

aromatic protons plus the low field olefinic proton), a styryl AB pattern (3.99 and 4.69 τ , $J_{AB} = 13.0$ c.p.s.), a higher field AB pattern (5.36 and 5.73 τ ; $J_{AB} = 5.0$ c.p.s.) due to the adjacent, non-equivalent bridgehead protons and the high field half of an AX system (5.64 τ , $J_{AX} = 9.7$ c.p.s.). A double resonance experiment identifies the low field olefinic proton as the other half of the AX system. Saturation of the low field olefinic proton (151 c.p.s. downfield from the doublet) collapsed the high field doublet to a sharp singlet. Reduction of IIIa gives a diol (VII) which shows all the expected physical properties including an olefinic doublet (4.33 τ , $J_{AX} = 10.7$ c.p.s.) due to the vinyl proton of the enol ether function and exchanges two protons on shaking with deuterium oxide. Attempted acid hydrolysis of the enol ether function in VII gives the ether VIII which exchanges only one proton and forms a monoacetate. Catalytic reduction of IIIa gives a novel dihydro derivative IX, 5.68 μ , $\lambda_{\text{max}}^{\text{EtOH}}$ 264 (12,290), 272 (11,440), 287 (infl., 2,900) and 297 $m\mu$ (1,520) in good yield. IX shows an exchangeable hydroxyl proton (5.84 τ), a styryl AB system (3.98 and 4.66 τ , $J_{AB} = 6.5$ c.p.s.) and an ABX pattern (6.40, 6.76 and 7.88 τ , $J_{AB} = 7.1$ c.p.s., $J_{AX} \sim 0$, $J_{BX} = 12.9$ c.p.s.).

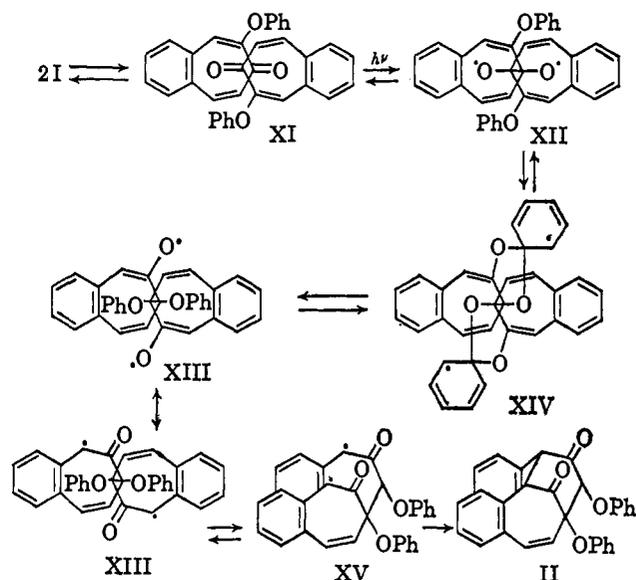
The dimers (II and III) appear to be derived formally from X rather than I. All attempts to trap X with dienophiles have failed. Dimer formation continues in the presence of dicarbomethoxyacetylene, maleic anhydride and tetracyanoethylene suggesting that dimerization does not involve X as an intermediate. Formation of II and III may be accounted for in the following manner. Complex formation between two molecules of I should lead to XI in which the ground state dipoles are properly oriented and the bulky phenoxy groups are on opposite sides of the complex.⁴ Excitation gives XII in which there is now a bond between the carbonyl carbons. An oxygen-oxygen phenyl shift analogous to previously observed carbon-oxygen phenyl shifts⁵⁻⁷ gives XIII via XIV. Rotation

(4) It is not necessary to assume complex formation in this mechanism. The same net result could be accomplished formally by addition of an excited molecule to a ground state molecule. 2-Phenoxy-4,5-benzotropone deviates significantly from Beer's law even in dilute (10^{-4} M) solution suggesting that complex formation does occur.

(5) H. Schmidt, H. Hochweber and H. von Halban, *Helv. Chim. Acta*, **30**, 1135 (1947), and references therein cited.

(6) G. W. Griffin and E. J. O'Connell, *J. Am. Chem. Soc.*, **84**, 4148 (1962).

(7) H. E. Zimmerman, H. G. C. Durr, R. G. Lewis and S. Bram, *ibid.*, **84**, 4149 (1962).



(180°) about the bond joining the two halves of the dimer gives XV which collapses to II. III may be produced by thermal rearrangement of dimer II molecules formed in a vibrationally excited state or by a separate photochemical process.⁸

Satisfactory analyses have been obtained for all new compounds.

Acknowledgment.—The authors acknowledge financial support of this investigation by grant CA-04253 from the National Institutes of Health, Public Health Service, and technical assistance by Miss Alice K. Peterson. The authors are indebted to Professor L. M. Jackman for stimulating discussion.

(8) It has been established that IIa is not derived from IIIa, but it has not been established that IIIa is derived from IIa.

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Tetracyanoethylene Oxide

Sir:

Unique reactivity has been uncovered for the previously unreported tetracyanoethylene oxide (I, TCNEO).¹ For example, TCNEO readily adds to olefinic, acetylenic, and aromatic systems to yield products derived from carbon-carbon cleavage of the epoxide molecule.

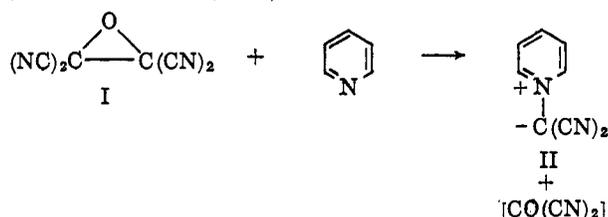
TCNEO, obtained in 65% yield by reaction of tetracyanoethylene with aqueous hydrogen peroxide in acetonitrile, is a colorless, sublimable compound, m.p. 177–178° (*Anal.* Calcd. for C₆N₄O: C, 50.00; N, 38.88; mol. wt., 144. Found: C, 50.00; N, 38.85, mass spectrum has parent peak at m/e 144). The compound shows no absorption in the ultraviolet, and the infrared spectrum (Nujol) is simple with absorption at 4.38, 7.68, 8.47, 8.66, 10.54 and 11.23 μ .

The strong electron-withdrawing character of the cyano groups is manifested in the ease with which TCNEO undergoes nucleophilic attack. Reaction with iodide ion gives cyanogen iodide and tricyanovinyl alcoholate.² With pyridine at 0°, the stable nitrogen

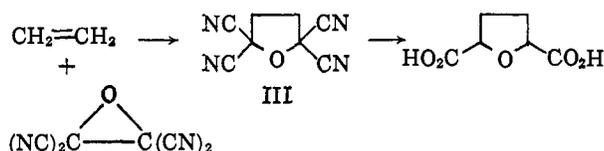
(1) Subsequent to our studies, we have learned that TCNEO has been isolated from ozonizations conducted in the presence of tetracyanoethylene (private communication from Prof. R. Criegee, Institut für Organische Chemie, Technische Hochschule, Karlsruhe, Germany).

(2) W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).

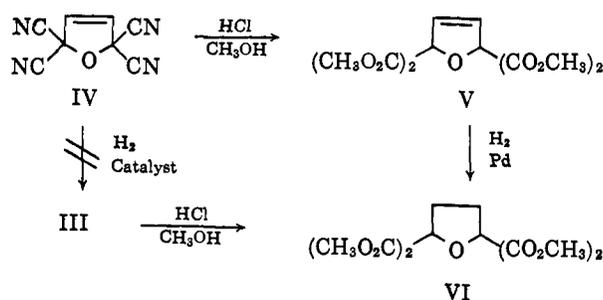
ylide II, m.p. 245–246°, is obtained in 80% yield. (*Anal.* Calcd. for $C_8H_5N_3$: C, 67.14; H, 3.52; N, 29.37; mol. wt., 143. Found: C, 67.30; H, 3.61; N, 29.43; mol. wt., 142).



The most striking reaction of TCNEO is the addition to olefinic and acetylenic compounds to give tetracyano-tetrahydro- and tetracyanodihydrofurans, respectively. Ethylene and TCNEO condense smoothly at 130° to give 2,2,5,5-tetracyanotetrahydrofuran (III), m.p. 107–108°, in 87% yield (*Anal.* Calcd. for $C_8H_4N_4O$: C, 55.84; H, 2.34; N, 32.56; mol. wt., 172. Found: C, 56.05; H, 2.50; N, 32.52; mol. wt., 184.) The ethylene adduct shows an unsplit proton resonance at 6.68 τ and is hydrolyzed with partial decarboxylation to the known tetrahydrofuran-*cis*-2,5-dicarboxylic acid.³

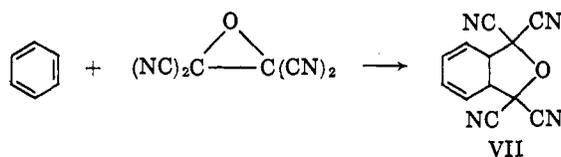


Under similar conditions, acetylene and TCNEO give 2,2,5,5-tetracyanodihydrofuran (IV), m.p. 160–161°, in 71% yield (*Anal.* Calcd. for $C_8H_2N_4O$: C, 56.50; H, 1.19; N, 32.96. Found: C, 56.73; H, 1.22; N, 32.54.)



It has not yet been possible to reduce IV to III catalytically, but IV has been converted to the corresponding tetraester V,⁴ m.p. 96.5–97°. Catalytic reduction of V gives the saturated ester VI,⁴ m.p. 103–104°, which is identical with that synthesized from III.

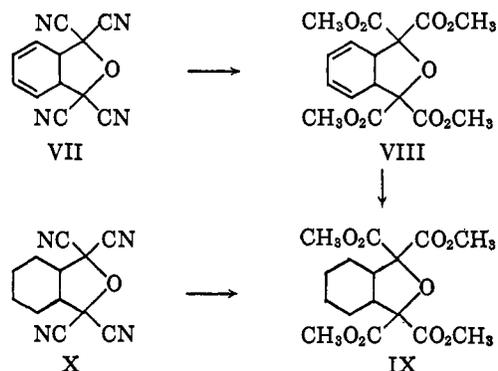
TCNEO also adds to aromatic systems, such as benzene and *p*-xylene, with surprising ease to form tetrahydroisobenzofurans.



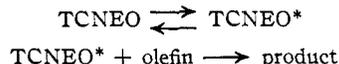
The monoadduct with benzene, 1,1,3,3-tetracyano-1,3,3a,7a-tetrahydroisobenzofuran (VII), m.p. 167–168° (*Anal.* Calcd. for $C_{12}H_8N_4O$: C, 64.84; H, 2.72; N, 25.21; mol. wt., 222. Found: C, 64.95; H, 2.87; N, 24.68; mol. wt., 228), is isolated in 35%

yield when TCNEO is heated in excess benzene at 130–150°.

The tetrahydroisobenzofuran VII shows an ultraviolet absorption spectrum typical of a 1,3-cyclohexadiene (λ_{max} 259 $m\mu$, ϵ 3800 in CH_3CN). The adduct VII is converted with hydrogen chloride-methanol to a tetraester VIII,⁴ m.p. 93.5–94.5°, that is reduced to a saturated tetraester IX,⁴ m.p. 114–115°. This latter product is identical with the tetraester derived from the adduct X of cyclohexene with TCNEO.



A kinetic study of the addition of TCNEO to styrene and to substituted stilbenes strongly indicates that the reaction involves preliminary promotion of TCNEO to an activated species. With a sufficiently reactive olefin, this step is rate-controlling.



Other polycyano olefins have also been epoxidized by hydrogen peroxide in acetonitrile with retention of the nitrile groups.⁵ The following oxides have been prepared by this method: phenyltricyanoethylene oxide, m.p. 78–80° (72% yield) (*Anal.* Calcd. for $C_{11}H_5N_3O$: C, 67.69; H, 2.57; N, 21.54. Found: C, 68.04; H, 2.89; N, 21.45), tricyanoethylene oxide, m.p. 76–77° (31% yield) (*Anal.* Calcd. for $C_5H_3N_3O$: C, 50.42; H, 0.85; N, 35.29. Found: C, 50.47; H, 0.90; N, 35.52), *t*-butyltricyanoethylene oxide, m.p. 44–45° (76% yield) (*Anal.* Calcd. for $C_9H_9N_3O$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.88; H, 5.41; N, 24.03) and 1,2-bis-(ethoxycarbonyl)-1,2-dicyanoethylene oxide, m.p. 61–70° (93% yield) (*Anal.* Calcd. for $C_{10}H_{10}N_2O_5$: C, 50.41; H, 4.23; N, 11.76. Found: C, 50.61; H, 4.25; N, 12.09). A catalytic amount of base, such as pyridine, may be used to increase the rate of epoxidation of these olefins.

(5) Epoxidation of α,β -unsaturated nitriles with alkaline hydrogen peroxide has previously led predominantly to the corresponding epoxyamide. See G. B. Payne and P. H. Williams, *J. Org. Chem.*, **26**, 651 (1961). Amide formation has been avoided by epoxidizing with an alkyl hydroperoxide [G. B. Payne, *ibid.*, **26**, 663 (1961)] or hypochlorite ion [D. H. Rosenblatt and G. H. Broome, *ibid.*, **28**, 1290 (1963)].

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A Stable Triplet State of Pentaphenylcyclopentadienyl Cation

Sir:

It is predicted by molecular orbital theory that cyclopentadienyl cation, or a derivative of it which retains the fivefold symmetry, could be a triplet in its ground state. Such a prediction is made for many other symmetric systems with $4n$ π -electrons, *e.g.* cyclobutadiene,

(3) A. C. Cope and W. N. Baxter, *J. Am. Chem. Soc.*, **77**, 393 (1955).

(4) Satisfactory analytical data have been obtained.