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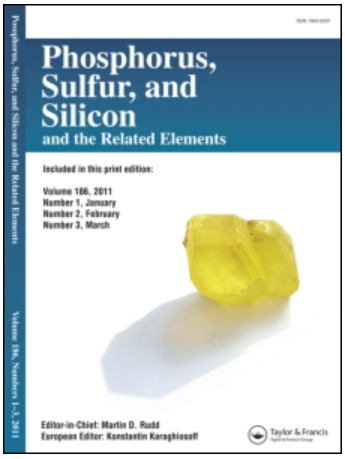

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NEW SYNTHESIS OF DIALKOXYTHIOXAPHOS-PHORANESULFENYL BROMIDES AND CHLORIDES

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NEW SYNTHESIS OF DIALKOXYTHIOXAPHOSPHORANESULFENYL BROMIDES AND CHLORIDES

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The synthesis of new pseudohalogen thioxaphosphoranesulfenyl bromides by simple bromination of bis(dialkoxythiophosphoryl)disulfides is presented. The new bromides turned out to be excellent thiophosphorylating agents, as well as substrates for a novel, highly efficient preparation of dialkoxythioxaphosphoranesulfenyl chlorides **4**.

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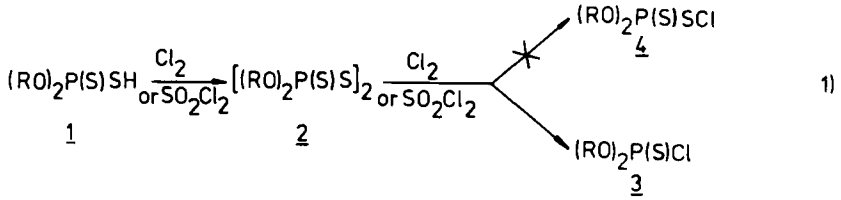
Organophosphorus compounds of the type $(RO)_2P(X)SCl$ (X = O,S), which contain a halogenosulfenyl moiety, belong to the class of thiophosphorylating agents with an electrophilic sulfur atom.[1,2]

Oxophosphoranesulfenyl chlorides are known, readily available compounds which can be obtained by direct chlorination of the corresponding monothioic organophosphorus acids, or from thionoesters in reaction either with chlorine, or with sulfuryl chloride.[3–7]

However, chlorination of dithioic acids **1** does not provide corresponding thioxaphosphoranesulfenyl chlorides **4**. Instead, chloridates **3** are formed exclusively (Equation 1).[8,9]



1 2 4 3 1)

R = Alkyl

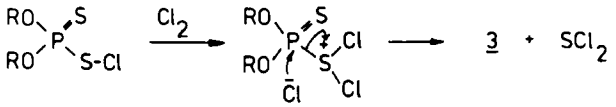
The only published procedure for the synthesis of thioxaphosphoranesulfenyl chlorides **4** utilizes the reaction of dialkoxythioxaphosphorane sulfenamides with dry HCl.[10] This approach however, suffers from two main drawbacks: (i) the thioxaphosphorane sulfenamides are not readily available, and (ii) products **4** synthesized according to that procedure are of low stability and easily eliminate sulfur to form the corresponding dialkyl phosphorothionochloridates **3**.[11] We present a convenient and highly efficient synthesis of the new thioxaphosphoranesulfenyl bromides **5** which is based on the reaction between bis(dialkoxythiophosphoryl)disulfides and bromine.† These compounds are demonstrated to be excellent dithiophosphorylating agents. Their evaluation as

† Preliminary paper: J. Michalski, M. Potrzebowski, A. Łopusiński, Angew. Chem., Internat. Edit., **94**, 135 (1982).

starting materials in the straightforward synthesis of the corresponding thioxaphosphoranesulfenyl chlorides of high purity and brief mechanistic discussion will also be presented.

RESULTS AND DISCUSSION

A facile cleavage of the phosphorus-sulfur bond in the reaction of chlorine with organophosphorus thioloesters >P(S)SR,[12] dithioic acids **1**, and disulfides **2**,[8,9] as well as thioxaphosphoranesulfenyl chlorides **4**[13] has been observed. This can be attributed to the greater affinity of the relatively hard basic chloride anion towards the hard electrophilic thiophosphoryl center.[14] However, the possibility of the reaction of chlorine with the thiolo sulfur center cannot be excluded. Such a process would make the thiolo sulfur atom a good leaving group susceptible to the substitution by the chloride anion (Equation 2). Analogous sulfonium ion structures $>P(O)\overset{+}{S}RClCl^-$ were recently encountered as intermediates in the chlorination reaction of organophosphorus thioloesters.[15]

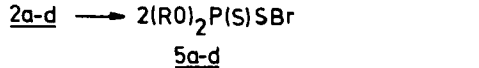


2)

On the other hand, the bromide anion which is softer than chloride anion, should preferably interact with softer thiono sulfur atom and not with the hard phosphorus center.[14] The "reluctance" of the bromide anion to take part in the formation of P–Br bond in tetracoordinate phosphorus compounds is strengthened by the tendency of Br^- to associate with bromine to produce Br_3^- which is a weaker nucleophile.[16,17] For this reason, the cleavage of the sulfur-sulfur bond by the bromide anion leading to sulfenyl bromides **5** should be a more preferred process than the cleavage of the phosphorus-sulfur bond which leads to the bromidates $(RO)_2P(S)Br$ **6**. A possibility of the nucleophilic atack of Br^- anion at centers different than phosphorus has also recurred in recent investigations of the bromination of the organophosphorus thioloesters.[18]

Reaction of bis(dialkoxythiophosphoryl)disulfides with bromine

Bromine in aprotic solvents such as toluene, methylene chloride, etc. at temperatures ranging from −80°C to −10°C reacts very readily with stoichiometric amounts of disulfides **2a–d**. In each case the quantitative formation of only one organophosphorus product, namely the sulfenyl bromides **5a–d**, was observed by ^{31}P NMR spectroscopy (Equation 3). This synthesis of the



3)

a R=CH_3^-; b R=$Bu^tCH_2^-$; c R=$i\text{-}C_3H_7^-$;
d R=$C_6H_5^-$;

bromides **5a–d** can also utilize dithioic acids **1**, their salts, or trialkylsilylesters as

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starting materials in a one-pot process in which the required disulfides are generated in situ (Equation 4). Thioxaphosphoranesulfenyl bromides are separated from the reaction mixture simply by removing the solvents at −5°C to 0°C under reduced pressure. The bromides thus obtained are sufficiently pure for further transformations. The identity of all new compounds **5a–d** was confirmed spectroscopically using ^{1}H, ^{31}P NMR, as well as by chemical transformations.

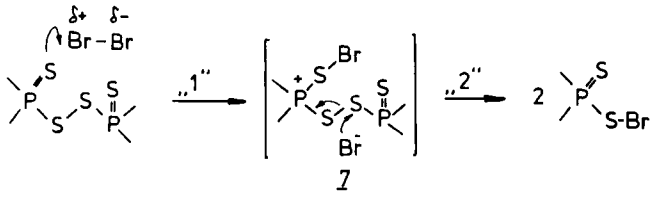
$$(RO)_2P(S)SY \xrightarrow{Br_2} \underline{2a\text{-}d} \xrightarrow{Br_2} 2\,\underline{5a\text{-}d} \qquad 4)$$

Y = H, Na, K, NHR_3, -SiAlkyl$_3$

Thioxaphosphoranesulfenyl bromides **5a–d** are more stable than the corresponding sulfenyl chlorides **4** prepared by the known procedure.[10,11] They can be kept for several days in the absence of moisture and nucleophilic impurities. However, they decompose rapidly during the attempts to distill them in vacuo. For example diisopropoxythioxaphosphoranesulfenyl bromide (**5c**) decomposes already at 40°C giving diisopropyl thiophosphorobromidate (**6c**) and sulfur in quantitative yield.

$$\underset{\underline{5c}}{(i\text{-}PrO)_2P(S)SBr} \xrightarrow{40^\circ C} \underset{\underline{6c}}{(i\text{-}PrO)_2P(S)Br} + \frac{1}{x}S_x \qquad 5)$$

The following mechanistic scheme (Equation 6) can be proposed for the bromination reaction of the bis(dialkoxythiophosphoryl)disulfides. In the first stage of this reaction, the nucleophilic attack of the thiono-sulfur atom of disulfide to the soft bromine molecule results in the formation of the phosphonium salt such as **7**. In the second stage, the attack of the Br^- anion at the soft electrophilic sulfur atom leads to the cleavage of the disulfide bond and the formation of thioxaphosphoranesulfenyl bromide. The investigation of the reaction involving disulfide **2b** by low temperature ^{31}P NMR technique at −85°C has not revealed any detectable amount of the possible intermediate **7**. At this temperature only the immediate formation of the sulfenyl bromide with resonance ^{31}P 74.4 ppm close to the starting **2b**, ^{31}P 84.4 ppm, has been observed. However, the formation of the intermediate **7** in this process cannot be totally excluded in the light of other results obtained by Michalski *et al.* during the study of halogenation of organophosphorus thionoesters.[7]



7 6)

Sulfenyl bromides act as electrophiles towards a variety of reagents such as olefins, amines, tricoordinate phosphorus compounds and others.

As can be seen from the Scheme, besides the electrophilic properties typical for sulfenyl halides in general, thioxaphosphoranesulfenyl bromides can also act as

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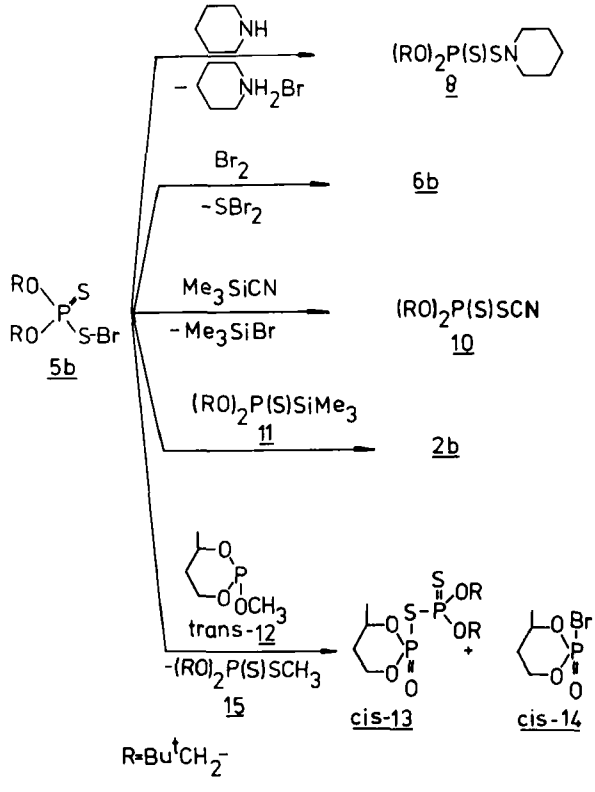
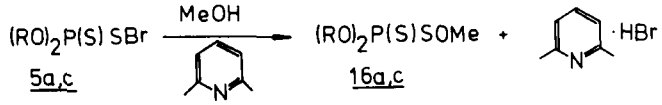


SCHEME 1.

brominating agents. This adds a novel element to the chemistry of organophosphorus sulfenyl halides and should possess some mechanistic implications.

Synthesis of dialkoxythioxaphosphoranesulfenyl chlorides

Sulfenyl bromides **5** turned out to be excellent starting materials in a new, efficient synthesis of thioxaphosphoranesulfenyl chlorides **4**. According to this method, the sulfenyl bromides **5a,c** react with methanol to give the corresponding dialkoxythioxaphosphorane methylsulfenates (**16a,c**).



7)

The reaction can be performed in non-polar solvents such as hexane or petroleum ether (b.p. 20–40°C) at room temperature in the presence of a stoichiometric amount of 2,6-lutidine. The esters **16a,c** are stable compounds; they can be isolated from the reaction mixture by vacuum distillation in 70–80% yield. The synthesis of esters **16** from **5** is of general character and different

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aliphatic alcohols can be used as exemplified in Equation (8).

$$\underline{5b} + Bu^tCH_2OH \longrightarrow (Bu^tCH_2O)_2P(S)SOCH_2Bu^t \quad 8)$$
$$\underline{16b}$$

However, the yield of esters **16** obtained by this method depends strongly on the nucleophilicity of the tertiary amine used. When triethylamine or pyridine is used instead of 2,6-lutidine, side reactions occur and lower the yield of **16**. The following products were identified by ^{31}P NMR in the reaction of **5b** with 2,2-dimethylpropanol in the presence of triethylamine (Equation 9): sulfenate **16b** (60%), disulfide **2b** (20%), bromidate **6b** (15%).

$$\underline{5b} + \frac{Bu\ CH_2OH}{Et_3N} \underline{16b}\,(60\%) + \underline{2b}\,(20\%) + \underline{6b}\,(15\%) + \text{unidentified products} \quad 9)$$

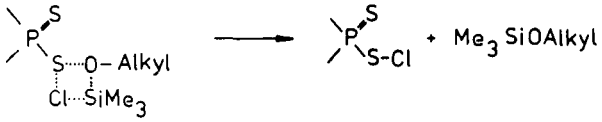
The formation of such side-products as the disulfide **2b** and the bromide **6b** in this reaction results probably from the possible interaction of the nucleophilic amine with sulfenyl bromide **5b**. Certainly the formation of the salt $>P(S)\overset{+}{S}NR_3Br^-$ is possible. It can decompose and/or react with another molecule of the bromide **5b** to give the observed by-products.

A similar species $[Et_3\overset{+}{N}SR]Hal^-$ was recently postulated as a disulfide precursor in the reaction of pyridine, or triethylamine with other sulfenyl halides.[19,20]

The thioxaphosphoranesulfenates **16** react smoothly with trimethylchlorosilane in non-polar solvents at room temperature to give the dialkoxythioxaphosphoranesulfenyl chlorides **4** in nearly quantitative yield.

$$\underline{16a\text{-}c} + Me_3SiCl \longrightarrow (RO)_2P(S)SCl + \ddot{R}OSiMe_3 \quad 10)$$
$$\ddot{R} = CH_3^-, \text{ or } Bu^tCH_2^- \qquad \underline{4a\text{-}c}$$

Sulfenyl chlorides **4a–c** are separated from the reaction mixture simply by removing the solvent and trimethylsilylalkylether at 0–5°C in vacuo. The products **4** exhibit good stability; they can be stored in the absence of nucleophilic impurities at room temperature for several days without formation of any detectable amount of dialkyl thiophosphorochloridates **3**. This compares favourably with previous observations and can be considered as the main virtue of the presented synthetic route to dialkoxythioxaphosphoranesulfenyl chlorides **4**. Most probably, the four-center mechanism indicated in Equation 11 can reasonably be assumed responsible for such a clean transformation.[21] In this respect the reaction studied resembles closely similar reactions of alkyl benzenesulfenates[22] and dialkoxyoxophosphorane alkyl sulfenate.[23]



11)

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EXPERIMENTAL

The solvents and reagents were purified by conventional methods before use. All b.ps. and m.ps. are uncorrected. ^{1}H NMR spectra were recorded on Bruker HX–72, Bruker Aspect 2000, Tesla BS–487C, Perkin Elmer R12B instruments with Me_4Si as internal standard. ^{31}P NMR spectra were measured with Jeol JNM-FX60 spectrometer with 85% H_3PO_4 as external standard. The preparation of *trans*-2-methoxy-1,3,2-dioxaphosphorinane (**12**) has been described.[24]

0,0-Di(2,2-dimethylpropyl)-S-trimethylsilylphosphorodithioate (**11**) was prepared in the reaction of (2,2-dimethylpropyl)phosphorodithioic acid (**1b**) with hexamethyldisilazane in the presence of catalytic amounts of imidazole. B.p. 78°C/0.01 Torr, yield 95%, ^{31}P NMR 86.2 (neat) (Found: C, 45.32; H, 8.94; P, 9.18; Calc. for $C_{13}H_{31}O_2PS_2Si$: C, 45.61; H, 9.04; P, 9.06).

Dimethoxythioxaphosphoranesulfenyl bromide (**5a**)

To a soln of **2a** (31.5 g; 0.1 mol) in 80 ml $CHCl_3$ was added dropwise with stirring at −80°C a soln of dry bromine (16.07 g; 0.1 mol) in 10 ml of $CHCl_3$. The stirring was continued for the next 20 min. The solvent was removed in vacuo (5 mmHg, temp. −5°C) and 46.8 g (84.3%) of **5a** was obtained ^{31}P NMR 79.9 ($CHCl_3$). The addition of 2.37 g (0.01 mol) of the crude **5a** to 0.85 g (0.0103 mol) cyclohexene in 15 ml CH_2Cl_2 gave 2.8 g (88%) 1-bromo-2-(S-dimethoxythiophosphoro)cyclohexane. ^{31}P NMR 92.3 ($CHCl_3$); b.p. 110°/0.01 Torr (Found: C, 29.60; H, 5.36; Br, 24.56; P, 10.30; S, 21.00; Calc. for $C_8H_{16}BrO_2PS_2$: C, 30.10; H, 5.01; Br, 25.04; P, 9.72; S, 20.10).

Dineopentoxythioxaphosphoranesulfenyl bromide (**5b**)

Bromine (16.0 g, 0.1 mol) in 50 ml of CCl_4 was added over 1 hr to a stirred soln. of **11** (34.2 g, 0.1 mol) in 100 ml of dry CCl_4 at −35°C. The solvent and trimethylbromosilane were removed at temp. 0–5°C under pressure of 2 Torr and **5b** was obtained as an oily, yellowish liquid. Yield 34.0 g (97%); ^{31}P NMR 74.4 (CH_2Cl_2) (Found: C, 33.80; H, 6.50; P, 9.00; S, 18.92; Calc. for $C_{10}H_{22}BrO_2PS_2$: C, 34.38; H, 6.34; S, 18.35).

Diisopropoxythioxaphosphoranesulfenyl bromide (**5c**)

Bromine (7.94 g, 0.05 mol) in 10 ml CH_2Cl_2 was added dropwise to a stirred soln. of disulfide **2c** (21.32 g, 0.05 mol) at −15°C. The stirring was continued for the next 20 min. The solvent was distilled off at 5°C under pressure of 2 Torr and **5c** was obtained as an oily liquid. Yield 13.9 (98%); ^{31}P NMR (CH_2Cl_2) 70.0 (Found: C, 24.11; H, 4.65; P, 11.02; Calc. for $C_6H_{14}BrO_2PS_2$: C, 24.57; H, 4.78; P, 10.58).

Diphenoxythioxaphosphoranesulfenyl bromide (**5d**)

To a stirred solution of acid **1d** (11.3 g; 0.04 mol) in a mixture of 15 ml of C_6H_6 and 20 ml of CH_2Cl_2 bromine (6.4 g; 0.04 mol) was added dropwise with stirring

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at −10°C. The stirring was continued for 20 min. The solvents were removed under pressure of 5 Torr at 0°C. The bromide **5d** (14.4 g) was obtained as a yellow, oily liquid. It solidified at −20°C. ^{31}P NMR 69.8 (CCl_4) (Found: C, 40.01; H, 2.60; P, 8.95; Calc. for $C_{12}H_{10}BrO_2PS_2$: C, 39.87; H, 2.80; P, 8.57).

The thermal decomposition of **5c**

A sample of diisopropoxythioxaphosphoranesulfenyl bromide in NMR tube was warmed to 40°C and the reaction was followed by ^{31}P NMR. After 40 min. the presence of only one product diisopropyl thiophosphorobromidate (**6c**) was detected. ^{31}P NMR 50.0 (CH_2Cl_2).

The reaction of **5b** *with piperidine*

A soln. of anhydrous piperidine (3.4 g, 0.04 mol) in 15 ml of CH_2Cl_2 was added dropwise at −10°C to a stirred soln. of **5b** (7.0 g, 0.02 mol) in 40 ml of CH_2Cl_2. The stirring was continued for the next 20 min. at 0–5°C. The hydrobromide was filtered off and solvent was removed in vacuo. The crude **8** was purified by crystallisation. Needles m.p. 67°C (EtOH), yield 3.1 g (88%); ^{31}P NMR 96.0 (C_6H_6) (Found: C, 51.20; H, 9.01; N, 4.01; P, 8.90; S, 18.02; Calc. for $C_{15}H_{32}NO_2PS_2$: C, 51.01; H, 9.06; N, 3.96; P, 8.77; S, 18.12).

The bromination of **5b**

Bromine (3.99 g; 0.025 mol) in 15 ml of CH_2Cl_2 was added at −5°C to a stirred soln. of **5b** (8.73 g; 0.025 mol) in 30 ml of CH_2Cl_2. The stirring was continued for the next 15 min. at temp. 0°C. After that time in the ^{31}P NMR spectrum the presence of signal characteristic only for dineopentyl thiophosphorobromidate (**6b**) was observed. The product was isolated from the reaction mixture by distillation, b.p. 64°C/0.01 Torr, yield 7.53 g (95%); ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 18H, $(CH_3)_3C-$), 3.28 (dd, 4H, —CH_2O—); ^{31}P NMR 51.1 (CH_2Cl_2) (Found: C, 38.11; H, 7.10; P, 9.96; Br, 25.58; S, 10.50; Calc. for $C_{10}H_{22}BrO_2PS$: C, 37.85; H, 6.94; P, 9.78; Br, 25.20; S, 10.10).

The reaction of trimethylsilyl cyanide with **5b**

A soln. of trimethylsilyl cyanide (3.47 g; 0.035 mol) in 10 ml of CH_2Cl_2 was added at 0°C to a stirred, freshly prepared soln. of **5b** (10.5 g, 0.03 mol) in 30 ml of dry CH_2Cl_2. The stirring was continued until the yellow colour had disappeared. The solvent and trimethylbromosilane were removed at 0–5°C under pressure of 1 Torr and the residual product was identified as 0,0-dineopentylthiophosphorothiocyanidate (**10**). Yield 8.41 g (95%), ^{31}P NMR 75.0; IR (CH_2Cl_2): ν_{SCN} 2185, $\nu_{P=S}$ 680. The distillation of **10** in vacuo gave the rearranged product 0,0-dineopentylthiophosphoroisothiocyanidate, b.p. 82.83°C/0.18 Torr, ^{31}P NMR 68.5 (CH_2Cl_2), IR (neat): ν_{NCS} 1980; $\nu_{P=S}$ 695 (lit.[26] b.p. 84–85°C/0.2 Torr; ^{31}P NMR (neat) 69.0).

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The reaction of **5b** *with 0,0-dineopentyl-S-trimethylsilylphosphoro-dithioate* (**11**)

A soln. of **5b** (10.5 g, 0.03 mol) in a 10 ml of CH_2Cl_2 was added to a stirred soln. of **11** (5.13 g, 0.015 mol) in 30 ml of CH_2Cl_2 at −15°C. The solvent was removed at 5°C under pressure of 5 Torr. The sirupy residue was purified by crystallisation to give **2b** 7.8 g (96%), m.p. 71–73°C (hexane); ^{31}P NMR 88.3 (CH_2Cl_2) (Found: C, 44.35; H, 8.15; P, 11.25; S, 22.9; Calc. for $C_{20}H_{44}O_4P_2S_2$: C, 44.58; H, 8.23; P, 11.49; S, 23.80).

The reaction of **5b** *with trans-2-methoxy-1,3,2-dioxaphosphorinane* (**12**)

A soln. of **5b** (7.0 g; 0.02 mol) in 15 ml of hexane was added at −10°C to a vigorously stirred soln. of trans-**12** (3.08 g; 0.02 mol) in 20 ml of hexane. The stirring was continued for the next 15 min. at 0°C. After that time in the ^{31}P NMR spectrum of the reaction mixture the following signals were observed: *cis*-2-bromo-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (**14**) ^{31}P NMR 19.0, yield 36% (lit.[26] *cis*-**14**, ^{31}P δ 19.0); *cis*-2-S-(dineopentylthiophosphoro)-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (**13**)[27] ^{31}P NMR 5.63 (P=O), 77.19 (P=S), yield 28%; 0,0-dineopentyl-S-methylphosphorodithioate **15** ^{31}P NMR 94.1, yield 36%. The ester **15** is identical with the product of the alkylation of triethylammonium 0,0-dineopentyldithioate with CH_3I, b.p. 88–90°C/0.015 Torr (Found: C, 46.38; H, 8.75; P, 10.45; Calc. for $C_{11}H_{25}O_2PS_2$: C, 46.45; H, 8.85; P, 10.88).

The reaction of sulfenyl bromides **5** *with alcohols*

General procedure: to a vigorously stirred soln. of **5** (0.03 mol) in 40 ml of petroleum ether, the corresponding alcohol (0.03 mol) and dry 2,6-lutidine (0.03 mol) was added dropwise at temp. −10°C to 5°C. The hydrobromide was filtered off in the closed system and sulfenyl esters **16** were isolated by distillation.

Dimethoxythioxaphosphorane methylsulfenate (**16a**)

B.p. 78°C/0.03 Torr; yield 68%, ^{31}P NMR 91.1 (Found: C, 19.7; H, 4.9; P, 16.45; Calc. for $C_3H_9O_3PS_2$: C, 19.14; H, 4.82; P, 16.45).

Diisopropoxythioxaphosphorane methylsulfenate (**16c**)

B.p. 65°C/0.01 Torr; yield 78%; ^{31}P NMR 86.6 (Found: C, 34.12; H, 7.30; P, 18.9; Calc. for $C_7H_{17}O_3PS_2$:C, 34.41; H, 7.01; P, 19.64).

Dineopentylthioxaphosphorane 2,2-dimethylpropylsulfenate (**16b**)

B.p. 70–72°C/0.01 Torr; Yield 90%; ^{31}P NMR 92.1: ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 18H, $(CH_3)_3C$-) δ 3.98 (m, 4H, —CH_2O—) (Found: C, 50.24; H, 9.09; P, 8.61; Calc. for $C_{15}H_{33}O_3PS_2$: C, 50.56; H, 9.2; P, 8.7).

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The reaction of sulfenyl bromide **5b** *with 2,2-dimethylpropanol in the presence of triethylamine*

The mixture of 2,2-dimethylpropanol (0.88 g; 0.01 mol) and triethylamine (1.01 g, 0.01 mol) in 10 ml of hexane was added to a stirred soln. of **5b** (3.5 g, 0.01 mol) in 20 ml of hexane at −5°C. The stirring was continued at 0°C for the next 15 min. and the following organophosphorus compounds were identified from the ^{31}P NMR spectra recorded immediately after; yields were estimated from the integration: the sulfenate **16b**, δ 91.8 (60%); disulfide **2b,** δ 84.5 (20%) and 15% of dineopentyl thiophosphorobromidate (**6b**) δ 51.1.

The reaction of sulfenyl esters **16a–c** *with trimethylchlorosilane*

General procedure: a stirred solution of crude, freshly prepared sulfenate **16a–c** (0.01–0.05 mol) in 20–50 ml of dry petroleum ether, b.p. (20–40°C) or hexane was treated at −20°C with 0.012 − 0.053 mol of trimethylchlorosilane. The stirring was continued for 1–2 hr, solvent and the corresponding trimethylsilyl alkyl ether were removed under pressure of 0.01 ÷ 1 Torr at temp. 0–5°C leaving the crude sulfenyl chloride **4**.

Dimethoxythiooxaphosphoranesulfenyl chloride (**4a**)

Yellow oily liquid; yield 90%; ^{31}P NMR 84.3 (CH_2Cl_2) (Found: C, 13.50; H, 3.25; P, 16.70; Calc. for $C_2H_6ClPS_2$: C, 12.47; H, 3.13; P, 16.08).

Diisopropoxythioxaphosphoranesulenyl chloride (**4c**)

Yellow oily liquid; yield 87%; ^{31}P NMR 75.0 (CH_2Cl_2). 1-(S-diisopropylthiophosphoro)-2-chlorocyclohexane was obtained in 90% yield in the addition reaction of the crude **4c** to cyclohexene. B.p. 95–97°C/0.01 Torr; ^{31}P NMR 89.2 (CH_2Cl_2) (Found: C, 43.2; H, 7.18; P, 9.42; Calc. for $C_{12}H_{24}ClO_2PS_2$: C, 43.56; H, 7.31; P, 9.36).

Dineopentoxythioxaphosphoranesulfenyl chloride (**4b**)

Yellow oily liquid which solidified at 0°C; yield 90%; ^{31}P NMR 79.5 (CH_2Cl_2). The crude **4b** was reacted with piperidine to give sulfenamide **8,** m.p. 65–67°C; ^{31}P NMR 95.8 (CH_2Cl_2) in 86% yield.

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