## SECTION C **Organic Chemistry**

## Tetracyanocyclopentadienide Anion and its Electrophilic Aromatic Substitution

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1.4-Diethoxycarbonyl-2,3-dicyanocyclopentadienide salts have been made from 1,4-diethoxycarbonylcyclopentane-2,3-dione by addition of hydrogen cyanide, acetylation, and treatment with base. The tetracyanocyclopentadienide anion was formed by dehydrogenation of all-trans-tetracyanocyclopentane with phosphorus pentachloride. The tetracyano-salts can be converted into halogeno-, nitro-, and acetyl derivatives by the appropriate electrophilic reagents.

PENTAMETHOXYCARBONYLCYCLOPENTADIENE<sup>1-4</sup> is an extremely strong acid.<sup>2</sup> The pentacyano-compound should be even stronger, not only because of the greater electron-accepting ability of CN, but also because the anion can maintain pentagonal symmetry with equal delocalisation of charge on to each C-CN group, whereas steric congestion prevents simultaneous conjugation of all five ester groups in the pentamethoxycarbonyl compound. Pentacyanocyclopentadienide would also be the lower member of the possible series of monocyclic aromatic cyanocarbons recently begun with hexacyanobenzene.<sup>5</sup> We therefore set out to synthesise it and some of its relatives.

Synthesis.—The diketo-diester  $(I)^6$  could be converted into the biscyanohydrin (II), but only by liquid hydrogen cyanide containing a catalytic amount of base. The biscyanohydrin (II) was unstable to moisture and decomposed slowly into its components. As with other compounds with oxygen and nitrile groups on the same carbon atom, neither the biscyanohydrin (III) nor its diacetate (III) showed any CN stretching vibration in their infrared spectra. Potassium t-butoxide in tbutyl alcohol caused elimination of acetic acid from the diacetate (III) to give the 2,3-dicyano-1,4-diethoxycarbonylcyclopentadienide anion, isolated as the tetramethylammonium salt (IV).

Application of the same reaction sequence to the corresponding dinitrile (V) should lead to tetracyanocyclopentadienide salts. By analogy with the formation of the diketo-diester (I) from diethyl glutarate and diethyl oxalate,<sup>6</sup> the diketo-dinitrile (V) could be made by condensation of glutaronitrile and diethyl oxalate with sodium hydride, although only in low yield. According to the infrared spectrum this compound, which gave a deep brown-violet colour with ferric chloride, was completely enolised. No reaction with hydrogen cyanide could be detected.

A successful synthesis of tetracyanocyclopentadienide

<sup>1</sup> O. Diels, Ber., 1942, 75, 1452.

<sup>2</sup> R. C. Cookson, J. Hudec, and B. R. D. Whitear, Proc. Chem. Soc., 1961, 117.

<sup>3</sup> P. Bamfield, R. C. Cookson, A. Crabtree, J. Henstock, J. Hudec, A. W. Johnson, and B. D. R. Whitear, *Chem. and Ind.*, 1964, 1313.

salts started with all the carbon atoms already linked. Cyclopentane-1,2,3,4-tetracarboxylic acid 7 (VI) needed treatment with thionyl chloride for two days for conversion into the acid chloride. Although the time could be reduced to less than 2 hr. by a catalytic amount of dimethylformamide,<sup>8</sup> a purer product resulted from the use of phosphorus pentachloride in benzene. Reaction



of the crude product with ammonia then gave the tetraamide (VII), dehydrated to the tetranitrile (VIII) by boiling a suspension in acetonitrile with phosphoryl chloride and sodium chloride. (The latter removes the resulting phosphoric acid as its sodium salt, which is filtered off with unchanged amide.) Of several methods

E. Le Goff and R. B. La Count, J. Org. Chem., 1964, 29, 423.
K. Wallenfels and K. Friedrich, Tetrahedron Letters, 1963,

1223.

W. Dieckmann, Ber., 1894, 27, 965.

7 K. Alder, H. H. Molls, and R. Reeber, Annalen, 1958, 611, 7.

Von H. H. Bosshard, R. Mori, M. Schmid, and H. Zollinger, Helv. Chim. Acta, 1959, 42, 1653.

tried for the last step, success was achieved only by treating the tetranitrile with phosphorus pentachloride.

Soon after this synthesis Webster reported another preparation of the tetracyanocyclopentadienide anion.<sup>9</sup> Since he also made the pentacyano-anion, we abandoned that objective.

*Chemical Properties.*—The dicyanodiethoxycarbonylcyclopentadienide and tetracyanocyclopentadienide anions could be isolated from their solutions in water by addition of tetra-alkylammonium salts, even in strongly acidic solutions. The alkali salts were much more soluble. The very insoluble silver salts could again be converted into the alkylammonium salts by dissolving them in aqueous ammonia and adding the respective cations.

Like pentamethoxycarbonylcyclopentadienide<sup>3</sup> the dicyanodiethoxycarbonyl and tetracyano-anions formed ferrous salts, which were not ferrocenes. Similarly, addition of tropylium fluoroborate to aqueous solutions of the anions produced the tropylium cyclopentadienide salts, rather than the dihydrosesquifulvalenes as reported for cyclopentadienide anion itself.<sup>10</sup> The infrared spectra of the two tropylium salts were very similar to those of the corresponding anions, and lacked the C=C absorption expected from the sesquifulvalenes. The salt-like character was further attested by the compounds' solubility in water, but not in organic solvents such as ether or benzene. The salts were unstable in solution in water or alcohol, their yellow to orange colour soon fading. The tetramethylammonium cyclopentadienide salts (IV and IX) could then be isolated by addition of tetramethylammonium chloride. Nevertheless an equilibrium with the dihydrosesquifulvalenes may exist in non-polar liquids, because suspensions of the tropylium salts in ether, dioxan, or chloroform became deep red when exposed to the air or treated with triphenylmethyl cations.

The aromatic tetracyanocyclopentadienide anion underwent typical substitution by electrophilic reagents. A suspension of the tetramethylammonium salt (IX) took up one mol. of bromine to give the bromo-derivative (X; Z = Br), and nitration was effected with concentrated nitric acid (X;  $Z = NO_2$ ). Friedel-Crafts acetylation with acetyl chloride and zinc chloride formed the acetyl derivative (X;  $Z = COCH_3$ ). On treatment of a suspension of the salt (IX) in ether with ethyl nitrite and hydrogen chloride no reaction occurred. Attempted nitrosation with ethyl nitrite and acetyl chloride resulted instead in formation of the chloro salt (X; Z = Cl).

Spectral Properties.—As might be expected, the carbonyl stretching bands of 2,3-dicyano-1,4-diethoxy-carbonylcyclopentadienide (IV) and acetyltetracyano-cyclopentadienide (X;  $Z = COCH_3$ ) had the rather low frequencies of 1675 and 1655 cm.<sup>-1</sup>, respectively. All the pentasubstituted cyclopentadienide anions lacked the absorption at about 850 cm.<sup>-1</sup> which is

present in the spectrum of the tetracyano-anion (IX), owing to the bending of the C-H out of the aromatic plane. (In tetra- and penta-substituted benzenes it occurs at 860-900 cm.<sup>-1</sup>.)

The ultraviolet spectra of the dicyanodiethoxycarbonyl salt (IV) and the tetracyano-salt (IX) are very similar, the maxima for the former appearing at about 17 m $\mu$  to longer wavelengths (see Table). The spectra closely resemble those of the methyltetramethoxycarbonyl and pentamethoxycarbonyl salts.<sup>2</sup>

Mainly because of the negative charge, the protons of cyclopentadienide anion resonate about 1.9 p.p.m. to higher field than those of benzene.<sup>11</sup> Comparison of the chemical shift of the proton in 1,2,4,5-tetracyanobenzene ( $\tau$  1.15 in deuterioacetone) with the figure for tetracyanocyclopentadienide ( $\tau$  3.31 in dueterioacetone) reveals a shift of similar magnitude (2.16 p.p.m.)

Ultraviolet spectra of cyclopentadienide anions

	1	
Compound	$\lambda_{max}$ (m $\mu$ )	$\epsilon_{max}$
(IV)	313	14,300
	302	14,300
	262	52,000
	$255 \mathrm{sh}$	45,000
(IX)	298	14,000
	288	13,300
	<b>243</b>	44,200
	235	37,600
	$232 \mathrm{sh}$	33,600
Potassium pentamethoxycarbo	nyl- 295	14,600
cyclopentadienide <sup>2</sup>	265	49,800

## EXPERIMENTAL

2,3-Dicyano-1,4-diethoxycarbonyl-2,3-dihydroxycyclopentane (II).—To a stirred suspension of 3,5-diethoxycarbonylcyclopentane-1,2-dione (10 g.: m. p. 120—121°, lit.,<sup>6</sup> 118°) in anhydrous hydrogen cyanide (30 ml.), kept at 13—15° by external cooling, 2 drops of 50% KOH were added. After 24 hr. a few drops of conc. phosphoric acid were added to neutralise the KOH and stabilise the cyanohydrin. Then the excess of hydrogen cyanide was removed at water pumppressure and 20°, and the residue, recrystallised from chloroform-carbon tetrachloride, gave colourless needles (8·5 g., 70%), m. p. 144° (Found: C, 52·8; H, 5·3; N, 9·4.  $C_{13}H_{16}N_2O_6$  requires C, 52·7; H, 5·4; N, 9·5%).

2,3-Diacetoxy-2,3-dicyano-1,4-diethoxycarbonylcyclopentane.—The cyanohydrin (2·1 g.) was refluxed for 10 min. with acetic anhydride (20 ml.) and 1 drop of conc. sulphuric acid. After cooling, the mixture was poured on crushed ice and stirred until the hydrolysis of the excess of acetic anhydride was complete. The white solid, filtered off, washed with water, and recrystallised from dilute acetic acid gave colourless needles (1·2 g., 45%), m. p. 120—121°. A better yield (70%) could be obtained by acetylation with acetic anhydride alone for 2 hr. (Found: C, 54·2; H, 5·8; N, 7·4; acetyl, 22·5.  $C_{17}H_{20}N_2O_8$  requires C, 53·7; H, 5·3; N, 7·4; acetyl 22·6%).

Tetramethylammonium 2,3-Dicyano-1,4-diethoxycarbonylcyclopentadienide.—The cyanohydrin acetate (1.92 g.) in t-butyl alcohol (30 ml.) was stirred under reflux for 4 hr. with potassium t-butoxide (from potassium, 0.6 g.). The

<sup>&</sup>lt;sup>9</sup> O. W. Webster, J. Amer. Chem. Soc., 1965, 87, 1820.

<sup>&</sup>lt;sup>10</sup> W. von E. Doering and H. Krauch, *Angew. Chem.*, 1956, **68**, 664.

<sup>&</sup>lt;sup>11</sup> G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, 1960, **82**, 5846.

mixture turned yellow immediately after the addition of the base. After removal of the solvent *in vacuo* the residue was dissolved in the minumum of water, neutralised, filtered, and an excess of tetramethylammonium chloride added. The resulting *salt*, recrystallised from water with addition of tetramethylammonium chloride, gave colourless crystals (1.01 g., 59%), m. p. 169° (Found: C, 61.1; H, 7.0; N, 12.5.  $C_{17}H_{23}N_3O_4$  requires C, 61.2; H, 6.95; N, 12.6%).

1,4-Dicyano-2,3-dihydroxycyclopentadiene. — This compound is formed as a by-product of the reaction between glutaronitrile and diethyl oxalate, which gives mainly ethyl 2-oxo-3,5-dicyanovalerate.<sup>12</sup> Diethyl oxalate (34.2 g.) was dissolved in dry benzene (250 ml.) and dimethoxyethane (10 ml.). To this well-stirred solution 11 g. of a 50% mineral oil suspension of sodium hydride was added. After the evolution of hydrogen had ceased, glutaronitrile (10 g.) was added during 1 hr., the temperature being kept at  $40^{\circ}$ . Stirring was continued for another 30 min. The yellow precipitate was filtered off, washed with ether, and dried. The decomposition of this sodium salt with an excess of cold dilute sulphuric acid gave a mixture of an oil and a solid, which could be separated by addition of benzene. The filtered yellow powder, several times recrystallised from ethanol-ethyl acetate, gave slightly yellow crystals (3.1 g., 20%), m. p. 225° (decomp). The compound gives an intense colour with ferric chloride and the infrared spectrum shows no carbonyl bands (Found: C, 57.4; H, 2.9; N, 16.1. C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>O<sub>2</sub> requires C, 56.8; H, 2.7; N, 18.9%).

Cyclopentane-all-trans-1,2,3,4-tetracarboxylic Acid.—The method of Alder et al.7 was followed except for minor changes necessary for larger quantities. The endo-cis-5-norbornene-2,3-dicarboxylic anhydride was oxidised in 20 g. portions with 240 ml. each of a mixture of 60% conc. nitric acid and 40% fuming nitric acid (d 1.50). Within 2 weeks about 70%of the product had crystallised from the yellow solution. After drying it was recrystallised from 75% formic acid and had m. p. 195° (lit., 7 195°). The all-cis-acid was then heated together with 9 parts of KOH and a few drops of water in an iron crucible until complete solution had occurred (about 20 min.). The mixture was cooled, dissolved in the minimum of water, and acidified with conc. hydrochloric acid. From this solution the all-trans-acid was extracted with ethyl methyl ketone in a continuous extractor. After drying (MgSO<sub>4</sub>) the ketone was removed under reduced pressure. The oily residue then started to crystallise after a short time: yield 80-90%. The product was pure enough for conversion into the acid chloride.

Cyclopentane-all-trans-1,2,3,4-tetracarbonamide.— To a mixture of all-trans acid (70 g.) and dry benzene (1 l.) was added during 1 hr. phosphorus pentachloride (237 g.). After the addition was complete stirring was continued overnight, then the clear solution evaporated under reduced pressure on a steam-bath. The oily residue could not be distilled without decomposition (b. p. 172-173°/4 mm.) and was therefore used directly. It was dissolved in dry benzene (1.5 l), and through the stirred solution a stream of dry ammonia was passed without external cooling for 20 hr. The thick suspension was then evaporated to dryness under reduced pressure and the residue, several times recrystallised from water (charcoal), gave colourless long *needles* (40.5 g., 59%), m. p. 335° (decomp.) (Found: C, 44.5; H, 5.7; N, 23.2. C<sub>9</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub> requires C, 44.6; H, 5.8; N, 23.1%)

1,2,3,4-*Tetracyanocyclopentane*.—The tetra-amide (34 g.) was suspended in dry acetonitrile (500 ml.); sodium chloride

(60 g.) and phosphoryl chloride (30 ml.) were added and the mixture stirred under reflux for 24 hr. The solid was filtered off, washed with acetonitrile, and again treated with the same amount of phosphoryl chloride in fresh acetonitrile for 24 hr. The combined filtrates were evaporated under reduced pressure on a steam-bath and the oily residue crystallised from water (charcoal) as colourless *crystals* (15·2 g., 64%), m. p. 221°. The yields were usually between 60 and 70% (Found: C, 63·35; H, 3·6; N, 32·9.  $C_9H_6N_4$  requires C, 63·5; H, 3·5; N, 32·9%).

Tetramethylammonium Tetracyanocyclopentadienide.—Alltrans-1,2,3,4-tetracyanocyclopentane (8.6 g.) was thoroughly mixed with finely powdered phosphorus pentachloride (32 g.) and heated in a flask with reflux condenser in an oil-bath to 125-130° for 2 hr. The evolution of hydrogen chloride had then ceased, and the cooled contents of the flask were ground together with carbon tetrachloride and the whole evaporated to dryness on a steam-bath in vacuo. The black-brown residue was then carefully treated with ice to decompose the excess of phosphorus pentachloride, the red solution was filtered, made neutral with NaOH, and an excess of tetramethylammonium chloride was added. The precipitated salt was filtered off, washed with a little icewater, then with ether, and recrystallised from water with addition of tetramethylammonium chloride (charcoal). (It was always useful to add tetramethylammonium chloride during recrystallisation of the cyclopentadienide salts to complete the separation of the products.) The slightly brown crystals (2.42 g., 20%) had m. p. 217-220°. In spite of repeated purification the analyses were never correct (Found: C, 63.8; H, 5.4; N, 26.25. C<sub>13</sub>H<sub>13</sub>N<sub>5</sub> requires C, 65.25; H, 5.5; N, 29.3%). Better results were obtained with the tetraethylammonium salt, m. p. 131-132° (lit., 9 130-132°) (Found: C, 68.2; H, 7.0; N, 24.1. C<sub>17</sub>H<sub>21</sub>N<sub>5</sub> requires C, 69.1; H, 7.2; N, 23.7%). The salts are sparingly soluble in cold water, more in ethanol or acetone.

Tropylium Tetracyanocyclopentadienide.—This salt was prepared by mixing together concentrated warm aqueous solutions of equimolecular amounts of tetramethylammonium tetracyanocyclopentadienide and of tropylium fluoroborate. The mixture turned yellow at once and deposited yellow *needles*. Recrystallisation is possible from water if prolonged heating is avoided: m. p. 183° (decomp.), yield 93% (Found: C, 71.0; H, 3.1; N, 19.65.  $C_{16}H_8N_4$ requires C, 75.0; H, 3.15; N, 21.9%). The salt could not be obtained pure owing to decomposition during recrystallisation.

Tropylium 2,3-Dicyano-1,4-diethoxycarbonylcyclopentadienide.—The same method gave yellow-orange crystals, m. p. 160° (decomp.) from water; yield 85% (Found: C, 68.7; H, 5.2; N, 7.8.  $C_{20}H_{28}N_2O_4$  requires C, 68.6; H, 5.2; N, 8.0%).

Tetramethylammonium Bromotetracyanocyclopentadienide. —Tetramethylammonium tetracyanocyclopentadienide (0·12 g.) was stirred in chloroform suspension and bromine (0·082 g.) in the same solvent was added. After being stirred for 1·5 hr., the solvent was evaporated and the residue recrystallised from water as colourless *needles* (0·120 g., 75%), m. p. 360—362° (decomp.) (Found: C, 49·2; H, 4·2; Br, 25·2; N, 22·3.  $C_{13}H_{12}BrN_5$  requires C, 49·1; H, 3·8; Br, 25·1; N, 22·0%).

Tetramethylammonium Tetracyanonitrocyclopentadienide. <sup>12</sup> A. Michael, Amer. Chem. J., 1903, **30**, 156; W. Dieckmann, Ber., 1911, **44**, 985.

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--Tetramethylammonium tetracyanocyclopentadienide (0·116 g.) was stirred with conc. nitric acid (5 ml.) at 20°. The mixture turned slowly to green and then blue. After 48 hr. water (5 ml.) was added and the product was precipitated by an excess of tetramethylammonium chloride. The blue by-product was formed in larger quantities if the nitration was carried out in 1: 1 conc. nitric acid-water for 36-48 hr. at 20°. Then only traces of the nitro-product could be isolated. By repeated recrystallisation from boiling water the blue compound is destroyed. The *nitrocompound* forms slightly yellow needles, which turn brownish-green during exposure to air (0·045 g., 33%), m. p. >385° (Found: C, 55·0; H, 4·3; N, 28·7. C<sub>13</sub>H<sub>12</sub>N<sub>6</sub>O<sub>2</sub> requires C, 54·9; H, 4·3; N, 29·6%).

Tetramethylammonium Acetyltetracyanocyclopentadienide. —Tetramethylammonium tetracyanocyclopentadienide dissolved in acetyl chloride was treated with zinc chloride (1 mol.). After 20 minutes' shaking at 20° the deep violet solution was evaporated, water was added, and the *product* was precipitated by addition of excess of tetramethylammonium chloride. After recrystallisation from water the crystals melted at 335° (decomp.) (Found: C, 62.9; H, 5.7; N, 24.5.  $C_{15}H_{15}ON_5$  requires C, 64.0; H, 5.4; N, 24.9%).

Tetramethylammonium Chlorotetracyanocyclopentadienide. —No reaction occurred on treating the tetramethylammonium tetracyanocyclopentadienide in ether suspension with ethyl nitrite and anhydrous hydrogen chloride, but passing a stream of gaseous ethyl nitrite through a boiling solution of the salt in acetyl chloride resulted in a reaction. The starting compound (0.234 g.) in acetyl chloride (30 ml.) was treated for 1 hr. with excess of ethyl nitrite. The green-blue solution was then evaporated and the residue recrystallised from water. During this the green compound was destroyed and only the chlorotetracyanocyclopentadienide could be isolated, as colourless needles (0.110 g., 41%), m. p. 353—355° (Found: C, 57.0; H, 4.3; Cl, 12.8; N, 25.6.  $C_{13}H_{12}ClN_5$  requires C, 57.0; H, 4.4; Cl, 12.9; N, 25.6%)

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