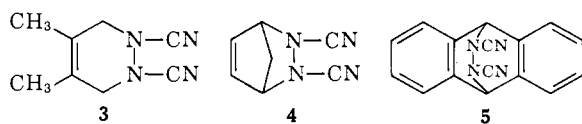
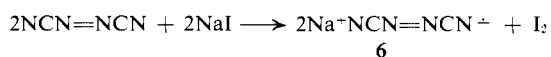


is formed in 3 days at room temperature (*Anal.* Calcd. for **5**: C, 74.4; H, 3.9; N, 21.7. Found: C, 75.2;



H, 4.1; N, 20.9). On heating at 120°, **5** reverts to **1** and anthracene.⁴

Azodicarbonitrile is reduced chemically or electrolytically to a stable anion radical. Sodium azodicarbonitrilide (**6**), prepared in 94% yield from **1** and sodium iodide in acetonitrile, is a bronze, explosive powder,



soluble and stable in water, methanol, and dilute base. *Anal.* Calcd. for **6**: C, 23.3; N, 54.4. Found: C, 23.2; N, 52.5; $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 222 (ϵ 5270), 372 (ϵ 4560), 525 $\text{m}\mu$ (ϵ 120); $\lambda_{\text{max}}^{\text{KBr}}$ 4.62 μ . Polarographic reduction of **1** to **6** is a reversible, one-electron process at $E_{1/2} + 0.40$ v. vs. s.c.e., *i.e.*, more facile than the reduction of tetracyanoethylene (+0.152 v.) or of tetracyanoquinodimethane (+0.127 v.).⁵ Molecular orbital calculations on **1** indicate an unfilled bonding orbital is present at +0.42 β . Electron spin resonance of **6** in acetonitrile shows 5 lines, each split to 5 lines, thus indicating two equivalent pairs of nitrogen atoms.

(4) J. Harley-Mason and J. C. W. Tims, *Proc. Chem. Soc.*, 345 (1963), report an analogous reaction, the formation of ethyl cyanoazofornate from its anthracene adduct.

(5) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).

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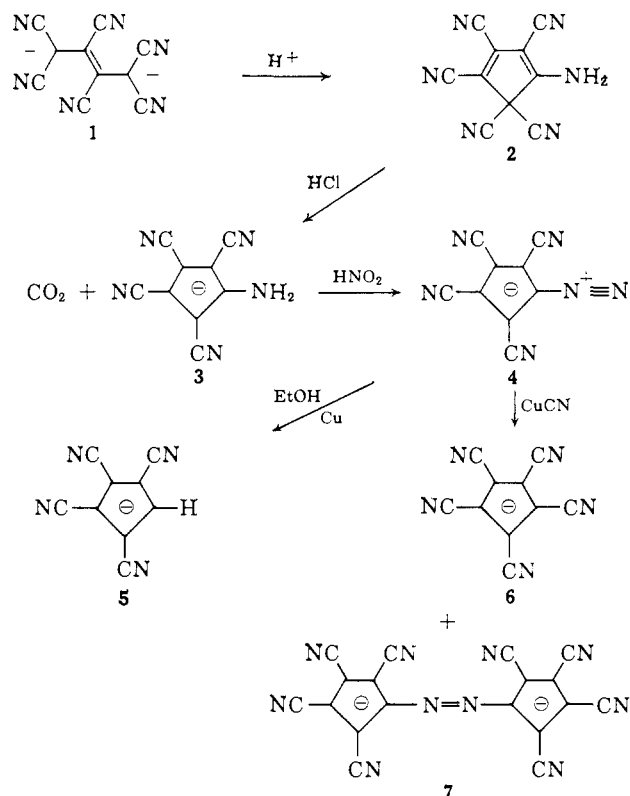
Diazotetracyanocyclopentadiene and Its Conversion to Tetracyanocyclopentadienide and Pentacyanocyclopentadienide

Sir:

We have synthesized diazotetracyanocyclopentadiene (**4**) from hexacyanobutenediide¹ (**1**) and used this "diazonium" compound to make the very stable tetra- and pentacyanocyclopentadienide anions **5** and **6**. Because of the marked stabilizing effect of the four cyano groups, the chemical properties of the "diazonium" group in diazotetracyanocyclopentadiene and the carbon-hydrogen bond in tetracyanocyclopentadienide parallel those of a benzene diazonium group and benzene carbon-hydrogen bonds. Thus, the aromaticity of the cyclopentadienide system can now be examined by classical chemical means.

In dilute aqueous acid, disodium hexacyanobutenediide cyclizes to 1-amino-2,3,4,5-pentacyanocyclopentadiene² (**2**), a bright yellow unstable solid, $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 413 $\text{m}\mu$ (ϵ 7000). One of the cyano groups at the 5-position

in **2** is hydrolyzed by concentrated hydrochloric acid at 15°, and the resulting carboxylic acid group spontaneously loses carbon dioxide to generate aminotetracyanocyclopentadienide (**3**), m.p. (tetraethylammonium salt) 126–127°. Its aqueous solutions are neutral, which indicates the tetracyanocyclopentadienidyl portion of the ion is withdrawing electrons from the amino group.



Diazotetracyanocyclopentadiene (**4**) results when aminotetracyanocyclopentadienide is diazotized under conditions ordinarily used to prepare aromatic diazonium compounds. Diazotetracyanocyclopentadiene, recrystallized from acetonitrile, is a light-yellow, water-insoluble solid which decomposes at ~200°. It does not appear to be shock sensitive. In view of its high dipole moment, 11.44 D., and chemical properties, which parallel aromatic diazonium compounds, a zwitterion structure is preferred.

Diazotetracyanocyclopentadiene reacts with cuprous cyanide to give pentacyanocyclopentadienide (**6**) and azotetracyanocyclopentadienide (**7**). Pentacyanocyclopentadienide salts are remarkably stable. For instance, the potassium salt can be heated at 400° in air without decomposition. Spectrophotometrically, we could not detect any protonation of the anion by perchloric acid in acetonitrile. The $\text{p}K_a$ of pentacyanocyclopentadiene in this solvent is therefore less than -2.³ For comparison, the $\text{p}K_a$ of sulfuric acid in acetonitrile is +7.25.⁴

Diazotetracyanocyclopentadiene is reduced by ethanol in the presence of copper powder to tetracyanocyclopentadienide (**5**), isolated as the tetraethylammonium salt, m.p. 130–132°. Its $\text{p}K_a$ in acetonitrile

(1) O. W. Webster, *J. Am. Chem. Soc.*, **86**, 2898 (1964).

(2) Satisfactory analytical results were obtained on all compounds.

(3) The $\text{p}K_a$ measurements were made by Dr. J. Fok.

(4) I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **83**, 3927 (1961).