methylene chloride and dried over calcium hydride. Upon removal of the methylene chloride and calcium hydride, 10 g., 60.6% yield, of a yellow oil was obtained which crystallized slowly (about 3 weeks) to yellow, mushy platelets.[5] The crude solid was washed with cold methanol giving 4.5 g. (27.2% yield) of a white residue, m.p. 106–107°.

Anal. Calcd. for $C_{11}H_{14}N_4$: C, 65.34; H, 6.93; N, 27.72. Found: C, 66.7, 66.83; H, 6.07, 6.04; N, 27.80, 27.51. Found: C, 65.74, 65.69; H, 6.35, 6.41; N, 27.80, 27.51.

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[5] The infrared analysis[4] of the crude product indicated above 90% (VI) with about 5% of a carbonyl containing impurity.

Synthesis and Some Reactions of 1,1-Bis-(2-cyanoethyl)hydrazine

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Monocyanoethylation of hydrazine with acrylonitrile is reported[1] to be accomplished in high yield with apparently little formation of the dicyanoethylation product when an equimolar ratio of reactants is employed. When an excess of acrylonitrile is employed we have found that a quantitative yield of 1,1-bis(2-cyanoethyl)hydrazine (I) results. In an attempt to extend this

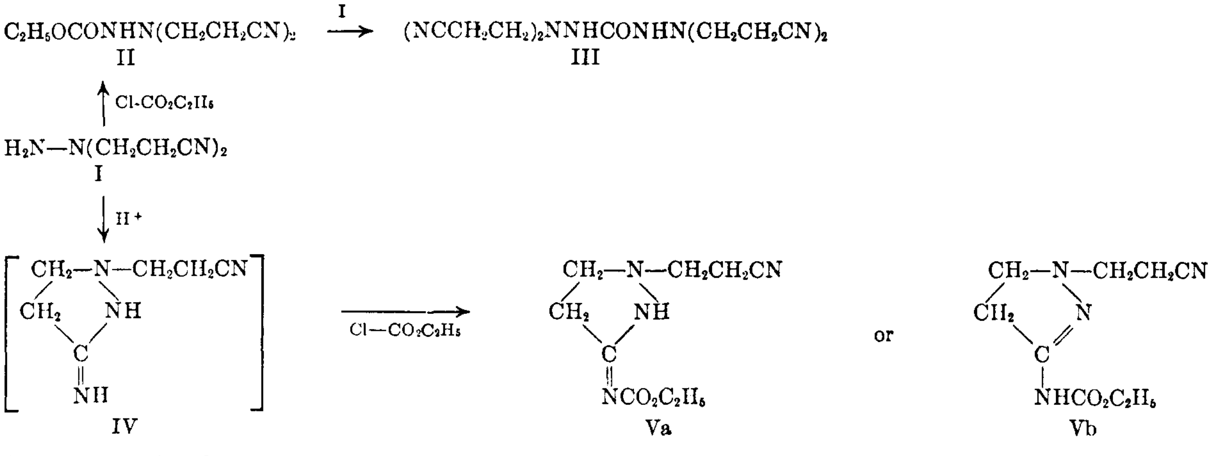
$$2\ CH_2{=}CHCN + H_2N{-}NH_2 \longrightarrow \underset{\text{I}}{H_2N{-}N(CH_2CH_2CN)_2}$$

synthesis to the use of other 2,3-unsaturated nitriles, methacrylonitrile and crotononitrile were treated with hydrazine in an analogous manner. However, only the mono-adducts were obtained and in quantitative yields. The failure of the mono-adducts to react further may be due to the combined effects of steric hindrance and decreased reactivity of the double bonds as has been previously noted in addition of hydrogen cyanide using cyanide ion catalysis.[2]

An attempt to percyanoethylate I by treatment with acrylonitrile in refluxing acetic acid proved unsuccessful as only I was recovered.

That I possesses the unsymmetrical structure proposed is confirmed by infrared maxima at 3.03 and 3.55 μ indicating primary amine function. The close comparison to the infrared spectrum of 1,1-dimethylhydrazine and the fact that phenylhydrazine reacts with acrylonitrile in the absence of catalyst to give 1-cyanoethyl-1-phenylhydrazine[3] is also substantiating evidence. Treatment of I with phenyl isocyanate gave only the *monophenylsemicarbazide* derivative expected from the unsymmetrical structure.

The reaction of I with ethyl chloroformate resulted in the formation of the expected carbazate II (3%), the carbohydrazide III (14%), and a pyrazolidine V (60%). Carbohydrazide III can be realized from aminolysis of II by I. The structure of compound V was assigned on the basis of elemental analysis, molecular weight and infrared spectrum. Pietra[3] and Papini[4] have reported analogous ring closures of substituted hydrazines to give 3-iminopyrazolidines. In the present case, acylation at the exocyclic imino group of the intermediate pyrazolidine, IV, by ethyl chloroformate probably occurred subsequent to the ring closure. Failure of V to react with phenyl isocyanate confirms the expected unreactive nature of the amidic —NH— groups of Va and Vb.



EXPERIMENTAL

All temperatures are uncorrected.

1,1-Bis(2-cyanoethyl)hydrazine (I). To 100 g. (2.0 moles) of hydrazine hydrate (64%) held at 35–40° by cooling there was added with stirring 633 g. (12.0 moles) of acrylonitrile during a 1-hr. period. The mixture was held at 30–40° for an additional 3 hr. and then distilled to remove un-

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[1] V. Hoffmann and B. Jacobi, U. S. Patent 1,992,615, February 26, 1935.

[2] P. Kurtz, *Ann.*, **572**, 28 (1951).

[3] S. Pietra, *Boll. sci. fac. chim. ind. Bologna*, **11**, 78–82 (1952).

[4] P. Papini, S. Checchi, and M. Ridi, *Gazz. chim. ital.*, **84**, 769 (1954).

changed acrylonitrile. I was obtained as amber colored residual oil in quantitative yield [n_D^{30} 1.4740, d_{20}^{20} 1.0665, infrared maxima at 3.03, 3.55 μ (NH_2), 4.3 μ ($C\equiv N$), 6.29, 6.75 μ (NH), 7.1, 7.4 μ (N—N), 8.05, 8.96 μ (C—N)].

Anal. Calcd. for $C_6H_{10}N_4$: C, 52.15; H, 7.25; N, 40.55. Found: C, 52.40; H, 7.30; N, 40.72.

Treatment of I with phenyl isocyanate in benzene gave *1,1-bis(2-cyanoethyl)-4-phenylsemicarbazide)* (m.p. 107° from methanol).

Anal. Calcd. for $C_{13}H_{15}N_5O$: C, 60.68; H, 5.88; N, 27.22. Found: C, 60.81; H, 5.91; N, 28.14.

3-Hydrazino-3-methylpropionitrile. A solution of 100 g. (2.0 moles) of hydrazine hydrate (64%) was held at 30–40° during the addition of 268 g. (4 moles) of crotononitrile and allowed to stand at ambient temperature overnight. The excess crotononitrile was removed by distillation and the residue stripped to 60° at 13 mm. to give a quantitative yield (200 g.) of impure mono-adduct [n_D^{30} 1.4651, d_{20}^{20} 1.0125, infrared maxima at 3.03, 3.55 μ (NH_2), 4.3 μ ($C\equiv N$), 6.22 μ (NH), 7.04, 7.41 μ (N—N) and 7.25 μ (CH_3)].

Anal. Calcd. for $C_4H_9N_3$: N, 42.39. Found: N, 40.1.

Treatment of the above compound with phenyl isocyanate in benzene gave *1-(2-cyanopropyl)-4-phenylsemicarbazide* (m.p. 128.5–129.5° from methanol).

Anal. Calcd. for $C_{11}H_{14}N_4O$: C, 60.53; H, 6.47; N, 25.67. Found: C, 60.52; H, 6.19; N, 26.19.

3-Hydrazino-2-methylpropionitrile. The same procedure as described above was employed using methacrylonitrile to give a quantitative yield of amber oil [n_D^{30} 1.4635, infrared maxima at 3.00, 3.06 μ (NH_2), 4.42 μ ($C\equiv N$), 6.20 μ (NH)].

Anal. Calcd. for $C_4H_9N_3$: C, 48.46; H, 9.08; N, 42.39. Found: C, 48.45; H, 9.08; N, 42.4.

Treatment of the above compound with phenyl isocyanate in benzene gave *1-(1-cyanoisopropyl)-4-phenylsemicarbazide* (m.p. 124–125.5°).

Anal. Calcd. for $C_{11}H_{14}N_4O$: C, 60.53; H, 6.47; N, 25.67. Found: C, 60.8; H, 6.17; N, 26.2.

Treatment of 1,1-bis(2-cyanoethyl)hydrazine (I) *with ethyl chloroformate.* A solution of 140 g. (1.0 mole) of I, 200 ml. of water, and 200 ml. of benzene was stirred at 5–10° during the separate addition in four equal portions of 106 g. (1.0 mole) of ethyl chloroformate and 40 g. (1.0 mole) of sodium hydroxide in 60 ml. of water. The mixture was held at 5° for 1 hr. and then filtered to separate 5 g. of a solid product. Crystallization of this solid from acetone gave a 3.3% yield crystalline product whose analysis indicates it to be III.

1,1,5,5-Tetra(2-cyanoethyl)carbohydrazide (III) [m.p. 191°, infrared maxima at 3.02, 3.12, 6.02, 6.61 μ (NH), 4.41 μ ($C\equiv N$), 5.81–5.83 μ (C=O), 7.06, 7.37 μ (N—N)].

Anal. Calcd. for $C_{13}H_{18}N_8O$: C, 51.85; H, 5.98; N, 37.20. Found: C, 51.93; H, 2.61; N, 38.8.

The aqueous, salt-containing layer of the filtrate was separated and extracted twice with 200 ml. portions of ethyl ether. The combined organic fractions were stripped of solvent on a rotary evaporator to 2 mm. The residual oil on standing partially crystallized. The solid (29 g.) was removed and crystallized from benzene-petroleum ether (b.p. 60–75°) to give a crystalline product whose analysis indicates it to be the expected product II.

Ethyl 2,2-bis(2-cyanoethyl)carbazate (II) [m.p. 91–93°, infrared maxima at 3.02, 6.65 μ (NH), 4.40 μ ($C\equiv N$), 5.80 μ (NH—C=O), 8.05 μ (C—O—C)].

Anal. Calcd. for $C_9H_{14}N_4O_2$: C, 51.42; H, 6.71; 26.68. Found: C, 51.7; H, 6.80; N, 27.3.

Analysis of the mobile amber colored filtrate (125 g.) indicated it was probably V, though this assignment of structure is quite tenuous since it is based solely on analogous reactions, analytical, and spectral data.

1-(2-Cyanoethyl)-3-carboethoxyiminopyrazolidine (Va). [n_D^{30} 1.4673, d_{20}^{20} 1.080, infrared maxima at 3.00 μ (ring NH), 4.40 μ ($C\equiv N$), 5.95 μ (N=C), 5.85 μ (C=O ester), 6.65 μ (ring NH), 7.05 μ (N—N), 8.03, 8.22 μ (C—O—C)]. Molecular weight. Calcd.: 210. Found: 200 ± 5.

Anal. Calcd. for $C_9H_{14}N_4O_2$: C, 51.42; H, 6.71; N, 26.68. Found: C, 51.39; H, 7.03; N, 27.4.

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The Rearrangement of *N*-(Methylaminoalkyl)anilides[1]

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Although the intramolecular migration of acyl groups from N→O is well known,[2] fewer examples of intramolecular N→N′ acyl migration have been recorded. Migrations involving loss of amine with the formation of lactams have been reported by Holley and Holley[3] and by Stirling[4] and rearrangements without loss of amine have also been described.[4,5,6] We would like to describe some additional intramolecular N→N′ acyl migrations observed in a series of *N*-[2-(and 3)*sec*-aminoalkyl]-anilides.

N-(2-Methylaminoethyl)acetanilide (I) was prepared by the reductive debenzylation of *N*-(2-benzylmethylaminoethyl)acetanilide. Distillation of the crude product resulted in a mixture of the expected compound (I) and *N*-(2-anilinoethyl)-*N*-methylacetamide (III). The latter compound resulted from the intramolecular rearrangement of I. The structure of III was proved by the lithium aluminum hydride reduction of III to *N*-ethyl-*N*-methyl-*N′*-phenylethylenediamine (IV) identical with the compound obtained by the reaction of 2-chloro-*N*-methyldiethylamine (V) with aniline.

This rearrangement appears to take place through a cyclic transition state (II). A similar mechanism has been described by Stirling[4] for the rearrangement of *N*-(2-aminoethyl)benzanilide, and by others[7] for a variety of intramolecular N→O and O→N acyl migrations.

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(1) Presented in part at the New York Meeting in Miniature, March 1960, and at the 138th meeting of the American Chemical Society, New York, N. Y., September 1960.

(2) Houben-Weyl, *Methoden der Organischen Chemie*, Thieme, Stuttgart, 1957, Vol. XI, Part 1, p. 936.

(3) R. W. Holley and A. D. Holley, *J. Am. Chem. Soc.*, **74**, 3069 (1952).

(4) C. J. M. Stirling, *J. Chem. Soc.*, 4531 (1958).

(5) O. Widman, *J. prakt. Chem.*, [2] **47**, 343 (1893).

(6)(a) H. Rupe, R. Paltzer, and K. Engel, *Helv. Chim. Acta*, **20**, 209 (1937); (b) A. Gassmann and H. Rupe, *Helv. Chim. Acta*, **22**, 1241 (1939); (c) H. Rupe and W. Frey, *Helv. Chim. Acta*, **22**, 673 (1939).