160°. A solution of the red solid in a minimum amount of hot dimethylformamide when cooled in a freezer deposited 2.7 g. of crude product, m.p. 221°. The product after four recrystallizations from dimethylformamide and washing with acetone was obtained as reddish green crystals; yield, 1.3 g.; 21.6%, m.p. 241°.

Anal. Calcd. for $C_{27}H_{23}N_5Cl_2O_7$: C, 54.01; H, 3.86. Found: C, 53.74, 54.03; H, 4.23, 4.39.[12]

The picrate was neutralized with ammonium hydroxide and the precipitate was recrystallized from octane to yield yellow crystals, m.p. 115–116°.

Anal. Calcd. for $C_{21}H_{20}N_2Cl_2$: Cl, 19.10. Found: 19.25, 19.19.[13]

Schiff Bases.—A mole to mole mixture of 4-aminostyryl base and the aldehyde was heated 10–20 min. without solvent (method A), or dissolved in a minimum volume of methanol (method B), or the aldehyde was added slowly with stirring at 110° to a solution of the amine in a minimum amount of dimethylformamide, then heated 15 min. at 120°–130° (method C). The crude product was precipitated by addition of water and was recrystallized from octane or from methanol.

(12) Analyses by Weiler and Strauss, Oxford, England.

(13) Analyses by Galbraith Laboratories, Knoxville, Tenn.

Base-Catalyzed Ring Opening of Diethyl 1,1,2,2-Tetracyanocyclopropane-3,3-dicarboxylate

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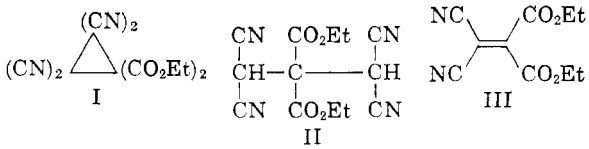
Polycarboxylic esters of cyclopropane are generally stable to bases with respect to ring cleavage.[1] Hydrolysis is often accompanied by decarboxylation but the cyclopropane ring remains intact unless very vigorous reaction conditions are employed. Herewith is reported an example of a cyclopropane ring cleavage under very mild conditions.

Diethyl 1,1,2,2 - tetracyanocyclopropane - 3,3-dicarboxylate (I) was synthesized using the technique of Mariella and Roth.[2] Condensation of malonitrile and diethyl ketomalonate catalyzed by a trace of piperidine yielded diethyl dihydroxymalonate and an intermediate, presumably II. Attempted isolation of this intermediate gave instead a compound assigned the structure diethyl 1,1 - dicyanoethylene - 2,2 - dicarboxylate (III).[3]



I II III

(1) W. E. Truce and L. B. Lindy, *J. Org. Chem.*, **26**, 1464 (1961).

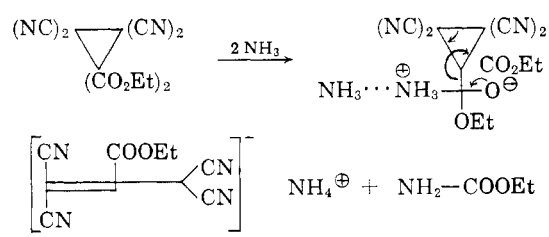
(2) R. P. Mariella and A. J. Roth, *J. Org. Chem.*, **22**, 1130 (1957).

(3) This compound was originally prepared by W. T. Tsatsos of the Central Research Dept., E. I. du Pont de Nemours & Co., *via* the condensation of malonitrile and diethylketomalonate.

Structural assignment was made on the basis of elementary analysis, infrared absorption, and reaction with anthracene to form initially the π-complex and then the Diels-Alder adduct. The reaction with anthracene is analogous to the reactions of tetracyanoethylene with aromatic compounds[4] to give the π-complexes and, where favorable, the Diels-Alder adducts.

Treatment of an ethanol solution of intermediate II with bromine gave the cyclic diester I in 87% yield.[5] When the diester I was added to aqueous or methanolic ammonia, a deep orange solution formed, but no tractable product could be isolated. In anhydrous ether, ammonolysis of the diester gave a nearly quantitative yield of an orange crystalline solid. The orange compound was soluble in water and alcohol and insoluble in nonpolar organic solvents. Its aqueous solutions gave instantaneous colored precipitates on addition of organic bases, *e.g.*, quinoline. The infrared spectrum had a sharp, intense nitrile band at 2190 cm.$^{-1}$ (4.57 μ), no absorption between 1710 and 1650 cm.$^{-1}$, but a strong band at 1510 cm.$^{-1}$ (6.62 μ). Cyclopropane nitriles absorb in the region 2250 cm.$^{-1}$ (4.45μ) and those containing carbethoxy groups characteristically have very weak nitrile bands[6]—*e.g.*, the diester I has only a barely perceptible nitrile band at 2240 cm.$^{-1}$ (4.46 μ). This sharp increase in nitrile band intensity coupled with the shift to lower frequency corresponds to the nitrile absorption of cyanopropenide ions as exhibited by sodium pentacyanopropenide and similar ions[7] which have high intensity absorption in the 2190-cm.$^{-1}$ (4.57μ) region. The polycyanopropanides also exhibit a strong low fequency shift in the C=C-stretching band from the region near 1625 cm.$^{-1}$ (6.1μ) to the region 1550–1400 cm.$^{-1}$ (6.45–7.41 μ)[7]; and in addition they form colored precipitates with organic bases such as quinoline.

These data lead to the structural assignment for the orange compound as ammonium 1,1,3,3-tetracyano-2-carbethoxypropenide. Further buttressing evidence is the fact that the ethereal



(4) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald, and H. E. Winberg, *J. Am. Chem. Soc.*, **80**, 2775 (1958).

(5) This compound was first synthesized in very small yield by Dr. R. M. Scribner of the Central Research Dept., E. I. du Pont de Nemours & Co., using the procedure of L. Ramberg and S. Widequist, *Arkiv. für Kemi*, **12A**, No. 22 (1937); **12B**, No. 37 (1941).

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., Wiley, New York, 1958, p. 266.

(7) C. E. Looney and J. R. Downing, *J. Am. Chem. Soc.*, **80**, 2840 (1958).

supernatant of the ammonolysis mixture gave a 50% yield of ethyl carbamate on work-up. Equation 1 is a rationalization of the reaction sequence.

At first glance the driving force for the reaction would seem to be the release of steric strain to give a resonance-stabilized product. However, construction of molecular models[8] indicates that a planar configuration of the propenide ion is subject to a much larger degree of steric crowding than is the cyclopropane. Even if the carbon-carbon bonds of the propane molecules are allowed to rotate freely, thus destroying allylic resonance, the most favorable conformation is not improved over the cyclopropane with respect to steric crowding. An acceptable rationale for the reaction is not evident.

Experimental

Diethyl 1,1-Dicyanoethylene-2,2-dicarboxylate (III).—Malonitrile (6.6 g., 0.10 mole) was dissolved in diethyl ketomalonate (17.4 g., 0.10 mole, Pierce Chemical Co.) contained a flask protected from moisture and cooled in an ice bath. One drop of base catalyst (2/3 dioxane, 1/3 piperidine) was added. At the end of 3 hr. the contents had become a solid waxy white mass. Filtration under nitrogen gave a white hygroscopic residue and a yellow oily filtrate.

The white solid was shown to be diethyl dihydroxymalonate by comparison (infrared) with an authentic specimen.

The yellow oil was fractionated through a spinning brush column: 1.2 g., b.p. 60–97° (1.5 mm.) and 13.1 g., b.p. 97–99° (1.5 mm.). The 97–99° fraction was redistilled through the spinning brush column: 11.7 g., b.p. 86.0° (1.0 mm.) collected in six fractions, $n^{24}D$ = 1.4620–1.4628. The center fraction, $n^{24}D$ 1.4628, was analyzed.

Anal. Calcd. for $C_{10}H_{10}N_2O_n$: C, 54.0; H, 4.5; N, 12.6; mol. wt., 222. Found: C, 54.23, 54.25; H, 4.56, 4.95; N, 12.80, 12.67; mol. wt., 203, 205.

The NMR spectrum (40 mc./sec.) shows only O—CH_2—CH_3 absorption. The infrared spectrum has a weak nitrile band at 2230 cm.$^{-1}$ (4.48 μ), a strong carbonyl at 1750 cm.$^{-1}$ (5.72 μ), and —C=C— at 1600 cm.$^{-1}$ (6.22 μ). The compound reduces permanganate readily but does not decolorize bromine in carbon tetrachloride, even on boiling. Its solution in benzene is colorless, but addition of anthracene gives a red-brown complex. An equimolar mixture of the compound and anthracene is red-brown, but after heating to 150° and cooling, a white adduct forms. Crystallization from ethanol–water, then from cyclohexane gave white crystals, m.p. 153.6–155.2°.

Anal. Calcd. for $C_{24}H_{20}N_2O_4$: C, 72.0; H, 5.0; N, 7.0. Found: C, 72.16, 71.84; H, 5.13, 5.19; N, 6.96, 6.94.

The adduct is thermochromic, turning red-brown on melting and white again on resolidifying.

Diethyl 1,1,2,2-Tetracyanocyclopropane-3,3-dicarboxylate (I).—To the product resulting from the reaction of malonitrile (38 g., 0.575 mole) and diethyl ketomalonate (100 g., 0.575 mole) (this time a yellow viscous fluid), ethanol (250 ml., commercial absolute) was added and the mixture stirred to effect solution. While cooling the mixture in an ice bath, bromine (52 g., 0.28 mole) was added dropwise slowly. The resulting dark red-brown solution was poured onto 1 kg. of ice to give a yellow oil, which crystallized on being stirred overnight. The precipitate was washed with water, then dried over phosphorus pentoxide under vacuum to give 71.5 g. (0.25 mole, 87%) of product, m.p. 129.4–130.8°. A sample crystallized from ethanol–water, carbon tetrachloride, and then hexane was sublimed at 1 mm. pressure and 110° to give white crystals, m.p. 129.6–131.2°.

(8) Godfrey Molecular Models, *J. Chem. Ed.*, **36**, 140 (1959).

Anal. Calcd. for $C_{13}H_{10}N_4O_4$: C, 54.5; H, 3.5; N, 19.6; mol. wt., 286. Found: C, 54.80, 54.70; H, 3.81, 3.51; N, 19.44, 19.37; mol. wt., 297, 280.

The NMR spectrum (40 mc./sec.) shows only O—CH_2—CH_3 absorption. The infrared spectrum has only a barely perceptible nitrile band at 2240 cm.$^{-1}$ (4.46 μ), a strong CO at 1765 cm.$^{-1}$ (5.70 μ), and no absorption between 1765 (5.70 μ) and 1500 cm.$^{-1}$ (6.7 μ) (*i.e.*, no —C=C—).

Ammonium 1,1,3,3-Tetracyano-2-carbethoxypropenide (IV).—Diethyl 1,1,2,2-tetracyanocyclopropane-3,3-dicarboxylate (I) (15.0 g., 0.052 mole) was suspended in ether (500 ml., distilled from calcium hydride) in a flask protected from moisture. Dry ammonia (approx. 15 g.) was allowed to distill from a solution of sodium in ammonia and drop from a Dry Ice–acetone cooled condenser into the ethereal suspension of I. The first drops of ammonia gave a yellow oily precipitate which soon solidified to a brown cake. After stirring overnight, the mixture was filtered to give 11.4 g. of brown amorphous solid, m.p. 192–201° dec. The filtrate was evaporated to dryness and the pasty orange residue was stirred with chloroform, leaving a yellow chloroform solution and 0.5 g. of yellow powder, m.p. 203° (decompn.). Mixed m.p. of this latter yellow powder with the first precipitate was 197–204° (decompn.). The chloroform-insoluble material was washed with excess chloroform and dried *in vacuo*.

Anal. Calcd. for $C_{19}H_{13}N_5O_2$: C, 52.1; H, 4.3; N, 30.3. Found: C, 52.34; H, 4.21; N, 30.50.

The chloroform solution was decolorized with charcoal and evaporated to dryness to give white crystals, m.p. 46.6–48.6°, whose infrared spectrum was superimposable on that from an authentic specimen of ethyl carbamate.

The infrared spectrum of the orange solid has a very strong nitrile band at 2190 cm.$^{-1}$ (4.57 μ), a strong CO at 1730 cm.$^{-1}$ (5.78 μ), no absorption between 1730 (5.8 μ) and 16.50 cm.$^{-1}$ (6.5 μ), but a strong band at 1510 cm.$^{-1}$ (6.62 μ) assigned to the —C=C—.

Quinolinium-1,1,3,3-tetracyano-2-carbethoxypropenide.—To an aqueous solution of IV was added a concentrated aqueous solution of quinolinium hydrochloride. An immediate orange precipitate formed, several recrystallizations of which from water gave a product of m.p. 51–52°. Drying in high vacuum over phosphorus pentoxide at 60° gave a product of m.p. 111.5–112.5°.

Anal. Calcd. for $C_{19}H_{13}N_5O_2$: C, 66.5; H, 3.8; N, 20.4. Found: C, 66.79, 66.88; H, 3.77, 4.00; N, 20.03, 20.0.

Recrystallization of the 111.5–112.5° product from water gave a product of m.p. 51–52°, presumably a hydrate.

S-Acylthiosemicarbazones

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While investigating methods for the preparation of 1-(5-nitro-2-furoyl)thiosemicarbazides,[1] a paper was found wherein the authors[2] treated *p*-nitrobenzoyl chloride and other acid chlorides with thiosemicarbazide in *acetone* to obtain 1-*p*-nitrobenzoyl and other 1-acylthiosemicarbazides. This reaction was verified in our laboratory. However, when 5-nitro-2-furoyl chloride was substituted for the nitrobenzoyl chloride, *S*-(5-nitro-2-furoyl)ace-

(1) W. R. Sherman, *J. Org. Chem.*, **26**, 88 (1961).

(2) M. Ohta and T. Higashijima, *J. Pharm. Soc. Japan.*, **72**, 376 (1952).