Reduction of Nitro- and Nitroso-compounds by Tervalent Phosphorus Reagents. Part 16.[1] Formation and Reactions of 2,3-Dihydro-1,3,2-benzothiazaphosph(v)oles [Amino(thiyl)phosphoranes] †

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In contrast to the corresponding ethers, which give 3-aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles [amino(oxy)phosphoranes] (1; X = O) on reaction with phosphorus(III) esters, aryl 2-nitroaryl sulphides give *N*-aryl-*N*-(2-alkylthiophenyl)phosphoramidates (4), in addition to N–S heterocycles. Yields of (4) are high (70%) when *o*-blocking methyl groups are present. Using ^{31}P Fourier-transform n.m.r. spectroscopy we have shown that compounds (4) are probably derived *via* the intermediacy and isomerisation of amino(thiyl)phosphoranes (1; X = S). This has been confirmed, using 2-phenyl-1,3,2-dioxaphospholan, by the isolation of the novel 2,3-dihydro-2-phenyl-3-(2,4,6-trimethylphenyl)-1,3,2-benzothiazaphosph(v)ole-2-spiro-2'-1',3',2'-dioxaphospholan (6; Q = Y = Me) and its 2,6-dimethylphenyl- and 2,6-dimethoxyphenyl-analogues (6; Q = Me, Y = H and 6; Q = MeO, Y = H) in 32—76% yield. These do not isomerise to amidates corresponding to (4). The use of methyl diphenylphosphinite (Ph_2POMe) in boiling toluene led to the first monocyclic amino(thiyl)phosphoranes, 2,3-dihydro-2,2-diphenyl-3-(2,6-dimethylphenyl)-2-methoxy-1,3,2-benzothiazaphosph(v)ole (7; Ar = 2,6-$Me_2C_6H_3$; 51%) and its 2,4,6-trimethylphenyl analogue (7; Ar = 2,4,6-$Me_3C_6H_2$; 48%). In boiling cumene (153 °C) these isomerised into *N*-(2,6-dimethylphenyl)-*N*-(2-methylthiophenyl)-*PP*-diphenylphosphinamidate (8) and its trimethylphenyl analogue. A kinetic study, using a programmed n.m.r. technique, showed that this reaction is first order (10^5k_1 at 451 K = 2.4 ± 1.2 s^{-1}), the high activation energy ($E_{act.}$ 220 ± 60 kJ mol^{-1}) pointing to a rate-determining fission of the phosphorane ring to give a quasi-phosphonium betaine (10), followed by fast alkyl transfer.

By-products in the formation of (7) and (8) from methyl diphenylphosphinite and aryl 2-nitrophenyl ethers include *N*-(2,6-dimethylphenyl)-*N*-(2-thiophenyl)-*PP*-diphenylphosphinamidate (11), formed by acidic hydrolysis of (7); 2-(2,6-dimethylphenylthio)phenylimino-*PP*-diphenyl-*P*-methoxyphosphorane (14) and its thermally derived isomer, *N*-methyl-*N*-2-(2,6-dimethylphenylthio)phenyl-*PP*-diphenylphosphinamidate (17), and products of the hydrolysis of (14), *N*-2-(2,6-dimethylphenylthio)phenyl-*PP*-diphenylphosphinamidate (13) and the derived amine (12). The formation of 2-methylthio-2',6'-dimethyldiphenylamine (15) is attributed to methylation of the thioquinone imine (16) postulated as an intermediate in the reaction. Analogous products were obtained from the 2,4,6-trimethylphenyl homologue.

The spirophosphoranes (6) exhibit classical temperature-dependent ligand reorganisation observable by n.m.r. with T_c = 110—126 °C and $\Delta G^{\ddagger}$ = 80.4—89.8 kJ mol^{-1}. Compounds (7) exhibit solvent chemical-shift changes from −37.8 δ($CDCl_3$) to +72.4 [$(CF_3)_2CHOH$–$CDCl_3$] indicating ring fission to the isomeric quasi-phosphonium betaines.

In Part 12 [2] we described a general method for the almost quantitative formation of 3-aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles [amino(oxy)phosphoranes] (1; X = O) on reaction of phosphorus(III) esters with aryl 2-nitroaryl ethers. Non-phosphorus containing heterocycles, *e.g.* 5,11-dihydrodibenz[*b*,*e*][1,4]oxazepines (2; X = O), or phenoxazines (3; X = O), were formed in only trace amounts, if at all. These results are in contrast to those obtained with the corresponding aryl 2-nitrophenyl sulphides.[3] In those cases where the *o*-positions in the aryl group were unblocked high yields of phenothiazines (3; X = S) were formed. Blocked *o*-positions in the aryl 2-nitroaryl sulphides led to *N*-aryl-*N*-alkylthiophenylphosphoramidates (4); yields were particularly high (*ca.* 70%) using *o*-methyl groups.

In Part 15 [1] we postulated that compounds (4) arose *via* isomerisation of the hitherto unknown amino(thiyl)-phosphoranes (1; X = S) (Scheme 1). This paper describes the results of experiments which not only support this hypothesis but also led to the isolation and characterisation of these elusive phosphoranes.

RESULTS AND DISCUSSION

Formation, Characterisation, and Isomerisation of 3-*Aryl*-2,3-*dihydro*-1,3,2-*benzothiazaphosph*(v)*oles*[*amino*-*(thiyl)phosphoranes*] (1; X = S).—(*i*) *Formation.* First, we used ^{31}P n.m.r. spectroscopy to establish that a phosphorane is, in fact, an intermediate in the reaction of trimethyl phosphite with 2-nitrophenyl 2,4,6-trimethylphenyl sulphide in boiling cumene (153 °C), the isolated product being dimethyl *N*-(2-methylthiophenyl)-*N*-(2,4,6-trimethylphenyl)phosphoramidate (4; R = Y = Q = Me). In this we used the well known fact that phosphoranes have negative ^{31}P chemical shifts relative to phosphoric acid (positive to high frequency) whereas phosphorus(III) esters and phosphoramidates have positive shifts. Control experiments carried out in the probe of the spectrometer established the appearance of a species (δ − 23.8) which gradually increased to a maximum and then decreased with the concomitant formation of the final isolated product, the phosphoramidate (4; R = Q = Y = Me) (δ +5.8). Similar results were obtained using 2,6-dimethylphenyl 2-nitrophenyl sulphide (δ, −24.0→+5.6) with trimethyl phosphite and the 2,4,6-trimethylphenyl homologue in the presence of dimethyl phenylphosphonite (δ, −26.4→+21.0).

These results strongly suggested the intermediacy of amino(thiyl)phosphoranes which isomerised under the reaction conditions. We therefore examined the reaction of the cyclic phosphorus(III) reagent, 2-phenyl-1,3,2-dioxaphospholan (5; Scheme 2) with 2,4,6-

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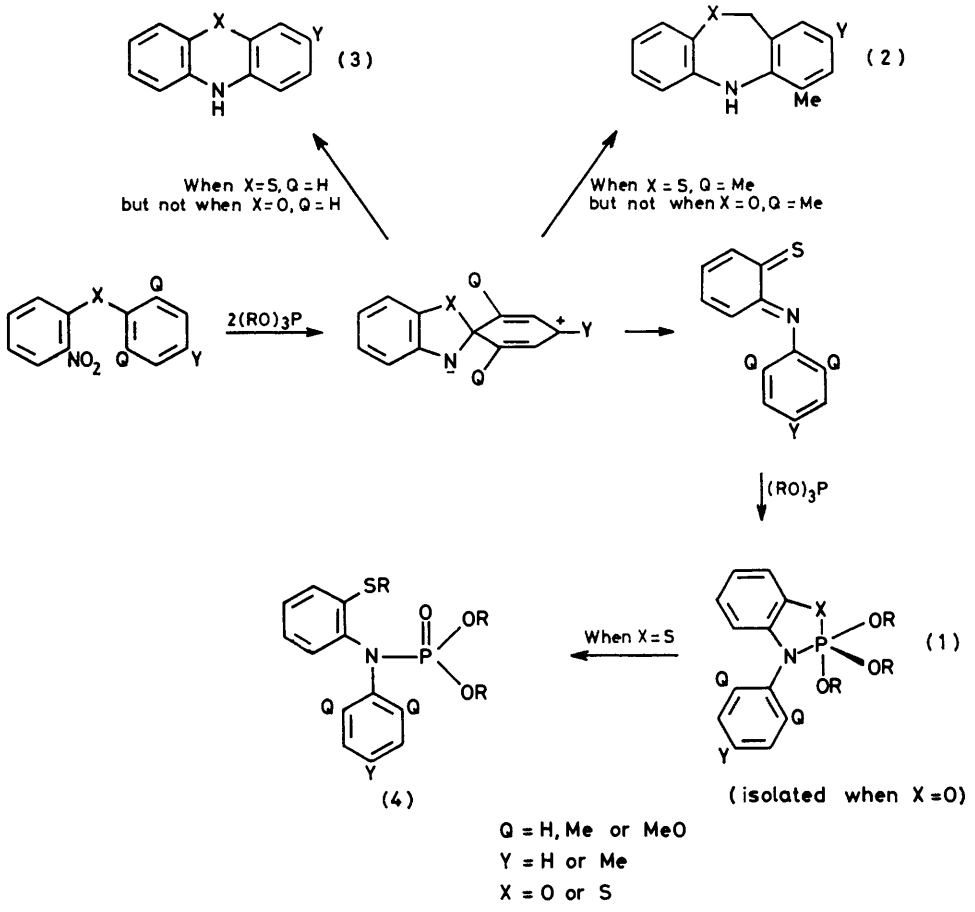
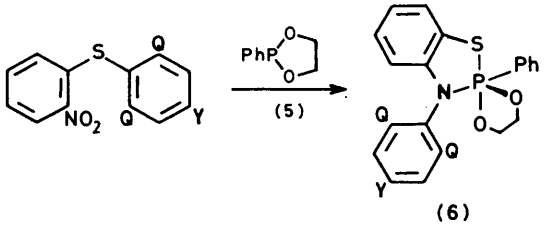
trimethyl-, 2,6-dimethyl-, and 2,6-dimethoxy-phenyl 2-nitrophenyl sulphides in the expectation that the resulting ' five-five ' spiro-bicyclic phosphorane would be stable enough to be isolated. This was realised by the isolation of 2,3-dihydro-2-phenyl-3-(2,4,6-trimethylphenyl)-1,3,2-benzothiazaphosph(v)ole-2-spiro-2'-1',3',-



SCHEME 1

2'-dioxaphospholan (6; Q = Y = Me) and its 3-(2,6-dimethylphenyl)- and 3-(2,6-dimethoxyphenyl)-analogues (6; Q = Me, Y = H and 6; Q = MeO; Y = H respectively) in 32—76% yields.

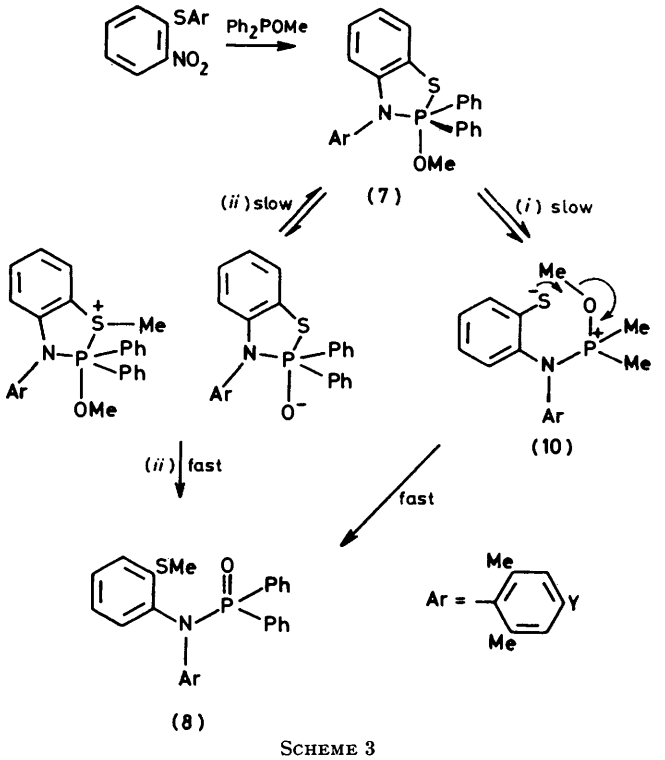


SCHEME 2

Control experiments having shown that the phosphoranes derived from trialkyl phosphite and dimethyl phenylphosphonite isomerised to the open chain amidates rapidly at 153 °C, we investigated the reactive deoxygenator [4] methyl diphenylphosphinite which can function at lower temperatures. Control experiments (^{31}P probe) showed that a phosphorane was indeed formed at a temperature low enough (110 °C) to provide a reasonable chance of its isolation. Thus reaction of methyl diphenylphosphinite (4 mol) with 2,6-dimethylphenyl 2-nitrophenyl sulphide and the 2,4,6-trimethyl analogue (1 mol) in boiling toluene led to the isolation, in *ca.* 50% yield, of the first monocyclic amino(thiyl)phosphoranes, 2,3-dihydro-2,2-diphenyl-3-(2,6-dimethylphenyl)-2-methoxy-1,3,2-benzothiazaphosph(v)ole (7; Ar = 2,6-$Me_2C_6H_3$) and the 3-(2,4,6-trimethylphenyl) analogue (7; Ar = 2,4,6-$Me_3C_6H_2$) (Scheme 3). These phosphoranes behaved analogously to the related tri- and di-alkoxyphenylphosphoranes (1; X = S) at 153 °C by rearranging to the isomeric phosphinamidates (8) (Scheme 3). In accord with this, deoxygenations of the sulphide carried out in boiling cumene (153 °C) gave the amidates (8) rather than the precursors (7).

(*ii*) *Characterisation.* Mass-spectral and elemental analytical data accord with the structures (7) and (8) but the key information was provided by ^{31}P and ^{1}H n.m.r. spectra. Each phosphorane exhibited the characteristic negative shift in the region δ −10.5 to −37.8 and each exhibited the expected phosphorus splitting of the methylene groups P–O–CH_2–R (6), or of the methyl

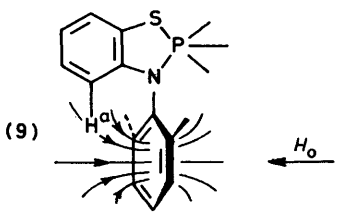
group in P–OMe (J_{P-H} = 11 Hz) (7). In each case the high-field complex multiplet (1 H) at *ca.* δ 5.8—6.0 (Table 1), which implies considerable shielding, is



SCHEME 3

assigned to the aromatic proton (H^a) at position 4 of the 1,3,2-benzothiazaphosph(v)ole system (*e.g.* 9).

These results point to highly restricted rotation of the pendant *N*-aryl group which is orthogonal to the second aryl group [see (9)]. This is supported by the appearance



of separate resonances for the *o*-methyl or methoxy-groups in (6). These spirophosphoranes exhibit classical temperature-dependant n.m.r. spectra expected from permutational isomerism of the trigonal bipyramid; coalescence of the signals of the *o*-groups occur only at high temperature [T_c = +110 °C, $\Delta G^{\ddagger}$ *ca.* 80 kJ mol^{-1}] (Table 1). As in the case of the corresponding benzoxazaphosph(v)ole [8] (ΔG^* *ca.* 96 kJ mol^{-1}), we attribute this to high-temperature regular permutational isomerisation in which the ethylenedioxy-group is placed equatorially. We discount the alternatives of (*a*) free rotation of the *N*-aryl group at high temperature, and (*b*) reversible ring fission of one of the spiro-linked rings because (*a*) fails to explain the observed accompanying change in the ethylenedioxy-resonance, and (*b*) is not in accord with the constancy of ^{31}P shift with marked change of solvent [$CDCl_3 \rightarrow (CF_3)_2CHOH$–$CDCl_3$] (Table 1).

TABLE 1

N.m.r. characteristics of the phosphoranes (6) and (7)

(6) Q	Y	Solvent	$\Delta\nu$ [a]/Hz	T_c [b] (°C)	$\Delta G^{\ddagger}$/kJ mol^{-1}	δ(^{31}P)	δ(H_a)
Me	H	Ph_2O	38.6	111 ± 2	80.6 ± 0.5		
Me	H	*o*-$Cl_2C_6H_4$	39.3	110 ± 2	80.4 ± 0.5		
Me	H	$PhNO_2$	37.0	114 ± 2	81.4 ± 0.5		
Me	H	$CDCl_3$				−10.6	5.82
Me	H	HFP–$CDCl_3$ [c]				−10.2	
Me	Me	Ph_2O	39.7	111 ± 2	80.6 ± 0.5		
Me	Me	$CDCl_3$				−10.5	5.85
Me	Me	HFP–$CDCl_3$ [c]				−10.1	
MeO	H	Ph_2O	6.5	126 ± 4	89.8 ± 1.0		
MeO	H	$CDCl_3$				−13.3	6.04
Y in (7)							
H		$CDCl_3$				−37.8	5.94
H		HFP–$CDCl_3$				+72.4	
Me		$CDCl_3$				−37.7	5.98
Me		HFP–$CDCl_3$				+71.6	

[a] Frequency separation between signals due to *o*-substituents at 28 °C. [b] T_c = coalescence temperature. [c] HFP: $(CF_3)_2$CHOH, HFP–$CDCl_3$, 1 : 1 v/v.

The markedly lower coalescence temperature shown by the thiazaphospholes, *e.g.* (6; Q = Y = Me; T_c = 111 °C; ΔG^* = 80.6 kJ mol^{-1}) compared with the oxaza-analogue [8] (T_c = 175 °C; ΔG^* = 96 kJ mol^{-1}) is of interest. We are currently investigating the reasons for this.

In the calculation of ΔG^* we used the Gutowsky–Holm [5] and Eyring [6] equations using a transmission coefficient of unity as favoured by others.[7] It should be noted that in a previous part [8] we used σ = 0.5. This however leads to almost negligible differences in $\Delta G^{\ddagger}$ (<1.5 kJ mol^{-1}).

The 2,3-dihydro-3-aryl-2-methoxy-2,2-diphenyl-1,3,2-benzoxazaphosph(v)oles (7), in which the methoxy-group is frozen in the apical position, in contrast to the spiro-compounds (6), exhibited a significant solvent effect of +110 p.p.m. in the ^{31}P n.m.r. shifts [$CDCl_3 \rightarrow (CF_3)_2CHOH$–$CDCl_3$] (Table 1), thus pointing to easy ring scission to the corresponding phosphonium betaine [9] *e.g.* (10). This is a point of significance, to which we return below, in discussion of the mechanism of isomerisation of the phosphoranes (7) to amidates (8) (Scheme 3). These structural conclusions have been confirmed by an *X*-ray crystallographic investigation of the spirophosphoranes (6) reported elsewhere.[10]

(*iii*) *Mechanism of the isomerisation of the thiaza-phosph*(v)*ole* (7; Y = H) *to the phosphinamidate* (8) (*Scheme* 3). The kinetics of the isomerisation of the phosphole (7; Y = H) to the phosphinamidate (8) (Scheme 3) were followed by ^{31}P spectroscopy using the kinetics version of the Varian Inc. program SSFT,[11] whereby a number of spectra were automatically recorded at selected intervals using the same sample. A typical result is illustrated in the Figure, which clearly shows the clean conversion of (7) into (8).

The kinetic results (Table 2) point to first-order

kinetics, thus ruling out the bimolecular route (*ii*) (Scheme 3). The high activation energy (E_{act}, 220 kJ mol^{-1}) is consistent with heterolytic ring scission in the rate-determining step, thus suggesting fast dealkylation of the first formed quasi-phosphonium betaine (10) [Scheme 3, route (*i*)], there being precedents for such *S*-dealkylations.[12]

In accord with this are the observed solvent effects: thus the phosph(v)ole is 80% rearranged after 18 h at 178 °C in deuteriobenzene–*o*-dichlorobenzene, 15% after 19 h in the less polar deuteriobenzene–*p*-t-butyltoluene ($10^6k_1 = 2.2$ s^{-1}), and completely rearranged after 45 min in the more polar deuteriobenzene–nitrobenzene.

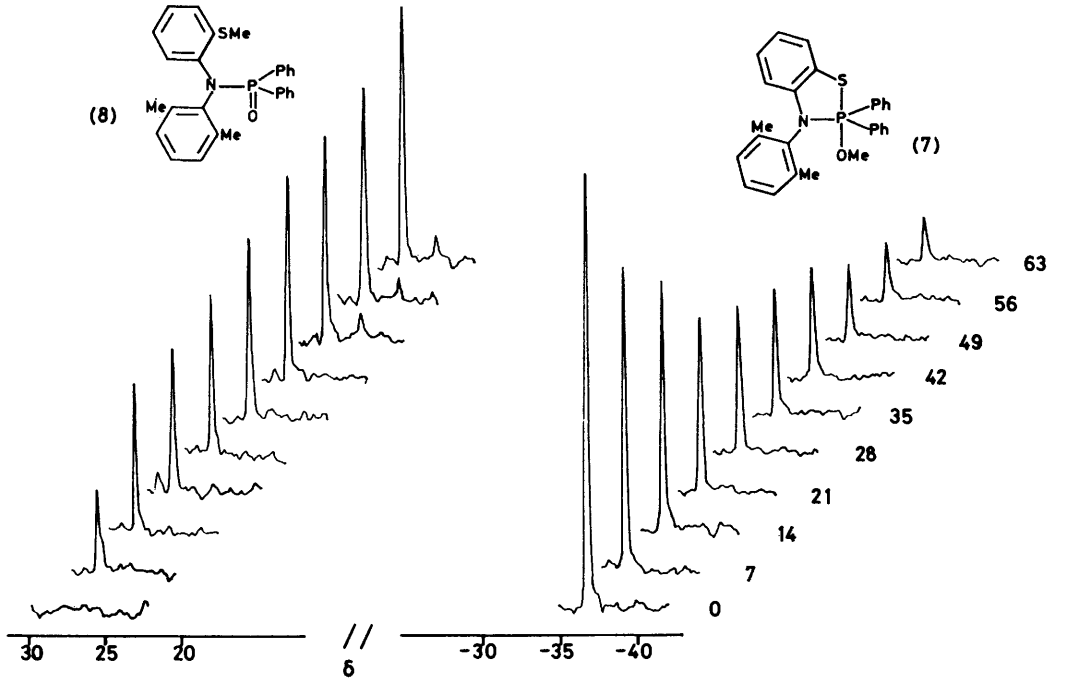


FIGURE Isomerisation of (7) to (8) followed by ^{31}P n.m.r. spectroscopy. Numbers by the spectra refer to elapsed time (10^3 s)

TABLE 2

Isomerisation of 2,3-dihydro-2-methoxy-2,2-diphenyl-3-(2,6-dimethylphenyl)-1,3,2-benzothiazaphosph(v)ole (7) [a]

T/K [b]	$10\,k_1$/s^{-1}
451	2.4 ± 1.2
451	2.4 ± 0.4
446	0.90 ± 0.10
442	0.59 ± 0.12
439	0.52 ± 0.16
431	0.13 ± 0.07

$E_{act.} = 22.0 \pm 60$ kJ mol^{-1}

[a] Concentrations; first experiment, 25 mg/0.5 ml solvent; all others, 75 mg/0.5 ml solvent. [b] Accurate to ±1 K.

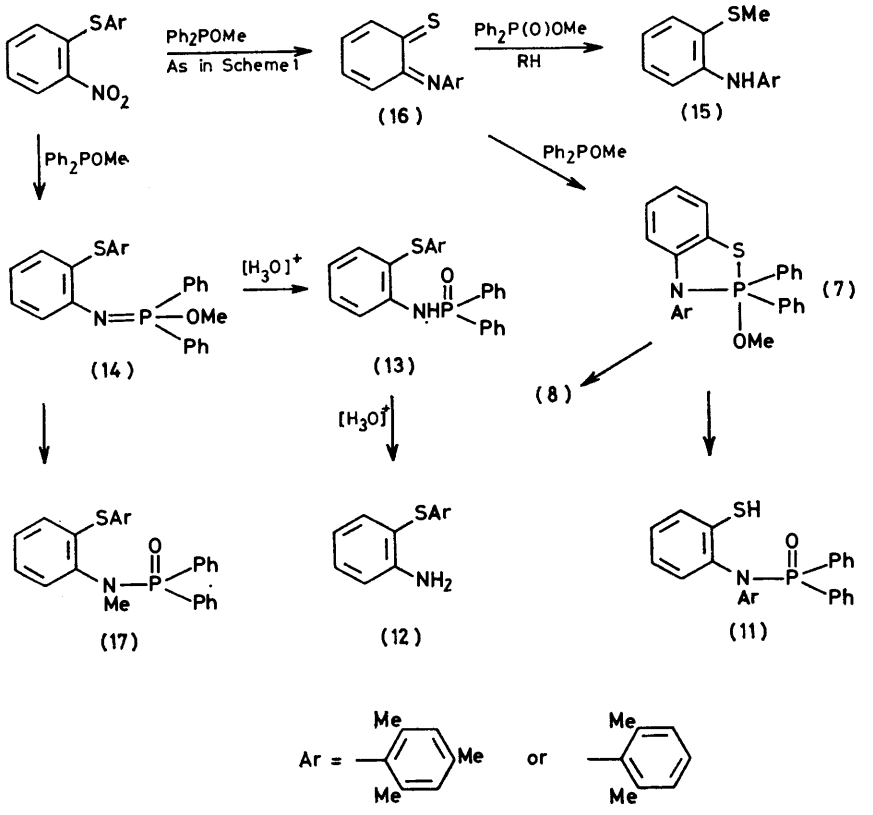
Further support is provided by n.m.r. evidence, given above, that ionisation to the betaine does occur in ionising solvents at room temperature. The mechanism of isomerisation of the far more easily isomerised and so far unisolated 2,2,2-trialkoxy-analogues (1; X = S) may, of course, be different.

Minor Products of Reactions of Methyl Diphenylphosphinite with Aryl 2-Nitroaryl Sulphides.—^{31}P N.m.r. showed that the only primary phosphorus-containing products of the reaction of methyl diphenylphosphinite with 2,6-dimethylphenyl 2-nitrophenyl sulphide in boiling toluene were the phosphorane (7; 42—50%) and the iminophosphorane (14; 3—17%). After isolation of the former by crystallisation, the minor products included the thiol (11; 0—14%) formed, as confirmed by control experiments, by fortuitous hydrolysis of the phosphorane, the substituted aniline (12; 0—13%), and the phosphinamidate (13; 1—5%), formed by hydrolysis of the iminophosphorane (14). The last-named compound provides further circumstantial evidence for the participation of nitrenes or nitrene precursors in deoxygenations of aryl 2-nitroaryl sulphides (Scheme 4).[3] It is of interest that the corresponding reactions of the analogous aryl 2-nitroaryl ethers do not give iminophosphoranes or their decomposition products. Whether the cause of this difference involves steric and/or electronic factors is unknown.

A significant by-product is the 2-methylthio-2′,6′-dimethyldiphenylamine (15). This was isolated in almost constant yield (16—21%) from four reactions carried out under very different conditions. We discount the possibility of formation *via* hydrolysis during work-up of the rearrangement product, the phosphinamidate (8), because the latter was not detected by ^{31}P n.m.r. spectroscopy before work-up, nor would we expect (8) to be present, from our kinetic studies, at this temperature. We attribute its formation to methylation of the postulated thioquinone imine intermediate (16) by methyl diphenylphosphinate in competition with trapping of the former by the phosphorus(III) reagent

(Scheme 4). The accountances of starting nitroaryl sulphides as identified products in these experiments were 89—91%.

Deoxygenations in boiling cumene, of course, led to isomerisation of the phosphorane (7) to the phosphinamidate (8), isolated in 55—57% yields. In addition 2-methylthiodiarylamines (15; 15—17%) were isolated. Also formed in one case was the *N*-methylated phosphinamidate (17; Ar = 2,4,6-$Me_3C_6H_2$; 8%), shown by a



SCHEME 4

control experiment to have arisen by isomerisation of the first formed iminophosphorane (14).

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded for solutions in $CDCl_3$ with tetramethylsilane as internal standard. Fourier-transform ^{31}P n.m.r. chemical shifts are recorded in p.p.m. (positive to high frequency) relative to phosphoric acid (85%). Tervalent phosphorus reagent, aryl 2-nitroaryl sulphides, and cumene were prepared and/or purified as described earlier.[1,2]

Formation of 2,3-*Dihydro*-2-*phenyl*-3-*aryl*-1,3,2-*benzothiazaphosph*(V)*ole*-2-*spiro*-2′-1′,3′,2′-*dioxaphospholans* (6) *by Reaction of* 2-*Phenyl*-1,3,2-*dioxaphospholan with Aryl* 2-*Nitrophenyl Sulphides*.—(*i*) *Aryl* = 2,6-*dimethylphenyl*. A mixture of the sulphide (1.3 g; 5 mmol) and 2-phenyl-1,3,2-dioxaphospholan (3.3 g; 20 mmol) in dry cumene (40 ml) was boiled under dry nitrogen with exclusion of light for 16 h, after which t.l.c. showed no residual sulphide. The solvent was removed *in vacuo* and the residual brown oil was distilled (Kugelrohre). After removal of unreacted 2-phenyl-1,3,2-dioxaphospholan and its oxide, 2,3-*dihydro*-2-*phenyl*-3-(2,6-*dimethylphenyl*)-1,3,2-*benzothiazaphosph*(V)*ole*-2-*spiro*-2′-1′,3′,2′-*dioxaphospholan* (1.44 g; 73%) was obtained as very viscous pale yellow oil (b.p. 218—227 °C at 0.05 mmHg) which slowly solidified to a white crystalline mass (m.p. 162—164.5 °C from dichloromethane–ether, 74% recovery) (Found: C, 66.9; H, 5.7; N, 3.5%; M^+, 395. $C_{22}H_{22}NO_2PS$ requires C, 66.8; H, 5.6; N, 3.5%; M^+ 395); $\nu_{max.}$ ($CHCl_3$) 1 580m, 1 470s, 1 440s, 1 370m, 1 310m, 1 280s, 1 180m, 1 115m, 1 070s, 960m, 945s, and 920s cm^{-1}; δ_H ($CDCl_3$) 7.62 [2 H, dm, collapses to multiplet δ 7.62 on ^{31}P irradiation, J(PH) *ca.* 16 Hz], 7.40—6.85 (7 H, m), 6.80—6.60 (2 H, m), 5.82 (1 H, m), 4.24—3.60 (4 H, m), 2.12 (3 H, s), and 1.68 (3 H, s); δ_P ($CDCl_3$) −10.6.

(*ii*) *Aryl* = 2,4,6-*trimethylphenyl*. Reaction as in (*i*) gave 2,3-*dihydro*-2-*phenyl*-3-(2,4,6-*trimethylphenyl*)-1,3,2-*benzothiazaphosph*(V)*ole*-2-*spiro*-2′-1′,3′,2′-*dioxophospholan* (1.55 g) (76%), b.p. 220—228 °C at 0.05 mmHg, as a pale yellow viscous oil which set to a crystalline mass, m.p. 165—167 °C (from dichloromethane–ether, 57% recovery) (Found: C, 67.5; H, 6.0; N, 3.3%; M^+, 409. $C_{23}H_{24}NO_2PS$ requires C, 67.5; H, 5.9; N, 3.4%; M^+, 409); δ_H ($CDCl_3$): 7.61 [2 H, dm, collapses to multiplet on ^{31}P irradiation, J(PH) *ca.* 16 Hz], 7.38—7.10 (4 H, m), 6.96—6.60 (4 H, m), 5.85 (1 H, m), 4.20—3.52 (4 H, m), 2.24 (3 H, s, *p*-Me), 2.08 (3 H, s), and 1.64 (3 H, s); δ_P ($CDCl_3$) −10.5.

(*iii*) *Aryl* = 2,6-*dimethoxyphenyl*. Reaction as in (*i*) gave 2,3-*dihydro*-2-*phenyl*-3-(2,6-*dimethoxyphenyl*)-1,3,2-*benzothiazaphosph*(V)*ole*-2-*spiro*-2′-1′,3′,2′-*dioxaphospholan* (32%) as a colourless oil (b.p. 225—234 °C at 0.05 mmHg) and then on trituration with ether a crystalline solid, m.p.

178—180 °C (decomp.) (from dichloromethane–ether, 64% recovery) (Found: C, 61.6; H, 5.1; N, 3.2%; M^+, 427. $C_{22}H_{22}NO_4PS$ requires C, 61.8; H, 5.2; N, 3.3%; M^+, 427); δ_H ($CDCl_3$): 7.75 [2 H, dm collapses to multiplet at δ 7.75 on ^{31}P irradiation, J(PH) *ca.* 15 Hz], 7.56—6.84 (5 H, m), 6.76—6.26 (4 H, m), 6.04 (1 H, m), 4.56—3.32 (4 H, m), 3.70 (3 H, s), and 3.64 (3 H, s); δ_P ($CDCl_3$): −13.3.

The trituration residues were chromatographed on alumina to give 1,2-dimethoxyphenothiazine (11%; m.p. and mixed m.p. 141—142.5 °C, from dichloromethane–ether).

Reactions of Methyl Diphenylphosphinite with Aryl 2-Nitrophenyl Sulphides in Boiling Cumene.—(*i*) *Aryl* = 2,6-*dimethylphenyl*. A mixture of the sulphide (1.3 g; 5 mmol) and phosphinite (4.32 g; 20 mmol) in dry cumene (40 ml) was boiled under reflux under dry nitrogen with exclusion of light for 65 h. The solvent was removed *in vacuo* and the resdiual dark brown oil was distilled (Kugelrohre), to give (*a*) an oil, consisting mainly of methyl diphenylphosphinite and its oxide, chromatography (Al_2O_3) of which gave 2-methylthio-2′,6′-dimethyldiphenylamine (0.212 g; 17%) and (*b*) a viscous pale yellow oil (1.40 g, b.p. 220—225 °C at 0.05 mmHg) which slowly solidified to a glass. Trituration of fraction (*b*) with dry ether afforded colourless crystals of N-(2,6-*dimethylphenyl*)-N-(2-*methylthiophenyl*)-PP-*diphenylphosphinamidate* (1.22 g; 55%), m.p. 211.5—213 °C (from methanol, 52% recovery) (Found: C, 72.9; H, 5.8 5; N, 3.2%; M^+, 443. $C_{27}H_{26}NOPS$ requires C, 73.1; H, 5.9; N, 3.2%; M^+ 443); δ_H ($CDCl_3$): 8.45—8.30 (1 H, m), 7.65—6.72 (16 H, m), 2.10 (9 H, s); δ_P ($CDCl_3$): +31.0.

(*ii*) *Aryl* = 2,4,6-*trimethylphenyl*. An analogue of the preceding experiment gave (*a*) 2-methylthio-2′,4′,6′-trimethyldiphenylamine, (15%): (*b*) N-(2,4,6-*trimethylphenyl*)-N-(2-*methylthiophenyl*)-PP-*diphenylphosphinamidate* (57%), m.p. 204—206 °C, as colourless crystals (methanol); δ_H ($CDCl_3$): 8.43—8.29 (1 H, m), 7.70—6.70 (13 H, m), 6.63 (2 H, s), 2.18 (3 H, s), 2.12 (3 H, s), and 2.07 (6 H, s). δ_P ($CDCl_3$): +30.9 (Found: C, 73.3; H, 6.0; N, 3.0%; M^+, 457. $C_{28}H_{28}NOPS$ requires C, 73.5; H, 6.2; N, 3.1%; M^+, 457): and (*c*) PP-*diphenyl*-N-*methyl*-N-2-(2,4,6-*trimethylphenylthio*)*phenylphosphinamidate* (8%) (from dichloromethane–ether), m.p. 183—186 °C, mixed m.p. 185—187 °C with an authentic sample (prepared as described below); δ_H ($CDCl_3$): 8.50—7.75 (4 H, mound), 7.75—6.95 (7 H, m), 7.04 (2 H, s), 6.95—6.65 (2 H, m), 6.22—6.06 (1 H, m), 3.10 [3 H, d, J(PH) 10.5 Hz, P–NMe], 2.36 (6 H, s), and 2.33 (3 H, s); δ_P ($CDCl_3$): +28.4 (Found: C, 73.7; H, 6.15; N, 3.0%; *M*, 457.164 175. $C_{28}H_{28}NOPS$ requires C, 73.5; H, 6.2; N, 3.1%; *M*, 457.162 915).

Reaction of Dimethyl Phenylphosphonite with 2,6-*Dimethylphenyl 2-Nitrophenyl Sulphide in Boiling Cumene.*—An analogue of the preceding experiment gave methyl N-2,6-*dimethylphenyl*-N-(2-*methylthiophenyl*)-P-*phenylphosphonamidate* (74%) as colourless crystals, m.p. 146.5—151 °C (from dichloromethane–ether); δ_H ($CDCl_3$): 8.04—7.66 (3 H, m), 7.48—6.80 (9 H, m), 3.52 [3 H, d, J(PH) 11 Hz, P–OMe], 2.40 (3 H, s), 2.36 (3 H, s), and 2.11 (3 H, s); δ_P ($CDCl_3$), +21.5 (Found: C, 66.3; H, 6.0; N, 3.75%; M^+, 397. $C_{22}H_{24}NOPS$ requires C, 66.5; H, 6.1; N, 3.5%; M^+, 397).

Preparation of 2-(2,4,6-*Trimethylphenylthio*)*phenylimino*-PP-*diphenyl*-P-*methoxyphosphorane, and its Rearrangement to* PP-*Diphenyl*-N-*methyl*-N-2-(2,4,6-*trimethylphenylthio*)-*phenylphosphinamidate.*—A solution of 2-azidophenyl 2,4,6-trimethylphenyl sulphide (500 mg; 1.86 mmol) in dry ether (10 ml) was added dropwise to a stirred solution of methyl diphenylphosphinite (400 mg; 1.85 mmol) in dry ether (5 ml) under nitrogen at room temperature, when evolution of nitrogen was observed. After 1 h the solvent was removed *in vacuo* to give 2-(2,4,6-*trimethylphenylthio*)*phenylimino*-PP-*diphenyl*-P-*methoxyphosphorane* (99%) as colourless crystals, m.p. 140—141 °C (CH_2Cl_2–ether): δ_H ($CDCl_3$): 8.14—7.88 (4 H, m, *o*-protons of PPh_2), 7.48—7.26 (6 H, m, Ar-H), 7.00 (2 H, s, Ar-H), 6.80—6.38 (3 H, m, Ar-H), 6.18 (1 H, dm, J 8 Hz, Ar-H), 3.82 [3 H, d, J(PH) 11.5 Hz, POMe], 2.42 (6 H, s, Ar-*Me*), and 2.30 (3 H, s, Ar-*Me*); δ_P ($CDCl_3$): +16.8 (Found: C, 73.3; H, 6.1; N, 3.0%; M^+, 457. $C_{28}H_{28}NOPS$ requires C, 73.5; H, 6.2; N, 3.1%; M^+, 457).

Distillation (Kugelrohre) at 210—220 °C and 0.1 mmHg gave *PP*-diphenyl-*N*-methyl-*N*-2-(2,4,6-trimethylphenylthio)phenylphosphinamidate (94%) as a colourless glass which on trituration with ether afforded white crystals, m.p. and mixed m.p. 185—187 °C.

Formation of 3-*Aryl*-2,3-*dihydro*-2-*methoxy*-2,2-*diphenyl*-1,3,2-*benzothiazaphosph*(v)*oles* (7) *by Reaction of Methyl Diphenylphosphinite with Aryl* 2-*Nitrophenyl Sulphides in Boiling Toluene.*—(*i*) *Aryl* = 2,6-*dimethylphenyl*.—A mixture of the sulphide (1.30 g; 5 mmol) and the phosphinite (4.32 g; 20 mmol) in dry toluene (40 ml) was boiled under reflux under dry nitrogen with exclusion of light for 30 h. The solvent was removed *in vacuo*, dry ether (25 ml) was added to the dark brown residual oil, and the mixture was set aside overnight at 0 °C, when a white crystalline mass separated from the mixture. The mother-liquors were decanted from the solid which was then extracted with boiling ether (3 × 10 ml) to remove methyl diphenylphosphinate, leaving colourless crystals of 2,3-*dihydro*-2-*methoxy*-2,2-*diphenyl*-3-(2,6-*dimethylphenyl*)-1,3,2-*benzothiazaphosph*(v)*ole* (1.124 g; 51%), m.p. 190—195 °C (decomp.) (from dichloromethane–ether, 69% recovery); $\nu_{max.}$ ($CHCl_3$): 2 840m, 1 575m, 1 470s, 1 440s, 1 275m, 1 250m, 1 180s, 1 100s, 1 060m, 1 040m, 935m, and 915m cm^{-1}; δ_H ($CDCl_3$): 8.02—7.68 (4 H, m), 7.50—7.02 (9 H, m), 6.80—6.64 (3 H, m), 5.94 (1 H, m), 2.55 [3 H, d, J(PH) 11 Hz, POMe], and 2.12 (6 H, s); δ_P ($CDCl_3$): −37.8 (Found: C, 72.85; H, 5.8; N, 3.1%; M^+, 443. $C_{27}H_{26}NOPS$ requires C, 73.1; H, 5.9; N, 3.2%; M^+, 443); *m/e* at 443, 428 (*m** 413.5), 396 (*m** 354), 366, 243, 232, 227, 211, 201, 195, and 77. The combined mother-liquors gave N-2-(2,6-*dimethylphenylthio*)*phenyl*-PP-*diphenylphosphinamidate* (5%), colourless crystals from dichloromethane–ether, m.p. 173—175 °C; δ_H ($CDCl_3$): 7.94—7.66 (4 H, m), 7.58—6.60 (13 H, m), 5.71 [1 H, br d, J(PH) 10 Hz, PNH], and 2.28 (6 H, s); δ_P ($CDCl_3$): +16.9 (Found: C, 72.4; H, 5.6; N, 3.2%; M^+, 429. $C_{26}H_{24}NOPS$ requires C, 72.7; H, 5.6; N, 3.3%; M^+, 429). Chromatography of the residues (Alumina, type H) gave 2-*methylthio*-2′,6′-*dimethyldiphenylamine* (16%); δ_H ($CDCl_3$): 7.43 (2 H, m), 7.20—6.90 (3 H, m), 6.64 (1 H, td J 7.5 and 1 Hz), 6.32 (1 H, mound, NH), 6.11 (1 H, dd, J 8 and 1.5 Hz), 2.39 (3 H, s), 2.18 (6 H, s) (Found: C, 73.95; H, 7.0; N, 5.5%; M^+, 229. $C_{15}H_{17}NS$ requires C, 74.0; H, 7.0; N, 5.8%; M^+, 229); and 2-(2,6-*dimethylphenylthio*)*phenylimino*-PP-*diphenyl*-P-*methoxyphosphorane* (17%), as colourless crystals from dichloromethane–ether, m.p. 133—134 °C; δ_H ($CDCl_3$): 8.14—7.86 (4 H, m), 7.50—7.36 (6 H, m), 7.17 (3 H, s), 6.82—6.36 (3 H, m), 6.16 (1 H, dm, J 7.5 Hz), 3.83 [3 H, d, J(PH) 11.5 Hz, POMe), and 2.46 (s, 6 H); δ_P ($CDCl_3$):

+16.9 (Found: C, 73.2; H, 5.9; N, 3.15%; M^+, 443. $C_{27}H_{26}NOPS$ requires C, 73.1; H, 5.9; N, 3.2%; M^+, 443). The total accountancy of starting sulphide was 89%.

In an otherwise replicate experiment fortuitous hydrolysis led to the conversion of some of the phosph(v)ole to N-2-*thiophenyl*-N-2,6-*dimethylphenyldiphenylphosphinamidate* (10%), identical with that characterised below, and 2-aminophenyl 2,6-dimethylphenyl sulphide, m.p. and mixed m.p. 60 °C (9%); total accountancy 90%.

(*ii*) *Aryl* = 2,4,6-*trimethylphenyl*. An experiment, analogous to (*i*), gave (*a*) 2,3-*dihydro*-2-*methoxy*-2,2-*diphenyl*-3-(2,4,6-*trimethylphenyl*)-1,3,2-*benzothiazaphosph*(v)*ole* (48%), as colourless crystals, m.p. 192—197 °C (decomp.) from dichloromethane–ether; δ_H ($CDCl_3$): 8.05—7.70 (Ar-H, 4 H, m), 7.44—7.10 (7 H, m), 6.92 (2 H, s), 6.80—6.63 (2 H, m), 5.98 (1 H, m), 2.56 [3 H, d, J(P) 11 Hz], 2.30 (3 H, s), and 2.09 (6 H, s); δ_P ($CDCl_3$): −37.7 (Found: C, 73.4; H, 6.3; N, 3.1%; M^+, 457. $C_{28}H_{28}NOPS$ requires C, 73.5; H, 6.2; N, 3.1%; M^+, 457): (*b*) N-2-*thiophenyl*-N-2,4,6-*trimethylphenyl*-PP-*diphenylphosphinamidate* (14%), as colourless crystals, m.p. 149—150 °C (decomp.) from dichloromethane–ether; δ_P ($CDCl_3$): 8.20 (1 H, dm, J *ca.* 7 Hz), 7.68—6.64 (15 H, m), 3.53 (1 H, s, SH), 2.21 (3 H, s), and 2.08 (6 H, s); δ_H ($CDCl_3$): +30.6 (Found: C, 66.0; H, 5.6; N, 4.95%; M^+, 443. $C_{27}H_{26}NOPS$ requires C, 65.9; H, 5.5; N, 5.1%; M^+, 443): (*c*) 2-*methylthio*-2′,4′,6′-*trimethyldiphenylamine* (15%), b.p. 127—130 °C at 0.1 mmHg, m.p. 34—35 °C; δ_P ($CDCl_3$): 7.42 (1 H, dd, J 7.5 and 1.5 Hz), 7.10—6.88 (3 H, m), 6.63 (1 H, td, J 7.5 and 1.5 Hz), 6.50—5.60 (1 H, br, NH), 6.10 (1 H, dd, J 8 and 1.5 Hz), 2.39 (3 H, s), 2.30 (3 H, s), and 2.14 (6 H, s) (Found: M, 257.122 766. $C_{16}H_{19}NS$ requires M, 257.123 815): (*d*) N-2-(2,4,6-*trimethylphenylthio*)*phenyl*-PP-*diphenylphosphinamidate* (2%), colourless crystals, m.p. 174—177 °C, from ether; δ_H ($CDCl_3$): 7.96—7.70 (4 H, m), 7.60—7.14 (8 H, m), 6.98—6.66 (4 H, m), 5.71 [1 H, br d, J(PH) 10 Hz, PNH], and 2.28 (9 H, s); δ_P ($CDCl_3$): +18.7 (Found: C, 73.0; H, 5.9; N, 3.1%; M^+, 443. $C_{27}H_{26}NOPS$ requires C, 73.1; H, 5.9; N, 3.2%; M^+, 443): and (*e*) 2-*aminophenyl*-2,4,6-*trimethylphenyl sulphide* (12%), m.p. and mixed m.p. 72—73 °C. Total accountancy 91%.

Acidic Hydrolysis of 3-*Aryl*-2,3-*dihydro*-2-*methoxy*-2,2-*diphenyl*-1,3,2-*benzothiazaphosph*(v)*oles*.—(*i*) *Aryl* = 2,6-*dimethylphenyl*. To a solution of the phosph(v)ole (320 mg; 0.72 mmol) in dry dioxan (4 ml) was added aqueous *p*-toluenesulphonic acid (100 µl; 0.3M); after 10 min the solvent was evaporated off leaving a white solid, which was washed with water-saturated ether (10 ml) to remove the *p*-toluenesulphonic acid and dried *in vacuo*. Residual dioxan was removed by dissolving the solid in chloroform, followed by evaporation of the solvent under a stream of dry nitrogen, to leave colourless crystals of N-(2,6-*dimethylphenyl*)-N-(2-*thiophenyl*)-PP-*diphenylphosphinamidate* (280 mg; 90%), m.p. 166—169 °C (decomp.) (from dichloromethane–ether, 73% recovery); δ_H ($CDCl_3$): 8.22 (1 H, dm, J *ca.* 8 Hz), 7.70—6.64 (16 H, m), 3.51 (1 H, s, SH), and 2.14 (6 H, s); δ_P ($CDCl_3$): +30.6 (Found: C, 72.4; H, 5.6; N, 3.2%; M^+, 429. $C_{26}H_{24}NOPS$ requires C, 72.7; H, 5.6; N, 3.3%; M^+, 429).

(*ii*) *Aryl* = 2,4,6-*trimethylphenyl*. This phosphole similarly gave *N*-2-thiophenyl-*N*-2,4,6-trimethylphenyl-*PP*-diphenylphosphinamidate (95%), identical with that characterised above.

Kinetics of the Thermal Isomerisation of 2,3-*Dihydro*-2-*methoxy*-2,2-*diphenyl*-3-(2,6-*dimethylphenyl*)-1,3,2-*benzothiazaphosph*(v)*ole*.—A solution of the phosph(v)ole (25—75 mg) in superdry [$^2H_6$]benzene–*o*-dichlorobenzene (0.5 ml; v/v, 1 : 4) was degassed and sealed in a 5-mm n.m.r. tube. The thermolysis was carried out in the probe of an XL-100 n.m.r. spectrometer and the ^{31}P n.m.r. spectrum of the reaction mixture was monitored using a kinetics programme,[11] which allowed the storage of a maximum of ten spectra measured at pre-selected time intervals. The accumulation time for the spectra was chosen to be no more than 10% of the time interval between the measurement of spectra.

Treatment of results. It was established that the ^{31}P n.m.r. responses of the phosph(v)ole and phosphinamidate were equal; the ratio of the peak height of the phosph(v)ole signal to the sum of the peak heights of the two signals was thus taken to be proportional to the concentration of phosph(v)ole. Treatment of the data according to first-order kinetics gave good linear correlations, while treatment in terms of second-order kinetics gave non-linear plots. The results are summarised in Table 2.

Detection of Intermediate Amino(thiyl)phosphoranes in the Reactions of Aryl 2-*Nitrophenyl Sulphides with Trimethyl Phosphite and Dimethyl Phenylphosphonite*.—Aliquots (0.6 ml) in sealed tubes of a solution of the sulphide (2.5 mmol) and phosphorus(III) reagent (15 mmol) in dry cumene (10 ml) were maintained at 130 °C in an oil-bath. At intervals tubes were removed and the ^{31}P n.m.r. spectra of the contents were recorded. In the early stages of the reactions the ^{31}P n.m.r. spectra of the reaction mixtures showed a signal in the region δ −20 to −30 characteristic of a phosphorane, in addition to the signals corresponding to the phosphorus(III) reagent and its oxide. After a time an additional signal, attributed to the isomeric phosphoroamidate or phosphonamidate, appeared, and increased in intensity as the signal due to the phosphorane decayed until eventually no phosphorane remained. In each case the phosphorane signal disappeared completely within 150 h. Relevant δ-values are given in the text.

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