Tetracyanocyclopentadienide Chemistry

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Tetracyanocyclopentadienide reacts with nitric acid, formaldehyde, bromine, chlorine, trifluoromethylsulfenyl chloride, and acetic anhydride to give nitro-, methylidene-, bromo-, chloro-, trifluoromethylthio-, and acetyltetracyanocyclopentadienides. Chlorotetracyanocyclopentadienide and chlorine produce 5,5-dichloro-1,2,3,4-tetracyanocyclopentadiene, an enophile, which reacts with ethylene at atmospheric pressure and room temperature. Acetyltetracyanocyclopentadienide was converted into vinyltetracyanocyclopentadienide.

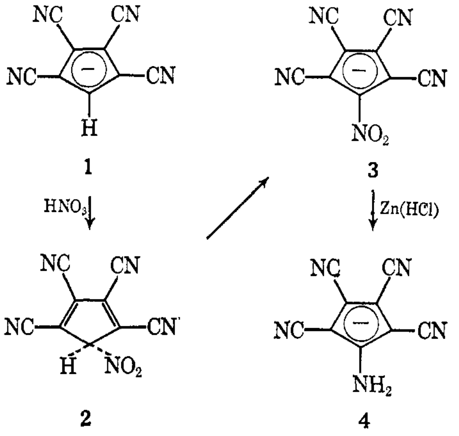
Electrophilic substitution reactions on the aromatic cyclopentadienide system[1] cannot ordinarily employ strongly acidic conditions because of the basicity of the cyclopentadienide. However, when the basicity of the cyclopentadienide ion is lowered by nitrile groups, strongly acidic conditions can be used. Tetracyanocyclopentadienide,[2] for example, is about as reactive as anisole. The nmr for the hydrogen in tetracyanocyclopentadienide (τ = 3.23 ppm) indicates that it is slightly more shielded than benzene hydrogens (τ = 2.68 ppm). However, methyltetracyanocyclopentadienide[2c] and toluene have their methyl nmr absorption at the same position (τ = 7.59 ppm).

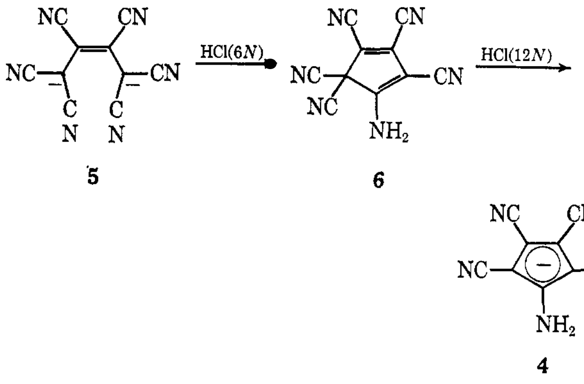
The chemical studies on tetracyanocyclopentadienides described here were conducted on the tetraethylammonium, potassium, or silver salts. All three types are surprisingly soluble in organic solvents. A change in cation had little affect on the course of the reactions studied. The most convenient cation for cyanocarbon anions is the tetraethylammonium ion as its salts are generally water insoluble and crystalline.

Unlike tetracarbomethoxycyclopentadiene, which can be isolated,[3] the more strongly acidic tetracyanocyclopentadiene ($\mathrm{p}K_a^{\mathrm{CH_3CN}} \sim 0$) or monosubstituted tetracyanocyclopentadienes appear to be too elusive to isolate. Indeed, some may exist only as transition states during the electrophilic reaction in which the cyclopentadienide is formed. For example, see 2. These transition states would be neutral, and thus the entropy of activation should be more positive than that for substitution on neutral aromatics where a charged transition state is involved.

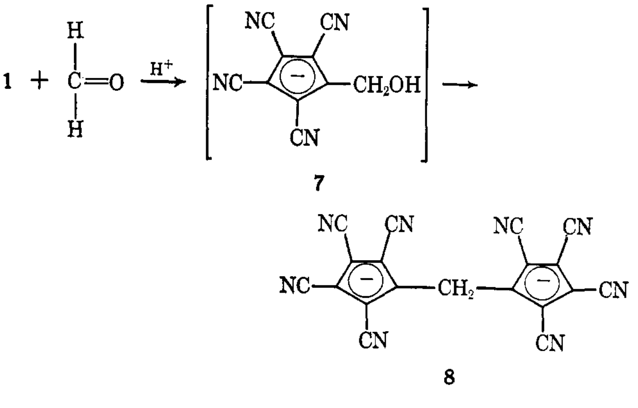
Nitration.—Cold, concentrated nitric acid[2b] nitrates tetracyanocyclopentadienide in 15 min (67% yield).

Powdered zinc in dilute hydrochloric acid reduces the nitro compound to aminotetracyanocyclopentadienide (4) which is also available from cyclization and decyanation of hexacyanobutene. Since aminotetracyclopentadienide readily produces diazotetracyanocyclopentadiene on treatment with nitrous acid,[2a] a new and shorter route to this reactive substance is now available.





Formaldehyde and Acetaldehyde.—Formaldehyde and acetaldehyde react with tetracyanocyclopentadienide to give methylene compounds rather than hydroxymethyl derivatives.



Halogenation.—Chlorine and bromine[2b] but not iodine halogenate tetracyanocyclopentadienide at room temperature. Chlorotetracyanocyclopentadienide (9) reacts with 1 mole of chlorine to produce 5,5-dichloro-

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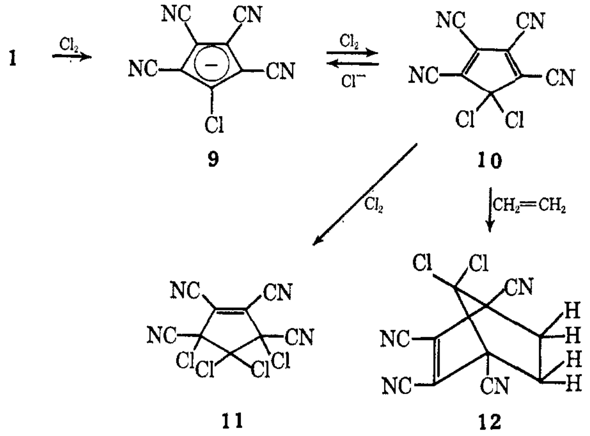
[1] (a) K. Hafner, K. H. Kafner, C. Konig, M. Kreuder, G. Ploss, G. Schulz, E. Sturm, and K. H. Vopel, *Angew. Chem.*, **75**, 35 (1963); formylation and other electrophilic substitution reactions of various fulvenes considered to be cyclopentadienide zwitterion systems are listed. (b) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2343 (1965); the polymethylation of cyclopentadienide is reported. (c) D. J. Cram and R. D. Partos, *J. Am. Chem. Soc.*, **85**, 1273 (1963); bromination, nitration, mercuration, and tricyanovinylation of diazocyclopentadiene, a cyclopentadienide zwitterion, are listed.

[2] (a) O. W. Webster, *ibid.*, **87**, 1820 (1965). (b) K. Friedrich, *Angew. Chem.*, **78**, 449 (1966); the nitration, bromination, and acylation of tetracyanocyclopentadiene are described. (c) O. W. Webster, *J. Am. Chem. Soc.*, **88**, 3046 (1966). (d) O. W. Webster, *ibid.*, **88**, 4055 (1966).

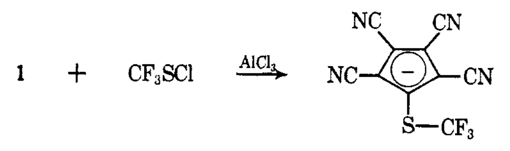
[3] R. C. Cookson, J. Hudec, and B. Whitear, *Proc. Chem. Soc.*, 117 (1961).

1,2,3,4-tetracyanocyclopentadiene (**10**) and reacts with a second mole to form a tetrachlorotetracyanocyclopentene (**11**). The chlorines on dichloro compound **10** are very positive, so much so that the substance reacts with chloride ion to produce chlorine.



The structure of the 5,5-dichloro compound follows from its reaction with ethylene at 1 atm and room temperature to give the tetracyanodichloronorbornene **12**. The mass spectrum of this substance contains a peak owing to the CCl_2^+ ion which confirms the presence of both chlorines on one carbon. Its nmr is an AA′BB′ pattern which is similar to that of the hexachloronorbornene from ethylene and hexachlorocyclopentadiene.

Trifluoromethanesulfenyl Chloride.—The pseudohalogen trifluoromethanesulfenyl chloride[4] reacts with tetracyanocyclopentadienide, but a Friedel–Crafts catalyst is required.[5]



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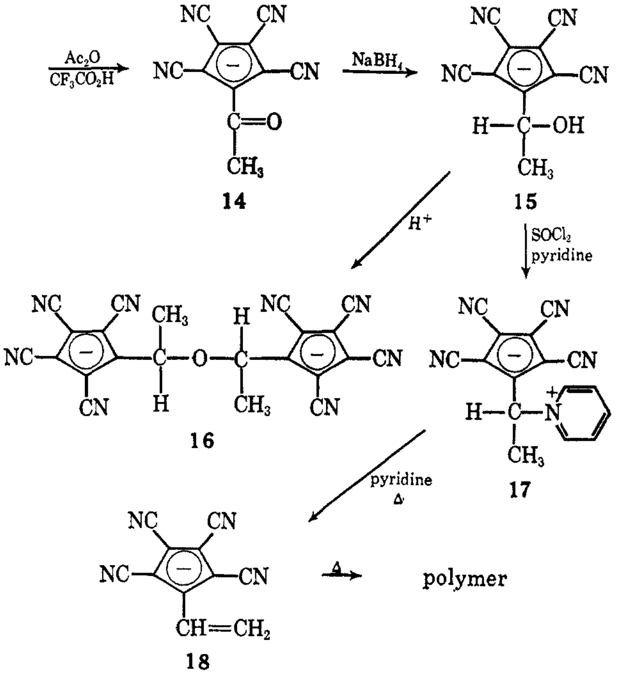
Acylation.—Tetracyanocyclopentadienide is acylated by acetic anhydride in trifluoroacetic acid (50% yield) or acetyl chloride[2b]–aluminum chloride. The keto group exhibited normal behavior in that it was readily reduced with sodium borohydride. Dilute acids caused the alcohol to form the ether **16** quickly, possibly through the intermediacy of the methyltetracyanofulvene. Treatment of the alcohol with thionyl chloride in pyridine gave the pyridinium zwitterion **17**. When this substance was warmed in pyridine, vinyltetracyanocyclopentadienide, isolated as the tetraethylammonium salt, was obtained. It polymerized readily at 135° to an acetonitrile-soluble polymer. A suspension of this polymer in water operated as an ion-exchange resin. (See Scheme I.)

Scheme I



Experimental Section

Nitrotetracyanocyclopentadienide (3).—A solution of potassium tetracyanocyclopentadienide (1.00 g, 4.90 mmoles) in concentrated nitric acid (20 ml) was allowed to stand at room temperature (15 min). The dark solution was then poured into ice water (100 ml) containing tetraethylammonium chloride (2.0 g). Tetraethylammonium nitrotetracyanocyclopentadienide (1.12 g, 67% yield, mp 372–374° dec) was collected on a filter and dried. The infrared spectrum of the product agreed with that of tetraethylammonium nitrotetracyanocyclopentadienide prepared from diazotetracyanocyclopentadiene and sodium nitrite.[2d]

Aminotetracyanocyclopentadienide (4).—A suspension of tetraethylammonium nitrotetracyanocyclopentadienide (0.73 g, 2.14 mmoles) and zinc powder (1.0 g) in water (75 ml) was treated with 6 *N* HCl (5 ml). When heated under reflux for 15 min, the tetraethylammonium nitrotetracyanocyclopentadienide dissolved. The hot solution was filtered, and the crystals which formed as the filtrate cooled were collected and stirred with $NaHCO_3$ (1.0 g) in acetonitrile (50 ml) at room temperature (15 min). The excess $NaHCO_3$ was separated by filtration, and the filtrate was concentrated to dryness. Tetraethylammonium aminotetracyanocyclopentadienide (0.35 g, 57% yield) remained. Its infrared spectrum agreed with that of tetraethylammonium aminotetracyanocyclopentadienide prepared from aminopentacyanocyclopentadiene.[2d] After one recrystallization from water, the product weighed 0.14 g and melted at 126–126.5°.

Bis(tetraethylammonium) Ethylidenebis(tetracyanocyclopentadienide).—A solution of potassium tetracyanocyclopentadienide (2.00 g, 9.82 mmoles), acetaldehyde (2.0 ml, 36 mmoles), water (5 ml), and concentrated hydrochloric acid (20 ml) was stirred at room temperature (20 min). The reaction mixture was poured into water containing excess tetraethylammonium chloride. Bis(tetraethylammonium) ethylidenebis(tetracyanocyclopentadienide) (2.5 g, 81% yield) was collected and recrystallized from methanol (three times). The pure product had mp 264.5–265.5°; $\lambda_{\max}^{\text{KBr}}$ 4.54, 7.32, 7.66, and 9.36 μ (Et_4N^+ bands not given); $\lambda_{\max}^{\text{CH}_3\text{CN}}$ 305 mμ (ϵ 26,800), 295 (24,700), sh 248 (67,800), and 242 (73,400).

Anal. Calcd for $C_{36}H_{44}N_{10}$: C, 70.1; H, 7.19; N, 22.7. Found: C, 70.1; H, 7.23; N, 22.5.

Bis(tetraethylammonium) Methylidenebis(tetracyanocyclopentadienide) (8).—A solution of tetraethylammonium tetracyanocyclopentadienide (10.0 g, 33.9 mmoles) and paraformaldehyde (3.5 g, 116 mmoles) in CF_3CO_2H (100 ml) was stirred at room temperature (1 hr). The mixture was then concentrated to about 20 ml under reduced pressure and was added to a solution of tetraethylammonium chloride (10 g) in water (200 ml). Bis(tetraethylammonium) methylidenebis(tetracyanocyclopentadienide) (9.73 g, 95% yield) precipitated. The pure product, recrystallized from ethanol–acetonitrile, had mp 260.5–262.5°; $\lambda_{\max}^{\text{KBr}}$ 3.35, 4.54, 6.74, 6.85, 6.92, 7.03, 7.17, 7.32, 8.54, 9.37, 9.50, 10.02, and 12.80 μ; $\lambda_{\max}^{\text{CH}_3\text{CN}}$ 375 mμ (ϵ 71.6), 305 (28,400), 293 (26,400), 248 (69,800), and 242 (74,600).

Anal. Calcd for $C_{35}H_{42}N_{10}$: C, 69.7; H, 7.06; N, 23.2. Found: C, 69.4; H, 7.22; N, 23.4.

Bromotetracyanocyclopentadienide.—A solution of potassium tetracyanocyclopentadienide (4.00 g, 19.6 mmoles) in aceto-

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[4] S. Andreades, J. F. Harris, Jr., and W. A. Sheppard, *J. Org. Chem.*, **29**, 898 (1964).

[5] The author is indebted to Dr. F. H. Dean for this result.

nitrile (100 ml) was stirred (0°), and a solution of bromine (1.1 ml, 21 mmoles) in acetonitrile (50 ml) was added dropwise (55 min). The solution was allowed to warm to room temperature and was stirred for 1 hr. Potassium carbonate (1.38 g) in 5 ml of water was then added, and the mixture was stirred for 15 min and filtered. The filtrate was concentrated to dryness, and the resulting potassium bromotetracyanocyclopentadienide was recrystallized from a saturated solution of potassium bromide in water. The recrystallized product weighed 3.0 g (53% yield). A small amount was converted into its tetraethylammonium salt, mp 218–222°. The identity of the product was further confirmed by comparison of its infrared spectrum with that of tetraethylammonium bromotetracyanocyclopentadienide prepared from diazotetracyanocyclopentadiene.[2d]

Chlorotetracyanocyclopentadienide (9).—A solution of tetraethylammonium tetracyanocyclopentadienide (11.75 g, 39.7 mmoles) in acetonitrile (500 ml) was cooled to −20° and liquid chlorine (3.0 ml, −34.6°, 66 mmoles) was allowed to condense into the solution. The reaction mixture was slowly warmed to room temperature (1 hr) and was concentrated to dryness. After one recrystallization from ethanol, tetraethylammonium chlorotetracyanocyclopentadienide (8.26 g, 63% yield) was obtained, mp 242.5–244°. Its structure was confirmed by comparison of its infrared spectrum with that of a sample prepared from diazotetracyanocyclopentadiene and CuCl.[2d]

A solution of tetraethylammonium chlorotetracyanocyclopentadienide (10.07 g, 30.5 mmoles) and silver nitrate (10.07 g, 60.3 mmoles) in acetonitrile (400 ml) was concentrated to about 50 ml. The concentrate was then diluted with water (300 ml), and the precipitate of silver chlorotetracyanocyclopentadienide which formed was collected and recrystallized from acetonitrile–water. The first crop of crystals amounted to 3.35 g. An additional 5.10 g was obtained by dilution of hot mother liquor to the cloud point with more water and cooling. The total yield was 8.45 g (90%).

5,5-Dichloro-1,2,3,4-tetracyanocyclopentadiene (10).—A solution of silver chlorotetracyanocyclopentadienide (8.45 g, 27.5 mmoles) in dry acetonitrile (200 ml), was cooled to −20° under nitrogen, and chlorine (2.0 ml, −34.6°, 44 mmoles) was condensed into the reaction flask. Silver chloride precipitated during the addition of the chlorine. The reaction mixture was allowed to warm to room temperature (2 hr) and was filtered. The filtrate was concentrated to dryness, and the resulting residue was extracted with benzene (200 ml). On concentration of the yellow benzene solution to dryness, 5,5-dichloro-1,2,3,4-tetracyanocyclopentadiene (4.84 g, 75% yield) remained. An analytical sample, mp 122–125° dec, was prepared by recrystallization twice from cyclohexane: $\lambda_{\max}^{\mathrm{Nujol}}$ 4.46, 6.17, 6.35, 7.53, 7.68, 8,34, 9.34, 9.68, 11.92, 12.20, 12.91, and 13.19 μ; $\lambda_{\max}^{\mathrm{CH_2Cl_2}}$ 338 mμ (ε 3420); association constant for π complex with benzene in CH_2Cl_2, 0.69; charge transfer band, $\lambda_{\max}$ 390 mμ (ε 5000); $E^{1/2}$ 0.35–0.40 v *vs.* sce 2 electron (Pt electrode).

Anal. Calcd for $C_9Cl_4N_2$: C, 46.0; Cl, 30.2; N, 23.8. Found: C, 46.4; Cl, 30.5; N, 24.0.

Chlorine gas was passed into a suspension of potassium tetracyanocyclopentadienide (3.90 g, 19.3 mmoles) in water (200 ml) until the yellow color of chlorine remained. The tarry precipitate was taken up in benzene, and the solution was dried and concentrated to dryness. The residue was recrystallized from cyclohexane. 5,5-Dichloro-1,2,3,4-tetracyanocyclopentadiene (0.83 g, 25% yield) was obtained. The product was identified by its infrared spectrum.

Tetrachlorotetracyanocyclopentene (9).—A solution of potassium tetracyanocyclopentadienide (2.75 g, 13.5 mmoles) in acetonitrile (50 ml) was cooled to −20° under nitrogen, and 50 ml of a 1.095 *N* solution of chlorine (27.4 mmoles) in acetonitrile was added in one portion. The reaction mixture was allowed to warm to room temperature (2 hr) and was filtered, and the filtrate was concentrated to dryness. A test with xylene showed that no dichlorotetracyanocyclopentadiene was present in the concentrate residue (no orange π-complex formation). The concentrate residue was washed with 200 ml of water. Tetrachlorotetracyanocyclopentene (1.25 g, 30% yield) remained insoluble. An analytical sample, mp 86.5–88.5°, was prepared by recrystallization once from cyclohexane and once from hexane: $\lambda_{\max}^{\mathrm{KBr}}$ 4.44, strong absorption 12–14 μ; $\lambda_{\max}^{\mathrm{dioxane}}$ 295 mμ (ε 616) and 237 mμ (ε 11,120).

Anal. Calcd for $C_9Cl_4N_4$: C, 35.3; Cl, 46.3; N, 18.3. Found: C, 35.2; Cl, 46.1; N, 18.5.

The Reaction of 5,5-Dichloro-1,2,3,4-tetracyanocyclopentadiene (10) with Tetraethylammonium Chloride.—To a solution of tetraethylammonium chloride (0.16 g, 1.00 mmole) in ethylene chloride (25 ml) was added dichlorotetracyanocyclopentadiene (0.23 g, 1.00 mmole) at room temperature. In a few minutes, tetraethylammonium chlorotetracyanocyclopentadienide (0.19 g) crystallized, mp 247–249°. An additional 0.12 g of tetraethylammonium chlorotetracyanocyclopentadienide was isolated by concentration of the reaction solution. The product was characterized by its infrared spectrum. A moist KI–starch test paper held over the solution turned dark, indicating the presence of chlorine gas.

7,7-Dichloro-1,2,3,4-tetracyanobicyclo[2.2.1]hept-2-ene (12).—To a saturated solution of ethylene in ethylene chloride was added 5.5-dichloro-1,2,3,4-tetracyanocyclopentadiene (1.00 g, 4.24 mmoles) at room temperature. The solution was allowed to stand for 1 week and was then concentrated to dryness. The residue was chromatographed on Woelm alumina (acid activity I) with ethyl acetate wash. The first product to be eluted was 7,7-dichloro-1,2,3,4-tetracyanobicyclo[2.2.1]hept-2-ene (0.34 g, 30% yield). An analytical sample, mp 226–228° dec, was prepared by recrystallization twice from benzene: $\lambda_{\max}^{\mathrm{KBr}}$ 3.30, 3.35, 4.40, 4.45, 6.25, 6.78, 6.86, 7.70, 7.82, 8.11, 9.28, 9,80, 10.35, 10.50, 11.45, 11.90, and 14.00 μ; $\lambda_{\max}^{\mathrm{CH_3CN}}$ 290 mμ (ε 22.6), 225 (6210), and 242 (9230); nmr [$(CD_3)_2CO$], a 20-line AA'BB' pattern centered at τ 7.16 ppm with a 47.6-cps separation between the first and last peak. The mass spectrum showed peaks at *m/e* 262 (parent ion), 234 (parent minus C_2H_4), 235 (parent minus HCN), 180 (parent minus CCl_2), 83 ($HCCl_2^+$), 82 (CCl_2^+), 49 (CH_2Cl^+), and 28 ($C_2H_4^+$).

Anal. Calcd for $C_{11}H_4N_4Cl_2$: C, 50.2; H, 1.52; N, 21.3. Found: C, 50.0; H, 1.65; N, 21.1.

Trifluoromethylthiotetracyanocyclopentadienide[4] (13).—Anhydrous aluminum chloride (3.03 g, 22.5 mmoles) was added to a cold solution (0°) of tetraethylammonium tetracyanocyclopentadienide (5.90 g, 20 mmoles) in acetonitrile (50 ml). The temperature rose to 50°. After the solution had cooled, trifluoromethanesulfenyl chloride (12 g, 88 mmoles) was passed into the solution as a gas (20 min). The temperature rose to 40°. The reaction mixture was heated under reflux (solid carbon dioxide–acetone cooled condenser) for 1.5 hr and was then allowed to stand overnight. The solvent was removed under reduced pressure. The residue was recrystallized from aqueous alcohol to give tetraethylammonium trifluoromethylthiotetracyanocyclopentadienide (6.90 g, 82.5% yield), mp 136–138°. Recrystallization again gave a sample with mp 137–138°; $\lambda_{\max}^{\mathrm{KBr}}$ 3.33, 3.65, 4.52, 6.72, 6.87, 7.18, 8.85, 9.10, 10.00, 12.75, 13.20, and 14.62 μ; F^{19} nmr (56.4 Mc, CD_3CN solution) showed a single sharp peak at +2477 cps from internal Freon 11®.

Anal. Calcd for $C_{15}H_{20}F_3N_5S$ (395): C, 54.7; H, 5.06; N, 17.7; S, 8.10. Found: C, 54.7; H, 4.94; N, 17.0; S, 8.09.

Acetyltetracyanocyclopentadienide[2b] (14).—Potassium tetracyanocyclopentadienide (9.0 g, 0.044 mole), acetic anhydride (9.0 ml), and trifluoroacetic acid (90 ml) were heated under reflux (1 hr). The solution was cooled and poured into water (300 ml) containing tetraethylammonium chloride (20 g). Tetraethylammonium acetyltetracyanocyclopentadienide (6.0 g, 40% yield) was obtained after chromatography of the crude precipitate (10.5 g) on acid alumina with ethyl acetate–acetonitrile eluent. An analytical sample, mp 237.5–240°, was prepared by recrystallization from water then ethylene chloride: $\lambda_{\max}^{\mathrm{Nujol}}$ 4.51, 6.02, 8.03, 8.45, 8.54, 9.13, 9.75, 10.00, 10.20, and 12.75 μ; $\lambda_{\max}^{\mathrm{CH_3CN}}$ 315 mμ (ε 6610), 300 (8610), 266 (70,850), and 257 (47,900).

Anal. Calcd for $C_{19}H_{23}N_5O$: C, 67.6; H, 6.87; N, 20.8. Found: C, 67.7; H, 7.41; N, 20.5.

(1-Hyroxyethyl)tetracyanocyclopentadienide (15).—A solution of tetraethylammonium acetyltetracyanocyclopentadienide (16.5 g, 45.9 mmoles), sodium borohydride (1.65 g, 43.6 mmoles), and ethanol (500 ml) was heated to reflux temperature, allowed to cool (0.5 hr), reheated to reflux, and allowed to cool (0.5 hr). The reaction mixture was concentrated to dryness. The residue was diluted with water (200 ml) and was titrated to about pH 8 with dilute sulfuric acid. Tetraethylammonium chloride (25 g) was added, and tetraethylammonium (1-hydroxyethyl)tetracyanocyclopentadienide was collected on a filter and dried. The product weighed 13.7 g (83% yield). An analytical sample was recrystallized from water three times. The pure product had mp 101–102°; $\lambda_{\max}^{\mathrm{KBr}}$ 2.86, 3.37, 4.52, 6.72, 6.86, 6.93, 7.16, 7.30, 8.52, 9.25, 9.80, 10.00, 10.90, and 12.75 μ; $\lambda_{max}^{CH_3CN}$ 300 mμ (ϵ 13,730), 290 (13,250), 247 (51,300), and 238 (43,480).

Anal. Calcd for $C_{19}H_{25}N_5O$: C, 67.2; H, 7.42; N, 20.6. Found: C, 67.0; H, 7.32; N, 20.5.

1,1′-Bis(tetracyanocyclopentadienido)ethyl Ether (**16**).—A mixture of tetraethylammonium acetyltetracyanocyclopentadienide (16.5 g, 55.9 mmoles), sodium borohydride (1.65 g, 43.5 mmoles), and ethanol (500 ml) was heated to reflux, allowed to cool (0.5 hr), and then reheated to reflux and allowed to cool (0.5 hr). The solution was concentrated to dryness, and the residue was treated with cold 1 *N* sulfuric acid (200 ml). Bis(tetraethylammonium) 1,1′-bis(tetracyanocyclopentadienido)methyl ether (13.0 g, 78% yield) was collected and recrystallized from water–CH_3CN three times and ethylene chloride once: mp 211–213°; λ_{max}^{KBr} 3.35, 4.54, 6.82, 7.15, 7.27, 7.55, 7.65, 8.45, 9.32, 9.70, 9.96, 10.45, and 12.60 μ; $\lambda_{max}^{CH_3CN}$ 303 mμ (ϵ 29,300), 292 (27,300), 248 (96,000), and 239 (84,100); nmr ($CD_3CN\cdot$), in addition to the tetraethylammonium peaks, a quartet at τ = 5.67 ppm (2 H) and a doublet at τ = 8.54 ppm (6 H, J = 7.0 cps).

Anal. Calcd for $C_{38}H_{48}N_{10}O$: C, 68.9; H, 7.30; N, 21.2. Found: C, 68.8; H, 7.29; N, 21.3.

(1-Pyridiniumethyl)tetracyanocyclopentadienide (**17**).—Tetraethylammonium (1-hydroxyethyl)tetracyanocyclopentadienide (12.7 g, 37.4 mmoles) was dissolved in pyridine (300 ml), thionyl chloride (3.0 ml, 41.7 mmoles) was added, and the solution was allowed to stand at room temperature (2.5 hr). The solution was concentrated to dryness, and the residue was washed with water. (1-Pyridiniumethyl)tetracyanocyclopentadiene (7.5 g, 75% yield) remained. An analytical sample (decomposition point 170°) was recrystallized from acetonitrile four times: λ_{max}^{KBr} 3.17, 3.24, 4.52, 6.18, 6.65, 6.72, 6.85, 7.15, 7.90, 8.45, 8.62, 9.45, 10.64, 12.96, and 14.88 μ; $\lambda_{max}^{CH_3CN}$ 297 mμ (ϵ 10,160), 283 (13,300), 266 (10,380), 247 (58,940), and 240 (46,700); nmr (CD_3COCD_3), complex multiplet centered at τ = 1.34 ppm (5 H), quartet at τ = 3.57 ppm (1 H), and doublet at τ = 7.79 ppm (3 H), J = 7.0 cps).

Anal. Calcd for $C_{16}H_9N_5$: C, 70.8; H, 3.34; N, 25.8. Found: C, 70.8; H, 3.30; N, 24.9.

Vinyltetracyanocyclopentadienide (**18**).—A solution of (1-pyridiniumethyl)tetracyanocyclopentadienide (9.40 g, 34.8 mmoles) in pyridine (200 ml) was heated under reflux (15 hr). The solution was concentrated to dryness and the residue was stirred with water (300 ml) containing tetraethylammonium chloride (10 g). Tetraethylammonium vinyltetracyanocyclopentadienide (11.5 g, quantitative yield) was collected. An analytical sample was recrystallized from ethylene chloride (three times): it melted and polymerized at 136°; λ_{max}^{KBr} 3.30, 3.35, 4.51, 6.12, 6.72, 6.86, 7.09, 7.16, 7.31, 8.52, 9.50, 10.00, 10.16, 11.29, 12.70, and 13.45 μ; $\lambda_{max}^{CH_3CN}$ sh 330 mμ (ϵ 3060), sh 315 (6620), 298 (9900), 271 (52,100), and 262 (45,600); nmr (CD_3CN), vinyl multiplet centered at τ = 3.9 ppm (J_{trans} = 17 cps, J_{cis} = 11 cps, and J_{gem} = 2 cps).

Anal. Calcd for $C_{19}H_{23}N_5$: C, 71.0; H, 7.21; N, 21.8; mol wt, 162. Found: C, 70.7; H, 7.16; N, 22.5; mol wt (freezing point of dimethyl sulfoxide), 173.

An acetonitrile-soluble polymer was obtained by heating the vinyl compound at 135–140° for 15 min under nitrogen. The nmr of the polymer showed no vinyl absorption.

Synthetic Approaches to Cyclohept[*f*]indenes[1a]

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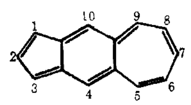
In the process of developing a method of synthesis of the cyclohept[*f*]indene derivatives **2b** and **3b**, a method of preparing benzo[*d*]tropones from *o*-bisbromomethylarenes and ketone enamines has been devised. Nitration and bromination of benzo[*d*]tropones in sulfuric acid solution have been observed to occur excusively in the α positions of the benzene ring. On quenching the carbanion of **2b** (formed in dimethyl sulfoxide) with deuterium oxide all three hydrogen atoms of the indene ring were exchanged, but the cyclohept[*f*]indenol was not produced. Attempts to obtain the cyclohept[*f*]indene system by removal of a proton from the tropylium ion **3b** were unsuccessful.

Some time ago we initiated a synthetic program designed to prepare derivatives of cyclohept[*f*]indene (**1**), a 14 π-electron system. In the meantime Bertelli[2] published the synthesis of the cyclohep[*f*]indene derivatives **2a** and **3a**. Since our synthetic approach and the derivatives prepared (**2b** and **3b**) differed somewhat from those described by Bertelli, we are hereby presenting a summary of our results.



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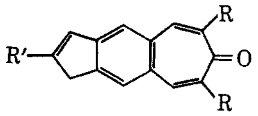
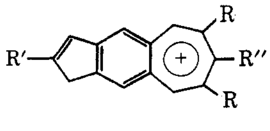
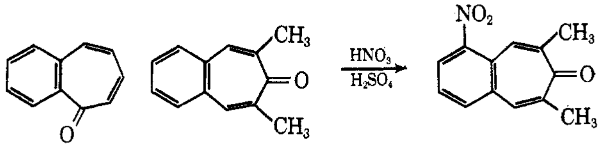


2a, R = C_6H_5; R′ = H
b, R = CH_3; R′ = C_6H_5



3a, R = C_6H_5; R′ = R″ = H
b, R = CH_3; R′ = R″ = C_6H_5

Reactions of Benzotropones with Electrophilic Reagents.—Our first approach to the cyclohept[*f*]indene system was to fuse a five-membered carbocyclic ring onto the benzene ring of a benzotropone system using a Friedel–Crafts or Meerwein reaction.[3] Although neither of these reactions succeeded, some useful information concerning electrophilic substitution of benzotropones was obtained. Tropone **4**, when treated with nitric acid, dinitrated in the seven-membered ring.[4] Under comparable conditions the dimethylbenzo[*d*]tropone **5** (readily obtained from phthalaldehyde and ethyl ketone[5]) failed to react; yet with nitric acid in sulfuric acid, **5** gave an almost quan-



4 **5** **6**

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[1] (a) Abstracted in part from the Ph.D. dissertation of M. Winn, Northwestern University, Aug 1965. (b) National Science Foundation Predoctoral Fellow 1962–1963; Texaco Fellow, 1963–1964; Ethyl Corp. Fellow, 1964–1965.

[2] D. Bertelli, *J. Org. Chem.*, **29**, 3032 (1964); **30**, 891 (1965).

[3] H. Meerwein, E. Büchner, and K. van Emster, *J. Prakt. Chem.*, [2] **152**, 237 (1939); C. F. Koelsch and V. Boekelheide, *J. Am. Chem. Soc.*, **66**, 412 (1944).

[4] G. L. Buchanan and D. R. Lockhart, *J. Chem. Soc.*, 3586 (1959).

[5] J. Thiele and E. Weitz, *Ann.*, **377**, 1 (1911); see also D. Meuche, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta*, **41**, 2220 (1958)