidine, prepared by dissolving 2 g. of the compound in the smallest possible amount of ethanol and adding water as long as the solution remained clear, was saturated with hydrogen sulfide. The solution gradually acquired a reddish-brown color and a few orange crystals appeared. After standing overnight the mixture was filtered and the orange solid recrystallized as follows: 2 ml. of water was added to remove any ammonium sulfide and the solid residue dissolved in ethanol at 40°. After filtration to remove sulfur, water was added until a cloudiness persisted, then a few drops of ethanol. The mixture was finally cooled in an ice bath. After three recrystallizations the melting point of the orange needles was 41.5–43.0°. The yield of crude material was 70%.

Anal. Calcd. for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_2$: N, 12.1; S, 27.6. Found: N, 12.1; S, 27.2.

(b) Di-*n*-butyldithiooxamide was also prepared by the method of Wallach.⁴ To a suspension of 12.0 g. (0.1 mole) of dithiooxamide in 48 g. of ethanol was added 15.6 g. (2.1 moles) of *n*-butylamine. Hydrogen sulfide and ammonia were evolved and some of the dithiooxamide went into solution. The mixture was heated until clear, after which a few drops of dilute sulfuric acid were added. Orange crystals formed on standing overnight. These were recrystallized as above and melted at 41.5–42.5°.

A mixed melting point with the product from (a) showed no depression. Infrared curves (10% solution in CHCl_3) of the two products were identical.

N,N'-Diethylthiooxamide. (a) Saturation with hydrogen sulfide of a concentrated ethanolic solution of diethyl-oxamidine produced orange needles melting at 57.5–59.0°. Recrystallization from ethanol-water was carried out below 55°. The yield of crude product was 45%.

This compound had previously been prepared by Wallach.⁴ A sample prepared by his method mixed with the product from above showed no depression of melting point. Infrared curves of the two products were identical.

(b) Oxamidines are often best isolated as dihydrochlorides. Saturation with hydrogen sulfide of either an aqueous or ethanolic solution of diethyl-oxamidine dihydrochloride failed to yield the dithiooxamide. Consequently a solution of 0.5 g. of diethyl-oxamidine dihydrochloride in the minimum amount of water was made basic to litmus with dilute sodium hydroxide and then treated with hydrogen sulfide until it became pale yellow and a few crystals appeared. More crystals formed overnight. Recrystallization gave orange needles which showed no melting point depression when mixed with the product from (a). The yield was 50%.

N,N'-Bis(3-methoxypropyl)-dithiooxamide. (a) One gram of *sym*-bis(3-methoxypropyl)oxamidine² was dissolved in 95% ethanol and saturated with hydrogen sulfide. The solu-

(5) H. M. Woodburn, B. Morehead, and M. C. Chen, *J. Org. Chem.*, **15**, 535 (1950).

tion turned orange-red and a few reddish crystals appeared on standing. These were filtered off and proved to be dithiooxamide. Water was added to the filtrate until it became cloudy and crystallization was completed by cooling in the ice chest. The product was obtained after one recrystallization from ethanol-water (below 40°) as orange-yellow needles melting at 44.0–45.5°. The yield of crude product was 60%.

Anal. Calcd. for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_2$: N, 10.6; S, 24.2. Found: N, 10.5; S, 23.7.

(b) Following the method of Wallach,⁴ dithiooxamide and 3-methoxypropylamine gave crystals which showed no melting point depression when mixed with the product from (a). Infrared curves (10% solution in CHCl_3) of the two products were identical.

N,N'-Bis(2-ethoxyethyl)dithiooxamide was prepared from *sym*-bis(2-ethoxyethyl)oxamidine² and hydrogen sulfide as described above. After recrystallization from ethanol-water, the yellow needles melted at 51–52°. Because of the small amount of starting material available, the yield of purified product was not sufficient for analysis.

N,N'-Bis(2-hydroxyethyl)dithiooxamide. (a) Hydrogen sulfide was passed into a solution of 1.0 g. of *sym*-bis(2-hydroxyethyl)oxamidine² in 20 ml. of water until an orange precipitate began to form. After standing for 4 hr. the mixture was filtered. The solid proved to be dithiooxamide.

The filtrate was extracted with 25-ml. portions of ether. Evaporation of the extracts produced 0.1 g. of yellow-orange crystals melting at 83–85°. The yield was 8.5%.

(b) To 12 g. (0.2 mole) of ethanolamine was added 6 g. (0.06 mole) of dithiooxamide. An immediate reaction produced much heat and hydrogen sulfide. After the initial reaction had subsided, the flask was heated gently with constant stirring for 0.5 hr.

After cooling, the mixture was diluted with 20 ml. of water and crystallization induced by scratching the inner surface of the flask. The yield of crude product was 29%. Recrystallization was accomplished from ethyl acetate-carbon tetrachloride. The yellow solid melted at 89–91° and gave no depression of melting point when mixed with the product from (a).

Anal. Calcd. for $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_2\text{S}_2$: N, 13.4; S, 30.7. Found: N, 13.2; S, 30.3.

Attempted reaction of *sym*-bis(2-methylaminoethyl)-oxaldiimidate² with hydrogen sulfide: One gram of the hydrochloride of *sym*-bis(2-methylaminoethyl)oxaldiimidate was dissolved in the minimum amount of water. The solution was made basic with dilute sodium hydroxide. Hydrogen sulfide was passed in until the solution was pale green in color. No crystals formed. The aqueous solution was extracted with ether and the extracts evaporated to dryness. No residue was obtained.

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A New Synthesis of 3-Indolesuccinic Acid

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Maleyldiindole,³ an addition product of indole and

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(2) Research Corporation Research Assistant, 1956–1957. We are indebted to the Research Corporation for a Frederick Gardner Cottrell grant in support of this research.

(3) O. Diels, F. Alder, and W. Lübbert, *Ann.*, **490**, 277 (1931).