Kinetics of Retro-cyanoethylation of Phosphonium Salts and the Question of Phosphole Aromaticity

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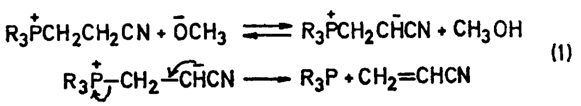
Summary Phospholium ion (**1**) is cleaved by sodium methoxide into 1,2,5-triphenylphosphole and acrylonitrile at a rate substantially greater than that observed for comparable phosphonium ions, a finding which is consistent with significant delocalization of the lone electron pair on phosphorus in phospholes.

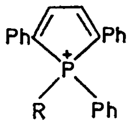
WHETHER phosphole may properly be regarded as an aromatic system akin to pyrrole and thiophen remains a subject of discussion[1] and controversy. Quin *et al.*,[2] noting that the n.m.r. and u.v. spectra of 1-methylphosphole point to extensive cyclic delocalization of the ring π electron system, felt justified on the basis of this and ancillary evidence in characterizing phosphole as "heteroaromatic". In harmony with this conclusion, we have interpreted the abnormally low barrier to inversion at phosphorus in several phosphole systems as a manifestation of cyclic $(3p\text{–}2p)\pi$ conjugation, which is at a maximum in the planar transition state, relative to the pyramidal ground state.[3] In contrast, Ozbirn *et al.*[4] recently concluded from an *X*-ray analysis of 1,2,5-triphenylphosphole that "All the structural evidence indicates that the heterocyclic ring exhibits little if any electron delocalization".

We have studied the kinetics of cleavage of phosphonium hexafluoroantimonates by sodium methoxide, equation (1). On the assumption that the rate-determining step involves heterolysis of the P–C bond, delocalization of the lone pair on phosphorus in the product phosphine, to the extent that it is felt in the transition state, will lead to an acceleration in the rate of retro-cyanoethylation. In particular, since the P–C σ bonding electrons in a cyanoethylphospholium ion become part of the cyclic 6π electron system in the phosphole produced, any heteroaromaticity should provide a substantial accelerating effect.†

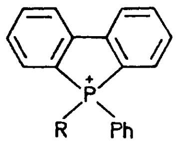


$$R_3\overset{+}{P}CH_2CH_2CN + \overset{-}{O}CH_3 \rightleftharpoons R_3\overset{+}{P}CH_2\overset{-}{C}HCN + CH_3OH$$
$$R_3\overset{+}{P}\text{–}CH_2\text{–}\overset{-}{C}HCN \longrightarrow R_3P + CH_2{=}CHCN \qquad (1)$$

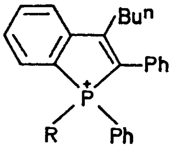
Our results are given in the Table. The salts were prepared by treatment of the appropriate phosphine with 3-bromopropionitrile, followed by treatment of the crude phosphonium bromide with $AgSbF_6$ in methylene chloride. The products were purified by crystallization from ethanol or chloroform.‡ Known concentrations (*ca.* 10^{-4} M) of phosphonium salt and sodium methoxide were allowed to react in methanol to *ca.* 90% completion, and the rate of reaction was monitored by u.v. spectrometry.§ Rate constants were calculated from least-squares plots for second-order reaction kinetics.[5]



(1)



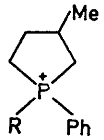
(2)



(3)

$Ph_3\overset{+}{P}R$

(4)



(5)

R = CH_2CH_2CN. The gegenion is SbF_6^-.

Comparison of the rate data at 41·6° reveals a substantial accelerating effect for (**1**), as compared to other phosphonium salts. According to the above line of reasoning, this finding

Second-order rate constants of retro-cyanoethylation

Phosphonium ion	T (°C)	k_2 (l mol^{-1} s^{-1})	Isosbestic points (nm)
(1)	−16·0	0·99	395
	−3·2	5·84	
	8·2	27·1	
	41·6	1130	
(2)	41·6	178	318, 252, 229
(3)	41·6	180	334, 250, 224
(4)	41·6	17·1	239, 218
(5)	41·6	0·4[a]	231, 216

[a] This value is an upper limit since the reaction appears to slow down significantly (for reasons yet unknown) beyond *ca.* 50% conversion.

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† Although equation (1) shows the retro-cyanoethylation as occurring in two discrete steps, this assumption is not essential to our argument, which would be equally valid if the process consisted of concerted proton abstraction and P–C bond cleavage.

‡ Satisfactory elemental analyses (C,H,P) were obtained and the ^{1}H n.m.r. spectra were consistent with the assigned structures.

§ After essentially complete conversion, the u.v. spectra of the reaction products were identical with those of the corresponding phosphines. Isosbestic points are listed in the Table.

supports the view that 1,2,5-triphenylphosphole exhibits aromatic character. Alternatively, this may reflect an antiaromatic destabilization of (**1**).

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