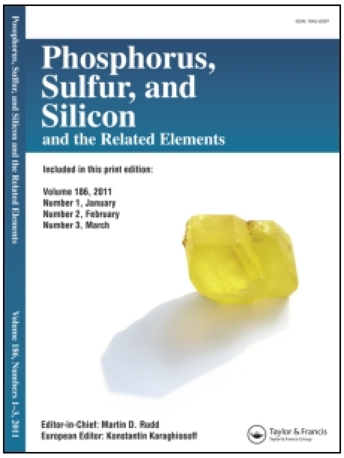

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CHLORINATION REACTIONS OF PHOSPHORUS THIONOESTERS > P(S)OSiMe$_3$; GENERAL SYNTHESIS OF COMPOUNDS CONTAINING > P(O)SCl FUNCTIONAL GROUP

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CHLORINATION REACTIONS OF PHOSPHORUS THIONOESTERS >P(S)OSiMe₃; GENERAL SYNTHESIS OF COMPOUNDS CONTAINING >P(O)SCl FUNCTIONAL GROUP

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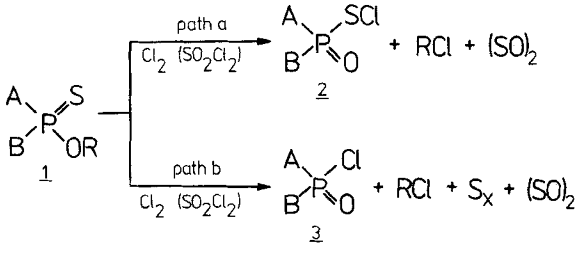
Efficient, general synthesis of oxophosphoranesulphenyl chlorides ABP(O)SCl **2** based on the reaction of phosphorus trimethylsilylthionoesters ABP(S)OSiMe$_3$ **7** with chlorinating agents is described.

Oxophosphoranesulphenyl chlorides **2** play an important role in synthetic, mechanistic, and stereochemical studies of organophosphorus compounds. They serve mainly as excellent electrophilic thiophosphorylating agents.[1] For example, **2** offer a unique possibility for the synthesis of compounds containing phosphorus-sulphur-phosphorus bridge.[2]

The methods of the synthesis of oxophosphoranesulphenyl chlorides have been extensively studied in our laboratory.[3] It has been found that the reactions of acyclic and cyclic 6-membered trialkylphosphorothionates **1a**, AB(RO)PS, A = B = RO with elemental chloride, or sulphuryl chloride provide the best method for preparation of dialkoxyoxophosphoranesulphenyl chlorides ABP(O)SCl **2**, A = B = RO (path a, Scheme I). However, this approach is unsatisfactory for the synthesis of structural analogues of **2** containing one or two direct phosphorus-carbon bonds. In contrast to **1a**, phosphorus thionoesters AB(RO)P = S **1b**, A = RO, B = R,Ar and AB(RO)PS **1c**, A = B = R,Ar, as well as other types of thionoesters **1** are chlorinated with release of alkyl chloride and elemental sulphur, and the formation of the corresponding chloridates **3** (path b, Scheme I). Cases in which both paths a and b are followed were also encountered.



SCHEME I

The mechanism of this complex chlorination process has been elucidated by low-temperature ^{31}P NMR studies.[4] It has been shown that the key intermediates

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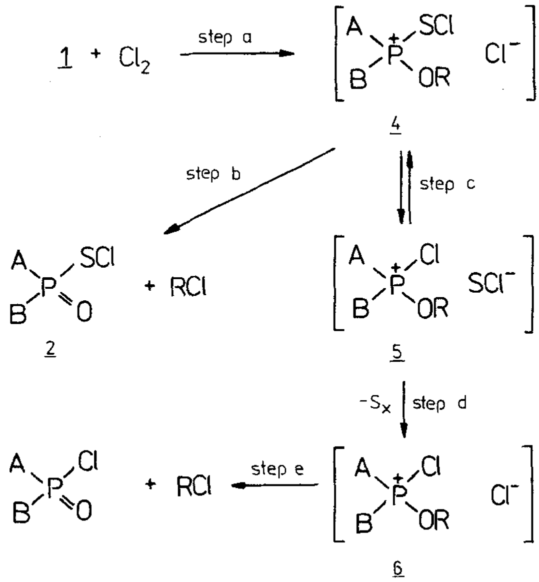
Dedicated to Prof. M. I. Kabachnik on occasion of his 80th birthday.

in all reactions of phosphorus thionoesters **1** are the phosphonium salts **4** (step a, Scheme II). These salts are transformed either by dealkylation into the sulphenyl chlorides **2** (step b), or by the ligand exchange via the salts **5** and **6** (step c, d) followed by the dealkylation of the latter into the chloridates **3** (step e). When suitable substituents induce high reactivity at the phosphorus centre, ligand exchange takes place. No competition between ligand exchange and dealkylation reaction in phosphonium salts **4** is observed when three alkoxy groups, or ligands causing steric hindrance are present.

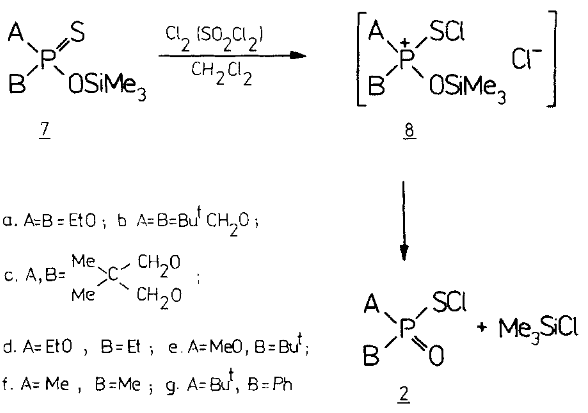


SCHEME II

In our recent investigations, we have found that dialkyltrimethylsilylphosphorothionates AB(Me$_3$SiO)PS **7a,b,c**, A = B = RO as well as trimethylsilyl esters **7d,e** and **7f,g** with one or two direct phosphorus-carbon bond respectively undergo very clean reaction with elemental chlorine, or sulphuryl chloride leading exclusively to the corresponding oxophosphoranesulphenyl chlorides. In the light of our previous work,[4] the above reactions proceed via phosphonium salts **8**, which are in turn selectively desilylated by the chloride anion. Therefore, in this case, desilylation occurs much faster than the ligand exchange at phosphorus in the phosphonium salts **8**.

The reaction between **7** and chlorinating agents can be recommended as the method of choice for the preparation of oxophosphoranesulphenyl chlorides **2** containing A,B = RO; A = R,Ph; B = RO; A,B = R and A = R, B = Ph. All sulphenyl chlorides **2** are prepared in quantitative yield and have NMR spectra consistent with the assigned structures.

The starting phosphorus thionoesters AB(Me$_3$SiO)PS **7** are readily available by the addition of elemental sulphur to the corresponding tricoordinate phosphorus esters, or by silylation of the corresponding salts of monothioacids. Thionesters **7**



SCHEME III

react readily with chlorinating agents at −20°C in methylene chloride solution. After the removal of solvent and trimethylsilyl chloride in vacuo at 0°C the sulphenyl chlorides **2** are of high purity and can be used directly for further transformation.

EXPERIMENTAL

Solvent and reagents were purified and dried by conventional methods. ^{31}P NMR spectra were recorded on a JEOL C-60 JNM-FX 60 TF Spectrometer operating at 24.3 MHz. Positive chemical shift values (ppm) were reported for compounds absorbing at lower field than 85% H_3PO_4. The purity of products were determined from the integrated ^{31}P NMR spectra.

I. *Materials*

0,0,0-dialkyltrimethylsilylphosphorothionates 2-trimethyl-silyloxy-2-thiono-5,5-dimethyl-2,3,2-dioxaphosphorinan, 0,0-alkyltrimethylsilyl alkylphosphonothionates and 0-trimethylsilyl dialkylphosphinothionates were obtained by the silylation of the corresponding salts of monothioacids,[5] or by addition of elemental sulphur to the corresponding tricoordinate phosphorus compounds.[6]

II. *Chlorination of Thionoesters* 7

A. *With sulphuryl chloride. General procedure*

Freshly distilled sulphuryl chloride (0.015 mol) was added dropwise with stirring to a solution of the corresponding thionoester **7** (0.015 mol) in methylene chloride (25 ml). The temperature of the mixture was kept at −15 to −20°C. Stirring was continued at 0°C for 10 min. The solvent and trimethylsilyl chloride were evaporated off in vacuo below 5°C. The crude product (100% yield) was examined by ^{31}P NMR spectroscopy.

B. *With chlorine*

The same procedure performed with **7** and a solution of chlorine in CH_2Cl_2 yields **2** (100% yield).

^{31}P NMR chemical shifts, δ ppm of sulphenyl chlorides **2** prepared from **7**

2a	2b	2c	2d	2e	2f	2g
+19.0	+18.8	+10.0	+61.7	+64.0	+69.7	+69.5

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