ligroin to give dichloroacetamide, m.p. 96–99° (sublimed easily); lit.,[8,11] m.p. 94.5°, 98°, sublimes easily.[11]

Anal. Calcd. for $C_2H_3ONCl_2$: C, 18.8; H, 2.34; 0, 12.5. Found: C, 19.0; H, 2.4; 0, 12.6.

The residue (II) from benzene extraction was extracted with acetone, solvent was removed, and the viscous water-soluble mass thus obtained was recrystallized twice from benzene to dichloromalondiamide, m.p. 199.5–202°, lit.,[8] m.p. 202°.

Anal. Calcd. for $C_3H_4O_2N_2Cl_2$: C, 21.07; H, 2.36; 0, 18.7. Found: C, 21.4; H, 2.6; 0, 18.4.

The residue left after acetone extraction of residue (II) was dissolved in water and acidified, whereupon carbon dioxide was evolved and identified by its formation of a precipitate with barium hydroxide.

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(11) A. Geuther, *Jahresbericht über die Fortschritte der Chemie*, **17**, 317 (1864).

Synthesis of 1,3,5,7-Tetracyanoheptane

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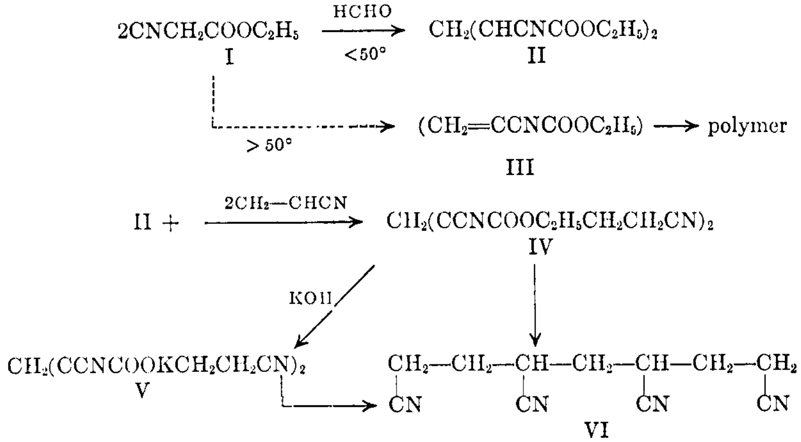
In a study of the solubility properties of polymers,[1] 1,3,5,7-tetracyanoheptane (VI) was synthesized as a short-chain model for the polyacrylonitrile molecule. VI has the features of a correct nitrile group spacing along a short hydrocarbon chain. The following reaction sequence was used to prepare VI from cyanoacetic ester (I), formaldehyde, and acrylonitrile.



The initial step in the synthesis was the addition of formaldehyde to I. The reaction temperature was very critical and, in numerous instances, only the α-cyanoethylacrylate (III) was formed. III polymerized immediately to a low molecular weight, sticky polymer that plugged the distillation column. Recently, Hellmann and Seegmüller[2] and Brown[3] reported the synthesis of II in which the formation of III was avoided.

EXPERIMENTAL

α,α′-Dicyanodiethylglutarate (II). Paraformaldehyde (60 g., 2 moles) was dissolved in 270 g. (2.39 moles) of cyanoacetic ester (I) and to this solution 4 ml. of 10% potassium hydroxide in ethanol was added during the course of 4 hr. Initially, the reaction was exothermic so it was necessary to cool it to maintain the temperature below 50°. However, in the latter stage of the addition of the potassium hydroxide, heat was required to maintain the desired temperature. After an additional 2 hr. heating and stirring, the reaction mixture was adjusted to a pH of 4 with alcoholic hydrochloric acid. It was vacuum-distilled without further treatment. II, 206 g. (73% yield), was collected boiling at 150.5–151.5°/0.4–0.6 mm., n^{24} 1.4500, d_{24} 1.1416.

Anal. Calcd. for $C_{11}H_{14}O_4N_2$: C, 55.46; H, 5.88; 0, 26,80; N, 11.75. Found: C, 55.55, 55.70; H, 5.9, 5.7; O, 26.8, 26.8; N, 11.64, 11.65.

1,3,5,7-Tetracyano-3,5-dicarbethoxyheptane (IV). To a solution of 180 g. (0.756 mole) of II, 300 ml. of dioxane and 102 ml. (1.51 moles) of acrylonitrile was added slowly (1 hr.) 38.5 g. of Triton B while maintaining the temperature between 30–35°. The solution was stirred an additional 16 hr. at this temperature and then poured into 3 l. of distilled water. After acidification to pH 4 with acetic acid, the reddish-yellow, oily layer was separated from the aqueous phase and dried by azeotropic distillation with benzene. The crude product (160 g., 60% yield) was not identified but was converted directly to V.

Potassium α,α′-dicyano-α,α′-bis(β-cyanoethyl)glutarate (V). Crude IV (160 g., 0.452 mole) was slowly mixed (0.5 hr.) into a solution of 84 g. of potassium hydroxide dissolved in a mixture of 600 ml. methanol and 400 ml. ethanol. A gummy, reddish-yellow salt precipitated immediately. The supernatent liquid was decanted from the salt and the latter was isolated by repeated washing with cold methanol. A white, free-flowing powder (39 g., 24% yield) was obtained, m.p. 198–206° dec.

Anal. Calcd. for $C_{13}H_8N_4O_4K_2$: C, 43.09; H, 2.21; N, 15.47; K, 21.54. Found: C, 42.9; H, 3.1, 3.4; N, 14.3, 14.4; K, 20.0, 19.8.

The infrared spectrum of V[4] is consistent with the proposed structure.

1,3,5,7-Tetracyanoheptane (VI). V, 30 g. (0.083 mole), was dissolved in 250 ml. of glacial acetic acid and maintained at 90–100° for 2.5 hr. After removal of the acetic acid by vacuum-distillation, the residue was extracted with

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(1) M. K. Phibbs, *J. Phys. Chem.*, 59, 346–53 (1955).

(2) H. Hellmann and K. Seegmüller, *Ber.*, **90**, 535 (1957).

(3) J. C. Brown, this laboratory, private communication.

(4) Dr. R. Zbinden, private communication.

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

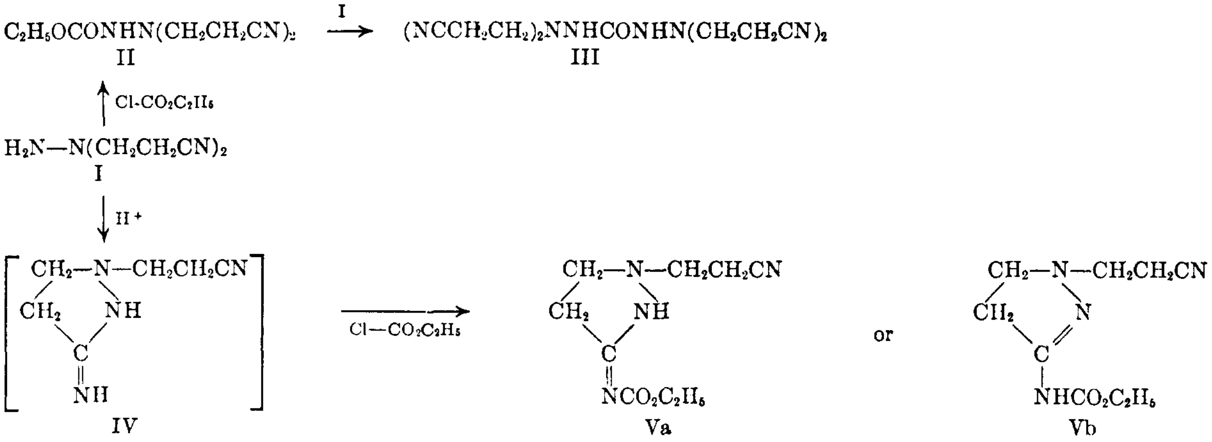
John W. Lynn

Received July 20, 1960

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).