The molarity of the solution with respect to magnesium was determined by adding a known volume to excess standard sulfuric acid, heating to dispel carbon dioxide, and back-titrating with sodium hydroxide. The carbon dioxide content of the reagent could be determined gasometrically; however, the interpretation of the result is not straightforward.[1] A magnesium methyl carbonate solution prepared in this fashion was used for seven months with no detectable change in its effectiveness. All the methyl esters were prepared in an identical fashion. The preparation of methyl α-nitrobutyrate is given as an illustration.

Methyl α-Nitrobutyrate. (a) **Carboxylation of Nitropropane.**—One liter of 2 *M* magnesium methyl carbonate was placed in a 2-l. flask equipped with a stirrer, a gas inlet tube, and a combination condenser and gas outlet. The reagent was heated, while stirring, to 60° under a carbon dioxide stream. When the temperature of the magnesium methyl carbonate solution had stabilized at approximately 60°, 89 g. of 1-nitropropane was added, and the carbon dioxide stream was replaced by a slow nitrogen stream.

After stirring for 6 hr. at 60°, the reaction mixture was cooled to 10° with an ice bath, and then either hydrolyzed or the magnesium chelate precipitated.

(b) **Hydrolysis and Esterification.**—The carboxylation mixture was poured with vigorous stirring into a mixture of 600 ml. of concentrated hydrochloric acid and 750 g. of ice that had been overlayed with 100 ml. of ether. The ether was separated and the aqueous layer extracted four times with 100-ml. portions of ether. The ether extracts were combined and given a preliminary drying for 15 min. with powdered anhydrous magnesium sulfate. After filtering off the magnesium sulfate, the drying was completed with phosphorus pentoxide. The essentially colorless ether solution was evaporated on a rotary film evaporator at room temperature or slightly below. While the ether was evaporating, 200 ml. of 2 *M* methanolic hydrogen chloride was cooled to −50°. This was poured into the flask containing the α-nitrobutyric acid and the mixture was allowed to warm spontaneously to room temperature and stand overnight. Approximately 100 ml. of the methanol was removed at room temperature, under vacuum, and the remaining reaction mixture was poured into 200 ml. of water. The aqueous solution was extracted five times with 50-ml. portions of ether, the ether dried over magnesium sulfate and distilled. The yield of methyl α-nitrobutyrate was 64.7 g. (44%), b.p. 77°/2.5, $n^{20}D$ 1.4249.

(c) **Precipitation and Esterification.**—The carboxylation mixture was poured with vigorous stirring into 2 l. of ether to precipitate the magnesium chelate of α-nitrobutyric acid and unchanged magnesium methyl carbonate. After decanting the supernatant liquid phase, 1 l. of methanol containing 200 g. of hydrogen chloride cooled to −50° was added to the solid precipitate. This mixture was allowed to warm spontaneously to room temperature and stand overnight. Approximately 600 ml. of methanol was distilled at room temperature under vacuum, and the remaining mixture was poured into 800 ml. of water. The aqueous system was extracted eight times with 50-ml. portions of ether. After drying the ether solution with magnesium sulfate, the product was distilled. The yield was 67 g. (45.5%) of methyl α-nitrobutyrate.

Preparation of Ammonium Salts.—Approximately 1.0 g. of the α-nitro ester was added to 25 ml. of 1 *M* ammoniacal methanol, and the reaction mixture was placed in the refrigerator overnight. The crystals were filtered off and recrystallized from 0.5 *M* ammoniacal methanol. The products were dried over potassium hydroxide in an ammonia atmosphere. All melting points were taken in sealed tubes. An analogous procedure gave the sodium salts of the methyl nitro esters when sodium methoxide was used in place of ammonia.

Preparation of Methyl α-Aminobutyrate Hydrochloride.—A solution of 1.47 g. (0.01 mole) of methyl α-nitrobutyrate in 40 ml. of methanol, in which was suspended 1.0 g. of 5% platinum on carbon (K&K Laboratories), was stirred, under hydrogen at 1 atm. until 670 ml. was consumed. The catalyst was filtered off, 10 ml. of 1.0 *M* methanolic hydrogen chloride was added to the filtrate, and the reaction mixture was evaporated to dryness in a film evaporator. The solid residue was recrystallized from ethanol–benzene, m.p. 136–138°, lit. 139°.[14]

Preparation of Methyl α-Ketobutyrate 2,4-Dinitrophenylhydrazone.—A sample of methyl α-nitrobutyrate (1.47 g.) was dissolved in 10 ml. of 2 *M* sodium methoxide. The mixture was poured into 20 cc. of ice cold concentrated hydrochloric acid. After filtering off the precipitated sodium chloride, the blue aqueous phase was extracted with ether and dried. After the blue color had faded, 2,4-dinitrophenylhydrazone reagent was added, the ether largely removed on the steam bath, and 10 ml. of methanol was added. The product crystallized after standing overnight in the refrigerator, m.p. 147–148°.

Anal. Calculated for $C_{11}H_{12}N_4O_6$: C, 44.90; H, 4.08; N, 19.05. Found: C, 44.9; H, 4.1; N, 19.2.

(14) T. Curtius and E. Müller, *Ber.*, **37**, 1274 (1904).

Dicyanoketenimine (Cyanoform)

S. TROFIMENKO

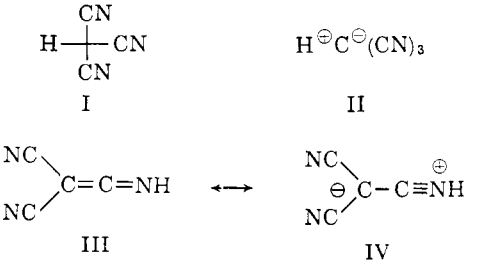
Contribution No. 807 from the Central Research Department Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

Received September 4, 1962

While salts and solutions of cyanoform have been known for a long time,[1] the nature of the free acid has not been established. Cox and Fontaine[2] reported the isolation of a material, m.p. 55–56°, "stable at room temperature for weeks, even when exposed to light and air," which they regarded as cyanoform. No such material could be isolated in our laboratories from aqueous or aquoethereal cyanoform solutions.

It was possible, however, to obtain by rapid evaporation of aquoethereal "cyanoform" a crystalline solid, obviously different from the material described by Cox and Fontaine. That it was indeed the anhydrous acid was established by analysis, by reaction with aqueous silver ion or *t*-butylamine to give, respectively, silver and *t*-butylammonium tricyanomethanide, and by reaction with ethanol to yield 1-amino-1-ethoxy-2,2-dicyanoethylene.

The free acid is unstable and forms an orange-red polymer on standing at room temperature, but can be purified by vacuum sublimation. The colorless, crystalline sublimate polymerizes slowly at room temperature, rapidly on heating above 70°, yet it has been stored unchanged for several days at −80°. The infrared spectra of the crude acid and of the sublimed material are essentially identical. The location of the nitrile band at 4.55 μ is sufficient to eliminate structures such as I and II and points to dicyanoketenimine, III, while the absence of ketenimine absorption[3] at 5.0–5.2 μ in conjunction with bands at 4.0, 4.4, and 5.6 μ, reminiscent of immonium bands,[4] is indicative of the



I II

III ⟷ IV

(1) (a) H. Schmidtman, *Ber.*, **29**, 1172 (1896); (b) A. Hantzsch and G. Oswald, *ibid.*, **32**, 641 (1899); (c) L. Birkenbach and K. Huttner, *ibid.*, **62B**, 153 (1929).

(2) E. Cox and A. Fontaine, *Bull. soc. chim. France*, 948 (1954).

(3) C. L. Stevens and C. J. French, *J. Am. Chem. Soc.*, **75**, 657 (1953); on the other hand, R. Dijkstra and H. J. Backer, *Rec. trav. chim.*, **73**, 569 (1954), report the ketenimine band at 4.61 μ for N-methylbisdiethylsulfonylketenimine.

(4) B. Witkop, *Experientia*, **10**, 420 (1954); *J. Am. Chem. Soc.*, **76**, 5597 (1954).

zwitterionic form IV, known to contribute appreciably to the structure of negatively substituted ketenimines.[5a,b]

Dicyanoketenimine is completely ionized in aqueous[6] or aquoethereal solutions as judged by ultraviolet[6] and infrared spectra. In the form of hydronium tricyanomethanide it is reasonably stable, since the addition of water proceeds slowly.[7] On dehydration, however, dicyanoketenimine is obtained instead of tricyanomethane. This fact is not too surprising, as it is known that negatively substituted malononitriles exist as the 1,1-dicyanoethylene tautomers,[8] probably favored on account of their resonance stabilization through structures analogous to IV, impossible in substituted dicyanomethanes. By the analogy between the $(NC)_2C{=}C\langle$ and $O{=}C\langle$ groups,[9] tricyanomethane and dicyanoketenimine are cyanocarbon analogs of cyanic and isocyanic acid. In fact, addition reactions of "cyanoform" resemble closely those of isocyanic acid, as does its facile autoaddition–polymerization. The dicyanoketenimine structure accounts readily for all these properties.

Experimental

Aquoethereal "Cyanoform."—This solution was prepared from potassium tricyanomethanide[7] as previously described.[1a,b] According to Hantzsch and Oswald,[1b] the composition is cyanoform–water–ether in 1:10:10 ratio. A nuclear magnetic resonance spectrum of this solution had, apart from the ethyl peaks (triplet and quadruplet centered at $\tau = 9.04$ and $\tau = 6.70$, respectively), a single proton peak at $\tau = 4.00$. The relative intensities of these peaks supported the earlier analysis.[1b]

The infrared spectrum of the aqueoethereal solution was characterized by tricyanomethanide bands at 4.61, 7.97, and 8.03 μ.[10]

Dicyanoketenimine.[11]—Five milliliters of aquoethereal "cyanoform" was placed on a watch glass and evaporated rapidly by directing a stream of air over the surface until a thick slurry was obtained. It was filtered immediately and the yellowish crystals pressed dry; yield 150–160 mg. Sublimation of this material at 1 mm. starting at a bath temperature of 60° and slowly raising it to 90° gave about 70 mg. of white crystals. The sublimate has no melting point but starts turning orange at 70° and decomposes to a red tar around 140°.

Anal. Calcd. for C_4HN_3: C, 52.7; H, 1.11; N, 46.1. Found: C, 52.2; H, 1.45; N, 45.6.

The infrared spectrum (Nujol mull) is characterized by bands at 4.0, 4.4, 4.55, 5.6, 7.98, 9.76, and 12.16 μ and is not significantly different from that of the crude solid.

A sample of the sublimate was dissolved in water and a portion of the solution was treated with aqueous silver nitrate. Silver tricyanomethanide precipitated immediately and was identified by its infrared spectrum.

Another portion of the solution was treated with excess *t*-butylamine yielding, on concentration of the solution, *t*-butylammonium tricyanomethanide, identified by comparison with authentic material[7] (mixed melting point and superimposition of infrared spectra).

Treatment of sublimed dicyanoketenimine with excess ethanol afforded, on evaporation of the solution, a solid identified as 1-amino-1-ethoxy-2,2-dicyanoethylene by comparison with authentic material[9] (mixed melting point and superimposition of infrared spectra).

(5) (a) R. K. Bullough and P. J. Wheatley, *Acta Cryst.*, **10**, 233 (1957); (b) Dinitroacetonitrile [C. O. Parker, W. D. Emmons, H. A. Rolewicz, and K. S. McCallum, *Tetrahedron*, **17**, 79 (1962)], which may be regarded as dinitroketenimine exhibits properties that parallel those of cyanoform. It could not be isolated in anhydrous state and infrared data are, consequently, lacking.

(6) R. H. Boyd, *J. Am. Chem. Soc.*, **83**, 4288 (1961).

(7) S. Trofimenko, T. L. Little, and H. F. Mower, *J. Org. Chem.*, **27**, 433 (1962).

(8) F. Arndt, H. Scholz, and E. Frobel, *Ann.*, **521**, 95 (1935).

(9) W. J. Middleton and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2788 (1958).

(10) F. A. Miller and W. K. Baer of Mellon Institute obtained values of 4.60 and 8.05 μ in aqueous solution and 4.60, 7.99, and 8.07 μ in the solid (private communication).

(11) Note: This procedure was found to be most convenient for preparing small samples of dicyanoketenimine. All of the operations must be conducted rapidly, as crude dicyanoketenimine and its concentrated solutions are unstable. Scaling up was not feasible as larger samples were much more prone to polymerize.

Nucleophilic Substitution at the Pyridazine Ring Carbons. I. Synthesis of Iodopyridazines

PETER COAD, RAYLENE ADAMS COAD, SHARON CLOUGH,[1] JUNE HYEPOCK, ROLLAND SALISBURY, AND CHARLES WILKINS[1]

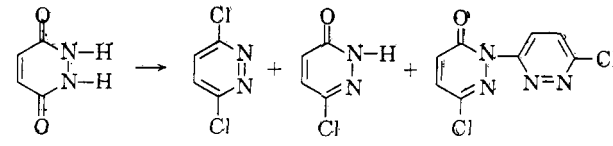
Department of Chemistry, Chapman College, Orange, California

Received August 17, 1962

In recent years interest has grown in the chemistry of the substituted pyridazines because of the theoretical aspects of the pyridazine ring system[2,3] and because of biological activity shown by many of these compounds.[4,5] A study of structure-reactivity correlations of substituted pyridazines is being conducted in this laboratory. A general procedure was sought by which satisfactory yields of iodopyridazines could be obtained from readily available starting materials. Previously, Horning and Amstutz[6] reported that substituted iodopyridazines might be formed as by-products in the reduction of highly substituted chloropyridazines with red phosphorus and hydriodic acid.

The route which appeared attractive was the nucleophilic substitution at the ring carbons using chloro- or bromopyridazines as the substrate and iodide ion as the nucleophile since chloro- and bromopyridazines can be prepared by one- or two-step syntheses from commercially available starting materials. For example, maleic hydrazide (I) can be converted to chloro or bromo compounds.

In spite of the fact that the synthesis of 3,6-dichloropyridazine (II) using phosphorus oxychloride is described several times in the literature,[7,8] Feuer and Rubenstein[9] showed by meticulous work that the product from such reactions is contaminated with 3-chloro-6-hydroxypyridazine (III) and to a lesser extent with 1-(3′-chloro-6′-pyridazyl)-3-chloro-6-pyridazone (IV). The over-all yield of pure dichloropyridazine was of the order of 30%. Difficulties in obtaining dichloropyridazine of high purity were also encountered



I II III IV

(1) Participants in Undergraduate Research Training Grant NSFG11835 from the National Science Foundation.

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(3) S. F. Mason, *ibid.*, 1240 (1959).

(4) J. Druey, Kd. Meier, and K. Eichenberger, *Helv. Chim. Acta*, **37**, 121 (1954).

(5) J. Druey, U.S. Patent 2,764,584 (1956).

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