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The Reactions of some Azides with an Anionic Phosphorus(III) Complex

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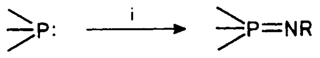
The first example of a Staudinger reaction involving an anionic phosphorus(III) species is reported; the ^{31}P chemical shift and reactivity of the resulting product indicate the formation of a novel iminophosphoranide(v).

The Staudinger reaction is a well known and useful method for preparing phosphorus–nitrogen double-bonded species by the action of covalent azides on phosphorus(III) compounds.[1] So far it has been used with phosphines [reaction (1)][1] and with di-co-ordinated neutral compounds [reaction (2)][2–4] or cations [reaction (3)].[5,6] We have now extended this type of reaction to a phosphoranide [*e.g.* (**1**)] in order to synthesise the previously unknown iminophosphoranide structure [*e.g.* (**2**)]. The most suitable compound for this purpose appeared to be $Et_4N^+PhP(CN)_2Cl^-$ (**1**), which has been recently synthesised in one of our laboratories[7] and characterised by *X*-ray diffraction.[8]

Addition of phenyl azide or tosyl azide to (**1**) in acetonitrile solution at room temperature led to the evolution of nitrogen and the formation of phosphorus-containing products (**2a**) or (**2b**), with ^{31}P n.m.r. chemical shifts of −91.5 and −90.9 p.p.m. respectively. These species were extremely moisture-sensitive, and could not be isolated in a completely pure state. Removal of solvent from the reaction product with PhN_3 yielded a viscous liquid, which gave ^{31}P shifts of −91.5 p.p.m. when redissolved in MeCN and −80.1 p.p.m. in $CHCl_3$. These results strongly suggest that the compound is anionic in character. Compound (**1**) similarly gave shifts of −86.0 p.p.m. in MeCN and −76.4 p.p.m. in $CHCl_3$. The phosphine $PhP(CN)_2$ did not react with either of the azides under the same conditions, showing that the reacting species is the phosphoranide. This is in keeping with the mechanism of the Staudinger reaction which involves the nucleophilic character of the phosphorus atom,[1] and should therefore be facilitated by using an anionic species. No reaction of (**1**) with PhN_3 was observed in $CHCl_3$, where compound (**1**) undergoes considerable dissociation to $PhP(CN)_2$ (δ ^{31}P −72.6 p.p.m.) from the chemical shift values. On the basis of these results, reaction (4) is a reasonable hypothesis for the initial reaction.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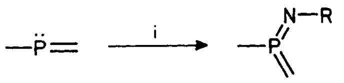
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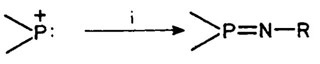
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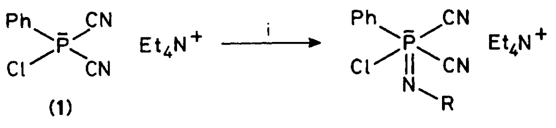

(4)

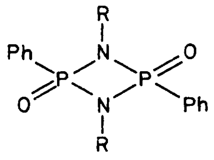
a; R = Ph, b; R = *p*-$MeC_6H_4SO_2$ (Tos)

i, + RN_3, $-N_2$.

Controlled hydrolysis of compound (**2a**) led to the formation of the diazadiphosphetidine (**3a**), which was fully characterised. Compound (**2b**) underwent conversion during 12 h into a new phosphorus species (**4**) (δ ^{31}P −19.0 p.p.m.), the chemical shift of which was not solvent-dependent. Controlled hydrolysis of (**4**) gave the diazaphosphetidine (**3b**), which was also fully characterised. The formation of (**3a**) and (**3b**) containing N–R groups confirms that a Staudinger reaction involving the organic azide has taken place.

The most probable rationalisation of this behaviour in the case of the tosyl compound is the conversion of the phosphoranide (**2b**) into the corresponding phosphazene (**4**) by loss of chloride ion [reaction (5)]. The chemical shift of −19.0 p.p.m. for (**4**) appears entirely as expected for a lower co-ordination number, and the assignment is strongly supported by the value of 13.7 p.p.m. for the analogous chloro-compound (**5**), prepared by reaction of $PhPCl_2$ with tosyl azide. A similar upfield shift of 29.1 p.p.m. caused by replacement of two chlorines by two cyano-groups has been reported for PCl_3O and $PCl(CN)_2O$.[9] Further support for this assignment is provided by the reaction of (**4**) with methanol, which led to two products $PhP(OMe)_2{=}N{-}Tos$ (10%) and $PhP(:O)(OMe){-}NH{-}Tos$ (80%), both of which were fully characterised. The identical products were obtained by reaction of methanol with the dichloro-compound (**5**). Final confirmation was adduced by reaction of the ion $[PhP(CN)_2Cl_3]^{-}$[7] with tosylamine in CH_2Cl_2 solution; the main product was (**4**) (δ −19.5 p.p.m.), together with some (**5**), while (**5**) (δ 16.2 p.p.m.) was obtained exclusively by reaction of $PhPCl_4$ with tosylamine, either in CH_2Cl_2 or in MeCN.

It is probable that the phosphazene analogous to (**4**) is present in a small proportion in the phenyl system also, but at or below the n.m.r. detection limit. The presence of the non-ionic species (**4**) could account for the high reactivity and moisture-sensitivity of the phosphoranides (**2a,b**), since there is no facile route for hydrolysis of the anion. We therefore conclude that the new phosphoranide species (**2**) are formed in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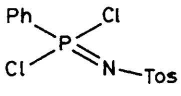
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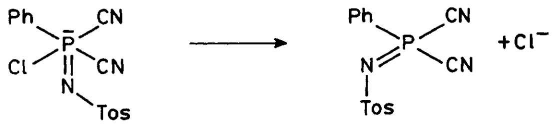
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solution, and that the reason for their high reactivity is the presence of at least a small quantity of the corresponding phosphazene; this species is stabilised by the presence of the tosyl group, and may then be readily detected in the n.m.r. spectrum. This deduction is supported, moreover, by the non-availability of an associative (S_N2)-type mechanism for substitution into the phosphoranides (**2**), which must react *via* a dissociative (S_N1)-type mechanism, necessarily involving a neutral phosphorus(v) species as an intermediate.

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