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Hexacyanobutadiene

BY O. W. WEBSTER

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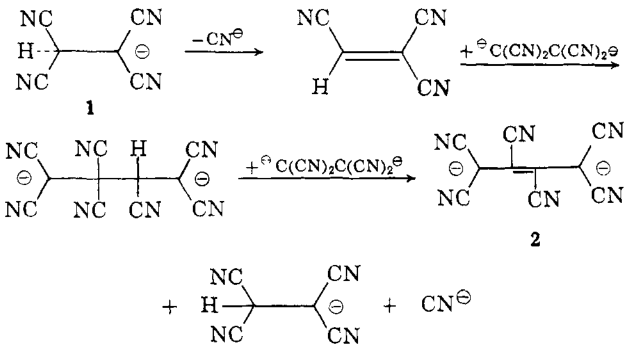
The synthesis of hexacyano-1,3-butadiene and its reactions with water, with malononitrile, and with butadiene are described.

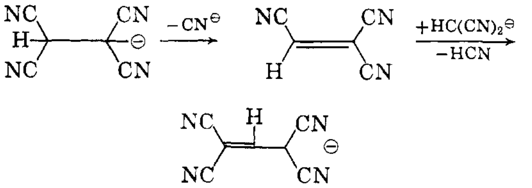
Although a large number of cyanocarbon anions[1] are known, only five neutral cyanocarbons have been reported: dicyanoacetylene,[2] dicyanodiacetylene,[3] tetracyanoethylene,[4] hexacyanoethane,[5] and hexacyanobenzene.[6]

This paper describes the synthesis of hexacyano-1,3-butadiene (HCBD), the first percyanodiene, from tetracyanoethanediide.[7] The reaction of HCBD with water, with malononitrile, and with butadiene, as well as its reduction to hexacyanobutadiene anion radical and hexacyanobutenediide, are also reported.

Disodium tetracyanoethanediide (prepared from tetracyanoethane and sodium hydride) is converted to disodium hexacyanobutenediide **2** (quantitative yield) when heated 1 hr. in 1,2-dimethoxyethane at 60–80°. No reaction occurs unless a small amount of the monosodium salt of tetracyanoethane is present. In fact the stability of tetracyanoethanediide prepared with excess NaH is remarkable. Even though it has two negative charges and four nitrile groups available for elimination as cyanides, it can be heated under reflux in 2,2′-dimethoxyethyl ether (~163°) for 24 hr. without change. On addition of a small amount of tetracyanoethane, the hot cream-colored suspension of disodium tetracyanoethanediide quickly yields orange HCBD^{-2}. Addition of tricyanoethylene[8] to the reaction mixture increased the yield of butenediide to greater than that theoretically possible unless the tricyanoethylene was utilized in the reaction. Therefore, a mechanism involving the elimination of cyanide from tetracyanoethanide **1** and addition of tetracyanoethanediide to the resulting tricyanoethylene is preferred.

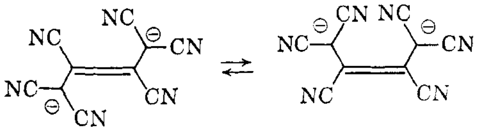


To establish that sodium tetracyanoethanide could function as a tricyanoethylene source, its reaction with sodium malononitrile was studied. When a solution of tetracyanoethane was slowly dropped into a mixture of sodium malononitrile and sodium hydride in 1,2-dimethoxyethane at about 80°, 1,1,3,3-tetracyanopropenide[9] was produced in 67% yield. Since tetracyanoethane itself is stable in solution at 80°, tetracyanoethanide must be the tricyanoethylene source.



Tetracyanoethylene anion radical also gives hexacyanobutenediide when heated in solution for long periods of time.

Interconvertible *cis–trans* isomers of HCBD^{-2} were isolated by fractional precipitation from 1,2-dimethoxyethane–acetonitrile solutions with ether.



The *cis* structure is tentatively assigned to the more soluble disodium salt since its infrared spectrum shows a much more intense carbon–carbon double bond absorption (6.53 μ) as expected for the less symmetrical structure. A heated solution of either *cis*- or *trans*-$\mathrm{Na_2HCBD}$ in 1,2-dimethoxyethane–acetonitrile equilibrates to approximately 25% of the *cis* and 75% of the *trans* form. Thus, there is an energy difference of only about 800 cal. per mole between the *cis* and *trans* forms.

One might expect that steric hindrance to a planar *cis* form would greatly favor the *trans* structure. However, Stuart–Brieglieb molecular models of the two forms show considerable hindrance in the *trans* form as well as in the *cis;* the 1–3 and 2–4 pairs of cyano groups are extensively eclipsed.

Hexacyanobutadiene.—Solid *cis*- or *trans*-$\mathrm{Na_2HCBD}$ is readily oxidized to HCBD (about 80% yield) by gaseous bromine at room temperature or by a solution of bromine in a nonpolar solvent. When the reaction of $\mathrm{Na_2HCBD}$ with bromine was conducted in acetonitrile, oxidation proceeded only to the ion radical state. Treatment of HCBD with bromide ion in acetonitrile readily produced $\mathrm{HCBD}^{\overline{\cdot}}$ in high yield, while cyanide reduced HCBD to HCBD^{-2}. Polarographic studies on the HCBD oxidation–reduction system

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[1] W. J. Middleton, E. L. Little, D. D. Coffman, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958). For a review of cyanocarbon chemistry, see T. L. Cairns and B. C. McKusick, *Angew. Chem.*, **73**, 520 (1961).

[2] C. Moureau and J. Bongrand, *Compt. rend.*, **170**, 1025 (1928).

[3] F. J. Brockman, *Can. J. Chem.*, **33**, 507 (1955).

[4] T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, and W. J. Middleton, *J. Am. Chem. Soc.*, **79**, 2340 (1957).

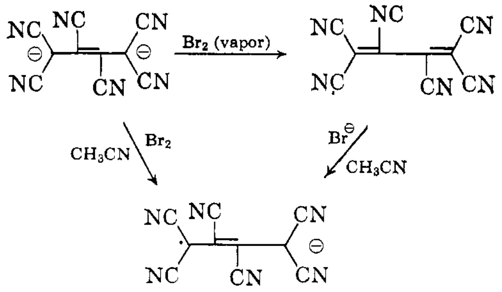
[5] S. Trofimenko and B. C. McKusick, *ibid.*, **84**, 3677 (1962).

[6] K. Wallenfels and K. Friedrich, *Tetrahedron Letters*, **19**, 1223 (1963).

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

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

[9] Y. Urushibara, *Bull. Chem. Soc. Japan*, **2**, 278 (1927); *Chem. Abstr.*, **22**, 579 (1928).



(carbon paste electrode) showed reversible waves at $\epsilon_{1/2}^{CH_3CN} = 0.6$ v. and 0.02 v. (*vs.* aqueous s.c.e.).

Hexacyanobutadiene is a colorless, crystalline solid which sublimes at 130° (0.3 mm.) and melts at 253–255°. Its infrared spectrum shows conjugated nitrile absorption at 4.45 μ and carbon–carbon double bond absorption at 6.46 μ. Although a Stuart–Briegleib model of HCBD could not be made without orthogonal tricyanovinyl groups, the ultraviolet spectrum, $\lambda_{max}^{CH_3CN}$ 302 mμ (ϵ 15,300), indicates the entire molecule is conjugated.[10]

Hexacyanobutadiene ion radical is readily formed by admixture of equimolar amounts of HCBD and HCBD^{-2}. Its e.s.r. spectrum[11] in 1,2-dimethoxyethane shows an over-all pattern of 9 peaks with 1.16 gauss separation, each peak in turn is split five times into peaks of 0.22 gauss separation. The over-all nine-line pattern is attributed to a hyperfine interaction of the unpaired electron with the four nitrogen atoms of the terminal nitrile groups. The quintets are ascribed to the hyperfine interaction of the unpaired electron with the nitrogen atoms of the two center nitrile groups. The tetraethylammonium and sodium salts of HCBD$^{\overline{\cdot}}$ proved to be remarkably stable to atmospheric conditions and were isolated and characterized. The resistivity of a compaction of NaHCBD· is in the semiconductor range at 4.4 × 10^7 ohm-cm.

Charge-Transfer Complexes.—Like Tetracyanoethylene (TCNE), hexacyanobutadiene is a strong π-acid and forms charge-transfer complexes with aromatic compounds. Thus, benzene solutions are yellow-orange; toluene, red; and xylene, purple. Black crystalline complexes of HCBD with pyrene and with hexamethylbenzene were isolated. In both cases, the complexes contain 2 moles of aromatic compound and 1 of HCBD. The compaction resistivities were 3.1 × 10^9 and 7.0 × 10^{10} ohm-cm., respectively. The association constants and stoichiometry of π-complex formation with benzene and with pyrene in methylene chloride were determined by the procedure outlined by Merrifield and Phillips.[12] Surprisingly, in solution pyrene as well as benzene forms a 1:1 complex with HCBD. For comparison, the association constants for HCBD and for TCNE are given in Table I.

Chemistry of Hexacyanobutadiene.—Butadiene reacts readily with HCBD at 0–25° to produce a white crystalline substance tentatively characterized as **3**.

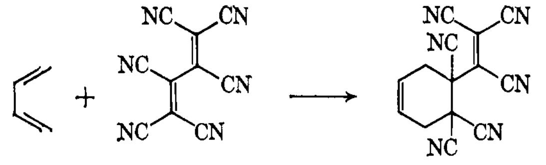


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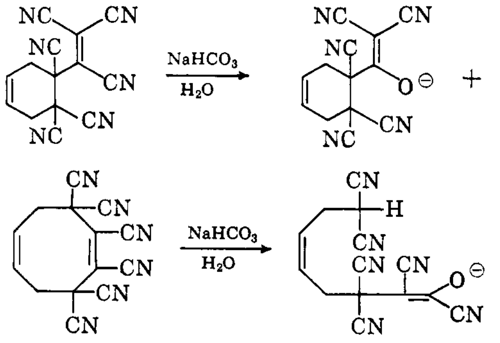
TABLE I

COMPARISON OF HCBD AND TCNE AS π-ACIDS IN CH_2Cl_2

π-Acid	π-Base	K	λ_{max}, mμ	ϵ, cm.$^{-1}$ mole^{-1}
HCBD	Benzene	1.02	440	4400
TCNE	Benzene	2.00	384	3570
HCBD	Pyrene	43.0	605	2630
			870	. .
TCNE	Pyrene	29.5	724	1137

The cyclooctadiene structure, **4**, for the adduct is unlikely because the hydrolysis product contains one less cyano group.[13] The expected product from hydrolysis of the hexacyanocyclooctadiene would be the open chain compound **5**,[13] containing the same number of cyano groups.

The n.m.r. spectrum consists of two poorly resolved multiplets, τ = 3.93 and 6.58, with an area ratio of 1:2. Comparison of 60- and 100-Mc. spectra showed that peaks within each multiplet were due to chemical shifts as well as couplings.[14] This complex pattern would more likely result from the six-membered structure **3** than from the eight-membered structure **4**.



4 **5**

One cyano group was displaced when HCBD reacted with aqueous sodium bicarbonate. The fact the same product is produced by reaction of tetracyanofuran[15] with cyanide demands that the displaced cyano group from HCBD be a terminal one. This clearly shows that HCBD is not functioning as two separate tricyano groups, for then attack would occur mainly at the 2-position.[16] The product is assigned structure **6** on the basis of its ultraviolet and infrared spectra, although a

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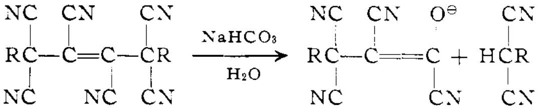
[10] For comparison, the longest wave length λ_{max} for tetracyanoethylene occurs at 265 mμ: C. E. Looney and J. R. Downing, *J. Am. Chem. Soc.*, **80**, 2840 (1958).

[11] The e.s.r. spectrum was obtained on a Varian 100-kc. spectrometer with a dual cavity arrangement. The *g*-value for HCBD$^{\overline{\cdot}}$ was approximately the same as that for TCNE$^{\overline{\cdot}}$ (2.0026) which was used as the standard: W. D. Phillips, J. C. Rowell, and S. I. Weissman, *J. Chem. Phys.*, **33**, 626 (1960).

[12] R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

[13] Unpublished work of Dr. E. L. Martin of this laboratory. Hydrolysis of dialkylhexacyanobutenes produced cleavage products rather than substitution products.



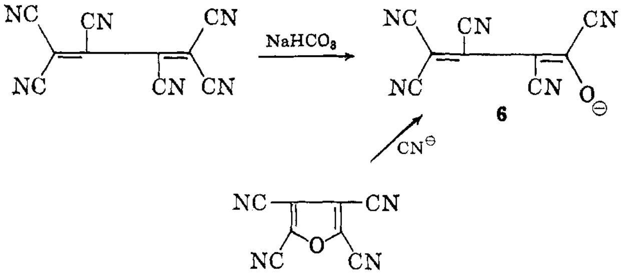
$$RC(CN)_2-C(CN)=C(CN)-C(CN)_2R \xrightarrow[H_2O]{NaHCO_3} RC(CN)_2-C(CN)=C(CN)O^{\ominus} + HC(CN)_2R$$

[14] The n.m.r. spectra (solvent CD_3COCD_3–$DCCl_3$) were obtained on Varian A-60 and HR-100 spectrometers. We thank Varian Associates for the latter result.

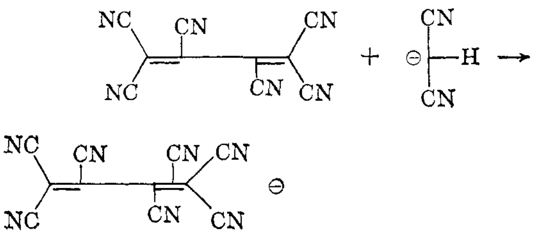
[15] C. D. Weis, *J. Org. Chem.*, **27**, 3514 (1962).

[16] G. N. Sausen, V. A. Engelhardt, and W. J. Middleton, *J. Am. Chem. Soc.*, **80**, 2815 (1958). Reactions of 1,2,2-tricyanovinyl compounds with nucleophilic reagents resulted in replacement of the 1-cyano group.

cyclized structure has not been rigorously excluded. 1,1,4,4-Tetracyanobuta-2,3-dionediide,[17] the expected product from substitution at both the 2- and 3-positions, was not detected in the crude reaction product (ultraviolet).



Products derived from substitution of cyano groups at both the 1- and 2-position were isolated from the mixture produced in the reaction of malononitrile anion with HCBD. Under conditions where HCBD was maintained in excess, a bright red cyanocarbon anion believed to be heptacyanopentadienide (**7**) was produced. When malononitrile anion was maintained in excess, a yellow cyanocarbon anion, the result of a double substitution by malononitrile anion, was isolated. This product was not produced from reaction of **7** with malononitrile anion. Therefore, it must result from a primary substitution at the 2-position. On the basis of the infrared and visible spectra, it is postulated that the second substitution occurs at the 3-position (at this stage of the reaction the position of lowest electron density) to give **8**.



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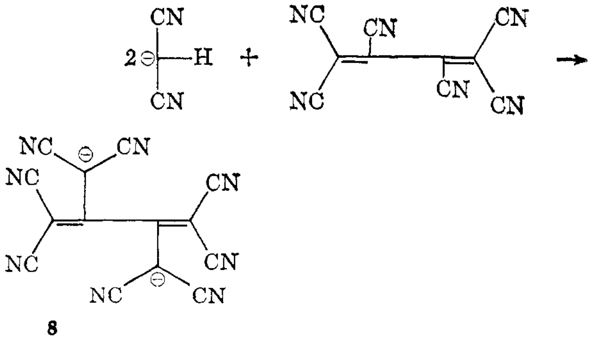

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In summary, the chemical behavior of HCBD indicates substantial interaction between the two double bonds.

Experimental

Sodium 1,1,2,3,4,4-Hexacyanobutenediide (Na_2HCBD).—A suspension of 63 g. (1.48 moles) of sodium hydride–mineral oil dispersion (56.5% NaH) in 500 ml. of glyme (1,2-dimethoxyethane) was cooled in an ice–salt water bath under nitrogen *and stirred vigorously. A solution of 98 g. (0.75 mole) of 1,1,2,2-tetracyanoethane*[18] in 400 ml. of glyme was added in a slow stream over a period of 2 hr.[19] The white suspension of sodium tetracyanoethanediide[7] was then refluxed (about 80°) for 1 hr. The color of the mixture changed to a deep orange, and an oil separated. The mixture was cooled to room temperature, and the top layer containing glyme and mineral oil was decanted and discarded. The remaining suspension was shaken with 500 ml. of acetonitrile and was filtered. Sodium cyanide (37 g.) remained on the filter. The orange filtrate was concentrated to dryness, and the residue was refluxed for 2 hr. in 500 ml. of acetonitrile. The mixture was cooled to room temperature, and crude *trans*-Na_2HCBD (50 g., 53% yield) was collected on a filter. Dilution of the acetonitrile solution with 3 l. of dry ether caused crude *cis*-Na_2HCBD (47 g., 50% yield) to crystallize. An analytical sample of *trans*-Na_2HCBD was prepared by two recrystallizations from acetonitrile and one from glyme; $\lambda_{\max}^{\text{KBr}}$ 4.48, 4.60, 4.67, 6.60, 7.82, 7.92, 9.72, and 12.40 μ; $\lambda_{\max}^{\text{CH}_3\text{CN}}$ 223 mμ (ε 5000) and 487 mμ (ε 14,570).

Anal. Calcd. for $C_{10}N_6Na_2$: C, 48.0; N, 33.6. Found: C, 47.9; N, 33.9.

An analytical sample of *cis*-Na_2HCBD was prepared by dilution of an acetonitrile solution with ether until crystals formed. It was necessary to heat *cis*-Na_2HCBD at 144° (0.3 mm.) to remove the last traces of water; $\lambda_{\max}^{\text{KBr}}$ 4.60, 4.70, 6.53, 7.36, 7.76, and 8.00 μ; $\lambda_{\max}^{\text{CH}_3\text{CN}}$ 487 mμ (ε 12,800), 392 mμ (ε 5360), and 325 mμ (ε 4450).

Anal. Calcd. for $C_{10}N_6Na_2$: C, 48.0; N, 33.6. Found: C, 48.4; N, 33.7.

The band at 6.53 μ in the infrared spectrum of *cis*-Na_2HCBD was strong while the corresponding band at 6.60 μ in *trans*-Na_2HCBD was weak.

When an acetonitrile solution of *cis*-Na_2HCBD was heated under reflux for about 5 min., *trans*-Na_2HCBD crystallized.

A solution of 9.20 g. of *trans*-Na_2HCBD in 200 ml. of glyme and 200 ml. of acetonitrile was refluxed for 18 hr. with 1 g. of sodium cyanide. The reaction mixture was cooled, filtered, and the filtrate was evaporated to dryness. The solid residue was extracted with 100 ml. of acetonitrile; *trans*-Na_2HCBD (5.2 g.) was isolated by filtration. On dilution of the filtrate with 250 ml. of ether, *cis*-Na_2HCBD (2.01 g.) crystallized. Additional dilution of the filtrate with 1 l. of ether caused 0.22 g. of *cis*-Na_2HCBD to crystallize. The total yield of *cis* product was 24%.

A solution of 0.25 g. of *trans*-Na_2HCBD in 10 ml. of glyme and 10 ml. of acetonitrile was refluxed 2 hr. under nitrogen in the presence of a trace of sodium cyanide. The reaction solution was cooled to room temperature and was poured into a solution of 2.0 g. of silver nitrate in 200 ml. of water. The orange Ag_2HCBD which formed was collected on a filter, was washed with water, and dried at 0.1 mm. Comparison of the infrared spectrum with those from a standard series of *cis*- and *trans*-Ag_2HCBD showed that the *cis–trans* ratio produced by equilibration was about 1:3 *cis–trans*.

When the above equilibration was carried out with 0.25 g. of *cis*-Na_2HCBD, the same equilibrium mixture was obtained.

Preparation of Na_2HCBD from Disodium Tetracyanoethanide and Tricyanoethylene.—A suspension of 1.30 g. (0.032 mole) of sodium hydride–mineral oil dispersion (56.5% NaH) in 100 ml. of glyme was cooled to 0°, and a solution of 2.00 g. (0.0154 mole) of tetracyanoethane in 100 ml. of glyme was added dropwise (1 hr.). The solution was stirred an additional 2 hr. at room temperature. To the now light yellow suspension there was added a solution of 1.00 g. (0.0097 mole) of tricyanoethylene[8] in 50 ml. of glyme (15 min.). The reaction mixture was heated at 60° for 0.5 hr. and was then refluxed for 1 hr. During this time, the color of the mixture turned from light orange to deep red. The reaction mixture was cooled and was concentrated to dryness. A solid remained which was refluxed in 100 ml. of acetonitrile for 8 hr. The acetonitrile solution which formed was cooled and diluted with 1 l. of diethyl ether to precipitate crude Na_2HCBD (3.30 g.). This product was recrystallized from acetonitrile to give pure *trans*-Na_2HCBD (2.46 g., 0.0098 mole).

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[17] R. Schenck and H. Finken, *Ann.*, **462**, 158 (1928). Disodium 1,1,4,4-tetracyanobuta-2,3-dionediide ($\lambda_{\max}^{\text{H}_2\text{O}}$ 281 mμ (ε 13,400)) can be made in quantitative yield by a modification of Schenck's procedure. Sodium malononitrile from malononitrile and sodium hydride was stirred at room temperature 24 hr. with diethyl oxalate in 1,2-dimethoxyethane. The product prepared in this manner is not orange.

[18] W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).

[19] If sufficient time is allowed for complete conversion of tetracyanoethane to its dianion (24 hr.), no $HCBD^{-2}$ is produced on heating.

The total amount of Na_2HCBD possible from 2.00 g. of tetracyanoethane alone is 1.92 g.

Reaction of Sodiomalononitrile with Tetracyanoethane.—A suspension of 8.50 g. (0.20 mole) of sodium hydride–mineral oil dispersion (56.5% NaH) in 500 ml. of glyme was cooled to 0° under nitrogen, and a solution of 6.60 g. (0.10 mole) of malononitrile in 100 ml. of glyme was added dropwise over 1 hr. The reaction mixture was then heated under reflux, and a solution of 13 g. (0.10 mole) of tetracyanoethane in 100 ml. of glyme was added over 1 hr. The reaction mixture was cooled, filtered, and the filtrate diluted with 3 l. of ether. Sodium 1,1,3,3-tetracyanopropenide (11.0 g., 67% yield) precipitated as a white solid and was characterized by comparison of its infrared spectrum with that of an authentic sample.[9]

Hexacyanobutadiene (HCBD).—*trans*-Na_2HCBD (71 g.) was dried for 24 hr. at 70° (20 mm.). The orange solid was then spread on the bottom of a large desiccator. On the upper plate of the desiccator was placed an evaporating dish containing 5 ml. of concentrated sulfuric acid. After the desiccator had been evacuated and filled with nitrogen, the cover of the desiccator was slid open about 0.25 in., and 15 ml. of bromine was introduced into the evaporating dish by means of a hypodermic syringe. The cover was then closed, and the system allowed to stand 20 hr. Excess bromine was removed by evacuation of the system to approximately 0.3 mm. for 3 hr. The light tan product which resulted (NaBr and HCBD) was extracted 1 hr. with 400 ml. of dry dioxane. The extract, bright yellow due to HCBD–dioxane π-complex, was concentrated to dryness in a rotating evaporator at about 0.3 mm. pressure to give crude hexacyanobutadiene (47 g., 81%). The product was purified by dissolution in 200 ml. of warm dry acetonitrile and concentration of the solution at room temperature in a rotating evaporator. When the total volume reached about 75 ml., crystals were collected on a filter under nitrogen, and dried. The purified HCBD, about 35 g., was placed in a percolator and was extracted with dichloroethylene containing a few milligrams of N-chlorosuccinimide. The nearly white HCBD which collected in the solvent flask, 33 g., was collected by filtration under nitrogen and was dried under reduced pressure.

An analytical sample was prepared by recrystallization from dichloroethane; $\lambda_{max}^{CH\ CN}$ 302 mμ (ϵ 15,300); λ_{max}^{Nujol} 4.45, 6.46, 8.14, 8.55, 9.67, 12.20, 12.55 μ.

Anal. Calcd. for $C_{10}N_6$: C, 58.8; N, 41.2. Found: C, 58.7; N, 41.3.

For preparing small amounts of HCBD, it was found convenient to use nitric acid as the oxidant. Concentrated nitric acid, 10 ml., was added in one portion to an ice-cold solution of of 1.22 g. (0.0049 mole) of Na_2HCBD in 5 ml. of water. HCBD (0.45 g., 45% yield) was collected on a filter, was washed with water, and dried. Its identity was confirmed by its infrared spectrum.

Hexacyanobutadiene–(Pyrene)$_2$ Charge-Transfer Complex.—A solution of 2.02 g. (0.010 mole) of pyrene and 1.02 g. (0.0050 mole) of HCBD in 40 ml. of acetonitrile was evaporated to approximately 10 ml. Hexacyanobutadiene–(pyrene)$_2$ charge-transfer complex crystallized as black needles (1.3 g., m.p. 188–195°). The product was collected on a filter and dried for 20 hr. at 0.3 mm. The visible spectrum of the product showed a charge transfer band at 870 mμ as well as bands at 477 and 509 mμ, indicative of $HCBD^{\overline{\cdot}}$. Its compaction resistivity was 3.1 × 10^9 ohm-cm.

Anal. Calcd. for $C_{42}H_{20}N_6$: C, 82.9; H, 3.3; N, 13.9. Found: C, 83.1; H, 3.4; N, 14.0.

Hexacyanobutadiene–(Hexamethylbenzene)$_2$ Charge-Transfer Complex.—A solution of 1.62 g. (0.010 mole) of hexamethylbenzene and 1.02 (0.0050 mole) of HCBD in 10 ml. of acetonitrile and 30 ml. of dichloroethane was evaporated to about 5 ml. Hexacyanobutadiene–(hexamethylbenzene)$_2$ charge-transfer complex (2.6 g.) crystallized as black needles, m.p. 145° dec. The complex was dried at 0.3 mm. for 18 hr. Its visible spectrum showed a charge-transfer band at 648 mμ as well as bands at 477 and 508 mμ, indicative of $HCBD^{\overline{\cdot}}$. The resistivity of the complex was 7.0 × 10^{10} ohm-cm.

Anal. Calcd. for $C_{34}H_{36}N_6$: C, 77.2; H, 6.9; N, 15.9. Found: C, 77.3; H, 6.9; N, 16.3.

Sodium Hexacyanobutadienide.—A mixture of 2.50 g. (0.010 mole) of Na_2HCBD and 2.02 (0.010 mole) of HCBD was stirred in 200 ml. of acetonitrile for 0.5 hr. The solution was filtered and concentrated to approximately 30 ml.; sodium hexacyanobutadienide (1.75 g.) crystallized. Solid NaHCBD· did not noticeably decompose when exposed to atmospheric conditions for several days. A solution of 9.3 mg. of NaHCBD· in 100 ml. of acetonitrile lost 20% of the ion radical when bubbled with oxygen 15 min. (ultraviolet). A solution of 10.1 g. of NaHCBD· in 100 ml. of water under nitrogen lost 12% of the ion radical in 5 hr. (ultraviolet); λ_{max}^{KBr} 4.45, 4.52, 6.75, and 7.30 μ; compaction resistivity 4.4 × 10^7 ohm-cm; $\lambda_{max}^{CH_3CN}$ 475 mμ (ϵ 18,600), 507 (43,500), 613 (2410), 667 (3720), 713 (2410).

Anal. Calcd. for $C_{10}N_6Na$: C, 52.9; N, 37.0. Found: C, 52.8; N, 37.2.

Tetraethylammonium Hexacyanobutadienide.—A mixture of 5 g. of $(Et_4N)_2HCBD$ and 21.8 g. of HCBD was dissolved in 50 ml. of acetonitrile. On evaporation to approximately 20 ml., 2.4 g. of Et_4NHCBD· crystallized. The product was collected on a filter and was recrystallized from 1,2-dichloroethane (long black needles). The product melted at 153–159° dec.; λ_{max}^{KBr} 3.30, 4.52, 6.70, 6.95, 7.18, 7.30, 8.53, 9.50, 10.00, and 12.75 μ.

Anal. Calcd. for $C_{18}H_{20}N_7$: C, 64.6; H, 6.03; N, 29.3. Found: C, 64.7; H, 5.90; N, 29.1.

The reaction of HCBD in acetonitrile solution with metals, even as unreactive as mercury, readily produced $HCBD^{\overline{\cdot}}$ (ultraviolet).

Reaction of Hexacyanobutadiene with NaCN.—To a refluxing suspension of 1.76 g. (35.9 mmoles) of sodium cyanide in 200 ml. of acetonitrile there was added a solution of 3.00 g. (14.7 mmoles) of HCBD in 50 ml. of acetonitrile over the course of 4 hr. The dark orange-red solution was cooled and 2.90 g. (79% yield) of Na_2HCBD was collected by filtration. The product was identified by its infrared spectrum.

4-(Tricyanovinyl)-4,5,5-tricyanocyclohexene.—A solution of 2.00 g. (0.0098 mole) of HCBD in 80 ml. of dry acetonitrile under nitrogen was cooled to 0°, and 7.9 g. (0.14 mole) of butadiene was condensed into the system. The reaction solution turned deep yellow. Stirring was continued 1 hr. at 0° and then 1 hr. at room temperature. The acetonitrile and excess butadiene were evaporated under reduced pressure. The residue (2.5 g.) was extracted with hot dichloroethane. On concentration of this extract, white crystals of 4-(tricyanovinyl)-4,5,5-tricyanocyclohexene, 0.90 g., formed. An additional 0.83 g. of product was obtained by complete evaporation of the dichloroethane. An analytical sample, m.p. 164–165°, was prepared by recrystallization from chlorobenzene; λ_{max}^{KBr} 3.25, 3.36, 4.50, 5.98, 6.75, 6.95, 7.45, 7.75, 8.03, 8.72, 8.90, 9.28, 9.50, 10.36, 11.57, 11.80, 14.86, and 15.15 μ; $\lambda_{max}^{CH_3CN}$ 252 mμ (ϵ 13,300).

Anal. Calcd. for $C_{14}H_6N_6$: C, 65.1; H, 2.34; N, 32.6. Found: C, 65.0; H, 2.39; N, 32.3.

Tetraethylammonium 1-(1,2,2-Tricyanocyclohex-4-enyl)-2,2-dicyanoethenolate.—A suspension of 1.00 g. of 4-(tricyanovinyl)-4,5,5-tricyanocyclohexene in 50 ml. of water and 25 ml. of acetonitrile was stirred with 1.0 g. of sodium bicarbonate 0.5 hr. The dark yellow solution was treated with 3.0 g. of Et_4NCl and the oil which separated was chromatographed on acid-washed Activity I alumina with ethylene chloride as eluent. Tetraethylammonium 1-(1,2,2-tricyanocyclohex-4-enyl)-2,2-dicyanoethenolate (0.4 g.) was the main product eluted. An analytical sample was prepared by recrystallization twice from water. The product melted at 113–114°; λ_{max}^{KBr} (Et_4N^+ bands not given) 4.55, 4.59, 6.27, 6.97, 7.46, 11.75, and 14.96 μ; $\lambda_{max}^{CH_3CN}$ 268 mμ (ϵ 11,980).

Anal. Calcd. for $C_{21}H_{26}N_6O$: C, 66.6; H, 6.92; N, 22.2. Found: C, 67.0; H, 6.81; N, 22.1.

Tetraethylammonium 1,1,2,3,4,5,5-Heptacyanopentadienide.—A solution of 1.32 g. (20.0 mmoles) of malononitrile and 4.08 g. (20.0 mmoles) of HCBD in 100 ml. of acetonitrile was stirred with 10 g. (102 mmoles) of potassium acetate under nitrogen for about 15 min. The resulting bright red solution was filtered and chromatographed on acid-washed alumina utilizing 4:1 ethyl acetate-diethyl ether as the eluent. Red potassium heptacyanopentadienide (0.85 g., 15% yield) was collected. For analysis, the tetraethylammonium salt was prepared by metathesis in water and was purified by chromatography on acid-washed alumina (Woelm) with methylene chloride eluent; λ_{max}^{KBr} 3.35, 4.50, 6.67, 6.85, 7.14, 7.20, 8.45, 9.96, 12.53, 12.65, and 14.65 μ. The intensity of the band at 6.85 indicates absorption due to the anion as well as Et_4N^+; $\lambda_{max}^{CH_3CN}$ 528 mμ (ϵ 33,000).

Anal. Calcd. for $C_{20}H_{20}N_8$: C, 64.5; H, 5.41; N, 30.1. Found: C, 64.9; H, 5.46; N, 29.6.

Tetraethylammonium 2,3-Bis(dicyanomethyl)-1,1,4,4-tetracyanobutadienediide.—To an ice-cold suspension of 1.70 g. (40.0 mmoles) of sodium hydride–mineral oil dispersion (56.5%

NaH) in 100 ml. of glyme was added 2.64 g. (40.0 mmoles) of malononitrile in 50 ml. of glyme. The resulting sodiomalononitrile solution was cooled to $-50°$ and a solution of 4.08 g. (20.0 mmoles) of HCBD in 50 ml. of acetonitrile was added dropwise (1.5 hr.). The color of the reaction solution was first orange, then changed to brown. The reaction solution was allowed to warm to room temperature and was diluted with 1 l. of ether. The gummy, insoluble solid which precipitated was collected and chromatographed on neutral alumina (Woelm). The major product, which was eluted with ethyl acetate and acetonitrile, was a yellow substance, λ_{max} 418 mμ. This yellow product was stirred overnight with 10 g. of tetraethylammonium chloride in acetonitrile. The solution was concentrated to dryness and was extracted with acetone. Tetraethylammonium 2,3-bis(dicyanomethyl)-1,1,4,4-tetracyanobutadienediide (0.52 g., m.p. 205–211°) was recovered from the acetone extract after it was passed through neutral alumina. An analytical sample was prepared by recrystallization from water; λ_{max}^{KBr} (Et_4N^+ bands not given) 4.56 (s), 6.88, (s), 7.71 (w), and 8.07 (w) μ; $\lambda_{max}^{CH_3CN}$ 420 mμ (ε 20,100), 328 mμ (ε 20,100).

Anal. Calcd. for $C_{30}H_{48}N_{10}$: C, 66.6; H, 7.46; N, 25.9. Found: C, 66.7; H, 7.42; N, 26.1.

The dipotassium salt of the bis(dicyanomethyl) compound was prepared by ion exchange and was recrystallized from acetonitrile–ethylene chloride.

Anal. Calcd. for $C_{14}N_8K_2$: C, 46.9; N, 31.3. Found: C, 47.1; N, 31.2.

Tetraethylammonium 1,2,3,4,4-Pentacyanobutadienolate.—A solution of 1.20 g. of sodium bicarbonate in 50 ml. of water was treated with 3.00 g. (14.7 mmoles) of HCBD. The mixture was stirred 15 min. and was filtered. The dark brown filtrate was treated with 2 g. of tetraethylammonium chloride. The product which precipitated (3.00 g.) was dissolved in methylene chloride, and the solution was diluted with about an equal amount of ether. Yellow tetraethylammonium pentacyanobutadienolate (2.6 g., 55% yield) precipitated. Further dilution of the solution with about 10 volumes of ether caused 0.35 g. of red sodium heptacyanopentadienide (identified by infrared and ultraviolet) to precipitate. An analytical sample of the pentacyanodienolate (m.p. 214.5–216.5°) was prepared by recrystallization from chloroform; λ_{max}^{KBr} 4.50, 4.55, 6.13, 6.71, 7.75, 9.90, and 13.75 μ; $\lambda_{max}^{CH_3CN}$ 442 mμ (ε 28,600), 424 (25,300), and 266 (3950).

Anal. Calcd. for $C_{17}H_{20}N_6O$: C, 62.9; H, 6.21; N, 25.9. Found: C, 62.8; H, 6.42; N, 26.3.

A solution of 0.75 g. (4.46 mmoles) of tetracyanofuran[15] in 30 ml. of acetonitrile was stirred overnight at room temperature with 0.30 g. (4.6 mmoles) of KCN. The yellow-brown solution was filtered and was concentrated to dryness. The residue was dissolved in water, and a tacky solid was obtained by addition of a solution of 2.0 g. of Et_4NCl in 10 ml. of water. Yellow crystals of tetraethylammonium pentacyanobutadienolate (0.08 g., m.p. 213–216°) formed on recrystallization of the solid from chloroform. Its identity was confirmed by its infrared spectrum.

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The Formation of *cis*- and *trans*-Perhydrobenzofurans from 2-(2-Methoxycyclohexyl)ethanol Derivatives. Reactions Proceeding through Methoxyl Participation[1]

BY STEPHEN E. CANTOR[2a] AND D. STANLEY TARBELL[2b]

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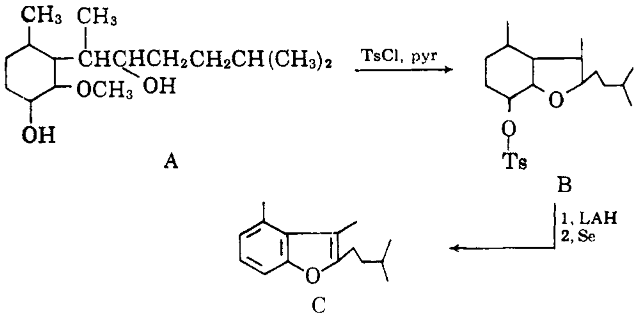
cis- and *trans*-(2-methoxycyclohexylethanol and homologs have been synthesized and are shown to form *cis*- and *trans*-perhydrobenzofurans when treated with tosyl chloride–pyridine. An oxygen-18 labeling study has shown that the methoxyl oxygen is retained during the cyclization; the hydroxyl oxygen is the one eliminated. The cyclization is believed to involve a cyclic oxonium ion intermediate; this is supported by the isolation of chloro compounds, which could be formed by the attack of chloride ion on a methine carbon atom in the oxonium ion.

We observed,[3] during degradative work on the antibiotic fumagillin, a number of reactions in which a perhydrobenzofuran ring was formed, involving interaction of a 2-methoxy group on a cyclohexane ring with an oxygen function on the side chain, with cleavage of the methoxyl group and cyclization. The most important example of this reaction, from the standpoint of the fumagillin work, is illustrated by the transformation of A to B in good yield; B was dehydrogenated to C, whose structure was proved by synthesis.



The present paper describes a study of this type of cyclization on simpler compounds; it is demonstrated that the cyclization can occur from both *cis* and *trans* precursors to form the *cis*- and *trans*-perhydrobenzofurans, and it is shown by oxygen-18 studies that the methoxyl oxygen is the one which is retained in the cyclization. The reaction is discussed in relation to earlier work on methoxyl participation and methoxonium ion intermediates.

2-Methoxyphenylacetone[4](D) was most readily prepared by Hauser's[5] procedure for methyl ketones, by acylation of malonic ester with 2-methoxyphenylacetyl chloride, followed by hydrolysis and decarboxylation. The aromatic ring was reduced catalytically with rhodium-on-alumina[6] in acetic acid to give the *cis*-ketone E.

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(2) (a) Abbott Laboratories Fellow, 1961–1962; (b) to whom inquiries should be addressed.

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