# The Reaction of Cyclopentadienylidenetriphenylphosphorane with Cyano-olefins

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EQUIMOLAR quantities of cyclopentadienylidenetriphenylphosphorane[1] (I) and tetracyanoethylene (IIa), when mixed in methylene chloride solution in the presence of a 20 molar excess of triethylamine, gave a quantitative yield of triphenyl-2-(1,2,2-tricyanovinylcyclopentadienylidene)phosphorane.† (III), m.p. 222—224°, $\nu_{max}$ (cm.$^{-1}$) (KBr), 2205s CN conj., 1510s C=C str., 1435s P–Ph;[2] $\lambda_{max}$ (EtOH) 462 m$\mu$ ($\epsilon$ 42,000); the n.m.r.‡ was consistent with (III) being the 2-tricyanovinyl isomer.

Compound (III) was an extremely weak base but addition of a large excess of 72% perchloric acid in glacial acetic acid to a methylene chloride solution of (III) gave $\lambda_{max}$ 372 m$\mu$. Assuming protonation occurs to give (V), the calculated value[3] is 369 m$\mu$. Attempts to isolate (V) by precipitation with ether resulted in regeneration of (III).

An equimolar mixture of (I) and tricyanovinyl chloride[4] (IIb) in methylene chloride reacted spontaneously (without the addition of base) to give (III), again quantitatively. However, an equimolar mixture of (I) and (IIa) in methylene chloride (no base) gave a product, $\lambda_{max}$ 482 m$\mu$ ($\epsilon$ 32,000), but attempts to isolate this material by chromatography resulted in decomposition, apparently to polymeric products. By removal of the solvent at −10° an orange, crystalline compound§ was obtained, $\lambda_{max}$ ($CH_2Cl_2$) 482 m$\mu$ ($\epsilon$ 32,000) unstable, $\lambda_{max}$ ($Me_2CO$) 478 m$\mu$ ($\epsilon$ 30,000) stable in dilute solution; $\nu_{max}$ (cm.$^{-1}$), 2195s CN conj., 2165, 2155m CN highly conj., 1535s C=C, 1440s P–Ph, 1410vs.

On the basis of the i.r. and u.v. data the compound was assigned structure (VI), with (VIb) as the major contributor to the resonance hybrid. Compound (VI) is the geometrical isomer of (III). Cyanide absorption in the i.r. at 2165 and 2155 cm.$^{-1}$ is analogous to that observed with sodium pentacyanoethanide,[5] and the absorption at 1535 cm.$^{-1}$ is

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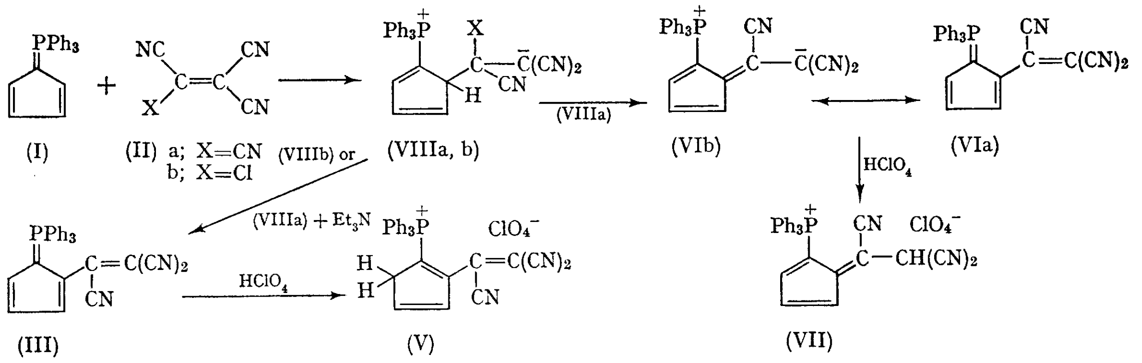
† Satisfactory elemental analyses obtained for C, H, N and P.

‡ All n.m.r. spectra relative to $Me_4Si$ except for $^{31}P$ spectra.

§ Elemental analysis for C, H, N, and P were unsatisfactory, giving variable results on the same sample.

attributed to the exocyclic double bond of (VIb). It is suggested that the very strong band at 1410 cm.$^{-1}$ is due to the carbon–carbon bond, C–$\bar{C}$(CN)$_2$ of (VIb). Owing to the instability of the compound in a variety of solvents at practical concentrations, no definitive information has yet been obtained from the n.m.r. spectrum.

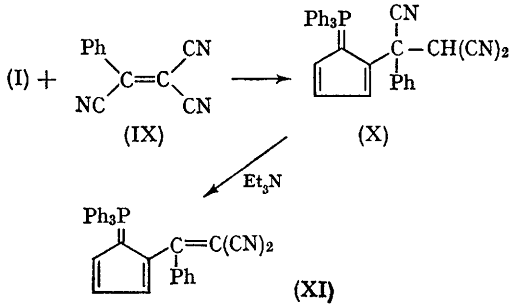


Compound (VI), in methylene chloride, was easily protonated (HClO$_4$, 72%), the product (VII) having $\lambda_{max}$ 430 m$\mu$ [calculated[3] for (VII) $\lambda_{max}$ 465 m$\mu$], isolated by precipitation with ether as pale yellow crystals, $\nu_{max}$ (cm.$^{-1}$), 2230, 2190w CN, 1590s C=C, 1080 (s and br) ClO$_4^-$; the n.m.r. [(CD$_3$)$_2$SO] was poorly resolved, probably due to proton exchange and consequently no unequivocal structure assignment could be made. However, the presence of weak, saturated cyanide absorption in the i.r. at 2230 cm.$^{-1}$ is consistent with (VII).

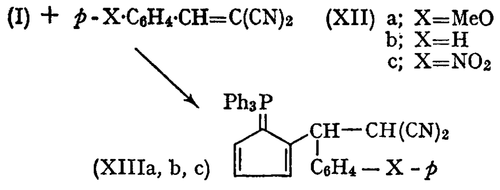
The suggested reaction scheme involves the formation of a betaine intermediate (VIIIa, b). In the presence of triethylamine, (VIIIa) eliminates hydrogen cyanide to give (III), also formed by the spontaneous elimination of hydrogen chloride from (VIIIb). Without triethylamine however, (VIIIa) loses hydrogen cyanide spontaneously to give (VI). A kinetic investigation is in progress in order to establish the factors controlling the formation of (III) or (VI).

Reaction of (I) with tricyanovinylbenzene[6] (IX) in methylene chloride at ambient temperature proceeds in a 1 : 1 molar ratio to give triphenyl-2-(1,2,2-tricyano-1-phenylethyl)cyclopentadienylidenephosphorane (X).†[7] The structure of (X) was assigned on the basis of i.r., u.v., and n.m.r. spectra, the latter showing a sharp singlet at $\tau$ 5·1 [C*H*(CN)$_2$]. In this case therefore, the betaine intermediate [equivalent to (VIIIa, b)] undergoes proton rearrangement to yield a stable substituted ylid. At present there is no evidence for a similar proton shift prior to elimination, in the reactions of (I) with (IIa) and (IIb).

Treatment of (X) in methylene chloride with triethylamine gave (XI), $\lambda_{max}$ (EtOH) 415 m$\mu$; the i.r. and n.m.r. spectra were consistent with the structure suggested.



Similarly, (I) reacts with *p*-substituted benzylidene malonitriles[8] (XIIa, b, c) in a 1 : 1 molar ratio to give (XIIIa, b, c),†[7] the structure being assigned on the basis of u.v., i.r., and $^1$H and $^{31}$P n.m.r. data.



Qualitatively, the rates increased in the order (XIIa < b < c) in parallel with the increasing electron affinity of the cyano-olefins, and a kinetic study is in progress in an attempt to correlate the rates of nucleophilic addition with the appropriate substituent constants. As expected, compounds (XIII a, b, c) were inert to an excess of triethylamine, there being no suitable leaving group on the α-carbon atom of (XIII).

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