

Registry No.—Cyclobutylcarbanyl radical, 16447-31-7; cyclobutylcarbanyl iodide, 16408-62-1.

Acknowledgment.—We are grateful to Professor W. D. Walters for a sample of methylcyclobutane.

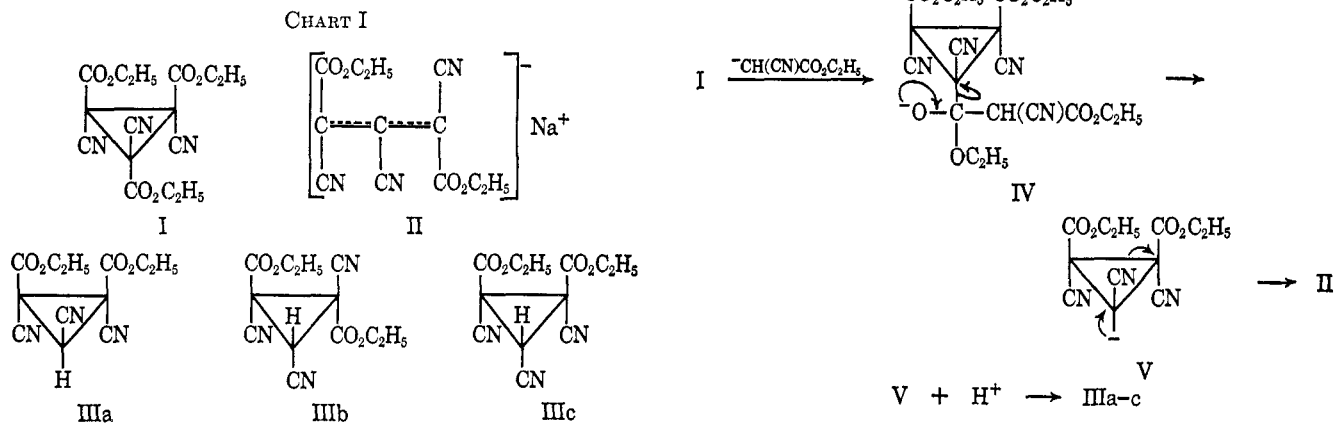
**The Reaction of Triethyl *trans*-1,2,3-Tri-
cyanocyclopropane-1,2,3-tricarboxylate with
Base. Formation of a Substituted
Cyclopropane Anion Radical**

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In the synthesis of triethyl *trans*-1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate (I) by reaction of ethyl sodiocyanoacetate and ethyl bromocyanoacetate according to the general procedure of Felton,^{1b} we obtained, in addition to I, two other compounds, sodium 1,2,3-tricyano-1,3-dicarbethoxypropenide (II) and diethyl 1,2,3-tricyanocyclopropane-1,2-dicarboxylate (IIIa-c) (21 and 6% yield, respectively) (Chart I).



Compounds II and IIIa-c were characterized and identified as follows. The yellow salt II gave the correct elemental analysis and was soluble in water and insoluble in nonpolar solvents. The infrared spectrum showed the presence of conjugated nitrile,² exhibiting a strong, sharp absorption peak at 4.51 μ and a less intense peak at 4.47 μ . The absorption bands at 5.88 and 6.78 μ are assigned to C=O and C=C stretching vibrations, respectively. The ultraviolet spectrum of II showed $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 425 m μ (ϵ 22,203) and 218 (13,192). These ultraviolet absorption features are similar to those reported for pentacyanopropenides.³

Assignment of structures IIIa-c is based primarily on analysis of spectral data. The proton nmr spectrum exhibited signals centered at δ 4.55 (two protons, quartet), 4.54 (two protons, quartet), 3.58 (one proton),

and 1.45 ppm (six protons, triplet). The two low-field signals are attributed to the ester methylene protons, the 3.58-ppm signal to the cyclopropyl proton,⁴ and the 1.45-ppm triplet to the ester methyl protons. Absorption bands in the infrared spectrum at 3.29 (cyclopropyl C—H),⁵ 5.73 (C=O), and 4.44 μ (C \equiv N) and elemental analysis also indicate structures IIIa-c. The spectra are compatible with the structures IIIa-c for the cyclopropane derivative.

Regan⁶ has observed propenide formation in the reaction of diethyl 2,2,3,3-tetracyanocyclopropane-1,1-dicarboxylate with ammonia. It would appear that formation of compound II results from base-catalyzed ring opening of I and that this type of ring opening could be general for highly negatively substituted cyclopropane derivatives with at least one carbalkoxy group. These results are consistent with the initial involvement of a Haller-Bauer⁷ type of cleavage reaction. The transformations involved in the derivation of II and IIIa-c might be rationalized by initial formation of pentasubstituted cyclopropyl carbanion (V), which is formed by the elimination of diethyl cyanomalonate from intermediate IV, which, in turn, results from the nucleophilic addition of ethyl cyanoacetate anion to an electron-deficient ester carbonyl of I. Rearrangement of V would lead to the propenide (II) while proton capture would give IIIa-c. This rationalization is sup-

ported by the fact that compound II and its potassium salt were formed upon treatment of I with ethyl sodiocyanoacetate and potassium acetate in anhydrous 1,2-dimethoxyethane in 78 and 51% yield, respectively. Moreover, reaction of I with ethyl sodiocyanoacetate gave IIIa-c in 4-8% yield. On the other hand, the strongly basic sodium hydride gave an 11% yield of II and no cyclopropane product could be detected after 1 week at room temperature. These products are identical with those isolated in the original reaction as evidenced by comparison of infrared and ultraviolet absorption spectra and mixture melting point determinations.

That the cyclopropane derivative (IIIa-c) did not arise from a mechanism involving protonation of II was demonstrated by treating II with *p*-toluenesulfonic acid in ethanol. Only 1,2,3-tricyano-1,3-dicarbethoxy-

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

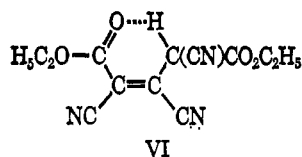
(3) W. J. Middleton, E. L. Little, D. D. Coffman, and V. A. Engelhardt, *ibid.*, **80**, 2795 (1958).

(4) H. Hart and F. Freeman, *J. Org. Chem.*, **28**, 1220 (1963).

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 18.

(6) T. H. Regan, *J. Org. Chem.*, **27**, 2236 (1962).

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propene (VI) was obtained. The structure of the acid (VI) was confirmed by carbon and hydrogen analysis, molecular weight, and infrared and nmr spectral data. The nmr spectrum supports a *cis* configuration for VI which showed an extremely low-field absorption for the acidic proton at δ 14.65 ppm, characteristic for a hydrogen-bonded proton. Also, Dreiding models indicated a steric preference for this *cis* configuration and a normal hydrogen-bond distance of 2.6 Å for the C-H-O bond in VI.⁸

The stability of IIIa-c under the alkaline conditions of the reaction is interesting and deserves comment. The yields of cyclic product from treatment of I with various bases indicate the formation of V and proton abstraction by V to be a function of the nucleophilicity and structure of the attacking reagent. A rationale for ring-strain relief and product resonance stabilization is provided by propenide formation. Probably the latter accounts for the irreversibility of the cyclopropane forming reaction. Dreiding stereo models suggest no driving force for the rearrangement of V owing to steric interaction of the carboxy groups. In contrast to the reported⁶ steric interference existing in ammonium 1,1,3,3-tetracyano-2-carboxypropenide no steric effects were observed in models of II. In view of the known double-bond character of cyclopropanes⁹ the stability of V must be attributed to its similarity to a carbanion formed at a trigonal carbon atom through delocalization of its charge by interaction with the α -cyano group.¹⁰

On mechanistic grounds it appears reasonable that the cyclopropane product be assigned the configuration as shown by IIIa. This would be expected from attack by base on the least hindered carboxy group of I followed by proton capture. On the other hand, isomerization of the intermediate carbanion V would be expected to lead to the thermodynamically stable isomer, IIIb. Indeed, Walborsky¹⁰ has shown that the energy barrier for the inversion of a α -cyano cyclopropane carbanion in aprotic solvents is lower than expected and that racemization occurs readily.

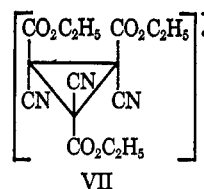
The nmr spectrum agrees with the proposed structure IIIb. In addition to the cyclopropyl proton, the nmr spectrum showed two equivalent carboxy methyl groups and a quartet due to the methylenic protons of the ester which under resolution were discernible as two quadruplets. On the other hand, the nonequivalency of the ester groups of starting *trans* I is clearly shown by its nmr spectrum which exhibited two overlapping quadruplets centered at δ 4.47 and 4.54 ppm and two overlapping triplets centered at δ 1.40 and 1.45 ppm, each in a 2:1 proton ratio, respectively. The assignment of configuration to IIIa-c with certainty must await the synthesis of all three isomers.

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(9) M. Yu. Lukina, *Russ. Chem. Rev.*, **31**, 419 (1962).

(10) H. M. Walborsky and F. M. Hornyak, *J. Amer. Chem. Soc.*, **78**, 872 (1956), and references therein.

In the course of investigating the reactions of I, formation of the stable anion radical VII was observed. Treat-



ment of I with potassium iodide in acetone solution under an inert atmosphere proceeded with the liberation of iodine and gave an orange solution. Likewise, colored solutions were obtained when potassium cyanide and triethylamine were used in the reaction. Anion radical formation in these reactions was substantiated by examination of an esr spectrum of the electrolytic reduction product of I with $n\text{-Bu}_4\text{N}^+\text{ClO}_4^-$ as the electrolyte in acetonitrile. A spectrum consistent with the cyclopropane structure VII was obtained with $a_N = 0.70$, $a_H = 1.48$ Oe, and $g = 2.0033$. In contrast to I, *cis*- and *trans*-1,2,3-tricyanocyclopropanes failed to oxidize potassium iodide, cyanide ion, and triethylamine and to undergo electrolytic reduction under the conditions described for I.

The observed influence of substituents on anion radical formation of cyclopropane derivatives is of significance in view of the current confusion that exists in the literature concerning anion radical existence of the parent cyclopropane.¹¹

Experimental Section¹²

Reaction of Ethyl Sodicyanoacetate and Ethyl Bromocyanacetate.—The reaction was carried out by a modification of the procedure of Fenton.^{1b} To a suspension of 2.0 mol of ethyl sodicyanoacetate [prepared by adding 226 g (2.0 mol) of ethyl cyanoacetate in 500 ml of anhydrous 1,2-dimethoxyethane (glyme) to a suspension of 90 g (2.0 mol) of 50% sodium hydride dispersion in mineral oil in 1 l. of anhydrous glyme at 5°] was added 160 g (1.0 mol) of liquid bromine at -60 to -70° during 1.5 hr. When the addition was complete, the reaction mixture was held at room temperature overnight. The reaction mixture was filtered to remove sodium bromide, and the filtrate was concentrated under reduced pressure to a yellow oil. The oil was washed with two 50-ml portions of petroleum ether (bp 35–60°) and the solvent discarded. The semisolid was filtered to give 57.0 g (51%) of crude colorless triethyl *trans*-1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate (I). Recrystallization from ethanol afforded 45.7 g (41%) of pure product, mp 119–120° (lit.^{1b} mp 122–123°). A mixture melting point with an authentic sample of I prepared by the reaction of ethyl bromocyanacetate and potassium acetate in anhydrous glyme^{13,14} showed no depression, 119–120°.

Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_6$: C, 54.05; H, 4.54; N, 12.61. Found: C, 54.19; H, 4.64; N, 12.72.

The infrared absorption spectrum was consistent with that reported for I.¹⁵ There is a very weak absorption at 4.43 attributable to nitrile and at 5.68 μ for carbonyl.

The filtrate, a yellow oil, was extracted with two 50-ml portions of water. The combined water layers were evaporated to dryness to give 20 g (21%) of crude yellow product. Recrystal-

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(12) Melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 21, ultraviolet on a Cary Model 14, and nmr spectra on a Varian Associates 60-Mc high-resolution spectrometer. Nmr spectra were obtained in deuteriochloroform using tetramethylsilane as internal standard.

(13) G. W. Griffin and L. I. Peterson, *J. Org. Chem.*, **28**, 3219 (1963).

(14) T. Sadeh and A. Berger, *Bull. Res. Council Israel*, **7A**, 98 (1958).

(15) D. G. I. Felton and S. F. D. Orr, *J. Chem. Soc.*, 2170 (1955).

lization from ethanol-ether gave 8.0 g (9%) of bright yellow salt, sodium 1,2,3-tricyano-1,3-dicarbethoxypropene (II), mp 241–246° dec. An analytic sample was prepared by recrystallization from ethanol, mp 299–300° dec.

Anal. Calcd for $C_{12}H_{10}NaN_3O_4$: C, 50.89; H, 3.56; N, 14.84. Found: C, 50.71; H, 3.80; N, 14.51.

The water-insoluble oil crystallized on standing 1 week. The solid was washed with ether and dried: yield 5.0 g (6%) of crude, colorless diethyl 1,2,3-tricyanocyclopropane-1,2-dicarboxylate (IIIa-c), mp 109–111°. Recrystallization from ethanol gave 4.1 g (5%) of pure IIIa-c, mp 118–119°. A mixture melting point with I was depressed, 100–104°.

Anal. Calcd for $C_{12}H_{11}N_3O_4$: C, 55.17; H, 4.24; N, 16.09. Found: C, 55.15; H, 4.48; N, 15.78.

Reaction of Triethyl *trans*-1,2,3-Tricyanocyclopropane-1,2,3-tricarboxylate (I) with Potassium Acetate.—Powdered anhydrous potassium acetate (3.0 g, 0.03 mol) was added to a solution of triethyl *trans*-1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate in 300 ml of anhydrous glyme at 23°. The mixture was stirred for 2 days at room temperature and then evaporated to dryness under reduced pressure. The residue was recrystallized from 95% ethanol to give 4.6 g (51%) of yellow potassium 1,2,3-tricyano-1,3-dicarbethoxypropene, mp 244–246° dec.

Anal. Calcd for $C_{12}H_{10}KN_3O_4$: C, 48.15; H, 3.37; K, 13.06; N, 14.04. Found: C, 47.96; H, 3.65; K, 13.30; N, 13.90.

The infrared absorption spectrum revealed bands at 4.54 (s) and 4.49 (w) attributable to conjugated nitrile, 5.87 (C=O), and 6.78 μ (C=C). The ultraviolet spectrum showed absorption at $\lambda_{max}^{C_2H_5OH}$ 425 m μ (ϵ 22,806) and 218 (13,678).

Reaction of Triethyl *trans*-1,2,3-Tricyanocyclopropane-1,2,3-tricarboxylate (I) with Ethyl Sodiocynoacetate.—A suspension of ethyl sodiocynoacetate (0.03 mol) in anhydrous glyme was prepared by adding 3.4 g (0.03 mol) of ethyl cyanoacetate to a mixture of 1.4 g (0.03 mol) of sodium hydride (as a 50% dispersion in mineral oil) in 200 ml of anhydrous glyme at 10°. The mixture was stirred and warmed at 30° until the theoretical amount of hydrogen gas had evolved. Triethyl *trans*-1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate (I, 10.0 g, 0.03 mol) in 150 ml of anhydrous glyme was added at 5–10° during 40 min. After stirring overnight at room temperature, the solvent was evaporated under reduced pressure, and the red oil (approximately 30 ml) was shaken with three 100-ml portions of ether and the combined ether washings were saved. The precipitated solid, from treatment with ether, was dissolved in warm water and filtered (in several experiments some unreacted I was recovered at this point) and the filtrate evaporated to dryness. Recrystallization of the residue from ethanol gave sodium 1,2,3-tricyano-1,3-dicarbethoxypropene (II): yield 6.6 g (78%), mp 295° dec. A mixture melting point and comparison of infrared spectra with authentic II showed them to be identical.

The ether washings were evaporated to give a mixture of orange oil and solid. The solid was collected by filtration, washed with cold ethanol and ether, and dried: yield 1.1-g (11%) recovery of starting cyclopropane I, mp 120–122°; mixture melting point with authentic I, 120.5–122°. (I was recovered in yields up to 14% in one experiment.)

The red oily filtrate was washed with water and then allowed to stand at room temperature for 1 week. During this time a white solid crystallized. The product solid was separated from the mineral oil by filtration, washed with cold ethanol and ether, and dried: yield 0.6 g (8%) of diethyl 1,2,3-tricyanocyclopropane-1,2-dicarboxylate (IIIa-c), mp 114–116°. Recrystallization from ethanol raised the melting point to 117–119°. Mixture melting point with starting cyclopropane I was depressed, 99.5–104°. Mixture melting point with authentic IIIa-c was not depressed, 118–119°. An infrared spectrum was identical with that of authentic IIIa-c. In three experiments yields of IIIa-c ranged from 4 to 8%.

Reaction of Sodium 1,2,3-Tricyano-1,3-dicarbethoxypropene (II) with *p*-Toluenesulfonic Acid.—A solution of 2.68 g (0.014 mol) of *p*-toluenesulfonic acid in 150 ml of absolute ethanol was added to 4.0 g (0.014 mol) of sodium 1,2,3-tricyano-1,3-dicarbethoxypropene (II) in 100 ml of absolute ethanol all at one time, with swirling, and the mixture was allowed to stand for 2 days. The red mixture was concentrated to a total volume of about 15 ml and filtered. The white solid which had been collected by filtration was washed with a small portion of cold ethanol and dried, yield 2.4 g. The solid product was then washed thoroughly with water to remove sodium *p*-toluenesulfonate and dried: yield 0.40 g (11%) of *cis*-1,2,3-tricyano-1,3-di-

carbethoxypropene (VI). Recrystallization from ethanol gave 0.30 g (8.2%) of white product, mp 149.5–151°.

Anal. Calcd for $C_{12}H_{11}N_3O_4$: C, 55.17; H, 4.24; N, 16.09; mol wt, 261. Found: C, 55.05; H, 4.24; N, 15.98; mol wt (cryoscopic method in DMSO), 245.

An infrared spectrum had absorption bands at 3.20 (C–H), 4.48 (CN), 5.95 (C=O), and 6.05 μ (C=C). The nmr spectrum showed two overlapping quadruplets (δ 4.63 and 4.60 ppm, four protons) and two overlapping triplets (δ 1.53 and 1.49 ppm, six protons), in addition to acidic proton (δ 14.65 ppm).

The filtrate from the original reaction mixture was evaporated to dryness to give an orange tacky residue. Various attempts at isolating other reaction products were unsuccessful.

Registry No.—I, 16408-63-2; II, 12259-90-4; IIIa, 16408-64-3; IIIb, 16408-65-4; IIIc, 16408-66-5; VI, 16408-67-6; potassium 1,2,3-tricyano-1,3-dicarbethoxypropene, 12259-91-5.

Acknowledgment.—The author is deeply indebted to Dr. M. T. Jones of the Central Research Department for obtaining and interpreting the esr spectra.

Kinetics of Neutral and Alkaline Hydrolyses of Trimethylsulfonium and Benzylmethylphenylsulfonium Salts^{1,2}

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Neutral Hydrolyses.—The decomposition of neutral trimethylsulfonium halides in aqueous acetone³ or absolute ethanol⁴ is a second-order process involving nucleophilic displacement of dimethyl sulfide by the anion. In contrast, trimethylsulfonium salts incorporating such relatively inert anions as perchlorate, picrate, and arenesulfonate have now been found to decompose in water solution by a first-order process. Seven different salts liberate acid at the same rate at 158°, with no important change in rate accompanying a tenfold increase in anion concentration (Table I).

TABLE I
HYDROLYSIS OF $(CH_3)_3SX$

X	Concn, M at 25°	Addend	Concn, M at 25°	Temp, °C	10 ³ k _w , sec ⁻¹
ClO ₄	0.0100	None		157.8	0.37
ClO ₄	0.0100	NaClO ₄	0.100	157.8	0.37
ClO ₄	0.0100	HClO ₄	0.0100	157.8	0.39
O ₃ SC ₆ H ₅	0.0100	None		157.8	0.41
O ₃ SC ₆ H ₄ - <i>p</i> -CH ₃	0.0100	None		157.8	0.38
O ₃ SC ₆ H ₄ - <i>p</i> -Br	0.0100	None		157.8	0.36
O ₃ SC ₆ H ₄ - <i>p</i> -NO ₂	0.0100	None		157.8	0.37
O ₃ S- β -C ₁₀ H ₉	0.0100	None		157.8	0.37
OC ₆ H ₂ -2,4,6-(NO ₂) ₃	0.0100	None		157.8	0.37
ClO ₄	0.0100	None		138.0	0.055

(1) Supported in part by the National Science Foundation and by the National Institutes of Health.

(2) For further details on benzylmethylphenylsulfonium salts, see the Ph.D. Thesis of B. J. Schowen, Massachusetts Institute of Technology, Cambridge, Mass., 1964.

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