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Cyanocarbon Chemistry. XX.[1,2] 1,2,2-Tricyano-1,3-butadienes

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Tricyanovinyl chloride reacts with electron-rich olefins such as methyl vinyl ether, anethole and N-vinylpyrrolidone to give 1,1,2-tricyano-1,3-butadienes. Some of these butadienes can also be synthesized by the cleavage in hot alcohol of 3-substituted 1,1,2,2-tetracyanocyclobutanes obtained from tetracyanoethylene.[1] 1,1,2-Tricyano-4-methoxy-1,3-butadiene reacts readily in alcohol to give the intensely blue cyanocarbon acid, 1,1,2,6,7,7-hexacyano-1,3,5-heptatriene.

The facile reaction of tetracyanoethylene with electron-rich olefins to give 3-substituted-1,1,2,2-tetracyanocyclobutanes[1] has prompted us to investigate the analogous reaction with tricyanovinyl chloride.[3] Interestingly, the expected cyclobutane adducts could not usually be isolated because of spontaneous loss of hydrogen chloride accompanied by ring cleavage to give 4-substituted-1,1,2-tricyano-1,3-butadienes. For example, anethole reacted with tricyanovinyl chloride at room temperature to give 1,1,2-tricyano-4-anisyl-3-methyl-1,3-butadiene (I) in 43% yield. Similarly, reaction with methyl vinyl ether gave 1,1,2-tricyano-4-methoxy-1,3-butadiene (II).

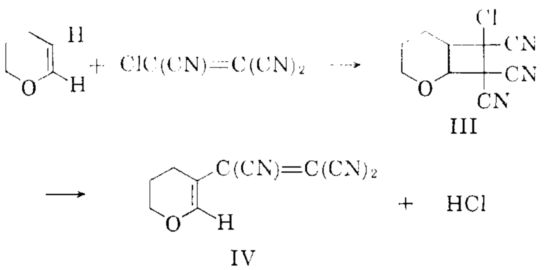
$$p\text{-}CH_3OC_6H_4CH{=}CHCH_3 + ClC(CN){=}C(CN)_2 \longrightarrow p\text{-}CH_3OC_6H_4CH{=}C(CH_3)C(CN){=}C(CN)_2 + HCl$$

I

$$CH_3OCH{=}CH_2 + ClC(CN){=}C(CN)_2 \longrightarrow CH_3OCH{=}CHC(CN){=}C(CN)_2 + HCl$$

II

The reactions appeared to be quite dependent on solvent polarity, proceeding rapidly at room temperature in acetonitrile or tetrahydrofuran. In ether or benzene solution, the reaction was quite slow, and in the case of dihydropyran it was possible to isolate a relatively unstable 1:1 cyclobutane adduct (III). The structure of III was confirmed by its infrared and proton magnetic resonance absorption spectra and its ready conversion to the corresponding tricyanobutadiene IV. The adduct was quite sensitive to heat and polar solvents. For example, just dissolving the colorless adduct in acetonitrile at room temperature caused a rapid evolution of hydrogen chloride accompanied by the formation of the yellow tricyanovinyl dihydropyran IV.

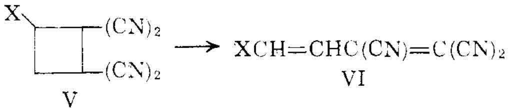


III

IV

Styrene, which did not give a cyclobutane derivative with tetracyanoethylene,[1] reacted with tricyanovinyl chloride only upon refluxing in acetonitrile or tetrahydrofuran to give a low yield of 1,1,2-tricyano-4-phenyl-1,3-butadiene.

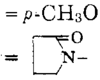
An alternative synthesis of these 4-substituted-1,1,2-tricyanobutadienes has been accomplished *via* some of the tetracyanocyclobutanes synthesized from tetracyanoethylene and electron-rich olefins.[1] For example, refluxing 3-anisyl-1,1,2,2-tetracyanocyclobutane (Va) in alcohol resulted in ring cleavage with loss of hydrogen cyanide to give 4-anisyl-1,1,2-tricyano-1,3-butadiene (VIa). N-(3,4,4-Tricyano-1,3-butadienyl)-pyrrolidone (VIb) was obtained by heating N-(2,2,3,3-tetracyanocyclobutyl)-pyrrolidone (Vb) in methanol and alternatively by treating N-vinylpyrrolidone with tricyanovinyl chloride.



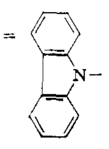
V VI

V and VIa, X = p-$CH_3OC_6H_4$ c, X = $C_6H_5SO_2N(CH_3)$-

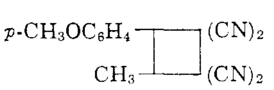
b, X =



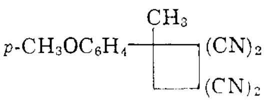
d, X =



Alcohols seem to be essential for the ring cleavage reaction, for no diene was detected when Va was heated in dioxane, acetonitrile or benzene solution. A sixth substituent on the cyclobutane ring in addition to the four cyano groups and the electron-releasing group seems to inhibit the reaction. For example, no diene was obtained from the anethole adduct 1,1,2,2-tetracyano-3-anisyl-4-methylcyclobutane (VII) or the isomeric 1,1,2,2-tetracyano-3-anisyl-3-methylcyclobutane (VIII) by heating them in methanol. On the other hand, the compound obtained from tetracyanoethylene and N-vinylcarbazole (Vd) cleaves so readily that its isolation in analytical purity was not accomplished. When crude Vd was heated in alcohol a good yield of the diene VId was obtained.



VII



VIII

The 4-alkoxy-1,1,2-tricyanobutadienes are considerably more reactive than the 4-aryl or 4-

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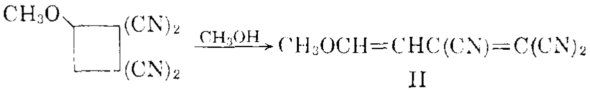
[1] Paper XIX, J. K. Williams, D. W. Wiley and B. C. McKusick, *J. Am. Chem. Soc.*, **84**, 2210 (1962).

[2] Presented at the St. Louis Meeting of the American Chemical Society, March, 1961.

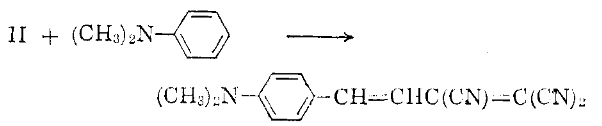
[3] C. L. Dickson, D. W. Wiley and B. C. McKusick, *J. Am. Chem. Soc.*, **82**, 6132 (1960); U. S. Patent 2,942,022.

amido dienes and are consequently more difficult to isolate. Thus when 3-methoxy-1,1,2,2-tetracyanocyclobutane (IX) was heated in methanol only a low yield of II could be isolated because the compound reacts further with the solvent to give intensely colored solutions (see below).


IX II

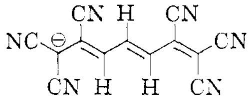
Consideration of the available data concerning the mechanism of these concomitant ring cleavage and elimination reactions has led to no simple common plausible explanation. For that matter it is not even clear that the two methods of butadiene synthesis are necessarily related by proceeding through similar cyclobutane intermediates. Thus even though it was possible to isolate a cyclobutane adduct from dihydropyran and tricyanovinyl chloride in ethereal solutions, spectroscopic examination of the reaction of *p*-methoxystyrene and tricyanovinyl chloride indicated that in the three solvents, acetonitrile, ether and cyclohexane, the rate of disappearance of *p*-methoxystyrene was almost exactly equal to the rate of appearance of the related butadiene. However, there was a marked difference in rates in the three solvents of 200:80:1, respectively.

The 1,1,2-tricyanobutadiene structure for the products is supported by the fact that their infrared spectra have in common bands at 4.45–4.52 μ (—CN), 6.23–6.31 μ $(-\overset{\diagdown}{C}=\overset{\diagup}{C}-)$ and 6.52–6.60 μ $(-\overset{CN}{\overset{|}{C}}=C(CN)_2)$, as well as the expected absorption for the appropriate additional functional groups. The most compelling structural argument is the fact that the dienes all absorb strongly (ϵ 18,000–40,000) above 350 mμ, as would be expected for such compounds by analogy with a large number of known tricyanovinyl compounds.[4] No alternative covalent structures can account for the intense color of these materials. Supporting evidence is found in the condensation of II with N,N-dimethylaniline to give X, a known compound.[4]

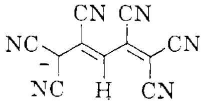

X

The exceptional reactivity of the 4-alkoxy-1,1,2-tricyanobutadienes is illustrated by their ready conversion to an intensely blue cyanocarbon acid upon treatment with alcohol. The same blue acid is obtained more slowly from the sulfonamide Vc. When the methoxy compound II or its precursor, the cyclobutane IX is heated in methanol for 30 minutes or 24 hours, respectively, a blue acid is obtained in 20–30% yield. The acid can be isolated as the tetramethylammonium, ammonium or sodium salt. Analyses of these salts indicate an empirical formula $C_{13}H_3N_6^-$ for the anion with an extinction coefficient of 165,000 at its absorption maximum of 635 mμ. The apparent molecular weights of the sodium and tetramethylammonium salts, determined ebullioscopically in acetone, are one-half those corresponding to the empirical formulas, indicating complete ionization. The infrared spectra of these salts contain strong conjugated C≡N and conjugated C=C absorption peaks.

The remarkable intensity of the visible absorption strongly suggests a symmetrical, planar anion. From these data, the anion is postulated to be 1,1,2,6,7,7-hexacyanoheptatrienide (XI), where the negative charge is stabilized by resonance throughout the conjugated system.

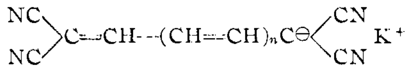

XI

When a methanol solution of the methoxy compound II was treated with tricyanovinyl chloride, a related anion, $C_{11}HN_6^-$, of an intense red color (λ_{max} 538 mμ, ϵ 82,000), was isolated in low yield as the tetramethylammonium salt. The infrared spectrum is similar to that of the blue anion, with strong conjugated C≡N and C=C absorption bands. This anion is postulated to be the salt of 1,1,2,4,5,5-hexacyanopentadiene (XII).


XII

The salts of 1,1,7,7-tetracyanoheptatriene (XIII, where n = 2) and 1,1,5,5-tetracyanopentadiene (XIII, where n = 1) have been described by Strell.[5] The visible absorption maxima of the series of related compounds are listed in Table I. The pentacyanopropenide ion has also been described[6]; it has maximum absorption at 395–410 mμ (doublet, ϵ 22,000). It is interesting to note that the substitution of one CN for the one hydrogen in tetracyanopropenide causes a bathochromic shift of about 50–60 mμ and increases the intensity about sevenfold. Thus it does not seem unreasonable that the substitution of two CN's for two hydrogens in XIIIb and XIIIc should cause a bathochromic shift of about

TABLE I


XII

	λ_{max} mμ (ϵ)
a, n = 0	346 (3,150)
b, n = 1	440 (8,300)
c, n = 2	540 (16,000)
d, n = 3	632 (not isolated)

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[4] B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *J. Am. Chem. Soc.*, **80**, 2806 (1958).

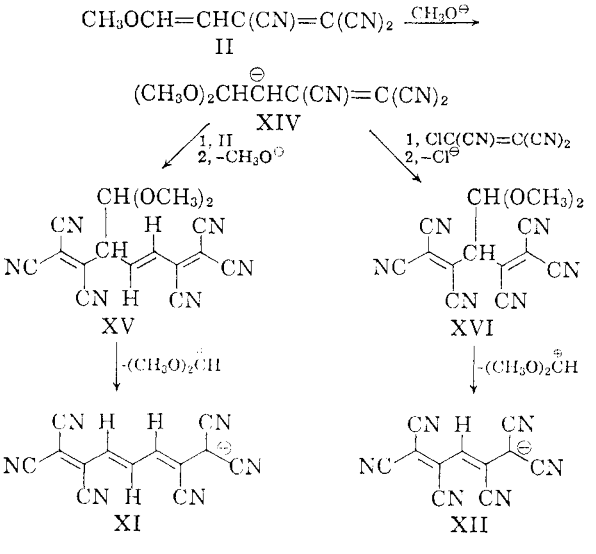
[5] M. Strell, W. B. Braunbruck, W. F. Fuhler and O. Huber, *Ann.*, **587**, 177 (1954).

[6] W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).

100 mμ and a tenfold increase in intensity. Examination of Stuart–Briegleb models of XI and XII using ethylenic carbon models for the backbone carbons indicates that these anions can be planar with little or no strain, which is quite favorable for the observed high extinction coefficients.

The formation of these anions is rationalized to proceed by the sequence shown in Chart I. The addition of a base to II would most likely occur at the 4-position of the butadiene to give an anion (XIV) stabilized by resonance. This intermediate anion then can react with a second molecule of butadiene or with the more reactive tricyanovinyl chloride to give intermediates XV or XVI. The heterolytic fission of a carbon–carbon bond in XV or XVI gives the stable anions XI or XII and dimethoxymethyl carbonium ion. An analogy can be noted in the SN1 solvolysis of an α-haloether.[7] The reaction of dimethoxymethyl carbonium ion with the solvent methanol would give methyl orthoformate.

Chart I



Experimental

1,1,2-Tricyano-4-(*p*-methoxyphenyl)-1,3-butadiene (VIa). a. From 1,1,2,2-Tetracyano-3-(*p*-methoxyphenyl)-cyclobutane (Va).—A mixture of 5 g. (19 mmoles) of 1,1,2,2-tetracyano-3-(*p*-methoxyphenyl)-cyclobutane and 100 ml. of absolute methanol was heated under reflux for 24 hours. The reaction mixture was chilled in ice, the dark-red crystalline 1,1,2-tricyano-4-(*p*-methoxyphenyl)-1,3-butadiene was collected and washed with methanol. The crude diene weighed 2.9 g. (64%) and melted at 213–214°. A sample prepared for analysis by two crystallizations from acetonitrile showed no increase in melting point. The ultraviolet spectrum in acetonitrile showed λ_{max} 278 mμ (ε 8,840), λ_{max} 445 mμ (ε 38,500) with shoulders at 303 and 320 mμ. The infrared spectrum showed bands at 4.51 (conj. —CN), 6.31 and 6.57 μ (C=C), 6.20 and 6.69 μ (benzene ring), and at 11.95 μ (1,4-disubstituted benzene).

Anal. Calcd. for $C_{14}H_9N_3O$: C, 71.5; H, 3.9; N, 17.9; mol. wt., 235. Found: C, 71.6; H, 4.0; N, 17.8; mol. wt., 260.

A similar reaction carried out in ethanol rather than methanol gave a 39% yield of the same diene, m.p. 214–215°, alone or mixed with the methanol product.

When 1.0 g. of 1,1,2,2-tetracyano-3-(*p*-methoxyphenyl)-cyclobutene was heated under reflux with 20 ml. of benzene or acetonitrile for 18 to 24 hours, the solution remained clear but became pale yellow. Cooling the reaction mixture to room temperature gave essentially quantitative recovery of unchanged starting material, as identified by undepressed mixed melting point.

b. From Tricyanovinyl Chloride and *p*-Methoxystyrene.—A mixture of 2.74 g. (20 mmoles) of tricyanovinyl chloride and 2.68 g. (20 mmoles) of *p*-methoxystyrene was dissolved in 8 ml. of tetrahydrofuran to give a deep red solution. The temperature rose slowly to 40° and then dropped back to room temperature with gradual evolution of HCl and deposition of red crystals. After 3 hours, the mixture was chilled and filtered to give 1.80 g. of 1,1,2-tricyano-4-(*p*-methoxyphenyl)-1,3-butadiene, m.p. 214.5–215°. Infrared and ultraviolet spectral analyses and a mixed melting point, 213.5–215°, showed this material to be identical with a sample prepared by method a above.

Additional material was obtained by adding 2.68 g. of *p*-methoxystyrene to the above filtrate. After standing overnight the solution had deposited 0.98 g. of large red prisms, m.p. 210–212°, giving a total yield of 2.8 g. (60%).

1,1,2-Tricyano-3-methyl-4-(*p*-methoxyphenyl)-1,3-butadiene (I) from Tricyanovinyl Chloride and Anethole.—To a solution of 2.74 g. (20 mmoles) of tricyanovinyl chloride in 10 ml. of tetrahydrofuran, 2.96 g. (20 mmoles) of anethole was added with swirling. The dark red solution was allowed to stand overnight at room temperature. The solvent was removed in vacuum and the residue was chromatographed on 150 g. of alumina (acid, Woelm, Activity I) using benzene and ether as eluants. The column was developed with 300–400 ml. of benzene and the following fractions were obtained: 1, 150 ml. of benzene yellow solution orange oil; 2, 250 ml. of benzene yellow solution 0.59 g. of gummy red solid; 3, 200 ml. of benzene bright yellow solution 0.26 g. of red solid; 4, 250 ml. of benzene–ether 1.87 g. of red solid; 5, 250 ml. of ether 0.37 g. of red solid; 6, 250 ml. of ether 0.09 g.; 7, 400 ml. of ether and 10% acetone–ether 0.29 g. of gummy red solid.

Fraction 1 gave 0.04 g. of recovered tricyanovinyl chloride upon sublimation. Fractions 3 through 6 were combined and recrystallized from methanol to give 1.79 g. of 1,1,2-tricyano-3-methyl-4-(*p*-methoxyphenyl)-1,3-butadiene as maroon crystals, m.p. 137.5–139°. An additional 0.35 g. of maroon crystals was obtained from fractions 2 and 7 to give a total yield of 2.14 g. (43% of theory). Additional recrystallizations from methanol gave an analytical sample, m.p. 138–139°. The ultraviolet spectrum (in EtOH) contained absorption peaks at 260 mμ (ε 11,300) and 444 mμ (ε 16,600). The infrared spectrum (in KBr) contained the following major absorption peaks 4.51 (C≡N), 6.24, 6.42, 6.61, 6.74, 7.00, 7.26, 7.51, 7.80, 7.92, 8.12, 8.46, 8.87, 9.35, 9.82, 10.28, 10.98, 11.83, 11.92, 13.0 and 14.4 μ.

Anal. Calcd. for $C_{15}H_{11}N_3O$: C, 72.3; H, 4.5; N, 16.9; mol. wt., 249. Found: C, 71.5; H, 4.7; N, 16.8; mol. wt., 258.

Reaction of Tricyanovinyl Chloride with Styrene.—A solution of 2.75 g. (20 mmoles) of tricyanovinyl chloride and 4.16 g. (40 mmoles) of styrene in 7 ml. of tetrahydrofuran was refluxed for 2 days. The volatile solvents were removed *in vacuo* and the black residue was chromatographed on 150 g. of alumina (acid, Woelm, Activity I) using benzene as eluant. A total of 2000 ml. of bright yellow benzene solution was collected and concentrated to give 0.24 g. of yellow solid, m.p. 135–204°. This material was rechromatographed and then recrystallized three times from 1,2-dichloroethane to raise the melting point to 199–205° dec. An analytical sample of 1,1,2-tricyano-4-phenyl-1,3-butadiene was prepared by sublimation at 120° (0.1 mm.) to give orange prisms, m.p. 202–205° dec. The ultraviolet spectrum in methylene chloride showed λ_{max} 402 mμ (ε 32,800) and in ethanol λ_{max} 390 mμ (ε 28,500). The infrared spectrum contained absorption peaks characteristic for aromatic CH (3.30 μ), unsatd. CH (3.32 μ), conj. CN (4.53 μ), aromatic and conj. C=C (6.26, 6.42 and 6.62 μ), *trans*-CH=CH (10.32 μ) and monosubstituted benzenes (13.20 and 14.62 μ).

Anal. Calcd. for $C_{13}H_7N_3$: C, 76.1; H, 3.4; N, 20.5. Found: C, 75.6; H, 3.5; N, 20.7.

The tricyanobutadiene was also obtained by refluxing a solution of tricyanovinyl chloride and styrene in ethylene glycol dimethyl ether (glyme) with sodium fluoride for 21

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[7] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 333.

hours. The yield of purified, sublimed material was 11% of theoretical.

N-(3,4,4-Tricyano-1,3-butadienyl)-pyrrolidone (VIb). a. From N-(2,2,3,3-Tetracyanocyclobutyl)-pyrrolidone (Vb).—After a solution of 2.7 g. (11 mmoles) of N-(2,2,3,3-tetracyanocyclobutyl)-pyrrolidone in 20 ml. of methanol had been heated under reflux for 1 hour, a yellow crystalline solid had almost caused the reaction mixture to solidify. At this point the solid was separated from the cooled reaction mixture to give 1.9 g. (79%) of N-(3,4,4-tricyano-1,3-butadienyl)-pyrrolidone as bright yellow needles, m.p. 169–170°.

A sample that was prepared for analysis by two recrystallizations from acetonitrile melted at 174–175°. The ultraviolet spectrum was measured in acetonitrile; $\lambda_{\max}$ 245 mμ (ϵ 5,570), 250 mμ (ϵ 6,000), 265 mμ (ϵ 3,700) and 398 mμ (ϵ 40,400). The infrared spectrum showed bands at 4.49 (conj. —CN), 6.25 and 6.50 μ (C=C). The carbonyl stretching vibration was at 5.72 μ, which is quite low for a γ-lactam (usually at 5.87). This short wave length shift can be explained as a result of the electron-withdrawing action of the tricyanovinyl group. For example, acetanilide shows absorption at 6.00 μ, whereas *p*-tricyanovinylacetanilide has the carbonyl absorption at 5.90 μ.

Anal. Calcd. for $C_{11}H_8N_4O$: C, 62.3; H, 3.8; N, 26.4. Found: C, 62.3; H, 3.9; N, 26.8.

b. From Tricyanovinyl Chloride and N-Vinylpyrrolidone.—A mixture of 1.37 g. (10 mmoles) of tricyanovinyl chloride, 1.11 g. (10 mmoles) of N-vinylpyrrolidone, 2.10 g. (50 mmoles) of sodium fluoride and 10 ml. of glyme was stirred overnight. The organic solution was then separated from the inorganic salts and concentrated to give a dark red, gummy residue. Two recrystallizations from ethanol gave 1.08 g. (51% of theory) of N-(3,4,4-tricyano-1,3-butadienyl)-pyrrolidone as yellow needles, m.p. 175–177°. The ultraviolet and infrared spectra were identical to those of a sample prepared by method a.

N-Methyl-N-(3,4,4-tricyano-1,3-butadienyl)-benzenesulfonamide (VIc).—A mixture of 5 g. (15 mmoles) of N-methyl-N-(2,2,3,3-tetracyanocyclobutyl)-benzenesulfonamide and 25 ml. of methanol was heated at reflux for 17 hours. The deep blue-green solution was allowed to cool to 25° and the yellow-green solid was collected by filtration and washed with methanol. It weighed 2.7 g. (59%). Recrystallization of the crude product from acetonitrile gave 1.9 g. of N-methyl-N-(3,4,4-tricyano-1,3-butadienyl)-benzenesulfonamide, m.p. 174–176°, and a second crop of 0.3 g., m.p. 173–174.5°.

Three crystallizations of the second crop from acetonitrile gave yellow prisms, m.p. 172.5–173.5°. The ultraviolet spectrum in acetonitrile showed $\lambda_{\max}$ 385 mμ (ϵ 38,700).

Anal. Calcd. for $C_{14}H_{10}N_4SO_2$: C, 56.4; H, 3.4; N, 18.8. Found: C, 56.5; H, 3.5; N, 18.9.

A sample of the methanol solution from the reaction mixture showed $\lambda_{\max}$ 635 mμ with a shoulder at 590 mμ. This absorption is characteristic of the 1,1,2,6,7,7-hexacyanoheptatrienide ion.

N-Methyl-N-(3,4,4-tricyano-1,3-butadienyl)-*p*-toluenesulfonamide.—A mixture of 0.34 g. (2.5 mmoles) of tricyanovinyl chloride, 0.53 g. (2.5 mmoles) of N-methyl-N-vinyl-*p*-toluenesulfonamide, 1.0 g. of sodium fluoride and 3 ml. of glyme was stirred overnight at room temperature. The inorganic salts were removed by filtration. After removal of the solvent in vacuum, the dark-colored residue was taken up in hot ethanol, filtered and chilled. The resulting yellow-orange needles weighed 0.49 g. (62%) and melted at 168–171°. An analytical sample of N-methyl-N-(3,4,4-tricyano-1,3-butadienyl)-*p*-toluenesulfonamide, m.p. 170–171°, was obtained by 4 recrystallizations from benzene–cyclohexane (1:1). The use of ethanol for recrystallization was accompanied by some conversion to the intensely blue hexacyanoheptatrienide. The ultraviolet spectrum in acetonitrile contained a major absorption with $\lambda_{\max}$ at 388 mμ (ϵ 25,600).

Anal. Calcd. for $C_{15}H_{12}N_4O_2S$: S, 10.3. Found: S, 10.3.

1-(1′-Carbazolyl)-3,4,4-tricyano-1,3-butadiene (VId).—To a solution of 1.3 g. (10 mmoles) of tetracyanoethylene in 10 ml. of tetrahydrofuran was added 2.1 g. of N-vinylcarbazole. The violet-colored solution became warm and, after 2 minutes, its color had faded to pink. The solution was kept at 25° for 2 hours and then diluted with 35 ml. of petroleum ether. The solid that precipitated was collected and washed with ether to give 3.3 g. of 1-(2′,2′,3′,3′-tetracyanocyclobutyl)-carbazole that had no definite melting point but decomposed slowly above about 70–80°. Purification of the crude material by crystallization was rendered difficult by its instability in solution.

When 0.5 g. of 1-(2′,2′,3′,3′-tetracyanocyclobutyl)-carbazole and 10 ml. of methanol were heated under reflux, red crystals began to precipitate after 0.5 hour. After the reaction mixture had been heated for 18 hours, it was cooled to 25° and the deep red, crystalline 1-(1′-carbazolyl)-3,4,4-tricyano-1,3-butadiene was collected and washed with methanol. It weighed 0.34 g. (74%).

Two recrystallizations from acetonitrile gave an analytical sample melting at 270–271°. The ultraviolet spectrum in acetonitrile gave $\lambda_{\max}$ 235 mμ (ϵ 36,500), 273 mμ (ϵ 18,200), sh 300 mμ (ϵ 8,260), 465 mμ (42,600). The infrared spectrum showed bands at 4.50 μ (conj. —CN) and at 6.20, 6.31 and 6.57 μ (conj. C=C) in addition to those associated with the carbazole ring system.

Anal. Calcd. for $C_{19}H_{10}N_4$: C, 77.5; H, 3.4; N, 19.0. Found: C, 77.7; H, 3.5; N, 19.1.

1,1,2-Tricyano-4-methoxy-1,3-butadiene (II). a. From 3-Methoxy-1,1,2,2-tetracyanocyclobutane.—A mixture of 3.72 g. (20 mmoles) of 3-methoxy-1,1,2,2-tetracyanocyclobutane, 0.2 g. of toluenesulfonic acid hydrate and 20 ml. of methanol was refluxed for 2 hours. The methanol was then distilled into a 10% silver nitrate solution, giving an immediate precipitate of silver cyanide. The residual tar was stirred with 15 g. of dry alumina and added to a column of 25 g. of alumina (Woelm, acid, Activity I) constructed in benzene. The first 200 ml. of benzene eluate was collected and concentrated to give an oil which contained 4-methoxy-1,1,2-tricyano-1,3-butadiene, identified by its ultraviolet spectrum ($\lambda_{\max}$ in CH_2Cl_2, 352 mμ) and by its ready reaction with alcohol and dimethylformamide to give an intense blue color, with tricyanovinyl chloride and dimethylformamide to give an intense red color, and with dimethylaniline to give a red π-complex which was dissipated by dilution. These color tests are characteristic of 4-alkoxy-1,1,2-tricyanobutadienes. Attempts to isolate 4-methoxy-1,1,2-tricyano-1,3-butadiene by additional chromatography on alumina were unsuccessful.

Similar results were obtained when the reaction was carried out using *t*-butyl alcohol as the solvent. Only an oil was obtained that again gave the characteristic color tests for the butadiene.

b. From Tricyanovinyl Chloride and Methyl Vinyl Ether.—A solution of 1.37 g. (10 mmoles) of tricyanovinyl chloride in 5 ml. of tetrahydrofuran was stirred under an atmosphere of methyl vinyl ether. The temperature rose to 51° and remained there for 20 minutes before starting to drop. After 40 minutes, the resulting solution, fuming with hydrogen chloride vapors, was concentrated to give a dark crystalline mass that was taken up in benzene and passed over a short (10 × 2 cm.) column of alumina (acid, Woelm, Activity I). The first 250 ml. of benzene was collected and concentrated to give 0.84 g. (53%) of yellow solid, m.p. 98–101°. (There developed a deep red color on the column which could be eluted with acetone to give the red anion XII; see below.) The initial solid was recrystallized from carbon tetrachloride to give brown needles, m.p. 100.5–102°. Rechromatography as above gave 0.45 g. of 1,1,2-tricyano-4-methoxy-1,3-butadiene as bright yellow needles, m.p. 101–103°. An analytical sample was recrystallized twice from ethylene dichloride–cyclohexane without raising the melting point.

Anal. Calcd. for $C_8H_5N_3O$: C, 60.4; H, 3.2; N, 26.4. Found: C, 60.3; H, 3.2; N, 26.6.

The ultraviolet and infrared spectra were consistent with the assigned butadiene structure with $\lambda_{\max}$ 352 mμ (ϵ 27,000 in methylene chloride) and strong absorption peaks at 4.47 (conj. C≡N), and at 6.20, 6.25 and 6.55 μ (highly conjugated system). The yellow butadiene rapidly darkened on exposure to air and light and appeared to be extremely sensitive to water and other protolytic or basic solvents. Warming in methanol gave the blue anion XI (see below). When heated in inert solvents, a slow decomposition occurred. It could be sublimed at 60° and 0.1 mm., giving a bright yellow solid but always leaving a small amount of dark fluffy residue.

4-Benzyloxy-1,1,2-tricyano-1,3-butadiene.—To a solution of 6.85 g. (50 mmoles) of tricyanovinyl chloride in 25 ml. of ether, 6.70 g. (50 mmoles) of benzyl vinyl ether in 20 ml. of ether was added with stirring under a nitrogen atmosphere. Even though an exothermic reaction appeared to occur, no solid had precipitated after 3 hours. Five milliliters of tetrahydrofuran was then added and the solution was allowed to stand overnight. A dark precipitate weighing 5.3 g. (45%) was separated from the fuming (HCl) solution. Two passes through an alumina column (acid, Woelm, Activity I), using benzene as wash liquid, gave 4-benzyloxy-1,1,2-tricyano-1,3-butadiene as a bright yellow solid, m.p. 102–105°. An analytical sample, fine tan needles, m.p. 106.5–107.5° dec., was obtained by three *quick* recrystallizations from *warm* ethyl acetate (50% loss each time).

Anal. Calcd. for $C_{14}H_9N_3O$: C, 71.5; H, 3.9; N, 17.9. Found: C, 71.8; H, 4.0; N, 17.9.

The ultraviolet and the infrared spectra were consistent with the assigned structure with λ_{max} at 357 mμ (ϵ 31,000 in methylene chloride) and strong absorption peaks at 4.49 (conj. C≡N) and 6.21 and 6.56 μ (see corresponding methoxy compound). The compound could be recrystallized from solvents other than ethyl acetate but there was some decomposition to give a darker colored product. The butadiene was very sensitive to water and turned green on exposure to air. Stored samples slowly turned dark upon standing at room temperature, but could be stored indefinitely at −80°.

3-(Tricyanovinyl)-5,6-dihydro-4H-pyran (IV) *via* **7-Chloro-7,8,8-tricyano-2-oxabicyclo[4.2.0]octane (III).**—To a solution of 2.75 g. (0.02 mole) of tricyanovinyl chloride in 10 ml. of ether, 6.4 g. (0.08 mole, excess) of 5,6-dihydro-4H-pyran in 5 ml. of ether was added. The orange-red solution was allowed to stand overnight, and the walls of the flask were scratched to induce crystallization. The mixture was cooled in ice and the solid was collected and washed with a small amount of ether to give 1.97 g. of 7-chloro-7,8,8-tricyano-2-oxabicyclo[4.2.0]octane as almost colorless fine needles that melted at 60–75° with evolution of gas (HCl), resolidified and then remelted at 111–112.5°. Two recrystallizations from warm benzene gave an analytical sample as colorless fine needles, melting at 74–76° with evolution of gas, resolidifying and remelting at 110–111°.

Anal. Calcd. for $C_{10}H_8ClN_3O$: Cl, 16.0. Found: Cl, 15.8.

The infrared spectrum was consistent with that of the oxabicyclic structure with weak absorption at 4.45 and 4.48 μ (C≡N), very strong absorption at 8.9–9.0 μ (C–O–C), and no absorption between 5 and 6.6 μ. The proton magnetic resonance spectrum (in $CDCl_3$) contained absorptions with relative intensities of 1:2:1:4 at 3.92 (doublet), 6.14 (multiplet), 6.60 (multiplet) and 8.17 τ (multiplet), respectively.[8]

The adduct was not stable at room temperature. It slowly evolved HCl to give the yellow 3-(tricyanovinyl)-5,6-dihydro-4H-pyran (described below). The transformation occurred rapidly in polar solvents such as acetonitrile or alcohol. Chromatography of the adduct on alumina (acid, Woelm) gave only the unsaturated product.

The preparation of 3-(tricyanovinyl)-5,6-dihydro-4H-pyran was most conveniently carried out by treating tricyanovinyl chloride with 2 equivalents of dihydropyran using tetrahydrofuran as a solvent. After 16 hours, the solvent was removed *in vacuo*, and the crude product recrystallized from ethyl ether to give bright yellow stubby needles, m.p. 113.5–114°, in 65% yield. An analytical sample was prepared by sublimation at 100° (0.1 mm.).

Anal. Calcd. for $C_{10}H_7N_3O$: C, 64.9; H, 3.8; N, 22.7. Found: C, 64.8; H, 3.9; N, 22.6.

The ultraviolet spectrum contained a major absorption peak in EtOH at 367 mμ with ϵ 20,500; whereas in CH_2Cl_2 the peak shifted to 370 mμ with ϵ 25,300. The infrared spectrum was consistent with the proposed structure with major peaks at 4.51 (C≡N), 6.35 and 6.66 (C=C), 7.43, 7.87, 8.04, 8.25, 8.40 and 10.15 μ. The proton magnetic resonance spectrum (in $CDCl_3$) contained absorptions with relative intensities of 1:2:2:2 at 2.23 (singlet, 2-H), 5.77 (triplet, J = 6 c./s., 6-H). 7.30 (triplet, J = 6 c./s., 4-H), and 7.97 τ (quintent of two superimposed triplets, J = 6 c./s., 5-H), respectively.

Reaction of 1,1,2-Tricyano-4-methoxy-1,3-butadiene with N,N-Dimethylaniline.—A solution of 0.32 g. (2 mmoles) of 1,1,2-tricyano-4-methoxy-1,3-butadiene in 2 ml. of dimethylformamide was treated with 2 ml. (excess) of N,N-dimethylaniline and warmed on a steam-bath for 1.5 hours. The deep blue-black solution was poured into 50 ml. of 1 N sulfuric acid. The resulting brown-black precipitate was collected, washed thoroughly with water, dried and extracted with xylene in a micro Soxhlet until the xylene extracts were colorless. The deep maroon xylene extract was concentrated to 5 ml. and chilled to give 0.15 g. (31% of theory) of 1,1,2-tricyano-4-(p-dimethylaminophenyl)-1,3-butadiene (X) as blue-gray needles, m.p. 255° (with decomposition starting at 230°). The infrared spectrum was identical to that of an authentic sample,[4] and the visible spectrum (in acetone) contained an absorption band at 582 mμ with k = 229. The intensity corresponds to 90% of that of a pure sample.

When the above reaction was carried out with only an equivalent amount of dimethylaniline (0.25 g., 2 mmoles), only 0.054 g. (11%) of the butadiene, λ_{max} 582 mμ, k = 241, or 94% pure, was isolated accompanied by 8% of the N,N-dimethylanilinium salt of 1,1,2,6,7,7-hexacyano-1,3,5-heptatriene, m.p. 210–215° dec., λ_{max} 638 mμ, ϵ 153,000.

1,1,2,6,7,7-Hexacyanoheotatriene (XI). a. From 3-Methoxy-1,1,2,2-tetracyanocyclobutane.—A solution of 145 g. (0.78 mole) of 3-methoxy-1,1,2,2-tetracyanocyclobutane in 1000 ml. of methanol was refluxed for 30 hours. The intensely blue solution which smelled strongly of HCN was filtered and concentrated to give a dark blue-black, tarry residue. An aliquot of the solution before concentration indicated the presence of roughly 30% of the blue anion XI as shown by the intensity of the absorption at 635 mμ. The residue was digested with 200 ml. of ethyl acetate. Filtering while still hot and washing with two additional 50-ml. portions of ethyl acetate afforded a dark green solid. The dark green solid was dissolved in 1 l. of hot water and treated with 10 g. of ammonium acetate and filtered. The residue was again taken up in hot water and treated with 10 g. of ammonium acetate and filtered. From the combined, cooled filtrates a total of 9 g. of dark green solid was obtained. The remaining residue above was continuously extracted in a Soxhlet with water until the extract was no longer blue. The cooled extract (300 ml.) afforded 8.5 g. of bright green needles. The green solids were each recrystallized once from water and combined to give 14.2 g. of glistening green needles. Two additional recrystallizations from 700 ml. of water yielded 13.1 g. (13% of theor.) of **ammonium 1,1,2,6,7,7-hexacyanoheptatrienide**, m.p. above 300° (with slow decomposition occurring at 230°). Each recrystallization was accompanied by some decomposition of the ammonium salt as shown by the formation of a small amount of black insoluble resin and free ammonia which could be detected above the hot solution.

Anal. Calcd. for $C_{13}H_7N_7$: C, 59.8; H, 2.7; N, 37.6. Found: C, 59.8; H, 2.9; N, 36.8.

A 200-mg. sample of crude XI prepared as described above was dissolved in 30 ml. of hot water, filtered and treated with 0.5 g. of tetramethylammonium chloride. The finely divided gray precipitate was filtered, dried and recrystallized from 100 ml. of ethanol to give 150 mg. of tetramethylammonium 1,1,2,6,7,7-hexacyanoheptatrienide as glistening dark green platelets, m.p. 278–283° (with dec.). The salt was only slowly soluble in hot ethanol and was usually recrystallized by successively percolating boiling ethanol up through a sintered glass funnel and then filtering hot until complete solution was obtained. From 150 mg. of salt, 133 mg. was obtained by cooling the resulting 25 ml. of solution. In this manner, three more recrystallizations were used to obtain an analytical sample, m.p. 277–279° dec. The analytical sample was dried under vacuum for 16 hours at 80°.

Anal. Calcd. for $C_{17}H_{15}N_7$: C, 64.3; H, 4.8; N, 30.9; mol. wt., 317. Found: C, 64.3; H, 4.8; N, 31.1; mol. wt., 165 (b.p. in acetone).

Other salts were qualitatively obtained by treating an aqueous solution of the ammonium salt with inorganic ions in a metathetical reaction. Water-insoluble salts (soluble in acetonitrile) were obtained from barium, ferric, cupric,

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[8] Nuclear magnetic resonance spectra were taken at 60 Mc. with tetramethylsilane as an internal standard. Chemical shifts are recorded in τ-values: G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

nickel, silver and zinc ions. Partially soluble salts (blue solutions with precipitates which were soluble in acetonitrile) were obtained from calcium, cadmium, cobaltous, ferrous, lithium, sodium and potassium ions. In the case of lead, magnesium and cuprous ions no precipitate was noted.

In one experiment, 23.6 g. (0.125 mole) of 3-methoxy-1,1,2,2-tetracyanocyclobutane was refluxed in 150 ml. of methanol for 24 hours and the resulting dark tarry residue was extracted with 700 ml. of hot benzene and then with hot ethyl acetate. The workup of the residue in the manner described above gave 1.63 g. (10% of theory) of the ammonium salt. The initial benzene extract was concentrated and passed through a column of 300 g. of alumina (acid, Woelm, Activity I) using benzene and ether as eluents. Upon selective solvent extractions of the resulting dark solid, 0.34 g. of 1,1,2-tricyano-4-methoxy-1,3-butadiene, m.p. 97–101° (identified by infrared spectral analyses), and 2.5 g. of a yellow solid, m.p. 187–189°, were obtained. The yellow solid (recrystallized from ethanol–water) contained absorption peaks in the infrared which were characteristic of NH_2, conj. CN and other conjugated C=C or C=N. The ultraviolet contained absorption bands at 235 (*k* 28.2), 267 (*k* 34.2) and 387 mμ (*k* 19.3). This solid remains unidentified.

Anal. Found: C, 57.4; H, 4.2; N, 26.2.

Attempts to isolate the 1,1,2,6,7,7-hexacyanoheptatriene as the free acid always resulted in extensive decomposition. However, aqueous solutions of the free acid obtained by passing a solution of the ammonium salt through an acidic ion-exchange column (Amberlite IR-120-H) titrated as a very strong acid. The free acid thus obtained could be converted to the sodium, ammonium or tetramethylammonium salt by titration or by precipitation upon addition of concentrated solutions of excess sodium, ammonium or tetramethylammonium chlorides, respectively.

b. From 4-Alkoxy-1,1,2-tricyano-1,3-butadiene.—A solution of 0.67 g. (2.85 mmoles) of 4-benzyloxy-1,1,2-tricyano-1,3-butadiene in 10 ml. of methanol was heated to reflux for 50 minutes. Aliquot portions were removed every 10 minutes and their visible spectra were measured. A maximum absorption developed after 30 minutes. The methanol solution was poured into 50 ml. of dilute sodium chloride solution and extracted continuously with ether. The resulting blue ethereal solution was concentrated and the residue chromatographed on alumina (acid, Woelm, Activity II). Ethyl acetate–acetone was used to develop the column. The column was extruded and the deep blue band was extracted with methanol–acetone. The sodium 1,1,2,6,7,7-hexacyanoheptatrienide thus obtained was recrystallized twice from methanol to give 47 mg. (11% of theor.) of green needles, m.p. above 300° dec. The analytical sample was vacuum dried at 80° overnight. The presence of sodium was indicated by emission spectra.

Anal. Calcd. for $C_{13}H_3N_6Na \cdot CH_3OH$: C, 56.4; H, 2.4; N, 28.2; O, 5.4; mol. wt., 298. Found: C, 56.4; H, 2.0; N, 29.5; O, 4.4; mol. wt., 151 (b.p. in acetone).

In other experiments, 1,1,2-tricyano-4-methoxy-1,3-butadiene was warmed in ethanol or isopropyl alcohol at 60° for 1–6 hours. Removal of the solvent followed by chromatographic purification and conversion to a silver salt gave 15–18% yields of XI whose ultraviolet visible spectrum (in acetonitrile) was practically superimposable on that of the salts described above.

c. From N-Methyl-N-(3,4,4-tricyano-1,3-butadienyl)-benzenesulfonamide.—A solution of 0.125 g. of N-methyl-N-(3,4,4-tricyano-1,3-butadienyl)-benzenesulfonamide (IIIc, 0.42 mmole) in 5 ml. of methanol was heated at reflux for 72 hours. The deep blue solution was diluted to 100 ml. with methanol and the spectrum was measured. The solution showed λ_{max} at 632 mμ (abs. 18.1) with a shoulder at 590 mμ (abs. 13.9) indicating the presence of the 1,1,2,6,7,7-hexacyanoheptatrienide ion at a concentration of 0.026 g./l., corresponding to a yield of 5.1%.

d. Spectral Properties of 1,1,2,6,7,7-Hexacyanoheptatriene.—The ultraviolet-visible spectra of both the salts and the free acid were identical in shape, the only differences being the specific intensities. The molecular extinction coefficients did not obey Beer's law upon dilution and are reported below where the observed optical density is about 1.0. For the strongest absorption peak at 635 mμ, this corresponds to a concentration of 6×10^{-6} mole/liter. The addition of aqueous 0.1 *N* hydrochloric acid shifted the major absorption from 635 to 643 mμ (ε 146,000) and its 590 shoulder to 600 mμ (ε 59,000). However, the addition of 0.1 *N* sodium hydroxide caused the blue color to slowly fade with the development of a broad peak at 450 mμ (ε 56,000).

Maxima in Ultraviolet-visible Spectrum of 1,1,2,6,7,7-Hexacyanoheptatrene[a]

λmax, mμ (ε)	λmax, mμ (ε)
245 (4600)	398 (3100)
270 (sh) (3100)	430 (1700)
320 (sh) (3700)	590 (sh) (53,000)
332 (5300)	635 (165,000)

[a] Tetramethylammonium, ammonium and sodium salts in ethanol.

The infrared spectra of the sodium, ammonium, tetramethylammonium and N,N-dimethylanilinium salts were very similar with the only differences attributable to the cations and molecules of solvation (methanol in the case of the sodium salt). The spectra (in KBr) contain the following peaks which appear to be characteristic of the 1,1,2,6,7,7-hexacyanoheptatriene anion (in μ): 3.28 (weak, unsatd. CH), 4.54 (very strong, conj. C≡N), 6.36 (strong, conj. C=C), 6.90 (very strong, conj. C=C), 7.20 (medium), 7.43 (medium strong), 7.75 (medium), 8.15–8.25 (strong and broad, sometimes resolved), 10.35–10.45 (medium, sometimes resolved) and 14.30 (medium and broad).

Tetramethylammonium Salt of 1,1,2,4,5,5-Hexacyano-1,3-pentadiene (XII).—To 1.20 g. (7.5 mmoles) of 1,1,2-tricyano-4-methoxy-1,3-butadiene dissolved in 10 ml. of cold methanol, 1.04 g. (7.5 mmoles) of tricyanovinyl chloride was added in small portions while stirring in an ice-bath. The intense red solution was allowed to warm slowly to room temperature over a 1-hour period. A solution of 1.0 g. of tetramethylammonium chloride in 3 ml. of methanol was added in one portion. The olive gray-green precipitate was filtered and washed with cold methanol and water. Additional material was obtained by diluting the wash liquors with water. A total of 0.14 g. (6.5% of theory) of crude tetramethylammonium 1,1,2,4,5,5-hexacyano-1,3-pentadienide was obtained. Three recrystallizations from methanol followed by drying at 80° under vacuum for 3 hours afforded an analytical sample, m.p. 297–299° (with dec. after first changing appearance around 265°). The ultraviolet-visible spectrum (in EtOH) contained a major absorption peak at 538 mμ (ε 82,000) with a shoulder at 504 mμ (ε 37,000). Other weaker maxima occurred at 296 (ε 6,200), 308 (ε 6900), 350 (ε 2,200) and 368 mμ (ε 2100). The infrared spectrum contained the following absorption peaks attributable to the anion (in μ): 4.56 (s, C≡N), 6.67(s), 6.77(s), 7.20(m), 7.75–7.85(s), 8.17(m), 8.48(w), 10.52(m) and 12.0(w) μ.

Anal. Calcd. for $C_{15}H_{13}N_7$: C, 61.8; H, 4.5; N, 33.7. Found: C, 62.1; H, 4.3; N, 33.6.