pleted in 12 hours, and work-up yielded 9.7 g. (53%) of pure 1,1,2,2-tetraphenyldisilane.

**1,2-Dimethyl-1,2-diphenyldisilane.**—A mixture of 31.3 g. (0.2 mole) of methylphenylchlorosilane, 4.9 g. (0.2 g. atom) of magnesium, 100 ml. of tetrahydrofuran and 5 drops of ethyl iodide was refluxed with stirring. The reaction was completed in 33 hours. Dry pentane (100 ml.) was added and the mixture was filtered through a glass filter. The solid was washed with an additional 20 ml. of pentane, and the filtrate was fractionated to give 13.6 g. (56%) of 1,2-dimethyl-1,2-diphenyldisilane, b.p. 81–83° (0.003 mm.), $n^{20}_D$ 1.5769, $d^{20}_{20}$ 0.980.

*Anal.* Calcd. for $C_{14}H_{18}Si_2$: C, 69.3; H, 7.49; *MR*, 82.0. Found: C, 69.01; H, 7.31; *MR*, 82.0.

**1,2-Diethyl-1,2-diphenyldisilane.**—A mixture of 25.2 g. (0.148 mole) of ethylphenylchlorosilane, 3.6 g. (0.15 g. atom) of magnesium, 75 ml. of tetrahydrofuran and 3 drops of ethyl iodide was refluxed and stirred for 65 hours. The reaction products were worked up as before. There was obtained 7.75 g. (39%) of 1,2-diethyl-1,2-diphenyldisilane, b.p. 110–111° (0.1 mm.), $n^{20}_D$ 1.5656, $d^{20}_{20}$ 0.969.

*Anal.* Calcd. for $C_{16}H_{22}Si_2$: Si, 20.7; *MR*, 91.2. Found: Si, 20.4; *MR*, 91.0.

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# Cyanocarbon Chemistry. XVII. Tricyanoethylene and Tricyanovinyl Chloride[1]

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Tricyanoethylene, hitherto the only unknown cyanoethylene, has been synthesized. It is chemically similar to tetracyanoethylene, but it reacts less vigorously. Addition of chlorine to tricyanoethylene is in striking contrast to the chlorination of most olefinic compounds in that initial attack seems to be by $Cl^-$ to give a carbanion rather than by $Cl_2$ to give a cation. The resultant dichloride has been converted to tricyanovinyl chloride, which has proved to be a more versatile tricyanovinylating reagent than tetracyanoethylene.

The novelty and great variety of the reactions that tetracyanoethylene undergoes[2] encouraged us to attempt the synthesis of tricyanoethylene, the only unknown member of the cyanoethylene family, in order to see to what extent its properties parallel those of tetracyanoethylene.

We have succeeded in preparing tricyanoethylene in 27% over-all yield by means of the five-step synthesis shown in Chart I. The first step is the reaction of ethyl cyanoacetate with glycolonitrile to give ethyl 2,3-dicyanopropionate.[3] The latter was converted to the corresponding amide, which was dehydrated to 1,1,2-tricyanoethane. This was readily brominated to 1-bromo-1,1,2-tricyanoethane, which was dehydrobrominated by triethylamine to give tricyanoethylene in excellent yield. The dehydrobromination is the most critical step in the synthesis; tricyanoethylene decomposes rapidly in the presence of bases, so that the use of even a slight excess of triethylamine will result in no product whatever being isolated. The best practice is to use 90 to 95% of the amount of triethylamine theoretically required.

CHART I

SYNTHESIS OF TRICYANOETHYLENE

$$NCCH_2OH + NaCH(CN)CO_2C_2H_5 \xrightarrow[55\%]{}$$

$$NCCH_2CH(CN)CO_2C_2H_5 \xrightarrow[74\%]{NH_3}$$

$$NCCH_2CH(CN)CONH_2 \xrightarrow[80\%]{POCl_3} NCCH_2CH(CN)_2$$

$$\xrightarrow[91\%]{Br_2/H_2O} NCCH_2CBr(CN)_2 \xrightarrow[91\%]{(C_2H_5)_3N} NCCH{=}C(CN)_2$$

Tricyanoethylene is a crystalline solid melting at 42°. It is much more sensitive to base than tetracyanoethylene, being readily resinified by even traces of base. It is considerably less stable than tetracyanoethylene, which can be stored at room temperature indefinitely provided moisture is excluded. Although a highly purified sample of tricyanoethylene can be stored at room temperature, a slightly impure sample must be stored at solid carbon dioxide temperature or it will decompose in less than a day. Tricyanoethylene therefore is intermediate in stability between tetracyanoethylene and vinylidene cyanide.[4]

Chemically, tricyanoethylene is similar to tetracyanoethylene, but it generally reacts less rapidly. Thus, like tetracyanoethylene,[5] tricyanoethylene forms a Diels-Alder adduct with anthracene, but at room temperature the reaction requires hours instead of minutes. The acid-catalyzed addition of ketones to tetracyanoethylene[5] has its parallel in the addition of acetone to tricyanoethylene to give 4,5,5-tricyano-2-pentanone (I). Like tetracyanoethylene,[6] tricyanoethylene condenses with aniline

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[1] Paper XVI, see R. M. Scribner, G. N. Sausen and W. W. Prichard, *J. Org. Chem.*, **25**, 1440 (1960).

[2] Paper I, 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, THIS JOURNAL, **80**, 2775 (1958).

[3] A. Higson and J. F. Thorpe, *J. Chem. Soc.*, **89**, 1455 (1906).

[4] A. E. Ardis, S. S. Averill, H. Gilbert, F. F. Miller, R. F. Schmidt, F. D. Stewart and H. L. Trumbull, THIS JOURNAL, **72**, 1305 (1950).

[5] W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *ibid.*, **80**, 2783 (1958).

[6] B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *ibid.*, **80**, 2806 (1958).

with loss of hydrogen cyanide to give an N-vinyl derivative (II). However, under the mild conditions that cause tetracyanoethylene to condense with N,N-dimethylaniline to give *p*-tricyanovinyl-N,N-dimethylaniline,[6] tricyanoethylene gave no detectable amount of the corresponding *p*-(2,2-dicyanovinyl) derivative. Tricyanoethylene is much more reactive toward water than is tetracyanoethylene; extraction of an ether solution of tricyanoethylene with water causes rapid and complete degradation to hydrogen cyanide and unidentified products.

$$\underset{\text{I}}{CH_3COCH_2CH(CN)CH(CN)_2} \qquad \underset{\text{II}}{C_6H_5NHCH{=}C(CN)_2}$$

The most interesting reaction of tricyanoethylene yet encountered is its chlorination, both because of the unusual mechanism involved and because it led to tricyanovinyl chloride, a most potent tricyanovinylating agent. Normally, the addition of chlorine to olefins is catalyzed by acids, and although there is some evidence for a nucleophilic process in selected cases,[7] this too is acid catalyzed. A highly negatively substituted olefin like tricyanoethylene is a special case, and when a solution in methylene chloride is treated with chlorine with no catalyst or with typical acidic catalysts such as iodine or ferric chloride, the addition is extremely slow. If a trace of tetramethylammonium chloride is added, a rapid, exothermic addition of chlorine is observed, and this is presumably the result of chloride ion attack on the olefin to form an intermediate such as III. This appears to be the first example of chlorine addition catalyzed by chloride ion.[8] We did not attempt to isolate 1,2-dichloro-1,1,2-tricyanoethane (IV). Instead we dehydrohalogenated it to tricyanovinyl chloride (V, 87% over-all yield) by adding slightly less than the calculated amount of triethylamine to the chlorine-free reaction mixture.

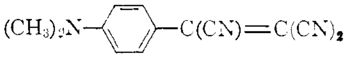
$$NCCH{=}C(CN)_2 \xrightarrow{Cl^-} \underset{\text{III}}{[NCCHCl\overset{\ominus}{C}(CN)_2]} \xrightarrow{Cl_2}$$

$$Cl^- + \underset{\text{IV}}{NCCHClCCl(CN)_2} \xrightarrow[-HCl]{Et_3N} \underset{\text{V}}{ClC(CN){=}C(CN)_2}$$

Tricyanovinyl chloride can also be made by treating the tetramethylammonium salt of tricyanovinyl alcohol[9] with oxalyl chloride. In this manner, tricyanovinyl chloride was obtained in 30-45% yields.

$$(CH_3)_4N^{+-}O{-}C(CN){=}C(CN)_2 + ClCOCOCl \longrightarrow ClC(CN){=}C(CN)_2$$

Tricyanovinyl chloride, m.p. 71-73°, is in many ways similar to tetracyanoethylene. It gives Diels-Alder adducts with dienes such as anthracene and 2,3-dimethylbutadiene, although it adds much more slowly than tetracyanoethylene or even tricyanoethylene. One of the most remarkable reactions of tetracyanoethylene is its condensation with amines, pyrroles and other nucleophiles to give tricyanovinyl derivatives,[6,10] and tricyanovinyl chloride shows the same behavior, except that it is considerably more reactive. Thus, tricyanovinyl chloride condenses completely with N,N-dimethylaniline to give *p*-tricyanovinyl-N,N-dimethylaniline (VI) within a few minutes under conditions where tetracyanoethylene requires hours. Similarly, both tricyanovinyl chloride and tetracyanoethylene react with ethanol to give tricyanovinyl ethyl ether (VII), but tricyanovinyl chloride reacts much faster.[11]



VI

$$\underset{\text{VII}}{C_2H_5OC(CN){=}C(CN)_2}$$

Not only are tricyanovinylations usually more rapid when tricyanovinyl chloride is used instead of tetracyanoethylene, but they sometimes take a different course. Thus, whereas tetracyanoethylene tricyanovinylates N-methylaniline in the *para* position, tricyanovinyl chloride tricyanovinylates it exclusively on the nitrogen.

Tricyanovinyl chloride reacts with water to give tricyanovinyl alcohol (VIII) accompanied by a trace of 1,1,2,3,3-pentacyanopropene (IX). As in the hydrolysis of tetracyanoethylene,[9] the course of hydrolysis seems to be dependent on the *p*H of the reaction solution, for when water is added to a tetrahydrofuran solution of tricyanovinyl chloride, the main product is pentacyanopropene (IX). The latter may arise by reaction of tricyanovinyl chloride with tricyanovinyl alcohol, for tricyanovinyl chloride reacts with tetramethylammonium salt of tricyanovinyl alcohol in anhydrous tetrahydrofuran to give tetramethylammonium pentacyanopropenide. However, the mechanism of formation of pentacyanopropene, whether from tetracyanoethylene or tricyanovinyl chloride, remains uncertain. Thus, malononitrile cannot be disregarded as a possible intermediate, for an equimolar mixture of malononitrile, tetracyanoethylene and pyridine in water has been found to give pentacyanopropene in such excellent yield that this is the preferred method of synthesis.

$$\underset{\text{VIII}}{HOC(CN){=}C(CN)_2} \qquad \underset{\text{IX}}{(NC)_2C{=}C(CN)CH(CN)_2}$$

The properties of ethyl tricyanovinyl ether were examined briefly. It formed a yellow π-complex with anthracene, but did not appear to give a Diels-Alder adduct with it. Like tetracyanoethylene, it condensed with N,N-dimethylaniline to give *p*-tricyanovinyl-N,N-dimethylaniline (V), but the condensation was relatively slow. By analogy with ethyl cyanoformate[9] one would have expected the cyano group to be lost in preference to the ethoxy

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[7] P. B. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 2838 (1950).

[8] The idea of catalyzing the chlorination of negatively substituted olefins by chloride ion was first suggested to one of us by Professor Stanley Cristol.

[9] W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, THIS JOURNAL, **80**, 2795 (1958).

[10] G. N. Sausen, V. A. Engelhardt and W. J. Middleton, *ibid.*, **80**, 2815 (1958).

[11] Earlier attempts to stop the reaction of tetracyanoethylene with alcohols at the alkyl tricyanovinyl ether stage were unsuccessful, only 1,1-dicyano-2,2-dialkoxy ethylenes being isolated.[12] We have now found that tricyanovinyl ethers can be obtained from alcohols by using a diluent and mild conditions.

[12] W. J. Middleton and V. A. Engelhardt, THIS JOURNAL, **80**, 2788 (1958).

group, but no *p*-(2,2-dicyano-1-ethoxyvinyl)-N,N-dimethylaniline[13] was detected. Another example of preferential elimination of the ethoxy group is the hydrolysis of ethyl tricyanovinyl ether with dilute ammonium hydroxide to give 1,1,2,3,3-pentacyanopropene in nearly quantitative yield.

Like tetracyanoethylene, tricyanoethylene and tricyanovinyl chloride are π-acids, for they form π-complexes with aromatic hydrocarbons. However, they do not appear to be nearly as strong π-acids; their complexes have absorption maxima at shorter wave lengths than do the corresponding complexes of tetracyanoethylene. Thus, whereas tetracyanoethylene forms a green complex with anthracene,[14] tricyanovinyl chloride and tricyanoethylene form magenta and orange complexes, respectively. The π-complexes of tricyanoethylene and tricyanovinyl chloride with toluene and durene were examined by the method as described by Merrifield and Phillips.[14] The association constants for complex formation ($K$), the wave lengths of maximum absorption ($\lambda_{max}$) and extinction coefficients for maximum absorption ($\epsilon_{max}$) are listed in Table I. Tetracyanoethylene is included for comparison.

TABLE I

π-COMPLEXES OF TOLUENE AND DURENE

SOLVENT, $CH_2Cl_2$; TEMPERATURE 22°

| π-Acid | $K$ | $\lambda_{max}$, mμ | $\epsilon_{max}$, cm.$^{-1}$ mole$^{-1}$ l. |
|---|---|---|---|
| | Toluene | | |
| Tricyanoethylene | 1.76 | 317 | 3,300 |
| Tricyanovinyl chloride | 1.09 | 334 | 3,300 |
| Tetracyanoethylene | 3.70 | 406 | 3,330 |
| | Durene | | |
| Tricyanoethylene | 6.6 | 365 | 2,200 |
| Tricyanovinyl chloride | 8.9 | 410 | 1,300 |
| Tetracyanoethylene | 54.2 | 480 | 2,075 |

From these data it appears that the variation of $\lambda_{max}$ is most indicative of relative π-acid strength toward a given π-base. Thus, the decreasing order or π-acid strength would be tetracyanoethylene, tricyanovinyl chloride, tricyanoethylene, corresponding to the relative electron-withdrawing character of cyano, chloro and hydrogen.

## Experimental

**Ethyl 2,3-Dicyanopropionate.**—The following is a modification of the method of Higson and Thorpe.[3] Ethyl cyanoacetate (1131 g., 10 moles) was added to a refluxing solution of 540 g. (10 moles) of sodium methoxide in 2400 ml. of absolute ethanol. The thick mixture was cooled to 30° and added to a cooled, stirred solution of 572 g. (10 moles) of freshly distilled glycolonitrile in 1100 ml. of ethanol. The temperature was maintained between 15 and 19° during the addition and for 1 hour thereafter, and the solution was then allowed to warm slowly to 30–35°. After 2 hours, the solution was divided into five portions, and each portion was poured onto a mixture of 140 ml. of concentrated hydrochloric acid and 800 g. of ice. The resulting neutral solutions were then each diluted with 2 liters of water and extracted with four 500-ml. portions of ether. The total combined ether extracts were dried and concentrated on a steam-bath, and the ethanol was removed under vacuum. The dark residue was flash-distilled at as low a pressure as possible. The considerable decarboxylation that occurred during the distillation maintained the pressure between 3 and 25 mm. Redistillation gave 829 g. (55%) of crude ethyl 2,3-dicyanopropionate, b.p. 120–135° (1 mm.).

The formation of ethyl 2,3-dicyanopropionate in the above preparation is undoubtedly more complex than displacement of hydroxyl by the anion of ethyl cyanoacetate. One possibility is that under the basic conditions glycolonitrile is in equilibrium with formaldehyde and cyanide ion. The former might condense with the cyanoacetate to give methylenecyanoacetate which might add cyanide ion to give the product.

**2,3-Dicyanopropionamide.**—The crude ethyl 2,3-dicyanopropionate from the preceding preparation (829 g.) was added with stirring to 1.5 l. of concentrated ammonium hydroxide that was cooled in an ice–salt-bath. The reaction mixture was maintained between 0 and 5° for 3 hours, and the 2,3-dicyanopropionamide was collected, washed with water and air-dried; yield 497 g. (74%), m.p. 128–131°. An analytical sample was prepared by recrystallization from water, m.p. 131–132°.

*Anal.* Calcd. for $C_5H_5N_3O$: C, 48.8; H, 4.1; N, 34.2. Found: C, 48.8; H, 4.0; N, 34.1.

**1,1,2-Tricyanoethane.**—A mixture of 73.8 g. (0.60 mole) of 2,3-dicyanopropionamide, 100 g. of sodium chloride and 300 ml. of acetonitrile was stirred for 5 minutes, and 49.2 g. (0.36 mole) of phosphorus oxychloride was added. The mixture was stirred and heated under reflux for 9.5 hours. The inorganic solid was removed by filtration and thoroughly washed with acetonitrile. The bulk of the acetonitrile was removed from the filtrate under vacuum, and 150 ml. of water was added to give the 1,1,2-tricyanoethane. It was recrystallized from water (decolorizing charcoal); yield 50.5 g. (80%), m.p. 112–113.5°. It is a weak acid with a $pK_a$ of 7.80 (determined in aqueous ethanol).

*Anal.* Calcd. for $C_5H_3N_3$: C, 57.1; H, 2.9; N, 40.0; neut. equiv., 105. Found: C, 57.2; H, 2.8; N, 40.2; neut. equiv., 105.

**1-Bromo-1,1,2-tricyanoethane.**—Bromine (320 g., 2.0 moles) was added to a stirred slurry of 210 g. (2.0 moles) of 1,1,2-tricyanoethane in 2 l. of ice-water. The temperature of the reaction mixture was kept below 12° by means of an ice-bath. Ten minutes after the addition was complete, the precipitate of 1-bromo-1,1,2-tricyanoethane was collected and washed with water. The moist solid was dissolved in dichloromethane, a water layer was discarded, and the organic layer was dried over magnesium sulfate. Evaporation of the dichloromethane at a water-pump gave 334 g. (91%) of 1-bromo-1,1,2-tricyanoethane as light yellow crystals, m.p. 65–67°. An analytical sample was prepared by recrystallization from benzene–chloroform followed by sublimation, m.p. unchanged.

*Anal.* Calcd. for $C_5H_2N_3Br$: C, 32.6; H, 1.1; N, 22.8; Br, 43.5. Found: C, 32.6; H, 1.0; N, 23.4; Br, 43.3.

Unless pure, 1-bromo-1,1,2-tricyanoethane does not store well, so its dehydrohalogenation was carried out as soon as possible.

**Tricyanoethylene.**—A solution of 334 g. (1.82 moles) of 1-bromo-1,1,2-tricyanoethane in 1.8 l. of ether was stirred and cooled in an ice-bath, and 172 g. (1.70 moles) of triethylamine in 900 ml. of ether was added dropwise. The dark mixture was filtered and the filtrate was concentrated to 600 ml. under vacuum. This dark solution was passed through a chromatographic column of 450 g. of *acid* alumina (Woelm, Activity I) and eluted with ether. The first 2 l. of ether that was collected was concentrated *in vacuo* and gave 169 g. (91%) of orange crystalline tricyanoethylene, m.p. 35–38°. A colorless analytical sample, m.p. 42°, was prepared by passing the compound over acid alumina three times and resubliming at 60° (0.1 mm.) three times, $\lambda_{max}$ 237 mμ (ether), $\epsilon_{max}$ 13,100. The infrared spectrum shows ethylene CH at 3.3 μ, conjugated -CN at 4.5 μ, and a double bond at 6.65 μ.

*Anal.* Calcd. for $C_5HN_3$: C, 58.3; H, 1.0; N, 40.8. Found: C, 58.8; H, 1.3; N, 40.9.

Since tricyanoethylene is base-sensitive, extreme care must be taken to use less than the theoretical amount of amine. Unless the tricyanoethylene is highly purified, it must be kept at −80° (solid carbon dioxide) where it is stable for months.

**Tricyanovinyl Chloride. A. From Tricyanoethylene.**—Three drops of triethylamine was added to a solution of 71.6 g. (0.695 mole) of tricyanoethylene in 280 ml. of methylene

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[13] This compound will be described in a subsequent paper by A. D. Josey.

[14] R. E. Merrifield and W. D. Phillips, THIS JOURNAL, **80**, 2778 (1958).

chloride. The dark solution was stirred, and chlorine gas was immediately bubbled in at a rate that maintained gentle reflux. The temperature began to drop when the reaction was complete, and the addition of chlorine was stopped. The excess chlorine was removed by stripping 50 ml. of the solution under vacuum. The orange solution was cooled in ice and stirred, and 67 g. (0.684 mole) of triethylamine in 300 ml. of methylene chloride was added. The dark mixture was concentrated under vacuum at 30°, and the residue was taken up in 600 ml. of benzene and passed through a column of 500 g. of acid alumina (Woelm, Activity I). Two liters of light yellow benzene solution was collected and concentrated to give 83.7 g. (87%) of almost colorless tricyanovinyl chloride, m.p. 70–72°, $\lambda_{max}$ 266 m$\mu$ ($CH_2Cl_2$), $\epsilon_{max}$ 13,200. Two sublimations at 80° (20 mm.) gave an analytical sample. The infrared spectrum showed conjugated CN at 4.48 $\mu$ and a double bond at 6.38 $\mu$.

*Anal.* Calcd. for $C_5N_3Cl$: C, 43.7; N, 30.5; Cl, 25.8. Found: C, 43.9; N, 30.0; Cl, 25.9.

Tricyanovinyl chloride is base-sensitive and care must be taken to use less than the theoretical amount of triethylamine. The compound tends to decompose when kept at room temperature unless highly purified, and it is best kept at −80° (solid carbon dioxide).

B. **From Tetramethylammonium Tricyanoethenolate.**—Ten milliliters of oxalyl chloride was added to a stirred solution of 9.6 g. (0.05 mole) of tetramethylammonium tricyanoethenolate[6] in 50 ml. of 1,2-dimethoxyethane in one portion. After 2 hours, the dark mixture was stripped of solvent and triturated with ether. The ethereal solution was concentrated and the residue of crude tricyanovinyl chloride was purified by two sublimations; yield 3.1 g. (45%), m.p. 70–72°.

**Tricyanovinyl Ethyl Ether.**—To a slurry of 32 g. (0.25 mole) of finely powdered tetracyanoethylene and 3.0 g. of urea in 75 ml. of tetrahydrofuran was added 40 ml. of ethanol dropwise over a 5-minute period with stirring and warming on a steam-bath. The temperature was maintained at 70° for 20 minutes. A slow evolution of hydrogen cyanide occurred. The dark solution was poured into 600 ml. of ice and water and extracted with ether. The ether extract was dried and concentrated to an oil that was dissolved in benzene, and the solution was passed over a 200-g. column of acid alumina (Woelm, Activity I). The 500 ml. of yellow benzene solution that was collected was concentrated and the oil was distilled through a short-path still at 45–60° (0.1 mm.); yield 17.3 g. (47%), $n^{24}D$ 1.4961–1.4948, m.p. 5.0–9.7°. The tricyanovinyl ethyl ether was redistilled through a small Vigreux column to give a colorless analytical sample; b.p. 60° (0.15 mm.), m.p. 10.5–11.7°, $n^{24}D$ 1.5009, $\lambda_{max}$ 283 m$\mu$ ($CH_2Cl_2$), $\epsilon$ 13,800.

*Anal.* Calcd. for $C_7H_5N_3O$: C, 57.2; H, 3.4; N, 28.6. Found: C, 57.5; H, 3.6; N, 28.6.

Tricyanovinyl ethyl ether was also prepared in high yield by adding alcohol to a solution of tricyanovinyl chloride in tetrahydrofuran, followed by removal of the solvent and evaporative distillation. The infrared spectrum was identical with that of the compound prepared from tetracyanoethylene.

**β-Anilino-α-cyanoacrylonitrile.**—A solution of tricyanoethylene in ether obtained directly from dehydrohalogenation was treated with aniline, and in a short time a solid separated. After recrystallization from methanol, it melted at 243–246° alone or mixed with an authentic sample of β-anilino-α-cyanoacrylonitrile.[15]

Tricyanoethylene gave a magenta complex with N,N-dimethylaniline in ether, but no condensation occurred.

**Diels–Alder Adduct of Tricyanoethylene and Anthracene.**—An ethereal solution of tricyanoethylene obtained from 1.85 g. (0.01 mole) of 1-bromo-1,1,2-tricyanoethane and 0.95 g. (0.0095 mole) of triethylamine was treated with a solution of 1.78 g. (0.01 mole) of anthracene in 100 ml. of benzene. The bright orange solution became colorless upon standing overnight, and the colorless, crystalline tricyanoethylene–anthracene adduct (9,10-dihydro-9,10-ethanol-11,11,12-tricyanoanthracene) that separated was collected; yield 2.21 g. (84%; based upon triethylamine), m.p. 222–225°. Several recrystallizations from benzene raised the melting point to 225–227°.

*Anal.* Calcd. for $C_{19}H_{11}N_3$: C, 81.1; H, 3.9; N, 15.0. Found: C, 81.3; H, 4.0; N, 15.2.

**4,5,5-Tricyano-2-pentanone.**—A solution of 2.06 g. (0.02 mole) of tricyanoethylene and 2 drops of boron trifluoride etherate in 5 ml. of acetone was allowed to stand for 2 days. Removal of the solvent left the tricyano ketone as an oily solid. After recrystallization from benzene–ethyl acetate, it weighed 1.25 g. (39%), m.p. 93–94.5°.

*Anal.* Calcd. for $C_8H_7ON_3$: C, 59.6; H, 4.4; N, 26.1. Found: C, 59.8; H, 4.4; N, 26.5.

In assigning the structure it was assumed that the methylene group became attached to the ethylenic carbon with the lower electron density, perhaps via attack of tricyanoethylene on the enolic form of acetone.

**Diels–Alder Adduct of Tricyanovinyl Chloride and Anthracene.**—A solution of 1.00 g. of anthracene and 0.67 g. of tricyanovinyl chloride in 50 ml. of benzene was heated under reflux for 2.5 hours. During this time the originally magenta solution became almost colorless. The white crystalline adduct (9,10-dihydro-9,10-ethano-11-chloro-11,12,-12-tricyanoanthracene) that separated upon cooling was collected; yield 0.60 g. (45%). The compound does not have a characteristic melting point, but it appears to dissociate into tricyanovinyl chloride and anthracene at 210–215°.

*Anal.* Calcd. for $C_{19}H_{10}N_3Cl$: C, 72.3; H, 3.2; N, 13.3; Cl, 11.2. Found: C, 72.2; H, 3.3; N, 13.4; Cl, 11.0.

**N-Methyl-N-tricyanovinylaniline.**—N-Methylaniline (2.14 g., 0.02 mole) was added dropwise to a stirred solution of 1.27 g. (0.01 mole) of tricyanovinyl chloride in 30 ml. of ether. The mixture was filtered to remove N-methylaniline hydrochloride, and the ethereal filtrate was evaporated to dryness. Recrystallization of the residue from benzene gave 1.25 g. (65%) of N-methyl-N-tricyanovinylaniline as light-yellow crystals, m.p. 124–126°. The infrared spectrum showed no N–H, and was not inconsistent with N-tricyanovinylaniline.[6]

*Anal.* Calcd. for $C_{12}H_8N_4$: C, 69.2; H, 3.8; N, 26.9. Found: C, 68.9; H, 3.9; N, 26.8.

***p*-Tricyanovinyl-N,N-dimethylaniline.**—N,N-Dimethylaniline (1.20 g., 0.01 mole) was added to a solution of 0.68 g. (0.005 mole) of tricyanovinyl chloride in 15 ml. of ethyl acetate. The solution became red immediately and deposited 0.20 g. of an irridescent blue solid on standing overnight. This was identified as N,N-dimethyl-*p*-tricyano-vinylaniline[6] by means of its visible spectrum.

**4-Chloro-1,2-dimethyl-4,5,5-tricyanocyclohexene.**—To a solution of 1.77 g. (0.013 mole) of tricyanovinyl chloride in 5 ml. of benzene was added 2.05 g. (0.025 mole) of 2,3-dimethylbutadiene with swirling. After 5 minutes, the warm solution was heated under reflux for 15 minutes. The resultant dark solution was diluted with 10 ml. of benzene and passed through a column of neutral alumina (30 g.), the first 140 ml. of benzene being collected. Concentration of the eluate followed by sublimation of the residue gave 1.50 g. (55%) of 4-chloro-1,2-dimethyl-4,5,5-tricyanocyclohexene, m.p. 116–119°. An analytical sample, m.p. 121.5–122°, was obtained by recrystallization from benzene–cyclohexane.

*Anal.* Calcd. for $C_{11}H_{11}N_3Cl$: C, 60.1; H, 4.6; N, 19.1. Found: C, 60.3; H, 4.6; N, 19.0.

**Tetramethylammonium Pentacyanopropenide.**—A solution of 6.6 g. (0.10 mole) of malononitrile, 8.7 g. (0.11 mole) of pyridine and 25 ml. of water contained in a 125-ml. erlenmeyer flask equipped with a stirrer was treated with 12.8 g. (0.10 mole) of powdered tetracyanoethylene added rapidly in small portions. The resulting mixture was warmed on a hot-plate with stirring until complete solution occurred (5–10 minutes, accompanied by evolution of HCN). The hot dark solution was transferred to a solution of 12.1 g. (0.11 mole) of tetramethylammonium chloride in 500 ml. of water. The mixture was heated almost to boiling to give a dark red solution which was cooled in an ice-bath. The orange needles of tetramethylammonium 1,1,2,3,3-pentacyanopropenide[9] were collected, washed with ice-water and recrystallized from 500 ml. of water containing 5 g. of activated carbon. The yield of recrystallized product obtained as bright yellow-orange needles, m.p. 314–315°, was 20.5 g. (85%).

**Hydrolysis of Tricyanovinyl Chloride.**—A mixture of 0.137 g. (1.0 mmole) of tricyanovinyl chloride in 10 ml. of water was stirred for 1.5 hours until complete solution occurred.

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[15] C. C. Price and V. Boekelheide, THIS JOURNAL, 68, 1246 (1946).

The tan solution was examined by visible–ultraviolet spectroscopy and shown to contain 0.99 mmole of tricyanovinyl alcohol ($\lambda_{max}$ 297 m$\mu$, $\epsilon$ 11,300) and 0.01 mmole of 1,1,2,3,3-pentacyanopropene ($\lambda_{max}$ 397 and 414 m$\mu$, $\epsilon$ 22,600 and 22,100, respectively).

When a solution of 0.81 g. (5.9 mmoles) of tricyanovinyl chloride in 4 ml. of tetrahydrofuran was treated with 2 ml. of water, a rapid (45 seconds) exothermic reaction took place with evolution of carbon dioxide (identified by the white precipitate it gave with lime water). The addition of 1.0 g. of tetramethylammonium chloride in 15 ml. of water followed by the removal of the tetrahydrofuran under vacuum gave 0.364 g. (51%) of tetramethylammonium pentacyanopropenide, m.p. 310–312°. The ultraviolet–visible spectrum was identical with that of an authentic sample.

**Reaction of Tricyanovinyl Chloride with Tricyanovinyl Alcohol.**—A mixture of 1.37 g. (0.01 mole) of tricyanovinyl chloride, 1.92 g. (0.01 mole) of the tetramethylammonium tricyanoethenolate and 15 ml. of tetrahydrofuran was heated under reflux on a steam-bath for 4 hours. The solid that separated weighed 2.35 g. It was shown to contain 0.0068 mole of pentacyanopropenide anion by spectroscopic examination. The filtrate yielded 0.45 g. (33%) of unreacted tricyanovinyl chloride after concentration and sublimation.

**Reaction of Tricyanovinyl Ethyl Ether with N,N-Dimethylaniline.**—A solution of 1.47 g. (0.01 mole) of tricyanovinyl ethyl ether in 5 ml. of N,N-dimethylaniline was heated in a boiling water-bath for 30 minutes. The resultant deep red solution was taken up in 30 ml. of methylene chloride and extracted successively with two 25-ml. portions of cold 2 *N* hydrochloric acid, 25 ml. of water and 10 ml. of saturated sodium chloride solution. The organic layer was then concentrated and chromatographed on acid alumina (Woelm) using ethyl acetate–acetone for elution. The deep-red gummy solid weighed 0.95 g. and contained 0.74 g. (34% yield) of N,N-dimethyl-*p*-tricyanovinylaniline as shown by the visible absorption intensity at 515 m$\mu$. The infrared spectrum of this gum indicated the absence of N,N-dimethyl-*p*-(2,2-dicyano-1-ethoxyvinyl)-aniline.[13]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS, AUSTIN 12, TEX.]

# The Initial Attack of Ozone on Unsaturated Systems. Ozonolyses of Unsymmetrical Derivatives of 1,2-Dibenzoylethylene[1]

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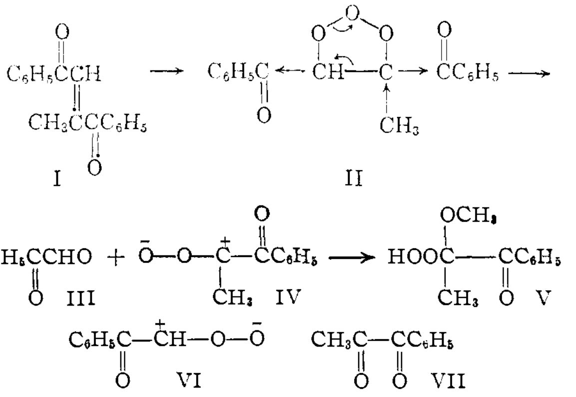
The study of the specificity of ozone attack on unsymmetrical olefins is continued with *cis*-1,2-dibenzoylpropene, *cis*-1,2-dibenzoyl-1-methoxyethylene, *cis*-1-amino-1,2-dibenzoylethylene and *cis*- and *trans*-1,2-dibenzoylstyrene. The results of this study and of studies made elsewhere make it clear that there is no single type of initial ozone attack, nor is there a single route to peroxidic and non-peroxidic ozonation products after the inital ozone attack. With most olefinic double bonds, however, it appears that a five-membered ring intermediate is produced *via*, at least in protolytic solvents, a $\pi$-complex involving the terminal electrophilic atom of the ozone molecule.

## Introduction

The Criegee mechanism[2,3] for ozonolysis does not attempt to elucidate the manner in which ozone initially attacks an unsaturated system. Various suggestions and discussions concerning this problem can be found in the literature.[3–7]

One approach to the problem of the initial ozone attack has involved the identification of the zwitterion and carbonyl moieties which are predominantly found during ozonolyses of unsymmetrical olefins.[8,9] For example, ozonolysis of *trans*-1,2-dibenzoylpropene (I) in the presence of methanol gave preferentially phenylglyoxal (III) and zwitterion IV (isolated as the methanol adduct V) rather than moieties VI and VII.[9] This result, as well as most other examples of the specificity of ozone attack reported up to the present time, can be explained by any of three ways: (1) a two-step addition in accordance with Markownikoff's rule to give a four-membered ring intermediate,[3,9] (2) the collapse of a five-membered ring intermediate (*e.g.*, II → III + IV) formed either by a one-step or a two-step ozone attack,[3,9–12] (3) an ozone attack which leads to no addition intermediate, but produces through an activated complex the more stable of the two possible zwitterion intermediates.



The present paper reports the results of a continuation of the unsymmetrical olefin study with com-

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[1] A portion of this work was presented at the 132nd Meeting of the American Chemical Society, Organic Chemistry Division, Symposium on Mechanisms of Oxidation Reactions, New York, N. Y., September, 1957.

[2] (a) R. Criegee and G. Wenner, *Ann.*, **564**, 9 (1949); (b) R. Criegee, *ibid.*, **583**, 1 (1953); (c) R. Criegee, G. Blust and H. Zinke, *Chem. Ber.*, **87**, 766 (1954); (d) R. Criegee, A. Kerckow and H. Zinke, *ibid.*, **88**, 1878 (1955); (e) R. Criegee, *Record Chem. Progr. Kresge–Hooker Sci. Lib.*, **18**, 111 (1957).

[3] P. S. Bailey, *Chem. Revs.*, **58**, 925 (1958).

[4] P. S. Bailey, *Chemistry & Industry*, 1148 (1957).

[5] E. A. Blair and A. Maggiolo, Abstracts of Papers presented at the 134th Meeting of the American Chemical Society, Chicago, Ill., September, 1958, p. 6 P.

[6] F. T. Wallenberger, *Tetrahedron Letters*, No. 9, August, 1959, p. 5.

[7] (a) E. J. Moriconi, W. F. O'Connor and L. Taranko, *Arch. Biochem. and Biophys.*, **83**, 283 (1959); (b) E. J. Moriconi, W. F. O'Connor and F. T. Wallenberger, THIS JOURNAL, **81**, 6466 (1959).

[8] P. S. Bailey, *Chem. Ber.*, **88**, 795 (1955).

[9] (a) P. S. Bailey and S. S. Bath, THIS JOURNAL, **79**, 3120 (1957); (b) P. S. Bailey, S. S. Bath and J. B. Ashton, *Advances in Chem. Ser.*, **21**, 143 (1959).

[10] L. A. Subluskey, G. C. Harris, A. Maggiolo and A. Tumolo, *ibid.*, **21**, 149 (1959).

[11] R. Criegee, private discussions.

[12] A. Maggiolo, "Organic Ozone Reactions and Techniques," The Welsbach Corp., Ozone Processes Div., Philadelphia, Pa., 1957