

by measuring the relative areas of the *trans*-cyclooctene and cyclooctane peaks in the vapor phase chromatograms of the heated sample and an unheated sample of the same composition and calculating their ratio. Three vapor phase chromatograms were ob-

tained for each sample. With this correction, values for the specific rotation of each sample were calculated, and the decrease in this value with time was followed. In all cases the reactions were followed to 80–90% completion.

Tetracyanoethylene Oxide. I. Preparation and Reaction with Nucleophiles¹

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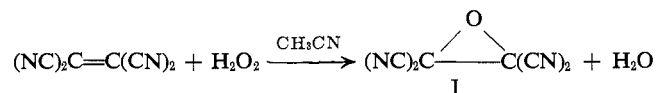
*Tetracyanoethylene oxide (TCNEO) is readily synthesized from tetracyanoethylene and hydrogen peroxide. Ethylenes substituted with two cyano groups and at least one other electronegative group may be epoxidized with hydrogen peroxide without conversion of nitrile to amide. Two different types of nucleophilic attack on TCNEO are described. Iodide and bromide ion attack at the nitrile group with the formation of cyanogen halide and tricyanovinyl alcoholate ion. Pyridine derivatives and dialkyl sulfides cleave the ring to give stable dicyanomethylides and carbonyl cyanide. A convenient high-yield synthesis of the latter has been developed using di-*n*-butyl sulfide.*

Reports of the epoxidation of α,β -unsaturated nitriles to the corresponding epoxy nitrile are limited to examples in which an alkyl hydroperoxide² or hypochlorite ion³ is the oxidizing agent. Alkaline hydrogen peroxide, the more common reagent, invariably gives the epoxyamide as the major product.⁴ Payne and co-workers have provided evidence that under controlled pH conditions the intermediate is a peroxyimidic acid which makes amide formation inevitable.⁴ Even with isopropylidenemalononitrile, an olefin which should be very susceptible to nucleophilic attack by the hydroperoxide anion, the product is primarily the epoxyamide.²

Preparation and Properties of Tetracyanoethylene Oxide

In contrast to these results, tetracyanoethylene is smoothly and rapidly converted to tetracyanoethylene oxide (TCNEO, I) with aqueous hydrogen peroxide in the absence of any added base.⁵ The reaction is best carried out by the dropwise addition of 30% aqueous hydrogen peroxide to a cooled solution of tetracyanoethylene (TCNE) in acetonitrile. When the reaction is

complete, the TCNEO is recovered in 65–70% yield by dilution of the reaction mixture with water. Such a procedure would result in the loss of any water-soluble amides, but these, if any, are minor products of the



reaction. A peroxyimidic acid from the acetonitrile is probably not the active epoxidizing agent, for the reaction may also be carried out in other water-miscible solvents for TCNE such as tetrahydrofuran, acetone, or ethanol. The reaction undoubtedly involves direct nucleophilic attack of the hydroperoxide anion or hydrogen peroxide to give a highly stable anionic intermediate.⁶

Tetracyanoethylene anion radical (TCNE⁻)⁷ is also oxidized to TCNEO with acidic hydrogen peroxide in aqueous solution. It is known that acidification of TCNE⁻ solutions gives an equimolar mixture of TCNE and tetracyanoethane (H₂TCNE), and this reaction may be partially involved as the initial step in the conversion to TCNEO. However, the yield of the epoxide in some instances was greater than 50%, indicating a more complicated mechanism. Although H₂TCNE was found in some preparations, it was not present in all of them. Furthermore, TCNE and aqueous, acidic hydrogen peroxide does not directly give TCNEO; a medium to dissolve the reactants appears necessary.

TCNEO is an easily crystallized, colorless solid, m.p. 177–178°. It is stable in air but slowly decomposes in the presence of water.

The structure of TCNEO is supported by elemental analysis and ultraviolet and infrared spectral data.

Electrophilic attack on the ring of TCNEO is not observed as a result of the presence of the strongly electron-withdrawing nitrile groups. As a consequence

(1) This work was presented in part at the XIXth International Congress of Pure and Applied Chemistry, London, July 10–17, 1963, Abstracts A, p. 247.

(2) G. B. Payne, *J. Org. Chem.*, **26**, 663 (1961).

(3) D. H. Rosenblath and G. H. Broome, *ibid.*, **28**, 1290 (1963).

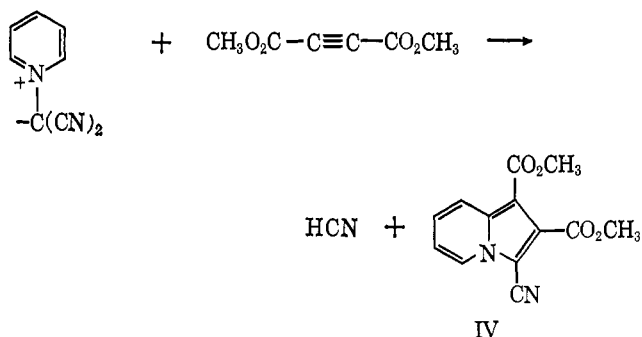
(4) G. B. Payne and P. H. Williams, *ibid.*, **26**, 651 (1961).

(5) These results have been communicated in preliminary form: W. J. Linn, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.*, **85**, 2032 (1963).

(6) TCNEO has also been isolated from ozonizations conducted in the presence of tetracyanoethylene: R. Criegee and P. Günther, *Chem. Ber.*, **96**, 1564 (1963). Subsequent to our first communication on the synthesis and reactions of TCNEO, a paper appeared which also reported the preparation of the epoxide from TCNE and either H₂O₂ or *t*-butyl hydroperoxide: A. Rieche and P. Dietrich, *ibid.*, **96**, 3044 (1963).

(7) O. W. Webster, W. Mahler, and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3678 (1962).

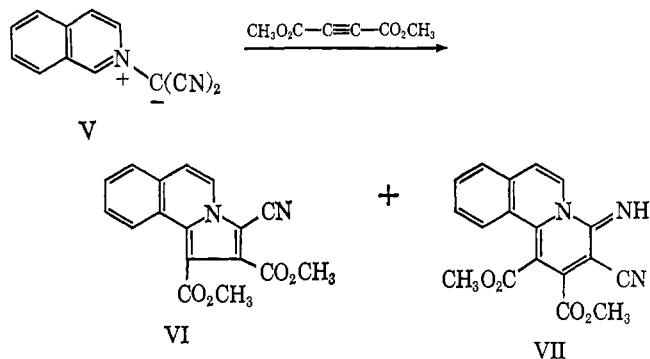
dicarboxylate (IV). The structure of IV was confirmed by the marked similarity of its ultraviolet spectrum to



that of trimethyl pyrrocoline-1,2,3-tricarboxylate¹⁴ and hydrolysis and decarboxylation to pyrrocoline-2-carboxylic acid.¹⁵

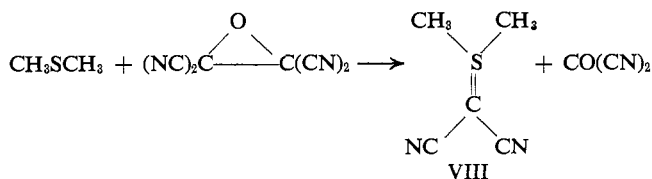
Isoquinolinium dicyanomethylide (V) also condenses with dimethyl acetylenedicarboxylate, but in this case two products are isolated. One of these corresponds to the expected pyrrocoline VI. The structure assignment is supported by the similarity of the ultraviolet spectrum to that reported for trimethyl benzo[*g*]-pyrrocoline-1,2,3-tricarboxylate.¹⁴

The second product has the composition of a 1:1 adduct of the ylide and the acetylenic ester. On the basis of some related unpublished work by Professor Boekelheide,¹⁶ we believe this material to be the iminoquinolizine derivative VII. The infrared spectrum is consistent with this formulation.



Reaction with Sulfides

Dialkyl sulfides are also sufficiently nucleophilic to cleave TCNEO to carbonyl cyanide and the dicyanomethylene fragment.¹⁷ The former can be isolated by distillation, and the latter is trapped as the sulfonium ylide. For example, addition of TCNEO to a cold ethereal solution of dimethyl sulfide results in the precipitation of dimethylsulfonium dicyanomethylide in better than 80% yield. This ylide VIII was first syn-



(14) R. H. Wiley and L. H. Knabeschuh, *J. Org. Chem.*, **18**, 836 (1953).

(15) E. T. Borrows and D. O. Holland, *J. Chem. Soc.*, 672 (1947).

(16) We are indebted to Professor Boekelheide, University of Oregon, for communicating his results to us prior to publication.

(17) W. J. Linn, U. S. Patent 3,115,517 to E. I. du Pont de Nemours and Co. (Dec. 24, 1963).

thesized by the condensation of dimethyl sulfoxide and malononitrile.¹⁸

The use of the less volatile di-*n*-butyl sulfide and a high-boiling solvent under slightly reduced pressure permit the distillation of carbonyl cyanide directly from the reaction mixture as it is formed in around 90% yield after purification.

The only other reported synthesis of carbonyl cyanide is a multistep process that suffers both from the small yield and lack of reproducibility.¹⁹ The ease of synthesis of TCNEO consequently makes the preparation from the epoxide the method of choice.

Synthesis of Other Cyano-Substituted Epoxides

On the basis of further work on the epoxidation of cyanoolefins it appears that three electronegative groups on a double bond are needed to achieve epoxidation without significant conversion of nitrile groups to the amides.

Tricyanoethylene, phenyltricyanoethylene, *t*-butyltricyanoethylene, and *trans*-1,2-diethoxycarbonyl-1,2-dicyanoethylene are readily converted to the corresponding epoxides by the technique described above for the preparation of TCNEO. A trace of pyridine was used to catalyze the formation of the last three epoxides.

All of the polycyano epoxides mentioned above are crystalline solids. The infrared spectrum of each is characterized by a nitrile band in the region associated with attachment to a saturated carbon atom. It has not been possible to assign a particular absorption with any certainty to the epoxide ring, although a strong band in the vicinity of 11 μ is present in each spectrum (see Table II).

Table II. Infrared Spectra of Polycyanoolefin Epoxides

Epoxide	C≡N	Wave length, μ^a	
		7.5-9	10.5-12
Tetracyanoethylene ^b	4.38	7.68 (m)	10.54
		8.47 (s)	11.23
		8.66 (s)	
Tricyanoethylene ^b	4.40	7.85 (m)	11.03
		8.37	
Phenyltricyanoethylene ^c	4.42 (4.62 sh)	7.70 (complex with 4 shoulders)	11.42
		8.05 (m)	
		8.55 (s)	
		7.79 (m)	11.12
<i>t</i> -Butyltricyanoethylene ^c	4.44	8.20 (m)	
		8.63 (m)	
		7.73 (br)	10.80
1,2-Dicyano-1,2-diethoxycarbonyl-ethylene ^b	4.43	8.75 (w)	11.75

^a Abbreviations: m, medium; s, strong; br, broad; w, weak.

^b Determined as a Nujol mull. Reaction with bromide ion precludes determination in a KBr pellet. ^c KBr pellet.

Even when analytically pure, the epoxide of 1,2-dicyano-1,2-diethoxycarbonyl-ethylene melts over a wide range (61-70°). The product is very likely a mixture of *cis* and *trans* isomers although the starting material was pure *trans*-olefin.²⁰ Attempts to separate the product into two isomers, however, were not suc-

(18) W. J. Middleton, E. L. Buhle, J. G. McNally, Jr., and M. Zanger, *J. Org. Chem.*, **30**, 2384 (1965).

(19) R. Malachowski, L. Jurkiewicz, and J. Wojtowicz, *Ber.*, **70B**, 1012 (1937).

(20) D. G. I. Felton, *J. Chem. Soc.*, 516 (1955).

cessful. Two isomers are to be expected if the intermediate is a carbanion produced by attack of HOO^- on the olefinic bond as postulated. Support for this mechanism is also provided by the greater reaction rate when pyridine is added.

Experimental

Tetracyanoethylene Oxide (I). A solution of 25.6 g. (0.2 mole) of tetracyanoethylene in 150 ml. of acetonitrile was cooled to $3-4^\circ$, and 22.5 ml. of 30% hydrogen peroxide was added at a rate such that the temperature remained between 25 and 30° . When the addition was complete, the reaction mixture was stirred for 3-4 min. and diluted with 750 ml. of ice-cold water. The precipitated solid was collected by filtration, washed with water, and air-dried for 3 to 4 hr. The crude product was recrystallized from ethylene dichloride (10 ml./g.) to give 19.1 g. (66.3%) of long, colorless needles. An analytical sample of tetracyanoethylene oxide melts at $177-178^\circ$ (sealed tube).

Anal. Calcd. for $\text{C}_6\text{N}_4\text{O}$: C, 50.00; N, 38.88; mol. wt., 144. Found: C, 50.00; N, 38.71, 39.06; mol. wt., 144 (mass spectrometry).

Caution: It is crucial that crude preparations of TCNEO be washed thoroughly and dried as rapidly as possible. This is especially true when the reaction is carried out on a large scale. Failure to do so can result in the onset of rapid hydrolysis resulting in heat buildup sufficient to set the crystalline material on fire.

Acetonitrile or methylene chloride solutions of TCNEO do not absorb in the ultraviolet region $220-440 \text{ m}\mu$.

Ethyl acetate, acetonitrile, tetrahydrofuran, 1,2-dimethoxyethane, acetone, and dioxane are all good solvents for TCNEO. If the exposure times are not long, it is possible to use methanol, ethanol, and glacial acetic acid, although TCNEO is eventually destroyed by reaction with these solvents. Benzene and diethyl ether will dissolve small amounts of the epoxide as will certain halogenated hydrocarbons such as 1,2-dichloroethane and 1,2-dibromoethane. The latter are especially good for recrystallization.

Tetracyanoethylene Oxide from K^+TCNE^- . The potassium salt of TCNE anion radical was prepared according to the method of Webster, Mahler, and Benson.⁷ A solution of 20.0 ml. of 4 *N* H_2SO_4 , 5.0 ml. of 30% H_2O_2 , and 5.0 ml. of water was cooled to 10° , and 6.69 g. (0.04 mole) of K^+TCNE^- was added all at once with stirring. Shortly thereafter, an exothermic reaction occurred which produced some foaming. Another 25 ml. of water was added to keep the mixture fluid. The reaction mixture was cooled and stirred for 30 min. and filtered. The precipitate was washed with 50 ml. of cold water and dried in a desiccator to give 3.85 g. of light gray solid which was recrystallized from 1,2-dichloroethane to give 3.33 g. (58%) of long, colorless needles of TCNEO, m.p. $176-177^\circ$. The ultraviolet spectrum in CH_2Cl_2 gave no indication of the presence of TCNE.

Reaction of TCNEO and Aqueous Potassium Bromide. To a solution of 0.83 g. (0.007 mole) of potassium bromide in 5 ml. of water there was added 1.00 g. (0.0069 mole) of TCNEO. The aqueous phase soon began to turn yellow, and after shaking for 5-10 min.

the TCNEO dissolved completely to give a yellow-orange solution. To this solution there was added 0.77 g. (0.007 mole) of tetramethylammonium chloride in 5 ml. of water. In a few seconds a precipitate began to form, and after 1 hr. the product was collected by filtration and air-dried to give 0.27 g. of feathery yellow needles, m.p. $208-209^\circ$. The filtrate, upon standing and with partial evaporation, gave an additional 0.34 g. of yellow needles, m.p. $208-210^\circ$. The combined sample, 0.61 g. (52%), was recrystallized from ethanol to give 0.55 g. of yellow needles of the tetramethylammonium salt of tricyanovinyl alcohol, m.p. $210-211^\circ$ (lit.⁸ m.p. $210-211^\circ$). The identity was further confirmed by comparison of the infrared spectrum with that of an authentic sample.

Reaction of TCNEO with Iodide Ion. Determination of TCNEO by Titration. TCNEO (0.1929 g.) was dissolved in a solution of 25 ml. of water containing 2.0 g. of potassium iodide and 1 ml. of 10% sulfuric acid (care must be taken not to have the pH of the solution too low or an indeterminate end point will result). The liberated iodine was titrated with 0.1010 *N* sodium thiosulfate solution to a starch end point. The titration required 26.50 ml. (2.676 mequiv.) of thiosulfate solution, corresponding to 2.00 mequiv. of iodine liberated per millimole of TCNEO.

Reaction of TCNEO with Potassium Iodide. Isolation of the Tetramethylammonium Salt of Tricyanovinyl Alcohol. To a solution of 3.32 g. (0.02 mole) of potassium iodide in 10 ml. of water was added 2.88 g. (0.02 mole) of TCNEO. There was an exothermic reaction, leaving an orange-yellow solution containing some suspended, colorless solid. This solid was collected by filtration and sublimed to give waxy needles of cyanogen iodide, m.p. $145-147^\circ$ (see below). To the filtrate there was added 2.2 g. of tetramethylammonium chloride. The reaction mixture was heated until solution was complete and was then cooled to room temperature. A precipitate of 1.62 g. of tan needles was identified by infrared spectroscopy as the tetramethylammonium salt of tricyanovinyl alcohol.⁸ For the quantitative determination of the yield of the alcohol anion by ultraviolet spectroscopy, an aqueous mixture of 0.0666 g. (4.2×10^{-4} mole) of TCNEO and 0.0833 g. (4.62×10^{-4} mole) of potassium iodide was diluted to 50 ml. with distilled water. When the pale yellow mixture was homogeneous, two tenfold dilutions were made and the ultraviolet spectrum was determined. There was observed only a single maximum at $295 \text{ m}\mu$ with an absorbance of 1.01 which corresponds to a 96.7% yield of the tricyanovinyl alcohol.⁹

Reaction of TCNEO with Iodide Ion. Isolation of Cyanogen Iodide. A solution of 3.32 g. (0.02 mole) of potassium iodide in 15 ml. of water was cooled in an ice bath and stirred. TCNEO (2.88 g., 0.02 mole) was added in small portions with stirring over a period of 0.5 hr. A yellow solution first formed, and eventually the separation of a solid precipitate was noted. When the addition was complete, the reaction mixture was stirred for 1 hr. and 15 ml. of cold ether was added. The solid dissolved in the ether layer which was then separated. The aqueous phase was extracted twice with cold ether. The combined ether extracts were concentrated at room temperature and reduced pressure to give a nearly colorless solid which was suspended in

15 ml. of water, and the mixture was heated under a slight vacuum at 40–50° for 10 min. The mixture was cooled and filtered. The product was air-dried in an efficient hood to give 1.7 g. (56%) of colorless solid, m.p. 148–149° alone, or in admixture with an authentic sample of cyanogen iodide,²¹ m.p. 147–149°. The product showed a single band in its infrared spectrum at 4.60 μ , as does authentic cyanogen iodide.

Pyridinium Dicyanomethylide (III). A solution of 23.7 g. (0.3 mole) of pyridine in 100 ml. of tetrahydrofuran was cooled in an ice bath, and a solution of 14.4 g. (0.1 mole) of TCNEO in 50 ml. of tetrahydrofuran was added dropwise with stirring over 1 hr. The mixture was stirred for an additional hour at ice-bath temperature and filtered. The dry, crude product, m.p. 245–246°, weighed 11.5 g. (80.5%). The melting point of pyridinium dicyanomethylide is unchanged on further recrystallization from acetonitrile or 50% aqueous ethanol. The ultraviolet spectrum was determined in acetonitrile: λ_{\max} 393 m μ (log ϵ 4.33), 243 (3.61), 238 (3.59), 214 (4.21).

Anal. Calcd. for C₈H₅N₃: C, 67.14; H, 3.52; N, 29.37; mol. wt., 143. Found: C, 67.30, 67.40; H, 3.61, 3.74; N, 29.43, 29.65; mol. wt., 141, 143 (ebullioscopic in ClCH₂CH₂Cl).

Dimethyl 3-Cyanopyrrocoline-1,2-dicarboxylate (IV). A suspension of 1.00 g. (0.007 mole) of pyridinium dicyanomethylide and 0.99 g. (0.007 mole) of dimethyl acetylenedicarboxylate in 10 ml. of acetonitrile was stirred at room temperature for 1 hr. By this time all of the solid had dissolved, and the dark red solution was drowned in ice-water. An oil separated and crystallized when scratched. The yellow solid was collected by filtration, washed with water, and dried. After recrystallization from ethanol there was obtained 0.86 g. (48%) of bright yellow crystals of dimethyl 3-cyanopyrrocoline-1,2-dicarboxylate, m.p. 129.5–130.5°. The melting point was raised to 131–131.5° by recrystallization from methanol.

Anal. Calcd. for C₁₃H₁₀N₂O₄: C, 60.48; H, 3.90; N, 10.85. Found: C, 60.52; H, 3.92; N, 10.96, 10.82.

The ultraviolet spectrum was determined in methanol: λ_{\max} 317 m μ (log ϵ 4.10), 273 (3.97), 241 (4.58), and 216 (4.28).

Acid Hydrolysis of Dimethyl 3-Cyanopyrrocoline-1,2-dicarboxylate. A solution of 1.00 g. of dimethyl 3-cyanopyrrocoline-1,2-dicarboxylate in 5 ml. of concentrated sulfuric acid was heated on a steam bath for 5 hr. The reaction mixture was poured onto ice, and the precipitated solid was collected by filtration and washed with water. The solid was resuspended in 25 ml. of concentrated hydrochloric acid, and the mixture was heated to boiling for 3 hr. (Attempted hydrolysis of the pyrrocoline directly with concentrated hydrochloric acid led to the precipitation of an extremely insoluble product which could not be further hydrolyzed.) The pale green solution was evaporated, the residue was dissolved in 10% sodium hydroxide, and the resulting solution was neutralized with 10% sulfuric acid. A light gray solid precipitated which was collected by filtration and washed with water. The product was recrystallized from aqueous ethanol to

give 0.1 g. of light green needles which turned dark at around 220° but did not melt until 240–242°. Pyrrocoline-2-carboxylic acid is reported to darken at 225° and melt at 238–240°.¹³ Identification was further confirmed by comparison of the ultraviolet and infrared spectra with that of an authentic sample.²²

Reaction of Isoquinolinium Dicyanomethylide and Dimethyl Acetylenedicarboxylate. A suspension of 1.00 g. of isoquinolinium dicyanomethylide and 0.74 g. of dimethyl acetylenedicarboxylate in 10 ml. of acetonitrile was shaken. After 15–20 min. all of the solid went into solution. The solution was then allowed to stand overnight at room temperature. During this time orange crystals deposited, and these were collected by filtration and washed with acetonitrile to give 0.83 g., m.p. 228–228.5°. Recrystallization from ethylene dichloride gave colorless crystals, m.p. 228–228.5°.

Anal. Calcd. for C₁₇H₁₂N₂O₄: C, 66.21; H, 3.92; N, 9.09. Found: C, 66.42; H, 3.94; N, 9.23.

On the basis of analysis and ultraviolet spectrum this product is believed to be dimethyl 1-cyanobenzo-[g]pyrrocoline-2,3-dicarboxylate: λ_{\max} 242 m μ (sh) (log ϵ 4.33), 263 (4.74), and 340 (3.95) (CH₃CN).

After removal of the pyrrocoline derivative, the reaction mixture was diluted with water to precipitate another solid which was collected by filtration, washed with water, and air-dried to give 0.81 g., m.p. 143–148°. After recrystallization from absolute ethanol there was obtained bright yellow needles, m.p. 154.5–155.5°. The analysis and spectra are consistent with the iminoquinolizine structure VII.

Anal. Calcd. for C₁₃H₁₃N₃O₄: C, 64.47; H, 3.91; N, 12.53. Found: C, 63.98; H, 3.96; N, 12.66, 12.58.

The infrared spectrum of the 1:1 adduct (KBr) shows absorption at both 3.25 and 3.37 μ for unsaturated and saturated CH, respectively. There is also absorption at 5.73 and 5.9 μ . The ultraviolet spectrum determined in methanol showed absorption at 220, 240, 262, 281, and 297 m μ . It is impossible to determine accurately the extinction coefficient, as solutions of the compound do not obey Beer's law.

Dimethylsulfonium Dicyanomethylide (VIII). A solution of 1.86 g. (0.03 mole) of dimethyl sulfide in 25 ml. of ether was cooled in an ice bath and stirred. To the stirred solution there was added all at once 1.44 g. (0.01 mole) of TCNEO. The reaction mixture was stirred at the temperature of the ice-bath for 1 hr. and filtered. The solid was washed with ether to give 1.04 g. (82.5%) of dimethylsulfonium dicyanomethylide, m.p. 101–102° (lit.¹⁸ m.p. 100–101°). The melting point was unchanged by recrystallization from 2-propanol. The infrared spectra of this product and an authentic sample of dimethylsulfonium dicyanomethylide were identical.

*Carbonyl Cyanide.*²³ A 500-ml., three-necked flask was fitted with a thermometer, a pressure equalizing dropping funnel, and a 10-in. Vigreux column attached to a trap cooled in a Dry Ice-acetone mixture. To the flask there was added 75–100 ml. of "topped" diethyl phthalate and 43 g. (0.3 mole) of tetracyano-

(22) We are indebted to Professor Virgil C. Boekelheide, University of Oregon, for an authentic sample of pyrrocoline-2-carboxylic acid.

(23) We are indebted to Dr. E. L. Martin of this laboratory who worked out this procedure for the preparation of carbonyl cyanide.

(21) R. Bak and A. Hillebert, *Org. Syn.*, 32, 29 (1952).

ethylene oxide. The reaction mixture was stirred with a magnetic stirrer, and the reaction flask was surrounded with a water bath at 50°. The pressure was reduced to 7–8 mm. by means of a water aspirator, and 44 g. (0.3 mole) of distilled *n*-butyl sulfide was added dropwise during the course of 20–25 min. An internal temperature of 50 ± 2° was maintained by controlling the temperature of the water bath. The reaction was exothermic at the start, but it was necessary to supply heat toward the end of the addition. As soon as the addition of the *n*-butyl sulfide was complete, the internal temperature was increased to 80° during the course of 10–15 min. The pressure of the reaction system was then increased to atmospheric by the introduction of nitrogen.

The carbonyl cyanide collected in the trap was allowed to warm to room temperature under nitrogen and 2 g. of tetracyanoethylene oxide was added to remove a small amount of *n*-butyl sulfide that had distilled along with the carbonyl cyanide. After warming to 50°, the carbonyl cyanide was distilled under reduced pressure (7–10 mm.) to a second trap cooled in Dry Ice–acetone mixture. After warming to room temperature, a 1-g. portion of tetracyanoethylene oxide was added, and the carbonyl cyanide was warmed to 50° and distilled under reduced pressure (7–10 mm.) into a distillation flask cooled in a Dry Ice–acetone mixture. Fractionation of this material using a 10-in. jacketed column packed with glass rings gave 20.8–21.8 g. (86–91%) of faintly yellow carbonyl cyanide, b.p. 65–66° (lit.²⁴ b.p. 65.6°).

A derivative was prepared by the addition of carbonyl cyanide to *N,N*-dimethylaniline in glacial acetic acid. The resulting bis(*p*-dimethylaminophenyl)dicyanomethane melted at 192–193° (lit.²⁵ m.p. 192–193°).

Phenyltricyanoethylene Oxide. To a solution of 1.79 g. (0.010 mole) of phenyltricyanoethylene²⁶ in 10 ml. of acetonitrile there was added 1 drop of pyridine. The solution was cooled in an ice bath to 5° and there was added all at once 1.5 ml. of 30% hydrogen peroxide. The temperature rose to 18°. The reaction mixture was stirred for 10 min. at ice-bath temperature and diluted with ice–water. The precipitated solid was collected by filtration and dried in a vacuum desiccator to give 1.84 g. of crude product which was recrystallized once from cyclohexane to give 1.41 g. (72%) of phenyltricyanoethylene oxide as colorless needles, m.p. 78–80°. Further recrystallization raised the melting point to 79–80°.

Anal. Calcd. for C₁₁H₅N₃O: C, 67.69; H, 2.57; N, 21.54. Found: C, 68.04; H, 2.89; N, 21.45.

(24) O. Glemser and V. Hausser, *Z. Naturforsch.*, **38**, 159 (1948).

(25) R. Malachowski and J. Jankiewicz-Wasowska, *Roczniki Chem.*, **25**, 34 (1951).

(26) G. N. Sausen, V. A. Engelhardt, and W. J. Middleton, *J. Am. Chem. Soc.*, **80**, 2819 (1958).

Tricyanoethylene Oxide. A solution of 1.03 g. (0.01 mole) of tricyanoethylene²⁷ in 10 ml. of acetone was cooled to 0° and 1.5 ml. of 30% hydrogen peroxide was added dropwise at such a rate that the temperature remained at about 10°. The resulting reaction mixture was evaporated on a rotary evaporator leaving a red oil which was taken up in methylene chloride. The aqueous layer was separated and extracted two more times with methylene chloride. The combined organic extracts were dried, and the solvent was removed leaving 0.78 g. of light yellow solid. This product was recrystallized from chloroform using charcoal. There was obtained 0.37 g. (31%) of light tan solid, m.p. 73–74°. The product was further purified by sublimation at 50–60° (0.1 mm.) to give 0.33 g. of tricyanoethylene oxide as colorless crystals, m.p. 76–77°.

Anal. Calcd. for C₅HN₃O: C, 50.42; H, 0.85; N, 35.29. Found: C, 50.47; H, 0.90; N, 35.52.

***t*-Butyltricyanoethylene Oxide.** A solution of 1.59 g. (0.01 mole) of *t*-butyltricyanoethylene²⁶ in 10 ml. of acetonitrile was stirred and cooled to +5°. There was added all at once 1.5 ml. of 30% hydrogen peroxide followed by 2 drops of pyridine. The temperature rose to 15° and when the mixture had recooled to 5° (about 5 min.) it was diluted with water. An oil separated and crystallized with repeated stirring. The solid was filtered, washed with ice–water, and air-dried to give 1.33 g. of colorless solid which was recrystallized from petroleum ether and then sublimed to give *t*-butyltricyanoethylene oxide as colorless crystals, m.p. 44–45°.

Anal. Calcd. for C₉H₉N₃O: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.88; H, 5.41; N, 24.03.

1,2-Diethoxycarbonyl-1,2-dicyanoethylene Oxide. To a solution of 1.11 g. (0.005 mole) of *trans*-1,2-diethoxycarbonyl-1,2-dicyanoethylene²⁰ in 5 ml. of acetonitrile there was added 1.0 ml. of 30% hydrogen peroxide followed by 1 drop of pyridine. There was an exothermic reaction and the temperature rose 25–50°. The reaction mixture was allowed to stand for 2 min. and was then diluted with cold water. An oil separated and crystallized with repeated stirring and scratching. The solid was collected by filtration, washed with water, and air-dried to give 1.1 g. (93%) of dicyanodiethoxycarbonylethylene oxide, m.p. 61–70°. The product was recrystallized by solution in boiling ether and addition of petroleum ether to incipient precipitation. Repeated recrystallization in this manner gave material with an unchanged melting point, 61–70°.

Anal. Calcd. for C₁₀H₁₀N₂O₅: C, 50.41; H, 4.23; N, 11.76. Found: C, 50.61; H, 4.25; N, 12.09.

(27) C. L. Dickinson, D. W. Wiley, and B. C. McKusick, *ibid.*, **82**, 6132 (1960).