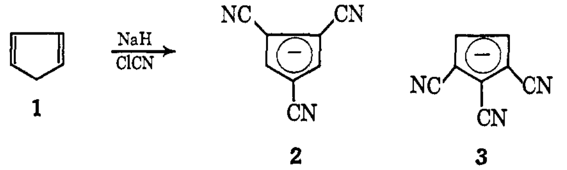
# Polycyanation. The Reaction of Cyanogen Chloride, Cyclopentadiene, and Sodium Hydride

O. W. Webster

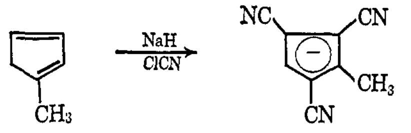
*Contribution No. 1185 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898.* *Received March 25, 1966*

**Abstract:** All of the possible cyanocyclopentadienides have been made by the stepwise cyanation of cyclopentadiene with cyanogen chloride. The first three cyano groups were introduced with the aid of sodium hydride, the fourth and fifth with aluminum chloride.

The high reactivity of sodium hydride to slightly acid hydrogens and low reactivity to other bonding situations makes it an attractive coreagent for the preparation of polyfunctional compounds.[1] With cyanogen chloride and sodium hydride, for example, we have found that cyclopentadiene, methylcyclopentadiene, or indene can be tricyanated.[2]



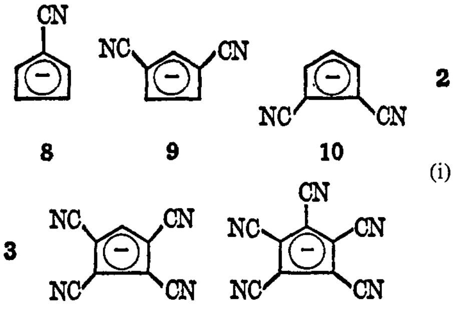
1 2 3



4 5

6 7

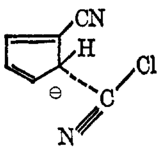
During the cyanation reaction as each additional cyano group is introduced, the resulting cyanocyclopentadienide (regenerated by sodium hydride) is less nucleophilic. Thus, the reaction can be stopped at the mono-, di-, or tricyano stage merely by limiting the amount of cyanogen chloride. Tricyanocyclopentadienide can be cyanated further to tetra- and pentacyanocyclopentadienide[3] but a Friedel–Crafts catalyst is required. A potassium or tetraalkylammonium salt of each cyanocyclopentadiene was isolated and characterized. Thus, the complete series (i) of cyanated cyclopentadienides is available for study. No products resulting from cyanation twice on the same carbon were isolated. In general, cyanocyclopentadienes form white salts with stability increasing gradually from the unstable monocyano-[4] to the very stable pentacyanocyclopentadienide. They undergo classical aromatic electrophilic substitution reactions; the fewer the cyano groups, the greater the reactivity.[5]



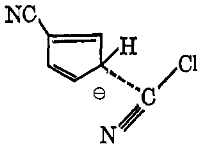
8 9 10 11 12 (i)

**Isomer Distribution.** The ratio of 1,2 (**10**) to 1,3 isomer (**9**) in the dicyano product, determined by nmr, is about 6:1. Nmr was also used to differentiate between the two isomers. The 3,4 hydrogens have a coupling constant of 4.0 cps for the 1,2 isomer (**10**), and the 2,4 hydrogens have 2.1 cps for the 1,3 isomer (**9**). The hydrogen between the two nitrile groups in the 1,3 isomer is deshielded more than any of the other hydrogens in either ion and appears at $\tau$ 3.41.

The ratio of 1,2,3 (**3**) to 1,2,4 isomer (**2**) in tricyanated cyclopentadiene is about 2:1. Salts of the 1,2,4 isomer were less soluble than the corresponding salts of the 1,2,3 isomer. The 1,2,4 isomer's proton resonance occurred at lower field than the 1,2,3 isomer's ($\tau$ 3.33 *vs.* $\tau$ 3.73) because of the greater deshielding from two adjacent nitrile groups in the former. In addition, the hydrogen out-of-plane vibration in the infrared of the 1,2,3 isomer (two adjacent hydrogens) was at longer wavelength (13.47 $\mu$) than the corresponding band for the 1,2,4 isomer (12.33 $\mu$) with no adjacent hydrogens. The larger amount of isomers with adjacent nitrile groups in both the dicyano and tricyano compounds reflects a lower transition state energy for substitution next to a cyano group (**13**) (conjugated) *vs.* nonadjacent substitution (**14**) (cross conjugated).[6]



13



14

---

[1] C. R. Hauser, *et al.*, *J. Am. Chem. Soc.*, **85**, 3884 (1963), use methyl benzoate and excess sodium hydride to dibenzoylate acetylacetone on its terminal methyl groups. C. R. Hauser, *et al.*, *J. Org. Chem.*, **29**, 2329 (1964), report a similar dibenzoylation of dimethyl sulfone.

[2] J. K. Williams, E. L. Martin, and W. A. Sheppard, *ibid.*, **31**, 919 (1966), have shown that arylacetonitriles can be converted to aryltricyanomethyl compounds by cyanogen chloride and sodium hydride.

[3] O. W. Webster, *J. Am. Chem. Soc.*, **87**, 1820 (1965).

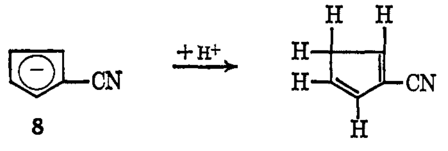
[4] (a) V. Grignard and G. Coulot, *Compt. Rend.*, **158**, 1763 (1914); (b) D. Peters, *J. Chem. Soc.*, 1832 (1960).

[5] A study of the chemistry of these anions is under way and will be reported as the work progresses.

[6] S. McLean and P. Haynes, *Tetrahedron*, **21**, 2341 (1965), found similar predominance of 1,2 over 1,3 isomer, and 1,2,3 over 1,2,4 isomer in the polymethylation of cyclopentadienide.

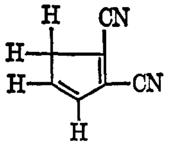
**Position of Protonation.** The position for protonation of mono-, di-, and tricyanocyclopentadienides was determined by nmr studies of solutions in trifluoroacetic acid.

Surprisingly, cyanocyclopentadienide (**8**) is protonated mainly at the cross-conjugated 3 position rather than at the 2 position. This may be the result of kinetic rather than thermodynamic[7] control since the acidities of monocyanocyclopentadiene and trifluoroacetic acid differ greatly.

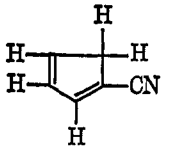


**8** **15**

Cyanocyclopentadiene can be isolated by distillation but it quickly dimerizes.[4] The nmr spectrum of protonated cyanocyclopentadienide is similar to that of **16**



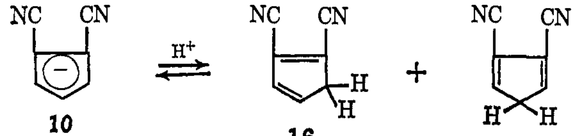
**16**



**17**

with one additional peak at $\tau$ 2.49 due to the replacement of the 1-cyano group of **16** with hydrogen. The experimental spectrum agrees with a computer-calculated spectrum of **15** rather than **17**.

1,2-Dicyanocyclopentadienide (**10**) is protonated with equal ease at positions 3 and 4. The nmr spectrum



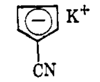
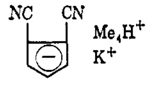
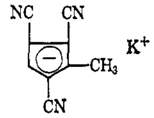
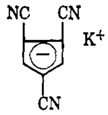
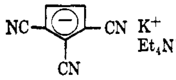
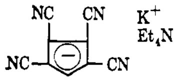
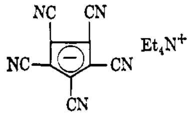
**10** **16** **18**

of the dicyanocyclopentadiene **16** consists of a weak–strong–strong–weak pattern in the vinyl region and a triplet in the allylic region, while that of **18** consists of a triplet in the vinyl region and a triplet in the allylic region.

The individual p$K_a$ values of these cyclopentadienes can be calculated from the observed p$K_a$ of their mixture (Table I), using the expression[8]

$$pK_a^{\text{acid }1} = pK_a^{\text{obsd}} - \log\left(1 + \frac{[\text{acid } 2]}{[\text{acid } 1]}\right)$$

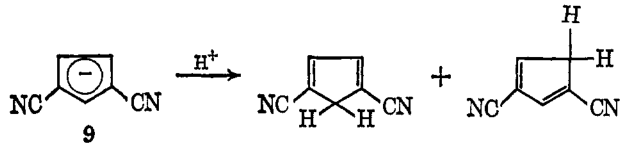
**Table I.** p$K_a$ Values of Cyanocyclopentadienes Measured in Water and in $CH_3CN$[a]

| Conjugate base | | p$K_a^{H_2O}$ | p$K_a^{CH_3CN}$ | p$K_a^{H_2O}$ calcd[c] |
|---|---|---|---|---|
|  | (**1**) | 15[b] | | |
|  | (**8**) | 9.78 | | |
|  | (**10**) | 2.52 | | |
|  | (**9**) | 1.11 | 10.17<br>10.17 | 1.1 |
|  | (**5**) | | 3.40 | −5.7 |
|  | (**2**) | | 3.00 | −6.1 |
|  | (**3**) | | 1.44<br>1.99 | −7.8<br>−7.2 |
|  | (**11**) | | ~0.0<br>~0.2 | −9.1<br>−8.9 |
|  | (**12**) | | <−2 | <−11 |
| $HClO_4$ | | | 1.83 | −7.3<br>−6.7[a] |

[a] p$K_a$ values in water were determined spectroscopically. The p$K_a$ values in acetonitrile were measured by the method of J. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **83**, 3927 (1961). [b] See ref 7, p 19. [c] To get a continuous although possibly not reliable scale, which could be dovetailed with Boyd's scale (R. H. Boyd, *J. Am. Chem. Soc.*, **83**, 4288 (1961); R. H. Boyd and C. H. Wang; *ibid.*, **87**, 430 (1965); and R. H. Boyd, *J. Phys. Chem.*, **67**, 737 (1963)), the p$K_a$ values of the cyanocyclopentadienides we could not measure in water were calculated by subtracting 9.1 from the p$K_a$ value in acetonitrile. This value was obtained from the p$K_a$ of 1,2-dicyanocyclopentadienide which was measured in both solvents.

The p$K_a$ of **16** (which equals that of **18**), calculated from the observed p$K_a$ (1.11) is 0.81.

1,3-Dicyanocyclopentadienide (**9**) is protonated on position 2 and position 4 in about a 10:1 ratio. Thus, the p$K_a$ of **19** is 2.40, and the p$K_a$ of **20** is 1.40. The



**9** **19** **20**

---

(7) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 204 ff.

(8) The relationship is readily derived.

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$pK_a = pH - \log\frac{[A^-]}{[HA]}$$

At half-neutralization

$$[A^-] = [HA]$$

and

$$pK_a = pH$$

but where two acids are present at half-neutralization

$$[A^-] = [HA'] + [HA'']$$

and

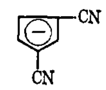
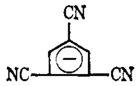
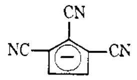
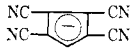
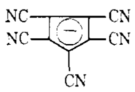
$$pK_a' = pH - \log\frac{[A^-]}{[HA']}$$

since $pH = pK_a^{\text{obsd}}$

$$pK_a' = pK_a^{\text{obsd}} - \log\frac{[HA'] + [HA'']}{[HA']}$$

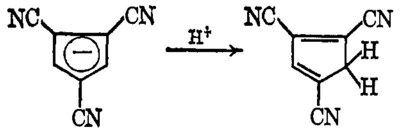
$$= pK_a^{\text{obsd}} - \log\left(1 + \frac{[HA'']}{[HA']}\right)$$

**Table II.** Ultraviolet Spectra of Cyanocyclopentadienides

| Cyclopentadienide | Cation | Solvent | $\lambda_{max}$, m$\mu$ (log $\epsilon$) |
|---|---|---|---|
|  | $K^+$ | $H_2O$ | 264 (4.20) |
| | Conjugate acid | $H_2O$ | 268 (3.90) |
|  | $Pr_4N^+$ | $CH_3CN$ | 224 (4.51), 273 (4.35), 277 (4.36) |
| | Conjugate acid | $CH_3CN$ | 226 (3.35), 243 (3.45), 278 (4.07), 292 (3.71) |
| | Conjugate acid | $H_2O$ | 279 (4.07), 286 (4.06), 298 (3.80) |
| | $K^+$ | $H_2O$ | 218, 274 (4.32) |
|  | $Me_4N^+$ | $H_2O$ | 267 (4.11), 283 (4.16) |
| | Conjugate acid | $H_2O$ | 290 (3.59) |
| | $Pr_4N^+$ | $CH_3CN$ | 265 (4.13), 282 (4.21) |
|  | $K^+$ | $CH_3CN$ | 236 (4.49), 267 (3.75) |
| | Conjugate acid | $CH_3CN$ | 283 |
| | $Pr_4N^+$ | $CH_3CN$ | 236 (4.78), 265 (4.05) |
|  | $K^+$ | $CH_3CN$ | 220 (4.35), 288 (4.27), 298 (4.26) |
| | $Et_4N^+$ | $CH_3CN$ | 220, 288, 298 |
|  | $Et_4N^+$ | $CH_3CN$ | 237 (4.63), 244 (4.75), 287 (4.13), 298 (4.16) |
|  | $Et_4N^+$ | $CH_3CN$ | 246 (4.60), 255 (4.98), 281 (4.04), 291 (4.01) |

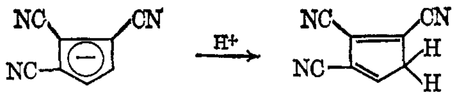
nmr spectrum of **19** consists of a triplet in the vinyl region and a triplet in the allylic region. The cyclopentadiene **19** was isolated in low yield as a crystalline solid, mp 119–121°.

A proton adds to one of the positions already possessing a hydrogen in 1,2,4-tricyanocyclopentadienide (**2**). The nmr spectrum consists of two peaks, one in the vinyl region and one in the allylic region with an area ratio of 1:2.



**2** **21**

1,2,3-Tricyanocyclopentadienide (**3**) is not completely protonated in $CF_3CO_2H$ solutions. The allylic and vinylic proton peaks in the nmr are about equal in area and are broad (proton exchange). When a small amount of $H_2SO_4$ is added, the peaks become sharp, and the ratio of allylic to vinylic hydrogen is 2:1.



**3** **22**

**Acidities of Cyanocyclopentadienides.** The p$K_a$ values of a number of cyanocyclopentadienes in water and in acetonitrile are compared in Table I.[9] It is noteworthy that tricyanocyclopentadiene is a stronger acid than perchloric acid. The 1,3-dicyano isomer (**9**) is a stronger base (1.4 p$K_a$ units) than the 1,2 isomer (**10**), and the 1,2,4-tricyano (**2**) is a stronger base (1.6 p$K_a$ units) than the 1,2,3 isomer (**3**). One might expect the delocalization of the charge to adjacent nitrile groups to decrease their respective electron-withdrawing ability and consequently provide ring positions of higher electron density (more basic) for protonation. However, the cyclopentadienides with separated nitrile groups can be protonated to form cyclopentadienes with cyano groups at the ends of the diene system. Since this is no doubt a more stable system than the cross-conjugated cyanocyclopentadienes which must result from protonation of the 1,2 and 1,2,3 isomers, there is less driving force for ionization in the former; *i.e.*, they are weaker acids.

**Ultraviolet Spectra.** The ultraviolet spectra of cyanocyclopentadienides show remarkable little variation over the series (see Table II). All of the cyanocyclopentadienides absorb in the 200–300-m$\mu$ range.

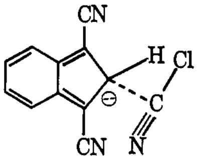
**Methyltetracyanocyclopentadienide.** The structure of 3-methyl-1,2,4-tricyanocyclopentadienide from cyanation of methylcyclopentadienes follows from the position of the ring proton in the nmr spectrum ($\tau$ 3.43) which has been deshielded from two adjacent nitrile groups (compare with 1,2,4-tricyanocyclopentadienide ($\tau$ 3.33)).

The methyltricyanocyclopentadienide **5** was cyanated further with cyanogen chloride and aluminum chloride to give methyltetracyanocyclopentadienide. Its nmr methyl absorption is about in the same place as that of toluene.

---

(9) For comparison with the acidities of other cyanocarbon acids see Boyd in footnote *c* of Table I.

**Cyanation of Indene.** In the case of indene, the third cyano group is introduced on a carbon already bearing a nitrile rather than on the vacant position, no doubt because cyanation on the 2 position would require a high-energy *o*-quinodimethan-type transition state (**23**).



**23**

## Experimental Section

**Potassium Cyanocyclopentadienide (8).** To a suspension of sodium hydride (54.5 g, 2.26 moles, dispersed in mineral oil) in 1,2-dimethoxyethane (500 ml) was added (3 hr) cyclopentadiene (82 ml, 1.02 moles) at room temperature. Hydrogen (30 l.) was evolved. The mixture was stirred at room temperature, and cyanogen chloride[10] (60.0 g, 0.97 mole) was added over 3 hr. After 1 day, the reaction mixture was filtered, and the filtrate was concentrated to dryness under reduced pressure. The residue was dissolved in water (500 ml), and $H_2SO_4$ (200 ml, 6 *N*) was added. The crude cyanocyclopentadiene was taken up in ethyl acetate and was distilled. Considerable cyanocyclopentadiene dimer was present since a pot temperature of 150–170°, the cracking temperature of the dimer,[4b] was necessary to maintain a head temperature of 49–55° (4 mm). Cyanocyclopentadiene (23.60 g, 26% yield) was collected. A center cut was analyzed.

*Anal.* Calcd for $C_6H_5N$: C, 79.1; H, 5.53; N, 15.4. Found: C, 78.9; H, 5.75; N, 15.3.

Although the product was quickly cooled, its nmr spectrum indicated it was over 50% dimer. The partially dimerized cyanocyclopentadiene was stirred with $K_2CO_3$ (20 g) in acetonitrile (200 ml) for 4 hr. The solution was filtered and concentrated to dryness, and the residue was washed with ether. Potassium cyanocyclopentadienide (5.0 g) remained. An analytical sample, mp 200.5–202.5°, was obtained by three precipitations from acetonitrile with ether; $\lambda_{\max}^{\mathrm{KBr}}$ 3.21, 4.54, 4.57, 6.86, 7.40, 7.87, 9.52, 9.65, 10.85, 12.15, and 13.64 $\mu$.

*Anal.* Calcd for $C_6H_4NK$: C, 55.7; H, 3.10; N, 10.9. Found: C, 56.0; H, 3.35; N, 10.7.

The nmr spectrum of the anion in acetonitrile was a 20-line AA′BB′ pattern centered at $\tau$ 4.18 with 31.5 cps between the first and last peaks. In trifluoroacetic acid the anion was completely protonated; the nmr spectrum showed peaks at $\tau$ 2.49, 3.19, and 6.59; relative intensities, 1:2:2. The $\tau$ 2.49 peak is a poorly resolved triplet ($J$ = ~1.5 cps). The peak at $\tau$ 3.19 is a poorly resolved weak–strong–strong–weak pattern with about 16 cps between the weak peak and 7 cps between the strong peaks. Each peak was in turn split into triplets ($J$ = ~1 cps). The peak at $\tau$ 6.59 has a shoulder on its high-field side indicating the presence of a small amount of another isomer.

**Dicyanocyclopentadienides.** A suspension of sodium hydride (187 g, 7.81 moles dispersed in mineral oil) in 1,2-dimethoxyethane (1500 ml) was cooled to 0°, and cyclopentadiene (165 ml, 2.00 moles) was added (3 hr). Hydrogen (55 l.) was evolved. Cyanogen chloride (250 g) was then condensed into the system (8 hr). Additional hydrogen (100 l.) was evolved. The solution contained mostly sodium 1,2-dicyanocyclopentadienide and sodium 1,3-dicyanocyclopentadienide in about a 6:1 ratio, as indicated by its nmr spectrum. The reaction mixture was filtered, and the filtrate was concentrated to dryness.

**Tetramethylammonium 1,2-Dicyanocyclopentadienide (10).** Tetramethylammonium 1,2-dicyanocyclopentadienide was isolated by addition of $Me_4NCl$ (200 g) to an aqueous solution (300 ml of water) of the crude reaction product above. The crude salt which precipitated was dissolved in methylene chloride (3 l.), and the solution was concentrated to dryness. A solution of the residue in methylene chloride (500 ml) was cooled to −75°, and the tetramethylammonium 1,2-dicyanocyclopentadienide (56.0 g) which crystallized was collected on a filter and dried. An analytical sample was recrystallized three times from methylene chloride, mp 97–99°; $\lambda_{\max}^{\mathrm{KBr}}$ 3.30, 4.57, 6.71, 6.97, 7.33, 7.76, 8.25, 8.95, 9.50, 10.55, and 14.02 $\mu$.

*Anal.* Calcd for $C_{11}H_{15}N_3$: C, 69.8; H, 7.99; N, 22.2. Found: C, 70.9; H, 8.02; N, 21.7.

The nmr spectrum in acetonitrile has a doublet at $\tau$ 3.71 and a triplet at 4.24 with relative intensity 2:1 ($J$ = 4.0 cps). The anion was protonated by dissolution in trifluoroacetic acid. The nmr spectrum of the solution had a triplet at $\tau$ 2.4 ($J$ = 1.3 cps), and a weak–strong–strong–weak pattern centered at 3.1 with 22 cps between the two weak peaks and 11 cps between the two strong peaks. Each peak was in turn split into triplets ($J$ = 1.3 cps). The allylic position contained two overlapping triplets, $\tau$ 6.23 and 6.30 ($J$ = 1.2 cps). The area of the triplet in the vinyl region about equaled the area under the weak–strong–strong–weak peaks.

**Tetrapropylammonium 1,2-Dicyanocyclopentadienide (10).** Tetrapropylammonium 1,2-dicyanocyclopentadienide was prepared by treatment of an aqueous solution of tetramethylammonium salt with tetrapropylammonium bromide. An analytical sample, mp 96–97°, was obtained by recrystallization from water two times; $\lambda_{\max}^{\mathrm{KBr}}$ 3.35, 3.46, 4.57, 6.76, 6.96, 7.35, 8.27, 8.52, 8.97, 9.55, 10.15, 10.31, 11.44, 11.75, 13.30, and 13.78 $\mu$.

*Anal.* Calcd for $C_{19}H_{31}N_3$: C, 75.7; H, 10.37; N, 13.9. Found: C, 75.3; H, 10.13; N, 13.8.

**1,3-Dicyanocyclopentadiene (19).** 1,3-Dicyanocyclopentadiene was isolated from 5.0 g of the crude reaction product from another run by chromatography on acid alumina with ethyl acetate–ether wash. The first product to be eluted was 1,3-dicyanocyclopentadiene (0.45 g). An analytical sample, mp 119–121°, was prepared by recrystallization from benzene and then carbon tetrachloride; $\lambda_{\max}^{\mathrm{KBr}}$ 3.22, 3.44, 4.50, 7.32, 8.80, 11.05, and 11.73 $\mu$.

*Anal.* Calcd for $C_7H_4N_2$: C, 72.4; H, 3.47; N, 24.1. Found: C, 72.1; H, 3.36; N, 23.5.

Its nmr spectrum in $CDCl_3$ had two triplets at $\tau$ 2.75 and 6.32 ($J$ = 1.6 cps). Extraneous peaks with a total integrated intensity of about $^1/_{10}$th the intensity of the combined triplet areas were present.

**Potassium 1,3-Dicyanocyclopentadienide (9).** Potassium 1,3-dicyanocyclopentadienide was produced when a small amount of 1,3-dicyanocyclopentadiene was stirred with a suspension of $K_2CO_3$ in acetonitrile (2 hr); $\lambda_{\max}^{\mathrm{Nujol}}$ 4.57, 4.59, 6.85, 7.46, 8.85, 9.00, 9.52, 10.52, 12.21, 13.75, and 13.93 $\mu$; nmr ($CH_3CN$) showed a triplet at $\tau$ 3.41 and a doublet at 3.92 with relative intensities 1:2 ($J$ = 2.1 cps).

**Tetrapropylammonium 1,3-Dicyanocyclopentadienide (9).** Tetrapropylammonium 1,3-dicyanocyclopentadienide was prepared by treatment of an aqueous solution of the potassium salt with tetrapropylammonium bromide. An analytical sample, mp 115–116°, was obtained by recrystallization from water three times; $\lambda_{\max}^{\mathrm{KBr}}$ 3.35, 3.45, 4.58, 6.54, 6.70, 6.75, 6.90, 7.19, 7.88, 8.79, 10.27, 10.58, 12.66, 13.20, and 14.35 $\mu$.

*Anal.* Calcd for $C_{19}H_{31}N_3$: C, 75.7; H, 10.36; N, 13.9. Found: C, 75.9; H, 10.31; N, 14.0.

**Tricyanocyclopentadienide (2, 3).** Cyclopentadiene (32.8 ml, 0.397 mole) was added dropwise (1 hr) to a suspension of 80.0 g (1.78 moles) of NaH–mineral oil (54.5% NaH) in 1 l. of 1,2-dimethoxyethane maintained at room temperature. The mixture was cooled to 0°, and 100 g (1.63 moles) of cyanogen chloride was slowly condensed into the system (3 hr). A Dry Ice cold finger was used to trap ClCN entrained with the hydrogen which smoothly evolved. After addition of the ClCN, the reaction mixture was slowly heated to reflux (2 hr) and then was cooled to room temperature. A total of 39 l. (1.59 moles) of $H_2$ was evolved.

The reaction mixture was filtered, and the filtrate was concentrated to dryness. The residue was dissolved in 400 ml of water and was washed with toluene to remove mineral oil. To remove colored impurities and dissolved toluene, the water solution was then treated with 10 g of powdered zinc and was boiled until its boiling point reached 99°. The solution was treated with carbon black and was filtered. Potassium chloride (120 g) was dissolved in the filtrate, and the precipitate which formed was collected and dried. The dry precipitate was extracted with acetonitrile, and the extract was concentrated to dryness. There remained 16.0 g (22% yield) of potassium 1,2,4-tricyanocyclopentadienide. An analytical sample, mp 380–383°, was prepared by recrystallization twice from water; $\lambda_{\max}^{\mathrm{KBr}}$ 3.22, 4.54, 6.18, 6.17, 6.90, 7.45, 8.53, 8.95, 10.40, 12.06, and 12.33 $\mu$; nmr ($CH_3CN$) showed a single peak at $\tau$ 3.33.

---

[10] Cyanogen chloride is an extremely toxic gas. All operations were therefore conducted in a fume hood. Cyanogen chloride was passed into the reaction system as a gas and maintained there by an efficient ice–water condenser.

*Anal.* Calcd for $C_8H_2N_3K$: C, 53.7; H, 1.12; N, 23.5. Found: C, 53.6; H, 1.07; N, 23.6.

After isolation of potassium 1,2,4-tricyanocyclopentadienide, the KCl-saturated solution was extracted with 500 ml of ethyl acetate. On concentration of the extract to dryness, there remained 36.0 g (50% yield) of potassium 1,2,3-tricyanocyclopentadienide. Althrough dark impurities were present, a comparison of the infrared of this product with that of the analytical sample showed that the isolated product was substantially pure. An analytical sample, mp 286–287° dec, was prepared by chromatography on Woelm alumina (neutral, activity I) with 1:1 ethyl acetate–ether as wash, followed by recrystallization two times from saturated KCl–water. The analytical sample was separated from occluded KCl by extraction with ethyl acetate; $\lambda_{\max}^{\mathrm{KBr}}$ 4.56, 6.80, 7.33, 8.31, and 13.47 $\mu$; nmr ($CH_3CN$) showed a single peak at $\tau$ 3.73.

*Anal.* Calcd for $C_8H_2N_3K$: C, 53.7; H, 1.12; N, 23.5. Found: C, 53.5; H, 1.16; N, 23.5.

**Tetraethylammonium 1,2,3-Tricyanocyclopentadienide (3).** A solution of potassium 1,2,3-tricyanocyclopentadiene in water was treated with excess tetraethylammonium chloride. Tetraethylammonium 1,2,3-tricyanocyclopentadienide crystallized. A sample for analysis (mp 68–69.5°) was recrystallized from ethanol.

*Anal.* Calcd for $C_{16}H_{22}N_4$: C, 71.1; H, 8.20; N, 20.7. Found: C, 71.0; H, 8.18; N, 20.8.

**Tetracyanocyclopentadienide (11).** Cyanogen chloride (2.0 ml, 39.1 mmoles, measured as liquid at 0°) was condensed into a solution of 1.00 g (5.54 mmoles) of dry potassium 1,2,3-tricyanocyclopentadienide and 0.49 g (3.67 mmoles) of $AlCl_3$ in 50 ml of acetonitrile at 0°. The solution was stirred overnight at room temperature and then was concentrated to dryness. The residue was dissolved in hot water, and 2.0 g of $Et_4NCl$ was added. Tetraethylammonium tetracyanocyclopentadienide (1.00 g, 60% yield), mp 125–130° (lit.[3] mp 130–132°), was collected on a filter and dried. The infrared spectrum agreed with that of a sample prepared from diazotetracyanocyclopentadienide.[3]

Into a suspension of 1.00 g (5.54 mmoles) of potassium 1,2,4-tricyanocyclopentadienide in 25 ml of dry acetonitrile at 0° was condensed 2.0 ml (39.1 mmoles) of cyanogen chloride (measured at 0°). $AlCl_3$ (0.34 g, 3.67 mmoles) was added, and the mixture was stirred at room temperature for 24 hr. The resulting dark solution was concentrated to dryness, and the residue was dissolved in 100 ml of hot water. $Et_4NCl$ (2.0 g) was added, and the warm solution was filtered. Tetraethylammonium tetracyanocyclopentadienide, 0.82 g (50% yield), remained on the filter. The identity of the product was confirmed by its infrared spectrum.

**Tetra- and Pentacyanocyclopentadienides (11, 12).** Crude silver tricyanocyclopentadienide containing both 1,2,3 and 1,2,4 isomers (550 g) was suspended in acetonitrile (3 l.), and $AlCl_3$ (114 g) was added. The mixture was cooled to 0°, and ClCN (256 g) was allowed to condense into the solution. The mixture was stirred for 2 days and was filtered. The filtrate was concentrated to about 1 l., diluted with 2 l. of ice–water, and filtered again. The filtrate was then treated with $Et_4NCl$ (165 g), and the mixture of tetraammonium tetra- and pentacyanocyclopentadienide (307 g) which precipitated was collected and air dried. Its ultraviolet spectrum indicated that the product was about 80% tetraethylammonium tetracyanocyclopentadienide and 20% tetraethylammonium pentacyanocyclopentadienide. The two products were separated by fractional recrystallization in ethanol (the pentacyano derivative is the least soluble) and were identified by their infrared and ultraviolet spectra.

**Potassium 1,2,4-Tricyano-3-methylcyclopentadienide (5).** A suspension of sodium hydride (160 g, 6.97 moles, dispersed in mineral oil) in 1,2-dimethoxyethane (1500 ml) was cooled to 0°, and methylcyclopentadiene (200 ml, 2.00 moles) was added dropwise (3 hr). Hydrogen (55 l.) was evolved. Then cyanogen chloride (250 g, 4.09 moles) was condensed into the system at 0–20° (8 hr). The nmr spectrum of the solution indicated that it contained mainly sodium 1,3-dicyano-2-methylcyclopentadienide (absorption at $\tau$ 4.11) and sodium 1,2-dicyano-3-methylcyclopentadienide (absorption at $\tau$ 3.84, 3.91, 4.46, and 4.52).

To the above mixture was added NaF powder (250 g) as a proton acceptor. After stirring overnight at room temperature, the mixture's nmr spectrum showed that the major soluble product was sodium 1,2,4-tricyano-3-methylcyclopentadienide.

The reaction mixture was filtered, and the filtrate was concentrated to dryness under reduced pressure. The residue was taken up in water (1.5 l.) and was washed with toluene to remove nonionic material. The water layer was then treated with ethyl acetate. The ethyl acetate extract was concentrated to dryness. The residue of crude tricyano product weighed 242 g. A sample of pure potassium 1,2,4-tricyano-3-methylcyclopentadienide (mp 285–287°) was isolated by dilution of a concentrated $CH_3CN$ solution of crude product with an equal amount of ether. The precipitate was chromatographed on neutral alumina (acetonitrile wash), and was recrystallized three times from water; $\lambda_{\max}^{\mathrm{KBr}}$ 3.55, 3.45, 3.50, 4.55, 6.32, 6.74, 7.12, 8.73, 9.00, 9.24, 11.25, 11.50, and 12.71 $\mu$; nmr ($CH_3CN$) showed a single peak at $\tau$ 3.43 (methyl group obscured by solvent).

*Anal.* Calcd for $C_9H_4N_3K$: C, 56.0; H, 2.09; N, 21.7. Found: C, 55.9; H, 2.30; N, 21.7.

**Potassium Methyltetracyanocyclopentadienide.** A solution of crude potassium tricyanomethylcyclopentadienide (236 g) in acetonitrile (1500 ml) was dried by passing through a column of alumina. The dried solution was cooled in an ice–water bath, and $AlCl_3$ (87 g) was added in 15-g portions. Cyanogen chloride (115 g) was condensed into the system (3 hr).

The solution was stirred at room temperature for 2 days and was then concentrated to dryness under reduced pressure. The residue was extracted with 1 l. of water. Potassium methyltetracyanocyclopentadienide which crystallized (54 g, 12% yield) was collected and dried. To get an analytical sample (mp 333–334°), it was chromatographed on neutral alumina with acetonitrile wash and was recrystallized from dioxane; $\lambda_{\max}^{\mathrm{KBr}}$ 4.50, 6.85, and 7.13 $\mu$; nmr ($CF_3CO_2H$) showed a single peak at $\tau$ 7.59 (no protonation was occurring).

*Anal.* Calcd for $C_{10}H_3N_4K$: C, 55.0; H, 1.39; N, 25.7. Found: C, 55.0; H, 1.51; N, 25.7.

**1,1,3-Tricyanoindene (7).** To a suspension of sodium hydride (6.2 g, 0.26 mole, dispersed in mineral oil) in glyme (200 ml) was added indene (5.8 ml, 0.050 mole) at room temperature. After hydrogen evolution had stopped (1200 ml), the mixture was cooled to 0°, and cyanogen chloride (10.0 ml, 0.198 mole) was added (4 hr). The reaction mixture was allowed to stand over the weekend and filtered, and the filtrate was concentrated to dryness. The residue was extracted with ether, and the extract was diluted with petroleum ether (bp 38–53°). 1,1,3-Tricyanoindene (2.63 g, 27% yield) crystallized. An analytical sample (mp 149–151°) was prepared by recrystallization from methylcyclohexane and then cyclohexane. The substance was neutral to litmus; $\lambda_{\max}^{\mathrm{KBr}}$ 3.22, 4.43, 6.00, 6.32, 6.78, 6.85, 7.43, 8.05, 9.30, 10.46, 12.05, 13.15, and 13.29 $\mu$; $\lambda_{\max}^{\mathrm{CH_3CN}}$ 292 m$\mu$ ($\epsilon$ 7800), 274 (9420), and 224 (32,000).

*Anal.* Calcd for $C_{12}H_5N_3$: C, 75.4; H, 2.64; N, 22.0. Found: C, 75.2; H, 2.89; N, 21.8.

**Acknowledgments.** The author thanks Miss Ellen Wallace and Dr. John Fok for determining the p$K_a$ values and Drs. R. E. Benson and W. A. Sheppard for much helpful discussion.