rial was removed by extraction with ether, and the solution was made acidic by addition of 25 ml. of concentrated hydrochloric acid. After the solution had stood for 2 hr., it was again extracted with ether. Concentration of the ether solution gave 1.3 g. (13%) of a yellow solid which, after sublimation at 70–80° at 0.5 mm., melted at 54–57°. Recrystallization from hexane gave 1.13 g. of yellow needles, m.p. 58–59°, which showed a greenish fluorescence. The infrared spectrum of this ketone had a single strong band at 6.04 μ in the carbonyl region.

Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.05, 76.25; H, 6.81, 6.65; N, 8.00.

The *2,4-dinitrophenylhydrazone* of 5-ketolilolidine was obtained after crystallization from a hexane-dioxane mixture as scarlet-black crystals, m.p. above 270° w. decomp.

Anal. Calcd. for $C_{17}H_{15}N_5O_4$: C, 57.78; H, 4.28. Found: C, 57.76; H, 4.39.

The *oxime* of 5-ketolilolidine was obtained after crystallization from hexane as yellow needles, m.p. 152–154°.

Anal. Calcd. for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43. Found: C, 69.79; H, 6.37.

Reduction of 5-ketolilolidine to lilolidine. To a solution of 510 mg. of 5-ketolilolidine in 20 ml. of trimethylene glycol there was added 4 ml. of hydrazine hydrate and 1.0 g. of potassium hydroxide, and the mixture was heated at 180° for 1.5 hr. The temperature was then raised to 215° and heating was continued for an additional 2 hr. After the solution had cooled, it was poured into water and extracted with chloroform. The chloroform extracts were dried, concentrated, and the residue was dissolved in ether. The ether solution was extracted with 6*N* hydrochloric acid. The aqueous layer was made basic and again extracted with ether. Concentration of the ether extract followed by distillation gave 90 mg. of a yellow oil, b.p. 90–100° at 0.5 mm. The *picrate* of this oil formed readily and was obtained, after crystallization from ethanol, as yellow plates, m.p. 167.5–168.5° (Barger and Dyer[4] report the m.p. of lilolidine picrate as 168–170°).

Anal. Calcd. for $C_{17}H_{16}N_4O_7$: C, 52.58; H, 4.15. Found: C, 52.75; H, 4.36.

5-Ketolilolidine cyanohydrin, IV. A solution of 600 mg. of 5-ketolilolidine and 10 mg. of potassium cyanide in 5 ml. of anhydrous hydrogen cyanide was allowed to stand at 5° for 3 hr. At the end of this time, the excess hydrogen cyanide was allowed to evaporate and the residue was extracted with boiling hexane. Concentration of the hexane solution followed by cooling gave 200 mg. (28%) of yellow needles, m.p. 110–112°. From the hexane-insoluble residue 360 mg. of 5-ketolilolidine was recovered.

Anal. Calcd. for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04. Found: C, 72.26; H, 6.30.

Lithium aluminum hydride reduction of the cyanohydrin of 5-ketolilolidine. A solution of 170 mg. of 5-ketolilolidine cyanohydrin in ether was added to a solution 1.0 g. of lithium aluminum hydride in ether. The mixture was boiled under reflux for 24 hr. and then decomposed by addition of 20 ml. of 10% aqueous sodium hydroxide solution. The ether layer was separated, dried, and concentrated. Distillation of the residue gave 50 mg. of a yellow oil, b.p. 130° at 0.005 mm., to which structure VI is assigned.

Anal. Calcd. for $C_{12}H_{16}N_2$: C, 76.56; H, 8.57. Found: C, 76.98; H, 8.73.

Schmidt Reaction with 5-ketolilolidine. To a solution of 1.0 g. of 5-ketolilolidine in 20 ml. of chloroform, there was added a prepared solution obtained by treating 2.0 g. of sodium azide in 70 ml. of chloroform with 1.2 g. of concentrated sulfuric acid. The rapidly stirred mixture maintained at 30° was then treated dropwise with an additional 2.0 g. of sulfuric acid. After stirring an additional hour, the mixture was poured into 30 ml. of water. Separation of the chloroform layer followed by concentration gave 420 mg. of an amorphous powder. Repeated crystallization of this from hexane gave 195 mg. (18%) of yellow plates, m.p. 140–141°, softening at 138°. The infrared spectrum of the crystals (VII or VIII) showed NH absorption at 2.52 μ and carbonyl absorption at 6.11 μ. The ultraviolet absorption spectrum of the crystals showed maxima at 227 mμ (log ϵ, 4.19), 263 (3.71), 310 (3.49) and 353 (3.40).

Anal. Calcd. for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.43; N, 14.9. Found: C, 69.7; H, 6.7; N, 14.8.

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Preparation of 7-Nitro-1-naphthylamine and 7,7′-Dinitro-1,1′-azonaphthalene

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Recent publications[1,2] on the chemistry of 7-nitro-1-naphthylamine prompt us to report some observations on the preparation of this amine, which was needed for diazo-coupling to 7,7′-dinitro-1,1′-azonaphthalene.

We have followed the method of Schroeter[3] in preparing the amine by a Semmler aromatization.[1] However, the directions given in the literature are rather scant,[1,3] and it was because of this that, in improvising on the directions, the following observations were made. These observations may be of interest and of help to others.

The oxime of 7-nitro-α-tetralone is best prepared by heating an aqueous ethanol solution of the ketone, hydroxylamine hydrochloride, and sodium acetate. Several attempts with the use of sodium hydroxide to neutralize hydroxylamine hydrochloride in preparing the oxime gave only starting material. The oxime acetate may be conveniently prepared by acetylating the oxime in pyridine with acetic anhydride.

The oxime acetate is very sensitive to light. Sunlight, both direct and indirect, and even electric light, cause the solid oxime acetate to turn pink. The discoloration occurs on the surface exposed to the light; under-surfaces remain white. The solid turns pink even when in suspension in the aqueous pyridine–acetic acid solution from which it is first precipitated. After observing this we carried out all subsequent preparations in subdued light and stored the oxime acetate in protected bottles. We do not know whether the use of pink material will affect subsequent reactions in which the oxime acetate is used. The color change is reversible if, after a few minutes of exposure, the solid is placed in the dark. However, exposures of longer than five minutes appear to be irreversible, and exposures of an hour or more turn the solid a tan color. From the directions

(1) A. Hardy, E. R. Ward, and L. A. Day, *J. Chem. Soc.*, 1979 (1956).

(2) A. Hardy and E. R. Ward, *J. Chem. Soc.*, 2634 (1957).

(3) G. Schroeter, *Ber.*, **63**, 1308 (1930).

given by Schroeter[3] 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 procedure[6] 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°.

Anal.[7] Calcd. for $C_{20}H_{12}N_4O_4$: C, 64.51; H, 3.25; N, 15.04. Found: C, 64.47; H, 3.28; N, 14.63.

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(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).

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

The Chemistry of Oxamidines. II. Reaction with Hydrogen Sulfide[1]

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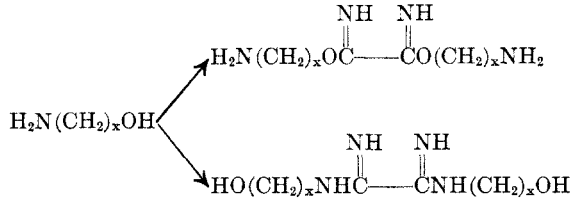
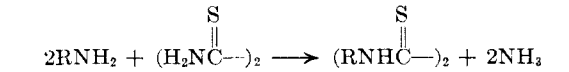
In a study of the reaction of cyanogen with alkanolamines, Graminski[2] had the problem of deciding under what conditions the product was an oxaldiimidate and when it was an oxamidine:



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).