

A Simple, One-flask Synthesis of Pentaco-ordinate Phosphoranes

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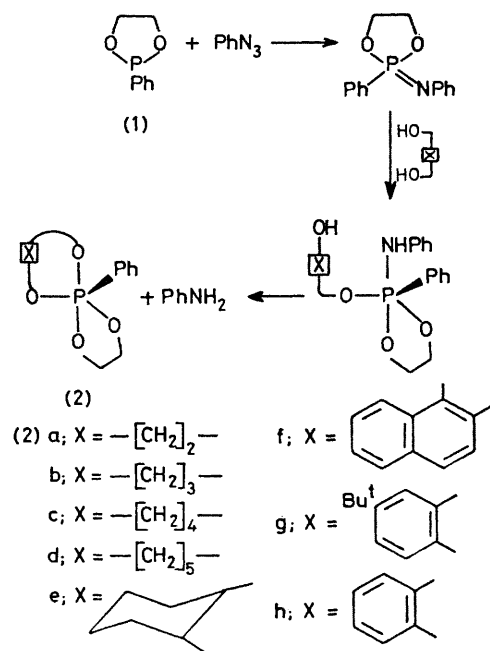
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Summary In a synthesis capable of extension, 2-phenyl-1,3,2-dioxaphospholan reacts at room temperature with phenyl azide followed by diols, *o*-dihydroxyarenes, or *o*-hydroxythiophenol to give phosphoranes (68–100%) including the first isolated phosphoranes containing 7- and 8-membered alicyclic rings, *i.e.* 2,2-ethylenedioxy-2-phenyl-1,3,2-dioxaphosph(v)epan and 2,2-ethylenedioxy-2-phenyl-1,3,2-dioxaphosph(v)ocan.

We here report a simple and convenient one-flask synthesis of pentaco-ordinate phosphoranes, *e.g.* (2), from trivalent phosphorus reagents, hydroxy-compounds, and azido-benzene.

We have observed^{1,2} that vicinal- or *o*-azido-hydroxy compounds, and related bifunctional azides react with phosphorus(III) reagents to give phosphoranes (*e.g.* Scheme in the preceding Communication²) *via* intramolecular addition of the $\text{XO}^{\delta-} \cdots \text{H}^{\delta+}$ unit across the imino-phosphorane ($\text{P}=\text{N}$) bond. We argued therefore that analogous intermolecular addition should also occur [$\text{R}_3^3\text{P}=\text{NR}^1 + \text{R}^2\text{OH} \rightarrow \text{R}_3^3\text{P}(\text{OR}^2)\text{NHR}^1$], and that further reaction *via* displacement of the amino group (R^1NH) by R^2OH should then lead to a new route to phosphoranes [$\text{R}_3^3\text{P}(\text{OR}^2)\text{NHR}^1 + \text{R}^2\text{OH} \rightarrow \text{R}_3^3\text{P}(\text{OR}^2)_2$].

We now report the realisation of this expectation. Thus, reaction under nitrogen of 2-phenyl-1,3,2-dioxaphospholan (1) in dry dichloromethane with phenyl azide (1 mol equiv.) over 10 min at room temperature followed by rapid addition of catechol (1 mol equiv.) in ether gave a quantitative conversion (by ^{31}P n.m.r.) into the phosphorane (2h). Reaction as in the Scheme is assumed. Removal of the solvent and aniline (78% recovery) at 0.05 mmHg, followed by crystallisation from ether afforded the pure phosphorane (71%), m.p. and mixed m.p. 113–115 °C (^{31}P δ –14.32 p.p.m.; CDCl_3).† The seven phosphoranes (2a–g) were produced (68–100%) similarly. Of particular interest are the phosphoranes (2c) and (2d); the former (m.p. 70–72 °C; ^{31}P δ –30.15 p.p.m.; CDCl_3) is the first isolated alicyclic phosphorane containing a seven-membered ring³ while the latter is the first isolated phosphorane containing an eight-membered ring. Compound (2d), an oil with the expected ^{13}C n.m.r. spectrum and exact mass spectrum,† exhibits two ^{31}P resonances in CDCl_3 (δ –36.14 and –36.46 p.p.m.)



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which we attribute to the presence of two equilibrating conformers. In accordance with this a variable temperature n.m.r. experiment in *o*-dichlorobenzene led to coalescence to a single ^{31}P resonance at δ –36.29 p.p.m. at *ca.* 120 °C.

Also produced in this way is the monothio analogue of (2h) [74%; m.p. 96–97 °C; ^{31}P δ +4.73 p.p.m.; CDCl_3] from *o*-hydroxythiophenol.

Preliminary experiments using ^{31}P reveal that the reaction is capable of extension to produce less stable phosphoranes, *e.g.* by the use of ethanol, phenol, or *o*-aminophenol in place of the above diols or dihydroxybenzenes.

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

¹ J. I. G. Cadogan, N. J. Stewart, and N. J. Tweddle, *J.C.S. Chem. Comm.*, 1978, 182.

² J. I. G. Cadogan, I. Gosney, E. Henry, B. Nay, T. Naisby, N. J. Stewart, and N. J. Tweddle, preceding communication.

³ L. B. Littlefield and G. O. Doak, *Phosphorus and Sulfur*, 1977, 3, 35; N. J. De'Ath and D. B. Denney, *ibid.*, p. 51.