A General Route to Pentaco-ordinate Amino(oxy)- and Diamino(oxy)-phosphoranes from Azido-compounds and Phosphorus(III) Reagents

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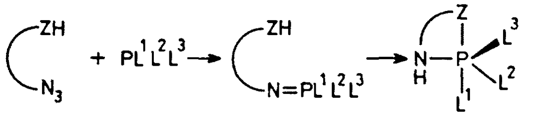
Summary Bifunctional azido-compounds such as benzohydroximic azide, α-azidobenzaldehyde 2,4-dibromophenylhydrazone, *trans*-1-azido-2-hydroxycyclohexane, 2-azido-1-phenylethanol, 2-azidobenzyl alcohol, *o*-azidoaniline, and α-azidoacetophenones react with a variety of phosphorus(III) reagents to give pentaco-ordinate amino(oxy)- and diamino(oxy)-phosphoranes.

WE report a synthesis of some new pentaco-ordinate phosphoranes by reaction of aliphatic bifunctional azides with organophosphorus(III) reagents. The general reaction, which proceeds *via* the formation of the iminophosphorane function followed by intramolecular cyclisation *via* addition to the P=N group (Scheme), is exemplified as follows: addition of benzohydroximic azide (3·08 mmol) in ether to 2-phenyl-1,3,2-dioxaphospholan (3·27 mmol) in ether at room temperature under nitrogen, followed by removal of solvent after 24 h gave 2,2-ethylenedioxy-2-phenyl-2,3-dihydro-4-phenyl-1,3,5,2-oxadiazaphosph(V)ole (**1**; *n* = 2; 91%; Table, footnote a).† Further phosphoranes similarly produced are listed in the Table. That the reaction is capable of extension follows from our preliminary observation of ^{31}P resonances characteristic of phosphoranes (large negative shifts) in reactions of α-azidoacetic acid, α-azidoacetamide, and α-azidophenylacetic acid, with a wide series of cyclic and acyclic phosphorus(III) reagents. The general reaction is thus complementary to the reaction of ω-amino-substituted phosphites with phenyl azide to give amino(oxy)phosphoranes.[1]



SCHEME

The isolation of phosphoranes such as the 2,2-ethylenedioxy-2-phenyl-2,3-dihydro-4-phenyl-1,3,2-oxazaphosph(V)oles (**2**; *n* = 2; Table, footnote g) from 2-azido-ketones and 2-phenyl-1,3,2-dioxaphospholan is of interest because reaction[2] of triphenylphosphine with the related azido-ketones, *e.g.* α-azidoacetophenone, does not give an isolable phosphorane; reaction at high temperature gives instead 1,4-diphenylpyrazine.

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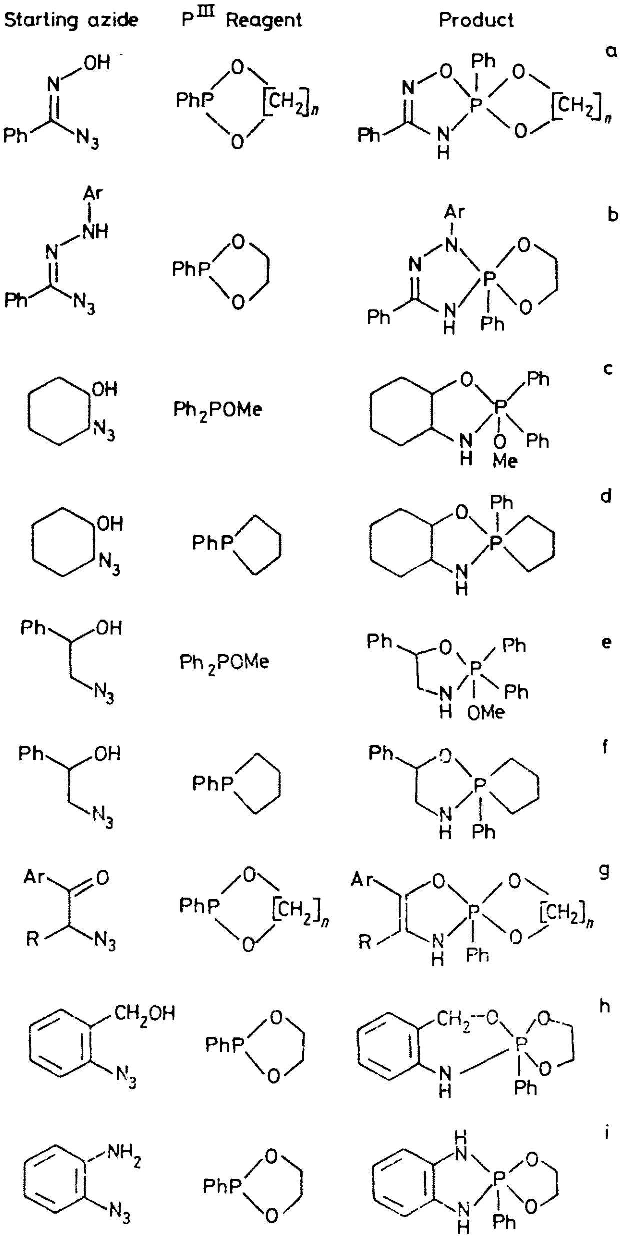
TABLE



[a] (**1**); *n* = 2, 91%, m.p. 123—124 °C, δ − 19·26 [all δ refer to. ^{31}P ($CDCl_3$) p.p.m.]; *n* = 3, 97%, m.p. 109 °C, δ − 34·99, [b] Ar = 2,4-$Br_2C_6H_3$; 96%, m.p. 164—166 °C, δ − 40·33. [c] 61% m.p. 71—73 °C, δ − 44·67. [d] 60%, m.p. 37—39 °C, δ − 40·14. [e] 85%, m.p. 103—105 °C, δ − 42·56. [f] 84%, m.p. 45—47 °C, δ − 36·91. [g] (**2**); Ar = R = Ph, *n* = 2, 89%, m.p. 88 °C (decomp.), δ − 29·7; Ar = R = Ph; *n* = 3, 96%, m.p. 94 °C (decomp.), δ − 45·6; Ar = Ph, R = H, *n* = 2, 61%, m.p. 84—86 °C (decomp.), δ − 25·4; Ar = Ph, R = H, *n* = 3, 82%, m.p. 87 °C (decomp.), δ − 41·1; Ar = *p*-BrC_6H_4, R = H, *n* = 2, 71%, m.p. 85 °C (decomp.), δ − 25·3; Ar = *p*-BrC_6H_4, R = H, *n* = 3, 85%, m.p. 105 °C (decomp.), δ − 40·8; Ar = *p*-$MeOC_6H_4$, R = H, *n* = 2, 73%, m.p. 99 °C (decomp.), δ − 25·6; Ar = *p*-$MeOC_6H_4$, R = H, n = 3, 74%, m.p. 102 °C (decomp.), δ − 41·2; Ar = *p*-PhC_6H_4, R = H, *n* = 2, 85%, m.p. 105 °C (decomp)., δ − 25·5. [h] 61%, m.p. 95—98 °C, δ − 44·46. [i] 72%, m.p. 137—141 °C, δ − 39·03.

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† All isolated phosphoranes had the expected elemental analyses and mass spectra.

[1] M. Sanchez, J-F. Brazier, D. Honalla, A. Munoz, and R. Wolf, *J.C.S. Chem. Comm.*, 1976, 730.
[2] E. Zbiral and J. Ströh, *Annalen*, 1969, **727**, 231.