Reduction of Nitro- and Nitroso-Compounds by Tervalent Phosphorus Reagents. Part XV.[1] Reactions of Certain Aryl 2-Nitrophenyl Sulphides and their 2-Azido-analogues leading to Evidence for the Intermediacy of 2,3-Dihydro-1,3,2-benzothiazaphosph(v)oles (Thiazaphosphoranes) and to the Formation of Dihydrodimethylphenothiazinones and Pyrimido- and Pyrido-[1,2-b]indazoles

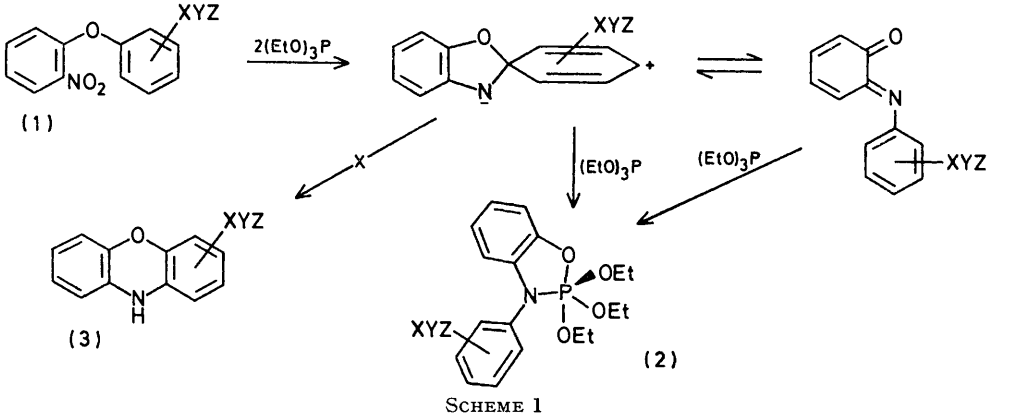
By **J. I. G. Cadogan** * and **Brian S. Tait**, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Deoxygenation by triethyl phosphite and, in two cases, by trimethyl phosphite, of aryl 2-nitrophenyl sulphides [aryl = 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, 2,6-$(MeO)_2C_6H_3$, 2,4,6-$(MeO)_3C_6H_2$, 2,5-$(MeO)_2C_6H_3$, 2-$MeO{\cdot}C_6H_4$, or 4-MeC_6H_4] gave, in addition to various heterocycles described previously, appreciable yields (6—87%) of dialkyl *N*-2-alkylthiophenyl-*N*-arylphosphoramidates, *e.g.* (9), where the alkyl group is derived from the phosphite and the aryl groups are as above. Some of these phosphoramidates were previously wrongly assigned the isomeric dialkyl *N*-alkyl-*N*-(2-arylthiophenyl)phosphoramidate structures, *e.g.* (6), and as such were previously considered to be unimportant and expected by-products [$ArNO_2 + (RO)_3P \longrightarrow (RO)_2P(O)NRAr$]. The present reassignment of structure points to the intermediacy of 2,2-dihydro-1,3,2-benzothiazaphosph(v)oles, *e.g.* (14), analogous to the oxazaphospholes (2) obtained from the deoxygenation of the corresponding aryl 2-nitrophenyl ethers (1), thus indicating mechanistic unity for the two series of reactions.

Deoxygenation of 4-hydroxy-2,6-dimethylphenyl 2-nitrophenyl sulphide (25) and its 2-hydroxy-4,6-dimethylphenyl analogue (26) gave 4-(2-ethylthioanilino)-3,5-dimethylphenol (29) (25%) and 2-(2-ethylthioanilino)-3,5-dimethylphenol (33) (21%), respectively, together with 4-ethoxy-2'-ethylthio-2,6-dimethyldiphenylamine (30) (24%) in the former case. These are hydrolysis products of the corresponding *N*-2-alkylthiophenylphosphoramidates. Spiro-dienones of the type (34) were not detected, but the corresponding 2-azidophenyl analogues gave the novel 4,4a-dihydro-1,4a-dimethylphenothiazin-3-one (36) (28%) and a mixture of 2,4a- and 4,4a-dihydro-3,4a-dimethylphenothiazin-1-one (40) (6.5%) and (41) (2.3%).

Deoxygenation of 2-nitrophenyl 2-pyridyl and 2-pyrimidyl sulphides by triethyl phosphite gave, respectively, pyrido[1,2-*b*]indazole (44) (2%) and the novel pyrimido[1,2-*b*]indazole (46) (5%), *via* cyclisation accompanied by desulphurisation not previously observed during phosphite deoxygenations.

In Part XII [2] we reported that the reaction of trialkyl phosphites and various other tervalent phosphorus reagents with aryl 2-nitroaryl ethers (1) led to high yields of novel oxyphosphoranes (2), but not to phenoxazines (3), and the reaction path outlined in Scheme 1 (*e.g.* Scheme 3). In the latter cases good yields of phosphoramidates were also obtained. These were assigned the structures (6) on the basis of the known propensity of simple nitro-compounds to react with trialkyl phosphites to give phosphorimidates (7), which



Scheme 1

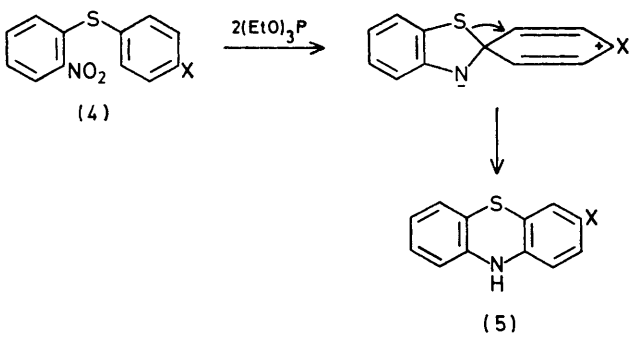
was proposed. This behaviour is in marked contrast to the corresponding reactions of aryl 2-nitrophenyl sulphides (4), which undergo high yield conversions into phenothiazines (5), when the *ortho*-positions in the receptor aromatic ring are free [3] (Scheme 2), and into heterocyclic compounds formed by a series of novel rearrangements when the *ortho*-positions are blocked [3a] on thermolysis either alone or in the presence of trialkyl phosphates (always present in the deoxygenation reaction mixtures) are known to give *N*-alkylphosphoramidates (8) (Scheme 4). The relatively high yields of phosphoramidates produced in the 'blocked *ortho*' (*e.g.* Scheme 3) as compared with the unsubstituted cases (4) were attributed to steric hindrance of the ring closure in the former cases, thus leading to the

[1] Part XIV, J. I. G. Cadogan, R. O. Gould, S. E. B. Gould, P. A. Sadler, S. J. Swire, and B. S. Tait, preceding paper.

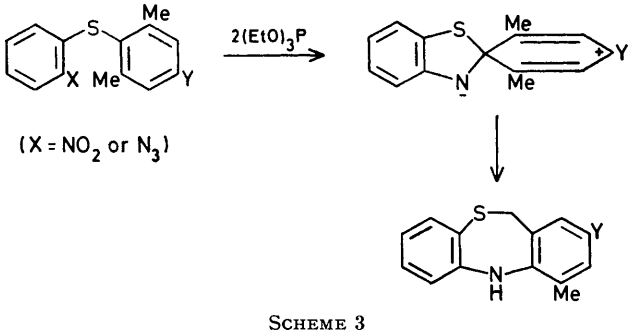
[2] J. I. G. Cadogan, D. S. B. Grace, P. K. K. Lim, and B. S. Tait, *J.C.S. Perkin I*, 1975, 2376.

[3] (*a*) J. I. G. Cadogan, S. Kulik, C. Thomson, and M. J. Todd, *J. Chem. Soc.* (*C*), 1970, 2437; (*b*) J. I. G. Cadogan and S. Kulik, *ibid*, 1971, 2621.

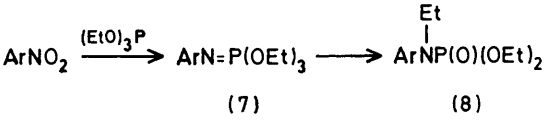
greater possibility of the competing formation of phosphoramidates, possibly by capture of intermediate



SCHEME 2



SCHEME 3



SCHEME 4

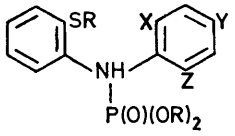
nitrenes by the phosphite. The need for an explanation of the difference in behaviour of the nitroaryl ethers, which gave oxazaphospholes (Scheme 1) as compared with nitroaryl sulphides, which apparently did not (Schemes 2 and 3), was the rationale for the investigation now described. Accordingly, reactions of aryl nitroaryl sulphides with triethyl phosphite have been reinvestigated with particular emphasis on the nature of the phosphorus-containing products, which could perhaps have contained hitherto undetected thiazaphospholes analogous to (2).

The significant result of these investigations is that the previous assignment of structures (6) (Scheme 5) to the phosphoramidates is incorrect. For reasons outlined below these are now considered to be the isomeric phosphoramidates (9). Thus the product previously assigned as diethyl *N*-ethyl-*N*-[*o*-(2-methoxyphenylthio)-phenyl]phosphoramidate (6; X = Y = H, Z = MeO) obtained in 17% yield from triethyl phosphite and 2-methoxyphenyl 2-nitrophenyl sulphide (10; X = Y = H, Z = MeO) is now shown to be diethyl *N*-2-ethylthiophenyl-*N*-2-methoxyphenylphosphoramidate (9; X = Y = H, Z = MeO). The key evidence was obtained in each case from ^{1}H n.m.r. spectra. Thus, in the latter case, the ^{1}H n.m.r. spectrum showed a quartet at τ 7.18 which is now assigned to the methylene part of the ethylthio-group, the alternative assignment (6) of an *N*-ethyl group being ruled out because of the high chemical shift value and the lack of phosphorus coupling in the signal, in contrast to the equidistant methylene part of the ethoxy-ligand on phosphorus, which showed a quintet at τ 5.84. The mass spectrum showed an intense primary fragmentation peak at M − 61 and exact mass studies on this peak confirmed that an ethylthio-group had been removed, hence providing good evidence for the reassigned structure (9). Similar features were noted in the ^{1}H n.m.r. and mass spectra of all other phosphoramidates (9) produced (Table 1).

The importance of the detection of these phosphoramidates lies in the mechanistic unity which it now imparts to the reactions of triethyl phosphite with aryl 2-nitroaryl sulphides and ethers, hitherto thought to be markedly different in character. Thus, the formation of the phosphoramidates can be rationalised by the mechanism outlined in Scheme 5 whereby the nitrene or 'nitrenoid' precursor reacts to form a spiro-diene

TABLE 1

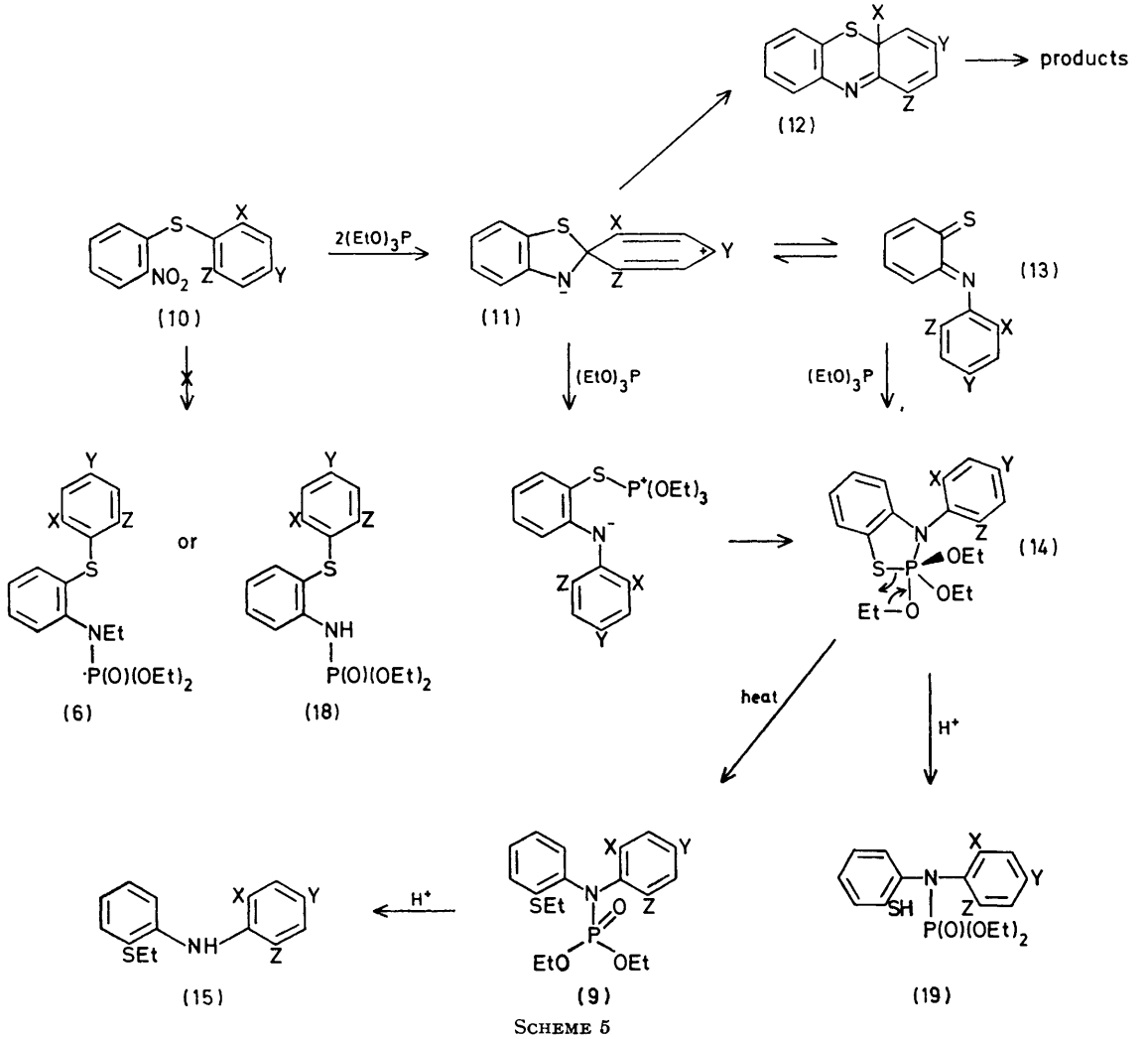
Formation and characterisation of phosphoramidates



					τ Values		
X	Y	Z	Yield (%)	R	S·CH$_2$	O·CH$_2$ (J_{PH}/Hz)	Abundance of M^+ − SR
Me	H	Me	50	Me	7.86	6.33 (12)	100
Me	H	Me	73	Et	7.45	5.9 (quintet) *	58
Me	Me	Me	66	Et	7.41	5.92 (quintet)	96
Me	Me	Me	87	Me	7.83 or 7.79	6.34 (12)	100
MeO	H	MeO	26	Et	7.28	5.81 (quintet)	42
MeO	MeO	MeO	26	Et	7.22	5.82 (quintet)	40
	[2,5(MeO)$_2$]		15	Et	7.18	5.82 (quintet)	40
MeO	H	H	17	Et	7.18	5.84 (quintet)	100
H	Me	H	6	Et	7.12	5.80 (quintet)	24

* Two overlapping quarters

intermediate (11) which can rearrange *via* a 1,2-sigmatropic shift of sulphur to give the hydroaromatic intermediate (12), which rearranges further to various products depending on the nature of X and Z, as previously described.[3] In competition with this, *via* the spirodiene intermediate or a thioquinone imine form (13), reaction with another molecule of triethyl phosphite can lead to the pentaco-ordinate thiazaphosphole (14), molecular case of the triethyl phosphorothiolates, reaction with alkylating agents at sulphur occurs readily.[4] In the present case we have the much reduced energy barrier which is associated with the intramolecular nature of the reaction, which is particularly favoured by the trigonal bipyramidal geometry of the system. That the phosphoramidates are formed by thermal rearrangement and not by hydrolysis during chromatographic

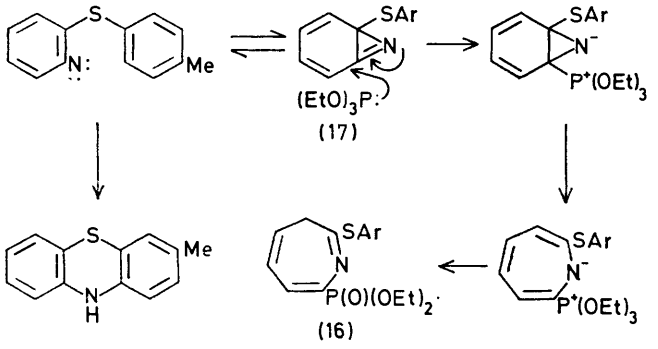


SCHEME 5

assumed to have the bulky and less electronegative thioligand in the equatorial position, although an apical siting would not affect the argument. Up to this point, therefore, the mechanism exactly parallels the corresponding conversion of aryl 2-nitrophenyl ethers into oxazaphospholes (2),[1] with the exception that heterocyclic by-products are formed to a greater extent in the thio-cases, which is in accord with the greater migratory aptitude of the more polarisable sulphur ligand. The observed formation of phosphoramidates [(14) ⟶ (9)] is attributed to the ease with which the more nucleophilic thiolates are alkylated as compared with the oxygen analogues, for even in the less favourable inter-work-up, was shown by the isolation of dimethyl *N*-2-methylthiophenyl-*N*-2,4,6-trimethylphenylphosphoramidate in very high yield (87%), by a completely anhydrous work-up based on distillation. Low yields (1—2%) of hydrolysis products, exemplified by 2-ethylthiodiphenylamine (15) were sometimes isolated when the products were worked up by chromatography. That significant yields of the phosphoramidates (9) appear only when the ease of cyclisation is reduced by the presence of *ortho*-groups is in accord with Scheme 5, as is the observation that even 2-nitrophenyl 4-methyl-

[4] A. J. Burn, J. I. G. Cadogan, and H. N. Moulden, *J. Chem. Soc.*, 1961, 5542.

phenyl sulphide, which has no such hindrance, can be induced to give the corresponding phosphoramidate (9; X = Z = H, Y = Me) (6%), in addition to 3-methylphenothiazine (49%), when the reaction is carried out in a 10 molar excess of triethyl phosphite in cumene. Under the standard conditions of these experiments (4 : 1 molar ratio of phosphite to nitro-compound in cumene as solvent), the phosphoramidate was not detected and the phenothiazine ring closure proceeded in 82% yield. The reaction carried out in

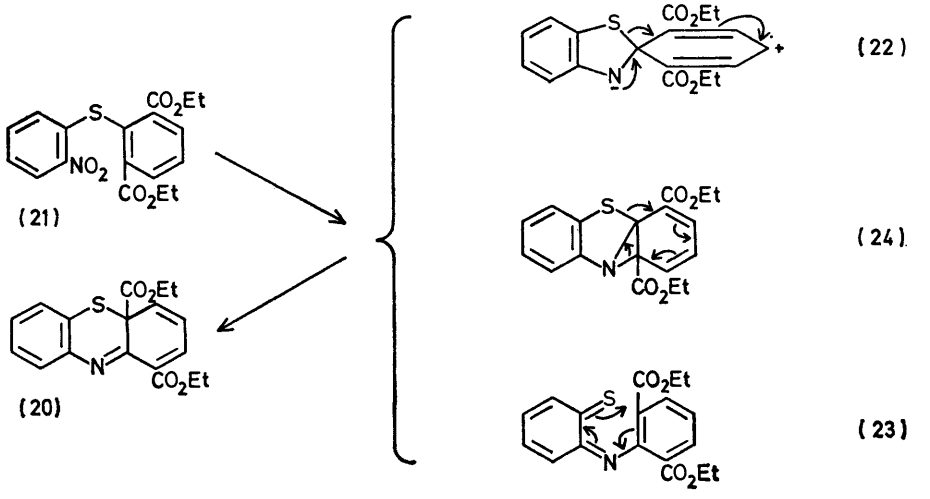


SCHEME 6 Ar = *p*-MeC_6H_4

neat triethyl phosphite also gave diethyl 2-(4-methylphenylthio)-3*H*-azepin-7-ylphosphonate (16) (2.5%), as shown by analytical and spectroscopic data as detailed

phenylphosphoramidate [Scheme 5; (18; X = Z = Me, Y = H)] [3] has been undertaken and this now leads to the assignment of the isomeric structure (19; X = Z = Me, Y = H), mainly because a sharp singlet at τ 7.60 previously assigned to the amido-proton in (18) shows no evidence of phosphorus coupling, thus indicating that the signal is derived from the isomeric thiol. The question which now arises is why only 2,6-dimethylphenyl 2-nitroaryl sulphide led to the free thiol in contrast to all others, including the 2,4,6-trimethylphenyl analogue, which give the *S*-ethyl derivative. A possible explanation is that the thiol (19) arose by fortuitous hydrolysis of the intermediate thiazaphosphole (14; X = Z = Me, Y = H) in this one instance (Scheme 5). Hydrolysis of the corresponding oxazaphosphole (2; X = Z = Me, Y = H) does indeed give the phenolic analogue of (19).[6] In further accord with this explanation, repetition of the experiment under strictly anhydrous conditions gave the expected *S*-ethyl phosphoramidate (9; X = Z = Me, Y = H), whereas the corresponding reaction with trimethyl phosphite and 2-nitrophenyl 2,6-dimethylphenyl sulphide similarly gave the *S*-methyl phosphoramidate corresponding to (9), rather than the free thiol.

Deoxygenation of 4-*Hydroxy*-2,6-*dimethylphenyl* 4-*Nitrophenyl Sulphide* (25) *and its* 2-*Hydroxy*-4,6-*dimethylphenyl Isomer* (26), *and Thermolysis of the Corresponding* 2-*Azidophenyl Analogues* (35) *and* (39).—These



SCHEME 7

in the Experimental section. The formation of this product can be rationalised by competitive ring expansion *via* the azirine (17) followed by nucleophilic attack by triethyl phosphite, followed by elimination of ethylene, there being ample precedent for this reaction [5] (Scheme 6).

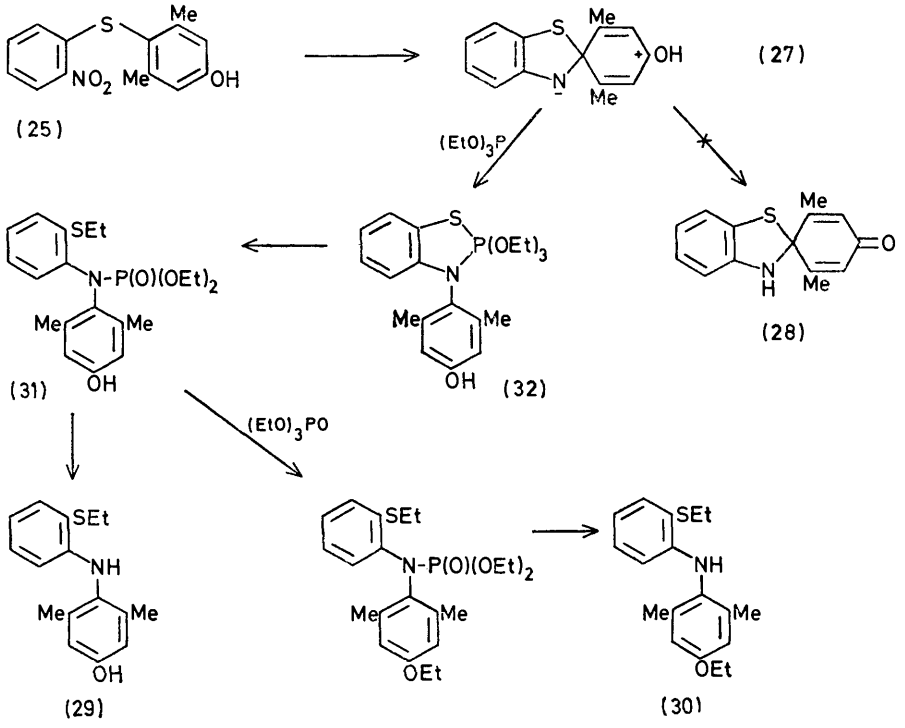
Thus, all the reactions of aryl nitroaryl sulphides described now and previously [3] can be explained with the exception of one apparent anomaly. In the light of the foregoing, reinvestigation of the material believed previously to be diethyl *N*-[*o*-(2,6-dimethylphenylthio)]-

experiments have a bearing on the question of the intermediacy of spiro-diene species such as (11) and hydroaromatic derivatives such as (12) in phosphite deoxygenations of aryl nitrophenyl sulphides leading to heterocyclic products *via* rearrangement [2,3] (*e.g.* Schemes 2, 3, 5, and 7). Good evidence in favour of the intermediacy of species such as (12) has been provided

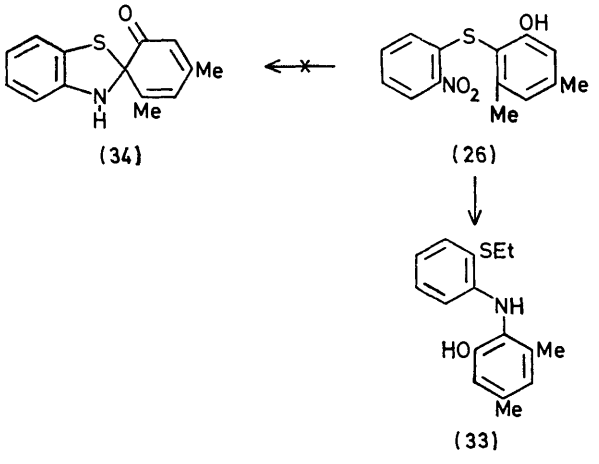
[5] (*a*) J. I. G. Cadogan, D. J. Sears, D. M. Smith, and M. J. Todd, *J. Chem. Soc.* (*C*), 1969, 2813; (*b*) J. I. G. Cadogan and R. K. Mackie, *ibid.*, p. 2819; (*c*) Th. de Boer, J. I. G. Cadogan, H. M. McWilliam, and A. G. Rowley, *J.C.S. Perkin II*, 1975, 554.

[6] J. I. G. Cadogan and D. S. B. Grace, unpublished results.

already,[3] particularly by the isolation of diethyl 4a*H*-phenothiazine-1,4a-dicarboxylate (20) from the deoxygenation of 2,6-bisethoxycarbonylphenyl 2-nitrophenyl sulphide (21) (Scheme 7), but there is no direct evidence which points to a spirodiene (22), a thioquinone imine (23), or an azabicyclo-species (24), all of which could equally well lead to the product (20). We have now examined the triethyl phosphite deoxygenation of 4-hydroxy-2,6-dimethylphenyl 2-nitrophenyl sulphide (25) (Scheme 8) and its 2-hydroxy-4,6-dimethylphenyl isomer (26) (Scheme 9) in the hope that the intermediacy of a spiro-diene species [*e.g.* (27)] would be revealed by its ready conversion into an isolable spiro-dienone such as (28). In the event, only 4-(2-ethylthioanilino)-3,5-dimethylphenol (29) (6.7%), identified by its analysis, and i.r., ^{1}H n.m.r., and mass spectra, and 4-ethoxy-2′-ethylthio-2,6-dimethyldiphenylamine (30) (6.5%), similarly identified, were found after chromatography on alumina. These are decomposition products of the usual *N*-2-alkylthiophenylphosphoramidate (31), thus indicating that reaction has occurred as in Scheme 5 *via* the thiazaphosphole (32). The ethylated diphenylamine (30) presumably arises *via* the well known ethylation action of triethyl phosphate on the phenolic hydroxy-group at some stage.



SCHEME 8



SCHEME 9

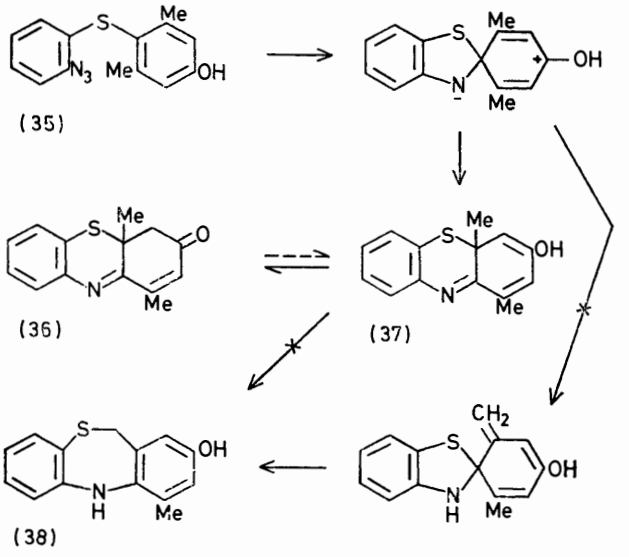
The low accountance of materials in the reaction was due to the polar nature of the phosphoramidate (31), which was not eluted from the column. The accountance of materials was much improved in a replicate reaction by hydrolysis of the reaction products prior to chromatography. This gave the phenol (29) (25%) and the diphenylamine (30) (24%).

Reduction of the isomeric sulphide, 2-hydroxy-4,6-dimethylphenyl 2-nitrophenyl sulphide (26), by triethyl phosphite similarly gave 2-(2-ethylthioanilino)-3,5-dimethylphenol (33) (21%), identified by its i.r., ^{1}H n.m.r., mass, and high resolution mass spectra as the only pure product, and no spiro-dienone (34) was found (Scheme 9).

Clearly, therefore, these experiments are not diagnostic because the preferred reaction is capture of whatever intermediate is present by phosphite to give the thiazaphosphole. Accordingly, we then investigated thermolysis of the corresponding 2-azidophenyl derivatives

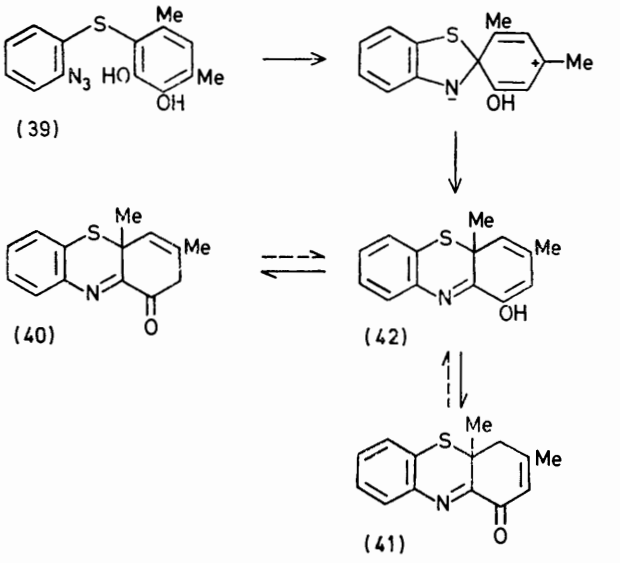
in which the unwanted competitive formation of the thiazaphosphole could not occur. These reactions gave much tar, and no spiro-dienones were isolated or detected, but products corresponding to the hydroaromatic species (20) were obtained. Thus thermolysis of 2-azidophenyl 4-hydroxy-2,6-dimethylphenyl sulphide (35) in decalin gave, after chromatography on alumina, 4,4a-dihydro-1,4a-dimethylphenothiazin-3-one (36) (28%), identified by its analysis and i.r., ^{1}H n.m.r., and mass spectra as detailed in the Experimental section.

The formation of this product can be rationalised by the mechanism outlined in Scheme 10 whereby the first formed intermediate, which for simplicity we assume is a



SCHEME 10

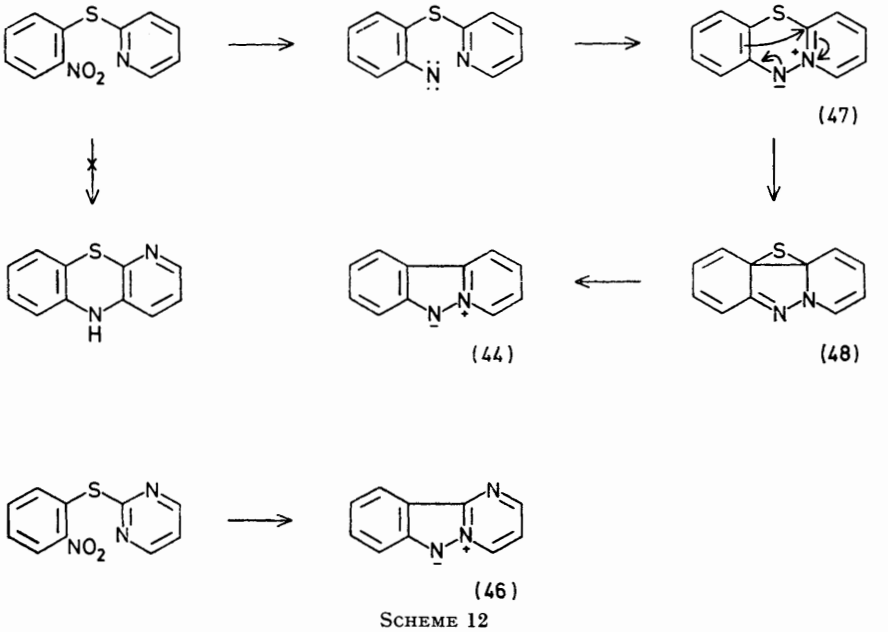
spiro-diene, does not form a spiro-dienone but prefers to rearrange *via* the usual shift of sulphur to give the hydroaromatic enol intermediate (37), stabilised by tautomerism forming the isolated oxo-compound (36).



SCHEME 11

The thiazepine (38) was not detected among the products. The behaviour of the 4-hydroxy-2,6-dimethylphenyl azide (35) is therefore markedly different from that of the 2,4,6-trimethylphenyl analogue, which gives a good yield of the thiazepine (Scheme 3).

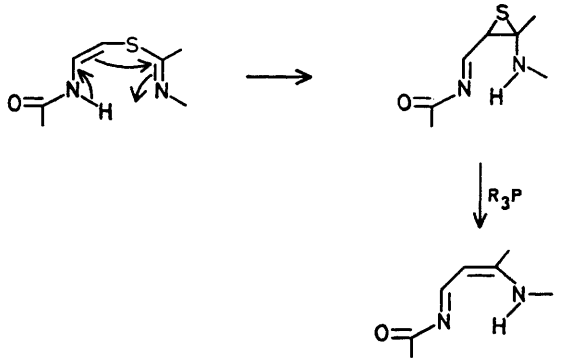
Thermolysis of the isomeric sulphide, 2-azidophenyl 2-hydroxy-4,6-dimethylphenyl sulphide (39), in decalin gave 2,4a-dihydro-3,4a-dimethylphenothiazine-1-one (40) (6.5%), and its 4,4a-dihydro-isomer (41) (2.3%), identified by analyses and i.r., ^{1}H n.m.r., mass, and high resolution mass spectra. A similar mechanism (Scheme 11) can be proposed and this time the hydroaromatic intermediate (42) can give two products *via* prototropic rearrangement, as observed.



SCHEME 12

Deoxygenation of 2-Nitrophenyl 2-Pyridyl and 2-Pyrimidyl Sulphides.—Finally, we briefly record the results of triethyl phosphite deoxygenation of 2-nitrophenyl 2-pyridyl sulphide (43) and its 2-pyrimidyl analogue, which both contain electron-rich nitrogen atoms in the '*ortho-*' positions in the receptor ring. Thus, in contrast to reactions of aryl nitroaryl sulphides described above and previously [3] (*e.g.* Schemes 2, 3, 7, 10, and 11) which all proceed *via* S-shifts, it was expected that direct attack by electron-deficient nitrogen (*e.g.* a nitrene) on ring nitrogen would occur. In the event this did occur but the reaction was accompanied by desulphurisation, never before observed in this type of reaction. Thus the 2-pyridyl derivative (43) gave a low yield (2%) of pyrido[1,2-*b*]indazole (44), as shown by comparison with an authentic specimen,[7] the phenothiazine analogue (45) being absent. In a similar reaction 2-nitrophenyl 2-pyrimidyl sulphide gave the new pyrimido[1,2-*b*]indazole (5%) (46).

A reasonable mechanism (Scheme 12) for the formation of these products involves direct attack of an electron-deficient nitrene on the electron-rich ring nitrogen atom, similar direct attack having been found in the phosphite deoxygenation of 2-(2-nitrosophenyl)pyridine [7] and in the cyclisation of the nitrene produced by thermolysis of 3-(2-pyridyl)anthranil.[8] The product (47) of this initial cyclisation is ideally set up for cyclisation to give the thiiran (48), which could be expected [9] to undergo ready desulphurisation. In this respect the proposed route [(47) ⟶ (48) ⟶ (44)] is closely related to Eschenmoser's synthesis of vinylogous amides [10] (Scheme 13).



SCHEME 13

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded for solutions in $CDCl_3$ with tetramethylsilane as internal standard. ^{31}P N.m.r. chemical shifts are recorded in p.p.m. upfield from phosphoric acid (85%).

Trialkyl phosphites and cumene were purified as described earlier.[3]

Aryl 2-nitrophenyl sulphides, prepared by Galt and Loudon's method,[11] were described earlier.[3] The following were kindly prepared by Drs. P. K. K. Lim and S. Kulik: *2-nitrophenyl 2-pyrimidyl sulphide*, m.p. 94—95° (yellow needles from ethanol) (Found: C, 51.7; H, 2.9; N, 17.8. $C_{10}H_7N_3O_2S$ requires C, 51.5; H, 3.0; N, 18.0%), *2-nitrophenyl 2-pyridyl sulphide*, m.p. 72—73° (yellow crystals from ethanol) (Found: C, 57.0; H, 3.6; N, 12.0. $C_{11}H_8N_2O_2S$ requires C, 56.9; H, 3.45; N, 12.0%), and *2-nitrophenyl 2,4,6-trimethoxyphenyl sulphide* (yellow prisms), m.p. 188—189° (from benzene) (Found: C, 56.6; H, 4.7; N, 4.7. $C_{15}H_{15}NO_5S$ requires C, 56.1; H, 4.7; N, 4.4%).

4-Hydroxy-2,6-dimethylphenyl and 2-hydroxy-4,6-dimethylphenyl 2-nitrophenyl sulphide. These were prepared by the method of Smiles and Learmonth.[12] *o*-Nitrophenylsulphur chloride [13] (62 g, 0.32 mol) in chloroform (200 ml) was slowly added to 3,5-dimethylphenol (39 g, 0.32 mol) in chloroform (200 ml), the temperature being kept at *ca.* 58 °C. After stirring for 10 h, the solvent was removed to leave a mixture of sulphides (90 g), separated by eluting batches (12 g) down a dry alumina column (20 × 2 in; activity III) with chloroform. The faster running isomer was the *2-hydroxy-4,6-dimethylphenyl compound* (31 g, 36%), m.p. 142—143° (crystals from benzene) (Found: C, 61.0; H, 4.7; N, 5.0. $C_{14}H_{13}NO_3S$ requires C, 61.1; H, 4.7; N, 5.1%). The 4-hydroxy-2,6-dimethylphenyl compound (21 g, 24%) had m.p. 154—156° (lit.,[12] 154°) (crystals from chloroform).

2-Aminophenyl 2-hydroxy-4,6-dimethylphenyl sulphide. Reduction of the corresponding nitro-isomer by hydrochloric acid and iron filings in aqueous ethanol gave the *amine*, m.p. 144—145° (from chloroform) (Found: C, 68.6; H, 6.4; N, 5.6. $C_{14}H_{15}NOS$ requires C, 68.6; H, 6.1; N, 5.7%).

A similar reaction of the other nitro-isomer gave *2-aminophenyl 4-hydroxy-2,6-dimethylphenyl sulphide* (91%), m.p. (sublimed) 124—126° (crystals from chloroform) (Found: C, 68.4; H, 6.1; N, 5.65%).

2-Azidophenyl aryl sulphides were prepared by the method of Smith *et al.*[14]

2-Azidophenyl 2-hydroxy-4,6-dimethylphenyl sulphide had m.p. 96—97° (crystals from light petroleum–ether) (Found: C, 62.1; H, 4.85; N, 16.0. $C_{14}H_{13}N_3OS$ requires C, 62.0; H, 4.8; N, 15.5%); the *4-hydroxy-isomer* had m.p. 136° (crystals from ether) (Found: C, 62.0; H, 5.0; N, 15.1%). Both azides had the expected i.r., mass, and ^{1}H n.m.r. spectra.

Deoxygenation of Aryl 2-Nitroaryl Sulphides with Trialkyl Phosphites.—General method. A solution of the nitro-compound (0.01 mol) and the tervalent phosphorus reagent (0.04 mol) in cumene (80 ml) was boiled under reflux, under dry nitrogen with stirring, for *ca.* 65 h. After removal of cumene and phosphorus esters by distillation (<160 °C at 11 mmHg), the residue was worked up by distillation and/or chromatography as indicated in each case.

Reactions of 2,6-Dimethylphenyl 2-Nitrophenyl Sulphide.—(i) *With trimethyl phosphite.* After reaction for 66 h low-vacuum distillation left a dark brown oil which, on trituration in light petroleum–ether gave fawn crystals identified as *dimethyl N-2,6-dimethylphenyl-N-2-methylthiophenylphosphoramidate* (0.76 g, 29%), m.p. 110—111° (Found: C,

[7] P. Bunyan and J. I. G. Cadogan, *J. Chem. Soc.*, 1963, 43; see also R. A. Abramovitch and K. Adams, *Canad. J. Chem.*, 1961, **39**, 2516.
[8] R. Ning, W. Chen, and L. Sternbach, *J. Heterocyclic Chem.*, 1974, **11**, 125.
[9] J. I. G. Cadogan and R. K. Mackie, *Chem. Soc. Rev.*, 1974, **3**, 87.
[10] M. Roth, P. Dubs, E. Gotschi, and A. Eschenmoser, *Helv. Chim. Acta*, 1971, **54**, 710.
[11] R. H. B. Galt and J. D. Loudon, *J. Chem. Soc.*, 1959, 885.
[12] S. Smiles and E. Learmonth, *J. Chem. Soc.*, 1936, 327.
[13] M. H. Hubacher, *Org. Synth.*, 1935, **15**, 45.
[14] P. Smith, B. Brown, R. Putney, and R. Reinisch, *J. Amer. Chem. Soc.*, 1953, **75**, 6335.

58.4; H, 6.4; N, 4.0. $C_{17}H_{22}NO_3PS$ requires C, 58.1; H, 6.3; N, 4.0%), $\nu_{max.}$ 1 260 (P:O), 1 220 (ArO), 1 175 (POMe), and 1 030 cm^{-1} (CO and PO), τ 7.86 (3 H, s, SMe), 7.63 (6 H, s, 2ArMe), 6.33 (6 H, d, 2POMe, J_{PH} 12 Hz), 2.8—3.1 (6 H, m, aromatic), and 2.1 (1 H, m, aromatic), ^{31}P δ −5.6, *m/e* 351 (M^+, 85%), 304 [100, *m** 263 (351 ⟶ 304)], 289 (1), 242 (4), 226 (10), and 194 (35).

The residue was chromatographed on alumina (activity I; 2 × 45 cm). Elution with light petroleum–ether (100 : 10) gave an oil identified as 2,6-*dimethyl*-2′-*methylthiodiphenylamine* (0.03 g, 1%), $\nu_{max.}$ 3 350 (NH) and 1 300 cm^{-1} (ArN), τ 7.90 (6 H, s, 2ArMe), 7.70 (3 H, s, SMe), and 2.5—4.0 (8 H, m, aromatic and NH), *m/e* 243 (M^+, 100%), 213 [40, *m** 187 (243 ⟶ 213)], and 196 [12, *m** 157.5 (243 ⟶ 196)] (Found: M^+, 243.107 584. $C_{15}H_{17}NS$ requires M, 243.108 166).

Elution with light petroleum–ether (100 : 30) gave starting material (0.1 g, 4%), identified by its i.r. spectrum. Elution with light petroleum–ether (1 : 1) gave a yellow oil identified as 5,11-dihydro-4-methyldibenzo[*b,e*][1,4]thiazepine (0.04 g, 2%) by comparison (i.r. and ^1H n.m.r. spectra) with an authentic specimen.[3]

Elution with ether–methanol (100 : 10) gave more of the phosphoramidate (0.72 g, 21%), identified by its i.r. spectrum (accountance 57%).

(ii) *With triethyl phosphite*.[3] After reaction for 66 h low-vacuum distillation left a dark brown oil which was chromatographed on alumina (activity I; 2 × 45 cm). Elution with light petroleum–ether (100 : 10) gave an oil identified as 2-*ethylthio*-2′,6′-*dimethyldiphenylamine* (0.013 g, 0.5%), $\nu_{max.}$ 3 360 (NH) and 1 310 cm^{-1} (ArN), τ 8.75 (3 H, t, SEt, J_{HH} 7 Hz), 7.85 (6 H, s, 2ArMe), 7.18 (2 H, q, SEt, J_{HH} 7 Hz), 3.9 (1 H, m, aromatic), and 2.4—3.6 (7 H, m, aromatic and NH), *m/e* 257 (M^+, 100%), 228 (4), 213 (60), 196 (5), and 194 (10) (Found: M^+, 257.123 787. $C_{16}H_{19}NS$ requires M, 257.123 814).

Elution with light petroleum–ether (100 : 30) gave a yellow oil identified as starting material (0.01 g, 0.4%) by its i.r. spectrum. Elution with light petroleum–ether (1 : 1) gave a dark yellow oil identified as crude 5,11-dihydro-4-methyldibenzo[*b,e*][1,4]thiazepine (0.04 g, 1.6%) by its i.r. and ^1H n.m.r. spectra.[3]

Elution with ether gave *diethyl* N-2,6-*dimethylphenyl*-N-2-*ethylthiophenylphosphoramidate* (2.86 g, 73%), m.p. 56° (from petroleum, b.p. 60—80°) (Found: C, 61.0; H, 7.2; N, 3.9. $C_{20}H_{28}NO_3PS$ requires C, 61.1; H, 7.1; N, 3.6%), $\nu_{max.}$ 1 260 (P:O), 1 220 (ArO), 1 170 (POEt), and 1 040 cm^{-1} (CO and PO), τ 8.95 (3 H, t, SEt, J_{HH} 7 Hz), 8.82 (6 H, dt, 2POEt, J_{HH} 7, J_{PH} 1 Hz), 7.62 (6 H, s, 2ArMe), 7.45 (2 H, q, SEt, J_{HH} 7 Hz), 5.9 (4 H, m, 2POEt), 2.65—3.10 (6 H, m, aromatic), and 2.02 (1 H, m, aromatic), ^{31}P δ −3.1, *m/e* 393 (M^+, 100%), 364 (4), 332 [58, *m** 280 (393 ⟶ 332)], 304 (7), and 276 [27, *m** 250 (304 ⟶ 276] (accountance 75.5%).

Reaction of 2-*Nitrophenyl* 2,4,6-*Trimethylphenyl Sulphide with Trimethyl Phosphite*.—After reaction for 65 h high-vacuum distillation gave the following fractions: (1) an oil identified as trimethyl phosphate by its i.r. spectrum; (2) a yellow oil (b.p. 160° at 0.05 mmHg) which solidified on cooling and was identified as *dimethyl* N-2-*methylthiophenyl*-N-2,4,6-*trimethylphosphoramidate* (3.2 g, 87%), m.p. 113—114° (from petroleum–ether; 62% recovery) (Found: C, 59.1; H, 6.7; N, 3.7. $C_{18}H_{24}NO_3PS$ requires C, 59.2; H, 6.6; N, 3.8%), $\nu_{max.}$ 1 260 (P:O), 1 060 and 1 030 (CO and PO), and 910 cm^{-1}, τ 7.83 and 7.79 (6 H, two s, SMe and ArMe), 7.68 (6 H, s, 2ArMe), 6.34 (6 H, d, 2POMe, J_{PH} 12 Hz), 3.20 (2 H, s, aromatic), 2.8—3.1 (3 H, m, aromatic), and 2.16 (1 H, m, aromatic), ^{31}P δ −5.7, *m/e* 365 (M^+, 70%), 350 (2), 332 (2), 318 [100, *m** 277 (365 ⟶ 318)], and 208 (35) (accountance 87%).

Reaction of 4-*Methylphenyl* 2-*Nitrophenyl Sulphide with Triethyl Phosphite*.—After reaction for 69 h low-vacuum distillation left a dark oil which was chromatographed on alumina (activity I; 2 × 45 cm). Elution with light petroleum–ether (100 : 25) gave a white solid identified as 10-ethyl-3-methylphenothiazine (0.11 g, 5%), m.p. (sublimed) 130—132° (lit.,[2] 131—132°), τ 8.67 (3 H, t, NEt, J_{HH} 7 Hz), 7.80 (3 H, s, ArMe), 6.19br (2 H, q, NEt, J_{HH} 7 Hz), and 2.7—3.5 (7 H, m, aromatic).

Elution with light petroleum–ether (1 : 1) gave a yellow solid identified as 3-methylphenothiazine (1.64 g, 77%), m.p. (from benzene; 83% recovery) and mixed m.p. 169—171° (lit.,[2] 169—171°).

Elution with ether–ethyl acetate (1 : 1) gave a brown liquid shown by its i.r. and ^1H n.m.r. spectra to be mainly triethyl phosphate (0.54 g) (accountance 82%).

A similar experiment with a larger excess of triethyl phosphite (0.1 mol) in cumene (20 ml) gave by chromatography 3-methylphenothiazine (49%), its 10-ethyl derivative (7%), and a brown oil (0.41 g) which on trituration with petroleum afforded a white solid identified as *diethyl* N-2-*ethylthiophenyl*-N-4-*methylphenylphosphoramidate* (0.22 g, 6%), m.p. 58—59° (Found: C, 60.4; H, 7.1; N, 3.5. $C_{19}H_{26}NO_3PS$ requires C, 60.2; H, 6.9; N, 3.7%), $\nu_{max.}$ 1 260 (P:O and ArO), 1 160w (POEt), 1 050 and 1 020 (CO and PO), and 970 cm^{-1} (POEt), τ 8.56—8.74 (9 H, overlapping triplets 2POEt and SEt), 7.74 (3 H, s, ArMe), 7.12 (2 H, q, SEt, J_{HH} 7 Hz), 5.80 (4 H, m, 2POEt, J_{HH} 7, J_{PH} 8 Hz), and 2.5—3.1 (8 H, m, aromatic), *m/e* 379 (M^+, 100%), 351 [0.2 *m** 325 (379 ⟶ 351], 318 [24, *m** 267 (379 ⟶ 318)], 290 (10), and 262 (28) (accountance 62%).

From a further experiment with even more triethyl phosphite (0.12 mol) *in the absence of cumene* were isolated 3-methylphenothiazine (47%), its 10-ethyl derivative (7%), the phosphoramidate (7%), and a brown oil which on trituration in petroleum gave a white solid identified as *diethyl* 2-(4-*methylphenylthio*)-3H-*azepin*-7-*ylphosphonate* (0.09 g, 2.5%), m.p. (sublimed) 71—73° (Found: C, 58.3; H, 6.6; N, 3.9. $C_{17}H_{22}NO_3PS$ requires C, 58.1; H, 6.3; N, 4.0%), $\nu_{max.}$ 1 240 (P:O), 1 165w (POEt), 1 110, 1 060, and 1 030 (CO and PO), and 975 cm^{-1} (POEt), τ 8.86 (6 H, t, 2POEt, J_{HH} 7 Hz), 7.68 (3 H, s, ArMe), 7.20 (2 H, d, CH_2, J_{HH} 7 Hz), 6.12 (4 H, m, 2POEt), 4.58 (1 H, m, azepine), 3.60 (1 H, m, azepine), 3.12 (1 H, d, azepine, J_{HH} 6, J_{PH} 14 Hz), 2.78 (4 H, m, aromatic), *m/e* 351 (M^+, 100%), 336 (2), 322 [4, *m** 297 (351 ⟶ 322)], 254 (7), 243 (33), and 242 (37) (accountance 63%).[5]

Reaction of 2-*Nitrophenyl* 2,4,6-*Trimethoxyphenyl Sulphide with Triethyl Phosphite*.—Work-up by distillation followed by chromatography gave unchanged nitro-compound (7%) and a dimethoxyphenothiazine fraction (33%), m.p. 84—85°, tentatively identified as a mixture of 1,3- and 2,4-isomers by spectroscopy (Found: M^+, 259.067 372. $C_{14}H_{13}NO_2S$ requires M, 259.066 696), τ ($CDCl_3$) 6.32 (3 H, s, MeO), 6.28 (3 H, s, MeO), 6.23 (3 H, s, Me), 6.21 (3 H, s, OMe), and 2.6—3.9 (14 H, complex, aromatic). Further elution gave *diethyl* N-2-*ethylthiophenyl*-N-2,4,6-*trimethoxyphenylphosphoramidate* (26%), m.p. 99—100°, τ 8.82 (3 H, t, SEt, J_{HH} 7.5 Hz), 8.80 (dt, 6 H, 2POEt, J_{HH} 7, J_{PH} 1 Hz),

7.22 (2 H, q, SEt, J_{HH} 7.5 Hz), 6.28 (9 H, s, 3ArOMe), 5.82 (4 H, quintet, 2POEt), 3.94 (2 H, s, aromatic), 2.8—3.0 (3 H, m, aromatic), and 2.0—2.2 (1 H, m, aromatic), *m/e* 455 (M^+, 100%), 394 [40, *m** 341 (455 ⟶ 394)], 366 (30), and 338 (10) (Found: C, 55.3; H, 6.6; N, 3.3. $C_{21}H_{30}NO_6PS$ requires C, 55.4; H, 6.6; N, 3.1%) (accountance 66%).

Reactions of 2-*Methoxyphenyl*, 2,6-*Dimethoxyphenyl, and* 2,5-*Dimethoxyphenyl* 2-*Nitrophenyl Sulphides with Triethyl Phosphite.*—Reinvestigation of these reactions [3] led to the reassignment of structures of the phosphoramidates obtained, as follows: from the 2-methoxyphenyl sulphide was obtained *diethyl* N-2-*ethylthiophenyl*-N-2-*methoxyphenylphosphoramidate* (17%), τ 8.80 (9 H, t, 2POEt and SEt), 7.18 (2 H, q, SEt), 6.34 (3 H, s, ArOMe), 5.84 (4 H, quintet, 2POEt), and 2.08—3.26 (8 H, m, aromatic), *m/e* 395 (70), 334 [100, *m** 282.5 (395 ⟶ 334)], 306 (33), and 278 (75) (Found: M^+, 334.121 436. $C_{17}H_{21}NO_4P$ requires *M*, 334.120 812).

Similarly the structures of the following compounds have been reassigned: *diethyl* N-2,6-*dimethoxyphenyl*-N-2-*ethylthiophenylphosphoramidate* (26%), τ 8.66—8.94 (9 H, overlapping triplets, 2POEt and SEt), 7.28 (2 H, q, SEt), 6.29 (6 H, s, 2ArOMe), 5.81 (4 H, quintet, 2POEt), and 1.96—3.57 (7 H, m, aromatic), *m/e* 425 (M^+, 100%), 364 [42, *m** 312 (425 ⟶ 364)], 336 [8, *m** 310 (364 ⟶ 336)], and 308 [17, *m** 282 (336 ⟶ 308)]; *diethyl* N-2,5-*dimethoxyphenyl*-N-2-*ethylthiophenylphosphoramidate* (15%), τ 8.78 (9 H, m, 2POEt and SEt), 7.18 (2 H, q, SEt), 6.40 (3 H, s, ArOMe), 6.23 (3 H, s, ArOMe), 5.82 (4 H, quintet, 2POEt), and 2.18—3.28 (7 H, m, aromatic), *m/e* 425 (M^+, 100%), 364 [40, *m** 312 (425 ⟶ 364)], 336 [20, *m** 310 (364 ⟶ 336)], and 308 [32, *m** 282 (336 ⟶ 308)]; *diethyl* N-2-*ethylthiophenyl*-N-2,4,6-*trimethylphenylphosphoramidate* (66%), τ 8.85 (9 H, m, 2POEt and SEt), 7.75 (3 H, s, ArMe), 7.62 (6 H, s, 2ArMe), 7.41 (2 H, q, SEt), 5.92 (4 H, quintet, 2POEt), and 2.0—3.21 (6 H, m, aromatic), *m/e* 407 (M^+, 100%), 346 [96, *m** 294 (407 ⟶ 346)], 318 [32, *m** 292 (346 ⟶ 318)], 290 [50, *m** 264 (318 ⟶ 290)], and 271 (60).

Reaction of 2-*Nitrophenyl* 2-*Pyridyl Sulphide with Triethyl Phosphite.*—After reaction for 64 h low-vacuum distillation left a black oil which was chromatographed on alumina, but no pure products were obtained.

In a similar reaction 2-nitrophenyl 2-pyridyl sulphide (2.32 g, 0.01 mol) and triethyl phosphite (20 g, 0.12 mol) were boiled under reflux for 5 h. The black oil isolated after low-vacuum distillation was chromatographed on alumina. Elution with ether gave a yellow oil, which slowly solidified and was identified as pyrido[1,2-*b*]indazole (0.037 g, 2.2%), m.p. and mixed m.p. (sublimed) 76—79° (lit.,[7] 83—84°), $\nu_{max.}$ 1 645 cm^{-1}, τ 1.1—3.0 (aromatic), M^+ 168.

Reaction of 2-*Nitrophenyl* 2-*Pyrimidyl Sulphide with Triethyl Phosphite.*—After reaction for 64 h low-vacuum distillation left a black oil which was chromatographed on alumina. Elution with ether gave a yellow solid identified as *pyrimido*[1,2-b]*indazole* (0.08 g, 4.7%), m.p. (sublimed) 122—123° (Found: C, 71,05; H, 4.5; N, 24.3. $C_{10}H_7N_3$ requires C, 71.0; H, 4.1; N, 24.85%), $\nu_{max.}$ 1 640 cm^{-1}, τ 1.0—3.0 (aromatic) (Found: M^+, 169.064 251. $C_{10}H_7N_3$ requires *M*, 169.063 994).

Reaction of 4-*Hydroxy*-2,6-*dimethylphenyl* 2-*Nitrophenyl Sulphide with Triethyl Phosphite.*—After reaction for 64 h high-vacuum distillation gave the following fractions: (1) a liquid shown by its i.r. spectrum to be triethyl phosphate; (2) a light yellow oil (b.p. 114—180° at 0.03 mmHg; 2.1 g) which was chromatographed on alumina. Elution with light petroluem–ether (100 : 1) gave a light yellow solid identified as 4-*ethoxy*-2′-*ethylthio*-2,6-*dimethyldiphenylamine* (0.19 g, 6.5%), m.p. (sublimed) 66—68° (Found: C, 72.0; H, 7.9; N, 4.55. $C_{18}H_{23}NOS$ requires C, 71.8; H, 7.6; N, 4.65%), $\nu_{max.}$ 3 360 (NH), 1 305 (ArN), 1 155 (CO), and 1 060 cm^{-1} (CO), τ 8.68 (6 H, overlapping triplets, OEt and SEt), 7.87 (6 H, s, 2ArMe), 7.20 (2 H, q, SEt, J_{HH} 7 Hz), 6.02 (2 H, q, OEt, J_{HH} 7 Hz), 3.93 (1 H, m, aromatic), 2.9—3.75 (5 H, m, aromatic and NH), and 2.60 (1 H, m, aromatic), *m/e* 301 (M^+ 100%), 272 [30, *m** 246 (301 ⟶ 272)], 257 (18), and 240 (1).

Elution with ethyl acetate gave a dark solid identified as 4-(2-*ethylthioanilino*)-3,5-*dimethylphenol* (0.18 g, 6.7%), m.p. (sublimed) 147—149° (Found: C, 70.0; H, 7.0; N, 5.1. $C_{16}H_{19}NOS$ requires C, 70.3; H, 7.0; N, 5.1%), $\nu_{max.}$ 3 595 and 3 100—3 450 (OH and NH), 1 305 (ArN), and 1 145 cm^{-1}, τ 8.75 (3 H, t, SEt, J_{HH} 7 Hz), 7.90 (6 H, s, 2ArMe), 7.18 (2 H, q, SEt, J_{HH} 7 Hz), 5.14br (1 H, s, OH), 3.92 (1 H, m, aromatic), 3.66br (1 H, s, NH), 3.3—3.5 (3 H, m, aromatic), 2.97 (1 H, m, aromatic), and 2.57 (1 H, m, aromatic), *m/e* 273 (M^+, 100%), 257 (8), 244 (4), 229 (70), and 212 (6) (accountance 13.2%).

In a replicate experiment the oil obtained after high-vacuum distillation was hydrolysed by boiling in aqueous ethanol. Chromatography [eluant light petroleum–ether (100 : 20)] gave 4-ethoxy-2′-ethylthio-2,6-dimethyldiphenylamine (0.35 g, 24%), identified by its i.r. spectrum. Elution with ethyl acetate gave 4-(2-ethylthioanilino)-3,5-dimethylphenol (0.34 g, 25%), identified by its i.r. spectrum (accountance 49%).

Reaction of 2-*Hydroxy*-4,6-*dimethylphenyl* 2-*Nitrophenyl Sulphide with Triethyl Phosphite.*—After reaction for 40 h work-up as described in the previous experiment gave a brown oil identified as 2-(2-*ethylthioanilino*)-3,5-*dimethylphenol* (0.61 g, 21%), $\nu_{max.}$ 3 250—3 550 (OH and NH), 1 310 (ArN), and 1 260 cm^{-1} (ArO), τ 8.74 (3 H, t, SEt, J_{HH} 7 Hz), 7.98 (3 H, s, ArMe), 7.77 (3 H, s, ArMe), 7.18 (2 H, q, SEt, J_{HH} 7 Hz), 3.8br (2 H, s, OH and NH), and 2.5—3.9 (6 H, m, aromatic), *m/e* 273 (M^+, 100%), 244 (4), 229 (37), 228 (30), 227 (20), and 212 [10, *m** 165 (273 ⟶ 212)] (Found: M^+ 273.118 149. $C_{16}H_{19}NOS$ requires *M*, 273.118 728).

Thermolysis of 2-*Azidophenyl* 4-*Hydroxy*-2,6-*dimethylphenyl Sulphide.*—The azide (2.71 g, 0.01 mol) was added over 30 min to decalin (80 ml) maintained at 150—160 °C under nitrogen. The solution was then boiled under reflux for 2 h. The decalin was removed by distillation and the dark residual oil was chromatographed on alumina. Elution with light petroleum–ether (1 : 1) gave a yellow solid identified as 4,4a-*dihydro*-1,4a-*dimethylphenothiazin*-3-*one* (36) (0.68 g, 18%), m.p. 74—75° (from petroleum–ether; 50% recovery) (Found: C, 69.2; H, 5.6; N, 5.7. $C_{14}H_{13}NOS$ requires C, 69.1; H, 5.35; N, 5.8%), $\nu_{max.}$ 1 675 cm^{-1} (C:O), τ 8.86 (3 H, s, 4a-Me), 7.73 (3 H, d, Me, J_{HH} 1 Hz), 7.09 (2 H, s, CH_2), 3.53br (1 H, s, olefinic), 2.6—2.8 (3 H, m, aromatic), and 2.49 (1 H, m, aromatic), *m/e* 243 (M^+, 100%), 228 (70), 214 (24), and 202 (65).

Thermolysis of 2-*Azidophenyl* 2-*Hydroxy*-4,6-*dimethylphenyl Sulphide.*—The azide (2.71 g, 0.01 mol) was added over 1 h to decalin (80 ml) maintained at 150—160 °C under nitrogen. The solution was maintained at this temperature overnight and then boiled under reflux for 1 h. The decalin was removed by distillation and the residual

tar was chromatographed on alumina. Elution with light petroleum–ether (100 : 10) gave a white solid identified as 2,4a-*dihydro*-3,4a-*dimethylphenothiazin*-1-*one* (40) (0.16 g, 6.5%), m.p. 102—103° (Found: C, 69.1; H, 5.4; N, 5.6%), $\nu_{max.}$ 1 680 cm^{-1} (C:O), τ 8.04 (3 H, s, 4a-Me), 7.96 (3 H, d, Me, J_{HH} 1.5 Hz), 7.14 (2 H, s, CH_2), 4.15br (1 H, s, olefinic), 2.60—2.95 (3 H, m, aromatic), and 1.68 (1 H, m, aromatic), *m/e* 243 (M^+ 100%), 228 (20), 214 (80), and 200 (35).

Elution with light petroleum–ether (100 : 25) gave a red oil identified as 4,4a-*dihydro*-3,4a-*dimethylphenothiazin*-1-*one* (41) (0.06 g, 2.3%), $\nu_{max.}$ 1 700 cm^{-1} (C:O), τ 8.34 (3 H, s, 4a-Me), 7.78br (3 H, s, Me), 7.25 and 6.16 (2 H, AB system, CH_2, J_{AB} 19 Hz, $\Delta\nu_{AB}$ 105.3 Hz), 4.06br (1 H, s, olefinic), 2.5—2.75 (2 H, m, aromatic), and 2.0—2.2 (2 H, m, aromatic), *m/e* 243 (M^+, 100%), 228 (30), 214 (100), and 200 (60) (Found: M^+, 243.071 287. $C_{14}H_{13}NOS$ requires M, 243.071 780).

The structures of compounds (36), (40), and (41) are considered to be well established by the data recorded, but additional support can be derived from a detailed consideration of their ^1H n.m.r. spectra (Table 2). The 4a-methyl protons resonate at lower field in compound (40), where they are adjacent to a double bond, than in compound (36). The methylene protons show a fairly sharp singlet in both compounds. The methyl group attached to the olefin in both compounds was shown by double resonance to be coupled to the olefinic proton, which itself gives a rather broad singlet. However, in compound (41) the methylene protons are non-equivalent and show signals typical of an AB system of interacting nuclei with J_{AB} 19 Hz and $\Delta\nu_{AB}$ 105.3 Hz. The 4a-methyl group now shows some coupling and the methyl group attached to the olefin shows only a broad singlet.

TABLE 2

Chemical shifts of compounds (36), (40), and (41)

	τ Values			
Compd.	4a-Me	CH_2	Olefinic Me (J_{HH}/Hz)	Olefinic H
(36)	8.86	7.09	7.73 (1)	3.53
(40)	8.04	7.14	7.96 (1.5)	4.15
(41)	8.34	AB system	7.78	4.06

We are grateful to the S.R.C. for grants for equipment, to the Carnegie Trust for the Universities in Scotland for a maintenance grant (to B. S. T.), and to Dr. P. K. K. Lim who carried out the deoxygenation of 2-nitrophenyl 2,4,6-trimethoxyphenyl sulphide.

[5/493 *Received*, 12*th March*, 1975