Reaction of Three-coordinate Phosphorus Compounds with Organophosphorus Pseudohalogens 3. Phosphonium and Phosphorane Intermediates in the Desulfurization and Deoxygenation of Bis(phosphinoyl) Disulfides. Influence of Lewis Acids on the Reaction Chemoselectivity

Ewa Krawczyk, Aleksandra Skowrońska* and Jan Michalski*
Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, 90-363 Łódź, Sienkiewicza 112, Poland

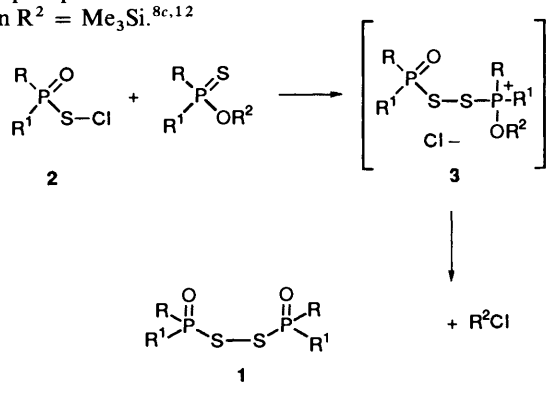
The reactions of bis(phosphinoyl) disulfides $RR^1P(O)S–S–P(O)RR^1$ **1** with P^{III} compounds have been investigated and various mechanistic features have been elucidated by variable-temperature ^{31}P NMR spectroscopy. These studies show that in most cases phosphonium intermediates $[>P(O)–S–\overset{+}{P}\leqslant {}^-O–P(S)<]$ **5** and $[>P(S)–O–\overset{+}{P}\leqslant {}^-O–P(S)<]$ **6** are involved. In cases where ligands on P^{III} increase the stability of the five-coordinate structures phosphorane intermediates are observed. In the isomerization **5** → **6**, the mode of decomposition (desulfurization, deoxygenation or dealkylation) to give stable end products is influenced by electronic and steric factors. The presence of the Lewis acid BF_3 influences considerably the stability of the transient species **5** and **6** and the chemoselectivity of the reaction.

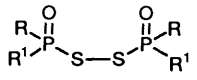
Disulfides RS–SR, an important class of organosulfur compounds with interesting chemistry, fulfill a variety of indispensable biological functions as a result of their structure, binding properties and reactivity. Organophosphorus disulfides $RR^1P(O)S–S–P(O)RR^1$ **1** display a variety of properties similar to those of elemental halogens, and hence the term pseudohalogens has been applied to them.[1] The pseudohalogen-like behaviour of the disulfides **1** was first described by Foss.[2] The high affinity of three-coordinate phosphorus compounds toward oxygen and sulfur is based on their tendency to form strong phosphoryl P=O or thiophosphoryl P=S bonds. Three-coordinate phosphorus compounds are readily oxidized by elemental oxygen or sulfur. In addition they bring about deoxygenation and desulfurization of a wide range of compounds that contain these elements. Little attention has been paid to systems containing both 'active' O and S atoms. Thiosulfonates RSO_2SR have been reported to undergo deoxygenation with triphenylphosphine[3] or desulfurization with trialkyl phosphites.[4] Reactions of thiosulfonates with aminophosphines, which proceed by nucleophilic attack on sulfenyl sulfur, are in marked contrast to the reaction of triphenylphosphine,[3] already mentioned, where deoxygenation is observed. This dichotomy does not extend to the corresponding reaction of phosphines with sulfenylthiosulfonates $RSO_2S–SR$, where nucleophilic attack on sulfenyl sulfur, is observed for both triphenylphosphine and tris(diethylamino)-phosphine.[5] Barton *et al.* described preferential deoxygenation of sulfenyl esters $RS–OR^1$ with triphenylphosphine.[6] Early observations of similar reactions in phosphorus chemistry with parallel desulfurization and deoxygenation of bis(phosphinoyl) disulfides **1** by triphenylphosphine have been reported by Edmundson.[7] Michalski, Skowrońska *et al.* investigated in detail the reaction of oxophosphoranesulfenyl chlorides $RR^1P(O)SCl$ **2** with three-coordinate phosphorus compounds.[8] These studies show that in all cases phosphonium intermediates containing a sulfur bridge $[RR^1P(O)–S–\overset{+}{P}R^2_3Cl^-]$ are formed. Depending on electronic and steric factors and reaction conditions, this primary phosphonium salt either decomposes by nucleophilic attack of the chloride counter ion on the phosphoryl centre (desulfurization pathway) or is transformed into the isomeric phosphonium salt $[RR^1P(S)–O–\overset{+}{P}R^2_3Cl^-]$. The latter decomposes by the attack of chloride ion on the thiophosphoryl centre (deoxygenation pathway).[8d,9c] Five-coordinate intermediates in the reaction of 2-neopentyloxy-1,3,2-benzodioxaphosphole with diethoxyoxophosphoranesulfenyl chloride **2** (R = R^1 = EtO) have been observed. Their role was rationalized by phosphorane–phosphonium equilibria shifted toward phosphorane structures.[10] Oxophosphoranesulfenyl chlorides **2** represent pseudohalogeno halogens containing a strongly electrophilic sulfur centre and in their reactions with nucleophiles the chloride ion acts as a leaving group.[9] It is expected that analogous reactions of the pseudohalogens **1** will follow a similar pattern in spite of the different character of the thiophosphate leaving group.

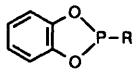
Here we describe our studies of the reactions between bis(phosphinoyl) disulfides **1** and three-coordinate phosphorus compounds. We combine chemical observations with those derived from variable temperature ^{31}P NMR experiments. Our aim was to disclose mechanistic features of the desulfurization and deoxygenation processes. We also compared the reactions of **1** with P^{III} compounds with those of sulfenyl chlorides **2**.

Results and Discussion

Substrates.—Bis(phosphinoyl) disulfides **1** are available from the corresponding phosphorus monothioacid salts $RR^1P(O)-S^-M^+$ by iodine–water oxidation[2] and by condensation of dialkyl phosphites with sulfur chloride.[11] Convenient syntheses of the disulfides **1** were accomplished in our laboratories by a route involving reaction of sulfenyl chlorides **2** with phosphorus thionoesters. The best results are obtained when R^2 = Me_3Si.[8c,12]

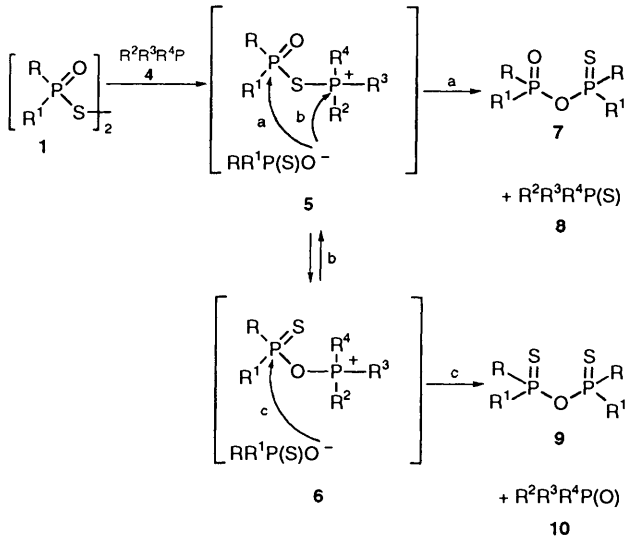




1	R	R^1	**4a**	$(Me_2N)_3P$		
a	OEt	OEt	**b**	$(Bu^tCH_2O)_3P$	**4h**	R = OEt
b			**c**	$(BuO)_3P$	**i**	R = OCH_2Bu^t
c	MeO	Bu^t	**d**	$(MeO)_2PPh$	**j**	R = NEt_2
d			**e**	Ph_2POMe	**k**	R = Bu^t
			f	$PrOPPh_2$		
			g	Ph_3P	**l**	$(PhO)_3P$

This reaction is most likely to proceed *via* the phosphonium intermediate **3** and can be performed as a one-flask procedure by the addition of the chlorinating reagent (Cl_2 or SO_2Cl_2) (1 mol equiv.) to the thionoester (2 mol equiv.). This simplified procedure involves formation of a sulfenyl chloride **2** which reacts immediately *in situ* with the thionoester. The three-coordinate phosphorus compounds **4a–l** were prepared by conventional methods and their reactions with the disulfides **1a–d** have been studied.

General Scheme for the Reaction Between Disulfides **1** *and* P^{III} *Compounds.*—Prior to more detailed discussion of our results it is advantageous to examine Schemes 1 and 2.

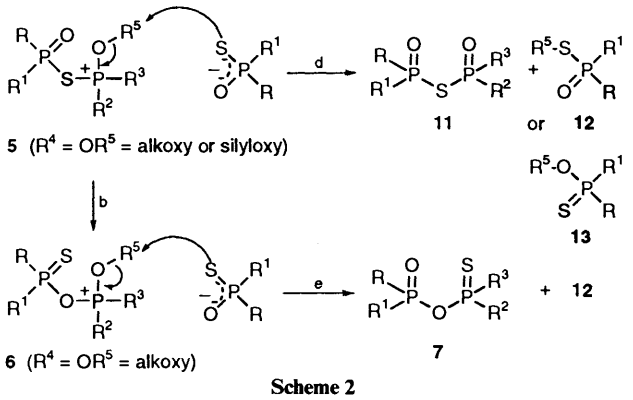


Scheme 1

The desulfurization shown in Scheme 1 (path a) proceeds by formation of the phosphonium intermediate **5** and its decomposition into the monothiopyrophosphate **7** and the thioester **8**. Deoxygenation has its origin in the isomerization **5** → **6** and decomposition of the latter into the dithiopyrophosphate **9** and the oxo ester **10** (Scheme 1, path b and c).

The pathways a and c are representative only for the reactions of P^{III} compounds in which ligands are resistant to dealkylation or desilylation. When an alkoxy or silyloxy group is present in a P^{III} system, the phosphonium intermediates **5** and **6** may undergo dealkylation or desilylation according to Scheme 2.

In the first case the monothiopyrophosphates **11** and the thioloesters **12** are formed *via* path d. Similarly the formation of the thiopyrophosphates **7** and the thiolester **12** takes place by



Scheme 2

dealkylation of the intermediate **6** (path e). When $R^5 = SiMe_3$ the reaction proceeds chemoselectively and forms compounds **11** and **13** in almost quantitative yield [13] (path d).

General Features of the Reaction of the Disulfides **1** *with* P^{III} *Compounds.*—The reaction of the disulfides **1** with P^{III} compounds is strongly exothermic and in most cases proceeds readily at −100 °C. The regioselectivity of this reaction depends on three factors: structure, temperature and the presence of a Lewis acid. In the reaction of the disulfide **1** with P^{III} compounds the influence of solvents of different polarity such as pentane, dichloromethane and nitropropane is marginal. In contrast, the influence of temperature is significant. For example the reaction of the disulfide **1a** with trineopentyl phosphite proceeds at −100 °C by the desulfurization pathway, while at −70 °C deoxygenation products are dominant (75%). In the reaction of the disulfide **1a** with triphenylphosphine, deoxygenation was observed exclusively at −100 °C and only in 83% when the temperature was raised to −70 °C.

The regioselectivity of this reaction for a representative pair of the substrates **1** and P^{III} compounds was evaluated in dichloromethane at −60 °C. The reproducibility of results was good. ^{31}P NMR Spectral data of new compounds are given in the corresponding schemes. The structures of products and their proportions were determined by means of ^{31}P NMR spectroscopy and GC chromatography and, in most cases, by comparison with the authentic samples. Our results are presented in Table 1 and arranged according to decreasing involvement of the desulfurization pathway.

The regioselectivity of the reactions between bis(phosphinoyl) disulfides **1** and P^{III} compounds exemplified in Table 1 depends on both substrates. General trends are similar to that observed in the case of the oxophosphoranesulfenyl chlorides **2**.[8d] Triphenylphosphine **4g** acts predominantly as a deoxygenation reagent. The same tendency applies to cyclic P^{III} compounds **4h–k**. In contrast tris(dimethylamino)phosphine **4a** acts as a highly selective desulfurization reagent. Bulky substituents at the phosphinoyl group in **1** and in the P^{III} compound affect the reaction course, but to a lesser extent than in the case of oxophosphoranesulfenyl chlorides **2**.[8d]

Variable Temperature ^{31}P *NMR Studies.*—These studies provided crucial information about short-lived phosphonium intermediates **5** and **6** and their interconversion and decomposition into the final products. The experiments were performed in temperature range of −100 to 20 °C in dichloromethane or ethyl chloride according to the protocol described in our earlier papers concerning analogous reactions of P^{III} compounds with oxophosphoranesulfenyl chlorides **2**.[8d,10] Only data reproducible in at least two experiments are presented.

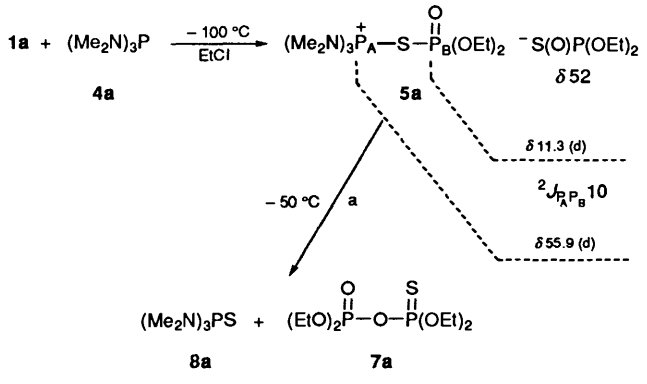
The reaction between the disulfide and tris(dimethylamino)-

Table 1 Desulfurization, dexoygenation and dealkylation of bis(phosphinoyl) disulfides **1** by P^{III} compounds **4**

Entry	Bis(phosphinoyl) disulfide **1**	P^{III} compounds **4**	Desulfurization (%)	Deoxygenation (%)	Dealkylation (%)
1	**1a**	**4a**	100	—	—
2	**1d**	**4b**	100	—	—
3	**1a**	**4c**	68	20	12
4	**1a**	**4b**	25 (100)[a]	75 (0)[a]	—
5	**1b**	**4g**	40	60	—
6	**1a**	**4g**	17 (0)[a]	83 (100)[a]	—
7	**1a**	**4l**	16	84	—
8	**1d**	**4g**	10	90	—
9	**1a**	**4h**	6	66	28
10	**1a**	**4i**	—	100	—
11	**1a**	**4j**	—	100	—
12	**1a**	**4k**	—	100	—
13	**1c**	**4g**	—	100	—
14	**1a**	**4f**	—	86	14
15	**1a**	**4e**	—	20	80
16	**1a**	**4d**	—	—	100

[a] These reactions were carried out at −100 °C.

phosphine **4a** takes the desulfurization course (Scheme 3). The thermally labile phosphonium salt **5a** was observed at −100 °C in ethyl chloride solution. This phosphonium salt decomposes gradually on warming and at −50 °C only the final products thiopyrophosphate **7a** and thioamide **8a** are observed.



Scheme 3

Variable-temperature ^{31}P NMR spectra of this system are presented in Fig. 1. The structure of the phosphonium salt **5a** containing two phosphorus centres bridged by a sulfur atom is evident from the ^{31}P NMR spectra [δ_{P_A} = 55.9 ppm (d), δ_{P_B} = 11.3 ppm (d), $^2J_{P_AP_B}$ = 10 Hz]. The spectral characteristics of **5a** are close to those of the phosphonium salt formed in the reaction of tris(dimethylamino)phosphine with diethoxyoxophosphoranesulfenyl chloride **2** (R = R^1 = OEt).[8d]

The reaction between the disulfide **1a** and trineopentyl phosphite **4b** takes both desulfurization and deoxygenation courses. Both of the crucial phosphonium intermediates **5b** and **6b** shown in Scheme 4 were recognized on the basis of ^{31}P NMR spectral data. The most important information differentiating structures of **5b** and **6b** are chemical shift values and coupling constants $^2J_{P_AP_B}$ 9 and 23 Hz characteristic of >P–S–P(O)< and >P–O–P(S)< groupings respectively. Lack of dealkylation products derived either from **5b** or **6b** is consistent with the known properties of the neopentyl group to resist nucleophilic displacement.

Chemical changes monitored by ^{31}P NMR spectroscopy at various temperatures are given in Fig. 2.

In the reaction between **1a** and tributyl phosphite **4c** where desulfurization, deoxygenation and dealkylation products are observed (Scheme 5), there was no trace of the phosphonium intermediate of the type **5c** at −100 °C. However, it was

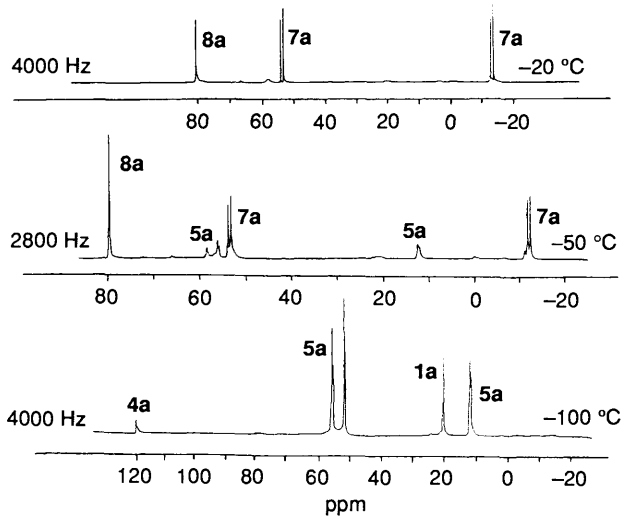


Fig. 1 ^1H-Decoupled ^{31}P NMR spectra of an equimolar mixture of $[(EtO)_2P(O)S]_2$ **1a** and $(Me_2N)_3P$ **4a**

probably an intermediate because products **7a** and **8c** were formed by the desulfurization pathway. At a slightly elevated temperature (−90 °C) it was possible to observe the intermediate phosphonium salt **6c** with two phosphorus centres linked by an oxygen bridge. The structure of **6c** is clearly seen from its ^{31}P NMR spectra. The salt **6c** decomposes by deoxygenation and dealkylation modes; these chemical changes and spectral data of **6c** are shown in Scheme 5.

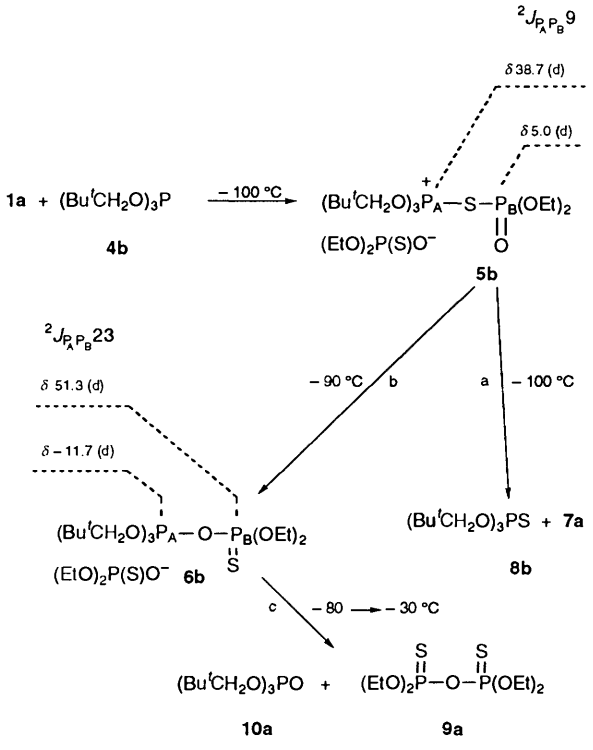
P^{III} Esters $PhP(OMe)_2$ **4d**, $Ph_2P(OMe)$ **4e** and $Ph_2P(OPr)$ **4f**, all of which contain C–P bonds, show higher affinity toward the disulfides **1** than trialkyl phosphites $P(OR)_3$. This feature, which expresses itself by fast reactions, even below −100 °C, can be explained in terms of the lower nucleophilicity of the former esters over the latter. In the reaction of the disulfide **1a** with dimethyl phenylphosphonite **4d** no phosphonium intermediates of the type **5** and **6** could be observed by ^{31}P NMR spectroscopy. The only products of this reaction were the monothiopyrophosphate **7c** and the thiolophosphate **12b**. The products **7c** and **12b** are likely to derive from the phosphonium intermediate **6d** as shown in Scheme 6.

Similarly, in the reaction of **1a** with methyl diphenylphosphinite Ph_2POMe **4e** two pairs of products **12b**, **7d** and **10c** and **9a**, are formed in a ratio of 80:20 as determined by ^{31}P NMR. They are derived from the phosphonium intermediate **6e** (Scheme 7).

As expected, when the methoxy group in a P^{III} compound is replaced by a propoxy group, dealkylation of the intermediate **6f** formed in the reaction between **1a** and propyl diphenylphosphinite **4f** is less important than its decomposition by the deoxygenation mode. In this case formation of the phosphonium salt **6f** is observed by ^{31}P NMR spectroscopy at −100 °C (Scheme 8).

That the structure of the disulfide **1** influences the reaction with triphenylphosphine is evident from observations described in Schemes 9, 10 and 11. In the reaction of **1a** with triphenylphosphine **4g** the final desulfurization and deoxygenation products are observed even at −100 °C, together with unchanged substrates. The reaction is complete at −40 °C.

Our failure to observe intermediate phosphonium salts of the type **5** and **6** in the reaction shown in Scheme 9 is in contrast to the analogous reaction of triphenylphosphine with diethoxyoxophosphoranesulfenyl chloride [$(EtO)_2P(O)SCl$ **2a**] where both intermediates [$Ph_3\overset{+}{P}$–S–P(O)$(OEt)_2$ Cl^-] and



Scheme 4

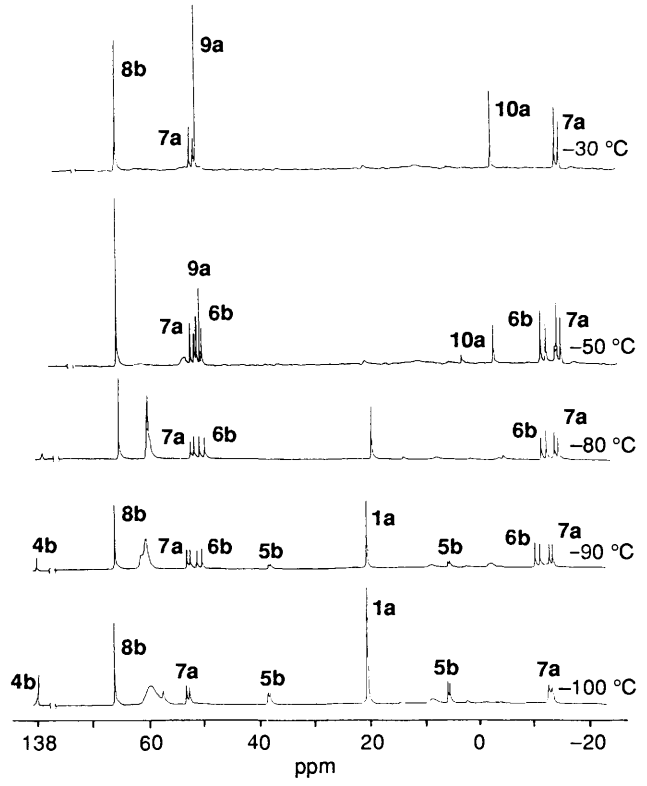
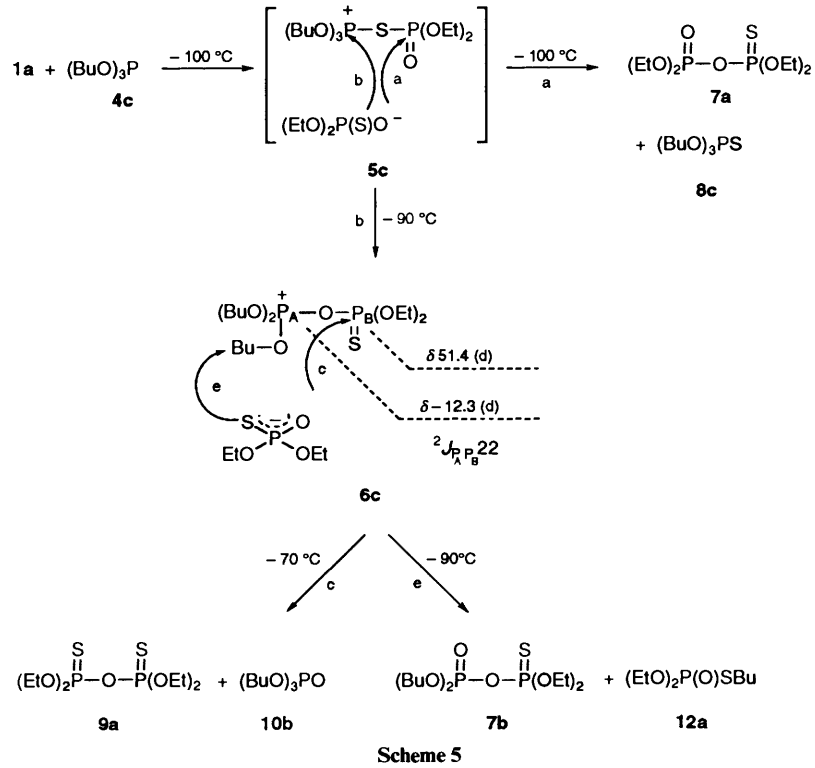
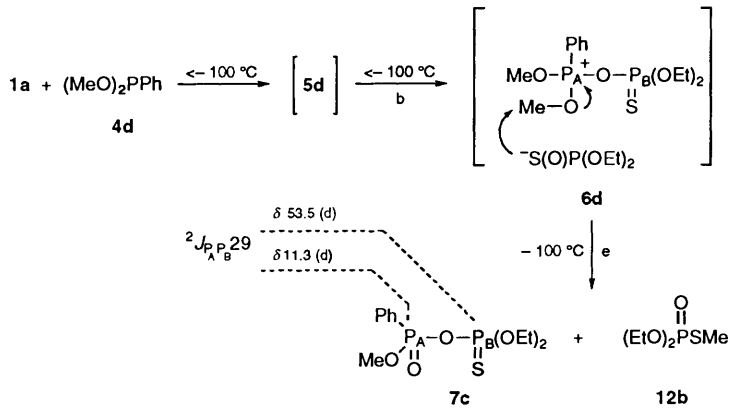


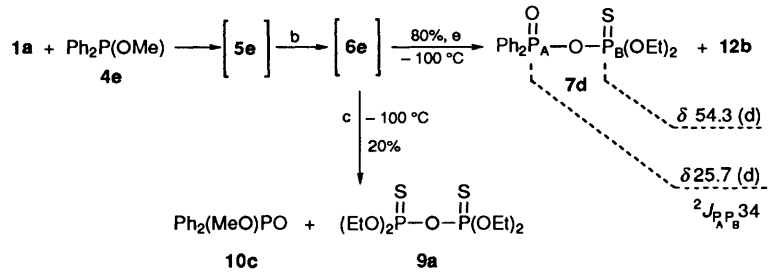
Fig. 2 ^1H-Decoupled ^{31}P NMR spectra of an equimolar mixture of $[(EtO)_2P(O)S]_2$ **1a** and $Bu'CH_2O)_3P$ **4b**



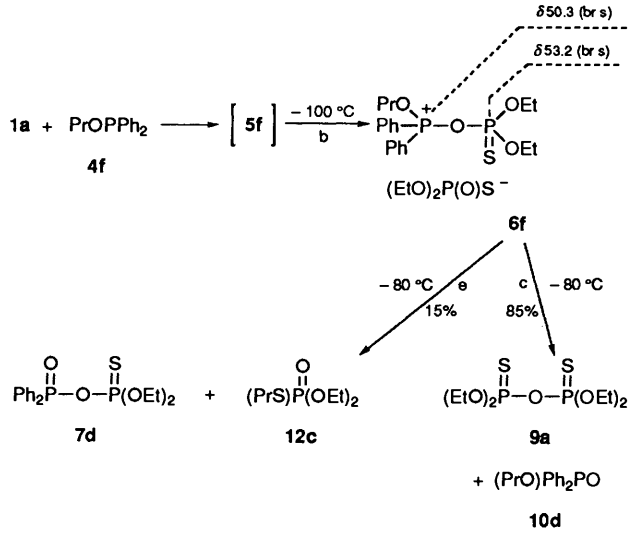
Scheme 5



Scheme 6



Scheme 7



Scheme 8

$[Ph_3\overset{+}{P}\text{-}O\text{-}P(S)(OEt)_2\ Cl^-]$ have been observed by ^{31}P spectroscopy.[8d] This difference may be explained by the affinity of the diethylphosphorothioate anion towards both phosphoryl and thiophosphoryl centres, which is higher than that of the chloride ion.

In the reaction of the disulfide derived from neopentyl glycol **1b** with triphenylphosphine **4g** the intermediate **6h** is observed and deoxygenation prevails. The relatively high thermal stability of the intermediate **6h** can be explained by steric hindrance which reduces the rate of nucleophilic displacement at the thiophosphoryl centre (Scheme 10).

The influence of such steric hindrance is even more pronounced in the reaction of triphenylphosphine **4g** with the disulfide **1c**. The intermediate phosphonium salt **6i** is observed up to −20 °C and the reaction takes entirely the deoxygenation course (Scheme 11).

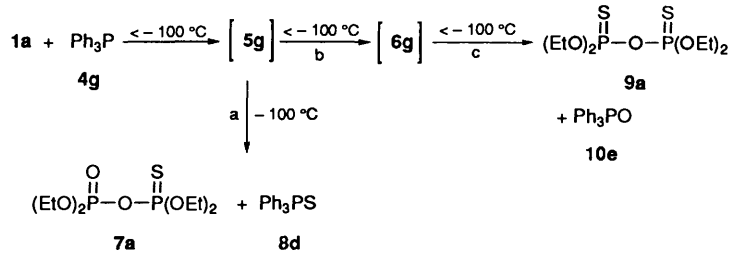
Reaction of the Disulfide **1** *with* P^{III} *Derivatives Containing Ligands which Increase the Stability of* P^{V} *Intermediates.*—It is well known that five-membered ring and aryloxy ligands increase the stability of five-coordinate intermediates. In our earlier studies formation of five-coordinate intermediates has been observed in the reaction of 2-neopentyloxy-1,3,2-benzodioxaphosphole with diethyoxyoxophosphoranesulfenyl chlorides. This reaction takes predominantly the deoxygenation course.[10]

The reaction of **1a** with 2-ethoxy-1,3,2-benzodioxaphosphole **4h** affords final products derived from desulfurization, deoxygenation and dealkylation pathways. At −80 °C the five-coordinate intermediate **15a** is accompanied by final products **7a**, **8e**, **9a**, **10f**, **7f**, **12d** and unchanged starting materials as shown in Scheme 12. This complex mixture clearly unfolded under ^{31}P NMR spectroscopy through comparison of spectral data with those of authentic samples of the components. The structure of the phosphorane **15a** was also confirmed by independent synthesis from the corresponding dichlorophosphorane and triethylammonium salt of diethylphosphorothioic acid.[14]

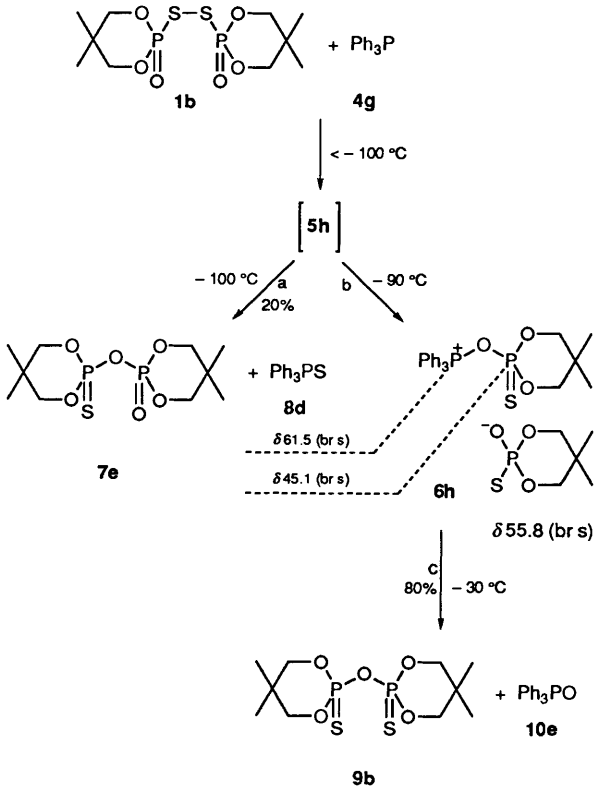
Formation of desulfurization products in the reaction described in Scheme 12 suggests that the primary phosphorane **14a** decomposes *via* the phosphonium salt **5j**.

This kind of oxidative addition already discussed in our earlier work is most likely to involve formation of the primary phosphorane **14** and its subsequent multi-step isomerization into the phosphorane **15**[15] (Scheme 13).

How the oxidative addition of the disulfide **1** to P^{III} compounds occurs stereochemically is an open question. Such addition can result in both apical, both equaltorial or one apical and one equatorial orientation. The frontier orbital method shows that axial–equatorial addition is forbidden, while the other two products can be formed in allowed modes.[16] The alternative reaction mechanism to concerted oxidative addition is a two-step process involving formation of the phosphonium salt which is in equilibrium with phosphorane structure. Without more detailed mechanistic studies, the mechanism of



Scheme 9



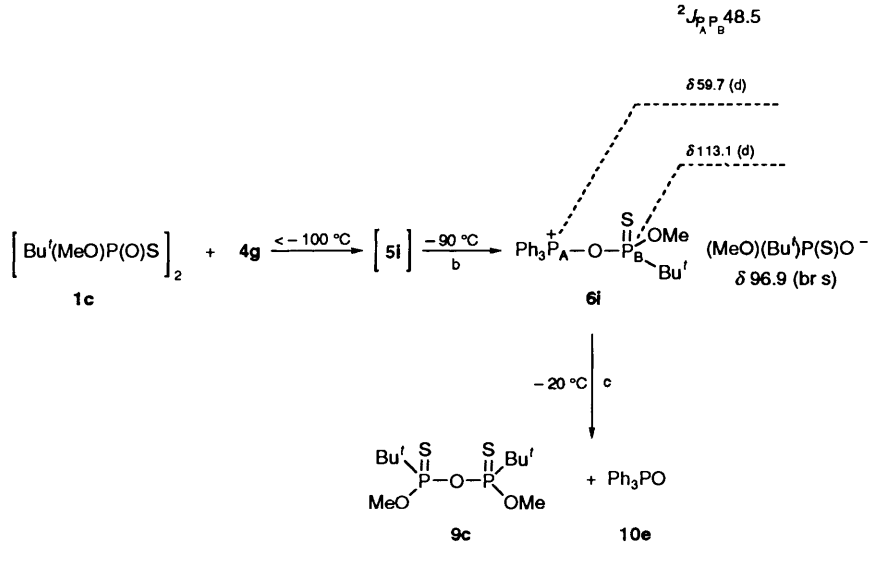
Scheme 10

formation of the intermediate **14a** cannot be defined. The same considerations apply equally well to our earlier studies on oxidative addition of oxophosphoranesulfenyl chlorides **2** to P^{III}-compounds.[10] One cannot exclude the possibility that the primary phosphorane has the e–e structure **14**, which after dissociations and redissociations is transformed into the isomeric structure **15**. The following possibilities can be considered. The a–a arrangement of thiophosphoryl groups is excluded because the five-membered ring is likely to occupy a–e positions. The e–e structure is supported by a lack of different signals for both thiophosphoryl groups in ^{31}P NMR spectra, but for an a–e structure fast ligand exchange would lead to the same spectral pattern. The experiment shown in Scheme 12 was performed using ^{31}P NMR 121.5 MHz frequency and in this case the two P^{IV} signals were equivalent.

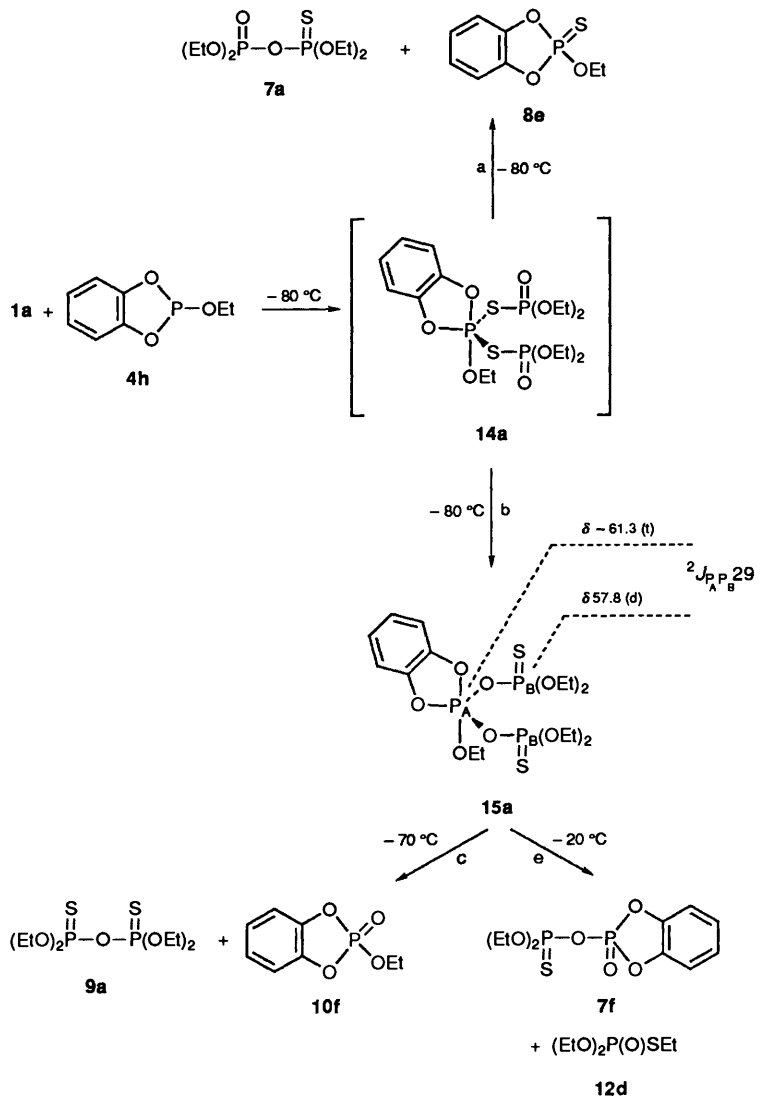
In the reactions of the disulfide **1a** with three other derivatives of 1,3,2-benzodioxaphosphole **4i–k**, the analogous five-coordinate intermediates **15b–d** were also observed. All these reactions proceed predominantly by deoxygenation mode yielding oxo esters **10g–i** and tetraethyl dithiopyrophosphate **9a** (Scheme 14).

The phosphorane **15e** is observed in the reaction of **1a** with triphenyl phosphite $P(OPh)_3$ **41** (Scheme 15).

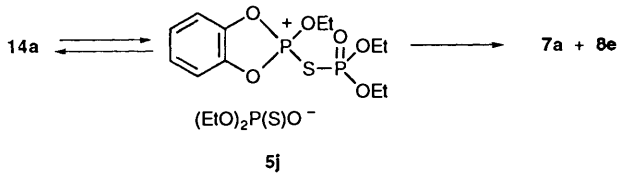
Reaction of Bis(diethoxyphosphinoyl) Disulfide **1a** *with* P^{III} *Compounds in the Presence of Boron Trifluoride–Diethyl Ether.*—A good example of complexation by BF_3 is the reaction between tributyl phosphite **4c** and the disulfide **1a**. In the absence of BF_3 this reaction proceeds according to Scheme 5. Existence of the primary intermediate **5c** is postulated on the basis of products derived from it *via* desulfurization. In the presence of BF_3 both transient phosphonium intermediates of the type **5** and **6** are observed. The intermediates **5c** and **6c** show increased thermal stability. The former is stable up to −70 °C and the latter decomposes into final products at −20 °C. The situation shown in Scheme 16 is valid for the reaction in which 1 equiv. of BF_3·Et_2O is added to the

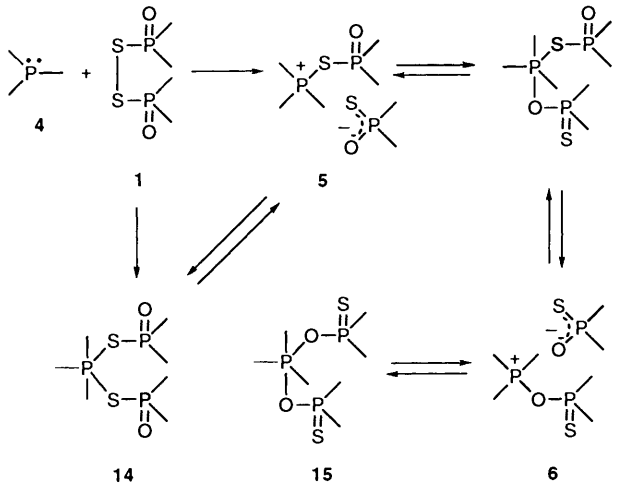


Scheme 11



Scheme 12



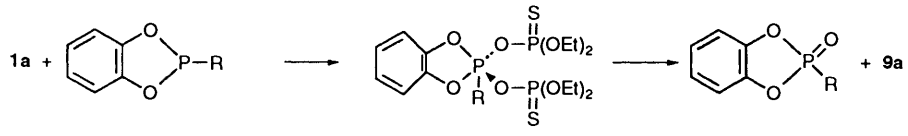


Scheme 13

system. When an equimolar amount or an excess of BF_3·Et_2O is added to a disulfides **1a** or **1b** prior to their interaction with **4b** and **4c** at −100 °C, the reaction takes the desulfurization pathway exclusively (Scheme 17).

Another spectacular example of the influence of BF_3 on the stability of intermediates **5g** and **6g** is the reaction between the disulfide **1a** and triphenylphosphine **4g**. In the absence of BF_3 only final products were evident (Scheme 9), while in the presence of BF_3 both intermediates were observed by ^{31}P NMR spectroscopy (Scheme 18). Also, in this case, the amount of BF_3 and the way it is added influence the final outcome. When an excess of BF_3 is present in the reaction medium prior to addition of **1a** to Ph_3P, only the complex **5g** is observed and its thermal decomposition gives products corresponding to the desulfurization pathway.

In the reaction between **1a** and triphenyl phosphite **4l** (Scheme 15) formation of the intermediate phosphorane **15e** was observed. It is assumed that deoxygenation pathway products are formed from the phosphonium salt **6j** which is in equilibrium with the phosphorane **15e**. Addition of BF_3 allows this equilibrium to be shifted entirely to the salt **6j** by lowering the nucleophilicity of the counter ion $(EtO)_2P(S)O^-$ by its complexation with BF_3 (Scheme 19 and Fig. 3).



4i – k 15b – d 10g – i

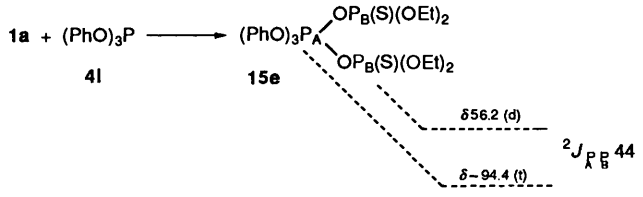
^{31}P data: δ (ppm); $J_{P_AP_B}$ (Hz)

4i (R = OCH_2Bu^t) → 15b δP^V – 69(t), P^{IV} 55.2(d); J_{PP} = 29 — 10g δ 11.3

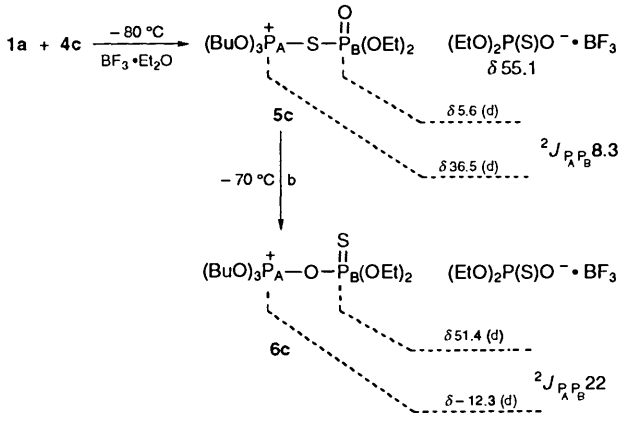
4j (R = NEt_2) → 15c δP^V – 63(t), P^{IV} 55.6(d); J_{PP} = 36 — 10h δ 20.9

4k (R = Bu^t) → 15d δP^V – 25.5(t), P^{IV} 55.5(d); J_{PP} = 51 — 10i δ 55.9

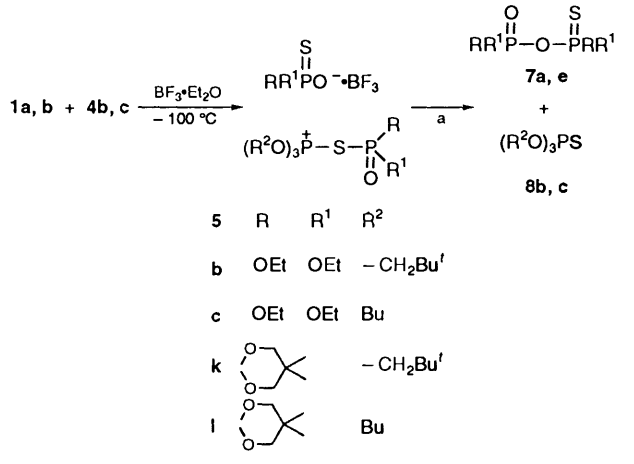
Scheme 14



Scheme 15

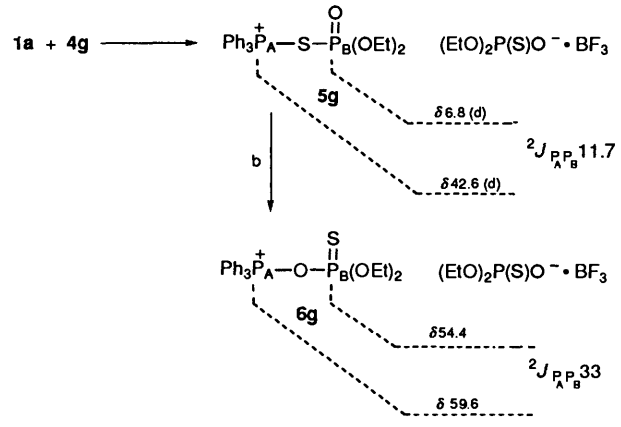


Scheme 16

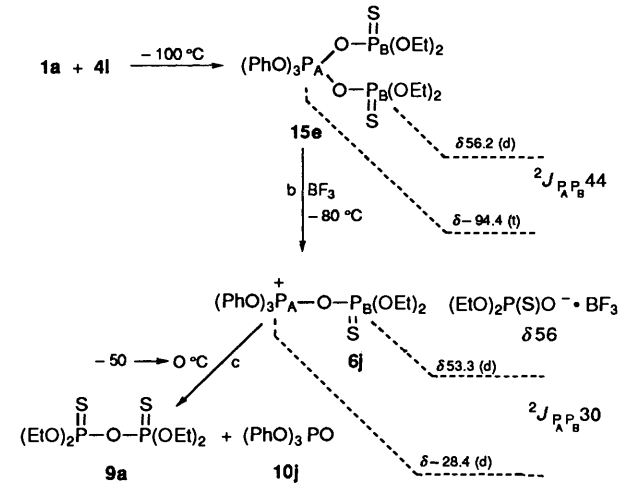


Scheme 17

In conclusion, complexation with BF_3 allows stabilization of the transient phosphonium intermediates **5** and **6** and, in consequence, the reaction course is steered in the desired direction.



Scheme 18



Scheme 19

Conclusion

The chemoselectivity of reaction between bis(phosphinoyl) disulfides **1** and P^{III} systems can be influenced by three factors: choice of ligands at P^{IV} and P^{III} centres, the temperature of reaction and complexation of counter-ions of phosphonium intermediates. The phosphonium intermediates **5** and **6** which are of crucial importance for the outcome of the reaction, are in dynamic equilibria with the corresponding P^V phosphoranes. The equilibria favour the phosphonium form except when phosphorus bears ligands which stabilize P^V species. But in every case reaction seems to proceed *via* phosphonium intermediates. The disulfide **1** and oxophosphoranesulfenyl chlorides **2** behave differently towards P^{III} species. This

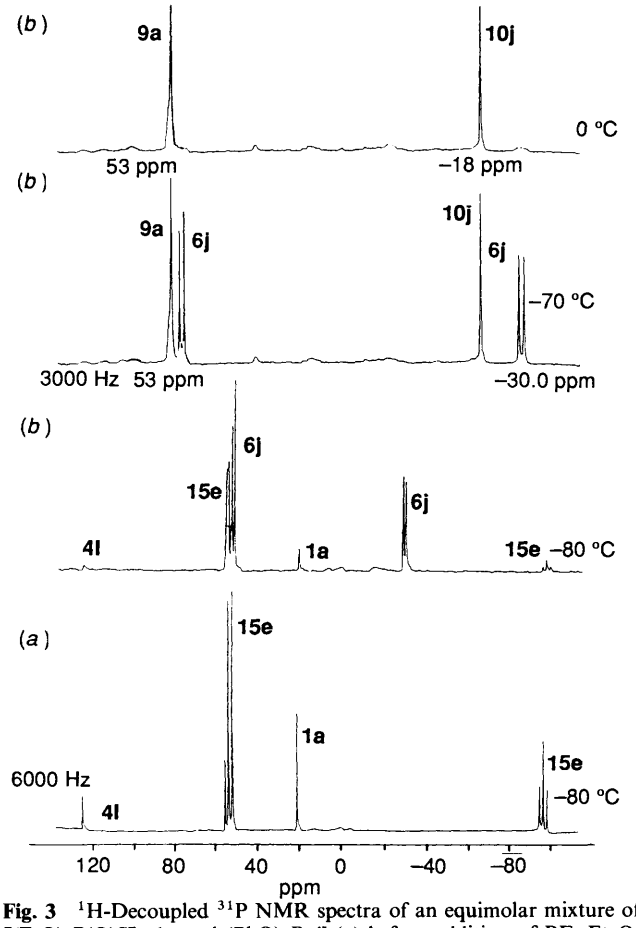


Fig. 3 ^{1}H-Decoupled ^{31}P NMR spectra of an equimolar mixture of $[(EtO)_2P(O)S]_2$ **1a** and $(PhO)_3P$ **4l** (*a*) before addition of BF_3·Et_2O, (*b*) after addition of BF_3·Et_2O

difference depends on the nature of the counter-ion in phosphonium salts **5** and **6**. There are three electrophilic centres in these phosphonium salts and they show diverse affinity toward Cl^- and $>P(O)S^-$ counter-ions.

Experimental

Boiling and melting points were uncorrected. Solvents and commercial reagents were purified by conventional methods. Products were identified with ^{31}P NMR spectroscopy and gas chromatography by comparison with authentic samples (unless specified otherwise). ^{31}P NMR Spectra were recorded on a FT JEOL FX-60H spectrometer at 24.3 MHz and on Bruker MSL 300 spectrometer at 121.5 MHz. Positive NMR chemical shifts were reported in parts per million (ppm) downfield from 85% H_3PO_4 as external standard.

Low-temperature ^{31}P *NMR Measurements.*—A 10 mm NMR tube (cooled in liquid N_2 or acetone–solid CO_2) was charged with equimolar amounts of bis(phosphinoyl) disulfides **1** and P^{III}-compounds **4** (0.5–1 mmol) in methylene dichloride or ethyl chloride (2.5 cm^3). All operations were carried out in a dry argon atmosphere. The tubes were closed tightly with rubber septa under argon. Variable-temperature spectra were monitored usually at intervals of 10 °C and 10 min.

Materials.—The following were prepared by literature procedures: tris(dimethylamino)phosphine **4a**,[17] trineopentyl phosphite **4b**,[17] tributyl phosphite **4c**,[17] dimethylphenylphosphonite **4d**,[18] methyl diphenylphosphinite **4e**,[19] propyl diphenylphosphinite **4f**,[20] ethyl *o*-phenylene phosphite **4h**,[21] neopentyl *o*-phenylene phosphite **4i**[21] [85%, b.p. 54/56 °C (0.4 mmHg) Found: C, 58.0; H, 6.4; P. 14.1. Calc. for $C_{13}H_{15}O_3P$: C, 58.4; H, 6.6; P, 13.7%; δ^{31}P 132], *o*-phenylene diethyl phosphoramidite **4j**[21] [94%, b.p. 68 °C (0.8 mmHg) Found: C, 56.5; H, 6.8; P. 14.8; N, 6.5. Calc. for $C_{10}H_{14}NO_2P$: C, 56.8; H, 6.6; P, 14.6; N, 6.6%, δ^{31}P 149], *tert*-butyl *o*-phenylene phosphonite **4k**[22] [86%, b.p. 46/47 °C (0.5 mmHg) Found: C, 60.9; H, 6.5; P, 15.3. Calc. for $C_{10}H_{13}O_2P$: C, 61.2; H, 6.68; P, 15.79%, δ^{31}P 208].

Bis(5,5-*dimethyl*-2-*oxo*-1,3,2-*dioxaphosphorinan*-2-*yl*) *Disulfide* **1b**.—(M.p. 130 °C, δ^{31}P 11.5) prepared by chlorination of the potassium salt of 2-hydroxy-2-mercapto-5,5-dimethyl-1,3,2-dioxaphosphorinane[23] with sulfuryl chloride according to Edmundson.[8]

Bis[*methoxy*-tert-*butyl*(*phosphinoyl*)] *Disulfide* **1c**.—(M.p. 76–78 °C, δ^{31}P 63) Obtained from the reaction of the potassium salt of *tert*-butylmethoxyphosphonothioic acid with sulfuryl chloride as described by Michalski *et al.*[24]

Bis(4-*methyl*-2-*oxo*-1,3,2-*dioxaphosphorinan*-2-*yl*) *Disulfide* trans, trans **1d**.—(δ^{31}P 11.4). Prepared according to Skowrońska *et al.*,[12] by treating *trans*-2-mercapto-2-methoxy-4-methyl-1,3,2-dioxaphosphorinane with a half an equimolar amount of sulfuryl chloride.

2,2′-*Oxybis*(4-*methyl*-1,3,2-*dioxaphosphorinane*) 2-*Oxide* 2′-*Sulfide*.—The solution of 2-chloro-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (3.4 g, 0.02 mol) in benzene (10 cm^3), prepared according to Stec,[25] was added to a stirred solution of the potassium salt of 2-hydroxy-2-mercapto-4-methyl-1,3,2-dioxaphosphorinane[23] (3.9 g, 0.02 mol) in benzene (10 cm^3). The reaction mixture was stirred at 30–40 °C for 5 h and was found by ^{31}P NMR spectroscopy to contain a mixture of 2,2′-oxybis-(4-methyl-1,3,2-dioxaphosphorinane) 2-oxide 2′-sulfide [yield 80%, δ^{31}P 46.5 (d), −21.6 (d), $^2J_{PP}$ 27] together with unchanged substrates (20%). The product (1 g, 0.0033 mol) was purified by preparative chromatography (R_f 0.23; C_6H_6–EtOAc 3:1). δ_H 1.45 (dd, CH_3, $^3J_{H-CH}$ 6.3, $^4J_{P-H}$ 1.6), 1.0–3.1 (m, CH_2 of ring).

Reactions of Bis(*phosphinoyl*) *Disulfides* **1** *with Three-coordinate Phosphorus Compounds* **4**: *General Procedure.*—A solution of compound **4** (0.015 mmol) in methylene dichloride (20 cm^3) was added dropwise at −70 °C to a stirred solution of the disulfide **1** (0.015 mol) in CH_2Cl_2 (25 cm^3) under a dry argon atmosphere. The reaction mixture was then allowed to warm slowly to ambient temperature and stirring was continued for 30 min. After evaporation of solvent the crude reaction mixture was analysed by ^{31}P NMR spectroscopy and GC chromatography. The products formed together with their yields are collected in Table 1 and their ^{31}P NMR data are given in Table 2.

Bis(4-*methyl*-2-*oxo*-1,3,2-*dioxaphosphorinan*-2-*yl*) *disulfide* trans,trans-**1d** *with trineopentyl phosphite* **4b**. Following the general procedure, compounds **1d** (3.34 g, 0.01 mol) and **4b** (2.92 g, 0.01 mol) gave a mixture of 2,2′-oxybis(4-methyl-1,3,2-dioxaphosphorinane) 2 oxide 2′-sulfide **7h** [δ^{31}P 46.5 (d), −21.7 (d), $^2J_{PP}$ 26.8, 50%] and **8b** (δ^{31}P 67.3, 50%). Compound **7h** was purified by preparative chromatography (R_f 0.25, C_6H_6–EtOAc 3:1) and analysed by ^{31}P NMR spectroscopy, by comparison with an authentic sample.

Bis(4-*methyl*-2-*oxo*-1,3,2-*dioxaphosphorinan*-2-*yl*) *disulfide* trans,trans-**1d** *with triphenylphosphine* **4g**. The general procedure was applied to the reaction of **1d** (3.34 g, 0.01 mol) and **4g** (2.62 g, 0.01 mol). ^{31}P NMR Analysis of the crude reaction mixture revealed the presence of **8d** (δ^{31}P 42.0, 5%), **7h** [δ^{31}P 47.5 (d), −21.9 (d), $^2J_{PP}$ 28, **7h** 5%], **10e** (δ^{31}P 29.2,

Table 2 ^{31}P NMR chemical shifts of products of the reactions of **1** and **4**

Entry[a]	$[RR^1P(O)S]_2$ **1**	R^2_3P **4**	$RR^1P_A(O)OP_B(S)RR^1$ **7** $\delta^{ref.}$ $J_{P_AP_B}$ [Hz]	$[RR^1P(S)]_2O$ **9** $\delta^{ref.}$ $J_{P_AP_B}$ [Hz]	$RR^1P_A(S)OP_B(O)R^2_2$ **7** $\delta^{ref.}$ $J_{P_AP_B}$ [Hz]	R^2_3PS **8** $\delta^{ref.}$	R^2_3PO **10** $\delta^{ref.}$	$RR^1P(O)SR^2$ **12** $\delta^{ref.}$
1	**1a**	**4a**	P_A − 14.9 (d), P_B 53.1 (d)[27] J 21	—	—	81[28]	—	—
2	**1d**	**4b**	P_A − 21.7 (d), P_B 46.5 (d)[b] J 26.8	—	—	67.4[29]	—	—
3	**1a**	**4c**	P_A − 14.6 (d), P_B 53.4 (d) J 21	51.8[30]	P_A 53.2 (d), P_B − 13.8 (d)[27] J 20	67.6[29]	−2.2[30]	27.4[19]
4	**1a**	**4b**	P_A − 14.5 (d), P_B 53.6 (d) J 20	52.1	—	67.4	−1.9[30]	—
5	**1b**	**4g**	P_A − 24 (d), P_B 44.4 (d)[8] J 30	44.2[18]	—	42[18]	35.3[18]	—
6	**1a**	**4g**	P_A − 15 (d), P_B 53.5 (d) J 21.5	52.4	—	42.9	29.2[18]	—
7	**1a**	**4l**	P_A − 13 (d), P_B 52.4 (d) J 20.5	51.8	—	53.2[30]	−18.2[19]	—
8	**1d**	**4g**	P_A − 21.9 (d), P_B 47.5 (d)[b] J 28	{P_A 46.8, P_B 42.7} AB[26] J_{AB} 31.7	—	42	29.2	—
9	**1a**	**4h**	P_A − 14.1 (d), P_B 55.5 (d) J 22	52.4	P_A 53.5 (d), P_B − 1.9 (d)[33] J 24.4	80[31]	12.1[19]	28.2[18]
10	**1a**	**4i**	—	52	—	—	11.2[19]	—
11	**1a**	**4j**	—	52.1	—	—	20.9[32]	—
12	**1a**	**4k**	—	51.9	—	—	55.5	—
13	**1c**	**4g**	—	103.3	—	—	30.6	—
14	**1a**	**4f**	—	51.9	P_A 54.1 (d) P_B 25.5 (d)[19] J 34	—	29.6[20]	27[19]
15	**1a**	**4e**	—	52	P_A 54.3 (d), P_B 25.7 (d)[19] J 34.2	—	31.7[28]	27.2[19]
16	**1a**	**4d**	—	—	P_A 53.5 (d), P_B 11.3 (d) J 29.3	—	—	27.5

[a] The entries are in the same order as in Table 1. [b] ^{31}P NMR data of original compound are cited in Experimental section.

Table 3 The ratio of the products formed in the reacting system **1a**–BF_3Et_2O + **4**

Reagents			Products	
1	**4**	BF_3Et_2O/ mol equiv.	Yield of desulfurization[a] **7** + **8** (%)	Yield of deoxygenation[a] **9** + **10** (%)
1a	**4b**	1	100	—
1a	**4b**	2	100	—
1a	**4c**	1	100	—
1a	**4c**	2	100	—
1a	**4g**	1	45	55
1a	**4g**	2	100	—

[a] Determined by ^{31}P NMR spectroscopy.

44%) and bis(4-methyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl)oxide **9d** [$\delta^{31}P$ 46.8, 42.7 (AB) $^2J_{PP}$ 31.7]. Compounds **7h** (R_f 0.23) and **9d** (R_f 0.44) were isolated by preparative chromatography (C_6H_6–EtOAc 3:1) and analysed by ^{31}P, ^1H NMR spectroscopy by comparison with an authentic sample (**7h**) or reported data (**9d**).[26] Compound **9d**: δ_H 0.85–1.03 (m, 6 H, CH_3–CH, $^4J_{PH}$ 2.6, 0.8), 1.8–2.9 (m, 4 H, CH_2 of ring).

Reactions of Bis(diethoxyphosphinoyl) Disulfide **1a** *with Three-coordinate Phosphorus Compounds* **4b**, **4c** *and* **4g** *in the Presence of Boron Trifluoride–Diethyl Ether.* To a solution of compound **1a** (0.001 mol) and borone trifluoride–dimethyl ether (0.001 mol or 0.002 mol) in ethyl chloride (5 cm^3) was added a solution of **4** (0.001 mol) in EtCl (5 cm^3) at −100 °C. After the temperature had risen to −20 °C, crude reaction mixtures were analysed by ^{31}P NMR spectroscopy. The proportions of the products formed are collected in Table 3.

References

1 (*a*) T. Moeller, *Inorganic Chemistry*, Wiley, New York, 1952; (*b*) J. E. Huheey, *Inorganic Chemistry*, Harper and Row, New York, 1978, p. 677.
2 O. Foss, *Acta Chem. Scand.*, 1947, **1**, 307.
3 L. Horner and H. Nickel, *Liebigs Ann. Chem.*, 1955, **599**, 20.
4 J. Michalski, T. Modro and J. Wieczorkowski, *J. Chem. Soc.*, 1960, 1665.
5 D. N. Harpp, J. G. Gleason and D. K. Ash, *J. Org. Chem.*, 1971, **36**, 322.
6 D. H. Barton, D. Manley and D. A. Widdowson, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1568.
7 R. S. Edmundson, *J. Chem. Soc. C*, 1967, 1635.
8 (*a*) J. Michalski and A. Skowrońska, *J. Chem. Soc. C*, 1970, 703; (*b*) J. Michalski, A. Skowrońska and R. Bodalski, in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, eds. J. G. Verkade and L. D. Quin, VCH (New York), 1987, ch. 8; (*c*) J. Michalski, A. Skowrońska and A. Łopusiński, *Phosphorus, Sulfur, Silicon*, 1991, **58**, 61; (*d*) E. Krawczyk, A. Skowrońska, J. Michalski and J. Mikołajczak, *J. Org. Chem.*, 1992, **57**, 4963 and references cited therein.
9 (*a*) J. Michalski, *Bull. Soc. Chim. Fr.*, 1963, 11 and references cited; (*b*) A. Markowska and J. Michalski, *Rocz. Chem.*, 1964, **38**, 1141; (*c*) A. Skowrońska, E. Krawczyk and J. Burski, *Phosphorus Sulfur Relat. Elem.*, 1983, **18**, 233 and references therein.
10 E. Krawczyk, A. Skowrońska, J. Michalski and J. Mikołajczak, *J. Chem. Soc., Perkin Trans. 1*, 1993, 851.
11 M. Zbirovsky and V. Ettel, *Chem. Listy*, 1956, **50**, 1261.
12 A. Skowrońska and E. Krawczyk, *Phosphorus Sulfur Relat. Elem.*, 1980, **9**, 189.
13 R. Dembiński, Ph.D. Thesis, Łódź, Poland, 1993.
14 A. Skowrońska, J. Burski, E. Krawczyk and M. Pakulski, *Phosphorus Sulfur Relat. Elem.*, 1986, **27**, 119.
15 E. Krawczyk, J. Michalski, M. Pakulski and A. Skowrońska, *Tetrahedron Lett.*, 1977, 2019.
16 R. G. Pearson, *Symmetry Rules for Chemical Reactions*, J. Wiley and Sons, New York, 1976, p. 289, 291.
17 Houben-Weyl, *Methoden der Organischen Chemie*, Georg Thieme Verlag, Stuttgart, 1963, vol. 12, ch. 2, pp. 45, 53, 108.
18 G. M. Kossolapoff and L. Maier, *Organic Phosphorus Compounds*, J. Wiley and Sons, New York, 1972, vol. IV, p. 32; vol. III, p. 431.
19 N. Mark and J. R. Van Wazer, *Topics in Phosphorus Chemistry*, J. Wiley and Sons, New York, 1967; vol. 5B.
20 F. M. Kharrasova and G. Kamou, *Zh. Obshch. Khim.*, 1964, **34**, 2195.
21 J. R. Van Wazer and V. Mark, *J. Org. Chem.*, 1967, **32**, 1187.
22 M. Wieber and W. R. Hoss, *Monats. Chem.*, 1970, **101**, 776.
23 M. Mikołajczyk and J. Łuczak, *Tetrahedron*, 1972, **28**, 5411.
24 A. Łopusiński, L. Łuczak and E. Brzezińska, *Phosphorus Sulfur Relat. Elem.*, 1987, **31**, 101.
25 W. J. Stec and M. Mikołajczyk, *Tetrahedron*, 1973, **29**, 539.
26 M. Mikołajczyk, B. Zimnicka, J. Karolak-Wojciechowska and M. Wieczorek, *J. Chem. Soc., Perkin Trans. 2*, 1983, 501.
27 A. Skowrońska, B. Młotkowska and J. Michalski, *J. Chem. Soc., Perkin Trans. 1*, 1974, 319.
28 A. Schmidpeter and H. Brecht, *Z. Naturforsch.*, 1969, **24**, 179.
29 J. Michalski, J Mikołajczak and A. Skowrońska, *J. Am. Chem. Soc.*, 1978, **100**, 5386.
30 G. Marell, *Annu. Rep. N.M.R. Spectrosc.*, ed. E. F. Mooney, Academic Press, London and New York, 1973, vol. 5B.
31 A. Skowrońska J. Mikołajczak and J. Michalski, *J. Chem. Soc., Chem. Commun.*, 1975, 986.
32 J. Perregaard, E. B. Pedersen and S.-O. Lawesson, *Rec. Trav. Chim. Pays-Bas*, 1974, **93**, 252.
33 K. M. Abraham and J. M. Van Wazer, *Inorg. Chem.*, 1975, **14**, 1099.

Paper 3/04361D
Received 23rd *July* 1993
Accepted 17th *August* 1993