frared spectrum of the product shows no absorption due to a carbonyl group, but displays strong absorption characteristic of ether groups at 1040–1090 cm.$^{-1}$ in agreement with the assigned structure.

Anal. Calcd. for $C_{15}H_{24}S_2O_7$: C, 47.35; H, 6.36; S, 16.86. Found: C, 47.20; H, 6.21; S, 17.24.

Methyl α,α-Bis-(ethylsulfonyl)-*p*-toluate (XIII).—To a solution of 145 mg. of α,α,α-trimethoxy-α′,α′-bis-(ethylsulfonyl)-*p*-xylene in 2 ml. of methanol was added 3 drops of 10% aqueous hydrochloric acid. The resulting mixture was diluted with water and filtered to give 120 mg. (94%) of white crystals of methyl α,α-bis-(ethylsulfonyl)-*p*-toluate, m.p. 164–165.5°. Recrystallization from methanol gave crystals of m.p. 164–165°. The infrared spectrum of the product shows absorption at 1720 (ester carbonyl); 1600, 1500 (aromatic); 1280–1320, 1105–1140, (sulfone); and 850 cm.$^{-1}$ (1,4-disubstituted benzene).

Anal. Calcd. for $C_{13}H_{18}S_2O_6$: C, 46.69; H, 5.42; S, 19.17. Found: C, 46.84; H, 5.64; S, 19.43.

Acknowledgment.—The authors wish to thank Dr. D. S. Acker for helpful suggestions.

[CONTRIBUTION NO. 743 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., INC., WILMINGTON 98, DEL.]

Substituted Quinodimethanes. V.[1] *p*-Tricyanovinylphenyldicyanomethide and Related Anions

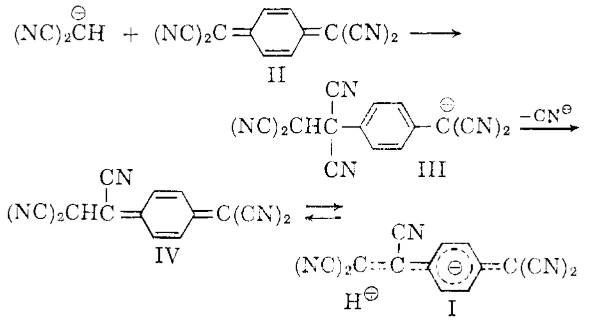
BY J. K. WILLIAMS

RECEIVED APRIL 7, 1962

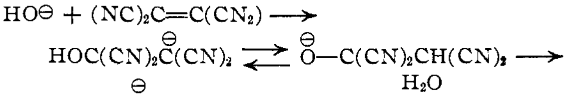
The deep-blue *p*-tricyanovinylphenyldicyanomethide (I) and two related anions have been prepared.

The deep-blue *p*-tricyanovinylphenyldicyanomethide ion (I) is the anion of a strong cyanocarbon acid[2] (pK_A 0.60) and owes its stability to the high degree of delocalization of its negative charge. It readily forms salts that are deep blue in solution (λ_{max}^{EtOH} 625, ε 52,200) and is best isolated as the tetramethylammonium salt.[3]

The most convenient method for preparing I (>90% yield) is to warm 7,7,8,8-tetracyanoquinodimethan[4] (II) with malononitrile in dimethylformamide solution. The steps leading to I probably involve the addition of the malononitrile anion to II to form the anion III. Elimination of cyanide ion from III can give IV, the conjugate acid of I.

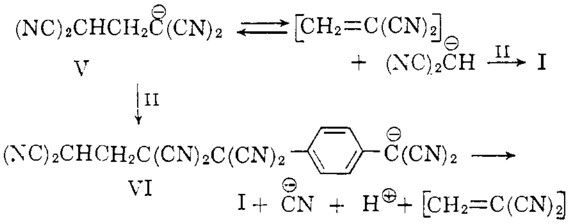


Two additional systems in which II is a reactant have been found to produce I, and in both the second component may function as a source of malononitrile. When II was allowed to react with tetracyanoethylene in moist dimethylformamide, compound I was formed in 45% yield. The formation of I in this system is analogous to the formation of the pentacyanopropenide anion[5] from tetracyanoethylene in moist dimethylformamide, a process that could involve the initial formation of the malonitrile anion as outlined below.



$$HO^{\ominus} + (NC)_2C{=}C(CN_2) \longrightarrow$$
$$HOC(CN)_2\overset{\ominus}{C}(CN)_2 \rightleftharpoons \overset{\ominus}{O}{-}C(CN)_2CH(CN)_2 \longrightarrow$$
$$\overset{\ominus}{C}H(CN_2) + [O{=}C(CN)_2] \xrightarrow{H_2O} 2HCN + CO_2$$

When II was allowed to react with 1,1,3,3-tetracyanopropane[6] in dimethylformamide, compound I was formed in 81% yield. In this system the anion V could be in equilibrium with vinylidene cyanide and malononitrile anion which would react with II to form I. Alternatively, V could add to II in an initial step to form the anion VI.



Elimination of cyanide ion, a proton and vinylidene cyanide from VI could then lead to I.

We have found another system that gives rise to I that does not include 7,7,8,8-tetracyanoquinodimethan. When phenylmalononitrile and potassium tetracyanoethylene anion radical (VII)[7] were allowed to react in dimethylformamide in the absence of moisture and oxygen, a 24% yield of I was obtained. Since no oxidizing agents were present it is unlikely that VII was converted to tetracyanoethylene, and thus the reaction cannot

$$\underset{\text{VII}}{K^{\oplus}(CN)_2CC(CN)_2{\cdot}^{\ominus}} + C_6H_5CH(CN)_2 \longrightarrow \text{I}$$

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[1] Paper IV, W. Hertler and R. Benson, *J. Am. Chem. Soc.*, **84**, 3474 (1962).

[2] We wish to thank Dr. R. H. Boyd for this spectrophotometric pK_A determination. Details of the technique used will be described by him elsewhere.

[3] An oxygen analog of I is the α,α-dicyano-*p*-toluoyl cyanide anion described in paper III of this series; W. R. Hertler, H. D. Hartzler, D. S. Acker and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3387 (1962).

[4] D. S. Acker, R. J. Hader, W. R. Hertler, W. Mahler, L. Melby, R. E. Benson and W. E. Mochel, *ibid.*, **82**, 6408 (1960).

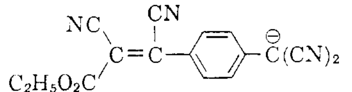
[5] W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *ibid.*, **80**, 2795 (1958); C. L. Dickinson, D. W. Wiley and B. C. McKusick, *ibid.*, **82**, 6132 (1960).

[6] O. Diels and B. Conn, *Ber.*, **56**, 2076 (1923).

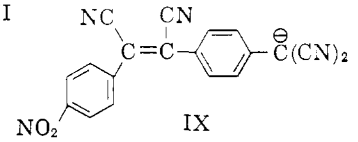
[7] O. W. Webster, W. Mahler and R. E. Benson, *J. Org. Chem.*, **25**, 1470 (1960).

be a simple ionic tricyanovinylation[8] of phenylmalononitrile by tetracyanoethylene. In fact there are preliminary indications that the reaction of tetracyanoethylene with phenylmalononitrile involves an oxidation–reduction in which the tetracyanoethylene is reduced to the anion radical while the phenylmalononitrile is oxidized.

Two anions related to I were prepared by reaction of 7,7,8,8-tetracyanoquinodimethan with other active methylene compounds. The anions, VIII (36% yield), $\lambda_{\max}$ 616 mμ (ε 45,000), and IX (64% yield, $\lambda_{\max}$ 590 mμ (ε 21,300), were prepared from ethyl cyanoacetate and *p*-nitrophenylacetonitrile and isolated as the tetramethylammonium salts.



VIII



IX

The assignment of structures to the ions I, VIII and IX is based on two considerations. The ultraviolet-visible and infrared spectra are compatible with the assigned structures. In addition, their structures follow from their mode of formation. The reaction of 7,7,8,8-tetracyanoquinodimethan with nucleophilic reagents is known to result in the replacement of one or more of the cyano groups by the nucleophilic moiety.[9] It is also well established that malononitrile and ethyl cyanoacetate undergo substitution by electrophilic reagents on the methylene carbon.[10]

Experimental

***p*-Tricyanovinylphenyldicyanomethide Ion. A. From Malononitrile and 7,7,8,8-Tetracyanoquinodimethan (II).**—A mixture of 3.0 g. (0.015 mole) of 7,7,8,8-tetracyanoquinodimethan,[4] 1.5 g. (0.023 mole) of malononitrile and 50 ml. of dimethylformamide was heated on a steam-bath for 0.5 hour. The deep-blue reaction mixture was poured into 500 ml. of cold water. Tetramethylammonium chloride (25 g.) was added to this solution. A micro-crystalline, black precipitate formed immediately and was collected by filtration. This solid was recrystallized from 250 ml. of absolute ethanol to give 4.2 g. (88%) of tetramethylammonium *p*-tricyanovinylphenyldicyanomethide as dark blue needles, m.p. 237°. The liquors from this crystallization were evaporated to a small volume, whereupon a second crop of salt was obtained weighing 0.15 g., m.p. 215–220°. An analytical sample, prepared by recrystallization from ethanol and then acetonitrile, melted at 237–238°. The spectrum in ethanol gave $\lambda_{\max}$ 292 mμ (ε 7,740), $\lambda_{\max}$ 350 mμ (ε 5,590) and $\lambda_{\max}$ 625 mμ (ε 52,200). The infrared spectrum showed bands at 3.28, 3.37, 4.51, 4.55, 4.62, 6.20, 6.57, 6.73, 6.88, 7.28 7.38, 10.52 and 12.07 μ.

Anal. Calcd. for $C_{18}H_{16}N_6$: C, 68.3; H, 5.1; N, 26.6. Found: C, 68.3; H, 5.1; N, 27.0.

B. From Tetracyanoethylene[11] and II.—A solution of 48.1 mg. of II in 100 ml. of dry dimethylformamide was prepared and to this was added 60.0 mg. of tetracyanoethylene and 1.00 ml. of water. The mixture was allowed to stand at room temperature for 6 days. The deep-blue reaction mixture was diluted to 250 ml. with alcohol. The spectrum of an aliquot diluted with absolute ethanol was measured. The absorption at $\lambda_{\max}$ 625 mμ corresponded to a 45% yield of the *p*-tricyanovinylphenyldicyanomethide ion.

C. From 1,1,3,3-Tetracyanopropane and II.—A mixture of 0.40 g. of II, 0.60 g. of 1,1,3,3-tetracyanopropane and 5 ml. of dimethylformamide was heated on a steam-bath for 0.25 hour. The deep-blue reaction mixture was diluted with absolute ethanol and its spectrum measured. Based on the absorption at $\lambda_{\max}$ 625 mμ, the yield of I was 81%.

D. From Phenylmalononitrile and Potassium Tetracyanoethylene Anion Radical (VII).—A mixture of 0.71 g. of phenylmalononitrile, 0.84 g. of VII and 5 ml. of dimethylformamide was stirred at room temperature under nitrogen for 23 hours. The deep-blue reaction mixture was diluted with ethanol and its spectrum was measured. The absorption at $\lambda_{\max}$ 625 mμ corresponded to a 24% yield of I.

Tetramethylammonium (*p*-[1,2-Dicyano-2-ethoxycarbonylvinyl]-phenyl)-dicyanomethide (VIII).—A mixture of 2.0 g. of ethyl cyanoacetate, 2.08 g. of 7,7,8,8-tetracyanoquinodimethan and 20 ml. of dimethylformamide was heated at reflux for 2.5 hours. The deep-blue solution was diluted to 100 ml. with acetonitrile. Measurement of the spectrum of a 1.00-ml. aliquot of this solution (diluted with ethanol) indicated the yield of VIII was 36% based on the extinction coefficient of the tetramethylammonium salt described below.

The remainder of the acetonitrile solution was chromatographed on 100 ml. of acid alumina (Woelm, activity grade II) with acetonitrile as the eluting solvent. The portion of the eluate that was blue (*ca.* 150 ml.) was evaporated to dryness. The dark-blue residue was dissolved in 200 ml. of hot water, treated with charcoal and filtered. When 30 g. of tetramethylammonium chloride was added to the filtrate, tetramethylammonium (*p*-[1,2-dicyano-2-ethoxycarbonylvinyl]-phenyl)-dicyanomethide (VIII) precipitated. After two crystallizations for absolute ethanol, deep-green needles were obtained, m.p. 175–176°. The infrared spectrum showed bands at 4.55 and 4.62 μ and 5.78 μ. The ultraviolet visible spectrum in ethanol showed $\lambda_{\max}$ 616 mμ (ε 45,000), shoulder 233 mμ (ε 6,280) and $\lambda_{\max}$ 290 mμ (ε 10,500).

Anal. Calcd. for $C_{20}H_{21}N_5O_2$: C, 66.1; H, 5.8. Found: C, 66.1; H, 6.0.

Tetramethylammonium (*p*-[1,2-Dicyano-2-(*p*-nitrophenyl)-vinyl]-phenyl)-dicyanomethide (IX).—A mixture of 0.24 g. of *p*-nitrophenylacetonitrile, 0.21 g. of 7,7,8,8-tetracyanoquinodimethan and 5 ml. of dimethylformamide was heated at reflux for 3 hours. The mixture was placed on a column packed with 30 g. of acid alumina in acetonitrile. Brown material was eluted with 100 ml. of acetonitrile and discarded. A deep blue band was eluted with 250 ml. of acetonitrile containing 1% ethanol. The blue eluate was evaporated to dryness and the residue was dissolved in alcohol. Spectral measurements of this solution indicated a yield of 64% of the *p*-(1,2-dicyano-2-[*p*-nitrophenyl]-vinyl)-phenyldicyanomethide ion (IX) based on the extinction coefficients found for the tetramethylammonium salt described below.

In another experiment on twenty times the scale of that described above, chromatography gave a blue eluate that was evaporated to dryness to give a dark residue. This residue was digested with 1 l. of boiling water and filtered. To the hot filtrate was added 100 g. of tetramethylammonium chloride. The mixture was allowed to cool and the solid that precipitated was collected. Two crystallizations from ethanol gave a sample of the tetramethylammonium salt of IX, m.p. 227–228°. The infrared spectrum showed bands at 4.50, 4.53, 4.59, 4.63, 6.27, 6.56, 6.67, 6.73, 7.45 and 7.53 μ. The ultraviolet-visible spectrum in ethanol showed $\lambda_{\max}$ 590 mμ (ε 21,300) and $\lambda_{\max}$ 307 mμ (ε 14,700) with a shoulder at 333 mμ (ε 12,600).

Anal. Calcd. for $C_{23}H_{20}N_6O_2$: C, 66.9; H, 4.9; N, 20.4. Found: C, 67.1; H, 5.1; N, 20.4.

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[8] G. N. Sausen, V. A. Engelhardt and W. J. Middleton, *J. Am. Chem. Soc.*, **80**, 2815 (1958).

[9] W. Hertler, H. Hartzler, D. Acker and R. Benson, *ibid.*, **84**, 3387 (1962).

[10] A. C. Cope, H. L. Holmes and H. O. House, "Organic Reactions," Vol. IX, R. Adams, ed., J. Wiley and Sons, Inc., New York, N. Y., 1957, p. 107; V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Corp., New York, N. Y., 1947.

[11] This reaction was carried out by Dr. D. S. Acker.