

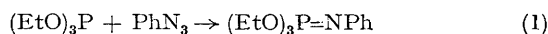
## Phosphorus-containing Heterocycles from Phosphorus(III) Reagents and *ortho*-Azidoaromatic Compounds: Synthesis of 2,2-Di(dimethylamino)-1,3,2-benzoxazaphosphole and Various 2,3-Dihydro-1,3,2-benzoxazaphosph(v)oles

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**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*-chlorodiisopropylamine; *o*-azidophenyl benzoate reacts with hexamethylphosphorous triamide to give 2,2-di(dimethylamino)-1,3,2-benzoxazaphosphole (**2**; 76%) and *NN*-dimethylbenzamide.

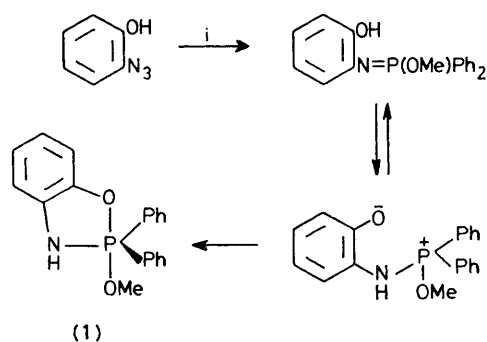
ORGANIC azides react readily with organophosphorus(III) reagents to give the corresponding imines<sup>1</sup> [*e.g.*, equation (1)]. We now report the adaptation of this reaction to



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%,

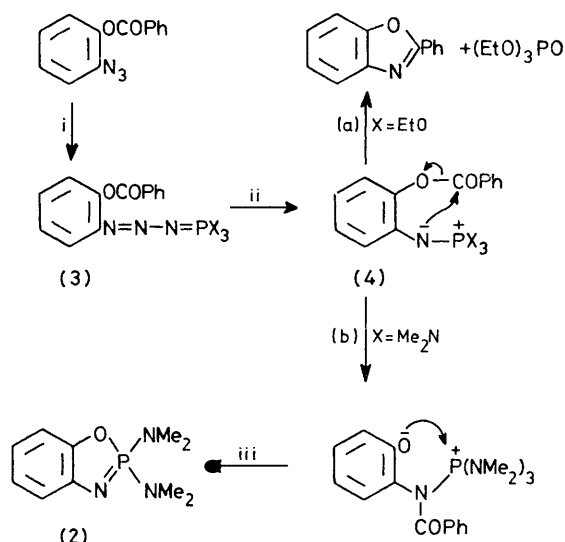
m.p. > 240 °C (decomp.)]. The material had correct elemental analysis and the expected n.m.r. spectra: <sup>31</sup>P (CDCl<sub>3</sub>) δ (positive to high frequency) –36.0 p.p.m.; <sup>1</sup>H (CDCl<sub>3</sub>) δ, 2.98 [d, 3H, *J*(<sup>31</sup>P–H) 11 Hz, POMe], 4.86 [d, 1H, *J*(<sup>31</sup>P–H) 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<sub>2</sub>). The structure was confirmed by an alternative synthesis (55% yield) from *o*-aminophenol, methyl diphenylphosphinite, and *N*-chlorodiisopropylamine in an analogue of a synthesis of oxaphosph(v)oles.<sup>2</sup> Trimethyl and triethyl phosphites and dimethyl phenylphosphonite similarly reacted with *o*-azidophenol, to give the corresponding oxazaphosph(v)oles, <sup>31</sup>P n.m.r. measurements indicating almost quantitative conversions (<sup>31</sup>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<sub>2</sub>); 94%; m.p. > 95 °C

SCHEME 1. i,  $\text{Ph}_2\text{POMe}$ ,  $-\text{N}_2$ .

(decomp.), correct elemental analysis and expected  $^1\text{H}$  n.m.r. data;  $^{31}\text{P}$  n.m.r.,  $\delta +42.4$  p.p.m.]. In a replicate experiment the triazene was not isolated but the mixture was boiled under reflux ( $80^\circ\text{C}$ ) for 24 h when crystalline 2,2-di-(dimethylamino)-1,3,2-benzoxazaphosphole (**2**; m.p.  $174$ — $177^\circ\text{C}$ ) was collected (75%). Chromatography of the mother liquors gave *NN*-dimethylbenzamide (86%). Compound (**2**) had the correct analysis and expected n.m.r. spectra:  $^{31}\text{P}$ ,  $\delta +68.0$ ;  $^1\text{H}$  ( $\text{CDCl}_3$ ),  $\delta 2.71$  [d, 12H,  $\text{PNMe}_2$ ,  $J(^{31}\text{P}-\text{H})$  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,  $\text{X}_3\text{P}$ ; ii,  $-\text{N}_2$ ; iii,  $-\text{PhCONMe}_2$ .

gives 2-phenyl-1,3-benzoxazole in good yield [Scheme 2, step (a)].<sup>3</sup> 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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<sup>2</sup> S. Antczak, S. A. Bone, J. Brierley, and S. Trippett, *J.C.S. Perkin I*, 1977, 278.

<sup>3</sup> L. J. Leyshon and D. G. Saunders, *Chem. Comm.*, 1971, 1608.