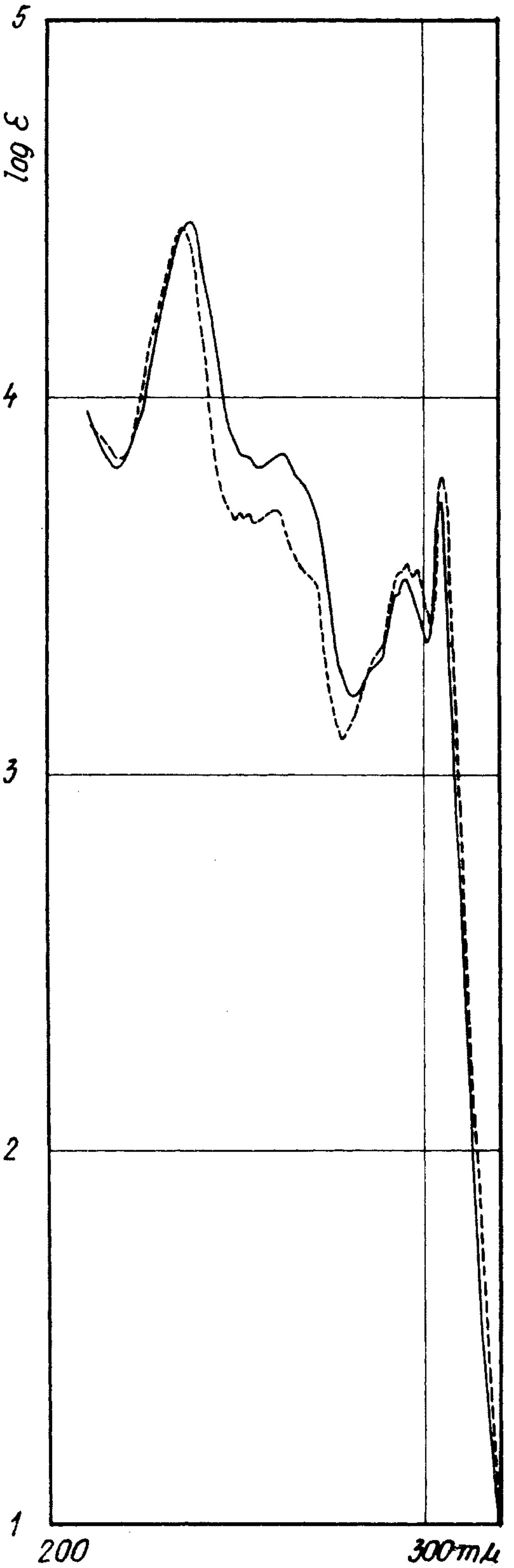

FIG. 2.—ULTRAVIOLET ABSORPTION SPECTRA IN HEPTANE. 2-Methylselenonaphthene (————); selenonaphthene (- - - - - -).

2,3-Dihydro-2-methylthianaphthene. 2-Methyl-3-oxothianaphthane (20.52 g., 0.125 mole) was dissolved in 54 ml. of toluene, then 54 g. of amalgamated zinc suspended in 40 ml. of water was added. During stirring the mixture was acidified with 44 ml. of acetic acid; then there was added 94 ml. of hydrochloric acid under reflux. This was repeated four times in every hour with 25.6 ml. of hydrochloric acid. After six hours the toluene portion was separated, washed with water, and dried over calcium chloride. The toluene was distilled and the residue was fractionated in a vacuum; b.p. 111–125°/18 mm.

2-Methylthianaphthene. 2,3-Dihydro-2-methylthianaphthene (8.5 g.) was heated for three hours at 220° with 1.82 g. of sulfur, and then was steam-distilled from a dilute alkaline solution to give white needles from ethanol, m.p. 51–52°.

Anal. Calc'd for C_9H_8S: C, 72,93: H, 5.44. Found: C, 72.25; H, 5.41.

The *picrate* of this substance had m.p. 108.5°.

α-(o-Carboxyphenylseleno)propionic acid. o,o′-Diselenodibenzoic acid (5.2 g., 0.013 mole) was dissolved in a solution of 2.6 g. of sodium hydroxide. It was heated and stirred for a half hour with 4 g. of zinc dust, then was filtered and to the clear solution was added an equivalent amount of α-bromopropionic acid neutralized with sodium carbonate. After short warming it was acidified with hydrochloric acid. Yield, 5.1 g. (72%), m.p. 212–213°, from a methanol-water mixture. The substance was soluble in most organic solvents.

Anal. Calc'd for $C_{10}H_{10}O_2Se$: C, 43.97; H, 3.69, Found: C, 43.83; H, 3.70.

2-Methylselenonaphthene. A mixture of 4 g. (0.014 mole) of α-(o-carboxyphenylseleno)propionic acid, 1.7 g. of anhydrous potassium acetate, and 4.4 ml. of acetic anhydride was heated to 115°. Carbon dioxide gas evolved and after subsidence of the gas evolution the temperature was raised to 135–140° and the mixture was kept at that temperature for 20 minutes. Then it was cooled and made alkaline with a solution of 10 g. of potassium hydroxide and refluxed for an hour. The solution was acidified with phosphoric acid and steam-distilled. The resulting oil was extracted with ether.

The 2-methyl-3-oxoselenonaphthane thus obtained was dissolved in dil. ethanol and 48 g. of amalgam, containing 4 per cent sodium, was added. Next day the solution was warmed, the ethanol was distilled off and the solution acidified with dil. hydrochloric acid. Hydrogen selenide gas was evolved and the separated oil was steam-distilled. The resulting red-brown crystals were steam-distilled once more to remove the traces of selenium. Yield: 0.8 g. (28.2%). It formed white, bright plates from methanol and was soluble in most organic solvents, insoluble in water. It sublimes in a vacuum, m.p. 63°.

Anal. Calc'd for C_9H_8Se: C, 55.4; H, 4.13. Found: C, 55.98; H, 4.60.

This compound gives a *picrate* in form of golden-yellow needles from ethanol. M.p. 118.5°. When dried in a vacuum it decomposes.

The spectra were determined with a Beckman quartz spectrophotometer Model DU in silica cells of 1 cm. thickness.

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2-Pyrrolidone

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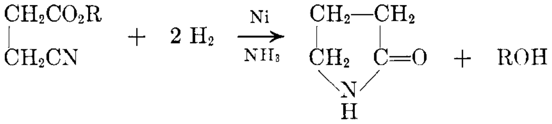
Catalytic hydrogenation of an alkyl 3-cyanopropionate over Raney nickel gives good yields of 2-pyrrolidone when carried out in the presence of ammonia.



This synthesis, as first reported by Adkins,[1] gave a 38% yield of 2-pyrrolidone when carried out in ether. It has been found that the use of at least two moles of ammonia per mole of alkyl 3-cyanopropionate leads to greatly increased yields of 2-pyrrolidone at the expense of high-boiling by-products. This is presumably due to a repression of secondary amine formation.

Ethanol proved to be superior to dioxane, ether, or heptane as solvent. Using 2–5% Raney nickel, based on the total charge, the hydrogenation of ethyl 3-cyanopropionate went smoothly at 90–130° and 1000 psi to give yields of 2-pyrrolidone up to 91%.

EXPERIMENTAL[2]

Ethyl 3-cyanopropionate was prepared by a modification of the method of Kurtz.[3] A mixture of 1000 g. (10 moles) of ethyl acrylate, 289 g. (11 moles) of hydrogen cyanide, and 6.5 g. of potassium cyanide was refluxed for 7 hours during which time the kettle temperature rose to 147°. The acidified reaction mixture was distilled to give ethyl 3-cyanopropionate (b.p. 100°/10 mm., $n_{\rm D}^{30}$ 1.4198; reported[4] b.p. 115°/18 mm.) in 91% yield.

2-Pyrrolidone. A mixture of 254 g. (2 moles) of ethyl 3-cyanopropionate, 750 ml. of ethanol, 50 g. of wet Raney nickel, and 117 g. (7 moles) of anhydrous ammonia was hydrogenated in a 3-liter stainless steel bomb at 90–95° and 1000 psi. for 1 hour. Distillation of the filtered reaction mixture gave 2-pyrrolidone (b.p. 126°/12 mm., $n_{\rm D}^{30}$ 1.4840, m.p. 24.6°; reported[5] b.p. 133°/12 mm., m.p. 24.6°) in 91% yield.

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[1] C. F. Winans and H. Adkins, *J. Am. Chem. Soc.*, **55**, 4167 (1933).

[2] All temperatures are uncorrected.

[3] P. Kurtz, *Ann.*, **572**, 52 (1951).

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The Reaction of Sodium Nitromalonaldehyde with Secondary Aromatic Amines[1]

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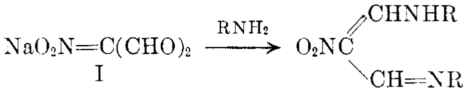
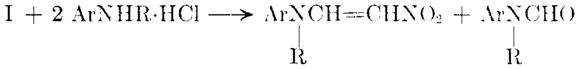
It has long been known that sodium nitromalonaldehyde (I) condenses with primary amines to



$$\underset{\text{I}}{\text{NaO}_2\text{N}{=}\text{C(CHO)}_2} \xrightarrow{\text{RNH}_2} \text{O}_2\text{NC}\begin{cases}\text{CHNHR}\\ \text{CH}{=}\text{NR}\end{cases}$$

produce Schiff bases.[2,3] However, no mention of this unusual salt's reaction with secondary amines has been recorded. It has now been found that sodium nitromalonaldehyde reacts with the salts of secondary aromatic amines to produce 1-amino-2-nitroethylenes (II); the formyl derivative of the amine employed is formed as a by-product. Only piperidinium and morpholinium nitromalonaldehyde were

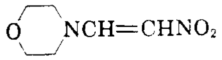


$$\text{I} + 2\,\text{ArNHR·HCl} \longrightarrow \underset{\text{R}}{\text{ArN}}\text{CH}{=}\text{CHNO}_2 + \underset{\text{R}}{\text{ArN}}\text{CHO}$$

II

isolated when piperidine and morpholine were employed in this reaction. Since the reaction is carried out under acidic conditions it is reasonable to presume that the reactive species is either nitromalonaldehyde or its *aci*-form. The isolation of the formanilide shows that the deformylation occurred by attack of the amine on the aldehyde. However, the timing of this step is unknown and thus little can be said about the actual path of the reaction.

The structure of the aminonitroethylenes was inferred from their elementary analyses and instability to alkali,[4] and was substantiated by the close similarity of their infrared and ultraviolet spectra to those of an authentic aminonitroethylene, 1-morpholino-2-nitroethylene (III).[4] The structure of this material had been proven previously[4]



III

by hydrolysis to the amine and the salt of nitroacetaldehyde by alkali and by reduction to the corresponding diamine. A comparison of the spectral characteristics of these materials may be found in Table I.

TABLE I

SPECTRAL CHARACTERISTICS OF 1-AMINO-2-NITROETHYLENES

Compound	$\lambda_{\max}$	$\epsilon_{\max}$	6μ Infrared Bands (cm^{-1})
III	232	2300	1625
	356	13800	
II, Ar = C_6H_5, R = CH_3	238	1600	1625
	362	3000	1590

Efforts to prepare these aminonitroethylenes by the method previously used[4] for the preparation of the morpholine compound were unsuccessful. The anilines condensed with diethyl ethoxymethylenemalonate to produce the corresponding aminomethylenemalonic ester but no reaction between these derivatives and nitromethane could be in-

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[1] This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

[2] Hill and Torrey, *Am. Chem. J.*, **22**, 89 (1899).

[3] Hale and Honan, *J. Am. Chem. Soc.*, **41**, 770 (1919).

[4] Hurd and Sherwood, *J. Org. Chem.*, **13**, 471 (1948).