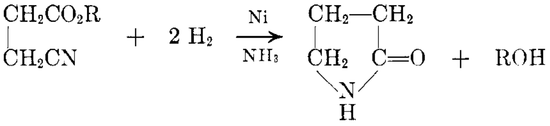

This synthesis, as first reported by Adkins,[1] gave a 38% yield of 2-pyrrolidone when carried out in ether. It has been found that the use of at least two moles of ammonia per mole of alkyl 3-cyanopropionate leads to greatly increased yields of 2-pyrrolidone at the expense of high-boiling by-products. 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_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_D^{30} 1.4840, m.p. 24.6°; reported[5] b.p. 133°/12 mm., m.p. 24.6°) in 91% yield.

Acknowledgment. The author is grateful to Messrs. H. C. Shue and J. Smith, Jr., for technical assistance.

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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).
(4) E. Carriere, *Ann. chim.*, **17**, 38 (1921).
(5) J. Tafel and M. Stern, *Ber.*, **33**, 2226 (1900).

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

Jeremiah P. Freeman and Charles O. Parker

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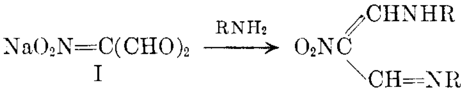
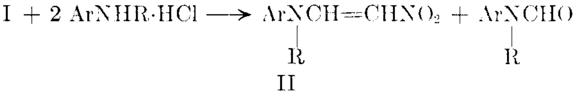
It has long been known that sodium nitromalonaldehyde (I) condenses with primary amines to produce Schiff bases.[2,3] However, no mention of this unusual salt's reaction with secondary amines has been recorded. It has now been found that sodium nitromalonaldehyde reacts with the salts of secondary aromatic 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 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.

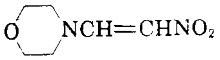


$$\underset{\text{I}}{NaO_2N{=}C(CHO)_2} \xrightarrow{RNH_2} O_2NC\begin{array}{l} \diagup\!\!\!\diagup CHNHR \\ \diagdown CH{=}NR \end{array}$$



$$I + 2\,ArNHR\cdot HCl \longrightarrow \underset{\text{II}}{Ar\underset{\displaystyle R}{\underset{|}{N}}CH{=}CHNO_2} + Ar\underset{\displaystyle R}{\underset{|}{N}}CHO$$

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] 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.



III

TABLE I

Spectral Characteristics of 1-Amino-2-nitroethylenes

Compound	λ_{max}	ϵ_{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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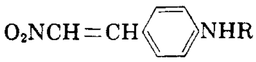
(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.
(2) Hill and Torrey, *Am. Chem. J.*, **22**, 89 (1899).
(3) Hale and Honan, *J. Am. Chem. Soc.*, **41**, 770 (1919).
(4) Hurd and Sherwood, *J. Org. Chem.*, **13**, 471 (1948).

duced. The specificity of this reaction for morpholine and piperidine has already been observed.[4]

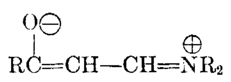
While all of the evidence cited supports the aminonitroethylene structure, there is another possible structure which should be considered. If reaction occurred in the aromatic nucleus rather than on the nitrogen atom,[5] the product would be a 4-alkylamino-β-nitrostyrene (IV). Since aromatic amines are known to undergo nuclear substitution



IV

by carbonyl compounds under acidic conditions, the production of this type of compound is not impossible. However, three pieces of evidence argue against this formulation. First, the infrared spectrum of the materials obtained show no bands attributable to an NH group. No NH group is present in the aminonitroethylene structure (II) but there is one in the nitrostyrene structure (IV). Secondly, alkaline hydrolysis of the product of the nitromalonaldehyde - methylaniline reaction produced methylaniline, the product to be expected from the aminonitroethylene, and not *p*-methylaminobenzaldehyde, the hydrolysis product of the nitrostyrene. Finally the ultraviolet spectrum of 4-dimethylamino-β-nitrostyrene, a good model of the nitrostyrenes, has been measured[6] and is quite different from the spectra of the products obtained in this study: λ_{max} 262, 435 mμ; $\epsilon_{max.}$ 10,250, 28,500 resp. (This nitrostyrene is bright red as compared to the yellow products obtained here.)

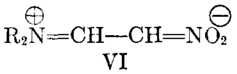
An interesting feature of the infrared spectra of all these compounds is the complete absence of any band in the 1500–1600 cm^{-1} region which might be assigned to the nitro group. A similar situation has been encountered with the infrared spectra of β-amino-α,β-unsaturated ketones[7] in which the carbonyl frequency was lowered considerably. This lowering was attributed to the contribution of structures such as V to the ground state of the



$$\overset{O\ominus}{\underset{|}{}}\!RC{=}CH{-}CH{=}\overset{\oplus}{N}R_2$$

V

molecule. In the present case a similar structure (VI) may be written for the aminonitroethylenes.



$$R_2\overset{\oplus}{N}{=}CH{-}CH{=}N\overset{\ominus}{O_2}$$

VI

The contribution of structures such as VI to the ground state of the aminonitroethylene molecule renders unambiguous assignment of the 1625 cm^{-1} band impossible. It may be associated with the carbon-carbon double bond or a carbon-nitrogen double bond. A detailed spectroscopic study of compounds containing this unique structural unit has been made and will be reported.[8]

EXPERIMENTAL

1-(N-Phenyl-N-methylamino)-2-nitroethylene. A solution of 5.4 g. (0.05 mole) of N-methylaniline in 17 ml. of 3 *N* hydrochloric acid was added all at once to a solution of 8.3 g. (0.053 mole) of sodium nitromalonaldehyde[9] in 50 ml. of water. The mixture was warmed on the steam-bath to hasten the separation of a brown oily product. When separation was complete (30–60 minutes), the mixture was cooled and extracted with 50 ml. of benzene. This extract was dried over sodium sulfate and then was treated with Norit to give a yellow solution which was concentrated to 20 ml. Addition of petroleum ether to this solution while it was immersed in an ice-bath caused crystallization of the product; yield 4.3 g. (48%),[10] m.p. 93–94°. Recrystallization from benzene-petroleum ether gave an analytical sample, m.p. 93.5–94.5°.

Anal. Calc'd for $C_9H_{10}N_2O_2$: C, 60.67; H, 5.62; N, 15.73. Found: C, 61.10; H, 5.72; N, 15.57.

When dissolved in 10% sodium hydroxide, this compound liberated methylaniline.

1-(N-Phenyl-N-ethylamino)-2-nitroethylene. Using the same procedure 4.8 g. (0.04 mole) of N-ethylaniline and 6.4 g. (0.04 mole) of sodium nitromalonaldehyde produced 2.3 g. (30%)[10] of the corresponding aminonitroethylene, m.p. 63–65° (from ether).

Anal. Calc'd for $C_{10}H_{12}N_2O_2$: C, 62.50; H, 6.25; N, 14.58. Found: C, 62.66; H, 5.90; N, 14.49.

The reaction was also carried out using N-propylaniline and N-butylaniline. In both cases reaction occurred but the oily products could not be induced to crystallize.

Infrared and ultraviolet spectra. The infrared spectra were measured as Nujol mulls on a Perkin Elmer Model 21 infrared spectrophotometer with a rock salt prism. The ultraviolet spectra were measured in absolute ethanol with a Beckman DK-1 ultraviolet spectrophotometer.

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(5) This possibility was suggested by a referee.

(6) Drain and Wilson, *J. Chem. Soc.*, 767 (1949).

(7) Cromwell, Miller, Johnson, Frank, and Wallace, *J. Am. Chem. Soc.*, **71**, 3337 (1949).

(8) Freeman and Emmons, *J. Am. Chem. Soc.*, In Press.

(9) Fanta, *Org. Syntheses*, **32**, 95 (1952).

(10) These experiments were carried out before the course of the reaction and thus its stoichiometry had been established. After the identity of the aminonitroethylene had been established, an experiment was made using a 2:1 ratio of amine to aldehyde and the formanilide was isolated. Thus the yields reported here do not represent a maximum as the amount of amine employed was insufficient.

A Synthesis of *o*-Carboxyphenyl β-D-Glucopyranosiduronic Acid

CARL D. LUNSFORD AND ROBERT S. MURPHEY

Received January 12, 1956

Much biological interest has been expressed in the glucuronides of salicylic acid, but no characteri-