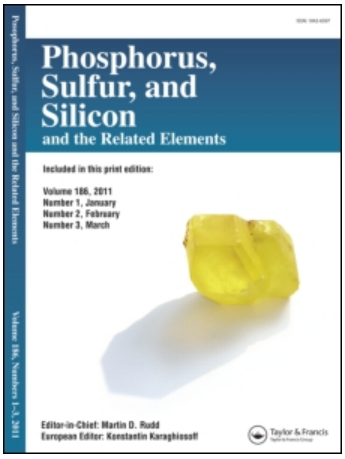

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ON THE REACTION OF BENZOTHIAZOL-2-YL SULPHENAMIDES WITH PHOSPHITES

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ON THE REACTION OF BENZOTHIAZOL-2-YL SULPHENAMIDES WITH PHOSPHITES

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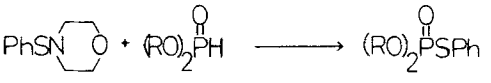
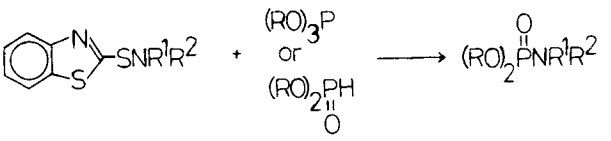
A study of the synthesis of phosphoramidates from phosphites and benzothiazol-2-yl-sulphenamides, indicates that a quinquecovalent phosphorane is an intermediate. Since the initial step in this reaction does not involve attack of phosphorus on nitrogen, it is unlikely that these sulphenamides will act as electrophilic aminating agents towards non-phosphorus nucleophiles. An efficient new method for preparing benzothiazol-2-yl-sulphenamides is reported.

In 1980, Torii *et al.* reported[1] that whereas the reaction of *N*-(phenylthio) amines with phosphites gave rise to *S*-phenyl phosphorothiolates (Scheme 1), the corresponding reaction of *N*-(benzothiazol-2-ylthio)amines produced phosphoramidates (Scheme 2). We were intrigued by this report, as it suggested that sulphenamides derived from 2-mercaptobenzothiazole (**1**) might act as electrophilic aminating agents.[2] We conducted a detailed examination of the reactions of these sulphenamides (**2**) with various nucleophiles, without finding any evidence for attack at sulphenamide nitrogen.[3] Therefore, we have investigated the reactions of **2** with phosphites in depth, in order to elucidate the mechanism of this process.



SCHEME 1



SCHEME 2

RESULTS AND DISCUSSION

Benzothiazol-2-yl sulphenamides (**2**) were prepared by two methods (Table I). Initially, the co-oxidation of 2-mercaptobenzothiazole and an amine by alkaline potassium triiodide[4] was used [method A], but this gave poor yields with sterically hindered amines. We later found that a very convenient procedure, which rapidly produces high yields of **2** even with hindered amines such as diisopropylamine and dicyclohexylamine, is to treat the amine with *N*-chlorosuccinimide and 2-mercaptobenzothiazole in dichloromethane (neutral, non-aqueous conditions) [method B].

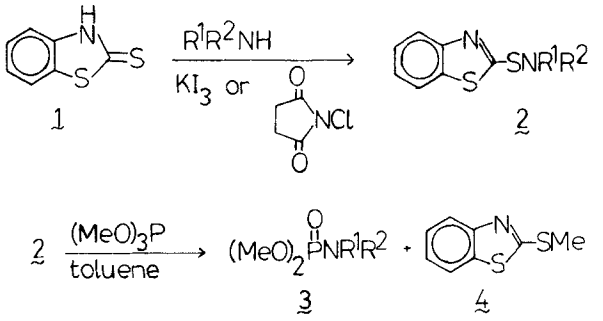
TABLE I

Preparation of benzothiazol-2-yl sulphenamides (**2**)

Entry	R^1	R^2	Method A yield (%)	Method B time (h)	Method B Yield (%)	m.p. (°C)	lit. m.p.
a	Me	Me	46	0.1	94	39–41	35[5]
b	$(CH_2)_2O(CH_2)_2$		56	3	90	84–6	85–6[4]
c	*n*-Bu	H	65	0.1	95	33–4	35–7[4]
d	*i*-Pr	H	23	0.5	96	92–3	93–4[4]
e	*t*-Bu	H	(Aldrich Chemical Co.)				
f	*i*-Pr	*i*-Pr	—	4	77	57–8	58.5–9.5[6]
g	*c*-C_6H_{11}	*c*-C_6H_{11}	—	4	84	99–101	101–2[6]

The reaction of the sulphenamides **2a–2e** was first studied with trimethyl phosphite (Scheme 3). In all cases the phosphoramidate **3** and 2-(methylthio)benzothiazole (**4**) were formed in good yield. It was noticeable, however, that the reaction was much slower with the more sterically hindered isopropyl and *t*-butyl sulphenamides **2d** and **2e** (Table II). In contrast, the substituents on phosphorus seem to have little effect, since triisopropyl phosphite reacted with **2a** rapidly and to give analogous products in high yield (Scheme 4).

There are three likely mechanisms for this reaction. As shown in Scheme 5, initial attack of phosphorus on sulphenamide nitrogen would lead directly to the

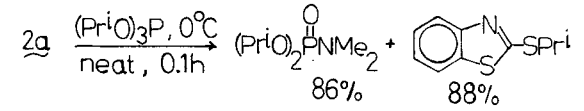


SCHEME 3

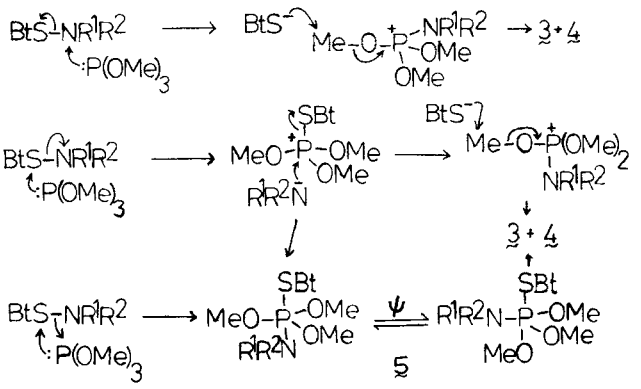
TABLE II

Reaction of **2** with trimethyl phosphite

2	Yield of **3** (%)	Reaction time (h, toluene at r.t.)	^{31}P nmr of **3** (δ, $CDCl_3/H_3PO_4$)
a	91	0.25	13.36
b	67 (91)[1]	0.33 (20)[1]	10.17
c	85	0.33	11.94
d	59	16	10.57
e	48	72	9.98



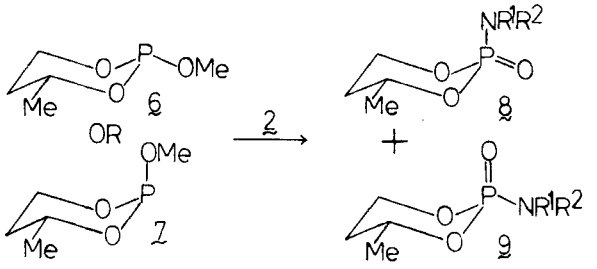
SCHEME 4



SCHEME 5

products **3** and **4**; in the case of unsymmetrical phosphites, inversion at phosphorus would be expected. If the phosphorus first attacked sulphenamide sulphur, the displaced amide ion would probably react at phosphorus; this could happen by addition to give the quinquecovalent phosphorane **5**, or by direct displacement (S_N2) of thiolate anion. In the latter case, overall retention at phosphorus is likely. Finally, a 'biphilic' addition to the sulphenamide would lead directly to the phorphorane **5**. The stereochemical result of the breakdown of this intermediate phosphorane obviously depends on its possible pseudorotation—assuming pseudorotation is faster than breakdown, we should expect the phosphoramidate product in unsymmetrical cases to be produced *stereoselectively* but *not stereospecifically*. Thus we have examined the interaction of the dioxaphosphorinans **6**[7] and **7**[7] with **2** to investigate the stereochemistry of this reaction (Scheme 6 and Table III).

The proportions of **8** and **9** produced were determined by ^{31}P nmr spectroscopy of the crude products and confirmed by the order of elution on flash column



SCHEME 6

TABLE III

Reaction of **2** with **6** and **7**

Entry	Sulphenamide	Phosphite	Yield (%) and ratio of **8**:**9** produced in benzene	in dichloromethane
1	2a	6	(76) 65:35	(69) 88:12
2	2b	6	(90) 26:74	(91) 51:49
3	2c	6	(97) 71:29	(65) 63:37
4	2d	6	(86) 71:29	(80) 52:48
5	2a	7	(79) 1:99	(79) 70:30
6	2b	7	(79) 29:71	(74) 38:62
7	2c	7	(93) 19:81	(93) 11:89
8	2d	7	(46) 60:40	(80) 38:62

chromatography. Based on previous experience (Table IV), the ^{31}P nmr signal of *trans*-2-amino-1,3,2-dioxaphosphorinan-2-oxides (**8**) is always to higher field than that of the *cis*-isomer.

The *tert*-butyl sulphenamide **2e** does not react cleanly with **6** and **7** to give phosphoramidates: a complex mixture is formed. The less hindered sulphenamides **2a–2d** give good yields of **8** and **9**. In only one case (Table III, entry 5 is benzene) is a 'stereospecific' reaction observed—all the other combinations resulted in a poor stereoselectivity. This agrees with a mechanism involving a phosphorane intermediate.

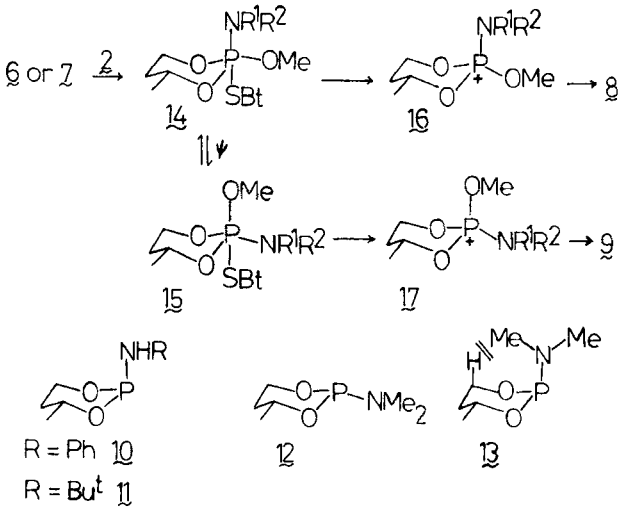
However, the ratios of **8** to **9** obtained from **6** and **7** under each set of conditions (entries 1 and 5, 2 and 6, 3 and 7, 4 and 8) are not the *same*, such as might be expected if a phosphorane with completely free pseudorotation were involved, nor are they the *opposite*, as we should expect if *no* pseudorotation takes place. In fact they appear to bear no relation to each other.

The ratio of **8** to **9** in each case is solvent dependent in a rather curious way: the proportion of **8** *increases* on going to the more polar dichloromethane when the sulphenamide is of a secondary amine, irrespective of whether **6** or **7** is used (entries 1, 2, 5, 6); the proportion of **8** *decreases* in dichloromethane with a primary sulphenamide (entries 3, 4, 7, 8).

TABLE IV

^{31}P nmr data of **8** and **9**

R^1	R^2	δ/H_3PO_4 **8**	**9**	Solvent	Reference
Me	Me (a)	5.05	7.06	$CDCl_3$	this work
$(CH_2)_2O(CH_2)_2$ (b)		1.66	4.60	$CDCl_3$	this work
n-Bu	H (c)	3.48	6.10	$CDCl_3$	this work
i-Pr	H (d)	1.86	5.21	$CDCl_3$	this work
Me	Me (a)	4.7	7.5	neat	8
Ph	H	−3.5	−1.1	CH_3OH	9
Ph	H	−3.7	−0.1	$CHCl_3$	10
$PhCH_2$	H	3.3	5.8	$CHCl_3$	10
t-Bu	H	0.4	4.6	$CHCl_3$	10
Et	Et	3.5	7	not stated	11
$(CH_2)_5$		2.5	4.5	not stated	11



SCHEME 7

These results can be explained in the following way (Scheme 7). It is widely known[12–14] that axial electronegative substituents (OMe, Cl, etc) on the phosphorus of dioxaphosphorinans are more stable than equatorial ones (e.g. **7** is more stable than **6**). This is also true for primary amino groups; but for secondary amino groups the equatorial isomer is more stable. Thus **10**[15], **11**[16] and **12**[14] are the more stable isomers for those compounds. The anomalous behaviour of dialkylamino substituents is explained[14] by an unfavourable 1,3 steric interaction of the alkyl group on (trigonal) nitrogen (**13**) which does not occur in **10** or **11** because the amine hydrogen is oriented towards the ring. We might expect similar arguments to hold true in the phosphoranes **14** and **15**, so that, *in the absence of any other effects* the preferred rotamers would **15a**, **15b**, **14c** and **14d**. However, superimposed upon this is the known apicophilicity of amino groups (good π-donors) in phosphoranes. This would reinforce the preference for **14c** and **14d**; in the cases **14a/15a** and **14b/15b** there is a balance—although since morpholino is a relatively poor electron donor (for an amine) and is larger than dimethylamino, there should be relatively more of **15b** than of **15a**.

The above arguments do, of course, have two flaws; the first is that we are assuming (perhaps unjustifiably) a chair structure in the phosphorane, with the ring bridging two equatorial positions; the second and more serious is that the relative stabilities of **14** and **15** will be only be reflected in the ratio of products **8**:**9** *if equilibrium has been reached* between **14** and **15**. A brief examination of Table III shows that this is not so. Only in the morpholino case (entries 2 and 6) in benzene is the ratio of **8**:**9** similar from either starting material. We would expect this to be the most likely case for equilibrium **14b/15b** to be established as the ionization step (**14/15**→**16/17**) will be the slowest in this case because, as mentioned above, morpholino is a poorer electron donor and so stabilizes the developing phosphonium ion less than the other alkylamino groups.

The ionization by which the phosphorane breaks down will, of course, be considerably more rapid in a more polar solvent. This explains the curious solvent

dependency mentioned above: in the less polar benzene there is more time for the phosphorane equilibrium **14** ⇌ **15** to be established than in dichloromethane, hence we observe in all cases that the ratio of **8** to **9** in benzene is nearer to the expected thermodynamic ratio than in dichloromethane (nearer **9a, 9b**, **8c**, **8d** in benzene).[17]

Reaction *via* a phosphorane has been suggested to explain the lack of stereospecificity at phosphorus in the Arbusov reaction;[18] a closer analogue is the reaction of phosphites with alkyl hypochlorites[19] and with *N*-chlorodialkylamines[11] which Denney found to show a similar variable, solvent dependent, relatively poor stereoselectivity.

ACKNOWLEDGEMENTS

We thank the SERC for a studentship (to I.C.J.) and Dr. C. D. Hall for helpful discussions.

EXPERIMENTAL

All m.ps. and b.ps. are uncorrected. Light petroleum refers to the fraction of b.p. 40–60°C. ^{1}H NMR were recorded on a Bruker WM 250 or a Jeol PMX 60SI spectrometer with TMS as internal standard. ^{31}P NMR were obtained on a Bruker HFX 90 instrument operating at 36.4 MHz with 85% phosphoric acid as external standard. Diastereomeric ratios were determined from integrated ^{1}H and ^{31}P NMR. IR spectra were obtained using a Perkin–Elmer 1310 spectrometer, and MS on a VG Analytical ZAB-SE machine. High-resolution mass spectra were recorded at the SERC Mass Spectrometry Centre, University College of Swansea.

Preparation of Benzothiazole Sulphenamides (**2**) (*Method B*).
The amine (30 mmol) was stirred at 0°C in dichloromethane (40 ml) and *N*-chlorosuccinimide (10 mmol) added. After the *N*-chlorosuccinimide had dissolved benzothiazole-2-thiol (10 mmol) was added and the mixture stirred until the reaction was complete (tlc).

For the dialkylamines (except morpholine) the reaction mixtures were put under vacuum to remove the dichloromethane and light petroleum (50 ml) added. After filtering off the succinimide and washing with more light petroleum (10 ml) the solutions were cooled to obtain the sulphenamides as pure crystalline solids.

For the more polar sulphenamides (e.g. from morpholine) the crude reaction mixture was washed with water (3 × 50 ml). After drying with magnesium sulphate and filtering the sulphenamides were crystallised by adding light petroleum to the dichloromethane solution and cooling. For data see Table I.

Reaction of Benzathiazole Sulphenamides (**2**) *with Trimethyl Phosphite*
The sulphenamide (2 mmol) was stirred at room temperature in toluene (10 ml) under nitrogen. Trialkyl phosphite (2 mmol) was added and the reaction stirred until complete.

The products were separated by flash chromatography using dichloromethane as eluant to remove the S-alkyl benzothiazole sulphide and in some cases a residual amount of benzothiazole-2-thiol. The phosphoramidate was eluted with acetone and further purified by bulb to bulb distillation. Prepared in this way (see Table II for yields and ^{31}P NMR data) were:

N,N-dimethyl-O,O-dimethylphosphoramidate (**3a**), n_D^{21} 1.4181(lit.[20] n_D^{25} 1.4175); IR (film) ν 1245 (P=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.66 (6H, d, J = 10 Hz, $PNMe_2$), 3.66 (6H, J = 10 Hz, POMe).

N,N-oxydiethylene-O,O-dimethylphosphoramidate (**3b**), n_D^{21} 1.4526 (lit.[20] n_D^{25} 1.4530); IR (film) ν 1250 (P=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.03–3.34 (4H, m, NCH_2), 3.59–3.77 (4H, OCH_2), 3.74 (6H, d, J = 11 Hz, POMe);

N-butyl-O,O-dimethylphosphoramidate (**3c**), n_D^{21} 1.4331 (lit.[21] n_D^{25} 1.4316); IR (film) ν 3200 (NH),

1235 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (3H, t, $J = 7.2$ Hz, $\underline{Me}CH_2$), 1.30–1.54 (4H, m, $MeC\underline{H_2}C\underline{H_2}$), 2.88 (2H, m, NCH_2), 3.27 (1H, br s, NH), 3.70 (6H, d, $J = 11$ Hz, POMe);

N-(1-methylethyl)-O,O-dimethylphosphoramidate (**3d**), m.p. 40–42°C (lit.[22] m.p. 42°C); IR ($CDCl_3$) ν 3220 (NH), 1235 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19 (6H, d, $J = 6$ Hz, $\underline{Me}_2CH$), 2.80 (1H, br s, NH), 3.35 (1H, m, $Me_2C\underline{H}NP$), 3.80 (6H, d, $J = 12$ Hz, POMe);

N-(1,1-dimethylethyl)-O,O-dimethylphosphoramidate (**3e**), m.p. 71–3°C (lit.[23] m.p. 64–5°); IR (nujol) ν 3180 (NH), 1245 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (9H, s, Me_3C), 2.69 (1H, br s, NH), 3.66 (6H, d, $J = 11.4$ Hz, POMe).

N,N-Dimethyl-O,O-bis(1-methylethyl)phosphoramidate (scheme 4) had n_D^{22} 1.4164 (lit.[24] n_D^{20} 1.4160); IR (film) ν 1250 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (12H, d, $J = 6$ Hz, $\underline{Me}_2CHO$), 2.70 (6H, d, $J = 10$ Hz, $PNMe_2$), 4.64 (2H, m, $Me_2C\underline{H}OP$); ^{31}P NMR ($CDCl_3$) δ 8.44.

Reaction of Benzothiazole Sulphenamides (**2**) *with cis- and trans-2-Methoxy-4-Methyl-1,3,2-Dioxaphosphorinans* (**6** *and* **7**). The sulphenamide (2 mmol) was stirred at 0°C in dry benzene or dichloromethane (10 ml) under nitrogen. The cis or trans-2-methoxy-4-methyl-1,3,2-dioxaphosphorinan (300 mg, 2 mmol) was added and the reaction stirred until complete.

The products were separated by flash chromatography as above. Prepared in this way (see Table III for yields and Table IV for ^{31}P nmr data) were:

trans-2-(N,N-dimethylamino)-4-methyl-1,3,2-dioxaphosphorinan-2-oxide (**8a**),[8] IR (film) ν 1260 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43 (3H, dd, $^3J_{HH} = 6.3$ Hz, $^4J_{PH} = 1.8$ Hz, $\underline{Me}CHOP$), 1.83–2.02 (2H, m $C\underline{H_2}CH_2O$), 2.67 (6H, d, $J = 11$ Hz, Me_2NP), 4.16–4.53 (3H, m, $CH_2OPOC\underline{H}Me$).

cis-2-(N,N-dimethylamino)-4-methyl-1,3,2-dioxaphosphorinan-2-oxide (**9a**),[8] IR (film) ν 1255 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (3H, dd, $^3J_{HH} = 6.2$ Hz, $^4J_{PH} = 2.2$ Hz, $\underline{Me}CHOP$), 1.71–2.15 (2H, m, $C\underline{H_2}CH_2O$), 2.73 (6H, d, $J = 9.9$ Hz, (Me_2NP), 4.18–4.34 (1H, m, $CH_{ax}H_{eq}O$), 4.56–4.66 (1H, m, $CH_{ax}H_{eq}O$), 4.81–4.85 (1H, m, $MeC\underline{H}O$);

trans-2-(N,N-oxydiethyleneamino)-4-methyl-1,3,2-dioxaphosphorinan-2-oxide (**8b**), m.p. 97–9°C (dichloromethane-ether); IR ($CDCl_3$) ν 1240 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47 (3H, dd, $^3J_{HH} = 6.4$ Hz, $^4J_{PH} = 1.4$ Hz, $\underline{Me}CHOP$) 1.68–2.12 (2H, m, $C\underline{H_2}CH_2OP$), 3.11–3.20 (4H, m, CH_2N), 3.64–3.70 (4H, m, $NCH_2C\underline{H_2}O$), 4.13–4.55 (3H, m, $C\underline{H_2}OPOC\underline{H}Me$); MS *m/e* 221 ($M^+$, 7%), 164 (100); anal. calcd. for $C_8H_{16}NO_4P$: C, 43.44; H, 7.29; N, 6.33; found: C, 43.14; H, 7.22; N, 6.23;

cis-2-(N,N-oxydiethyleneamino)-4-methyl-1,3,2-dioxaphosphorinan-2-oxide (**9b**), m.p. 75–7°C (ether-light petroleum); IR ($CDCl_3$) ν 1240 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (3H, dd, $^3J_{HH} = 6.2$ Hz, $^4J_{PH} = 2.2$ Hz, $\underline{Me}CHOP$), 1.68–1.96 (2H, m, $C\underline{H_2}CH_2OP$), 3.15–3.24 (4H, m, CH_2N), 3.61–3.68 (4H, m, $NCH_2C\underline{H_2}O$), 4.16–4.32 (1H, m, $CH_{ax}H_{eq}OP$), 4.49–4.60 (1H, m, $CH_{ax}H_{eq}OP$), 4.69–4.83 (1H, m, $MeC\underline{H}OP$); MS *m/e* 221 (M^+, 7%), 224 (100); anal. calcd. for $C_8H_{16}NO_4P$: C, 43.44; H, 7.29; N, 6.33; found: C, 42.69; H, 7.22; N, 6.23;

trans-2-(N-butylamino)-4-methyl-1,3,2-dioxaphosphorinan-2-oxide (**8c**), an oil; IR (film) ν 3200 (NH), 1240 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (3H, t, $J = 7.2$ Hz, $\underline{Me}CH_2$), 1.43 (3H, dd, $^3J_{HH} = 6.4$ Hz, $^4J_{PH} = 1.8$ Hz; $\underline{Me}CHOP$), 1.31–1.56 (4H, m, $MeC\underline{H_2}C\underline{H_2}$), 1.79–2.10 (2H, m, $C\underline{H_2}CH_2OP$), 2.66 (1H, br s, NH), 2.86–3.00 (2H, m, CH_2N), 4.20–4.59 (3H, m, $C\underline{H_2}OPOC\underline{H}Me$); MS *m/e* 207 ($M^+$, 10%), 164 (100); HRMS calcd. for $C_8H_{18}NO_3P$: 207.1024; found: 207.1019;

cis-2-(N-butylamino)-4-methyl-1,3,2-dioxaphosphorinan-2-oxide (**9c**), an oil; IR (film) ν 3200 (NH), 1240 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (3H, t, $J = 7.2$ Hz, $\underline{Me}CH_2$), 1.35 (3H, dd, $^3J_{HH} = 6.2$ Hz, $^4J_{PH} = 2.1$ Hz, $\underline{Me}CHOP$), 1.32–1.58 (4H, M, $MeC\underline{H_2}C\underline{H_2}$) 1.68–1.91 (2H, m, $C\underline{H_2}CH_2OP$), 2.86–2.99 (2H, m, CH_2N), 3.05 (1H, br s, NH), 4.16–4.34 (1H, m, $CH_{ax}H_{eq}OP$), 4.47–4.58 (1H, m, $CH_{ax}H_{eq}OP$), 4.69–4.81 (1H, m, $MeC\underline{H}OP$); MS *m/e* 207 (M^+, 14%), 110 (100);

trans-2-[N-(1-methylethyl)amino]-4-methyl-1,3,2-dioxaphosphorinan-2-oxide (**8d**) m.p. 86–8°C (dichloromethane-ether); IR ($CDCl_3$) ν 3200 (NH), 1245 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (6H, d, $J = 6.4$ Hz, $\underline{Me}_2CHN$), 1.42 (3H, dd, $^3J_{HH} = 6.3$ Hz, $^4J_{PH} = 1.7$ Hz, $\underline{Me}CHOP$), 1.77–2.09 (2H, m, $CH_2C\underline{H_2}OP$), 2.41 (1H, br, s, NH), 3.32–3.49 (1H, m, $Me_2C\underline{H}$), 4.17–4.61 (3H, m, $C\underline{H_2}OPOC\underline{H}Me$); MS *m/e* 194 ($MH^+$, 16%), 124 (100); anal. calcd. for $C_7H_{16}NO_3P$: C, 43.52; H, 8.35; N, 7.25; found: C, 42.81; H, 8.43, N, 7.17;

cis-2-[*N*-(1-*methylethyl*)*amino*]-4-*methyl*-1,3,2-*dioxaphosphorinan*-2-*oxide* (**9d**), m.p. 119–20°C (dichloromethane-light petroleum); IR ($CDCl_3$) ν 3200 (NH), 1250 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (6H, d, J = 6.5 Hz, $\underline{Me}_2CHN$), 1.35 (3H, dd, $^3J_{HH}$ = 6.3 Hz, $^4J_{PH}$ = 2.2 Hz, $\underline{Me}CHOP$), 1.67–1.96 (2H, m, $C\underline{H}_2CH_2OP$), 2.72 (1H, br s, NH), 3.34–3.46 (1H, m, $Me_2C\underline{H}$), 4.16–4.32 (1H, m, $CH_{ax}\underline{H}_{eq}OP$), 4.47–4.59 (1H, m, $C\underline{H}_{ax}H_{eq}OP$), 4.69–4.81 (1H, m, $MeC\underline{H}OP$); MS *m/e* 193 (M^+, 2%), 124 (100); anal. calcd. for $C_7H_{16}NO_3P$: C, 43.52; H, 8.35; N, 7.25; found: C, 43.42; H, 8.20; N, 7.09.

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17. We have also investigated the reaction of **2a** with trimethyl and triisopropyl phosphite using the corresponding alcohol as solvent. In both cases a mixture of phosphoramidate and phosphate was produced, as shown below (Scheme 8).

$$(RO)_3P + BtSNMe_2 \xrightarrow{ROH} (RO)_2P(O)NMe_2 + (RO)_3P{=}O + BtSR + BtSH$$
(**2a**)

SCHEME 8

R = Me	5%	87%	27%	67%
i-Pr	46%	52%	56%	40%

These results suggest that, at least in these polar solvents, a mechanism involving initial attack of phosphite on sulphenamide sulphur occurs to give a thiophosphonium ion which can then react with *either* dimethylamine to give (eventually) phosphoramidate *or* with the alcohol to produce phosphate—this latter being less rapid with more hindered 2-propanol.
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