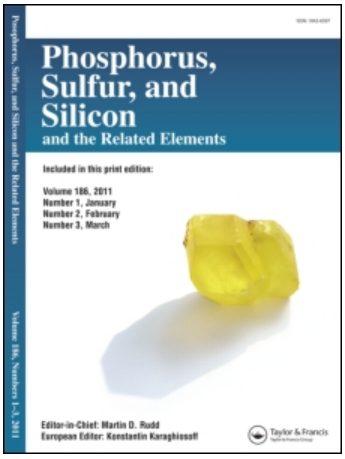

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REACTIONS OF COMPOUNDS OF PHOSPHORUS HAVING POSITIVELY POLARIZED DIVALENT SULFUR WITH DISILATHIANES. SYNTHETIC AND MECHANISTIC ASPECTS

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REACTIONS OF COMPOUNDS OF PHOSPHORUS HAVING POSITIVELY POLARIZED DIVALENT SULFUR WITH DISILATHIANES. SYNTHETIC AND MECHANISTIC ASPECTS

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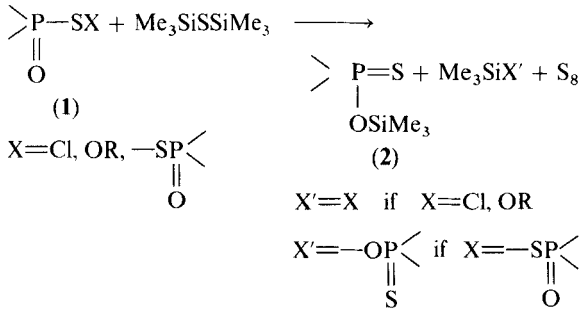
(*Received July 9, 1979*)

Reactions of hexamethyldisilathiane with oxophosphoranesulfenyl chlorides, oxophosphorane sulfenates and *bis*-phosphoranyldisulfides were studied. These processes lead to mono *o*-silyl thionesters of phosphorus. The mechanistic pathways are discussed.

Silylthioethers have interesting chemical properties making them useful as reagents in synthesis. It is now well recognized that silyalkyl and disilyl thioethers are very reactive towards some nucleophiles, mainly due to a high polarizability of the silicon-sulfur bond. They react particularly easily with oxygen nucleophiles like water and alcohol, which readily cleave the silicon-sulfur bond[1,2,3] and this reaction has been exploited in synthesis.[4,5] Silylthioethers are able to undergo addition to polarized double bonds[6,7] which can be also attributed to the high polarizability of Si—C bond. Silylthioethers are particularly prone to react with reagents having a soft electrophilic centre like a positively polarized divalent sulfur bound to a hard silicophilic atom like halogen or oxygen. A good example is the reaction between sulfenyl chlorides and silylakyl/aryl/thioethers, which led to disulfides[8] and was successfully used in synthesis of various unsymmetrical dialkyl/aryl/disulfides.[9]

Looking for general methods of synthesis of silyl derivatives of thioesters of phosphorus we found that Si—S bond in hexaalkyldisilathianes as well as hexaaryldisilathianes is cleaved under mild conditions by reagents of general formula $>P(=O)-\overset{\delta+}{S}-\overset{\delta-}{X}$ where X is halogen, alkoxide or eventually a phosphorothio group $-S-P(=O)<$. Though mechanisms of these reactions are complex, they lead to the formation of the same phosphorus containing product—O-silyl thionoester of phosphorus according to the following general scheme:



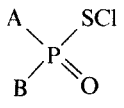
SCHEME 1

The reaction of phosphorosulfenyl chloride gives (**2**) with high yield. Since thionoesters of phosphorus are readily chlorinated to corresponding oxophosphoranesulfenyl chloride[10] the above reaction can be conveniently used as a preparative way to O-monosilyl substituted derivatives of these esters, which due to the possibility of selective removal of the silyl group are precursors of corresponding acids of phosphorus.

Mechanistic aspects of these processes seem to be interesting as well, because of the involvement of phosphoro and silyl polysulfides as intermediates. These intermediates can be observed experimentally.

RESULTS AND DISCUSSION

The reaction of various oxophosphoranesulfenyl chlorides of general formula (**3**) with hexamethyldisilathiane and hexaethyldisilathiane has been studied.



(**3**)

3a A = B = EtO
3b A = B = *t*-BuCH$_2$O
3c A = EtO, B = Et
3d A = MeO, B = *t*-Bu

The reaction is in most cases violent and highly exothermic if carried out at ambient temperature. When at least the stoichieometric amount of the disilathiane is used, the process leads to almost a hundred percent yield of mono O-silyl substituted ester of phosphorus. The excess of the silathiane is not able to substitute more than one alkyl ester group. The mechanism of this reaction must include several consecutive steps and when a sulfenyl chloride of structure (**3**) is used, two stages can be studied separately. The first stage involves reactions of sulfenyl chlorides which go much faster then the processes taking place at the second stage.

The First Stage—the Formation of Diphosphoranylpolysulfides

Neither the formation of silylated thionester nor the precipitation of sulfur was observed when half of the stoichieometric amount of the hexamethyldisilathiane was used. However, both substrates disappeared immediately in temperature as low as −70°C as shown by ^{31}P NMR spectrum. This corresponds to the situation for stoichieometric amounts of the substrates in which only half of the initial amounts of disilathiane is consumed at the moment when all the sulfenyl chloride is converted. The ^{31}P NMR spectrum of the reaction system revealed that the process at this stage almost exclusively leads to the formation of bisphosphoranylpolysulfides (scheme 2). The spectrum showed several new signals, all of them at about

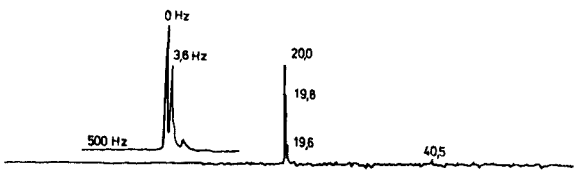
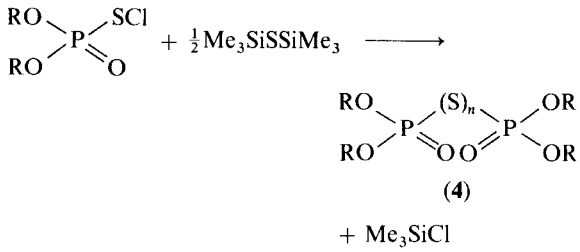


FIGURE 1 ^{31}P NMR spectrum of the polysulfides.

+20 ppm, which were attributed to the polysulfide (see Figure 1) on the known ^{31}P NMR characteristics of phosphoranyldisulfides.



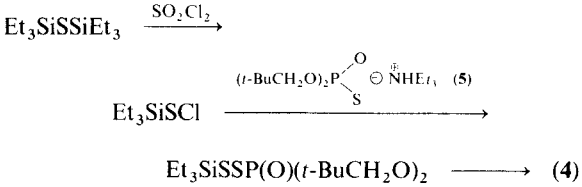
(**4**)

+ Me_3SiCl

SCHEME 2

Mass spectrum of these polysulfides proved the presence of compounds (**4**) with n = 2,3,4,5.

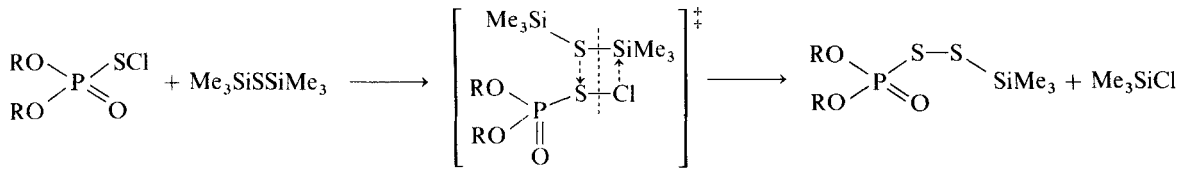
Presumably due to steric effect hexaethyldisilathiane reacts slower when the reaction is carried out at a sufficiently low temperature (−50°C) and another ^{31}P NMR signal appears at about 23 ppm (Figure 2). At first, the signal grows and then as the reaction proceeds it gradually declines. This should be attributed to a transient product. Additional experiments were carried out to identify this intermediate. First, hexaethyldisilathiane was converted to triethylsilylsulfenyl chloride according to[11] and then subjected to reaction with triethylammonium phosphorothioate (**5**), which was believed to occur according to Scheme 3 giving the same products and the same intermediate as the Reaction 2.



(**6**)

SCHEME 3

The thioate was introduced to the product of chlorination of hexathyldisilathiane at a temperature below −50° and ^{31}P NMR spectrum was monitored immediately at this temperature. The main products were (**4**) signals 19–20 ppm and again a small signal at 22–23 ppm was observed which disappeared after rising of the temperature (Figure 3). Therefore, this signal could be attributed to unsymmetrical disulfide (**6**) (eventually polysulfides of this type). Fast reactions of these intermediates involving also sulfenyl chlorides lead finally to (**4**).

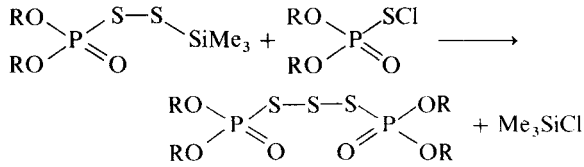


SCHEME 4

The position of the signal points to deshielding of phosphorus nucleus coming from the symmetrical to the unsymmetrical disulfide what is rather unexpected. A possible interaction of phosphoryl oxygen group with silicon atom could account for this effect.

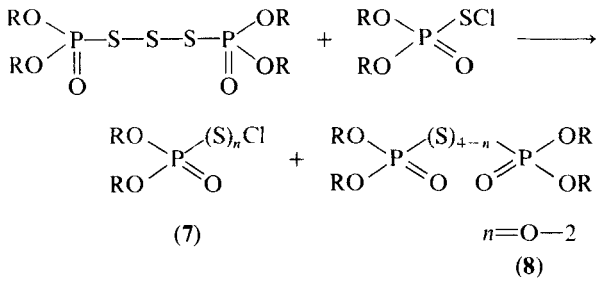
In the light of the above results the most probable route of the reaction of phosphorosulfenyl chloride with disilathiane seems to be one involving the nucleophilic attack of the disilathiane at the positively polarized sulfur atom of the sulfenyl chloride assisted by the attack of the chloride on silicon according to the Scheme 4.

Mixed phosphoro-silyl-disulfide transient product having electron donating silyl group and electron withdrawing phosphoryl group must be unstable and is expected to be involved in fast reaction with the sulfenyl chloride giving symmetrical diphosphorotrisulfide and trimethylchlorosilane (Scheme 5).



SCHEME 5

The diphosphorotrisulfide is expected to react with the sulfenyl chloride according to the Scheme 6:



SCHEME 6

Polysulfenyl chlorides (**7**) as well as the polysulfide (**8**) may enter into an analogous sequence of reactions to 4–6 giving symmetrical polysulfides with various numbers of sulfur atoms and trimethylchlorosilane.

Unsymmetrical polysulfides may also undergo symmetrization and symmetrical ones may undergo chain rearrangements, however, these processes which are important at the second stage, perhaps proceed too slowly to compete with processes 4–6 which are believed to dominate the reaction

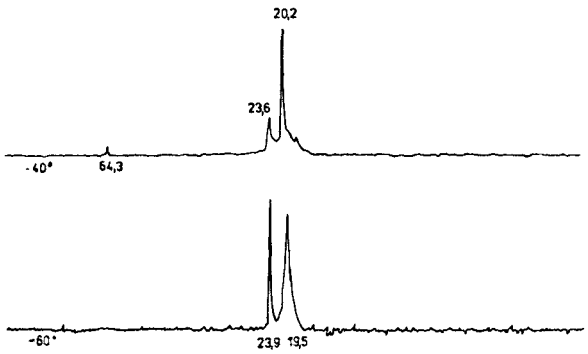


FIGURE 2 ^{31}P NMR spectrum of the products obtained in the reaction of the sulfenyl chloride with hexaethyldisilathiane.

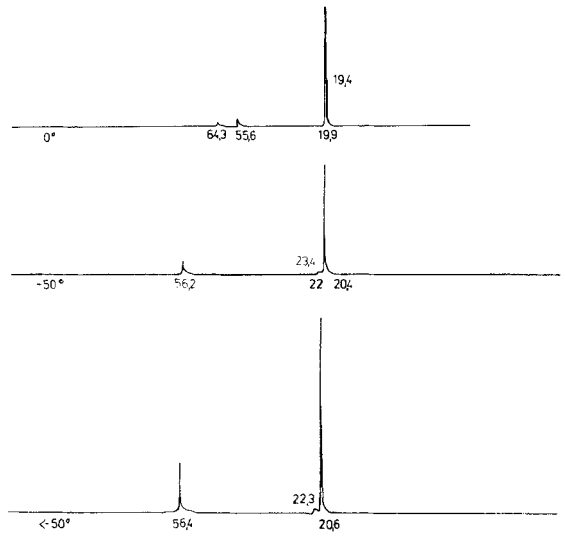
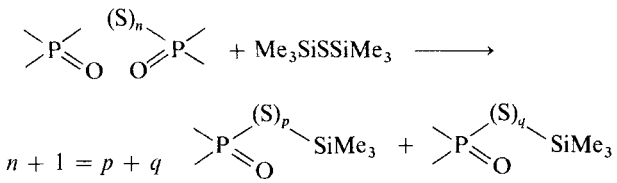


FIGURE 3 Identification of intermediate products.

pattern as long as sulfenyl chlorides are present in the system.

The Second Stage

The second stage occurs at a lower rate when all sulfenyl chlorides are consumed. Remaining disilathiane reacts with diphosphoropolysulfides according to the Scheme 7.



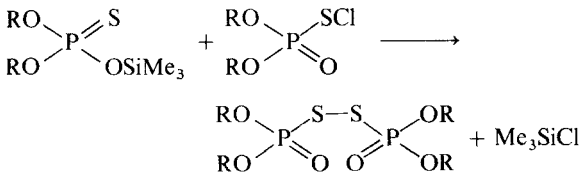
SCHEME 7

The intermediate having p or $q = 1$ undergoes isomerization giving the stable product O,O dialkyl-O-silylphosphorothioate[12] (Scheme 8).

(9)

SCHEME 8

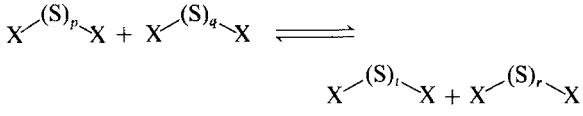
The thioate cannot be formed in the presence of a sulfenyl chloride because disulfide is immediately formed[13] (Scheme 9).



SCHEME 9

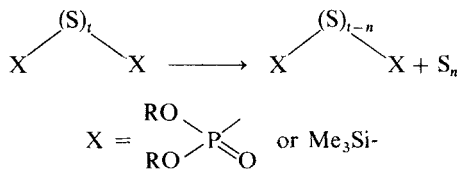
This may also be the reason why the thioate is not formed at the first stage of the reaction and can explain why the use of the excess of the sulfenyl chloride cannot lead to the introduction of more than one silyl group to the ester.

Various processes of rearrangement of the polysulfides represented by general Scheme 10 lead to elongation and shortening of the polysulfide chain and may lead to intermediates having sulfur chain long enough to produce cyclic sulfur oligomers (Scheme 11).



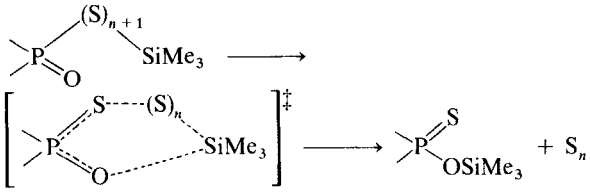
$p + q = t + r$

SCHEME 10



SCHEME 11

This product may be also formed synchronously with desulfuration (Scheme 12).



SCHEME 12

The second stage was studied separately. As a model the reaction of hexamethylsilathiane with *bis*-(diethoxyphosphinyl) disulfide was used. This investigation fully confirmed the above mechanism. The same polysulfide intermediates were detected by ^{31}P NMR and the reaction gave the thionate product with a hundred percent yield.

Acccording to the mechanism of the reaction between disilathiane and phosphorosulfenyl chloride postulated here, there is no cleavage or formation of a bond of phosphorus with its ligand. Consequently the reaction should not change the configuration at the phosphorus atom. This was demonstrated in a series of experiments including following the stereochemical cycle starting from both optical isomers of O-methyl *t*-butyl phosphonothioic acid, one after another (Figure 4). All reactions including the studied process occurred with full retention of the configuration at phosphorus giving support to the mechanism.

The analogous reaction of dialkylthio-oxophosphorane sulfenates[14] in principle, proceeds according to the same mechanism involving two stages. However, they are more complex because desulfuration of the esters competes with the formation of O-silyl thionoesters of phosphorus,

TABLE I

^{31}P NMR chemical shifts of products[a]

	A	B	R	A, B P—SCl (O) (3)	A, B P—SOR (O) (10)	A, B P=S (OSiMe$_3$) (2)
a	EtO	EtO	Et	18.2	23.7	55.5
b	*t*-BuCH$_2$O	*t*-BuCH$_2$O	Me	18.3	24.0	56.5
c	EtO	Et	Me	59.9	56.7	87.5
d	MeO	*t*-Bu	Et	62.5	64.7	97.7

[a] In ppm from H_3PO_4, 85%.

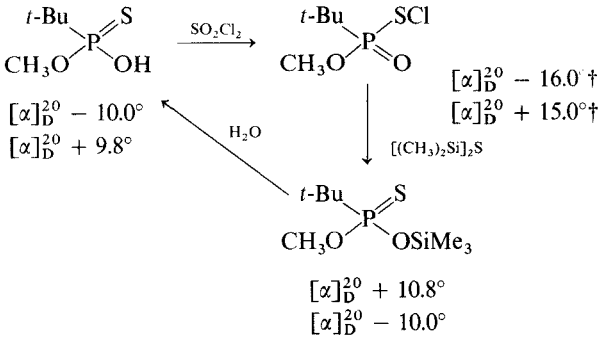
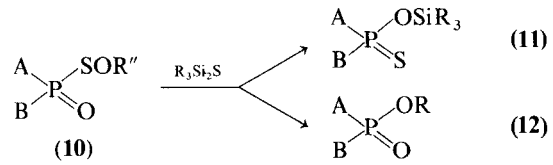


FIGURE 4

thus the process proceeds according to the Scheme 13:



SCHEME 13

The larger the stability of the used oxophosphorane sulfenate, the larger the yield of the thioester (**11**). There were observed molar contribution of product (**11**) in reaction of the sulfenate with hexamethyldisilathiane in methylene chloride at room temperature: (*t*-BuCH$_2$O)$_2$P(O)SOMe 100, (MeO) *t*-BuP(O)SOEt 75, (EtO)$_2$P(O)SOMe 37.5, (EtO) EtP(O)SOMe 25.

Reactions of oxophosphorane sulfenates with *bis*-trialkylsilyl thioethers occur slower than corresponding reactions of the sulfenyl chlorides. This may be partially due to the fact that the reaction of sulfenyl chloride is catalysed by small amounts of acid coming from hydrolysis of silyl or sulfenyl chloride with traces of water present in the system. In fact the addition of trifluoroacetic acid was found to accelerate considerably the reaction of sulfenate and also an increase of the yield of the O-silyl-thionoester of phosphorus was observed.

† Neat.

EXPERIMENTAL

Boiling points are uncorrected. Solvents were purified by conventional methods. Phosphorus NMR spectra were recorded at FX 60 Fourier transform spectrometers at 24.3 MHz with 85% phosphoric acid as external standard. Optical activity in benzene measurements were made with a Perkin-Elmer 241 MC photopolarimeter sensitivity ±0.002°.

O,O-dineopentyl-oxophosphorane sulfenyl chloride [10b] and O-methyl *t*-butyl oxophosphorane sulfenyl chloride[10c] being stable and easy for purification were convenient model sulfenyl chloride reagents in this study.

The chemical shifts ^{31}P NMR of all new compounds are presented in the table.

O-Methyl t-Butyloxophosphoranesulfenyl Chloride (**1d**)

The solution of sulfuryl chloride (0.01 mole, 1.35 g) in dichloromethane was added dropwise at 0–5° to ice-cooled, well-stirred solution of O-methyl *t*-butylphosphonothioic acid (0.01 mole, 1.7 g) in dichloromethane (10 ml). Then the mixture was allowed to warm up to room temperature. The solvent was removed under reduced pressure and a crude product was distilled to give 1.65 g (81.7%) of yellow liquid, bp 38°/0.1 mm. Other oxophosphoranesulfenyl chlorides were obtained according to this method.

O-Methyl t-Butyl O-Silylphosphonotioate (**2d**)

i) The solution of hexamethyldisilathiane (0.01 mole, 1.78 g) in dichloromethane was added slowly at room temperature to solution of (**3d**) (0.01 mole, 2 g) in dichloromethane. During the addition of hexamethyldisilathiane an exothermic effect and

precipitation of sulfur were observed. After standing over night sulfur was removed by filtration. The solvent was evaporated and residue was distilled *in vacuo* to give 1.9 g (79.2%) of colourless liquid. The same results were obtained when the reaction was carried out at lower temperatures 0–5°. Optically active *O*-methyl *t*-butyl-*O*-silylphosphonothioate were obtained according to the same method.

ii) The solution of hexamethyldisilathiane (0.01 mole, 1.78 g) was added to solution of O-methyl *t*-butyl *bis*-phosphoryl disulfide (0.01 m, 3.34 g) in dichloromethane while stirring at room temperature. Precipitation of sulfur was observed. After standing over night sulfur was removed by filtration. The solvent was evaporated and residue was distilled *in vacuo* to give 3 g (62%) of colourless liquid, bp 34°/0.01 mm, n_D^{20} 1.4582.

iii) The solution of hexamethyldisilathiane (0.01 mole, 1.78 g) was added to solution of (**10d**) (0.01 mole, 2.12 g) in dichloromethane in room temperature. Precipitation of sulfur was observed. After standing over night sulfur was removed by filtration. Products of reaction were monitored in ^{31}P NMR.

The Reaction of (**3b**) *with Hexamethyldisilathiane in Ratio 2:1*

The solution of hexamethyldisilathiane (0.005 mole, 0.089 g) was added at room temperature to a solution of (**3b**) (0.001 mole, 0.288 g) in dichloromethane placed in an NMR tube ^{31}P spectrometer. The spectrum showed several signals at about +20 ppm which were attributed to diphosphoropolysulfides.

Identification of Intermediate Products

This reaction was monitored by ^{31}P NMR at low temperature. To the solution of hexaethyldisilathiane (0.001 mole, 0.262 g) in dichloromethane placed in an NMR tube was added at room temperature the solution of sulfenyl chloride (0.001 mole, 0.135 g).

Gradual appearance of the yellow colour was observed being evidence of the formation of sulfenyl chloride Et_3SiSCl. Then NMR tube was refrigerated to −90° and the solution of (**5**) in dichloromethane was added. This reaction mixture was placed in ^{31}P NMR probe at −50°.

Spectra were recorded while the temperature was slowly raised from −50° to 0°.

Hydrolysis of (**2d**)

The mixture H_2O-dioxan were added at 5–10° to solution of (**2d**) (1.9 g); $[\alpha]_D^{20}$ − 10.0° in benzene. After removal of the solvent the residue was distilled *in vacuo* to give 1.1 g (85%) O-methyl *t*-butylphosphonothioic acid $[\alpha]_D^{20}$ + 8.9° bp 50°/0.05 mm.

O-Methyl t-Butyloxophosphorane Sulfenate (**10d**)

The mixture of ethanol (0.92 g, 0.02 mole) and triethylamine (2 g, 0.02 mole) in benzene (10 ml) was added dropwise at 0–5° to a solution of (**3d**) (4 g, 0.02 mole) in benzene (20 ml). After the addition had been completed the mixture was stirred at 0–5° for another 30 min. and then allowed to warm up to room temperature. The triethylamine hydrochloride was filtered off and the precipitate was washed with benzene 2 × 5 ml. The solvent was removed under reduced pressure and the crude product was purified by distillation *in vacuo*. Distillation gives 3.15 g (76% yield) of colourless liquid; bp 38°/0.1 mm n_D^{20} 1.4692.

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