Phosphorus-containing Heterocycles from Phosphorus(III) Reagents and *ortho*-Azidoaromatic Compounds: Synthesis of 2,2-Di(dimethylamino)-1,3,2-benzoxazaphosphole and Various 2,3-Dihydro-1,3,2-benzoxazaphosph(V)oles

By J. I. G. Cadogan,* Nevin J. Stewart, and Neil J. Tweddle
(*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh* EH9 3JJ)

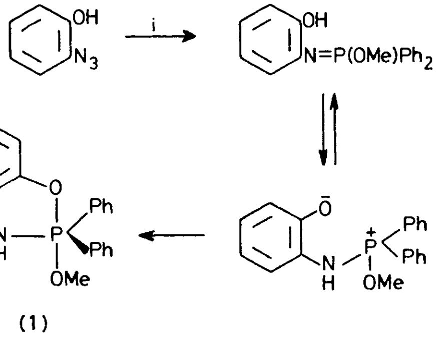
Summary *o*-Azidophenol reacts with methyl diphenylphosphinite to give the amino(oxy)phosphorane, 2-methoxy-2,2-diphenyl-2,3-dihydro-1,3,2-benzoxazaphosph(V)ole (**1**; 90%), which is also produced (55%) from *o*-aminophenol, the phosphinite, and *N*-chlorodi-isopropylamine; *o*-azidophenyl benzoate reacts with hexamethylphosphorous triamide to give 2,2-di(dimethylamino)-1,3,2-benzoxazaphosphole (**2**; 76%) and *NN*-dimethylbenzamide.

Organic azides react readily with organophosphorus(III) reagents to give the corresponding imines[1] [*e.g.*, equation (1)]. We now report the adaptation of this reaction to

$$(EtO)_3P + PhN_3 \rightarrow (EtO)_3P{=}NPh \qquad (1)$$

provide a simple, and mild, route to the amino(oxy)phosphorane system (**1**). Thus, addition under nitrogen of *o*-azidophenol (4·75 mmol) in dry light petroleum (13 ml, b.p. 40—60 °C) to methyl diphenylphosphinite (4·8 mmol) in the same solvent (5 ml) at 0 °C led to evolution of nitrogen with precipitation of 2-methoxy-2,2-diphenyl-2,3-dihydro-1,3,2-benzoxazaphosph(V)ole (**1**) as a colourless solid [90%, m.p. > 240 °C (decomp.)]. The material had correct elemental analysis and the expected n.m.r. spectra: ^{31}P (CDCl$_3$) δ (positive to high frequency) −36·0 p.p.m.; ^{1}H (CDCl$_3$) δ, 2·98 [d, 3H, *J*(^{31}P–H) 11 Hz, POMe], 4·86 [d, 1H, *J*(^{31}P–H) 20 Hz, NH], 6·45—6·80 (m, 4H, ArH), 7·20—7·45 (m, 6H, ArH), and 7·60—7·90 (m, 4H, Ar-*o*-H of –PPh$_2$). The structure was confirmed by an alternative synthesis (55% yield) from *o*-aminophenol, methyl diphenylphosphinite, and *N*-chlorodi-isopropylamine in an analogue of a synthesis of oxaphosph(V)oles.[2] Trimethyl and triethyl phosphites and dimethyl phenylphosphonite similarly reacted with *o*-azidophenol, to give the corresponding oxazaphosph(V)oles, ^{31}P n.m.r. measurements indicating almost quantitative conversions (^{31}P δ, −52·3, −53·9, and −39·8 p.p.m. respectively). Reaction as in Scheme 1 is suggested.

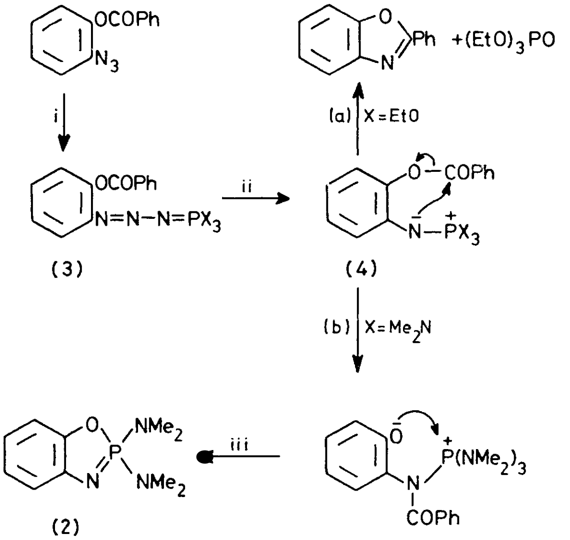
We also report a related novel synthesis of the 1,3,2-benzoxazaphosphole system (**2**). Addition under dry nitrogen of hexamethylphosphorous triamide (2·15 mmol) in super-dry cyclohexane (5 ml) to *o*-azidophenyl benzoate (1·99 mmol) in dry cyclohexane at 20 °C led to the precipitation of the triazene [(**3**; X = NMe$_2$); 94%; m.p. > 95 °C



Scheme 1. i, Ph_2POMe, $-N_2$.

(decomp.), correct elemental analysis and expected ^1H n.m.r. data; ^{31}P n.m.r., δ +42·4 p.p.m.]. In a replicate experiment the triazene was not isolated but the mixture was boiled under reflux (80 °C) for 24 h when crystalline 2,2-di(dimethylamino)-1,3,2-benzoxazaphosphole (**2**; m.p. 174—177 °C) was collected (75%). Chromatography of the mother liquors gave *NN*-dimethylbenzamide (86%). Compound (**2**) had the correct analysis and expected n.m.r. spectra: ^{31}P, δ +68·0; ^1H ($CDCl_3$), δ 2·71 [d, 12H, $PNMe_2$, $J(^{31}P\text{–}H)$ 11 Hz], and 6·38—6·60 (m, 1H, ArH) and 6·72—6·96 (m, 3H, ArH).

This reaction is noteworthy because the corresponding reaction of *o*-azidophenyl benzoate with triethyl phosphite



Scheme 2. i, X_3P; ii, $-N_2$; iii, $-PhCONMe_2$.

gives 2-phenyl-1,3-benzoxazole in good yield [Scheme 2, step (a)].[3] One possible explanation of the formation of the oxazaphosphole (**2**) is that it could be due to the high nucleophilicity of the nitrogen end of the P–N dipole (**4**) [step (b)] leading to reaction as in Scheme 2.

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