The Reactivity of Organophosphorus Compounds. Part 36.[1,2] Pyrolyses of 2-Alkoxy-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles

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Thermolysis of the phosph(v)oles [*e.g.* (**3**)] in the solid state, in suspension, or in solution, gives the 'phosphole dimer' (**6**) *via* dimerisation of the phosphinimine (**7**). This species, generated from the phosph(v)ole (**3**), or from the dimer (**6**), may be trapped by carbonyl compounds (aldehydes, ketones, or formamides) to give the phosphinates (**8**). Reaction with *p*-nitrobenzaldehyde converted the phosph(v)ole (**3**) into the benzoxazole (**13**).

We have shown that pyrolysis reactions of the 3-alkyl- and 3-aryl-1,3,2-benzoxazaphosph(v)oles (**1**) and (**2**) are controlled by cleavage of the heterocyclic ring to give products containing a four-co-ordinate phosphorus centre.[1] We now extend these studies to the readily available[3,4] *N*-unsubstituted compounds (**3**)—(**5**). Such thermolyses lead instead to highly reactive phosphinimine intermediates, which may be trapped by dimerisation or by reaction with carbonyl compounds.[2]

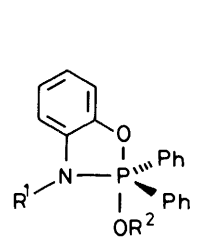
The phosph(v)oles (**3**)—(**5**) were synthesised by reaction of *o*-azidophenol with the appropriate phosphorus(III) reagent.[3,4] They were obtained as powders with high, ill-defined melting points and were extremely sensitive to hydrolysis. In subsequent work, therefore, apparatus and all reagents were thoroughly dried before use.

Early attempts to study the gas-phase reactions of (**3**)—(**5**) by flash vacuum pyrolysis (*cf.* ref. 1) gave a white insoluble material in the *inlet*, which passed unchanged through the furnace tube. Simply heating the phosph(v)ole *in vacuo* gave the same product, which was identified as the 'phosphole dimer' (**6**) by comparison with an authentic sample.[5,6] The appropriate alcohol (R^2OH) was also isolated in high yield.

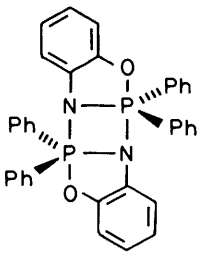
These products are best explained by a thermal elimination sequence [in which the phosph(v)ole behaves as a P–N analogue of a hemiacetal] to generate the alcohol and the reactive cyclic phosphinimine (**7**), which gives (**6**) by dimerisation (Scheme 1). It is of interest that a similar elimination (of HCl) takes place in the formation of *P,P*-tetra-alkoxy analogues of (**6**) from *o*-azidophenol and dialkyl or diaryl chlorophosphonites.[7,8]

The dimer (**6**) was also obtained in good yield under mild conditions, by thermolysis of the phosph(v)ole (**3**) in suspension in toluene (110 °C, 90 min, 71%) or in solution in chloroform (60 °C, 45 h, 65%). Surprisingly, no free methanol was detected in these cases, even though the reactions were carried out in sealed n.m.r. tubes and carefully monitored *in situ*. Either the elimination takes a different course, or the alcohol remains trapped within the lattice of the microcrystalline product.

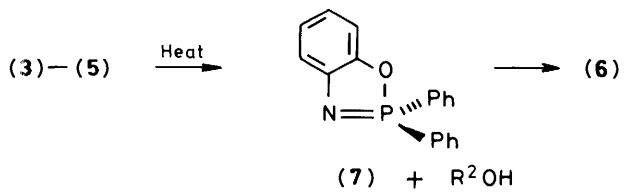
The intermediate phosphinimine (**7**), generated either by thermolysis of the phosph(v)ole (**3**) or by thermolysis of the dimer (**6**), may be trapped by carbonyl compounds to give the phosphinates (**8**), often in good to excellent yield (Scheme 2 and Table). The reaction is normally carried out with a four-fold excess of the carbonyl component, and has some generality, since aldehydes, ketones, and formamides may be used. The latter are of particular interest, since cyclic phosphinimines have been shown to react with aldehydes,[9] ketones,[10] isocyanates,[11] isothiocyanates,[12] and ketenes,[13] yet no previous report of attack at an amide carbonyl group has appeared. Such high reactivity is well known for cyclic phosphinimines, and has been



(**1**) R^1 = Aryl
(**2**) R^1 = Alkyl
(**3**) R^1 = H, R^2 = Me
(**4**) R^1 = H, R^2 = Et
(**5**) R^1 = H, R^2 = CH_2Bu^t



(**6**)



Scheme 1.

Table. The formation of phosphinates (**8**) from the oxazaphosph(v)ole (**3**) or the dimer (**6**)

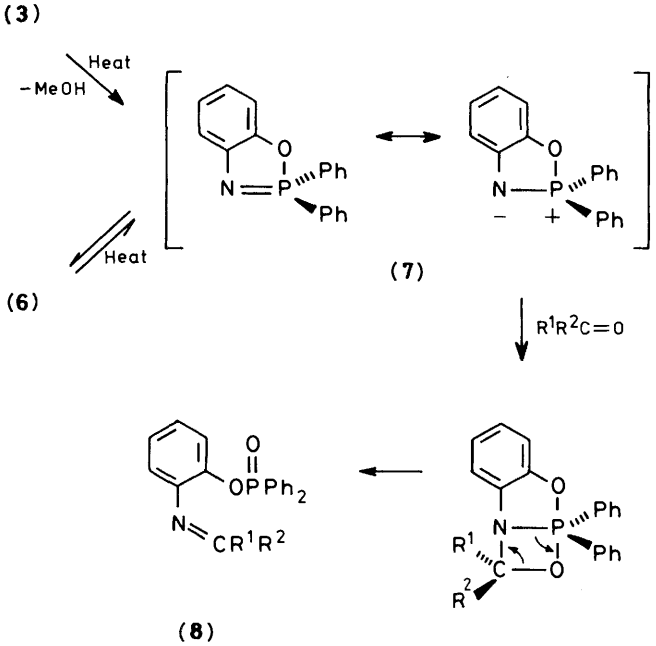
Compd.	R^1	R^2	*T*/°C	Reaction time (h)	Yield (%)
(**8a**)[a]	H	NMe_2	115—120	3	41
(**8a**)[b]	H	NMe_2	120—130	2.5	59
(**8b**)[a]	H	Piperidino	120—130	2.5	61
(**8c**)[a]	H	NMePh	130—140	2.5	13
(**8d**)[a]	Ph	Ph	150—160	5	71
(**8d**)[b]	Ph	Ph	125	10	*c*
(**8e**)[a]	Me	2-Naphthyl	120—165	8	*d*
(**8f**)[a]	Bu^t	Bu^t	135—140	21	0[e]
(**8g**)[a]	H	*p*-ClC_6H_4	130 140	2	41
(**8g**)[b]	H	*p*-ClC_6H_4	125	1	*c*
(**8h**)[a]	H	Ph	120—130	7	*d*

[a] From the phosph(v)ole (**3**). [b] From the dimer (**6**). [c] Small-scale experiment only, sole product by ^{31}P n.m.r. spectroscopy. [d] Mass spectroscopic evidence only. [e] Dimer (**6**) obtained in 49% yield.

ascribed to ring-strain effects.[10] In the present example the reactivity of (7) may be further enhanced by the vigorous conditions required for its formation.

The amidine group in (**8a**) and (**8b**) was characterised by variable-temperature ^1H and ^{13}C n.m.r. spectroscopy respectively, which shows the expected[14] restricted rotation about the C–N single bond [(**8a**), $\Delta G^{\ddagger}$ 62 kJ mol^{-1} : (**8b**), $\Delta G^{\ddagger}$ 60 kJ mol^{-1}].

The formation of methanol as a co-product was established by ^1H n.m.r. spectroscopy by the reaction of the phosph(v)ole (**3**) with [$^2H_7$]dimethylformamide in a sealed n.m.r. tube. Other aspects of Scheme 2 follow by analogy with Wittig and Staudinger mechanisms.

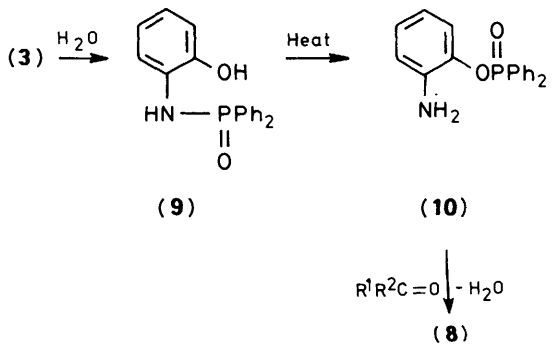


a ; $R^1 = H, R^2 = NMe_2$
b ; $R^1 = H, R^2$ = Piperidino
c ; $R^1 = H, R^2 = NMePh$
d ; $R^1 = R^2 = Ph$
e ; $R^1 = Me, R^2$ = 2-Naphthyl
g ; $R^1 = H, R^2 = p\text{-}ClC_6H_4$
h ; $R^1 = H, R^2 = Ph$

Scheme 2.

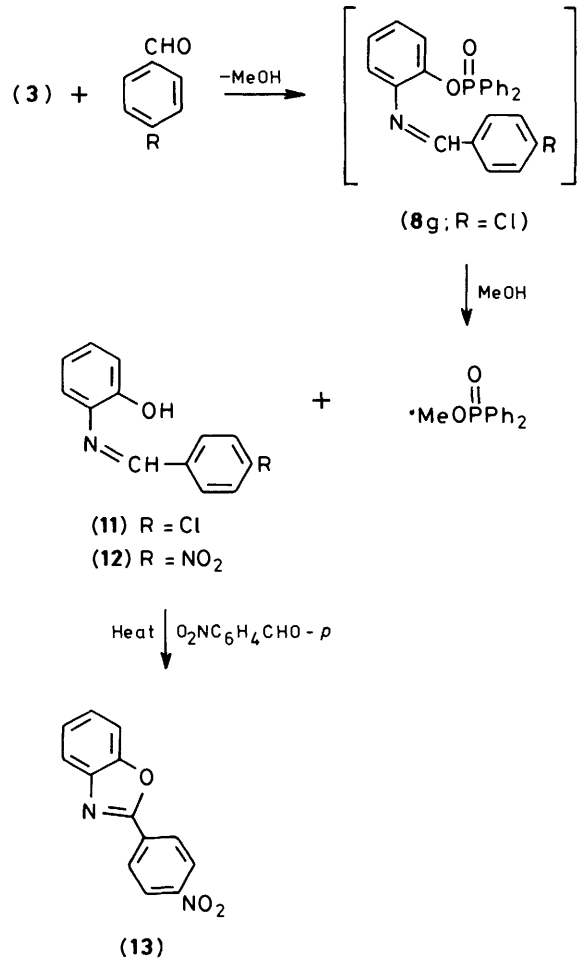
In view of the great sensitivity to hydrolysis of the phosph(v)ole (**3**) we have also considered an alternative mechanism for the formation of (**8**) (Scheme 3). This involves hydrolysis of (**3**) to the phosphinamide (**9**) followed by transphosphorylation to the phosphinate (**10**) (see Experimental section) and trivial condensation of the resulting free amino function with the carbonyl compound. Only a catalytic amount of water is therefore required. Independent treatment of (**9**) with benzophenone or with *p*-chlorobenzaldehyde indeed led to (**8d**) and (**8g**) respectively, under analogous reaction conditions to the phosph(v)ole experiments, though a similar control experiment with dimethylformamide gave only starting material. The mechanism of Scheme 3 cannot therefore be excluded for reactions of the oxazaphosph(v)ole with aldehyde or ketone substrates, though it must be emphasised that the reactions of the 'phosphole dimer' (**6**) are consistent *only* with the phosphinimine mechanism (Scheme 2).

The overall scope of these reactions is limited by a number of factors, including the reactivity of the carbonyl group. Thus the



Scheme 3.

phosph(v)ole (**3**) gives the dimer (**6**) by default, on being heated with di-t-butyl ketone. In some cases the phosphinate (**8**), although present, could not be isolated and fully characterised [see Table, entries (e) and (h)], while in other cases (*e.g.* benzyl methyl ketone) multi-component mixtures were obtained. This may be due in part to difficulties in purifying the reagent, but it is also possible that the product (**8**) may be unstable under the reaction conditions. For example, reaction of the phosph(v)ole (**3**) with *p*-chlorobenzaldehyde in solution in boiling chloroform gave methyl diphenylphosphinate (7%), together with the phenol (**11**) whose presence was confirmed by ^{13}C n.m.r. spectroscopy. These products are presumably derived from (**8g**) by methanolysis (Scheme 4). Surprisingly, a similar reaction



Scheme 4.

with *p*-nitrobenzaldehyde gave the oxazole (**13**) (17%) after work-up by distillation. This represents an unusual transformation of a benzoxazaphosph(v)ole into a benzoxazole. The phenol (**12**) was detected in the crude reaction mixture prior to work-up: confirmation that the excess of nitroaldehyde is capable of performing the final oxidation step to give (**13**) (Scheme 4) was obtained by a control experiment with authentic samples.

Experimental

^1H, ^{13}C, and ^{31}P N.m.r. spectra were recorded at 100, 20, and 24 MHz respectively, for solutions in deuteriochloroform, unless otherwise stated. I.r. spectra were recorded for Nujol mulls.

2-*Ethoxy*-2,3-*dihydro*-2,2-*diphenyl*-1,3,2-*benzoxazaphosph*(v)*ole*.—A solution of *o*-azidophenol (0.65 g, 4.8 mmol) in super-dry ether (6 ml) was added dropwise over a period of 5 min to a stirred solution of ethyl diphenylphosphinite (1.20 g, 5.2 mmol) in super-dry light petroleum (b.p. 40—60 °C) under an atmosphere of dry nitrogen. The mixture was stirred until evolution of nitrogen had ceased (15 min). The solvent was decanted from the precipitated solid, which was washed with a mixture of super-dry ether and light petroleum (b.p. 40—60 °C). Removal of the remaining solvents under high vacuum gave an analytically pure sample of the *phosph*(v)*ole* (1.31 g, 81%), m.p. >240 °C (decomp.) (Found: C, 71.1; H, 5.9; N, 3.95. $C_{20}H_{20}NO_2P$ requires C, 71.2; H, 6.0; N, 4.15%); δ_H 0.98 (3 H, t), 3.18 (2 H, apparent quintet), 4.81 (1 H, d, $^2J_{PH}$ 20 Hz), 6.4—6.9 (4 H, m), 7.2—7.5 (6 H, m), and 7.6—8.0 (4 H, m); δ_p −37.2; *m*/*z* 337 (M^+, 100%), 292 (64), 291 (71), and 201 (77).

The following 2,3-dihydro-2,2-diphenyl-1,3,2-benzoxazaphosph(v)oles were also prepared by this method: 2-methoxy (79%); δ_p −36.1 (lit.,[3] δ −36.0): 2-*neopentyloxy* (34%), m.p. >240 °C (decomp.) (Found: C, 72.75; H, 6.8; N, 3.6. $C_{23}H_{26}NO_2P$ requires C, 72.8; H, 6.9; N, 3.7%); δ_H 0.82 (9 H, s), 2.83 (2 H, d, $^3J_{PH}$ 5 Hz), 4.78 (1 H, d, $^2J_{PH}$ 21 Hz), 6.5—6.9 (4 H, m), 7.2—7.5 (6 H, m), and 7.6—7.9 (4 H, m); δ_p −38.7; *m*/*z* 379 (M^+, 49%), 309 (50), 291 (100), and 201 (42).

6,6,13,13-*Tetrahydro*-6,6,13,13-*tetraphenyl*[1,3,2,4]*diazadiphospheto*[2,1-b:4,3-b']*bis*[1,3,2]*benzoxazaphosph*(v)*ole* ('*Phosphole Dimer*') (**6**).—This compound, m.p. 210—220 °C (decomp.) was prepared (21%) by the method[5] which Stegmann and Bauer describe erroneously for the preparation of 2,2-diphenyl-1,3,2-benzoxazaphosph(v)ole monomer. In view of the discrepancy with the literature melting point (311 °C) the product was fully characterised (Found: C, 73.95; H, 4.85; N, 4.6. $C_{36}H_{28}N_2O_2P_2$ requires C, 74.2; H, 4.8; N, 4.8%); $\nu_{max.}$ 1 593, 1 247, 1 231, 1 121, 1 109, 1 022, 966, 923, 839, 742, 708, 700, 689, 662, and 645 cm^{-1}; δ_p −51.7; *m*/*z* 582 (M^+, <1%), 291 (100), 290 (58), and 183 (46) [lit.,[6] 582 (M^+, 1.6%), 291 (100), 290 (49.6), and 183 (12.4)].

Diphenyl-N-(2-*hydroxyphenyl*)*phosphinamide*.—An aqueous solution of toluene-*p*-sulphonic acid (0.225M; 50 μl) was added to a stirred solution of 2,3-dihydro-2-methoxy-2,2-diphenyl-1,3,2-benzoxazaphosph(v)ole (0.75 g, 2.3 mmol) in super-dry ether (30 ml). After 2 min, the *phosphinamide* (0.69 g, 97%) precipitated, m.p. 228—231 °C (from methanol) [lit.,[4] >200 °C (decomp.)].

Thermolysis Reactions of 2-Alkoxy-2,3-dihydro-2,2-diphenyl-1,3,2-benzoxazaphosph(v)oles

1. *Solid Phase Thermolyses*.—The phosph(v)ole was heated at 230 °C for 20—30 min under high vacuum (10^{-2}—10^{-3} Torr) and the volatile products were trapped with liquid nitrogen. An involatile compound was also obtained, at the exit point of the oven and this was shown to contain the 'phosphole dimer (**6**)' by ^{31}P n.m.r. spectroscopy. Further analysis was complicated by its low solubility. Identical results were obtained by incorporation of a hot zone (500 °C, 'flash vacuum pyrolysis') between the inlet heater and the trap.

The following results were obtained. 2-Ethoxy derivative: solid fraction, m.p. 200—210 °C; δ_p −51.7 [assigned as 'phosphole dimer (**6**)' by spiking with an authentic sample; other phosphorus-containing products were also present]: the volatile fraction contained ethanol (84%) identified by ^1H n.m.r. and g.l.c. (2% Carbowax 20M, 70 °C). 2-Neopentyloxy derivative: solid fraction, m.p. 215—225 °C; δ_p −51.6 (assigned as above): the volatile fraction contained neopentyl alcohol (77%). 2-Methoxy derivative: solid fraction, m.p. 215—225 °C (assigned by analogy with the above experiments).

2. *Thermolyses in Suspension*.—The 2-methoxyphosph(v)ole (0.15 g, 0.5 mmol) was heated under reflux in super-dry toluene (10 ml) for 90 min. The insoluble material (0.097 g) which remained was filtered off and identified as the 'phosphole dimer (**6**)' (71%), m.p. >250 °C, whose i.r. and ^{31}P n.m.r. spectra were identical with those of an authentic sample.

In a separate experiment, the phosph(v)ole (0.032 g, 0.1 mmol) was suspended in [$^2H_8$]toluene (0.3 ml) in a *sealed* n.m.r. tube, and was heated at 61 °C for 15 h, and then at 110 °C. The reaction was monitored by ^1H n.m.r. spectroscopy. No change in the spectrum was observed at 61 °C, though the reaction was complete after 2.5 h at 110 °C. No free methanol (δ 3.1) was formed during this process.

3. *Thermolyses in Solution*.—The 2-methoxyphosph(v)ole (0.33 g, 1 mmol) was dissolved in dry chloroform (20 ml) and the solution was heated under reflux for 45 h. The white solid (0.19 g) was filtered off and identified as the 'phosphole dimer (**6**)' (65%) by i.r. spectroscopy. Hydrolysis of unchanged starting material during work-up gave crystals of diphenyl-*N*-(2-hydroxyphenyl)phosphinamide (0.06 g, 19%) from the chloroform filtrate.

In a separate experiment, a sealed n.m.r. tube containing the phosph(v)ole (0.035 g) dissolved in dry deuteriochloroform (0.3 ml) was heated at 61 °C for 20 days. During this period, formation of free methanol (δ 3.47) could not be detected.

4. *Thermolyses in the Presence of Carbonyl Compounds*.—Reaction time and reaction temperature were optimised by performing the experiments on a small scale within the heated probe of a ^{31}P n.m.r. spectrometer. Certain carbonyl substrates gave complex mixtures on treatment with the 2-methoxyphosph(v)ole and these reactions were not attempted on a preparative scale. They included *N*-*p*-tolylformamide (150 °C, 90 min, 5 components), dry *N*,*N*-dimethylacetamide (100—110 °C, 2 h, 8 components) [use of untreated *N*,*N*-dimethylacetamide gave diphenyl-*N*-(2-hydroxyphenyl)phosphinamide (67%) by hydrolysis of the phosph(v)ole], benzyl methyl ketone (130—140 °C, 70 min, 5 components) and dibenzyl ketone (150—160 °C, 1 h, 4 components).

(a) N,N-*Dimethylformamide*. A solution of the 2-methoxyphosph(v)ole (0.40 g, 1.2 mmol) in dry dimethylformamide (4 ml) was heated at 115—120 °C for 3 h. The excess of dimethylformamide was removed by distillation at 45 °C (5×10^{-2} Torr) to leave a brown oil which crystallised on trituration with light petroleum (b.p. 60—80 °C). Recrystallisation from methanol gave 2-(3,3-*dimethyl*-1,3-*diazapropenyl*)-*phenyl diphenylphosphinate* (0.19 g, 42%), m.p. 161—163 °C (Found: C, 69.0; H, 5.75; N, 7.6. $C_{21}H_{21}N_2O_2P$ requires C, 69.2; H, 5.8; N, 7.7%); $\nu_{max.}$ 1 632, 1 587, 1 220, 1 185, 1 095, 975, 926,

898, 837, 762, 754, 730, and 700 cm^{-1}; δ_H 2.96 (6 H br s), 6.6—7.6 (11 H, m), and 7.8—8.2 (4 H, m); δ_p +30.2; *m/z* 364 (M^+, 83%), 363 (33), 201 (20), 147 (100), 146 (56), 145 (22), and 77 (39).

This reaction was also monitored by ^1H and ^{31}P n.m.r. spectroscopy, by heating a solution of the phosph(v)ole (0.036 g) in [$^2H_7$]dimethylformamide (0.3 ml) at 110 °C for 100 min in a sealed n.m.r. tube. After this time, no phosph(v)ole remained (^{31}P n.m.r.), and the ^1H n.m.r. spectrum showed the presence of methanol (δ 3.32, 65%) and methyl diphenylphosphinate [δ 3.67 (d), 23%] (both identified by spiking with authentic samples), in addition to the amidine (δ_p +27.8), as major product.

(b) N-*Formylpiperidine*. The 2-methoxyphosph(v)ole (0.98 g, 3.1 mmol) was heated with dry *N*-formylpiperidine (1.72 g, 15.2 mmol) at 120—130 °C for 2.5 h. After removal of the excess of amide under reduced pressure, the residual oil was triturated with ether to give 2-(3,3-*pentamethylene*-1,3-*diazapropenyl*)-*phenyl diphenylphosphinate* (0.75 g, 61%), after recrystallisation from benzene–light petroleum (b.p. 60—80 °C) (60:40). The amidine had m.p. 130—134 °C (Found: C, 71.5; H, 6.25; N, 6.65. $C_{24}H_{25}N_2O_2P$ requires C, 71.25; H, 6.25; N, 6.95%); $\nu_{max.}$ 1 626, 1 584, 1 350, 1 225, 1 215, 1 180, 1 098, 928, 911, 843, 759, and 696 cm^{-1}; δ_H 1.62 (6 H, br s), 3.46 (4 H, br s), 6.6—7.6 (11 H, m), and 7.8—8.2 (4 H, m); δ_p +29.9; *m/z* 404 (M^+, 43%), 201 (70), and 187 (100).

(c) N-*Methyl*-N-*phenylformamide*. Reaction of the 2-methoxyphosph(v)ole (0.48 g, 1.5 mmol) with dry *N*-methyl-*N*-phenylformamide (1.01 g, 7.5 mmol) at 130—140 °C for 2.5 h afforded, after work-up as in part (b) and recrystallisation from benzene–cyclohexane (50:50), 2-(3-*methyl*-3-*phenyl*-1,3-*diazapropenyl*)*phenyl diphenylphosphinate* (0.09 g, 14%), m.p. 100—103 °C (Found: C, 73.05; H, 5.45; N, 6.45. $C_{26}H_{23}N_2O_2P$ requires C, 73.25; H, 5.45; N, 6.55%); $\nu_{max.}$ 1 629, 1 586, 1 352, 1 230, 1 114, 1 103, 931, 922, 788, 761, 742, and 692 cm^{-1}; δ_H 3.49 (3 H, s), 6.7—7.5 (15 H, m), 7.8—8.1 (4 H, m), and 7.95 (1 H, s); δ_p +30.5; *m/z* 426 (M^+, 69%), 425 (46), 209 (18), 208 (13), 201 (45), 107 (45), 106 (34), and 77 (100).

(d) *Benzophenone*. The 2-methoxyphosph(v)ole (0.64 g, 2 mmol) and benzophenone (1.81 g, 10 mmol) were heated together at 150—160 °C for 5 h. After removal of the excess of ketone under reduced pressure the residual oil was triturated with light petroleum (b.p. 60—80 °C) to give 2-(*diphenylmethyleneamino*)*phenyl diphenylphosphinate* (0.69 g, 74%), m.p. 162—163 °C [from ethanol containing a trace of light petroleum (b.p. 60—80 °C)] (Found: C, 78.45; H, 5.15; N, 3.0. $C_{31}H_{24}NO_2P$ requires C, 78.65; H, 5.1; N, 2.95%); $\nu_{max.}$ 1 632, 1 590, 1 578, 1 317, 1 290, 1 239, 1 229, 1 194, 1 101, 960, 938, 926, 824, 757, 748, and 699 cm^{-1}; δ_H 6.3—8.1 (24 H, m); δ_p + 30.4; *m/z* 473 (M^+, 1%), 272 (49), 201 (100), 165 (45), 141 (10), 115 (13), and 77 (46).

(e) *Methyl 2-naphthyl ketone*. A mixture of the 2-methoxyphosph(v)ole (0.56 g, 1.7 mmol) and methyl 2-naphthyl ketone (1.46 g, 8.6 mmol) was heated at 120—130 °C (4 h) and then at 160—165 °C (5 h), whereupon the ^{31}P n.m.r. spectrum of the mixture showed a single peak (δ_p +30.5). Distillation of the excess of ketone gave a clear brown gum (0.81 g) which would not crystallise. The presence of 2-[*methyl*-(*2-naphthyl*)*methyleneamino*]*phenyl diphenylphosphinate* was inferred by mass spectroscopy (Found: M^+, 461.153. $C_{30}H_{24}NO_2P$ requires M^+, 461.154).

(f) *Di-t-butyl ketone*. The 2-methoxyphosph(v)ole (0.49 g, 1.5 mmol) was heated with di-t-butyl ketone (1.09 g, 7.7 mmol) at 135—140 °C for 21 h. Removal of the excess of ketone under reduced pressure gave a semisolid material which was triturated with ethanol to give the 'phosphole dimer (**6**)' (0.22 g, 49%), δ_p −51.6, whose i.r. spectrum was also identical with that of an authentic sample.

(g) 4-*Chlorobenzaldehyde*. A mixture of the 2-methoxyphosph(v)ole (0.42 g, 1.3 mmol) and the aldehyde (0.92 g, 6.6 mmol) was heated at 130—140 °C for 2 h, after which the excess of aldehyde was removed under reduced pressure. The resulting oil (0.58 g) crystallised on trituration with hot light petroleum (b.p. 60—80 °C), and was recrystallised from ethanol to give 2-[(4-*chlorobenzylidene*)*amino*]*phenyl diphenylphosphinate* (0.23 g, 41%), m.p. 148—150 °C (from ethanol) (Found: C, 69.25; H, 4.35; N, 3.05. $C_{25}H_{19}ClNO_2P$ requires C, 69.55; H, 4.45; N, 3.25%); $\nu_{max.}$ 1 628, 1 590, 1 582, 1 219, 1 130, 1 105, 1 084, 933, 917, 880, 817, 763, 745, and 690 cm^{-1}; δ_H 6.8—7.6 (12 H, m), 7.7—8.0 (6 H, m), and 8.26 (1 H, s); δ_p +30.8; *m/z* 434 (4%), 433 (^{37}Cl M^+, 12), 432 (10), 431 (34), 294 (22), 293 (100), 201 (30), 170 (22), and 77 (17).

Attempts to reproduce this experiment on a similar scale in solution in dry chloroform (20 ml) gave, after reflux for 20 h and fractional distillation of the residue, only methyl diphenylphosphinate (7%) together with unidentified products. A separate experiment using deuteriochloroform, confirmed the presence of 2-[(4-chlorobenzylidene)amino]phenol, since the ^{13}C n.m.r. spectrum of the crude reaction mixture showed the same signals as an authentic sample (δ_C 115.0, 115.7, 120.0, 128.9, 129.7, 134.1, 135.0, 137.4, 152.2, and 155.3). Attempts to isolate this material by medium-pressure chromatography gave instead 2-*aminophenyl diphenylphosphinate* (12%) by alternative solvolysis, m.p. 97—100 °C (Found: M^+, 309.092. $C_{18}H_{16}NO_2P$ requires M^+, 309.092); δ_H 3.98 (2 H, br s), 6.3—7.0 (4 H, m), 7.3—7.7 (6 H, m), and 7.7—8.1 (4 H, m); δ_p +32.5; *m/z* 309 (M^+, 100%), 202 (13), and 201 (83).

(h) *Benzaldehyde*. Reaction of the 2-methoxyphosph(v)ole (0.50 g, 1.6 mmol) with dry benzaldehyde (0.82 g, 7.8 mmol) at 120—130 °C for 7 h and removal of the excess of aldehyde under reduced pressure gave a yellow oil (0.58 g) which contained 4 components (^{31}P n.m.r.). These included 2-(*benzylideneamino*)*phenyl diphenylphosphinate* (Found: M^+, 397.122. $C_{25}H_{20}NO_2P$ requires M^+, 397.123). Use of untreated benzaldehyde gave a 26% yield of diphenyl-*N*-(2-hydroxyphenyl)phosphinamide.

(i) 4-*Nitrobenzaldehyde*. A solution of the 2-methoxyphosph(v)ole (0.52 g, 1.6 mmol) and 4-nitrobenzaldehyde (1.20 g, 8.0 mmol) in the minimum volume of dry chloroform was heated under reflux for 24 h. The crystals which had formed were filtered off, and identified as diphenyl-*N*-(2-hydroxyphenyl)-phosphinamide (0.077 g, 16%) by i.r., ^1H and ^{31}P n.m.r. spectroscopy. Fractional distillation of the yellow residue obtained by concentration of the filtrate gave a fraction of b.p. 130—135 °C (0.1 Torr) which consisted of 4-nitrobenzaldehyde contaminated by some methyl diphenylphosphinate (*ca.* 10%). The second fraction sublimed at 190—195 °C (0.1 Torr), and was 2-(4-nitrophenyl)benzoxazole (0.065 g, 17%), m.p. 257—263 °C, mixed m.p. 259—264 °C (lit.,[15] 268 °C), δ_H(TFA) 7.7—8.1 (4 H, m) and 8.60 (4 H, s), whose ^1H n.m.r. and mass spectra were identical with those of an authentic sample.

Two experiments were conducted to identify the source of the benzoxazole. In the first, the presence of 2-[(4-nitrobenzylidene)amino]phenol was confirmed by an *in situ* ^{13}C n.m.r. experiment as described in part (g) above (δ_C 115.5, 115.8, 120.2, 124.0, 129.1, 130.3, 130.5, 134.4, 141.0, 152.8, and 153.7). In the second experiment, an intimate mixture of this phenol and 4-nitrobenzaldehyde was heated *in vacuo* under similar conditions to those used in the work-up of the original reaction. The fraction with b.p. 160—165 °C (0.05 Torr) was identified as the benzoxazole by its ^1H n.m.r. and mass spectra.

Thermolysis Reactions of the 'Phosphole Dimer' (**6**).—(a) *With N,N-dimethylformamide*. The 'phosphole dimer (**6**)' (0.26 g, 0.45 mmol) was heated with dry dimethylformamide (1.33 g, 18.2 mmol) at 120—130 °C for 2.5 h, after which the excess of amide was removed under reduced pressure. The resulting oil (0.33 g) crystallised on trituration, and was recrystallised from

methanol to give 2-(3,3-dimethyl-1,3-diazapropenyl)phenyl diphenylphosphinate (0.20 g, 59%), m.p. 164—167 °C, δ_p +30.1.

(b) *With benzophenone.* The ^{31}P n.m.r. spectra of a mixture of the 'phosphole dimer (**6**)' (0.037 g, 0.06 mmol) and benzophenone (0.61 g, 3.4 mmol) at 125 °C were monitored over 10 h. After this time, the spectrum consisted of a single peak (δ_p +28.5), which was identified as that due to 2-(diphenylmethyleneamino)phenyl diphenylphosphinate by spiking with an authentic sample.

(c) *With 4-chlorobenzaldehyde.* A similar n.m.r. experiment to (b) above, using the 'phosphole dimer (**6**)' (0.047 g, 0.08 mmol) and 4-chlorobenzaldehyde (0.34 g, 2.4 mmol) at 125 °C gave the anticipated aryl diphenylphosphinate (δ_p +29.5) after 1 h.

*Thermolysis Reactions of Diphenyl-*N*-(2-hydroxyphenyl)-phosphinamide.*—(a) In vacuo (cf. *ref.* 1). The phosphinamide (0.04 g, 0.13 mmol) was sublimed at 200 °C and 10^{-3} Torr during a period of 1 h, through a silica tube (35 × 2.5 cm) maintained at 750 °C. ^1H and ^{31}P N.m.r. spectroscopy of the pyrolysate showed that 2-aminophenyl diphenylphosphinate (63%) was the major product.

(b) *With* N,N*-dimethylformamide.* The reaction between the phosphinamide (0.019 g, 0.06 mmol) and dry dimethylformamide (0.59 g, 8.1 mmol) was monitored directly by ^{31}P n.m.r. spectroscopy. After 2.5 h at 125—130 °C the spectrum showed the presence only of unchanged phosphinamide (δ_p +19.2).

(c) *With benzophenone.* In a similar n.m.r. experiment, the phosphinamide (0.017 g, 0.05 mmol) and benzophenone (0.46 g, 2.5 mmol) had not reacted after being heated at 135—140 °C for 1 h. However, after 12 h at 150—160 °C, the major product was 2-(diphenylmethyleneamino)phenyl diphenylphosphinate [δ_p +28.8 (100%)] together with an unidentified minor component [δ_p +30.4 (25%)].

(d) *With 4-chlorobenzaldehyde.* In a similar experiment to part (c) above, the corresponding phosphinate [δ_p +30.0 (100%)] and an unidentified minor product [δ_p +31.8 (46%)] were obtained after the mixture had been heated at 120—130 °C for 1 h.

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