Reduction of Nitro- and Nitroso-compounds by Tervalent Phosphorus Reagents. Part XII.[1] Conversion of Aryl 2-Nitroaryl Ethers into Novel 3-Aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles† (Oxazaphosphoranes) and their 2-Oxo-derivatives

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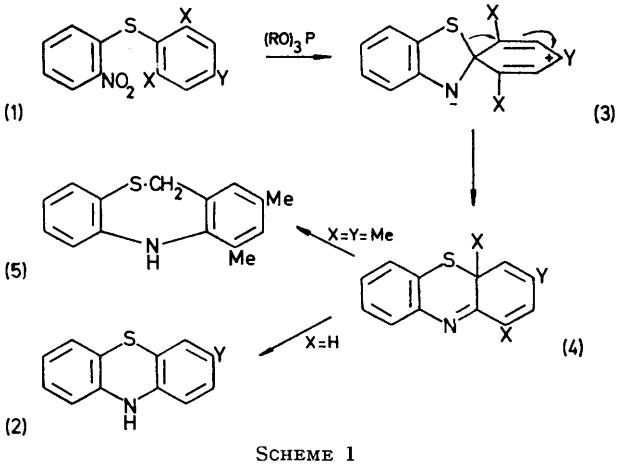
Reactions in cumene of aryl 2-nitroaryl ethers ($2\text{-}NO_2\cdot C_6H_4\cdot O\cdot C_6H_2R^3{}_2R^4$: R^3 = Me, R^4 = H; R^3 = R^4 = Me; R^3 = OMe, R^4 = H; R^3 = H, R^4 = OMe; R^3 = R^4 = H; R^3 = H, R^4 = Me; R^3 = Me, R^4 = CO_2Me) with tervalent phosphorus reagents (4 mol. equiv.) ($R^2R^1{}_2P$: R^1 = R^2 = MeO, EtO, or Pr^iO; R^1 = EtO, R^2 = Me; R^1 = MeO, R^2 = Ph; R^1 = Ph, R^2 = MeO; $R^1{}_2$ = $-O\cdot CH_2\cdot CH_2\cdot O-$, R^2 = Ph) give novel pentaco-ordinate phosphorus compounds, the 3-aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles (8) (12—95%). These are very rapidly hydrolysed in water to give tetraco-ordinate phosphorus compounds, 2-alkoxy-3-aryl-, 2-hydroxy-3-aryl-, 2-alkyl-3-aryl-, or 2,3-diaryl-2,3-dihydro-2-oxo-1,3,2-benzoxazaphospholes (15)—(17), according to conditions and the phosphorus ligands in the original oxazaphosphole (8). Hydrolysis in acid leads to 2-hydroxydiarylamines (13). The reaction of 4-methoxyphenyl 2-nitrophenyl ether with diethyl methylphosphonite gave as a major by-product (19.5%) a spiro-oxazaphosphole (32), probably *via* ligand exchange of the first-formed oxazaphosphole (8) with its hydrolysis product, 2-hydroxy-4′-methoxydiphenylamine. The reaction of ethane-1,2-diol with 2,3-dihydro-2,2-dimethoxy-2-phenyl-3-(2,4,6-trimethylphenyl)-1,3,2-benzoxazaphosphole (34) similarly gave the spiro-oxazaphosphole (35).

Small quantities, only, of non-phosphorus-containing heterocycles are formed as by-products in these reactions: 2,6-dimethylphenyl-, 2,4,6-trimethylphenyl-, and 2,6-dimethoxyphenyl 2-nitrophenyl ethers gave, respectively, 5,11-dihydro-4-methyldibenz[*b*,*e*][1,4]oxazepine, its 2,4-dimethyl analogue, and a mixture of 1,2-dimethoxyphenoxazine and 1- or 4-methoxy-phenoxazines in 1—5% yields.

The mechanisms of these reactions, which are markedly different from those of corresponding reactions of aryl 2-nitroaryl sulphides, are briefly discussed.

A WIDE variety of heterocyclic nitrogen compounds has been prepared by reductive cyclisation of suitable aromatic nitro-compounds with tervalent phosphorus reagents.[2] The synthesis of phenothiazines (2) from aryl 2-nitroaryl sulphides (1) by this method, besides being useful, is of mechanistic interest because it proceeds *via* rearrangement [2a] (Scheme 1) and, when the positions *ortho* to sulphur in the ring to be attacked by the nitrogen moiety are blocked, a new series of rearrangements arises leading to novel heterocycles, *e.g.* (4; X = CO_2Et; Y = H) or (5) (Scheme 1).[2a,3]

It was therefore of interest to investigate reactions of the corresponding aryl 2-nitroaryl ethers (6) with tervalent phosphorus reagents, in the expectation that the reduced migratory aptitude of oxygen in (7), should it be formed, compared with that of sulphur in (3) would lead to a new series of products.



SCHEME 1

At the start of this investigation it was known that the reaction of 2-nitrophenyl phenyl ether with an excess of triethyl phosphite in the absence of a solvent gave a

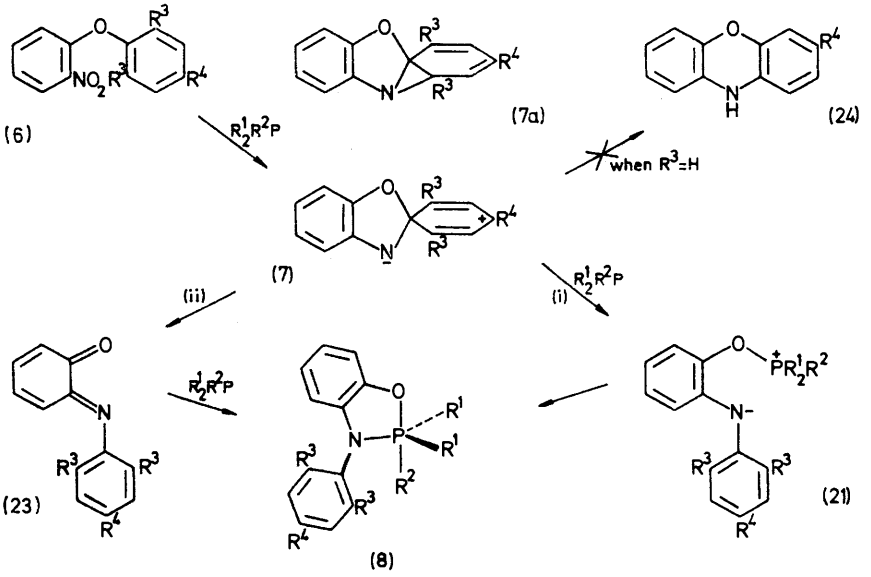
† Preliminary communication: J. I. G. Cadogan, D. S. B. Grace, P. K. K. Lim, and B. S. Tait, *J.C.S. Chem. Comm.*, 1972, 520.

[1] Part XI, M. A. Armour, J. I. G. Cadogan, and D. S. B. Grace, *J.C.S. Perkin II*, 1975, 1185.

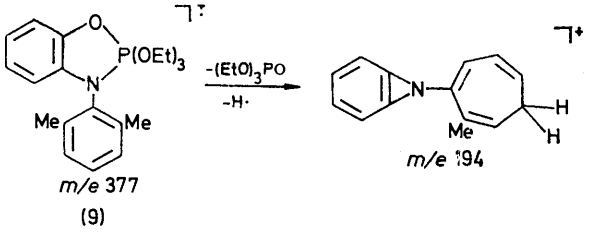
[2] J. I. G. Cadogan, (*a*) *Accounts Chem. Res.*, 1972, **5**, 303; (*b*) *Synthesis*, 1969, **1**, 11; (*c*) J. I. G. Cadogan and R. K. Mackie, *Chem. Soc. Rev.*, 1974, **3**, 87.

[3] J. I. G. Cadogan and S. Kulik, *J. Chem. Soc.* (*C*), 1971, 2621.

tarry mixture from which identifiable products could not be isolated.[4] Accordingly, we first investigated a series of aryl nitroaryl ethers in which the *ortho*-positions in the receptor ring were blocked (6), in the hope that this would reduce the possibility of side reactions and lead to cleaner reactions. In the event, as we describe below, this approach proved successful and led to the isolation of a new series of heterocycles, the 3-aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles (8), in yields of



SCHEME 2



SCHEME 3

up to 95%, in which the phosphorus atom, originally part of the reagent, is in the pentaco-ordinate, trigonal bipyramidal state and is incorporated in a heterocyclic ring. The scope of the reaction is indicated by Table 3 and the Summary, from which it can be seen that a wide range of phosphorus reagents and aryl nitroaryl ethers, including the unsubstituted case, undergo the reaction. The evidence for the structural assignment (8) is given below.

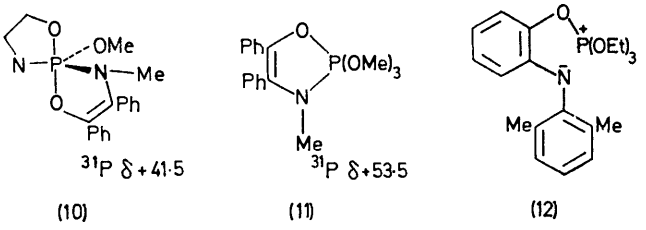
Mass Spectra.—The relevant data are contained in Table 4. A key observation in all cases was the loss of a fragment corresponding to the phosphorus moiety. For example, 3-(2,6-dimethylphenyl)-2,3-dihydro-2,2,

[4] J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 1965, 4831.

[5] M. Grayson and E. J. Griffith, *Topics Phosphorus Chem.*, 1967, **5**, 1.

2-triethoxy-1,3,2-benzoxazaphosphole (9) (Scheme 3) lost the fragment $(EtO)_3POH$. Also compatible with the proposed structure is the loss of ethylene by McLafferty rearrangement.

N.m.r. Spectra.—^{31}P Fourier transform and continuous wave n.m.r. spectra of twenty-three 3-aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles (8) are recorded in Table 3. Each exhibits one peak only with chemical shifts (upfield from H_3PO_4) in the range +33.3 to +62 p.p.m., characteristic of pentaco-ordinate phosphorus compounds,[5] closely related examples being (10) and (11).[6] In particular these values of chemical shifts exclude alternative dipolar structures such as (12) [7] (Scheme 4), and the very small downfield shift (<6 p.p.m.) observed when the ^{31}P spectrum of (8; $R^1 = OMe$, $R^2 = Ph$; $R^3 = R^4 = Me$) was recorded in $CDCl_3$–$(CF_3)_2CH{\cdot}OH$ (50% v/v), confirmed this, downfield shifts of up to 87



SCHEME 4

p.p.m. having been observed in established dipolar cases [8a] (Scheme 4). Also in accord with these assignments are the effects of substituents on the value of the

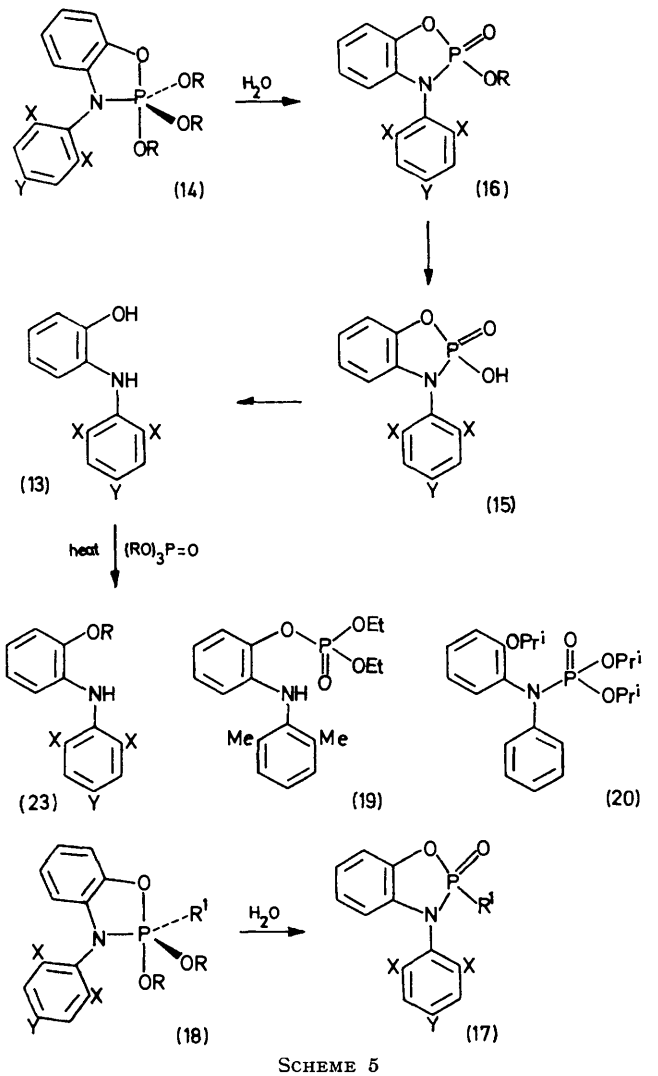
[6] (*a*) R. Burgada and D. Bernard, *Compt. rend.*, 1971, **272**, 2077; (*b*) F. Ramirez and N. Desai, *J. Amer. Chem. Soc.*, 1960, **82**, 2652; 1963, **85**, 3252.

[7] *Cf.* F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Amer. Chem. Soc.*, 1965, **87**, 4973.

[8] (*a*) F. Ramirez and I. Ugi, *Adv. Phys. Org. Chem.*, 1971, **9**, 25; (*b*) F. Ramirez, *Synthesis*, 1974, 90.

chemical shift. The successive replacement of alkoxy-groups by phenyl or methyl leads to the expected decreases in chemical shift (Table 3), and the introduction of a second five-membered ring into the molecule (compound U, Table 3) causes a decrease in chemical shift, again according to precedent.[9]

Also in accord with the assigned structure (8) are the ^{1}H n.m.r. spectra, described in the following paper, which



SCHEME 5

exhibit features of interest including a temperature-variation effect attributable to permutational isomerisation of the trigonal bipyramidal oxazaphosphole system.

Products of Hydrolysis.—As with other oxyphosphoranes,[10] the oxazaphospholes (8) are hydrolysed very rapidly ($t_{\frac{1}{2}}$ a few minutes in water at 20 °C); in some cases it was not possible to obtain them free from hydrolytic contaminants despite rigorous attempts to exclude water. As can be seen from Scheme 5 the nature of these products is in accord with the proposed structures (8).

Complete hydrolysis in acid solution leads to loss of the phosphorus moiety as an acid with the formation of *o*-hydroxydiphenylamines (13); partial hydrolysis occurs under milder conditions. Thus 3-(2,6-dimethylphenyl)-2,2,2-triethoxy-2,3-dihydro-1,3,2-benzoxazaphosphole (Scheme 5) (14; R = Et, X = Me, Y = H), in air, gave a high yield of 3-(2,6-dimethylphenyl)-2,3-dihydro-2-hydroxy-2-oxo-1,3,2-benzoxazaphosphole (15; X = Me, Y = H). Attempted recrystallisation of the trimethoxy- and tri-isopropoxy-analogues (14; R = Me or Pr^i, X = Me, Y = H) from light petroleum in the atmosphere led to less degraded products, *viz.* 3-(2,6-dimethylphenyl)-2,3-dihydro-2-methoxy-2-oxo-1,3,2-benzoxazaphosphole and its 2-isopropoxy-analogue (16; R = Me or Pr^i, X = Me, Y = H). Under similar conditions 3-(2,6-dimethoxyphenyl)-2,3-dihydro-2-methyl-2-oxo-1,3,2-benzoxazaphosphole (17; R^1 = Me, X = MeO, Y = H) was obtained from the 2,2-diethoxy-2-methyl precursor (18; R^1 = Me, R = Et, X = MeO; Y = H) (Scheme 5). The formation of these 2-oxo-benzoxazaphospholes (15)—(17) and others described in Table 5 support the proposed structure (8) and point to an overall reaction as in Scheme 5, although a more precise definition of mechanism must await the results of experiments in hand and will have to account for the formation of small amounts (<3%) of phosphoramidates such as (19) and (20).

The identities of the foregoing hydrolysis products were established by analysis and spectroscopy (Table 5).

The ^{1}H n.m.r. spectra contained particular points of interest which are described in the following paper.

X-Ray Crystallography.—*X*-Ray crystallographic analyses, described in a following paper,[11] of 3-(2,6-dimethylphenyl)-2,3-dihydro-2,2,2-trimethoxy-1,3,2-benzoxazaphosphole (8; R^1 = R^2 = MeO, R^3 = Me, R^4 = H) and its 2-hydroxy-2-oxo-analogue (15; X = Me; Y = H) obtained by hydrolysis also fully support the assigned structures.

Reaction Pathway and Mechanism.—We have discussed the general question of possible nitrene involvement in the phosphite–nitro-reaction elsewhere,[1-3] and we have no evidence which distinguishes between a nitrene or a precursor, *e.g.* $ArN^{-}-O-P^{+}(OEt)_3$, in the cyclisations described in this paper. In either event the products of the reaction can be accommodated by Scheme 2 whereby the nitrene or its precursor reacts to give the spiro-diene intermediate (7). This can then regain aromaticity either by undergoing direct nucleophilic attack by another molecule of the phosphorus reagent [step (i)], and hence, *via* (21), giving the product (8), or by rearrangement [step (ii)] to the quinone imine (22) fol-

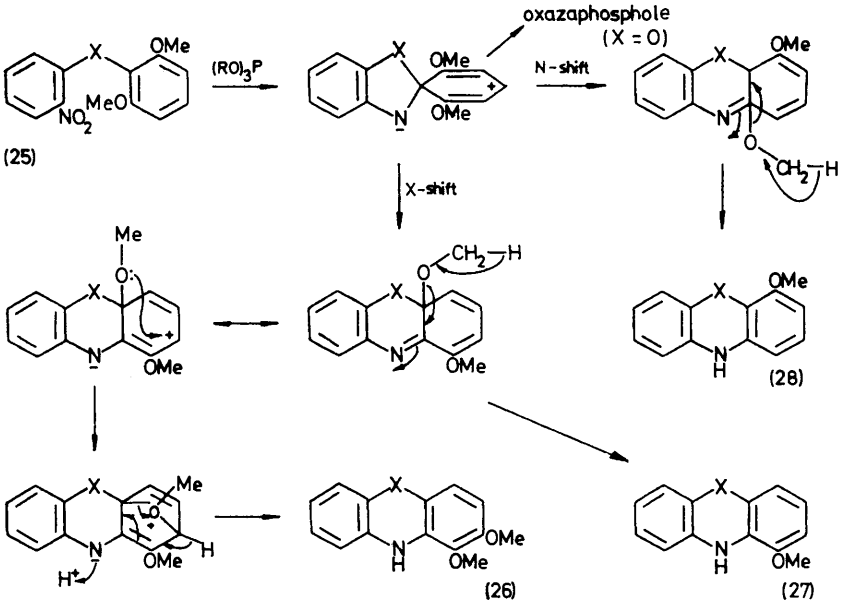
[9] F. Ramirez, A. J. Bigler, and C. P. Smith, *Tetrahedron*, 1968, **24**, 5041; F. Ramirez, K. Tasaka, and R. Hershberg, *Phosphorus*, 1972, **2**, 41.

[10] (*a*) W. C. Archie and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1973, **95**, 5955; (*b*) F. Ramirez, A. V. Patwardhan, N. B. Desai, and S. R. Heller, *ibid.*, 1965, **87**, 549.

[11] J. I. G. Cadogan, R. O. Gould, S. E. B. Gould, P. A. Sadler, S. J. Swire, and B. S. Tait, *J.C.S. Perkin I*, 1975, 2392.

lowed by trapping by the phosphorus reagent in a precedented reaction [6] to give the oxazaphosphole (8).*

The reactions usually proceeded in high yields, these being reduced occasionally by the ready formation of hydrolysis products described above (Scheme 5). In some cases the first formed *o*-hydroxydiphenylamines, produced by hydrolysis, underwent alkylation by trialkyl



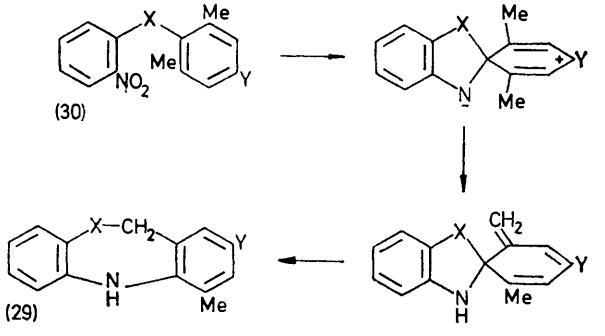
SCHEME 6 X = O or S

phosphate co-produced in the deoxygenation to give low yields of the corresponding 2-alkoxydiphenylamines (23) (Scheme 5).

Formation of Phenoxazines and 5,11-Dihydrodibenzoxazepines.—Unlike the corresponding reactions of aryl 2-nitroaryl sulphides (Scheme 1),[2,3] non-phosphorus-containing heterocycles were produced in very low yields (<3%) and only in a few cases. Phenoxazine (24; R^4 = H) (Scheme 2) was not detected even in the unsubstituted case, which might have been considered to have been the most favourable.

Reaction of 2,6-dimethoxyphenyl 2-nitrophenyl ether (25; X = O) (Scheme 6) with triethyl phosphite gave a good yield (52%) of the oxazaphosphole together with hydrolysis products (28%), but only low yields of 1,2-dimethoxyphenoxazine (26; X = O) (2%) and a monomethoxyphenoxazine, tentatively assigned the 1- or 4-methoxy-structure (27 or 28; X = O) (5%) were obtained. The latter products recall the formation of the corresponding methoxyphenothiazines, in much higher yields (total 65%) from 2,6-dimethoxyphenyl 2-nitrophenyl sulphide (25; X = S) (Scheme 6).[3]

Small quantities (1—3%) of 5,11-dihydro-4-methyldibenz[*b*,*e*][1,4]oxazepine (29; X = O, Y = H) and its 2,4-dimethyl analogue (29; X = O, Y = Me) were isolated from deoxygenation reactions of 2,6-dimethylphenyl 2-nitrophenyl ether (30; X = O, Y = H) and its 2,4,6-trimethyl homologue (30; X = O, Y = Me), respectively. Again, these products recall the formation of the corresponding 5,11-dihydrodibenz[*b*,*e*][1,4]-thiazepines (29; X = S, Y = H and Me) from the aryl 2-nitrophenyl sulphides (30; X = S, Y = H or Me) (Scheme 7).[3]

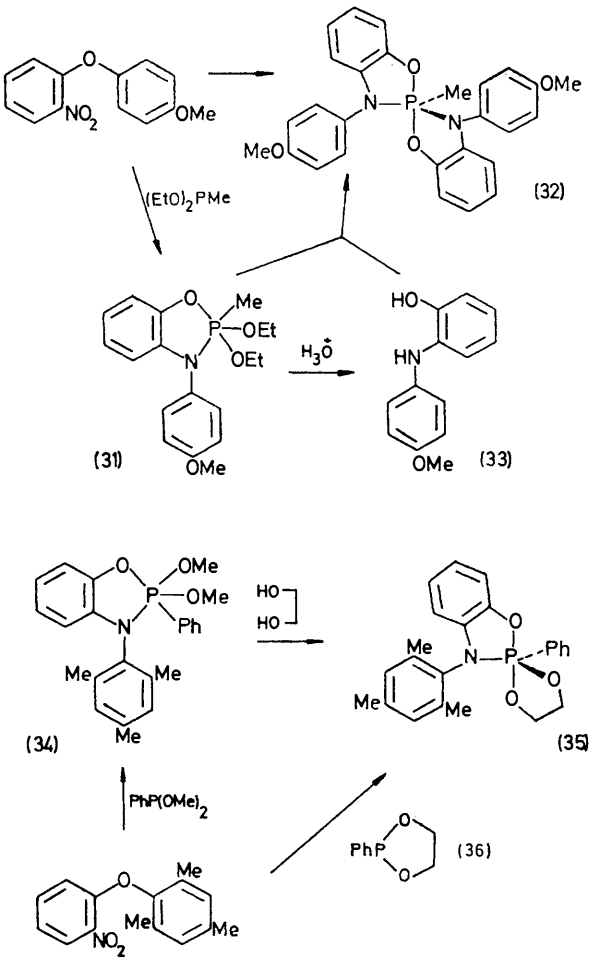


SCHEME 7 X = O or S

Formation of Spiro-1,3,2-benzoxazaphosph(v)oles (*Scheme* 8).—Whereas reaction of 4-methoxyphenyl 2-nitrophenyl ether with dimethyl phenylphosphonite [$(MeO)_2PPh$] gave a good yield of the corresponding oxazaphosphole (Table 3), reaction with diethyl methylphosphonite [$(EtO)_2PMe$] gave a mixture of the expected oxazaphosphole (31) and its hydrolysis products which, on attempted purification by distillation, gave 2,2′,3,3′-tetrahydro-3,3′-bis-(4-methoxyphenyl)-2-methyl-2,2′-spirobi-[1,3,2-benzoxazaphosphole] (32) (19.5%). This strongly suggested a ligand exchange

* The reaction may also be depicted in terms of the very strained azanorcaradiene (7a) derived from (7). We adhere to (7) for simplicity, although there is no direct evidence for either form.

reaction or ' transesterification ' between the first formed oxazaphosphole (31) and its hydrolysis product, 2-hydroxy-4'-methoxydiphenylamine (33).[12]



SCHEME 8

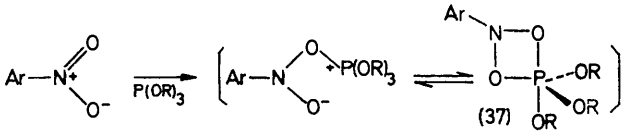
As a result of its hydrolytic instability it was not possible to test this explanation by first isolating the oxazaphosphole (31) and then allowing it to react with the hydroxydiphenylamine (33) to give, hopefully, the spiro-product (32).

That this is a reasonable explanation follows, however, from a related experiment in which 2,3-dihydro-2,2-dimethoxy-2-phenyl-3-(2,4,6-trimethylphenyl)-1,3,2-benzoxazaphosphole (34), on reaction with ethane-1,2-diol, gave, in excellent yield, 2,3-dihydro-2-phenyl-3-(2,4,6-trimethylphenyl)spiro{1,3,2-benzoxazaphosphole-2,2'-[1,3,2]dioxaphospholan} (35), identical with a sample produced directly by reaction of 2-nitrophenyl 2,4,6-trimethylphenyl ether with 2-phenyl-1,3,2-dioxaphospholan (36) (Scheme 8).

As expected [8] the spiro-compounds (32) and (35) derive considerable stability from the presence of two apical-equatorial five-membered rings. In accord with this, transesterification of (34) with propane-1,3-diol failed to give a spiro-derivative with both a five- and a six-membered ring.

Conclusions and Questions.—Deoxygenation of aryl 2-nitroaryl ethers by tervalent phosphorus reagents gives good yields of pentaco-ordinate oxazaphospholes (8). Phenoxazines and related heterocycles are formed by competitive cyclisation in trace amounts, if at all. This is in marked contrast to the case of the corresponding aryl 2-nitroaryl sulphides, where good yields of heterocycles were obtained but the corresponding pentaco-ordinate thiazaphospholes were not detected (Scheme 1). Although this can be attributed to the greater migratory aptitude of sulphur [(3) ⟶ (4)] *vs.* oxygen [(7) ⟶ (24)] (Scheme 2) it would be surprising if no thiazaphospholes were formed in the former case. An investigation of this point is described in a following paper.[13]

The ease of formation, and high thermal stability, of oxazaphospholes (8) prompts the question, now being investigated, of whether the first-formed intermediate in the deoxygenation of aromatic nitro-compounds by tervalent phosphorus reagents, in general, is also a nitrogen-containing phosphorane (37) (Scheme 9).



SCHEME 9

EXPERIMENTAL

N.m.r. Spectra.—^{1}H N.m.r. chemical shift values were recorded on the τ scale relative to tetramethylsilane as internal standard. Unless otherwise noted the solvent used was deuteriochloroform. ^{31}P N.m.r. spectra were obtained with a Varian HA-100 or XL100 spectrometer. Chemical shift values are given in p.p.m. to high field of external phosphoric acid (85%). The spectra obtained from the Varian XL100 instrument were proton noise-decoupled. In all these cases the solvent used was deuteriochloroform.

Mass Spectra.—These were obtained from an A.E.I. MS902 spectrometer. In each case the parent ion is given, followed by the percentage peak height in brackets. The major fragments and their relative abundances are also given along with any relevant metastable peaks. An A.E.I. MS20 spectrometer coupled to a Pye 104 gas chromatograph, with helium as carrier gas, was used for g.l.c.–mass spectrometry.

Reagents.—The tervalent phosphorus compounds used are widely described in the literature. Aryl 2-nitroaryl ethers (Table 1) were prepared [14] by reaction of the relevant *o*-chloronitrobenzenes with phenols in dimethyl sulphoxide in the presence of potassium hydroxide at 90 °C. The reaction was much improved when carried out under nitrogen.

Deoxygenation of Aryl 2-Nitroaryl Ethers: Formation of 3-Aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles.—(i) *General*

[12] F. Ramirez, K. Tasaka, N. B. Desai, and C. P. Smith, *J. Amer. Chem. Soc.*, 1968, **90**, 751; D. B. Denney, D. Z. Denney, R. Edelman, R. Powell, D. White, B. Chang, and W. Conrad, *ibid.*, 1971, **93**, 4004.

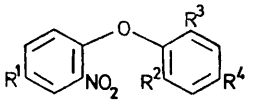
[13] J. I. G. Cadogan and B. S. Tait, *J.C.S. Perkin I*, 1975, 2396.

[14] J. Wright and E. C. Jorgensen, *J. Org. Chem.*, 1968, **33**, 1245.

method. A solution of the nitro-compound (0.01 mol) and the tervalent phosphorus reagent (0.04 mol) in freshly deperoxidised cumene (80 ml) was boiled under reflux, under dry nitrogen with stirring, for 65 h. *An absence of water*

TABLE 1

Aryl 2-nitroaryl ethers *



			Yield	M.p. (°C)	Analysis (%) †		
R^2	R^3	R^4	(%)	(lit. m.p.)	C	H	N
H	H	OMe	78	76—77	63.2	4.4	5.6
				(77)	63.7	4.5	5.7
‡Cl	Me	H	31	89—90	59.4	3.8	5.3
					59.2	3.8	5.3
Me	Me	H	72	75—76	69.0	5.2	5.4
				(73—74)	69.1	5.3	5.8
‡Me	Me	Me	52	74—75	70.3	6.0	5.2
					70.3	5.8	5.4
§Me	Me	H	51	98—99	69.9	5.8	5.2
					70.0	5.8	5.4
‡OMe	OMe	H	52	85—86	61.3	4.7	5.1
					61.1	4.7	5.1
Me	Me	CO_2Me	43	133—135	63.9	5.1	4.6
					63.8	5.0	4.7
H	H	Me	43	48 (49)			

* Except where indicated §, R^1 = H. † Upper row, ' Found ' values; lower row ' Required ' values. ‡ New compound. § R^1 = Me.

throughout the experiment was essential in order to prevent hydrolysis of the product.

The lower boiling fractions, *i.e.* cumene and phosphorus light esters were, as much as possible, removed by distillation at 12 mmHg (bath at 160 °C). The residue was transferred in a dry box under nitrogen to a distillation flask packed with glass wool and distilled at 0.01 mmHg (b.p. *ca.* 80—110°). The resulting oil or solid was examined analytically by n.m.r. and mass spectrometry and was usually the oxazaphosphole (see later), occasionally contaminated by hydrolysis products. Purification by distillation or crystallisation was effected where necessary. When contamination was extensive the reaction mixture was hydrolysed to remove the phosphorus moiety as an acid and to give 2-anilinophenols (see later), by use of ethanol–water (80 : 20; 50 ml) containing hydrochloric acid (10N; 10 drops) at the b.p. overnight (Method A). In many cases the residue from the distillation was similarly hydrolysed to give the same products and occasionally small quantities of dibenz[*b*,*e*][1,4]oxazepines (see later).

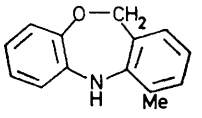
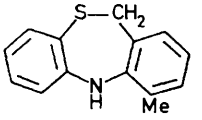
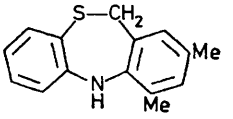
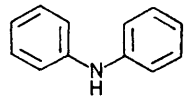
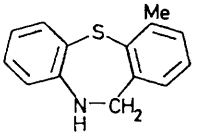
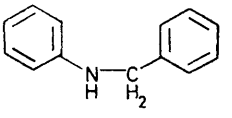
The above general method and the hydrolysis variation in work-up are exemplified by the case of reaction of 2,6-dimethylphenyl 2-nitrophenyl ether with triethyl phosphite, as follows: after reaction for 66 h, high-vacuum distillation gave the following fractions: (1) a colourless oil (b.p. 36° at 0.05 mmHg) identified by its i.r. spectrum as triethyl phosphate; (2) a yellow oil (b.p. 80° at 0.02 mmHg) which solidified on cooling and was identified as 3-(2,6-*dimethylphenyl*)-2,2,2-*triethoxy*-2,3-*dihydro*-1,3,2-*benzoxazaphosph*(v)*ole* (3.1 g, 82%), m.p. 36—38°, $\nu_{max.}$ 1 305 (ArN), 1 270 (ArO), 1 160w (POEt), 1 065 (CO), 980 (POEt), and 925 cm^{-1}; analytical, ^{31}P n.m.r., and mass spectral data are given in Tables 3 and 4. ^1H N.m.r. spectra are described in the following paper.

The residue from the distillation was hydrolysed by Method A to give 2-(2,6-*dimethylanilino*)*phenol* (0.23 g, 11%), m.p. 117—118° (Found: C, 79.2; H, 7.2; N, 6.7. $C_{14}H_{15}NO$ requires C, 78.9; H, 7.0; N, 6.6%), $\nu_{max.}$ 3 600 and 3 100—3 450 (OH and NH), 1 305 (ArN), 1 260 (ArO), 1 220, and 1 100 cm^{-1}, τ 7.80 (6, H s, 2ArMe), 4.8br (2 H s, OH and NH), 3.71 (1 H, m, aromatic), 3.20 (3 H, m, aromatic), and 2.91 (3 H, s, aromatic), *m/e* 213 (M^+, 100) and 107 (45).

The product of a replicate experiment was worked up by a different method: after low-vacuum distillation the residual dark brown oil was chromatographed on alumina (activity

TABLE 2

^1H N.m.r. data

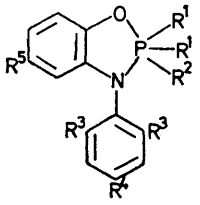
Compound	Chemical shifts (τ) NH	CH_2	Ref.
	4.43	5.11	
	4.34	6.10	3
	4.30	6.00	3
	4.60		
	6.15	5.30	3
	6.25	5.80	

I; 2 × 45 cm). Elution with petrol–ether (100 : 1) gave a solid identified as the above oxazaphosphole (1.31 g, 35%), m.p. 35—37°, with i.r. and ^1H n.m.r. spectra as expected.

Elution with petrol–ether (100 : 4) gave a colourless oil which solidified on cooling and was identified as 2-*ethoxy*-2′,6′-*dimethyldiphenylamine* (0.16 g, 6%), $\nu_{max.}$ (Nujol) 3 380 (NH), 1 250 (ArN), 1 220 (ArO), 1 120 (CO), and 1 050 (CO) cm^{-1}, τ 8.55 (3 H, t, OEt, J_{HH} 7 Hz), 7.82 (6 H, s, 2ArMe), 5.85 (2 H, q, OEt, J_{HH} 7 Hz), 4.3br (1 H, s, NH), 3.9 (1 H, m, aromatic), 3.1—3.3 (3 H, m, aromatic), and

TABLE 3

3-Aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles [a]



Compound [a]	R^1	R^2	R^3	R^4	Yield (%)	$^{31}P\delta$ (+)	M.p. (°C)	Analysis (%) [b] C	H	N	Other products [c] (%)	Accountance [d] (%)
A	OEt	OEt	Me	H	82	60	36—38	63.55	7.6	4.0	AP (11)	93
								63.7	7.4	3.7		
B	OMe	OMe	Me	H	62	57	129—130	60.8	6.5	4.4	DA (3)	83
								60.9	6.6	4.2	AP (18)	
C	OPr^i	OPr^i	Me	H	64	62	51—53	66.1	8.3	3.75	AP (33)	97
								65.9	8.1	3.3		
D	OEt	Me	Me	H	95	37	42—44	65.6	7.5	4.1		95
								65.7	7.5	4.0		
E	OEt	OEt	Me	H	87	60	51—53	64.8	7.7	3.7		87
								64.45	7.7	3.6		
F	OEt	OEt	Me	Me	85	60	34—37	64.5	7.6	4.0	Ox (1)	85
								64.45	7.7	3.6		
G	OMe	OMe	Me	Me	72	57.2	79—81	62.0	7.0	4.1	AP (17.5)	89.5
								61.9	6.9	4.0		
H [e]	OPr^i	OPr^i	Me	Me	12	62	62—64	66.3	8.3	3.2	DA (3), Ox (1.5)	83.5
								66.5	8.3	3.2	AP (66), PA (1)	
I	OEt	Me	Me	Me	95	37.5	63—65	66.5	8.1	3.9		95
								66.5	7.8	3.9		
J	OEt	OEt	OMe	H	52	57	83—84	58.4	6.8	3.7	AP (28)	80
								58.7	6.85	3.4		
K	OMe	Ph	H	OMe	78	45	164—165	65.9	5.8	3.6		78
								65.8	5.7	3.7		
L	OMe	Ph	H	H	70	45	104—106	68.4	5.8	3.9		70
								68.0	5.7	4.0		
M	OEt	Me	H	H	17	35.7	(Oil)				DA (6), AP (26)	49
N	OMe	Ph	Me	Me	86	46.7	162—163.5	70.1	6.4	3.7		86
								69.9	6.6	3.5		
O	Ph	OMe	Me	Me	64	44.2	196—198	76.1	6.4	3.1		64
								76.2	6.4	3.2		
P	OMe	OMe	H	Me	40	55.9	108—111				AP (22)	62
Q	OMe	Ph	H	Me	77	44.7	153—153.5	68.4	6.0	3.9		77
								68.7	6.0	3.8		
R	Ph	OMe	H	Me	76	39.9	188—189	75.5	5.9	3.3		76
								75.5	5.9	3.4		
S	OMe	Ph	Me	H	83	47.1	108—110	69.3	6.2	3.6		83
								69.3	6.3	3.7		
T	OMe	OMe	Me	CO_2Me	74	58.1	64—66	57.8	3.6	6.1		74
								58.0	3.6	6.2		
U	$-O(CH_2)_2O-$	Ph	Me	Me	89	33.3	189.5—191	70.0	6.2	3.4		89
								70.2	6.2	3.6		
V [f]	OEt	OEt	H	OMe	36	59					DA (24)	60
W [f]	OMe	Ph	OMe	H		41.6					OP	
X [g]	OEt	Me	H	OMe	19	35.8	225—226	68.7	5.5	5.95	OP (14),	44
								68.6	5.3	5.9	DA (11)	

[a] In compound E, R^5 = Me; in all other cases R^5 = H (Tables 2 and 3). [b] Upper row, ' Found ' values; lower row, ' Required ' values. [c] All structures were confirmed by comparison (i.r. spectrum) with an authentic sample or identified on the basis of i.r., ^1H n.m.r., and mass spectral data, and exact mass or analytical data as described in the Experimental section and Table 5. AP = an anilinophenol, DA = a diphenylamine, Ox = an oxazepine, PA = a phosphoramidate, OP = a 2-oxo-1,3,2-oxazaphospholine. [d] Accountance based on starting aryl 2-nitroaryl ether. Supporting mass spectral data are given in Table 4. ^1H n.m.r. data are given in the following paper. [e] Worked up by chromatography (Al_2O_3). [f] These experiments gave inseparable mixtures: data are derived from n.m.r. and g.l.c.–mass spectrometry. [g] Compound X was a ' bis-spiro '-compound; see Experimental section.

2.95 (3 H, s, aromatic), *m/e* 241 (M^+ 100), 212 (64), and 197 (85), m.p. 100—101° (Found: C, 80.1; H, 8.2; N, 6.1. $C_{16}H_{19}NO$ requires C, 79.7; H, 7.9; N, 5.8%).

Elution with petrol–ether (100 : 7) gave starting material (0.03 g, 2%), identified by its i.r. spectrum.

Elution with petrol–ether (100 : 50) gave a pale yellow oil which solidified on cooling. Sublimation gave 5,11-*dihydro-4-methyldibenz*[b,e][1,4]*oxazepine* (0.03 g, 3%), m.p. 120—121° (Found: C, 79.6; H, 6.1; N, 6.2. $C_{14}H_{13}NO$ requires C, 79.6; H, 6.2; N, 6.2%. Found: M^+, 211.099 437; required: 211.099 708. Found: $M^+ - CHO$, 182.096 761; required: 182.096 970), τ 7.79 (3 H, s, Me), 5.11 (2 H, s, OCH_2), 4.43br (1 H, s, NH), and 3.0—3.6 (7 H, m, aromatic).

The assignment of the 5,11-structure rather than the isomeric 10,11-form rests on the loss of the important CHO fragment in the mass spectrum and on comparison of the NH chemical shift with values for a series of related compounds (Table 2). The observed CH_2 chemical shift is also in agreement with the relative deshielding effect of the heteroatoms (O > N > S). Further elution gave 2-hydroxy-2′,6′-dimethyldiphenylamine (0.12 g, 6%), identical with the sample described above.

The results of a series of deoxygenation reactions of aryl 2-nitroaryl ethers are summarised in Table 3. Supporting mass spectral data are in Table 4; ^1H n.m.r. spectra are described in the following paper. By-products obtained from these reactions were identified as follows.

(i) *Reaction of trimethyl phosphite with 2,6-dimethylphenyl 2-nitrophenyl ether.* Hydrolysis of the distillation residue (Method A) followed by chromatography gave 2-*methoxy-2′,6′-dimethyldiphenylamine* (0.08 g, 3%), m.p. 82—84°, $\nu_{max.}$ 3 370 (NH), 1 290 (ArN), 1 240 (ArO), 1 110 (CO), and 1 030 cm^{-1} (CO), τ 7.8 (6 H, s, 2ArMe), 6.04 (3 H, s, OMe), 4.3br (1 H, s, NH), 3.8 (1 H, m, aromatic), 3.0—3.4 (3 H, m, aromatic), and 2.9 (3 H, s, aromatic), *m/e* 227 (M^+, 100), 212 (20), and 197 (43) (Found: M^+, 227.130 116. $C_{15}H_{17}NO$ requires *M*, 227.131 007). Further elution gave 2-(2,6-dimethylanilino)phenol (0.39 g, 18%), as described above.

(ii) *Reaction of 2-nitrophenyl 2,4,6-trimethylphenyl ether with trimethyl phosphite.* This reaction similarly gave 2-*(2,4,6-trimethylanilino)phenol* (17.5%), m.p. 102—103° (Found: C, 79.1; H, 7.6; N, 6.2. $C_{15}H_{17}NO$ requires C, 79.3; H, 7.5; N, 6.2%); i.r., n.m.r., and mass spectra as expected.

(iii) *Reaction of tri-isopropyl phosphite with 2-nitrophenyl 2,4,6-trimethylphenyl ether.* The product was worked up by chromatography on alumina. In addition to 2,3-*dihydro*-2,2,2-*tri-isopropoxy*-3-(2,4,6-*trimethylphenyl*)-1,3,2-*benzoxazaphosph*(v)*ole* was obtained 2-*isopropoxy*-2′,4′,6′-*trimethyldiphenylamine* (3%), $\nu_{max.}$ 3 400 (NH), 1 320 (ArN), 1 240

TABLE 4

Mass spectral characteristics of 3-aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles

Compound [a]	Exact mass [b]	*m/e* (%) Parent	$-HOPR^1{}_2R^2$	$-R^1$	McLafferty
A	377.174 496	377 (100)	194 (100)	332 (22)	$-C_2H_4$ (9)
	377.175 585				
B		335 (100)	194 (100)	304 (60)	
C		419 (50)	194 (65)		$-C_3H_6$ (63)
D		347 (45)	194 (100)	302 (22)	$-C_2H_4$ (3)
E		391 (100)	208 (100)	346 (24)	$-C_2H_4$ (10)
F	391.191 046	391 (100)	208 (75)	346 (23)	$-C_2H_4$ (15)
	391.191 234				
G	349.143 132	349 (66)	208 (100)	318 (21)	
	349.144 286				
H		433 (78)	208 (45)		$-C_3H_6$ (90)
I		361 (85)	208 (100)	316 (30)	$-C_2H_4$ (15)
J		409 (100)		364 (35)	$-C_2H_4$ (25)
K		383 (100)	196 (10)	352 (20)	
L		353 (100)		322 (20)	
M		319 (100)		274 (43)	$-C_2H_4$ (44)
N	395.165 326	395 (85)	208 (100)	364 (21)	
	395.165 021				
O	441.184 907	441 (100)	208 (100)	410 (23)	
	441.185 756				
P	321.112 904	321 (100)	180 (28)	290 (24)	
	321.112 987				
Q	367.132 773	367 (100)		336 (15)	
	367.133 723				
R	413.152 983	413 (100)	180 (12)	382 (19)	
	413.154 458				
S	381.148 179	381 (97)	194 (100)	350 (17)	
	381.149 372				
T	393.132 696	393 (100)	252 (92)	362 (40)	
	393.134 114				
U	393.148 603	393 (100)	208 (81)	349 (62) [c]	
	393.149 372				
V	379.154 353	379 (100)		334 (19)	$-C_2H_4$ (48)
	379.154 849				

[a] Compounds numbered as in Table 3. [b] Upper row, ' Found ' value; lower row, ' Required ' value. [c] Loss of $-CH_2{\cdot}CH_2{\cdot}O-$.

(CO), 1 115 (CO), and 1 015 cm^{-1} (CO), τ 8.62 (6 H, d, OPr^i, J_{HH} 7 Hz), 7.85 (6 H, s, 2ArMe), 7.72 (3 H, s, ArMe), 5.4 (1 H, septet, OPr^i, J_{HH} 7 Hz), 4.4br (1 H, s, NH), 3.87 (1 H, m, aromatic), and 3.0—3.4 (5 H, m, aromatic), *m/e* 269 (M^+, 100), 227 (100), 211 (50) (Found: M^+, 269.177 878. $C_{18}H_{23}NO$ requires *M*, 269.177 955).

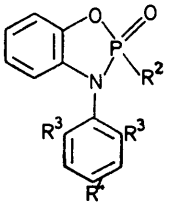
Also obtained was 5,11-*dihydro*-2,4-*dimethyldibenz*[b,e]-[1,4]*oxazepine* (1.5%), m.p. 119—120° (Found: C, 79.9; H, 6.6; N, 6.4. $C_{15}H_{15}NO$ requires C, 80.0; H, 6,6; N, 6.15%. Found: M^+, 225.115 246; required: 225.115 358.

with triethyl phosphite. Work-up by distillation and hydrolysis of the residue gave the oxazaphosphole (Table 3), and 2-*hydroxy*-2′,6′-*dimethoxydiphenylamine* (28%), m.p. 159—160° (Found: C, 69.0; H, 6.2; N, 5.8. $C_{14}H_{15}NO_3$ requires C, 68.6; H, 6.1; N, 5.7%); i.r., mass, and n.m.r. spectra as expected.

Material from a replicate experiment, worked up by chromatography, gave, additionally, a monomethoxyphenoxazine (5%), m.p. 81°, as pale yellow crystals on sublimation (Found: C, 73.4; H, 5.1; N, 6.6%; M^+,

TABLE 5

3-Aryl-2,3-dihydro-2-oxo-1,3,2-benzoxazaphospholes *



					Analysis (%) †			
R^2	R^3	R^4	M.p. (°C)	^{31}Pδ	C	H	N	Mass
OMe	Me	H	151	−13.5	62.3	5.5	4.85	289 ‡
					62.3	5.5	4.8	289
OPr^i	Me	H	113—114		64.4	6.1	4.8	317
					64.35	6.3	4.4	317
OMe	OMe	H	156—158		56.45	5.1	4.5	321
					56.1	5.0	4.4	321
Me	OMe	H	131—133					305.081 084
								305.081 689
OH	Me	H	230—232	−15.6	61.0	4.95	5.1	275
					61.1	5.1	5.1	275
OH	Me	Me	223	−15.9	62.5	5.9	4.9	289.086 828
					62.3	5.6	4.8	289.086 775
Ph	Me	Me	137.5—139	−28.6	72.1	5.8	4.0	349.121 743
					72.2	5.8	4.0	349.123 123
Ph	OMe	H	185—187	−28.8	65.1	4.8	3.8	367.097 467
					65.4	4.9	3.8	367.097 338
Ph	H	Me	148—150	−29.4	70.8	5.0	4.4	321.092 809
					71.0	5.0	4.4	321.091 861
Ph	H	H	127—128	−29.4	70.6	4.6	4.5	307
					70.4	4.6	4.6	307
Me	H	OMe	78—79		60.95	4.9	5.1	275
					61.1	5.1	5.1	275

* ^{1}H N.m.r. spectra are given in the following paper; i.r. spectra were as expected. † Upper row, ' Found ' values; lower row, ' Required ' values. ‡ All mass spectra had the expected cracking pattern, *e.g.* *m/e* 289 (100), 251 [25, *m** 228 (289 → 257)], and 194 [25, *m** 130 (289 ⟶ 194)].

Found: M^+ −CHO, 196.111 522; required: 196.112 619), τ 8.03 (6 H, s, 2Me), 5.14 (2 H, s, OCH_2) 4.54br (1 H, s, NH), and 3.2—3.5 (6 H, m, aromatic).

Elution with ether gave a green oil identified as *di-isopropyl* N-(2-*isopropoxyphenyl*)-N-(2,4,6-*trimethylphenyl*)-*phosphoramidate* (0.04 g, 1%), $\nu_{max.}$ 1 310 (ArN), 1 245 (P : O), 1 170w (POCH), and 1 000 cm^{-1} (CO), τ 8.5—8.9 (18 H, m, 3OPr^i), 7.90 (6 H, s, 2ArMe), 7.76 (3 H, s, ArMe), 5.3 (3 H, m, 3OPr^i), and 2.7—4.0 (6 H, m, aromatic), *m/e* 433 (M^+, 33), 391 (78), 349 (15), and 307 (100) (Found: M^+, 433.237 871. $C_{24}H_{36}NO_4P$ requires *M*, 433.238 182).

Elution with N-hydrochloric acid gave a dark brown oil which, after extraction into ether, drying, and removal of solvent, gave 2-(2,4,6-trimethylanilino)phenol (1.75 g, 66%) identified by its i.r. spectrum (accountance 85%).

(iv) *Reaction of* 2,6-*dimethoxyphenyl* 2-*nitrophenyl ether* 213.079 522. Calc. for $C_{13}H_{11}NO_2$: C, 73.3; H, 5.2; N, 6.6%; *M*, 213.078 973). The mass spectrum had an abundant fragment (75%) at *m/e* 198, attributable to loss of methyl and formation of a quinonoid ion, pointing to MeO *ortho* or *para* to the phenoxazine oxygen atom, τ (C_6D_6) 6.81 (3 H, s, MeO), 4.84br (1 H, s, NH), 4.10—4.20 (1 H, m, ArH), 3.93 (1 H, t, ArH, *J* 5 Hz), 3.46—3.60 (4 H, m, ArH), and 3.30—3.40 (1 H, m, ArH). The product is therefore 1- or 4-methoxyphenoxazine.

Further elution gave 1,2-*dimethoxyphenoxazine* (2%) as a yellow oil (Found: M^+, 243.091 37. $C_{14}H_{13}NO_3$ requires M, 243.089 537), *m/e* 228 (M^+ − Me), τ 6.25 (3 H, s, OMe), 6.19 (3 H, s, OMe), 4.42br (1 H, s, NH), and 3.2—3.9 (6 H, m, ArH) containing two prominent doublets (*J* 9 Hz) at 3.87 and 3.64.

Further elution gave 2-*ethoxy*-2′,6′-*dimethoxydiphenyl*-

amine (6%), m.p. 137—138° (Found: M^+, 273.135 573. $C_{16}H_{19}NO_3$ requires M, 273.136 485); i.r. and n.m.r. spectra as expected:

(v) *Reaction of 2-nitrophenyl phenyl ether with dimethyl phenylphosphonite.* Hydrolysis of the residue (Method A) gave 2-methoxydiphenylamine (1.5%) as shown by i.r., mass, and n.m.r. spectra, and 2-hydroxydiphenylamine (12%), m.p. 68—69° (lit.,[15] 69—70°); spectra as expected.

In addition to these experiments, most of which gave good yields of 3-aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles, some experiments yielded mixtures of the latter with their partially hydrolysed products such as 2,3-dihydro-2-oxo-1,3,2-benzoxazaphospholes, of mechanistic importance. In other cases the first-formed products were hydrolysed in air or on attempted recrystallisation. This is exemplified by the reaction of 2,6-dimethylphenyl 2-nitrophenyl ether with triethyl phosphite, during which the resulting 3-(2,6-dimethylphenyl)-2,2,2-triethoxy-2,3-dihydro-1,3,2-benzoxazaphosphole, in air, was hydrolysed in good yield to a white solid identified as 3-(2,6-*dimethylphenyl*)-2,3-*dihydro*-2-*hydroxy*-2-*oxo*-1,3,2-*benzoxazaphosphole*, m.p. (from benzene) 230—232° (see Table 5).

From a replicate experiment a mixture of hydrolysis products, derived from the benzoxazaphosphole was obtained. On eluting this mixture down a dry alumina column with benzene a light brown solid was obtained which was identified as 2-(2,6-*dimethylanilino*)*phenyl diethyl phosphate*, m.p. (sublimed) 63—65°, $\nu_{max.}$ (Nujol) 3 400 (NH), 1 320w (ArN), 1 275 (P : O), 1 250 (ArO), 1 180w (POEt), 1 030 (CO), 970 (POEt), and 750 cm^{-1} (PO), τ 8.61 (6 H, d t, 2POEt, J_{HH} 7, J_{PH} 1 Hz), 7.79 (6 H, s, 2ArMe), 5.72 (4 H, d q, 2POEt, J_{HH} 7, J_{PH} 8.5 Hz), 4.0—4.6br (1 H, s, NH), 3.8 (1 H, m, aromatic), 3.0—3.3 (2 H, m, aromatic), 2.86 (3 H, s, aromatic), and 2.66—2.8 (1 H, m, aromatic), ^{31}P δ +4.7, *m/e* 349 (M^+, 100) and 194 (40) (Found: M^+, 349.144 028. $C_{18}N_{24}NO_4P$ requires M, 349.144 286).

In an analogous experiment, the oxazaphosphole (1.02 g) obtained from the reaction with trimethyl phosphite, on attempted recrystallisation, gave 3-(2,6-*dimethylphenyl*)-2,3-*dihydro*-2-*methoxy*-2-*oxo*-1,3,2-*benzoxazaphosph*(v)*ole* (0.22 g), m.p. 151°, see Table 5.

Details of other 3-aryl-2,3-dihydro-2-oxobenzoxazaphospholes similarly obtained are given in Table 5.

Reaction of 4-Methoxyphenyl 2-Nitrophenyl Ether with Diethyl Methylphosphonite.—After reaction for 66 h low-vacuum distillation left an oil. Addition of ether to this oil gave a white solid (0.45 g). High-vacuum distillation of the residue gave the following fractions: (1) a colourless liquid shown by its i.r. spectrum to be diethyl methylphosphonate; (2) a light yellow oil (b.p. 140—145° at 0.04 mmHg) (2.30 g); (3) a yellow oil (b.p. 140° at 0.04 mmHg) (0.53 g); (4) the remaining distillable material [320 °C (bath)] (0.45 g). The precipitated solid and fraction (4) were shown by ^1H n.m.r. to be the same substance, which was identified as 2,2′,3,3′-*tetrahydro*-3,3′-*bis*-(4-*methoxyphenyl*) 2-*methyl*-2,2′-*spirobi*-[1,3,2-*benzoxazaphosphole*] (0.9 g, 19%), m.p. (from ether–chloroform; 60% recovery) 225—226° (Found: C, 68.7; H, 5.5; N, 5.95. $C_{27}H_{25}N_2O_4P$ requires C, 68.6; H, 5.3; N, 5.9%), $\nu_{max.}$ (Nujol) 1 290 (PMe and ArN), 1 245 (ArO), and 1 030 and 1 015 cm^{-1} (CO), τ 7.82 (3 H, d, PMe, J_{PH} 18 Hz), 6.20 (6 H, s, ArOMe), 3.89 (2 H, m, aromatic), 3.72 (2 H, m, aromatic), 3.40 (4 H, m, aromatic), and 2.82—3.16 (8 H, m, aromatic), ^{31}P δ +35.8, *m/e* 472 (M^+, 100), 457 [11, *m** 443 (472 ⟶ 457)], 349 (1),275 (3), 244 (32), and 236 (8), *m/2e* 236.5 (2).

Trituration of the oils of fractions (2) and (3) in petrol–ether gave a white solid identified as 2,3-*dihydro*-3-(4-*methoxyphenyl*)-2-*methyl*-2-*oxo*-1,3,2-*benzoxazaphosph*(v)*ole* (0.39 g, 14%), m.p. 78—79°, see Table 5.

The residues were hydrolysed by Method A and the dark oil obtained was run down a dry alumina column with ethyl acetate as solvent. A colourless oil was isolated which slowly solidified and was identified as 2-*ethoxy*-4′-*methoxydiphenylamine* (0.28 g, 11%), m.p. 49—51° (Found: C, 74.2; H, 7.1; N, 5.6. $C_{15}H_{17}NO_2$ requires C, 74.1; H, 7.0; N, 5.8%), $\nu_{max.}$ (Nujol) 3 410 (NH), 1 290 (ArN), 1 240 (ArO), 1 120 (CO), and 1 040 cm^{-1} (CO), τ 8.57 (3 H, t, OEt, J_{HH} 7 Hz), 6.24 (3 H, s, ArOMe), 5.90 (2 H, q, OEt, J_{HH} 7 Hz), 4.0br (1 H, s, NH), and 2.7—3.3 (8 H, m, aromatic), *m/e* 243 (M^+ 100), 214 [50, *m** 188 (243 ⟶ 214)], and 183 (50) (accountance 63%).

Reaction of 2,3-*Dihydro*-2,2-*dimethoxy*-2-*phenyl*-3-(2,4,6-*trimethylphenyl*)-1,3,2-*benzoxazaphosphole with Diols.*—(i) *With ethane*-1,2-*diol.* The oxazaphosphole (0.54 g, 1.2 mmol) was treated with ethane-1,2-diol (6 ml) in dry dioxan (40 ml) at room temperature for 112 h. Examination of the product after removal of solvents indicated the presence of starting material (10%) and a new substance (80%), separated by sublimation (180° and 0.2 mmHg), and shown to be 2,3-*dihydro*-2-*phenyl*-3-(2,4,6-*trimethylphenyl*)*spiro*-{1,3,2-*benzoxazaphosphole*-2,2′-[1,3,2]*dioxaphospholan*}, identical with that obtained by reaction of 2-nitrophenyl 2,4,6-trimethylphenyl ether with 2-phenyl-1,3,2-dioxaphospholan (Tables 3 and 4).

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