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SYNTHETIC AND MECHANISTIC ASPECTS OF THE REACTION OF TRIALKYLSILYL HALIDES WITH THIO AND SELENO ESTERS OF PHOSPHORUS

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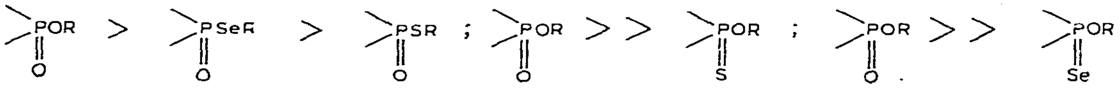
Summary

A study is described of the reaction of trimethylbromosilane and trimethyliodosilane with various esters of phosphorothioic and phosphoroselenoic acids of general structures $(RO)_2(RY)P{=}O$ (I) and $(RO)_3P{=}Y$ (II) (Y = S or Se, R = alkyl). The reaction results in replacement of the R groups by trimethylsilyl groups. No *S*-trimethylsilyl and *Se*-trimethylsilyl substituted esters were found among the products. Thus the displacement of the *O*-R group in II as well as the replacement of *S*-organyl or *Se*-organyl groups in I both lead to the corresponding *O*-trimethylsilyl isomer containing thiophosphoryl or selenophosphoryl groups. The following sequence of reactivity of the ester groups was observed:



$$>\underset{\overset{\|}{O}}{P}OR \;>\; >\underset{\overset{\|}{O}}{P}SeR \;>\; >\underset{\overset{\|}{O}}{P}SR \;;\quad >\underset{\overset{\|}{O}}{P}OR \;>>\; >\underset{\overset{\|}{S}}{P}OR \;;\quad >\underset{\overset{\|}{O}}{P}OR \;>>\; >\underset{\overset{\|}{Se}}{P}OR$$

The process involves initially the reversible formation of a phosphonium salt intermediate in a fast step, followed by slow dealkylation. It was shown by low temperature ^{31}P FT-NMR studies that in the reaction of trimethyliodosilane with an ester bearing a P=O phosphoryl group, the equilibrium for the phosphonium salt formation lies well over towards the intermediate and so the intermediate can be observed directly. These mechanistic proposals were confirmed by conductance studies on the reaction system and by investigation of the stereochemical course of the corresponding reaction of an optically-active model thiophosphonate.

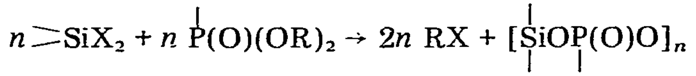
In some cases the reaction of the halosilanes with the phosphates takes a selective course which allows the reaction to be used as a convenient route to *O*-silyl substituted esters of phosphorothioic or phosphoroselenoic acids.

Introduction

O-Alkyl groups in esters of phosphorus oxy-acids can be replaced by trialkylsilyl groups by reaction with trialkylsilyl halides [1—10]. While the reaction with trialkylchlorosilane requires somewhat severe conditions [1—3], the reactions with bromosilane and iodosilane occur readily even at ambient temperature [1,4—7] and have been employed as a convenient method of removing *O*-alkyl groups from phosphorus esters in which advantage is taken of the ease of removal of the silyl group toward hydrolysis or alcoholysis [6—10].

$$>P(O)OR \xrightarrow[-RX]{R'_3SiX} >P(O)OSiR'_3 \xrightarrow{H_2O} >P(O)OH$$

The reactions of multifunctional halosilanes with alkylphosphates are also of interest as providing a method of synthesizing silicon- and phosphorus-containing copolymers [11—14].



$$n>SiX_2 + n\, \overset{|}{P}(O)(OR)_2 \rightarrow 2n\ RX + [\overset{|}{\underset{|}{Si}}O\overset{|}{\underset{|}{P}}(O)O]_n$$

These reactions have been rationalized in terms of nucleophilic attack by the phosphoryl oxygen, with transient formation of the phosphonium salt intermediate [3,4]. This route is supported by the isolation of tetrakis(trimethylsiloxy)phosphonium iodide from the reaction of trimethyl phosphate with an excess of trimethyliodosilane [4]. A synchronous one step mechanism involving a cyclic transition state has also been proposed [5], and also one involving nucleophilic attack by the P—O—R bridging oxygen on the silicon atom [14].

During studies of organo-thio and -seleno acids of phosphorus we have examined the reaction of trimethylbromosilane (**1a**) and trimethyliodosilane (**1b**) with thio and seleno esters of phosphorus of structures I and II (see Schemes 1 and 2). The aim of this paper is mainly to throw more light on the mechanism of the reaction of halosilane with esters of phosphorus. We thought it likely that a comparison of the reactivities in series of the thio and seleno phosphates in combination with low temperature ^{31}P NMR studies of unstable intermediates and also stereochemical and conductometric studies would give valuable information concerning this process. The other purpose was to examine the scope for the use of trialkylhalosilanes as reagents for the selective silylation of esters of thio- and seleno-acids of phosphorus.

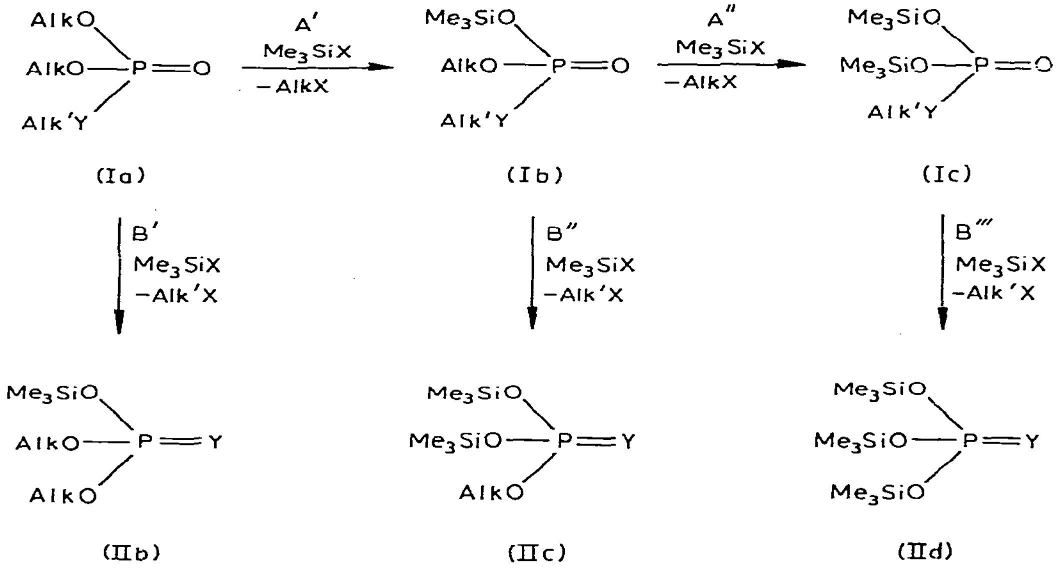
Results and discussion

1. General characteristic of the process

Reactions of thio and seleno esters of phosphorus of structures Ia and IIa with trimethylbromosilane (**1a**) and trimethyliodosilane (**1b**) were carried out in methylene chloride or in benzene and also in absence of solvent. The structures and proportions of products formed, as determined by ^{31}P NMR spectroscopy, are shown in Table 1. ^{31}P NMR assignments were confirmed with the aid of model compounds.

1.1. Silylation of the thiolates and selenolates. The reactions of phosphorothiolates and phosphoroselenolates of general structure Ia, Ib and Ic with trimethylbromosilane (**1a**) and trimethyliodosilane (**1b**) when carried out at low or ambient temperature can be represented by Scheme 1, which covers two types of reactions: A, replacement of an *O*-alkyl group by a trimethylsilyl group in thiolates or selenolates of structures Ia and Ib, and B, replacement of an *S*-alkyl or *Se*-alkyl group by the silyl group in thiolates or selenolates Ia, Ib and Ic followed by rearrangement to respective thionates or selenonates.

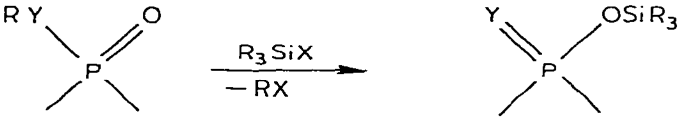
SCHEME 1



(X = Br, I ; Y = S, Se)

The reactivity of trialkyliodosilanes is much higher than that of the corresponding trialkylbromosilanes. While the introduction of trimethylsilyl in place of *O*-methyl or *O*-ethyl groups in the thiolates or selenolates takes usually several hours at room temperature when **1a** is used, whereas the analogous reaction with **1b** proceeds rapidly even at —30 to —20° C, and it usually proceeds violently at ambient temperature. This silicon—halogen bond cleavage is involved in an initial step of the process.

The reactivity of analogous compounds in the silylation involving the substitution of the alkyl group at oxygen, sulphur and selenium decreases in the sequence Y = O > Se > S in the general scheme:



Thiolates react more selectively than selenolates. Dealkylation involving *O*-alkyl bond cleavage occurs much more readily than that involving *S*-alkyl bond cleavage. Consequently the reaction of the thiolates follows the route A',

TABLE 1

YIELDS OF PRODUCTS OF REACTIONS OF TRIMETHYLBROMOSILANE AND TRIMETHYLIODOSILANE WITH MODEL THIO AND SELENO PHOSPHATES; YIELDS WERE DETERMINED BY ^{31}P NMR SPECTROSCOPY AND ARE GIVEN IN MOL %

Nb	Ester substrate	Silane substrate	Conditions [a]	Silane to ester molar ratio	Unreacted substrate Ia (IIa)	Products					Other products
						Ib	Ic	IIb	IIc	IId	
1	$(EtO)_2P(O)SMe$	1a	a	1 : 1	19	59	22	0	0	0	0
2	$(EtO)_2P(O)SMe$	1a	a	2 : 1	0	0	100	0	0	0	0
3	$(EtO)_2P(O)SMe$	1a	b	3 : 1	0	0	92	0	0	8	0
4	$(EtO)_2P(O)SMe$	1b	a	1 : 1	51	20	23	0	0	6	0
5	$(EtO)_2P(O)SMe$	1b	a	2 : 1	4	19	49	0	3	25	0
6	$(EtO)_2P(O)SMe$	1b	a	3 : 1	0	0	0	0	0	100	0
7	$(EtO)_2P(O)SMe$	1b	c	1.5 : 1	2	57	41	0	0	0	0
8	$(EtO)_2P(O)SeMe$	1a	a	0.6 : 1	47	38	11	3	1	0	0
9	$(EtO)_2P(O)SeMe$	1a	a	1.6 : 1	0	58	18	2	4	18	0
10	$(EtO)_2P(O)SeMe$	1a	b	3 : 1	0	0	51	2	4	20	23
11	$(EtO)_2P(O)SeMe$	1b	a	1 : 1	32	36	21	7	4	0	0
12	$(EtO)_2P(O)SeMe$	1b	a	2 : 1	0	11	53	10	9	7	0
13	$(EtO)_2P(O)SeMe$	1b	d	2 : 1	0	0	16	28	26	30	0
14	$(EtO)_3PS$	1a	e	3 : 1	100	0	0	0	0	0	0
15	$(EtO)_3PS$	1b	e	3 : 1	20	0	0	10	5	56	9
16	$(EtO)_3PS$	1b	f	3 : 1	73	0	0	14	2	0	11
17	$(EtO)_3PSe$	1a	e	3 : 1	100	0	0	0	0	0	0
18	$(EtO)_3PSe$	1b	f	3 : 1	18	0	0	6	3	34	39

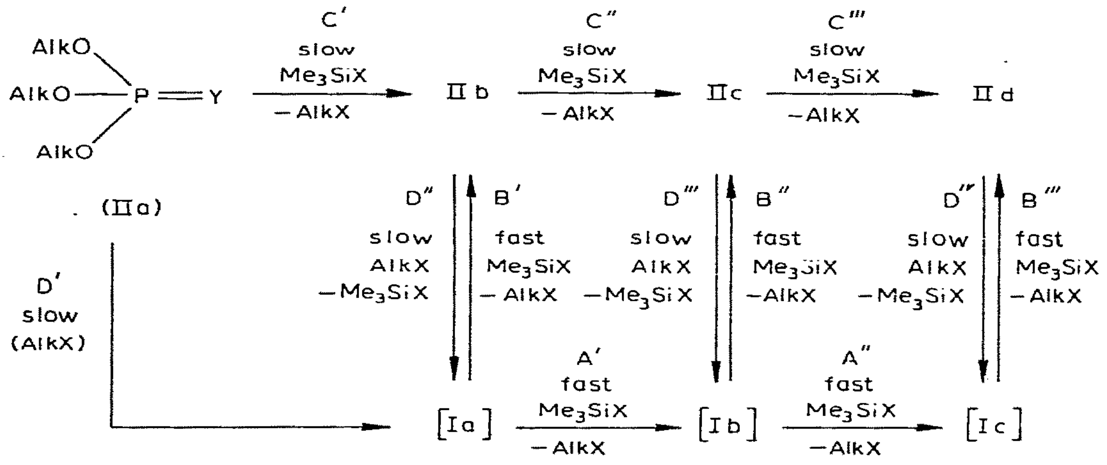
[a] (a) in methylene chloride 1/1 v/v, at room temp., to full conversion of the silane; (b) as in (a), for 24 h; (c) in methylene chloride 1/1 v/v, at −30°C, for 3 h full conversion of 1b; (d) in benzene 1/1 v/v, at room temp., to full conversion of 1b; (e) without solvent, at reflux (about 110°C), for 3 h; (f) without solvent, at 60°C, for 3 h.

A'', B''' of Scheme 1. Since the first two steps are much faster than the formation of the trisilylphosphorothionate IId, the reaction leads to high yields of mono- and di-silyl substituted thiolates when an appropriate proportion of the halosilane is used. The abstraction of the alkyl group from the selenium atom occurs more readily than the abstraction from sulfur, and may even compete with the replacement of an *O*-alkyl by a silyl group. Consequently both types of products, the selenolates Ib, Ic and the selenonates IIb, IIc, IId, are formed. It should be noted that the yields of various products vary considerably with the reaction conditions, in particular the temperature and nature of the solvent.

1.2. Silylation of the thionates and the selenonates. There is a considerable difference in the reactivity towards halosilanes between the esters of type Ia, Ib and Ic and the corresponding esters type IIa, IIb and IIc. For example only 27% of conversion occurs when triethyl phosphorothionate, a representative of type II, is heated with 3 molar equivalents of trimethyliodosilane at 60° C for about 3 h (Table 1). Under these conditions trimethylbromosilane is virtually unreactive towards both triethyl phosphorothionate and its selenone analogue. Thus the estimated sequences of reactivity of the homomorphic esters of phosphorus in the silylation processes are: $\geqslant$P=O >> $\geqslant$P=S and $\geqslant$P=O >> $\geqslant$P=Se. In consequence reactions of thionates of selenonates with halosilanes (reactions of series C in Scheme 2) are not taken into account in Scheme 1.

It should be noted that alkyl halides, which are generated during the reaction, also serve as catalysts of reagents in Pishchimuka thiono—thiolo or selenono—selenolo rearrangements [15—17] (reactions D in Scheme 2). These processes occur only at elevated temperature, and so are not included in Scheme 1, but they seriously complicate the course of silylation of the esters of structures IIa, IIb and IIc. These Pishchimuka reactions involve transient formation of the corresponding thiolates or selenolates Ia and Ib which, being very reactive towards the halosilanes at elevated temperatures, are immediately transformed

SCHEME 2



(X = Br, I ; Y = S, Se. $k_A > k_B$)

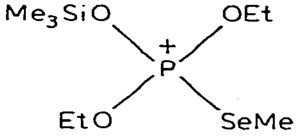
by reactions A into tri-*O*-silyl substituted thio- or seleno-phosphate IId. The over-all process is represented in Scheme 2. At an early stage in the silylation of IIa the concentration of the alkyl halide in the system is relatively low and the reaction proceeds mainly by route C, to give IIb as a main product (See Table 1, exp. no 16).

The importance of Pishchimuka rearrangements is reflected in the large proportions of IId among the products of the reactions of IIa with Ib at a high conversion of the silane (see Table 1). They seem to be especially important in the reactions involving selenonates.

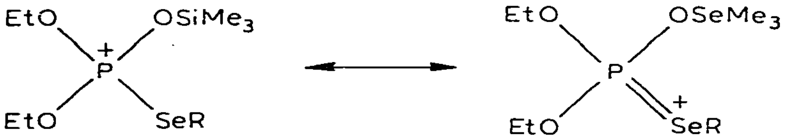
It is noteworthy that no *S*- or *Se*-trimethylsilyl substituted thiolo- or selenolo-phosphates were detected in the products of silylation of thionates or selenolates of structure IIa, although these products would be expected if direct nucleophilic attack by thio- or seleno-phosphoryl groups, P=Y, on silicon was involved.

2. *Studies of intermediates with aid of ^{31}P NMR spectroscopy*

No reaction of the type shown in Scheme 1 occurs at a temperature of —80° C. However, the signal from *O,O*-diethyl-*Se*-methyl phosphoroselenolate in methylene chloride shifts downfield at this temperature from +21 ppm to +31 ppm following the addition of an excess of trimethyliodosilane (Fig. 1a and 1b). Without ^{31}P—^{1}H decoupling the signal shows a complex multiplet structure presumably resulting from ^{31}POCH$_2$ and ^{31}PSeCH$_3$ couplings. The positions of the ^{31}P—^{77}Se coupling satellites indicate that there is a distinct change in the ^{31}P—^{77}Se coupling constant (Table 2). Data in the literature [18, 19] indicate that the changes in the chemical shift and the ^{31}P—^{77}Se coupling constant are consistent with formation of the corresponding phosphonium cation:



The coupling constant reflects the nature of the electron configuration in the intervening bonds, and increases markedly on going from the selenol bond P—Se—R (480 Hz in (EtO)$_2$P(O)SeMe) to selenone bond P=Se (920 Hz, in (EtO)$_3$P=Se). The coupling constant after the trimethyliodosilane is introduced to the selenolate at —80° C lies at an intermediate value (670 Hz), distinctly higher than that in the selenolate. The presence of a positive charge on the phosphorus atom causes contraction of the *d*-orbitals, which thus overlap more effectively with the *p*-orbitals of selenium. Hence a considerable contribution to the phosphonium cation from structure IV can be expected.



(III) (IV)

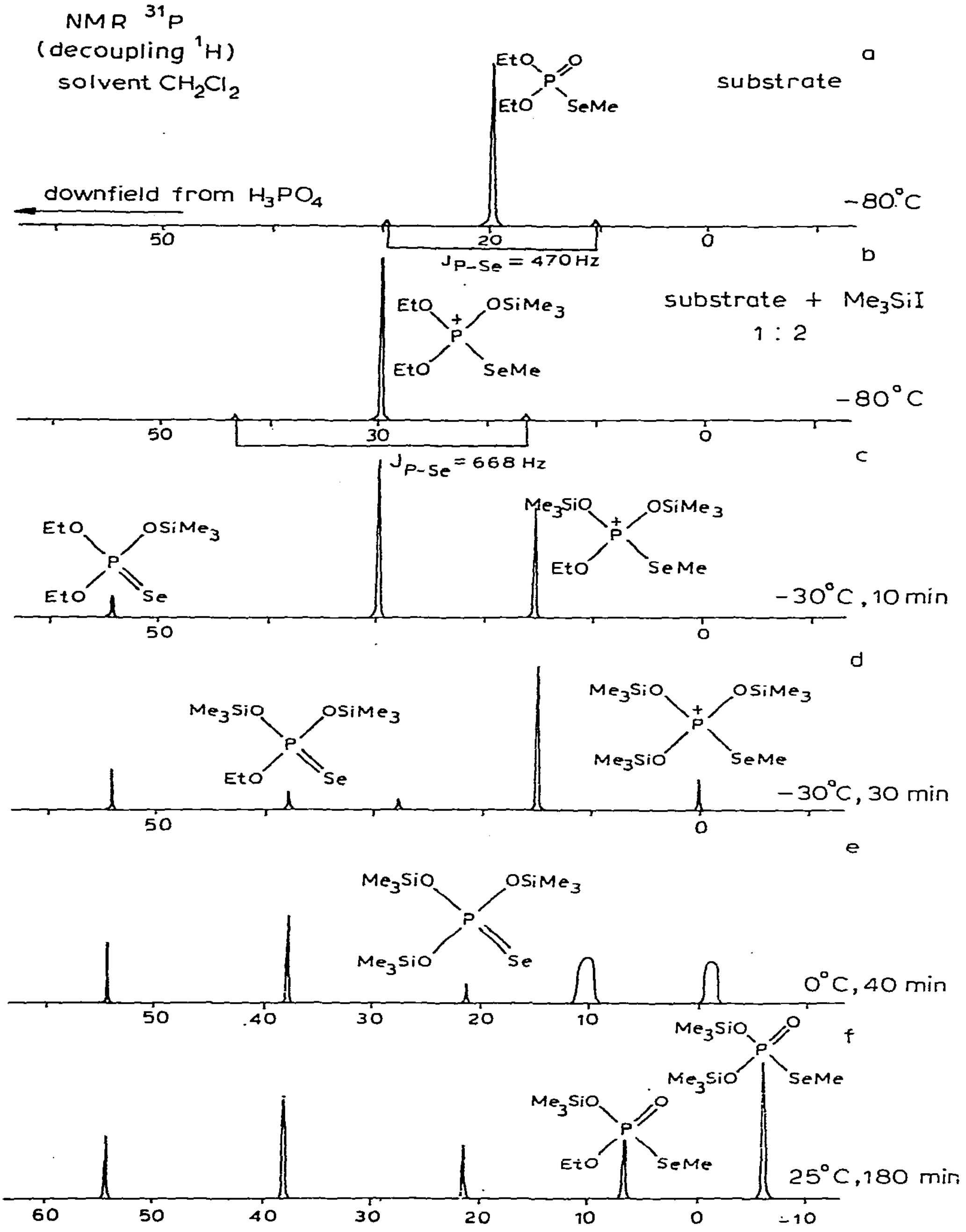


Fig. 1. The NMR spectra of the reaction mixture in silylation of *O,O*-diethyl-*Se*-methylphosphoroselenolate with trimethyliodosilane. (a) solution of the selenolate (1 mol dm^{-3}) in methylene chloride at −80°C; (b) after addition of the silane (2 mol dm^{-3}); (c) after raising the temperature to −30°C; (d) after keeping the mixture at the temperature −30°C for 20 minutes; (e) after raising the temperature to 0°C; (f) after complete conversion of the silane. Spin—spin coupling satellites are omitted in Fig.. 1c, 1d, 1e, and 1f.

TABLE 2

THE CHANGES OF THE ^{31}P NMR SPECTRA AT —80°C OF *O,O*-DIETHYL-*S*-METHYL PHOSPHOROTHIOLATE AND *O,O*-DIETHYL-*S*-METHYL PHOSPHOROSELENOLATE IN INTERACTION WITH TRIMETHYLIODOSILANE. A 1 mol dm^{-3} SOLUTION OF THE ESTER IN CH_2Cl_2 WAS USED

$(EtO)_2O(O)SMe$		$(EtO)_2P(O)SMe$		
Silane to ester ratio	δ (ppm)	Silane to ester ratio	δ (ppm)	$J(^{77}Se—^{31}P)$ (Hz)
0	26.8	0	21	480
0.25	29.5	0.4	25	545
0.5	31.3	1	30.6	662
0.75	33.3	2	30.6	668
1	35.8			
2	35.8			

The position of the ^{31}P NMR signal of the phosphonium cation is not affected by the amount of excess of the iodosilane. When the selenolate appears in excess only one signal is observed. Its chemical shift is intermediate between that for the phosphonium cation and that for the selenolate, while the $^{31}P—^{77}Se$ coupling constant is also an average of those in these two cations (Table 2). These results indicate that the reversible phosphonium salt formation is fast on the ^{31}P NMR time-scale and that the position of the equilibrium lies well over to the side of the salt, at least at low temperatures *.

No dealkylation was observed at —80° C, but the spectra taken after raising the temperature to —30° C reveal the existence of dealkylation products (Fig. 1c and 1d). The products of the selenonate series are stable under these conditions, and show a very low tendency, if any, to form a salt from the iodosilane, and so the signals of mono- and di-silyl-substituted selenones are observed in the spectra. On the other hand, the products of the selenolate series behave similarly to the substrate, and signals of the corresponding phosphonium salts are found, unless P=O containing compounds are present in the system in excess of the iodosilane (Fig. 1c and 1d). When such an excess is present averaged signals of the salts and the selenolates appear, and this is the situation depicted in Fig. 1e. These averaged signals shift towards the position of corresponding selenol signals as the reaction proceeds, which explains their considerable breadth (the scanning time was about 10 minutes). Only selenolate signals are observed if the iodosilane is fully converted into the stable ester products (Fig. 1f).

In contrast to the situation for the phosphonium iodide, the equilibrium for the phosphonium salt formation from *O,O*-dialkyl-*Se*-alkyl phosphoroselenolates and trimethylbromosilane lies well over towards the substrate, which underlines the importance of the heterolytic cleavage of the silicon—halogen bond in the reaction of phosphates with halosilanes. The pronounced drop in reactivity from iodo- to bromo- and to chloro-silanes may result from a

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* This is supported by preliminary kinetic study, which indicates that the rate of the reaction of the iodosilane with a phosphate does not depend on the concentration of the silane in excess of that of the phosphate.

decrease in the stationary concentration of the phosphonium salt intermediate in this sequence.

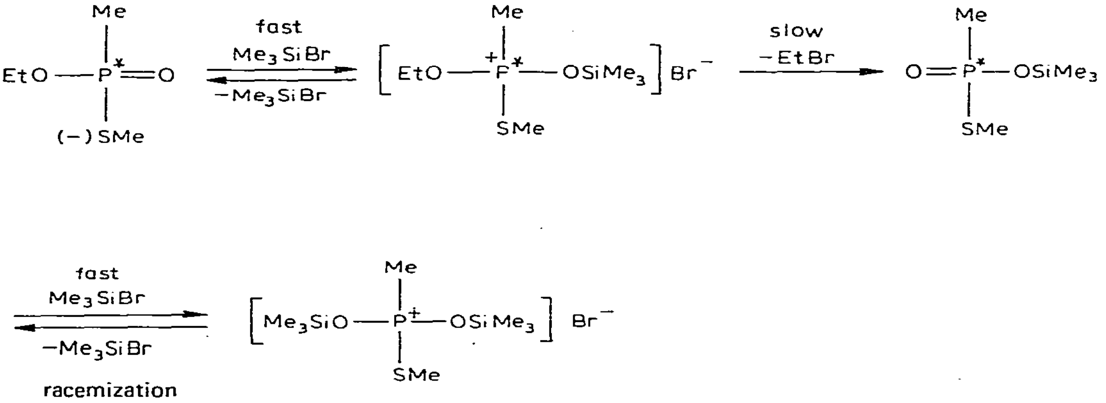
Reactions of the halosilanes with *O,O*-dialkyl-*S*-alkyl phosphorothiolates take an analogous course. Again the equilibrium for the phosphonium salt formation lies over to the side of the salt in the case of the reaction of trimethyliodosilane, while no salt intermediate was detected by ^{31}P NMR when trimethylbromosilane was used.

3. *Stereochemical studies*

The reaction of the optically active (—)-*O*-ethyl-*S*-methyl methylphosphonothiolate with trimethylsilyl bromide or iodide was found to proceed with complete racemization of the thioate. The reaction with trimethylsilyl bromide in CH_2Cl_2 at 25° C involving equimolar amounts of reagents was followed simultaneously by ^{31}P NMR analysis and measurement of optical activity. Experimental points obtained by both methods fitted well on to a single conversion-time curve (see Fig. 2).

This result fully confirmed the formation of the phosphonium salt in the fast and reversible step of the process. The racemization occurs as a result of the formation of an achiral phosphonium salt from the product and the bromosilane present in the system, according to Scheme 3.

SCHEME 3



4. *Conductometric studies*

The conductivity of both an 0.25 mol dm^{-3} solution of trimethyliodosilane in CH_2Cl_2 as well as 0.25 mol dm^{-3} solution of *O,O*-diethyl-*S*-methyl phosphorothiolate was found to be very low, i.e. at the level for the solvent itself. However, the conductivity of the corresponding CH_2Cl_2 solution containing equimolar amounts of both trimethyliodosilane and the thiolate, prepared and handled at a temperature low enough to prevent the silylation, was as high as could be expected for the solution of a strong electrolyte (molar conductivity at the concentration 0.1 *M* being at the level 15 ohm^{-1} cm^2 mol^{-1}). The solution of 0.25 mol dm^{-3} of the thiolate in CH_2Cl_2 was subjected to conductometric titration with trimethyliodosilane at −70° C. The conductivity increased strongly (Fig. 3) until an equimolar amount of the silane had been introduced.

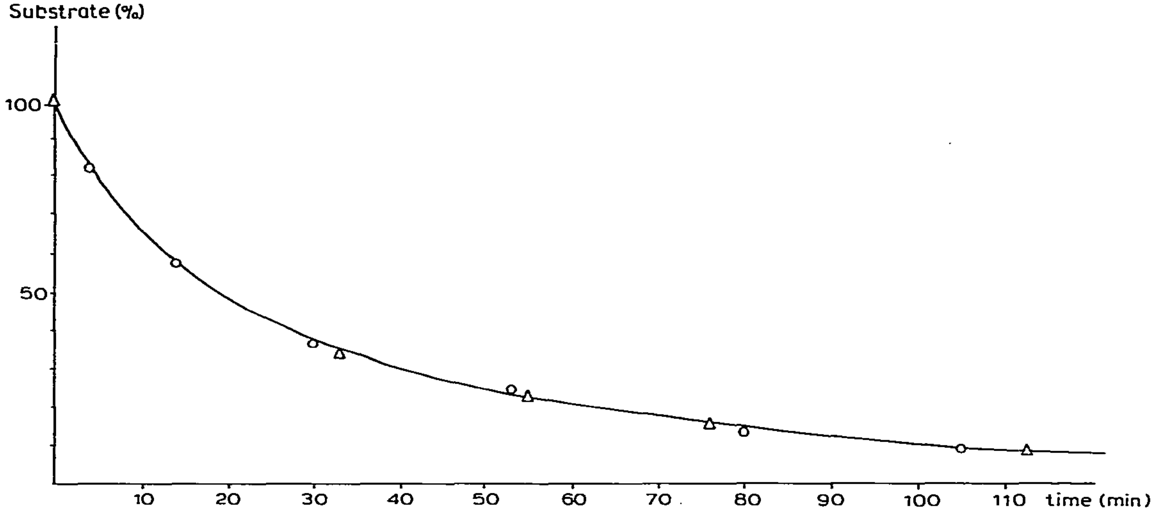


Fig. 2. Conversion-time curve for the reaction of (—)-$(C_2H_5O)(CH_3S)CH_3P(O)$ (0.9 mol dm^{-3}) with Me_3SiBr (0.9 mol dm^{-3}) in CH_2Cl_2 at 23 ± 1°. Experimental points are those obtained from ^{31}P NMR analysis (△) and optical rotation change (○). Second order rate constant was k(II) = 1.1 × 10^{-3} dm^3 mol^{-1} sec^{-1}.

Further addition of the silane caused no change in the conductivity.

In contrast a corresponding solution containing equimolar amounts of trimethylbromosilane and *O,O*-diethyl-*S*-methyl phosphorothiolate exhibits behaviour characteristic of a weak electrolyte, which is in agreement with the conclusion that position of equilibrium for the phosphonium salt formation lies well over to the side of substrates.

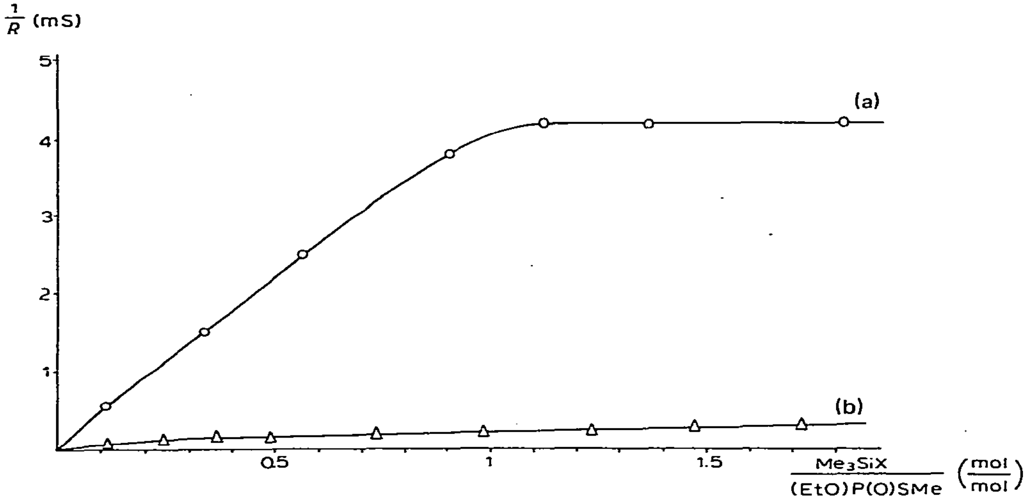
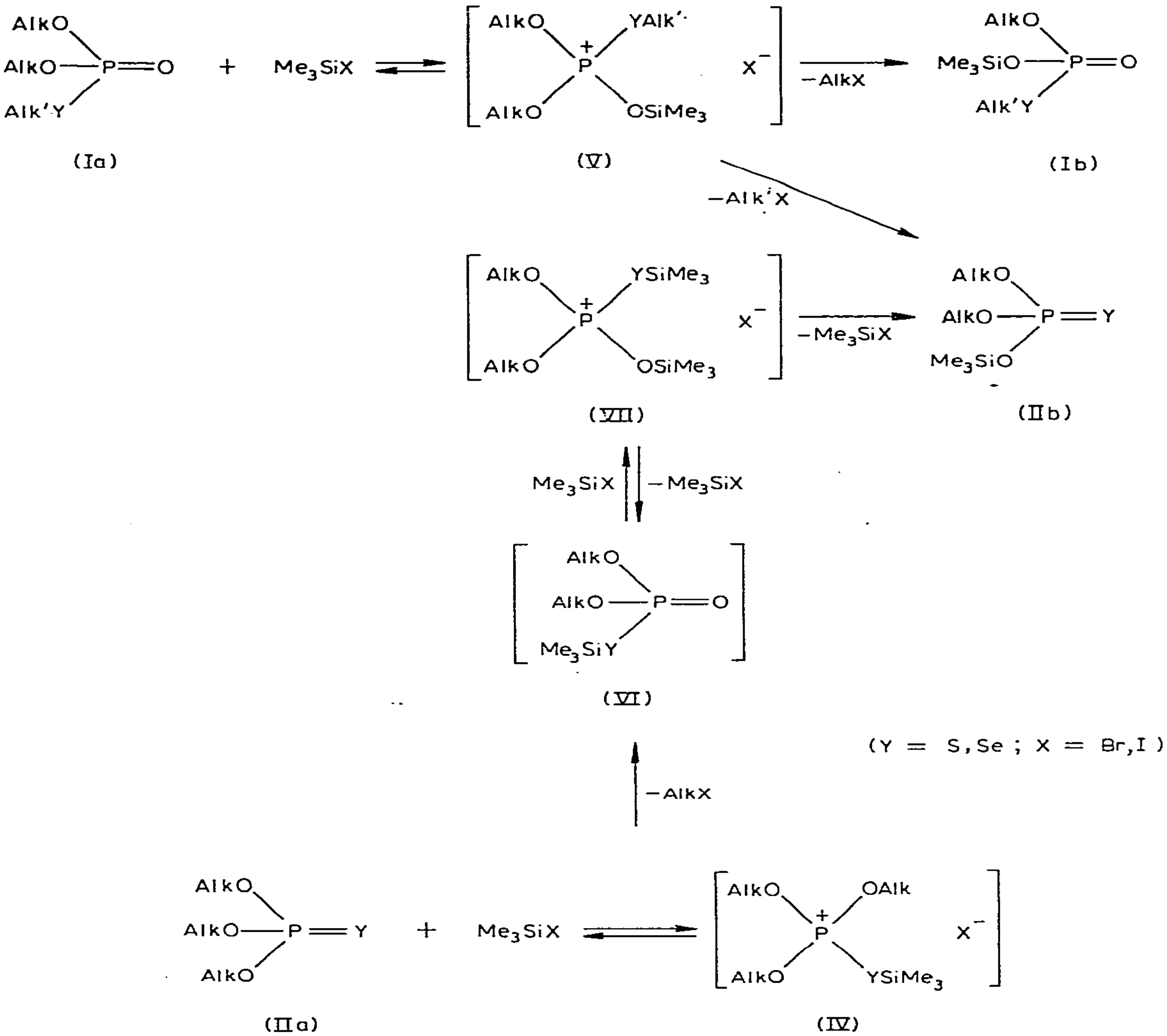


Fig. 3. Change of conductivity of the solution of $(EtO)_2(MeS)P{=}O$ (0.25 mol dm^{-3}) in CH_2Cl_2 at —70°C following addition of trimethylhalosilane: (a) on titration with Me_3SiI, (b) on titration with Me_3SiBr.

5. Mechanistic pathways of the silylation

Our results are best rationalised in terms of the mechanistic scheme 4.

SCHEME 4



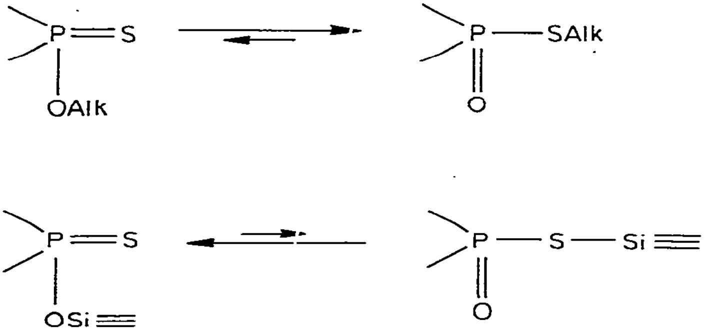
The nucleophilic attack of the phosphoryl oxygen of the thiolate or selenolate Ia on the silicon atom of 1a or 1b gives the phosphonium salt V, which subsequently undergoes cleavage in one of the three following ways, as determined by the position of the nucleophilic attack by the iodide or bromide ion: (1) Attack on silicon, which is strongly favoured, causes desilylation of the phosphonium cation and regeneration of the substrate. Thus the first step constitutes a fast equilibrium. (2) Attack at the alkyl bonded to oxygen results in the formation of the thiolate or selenolate Ib. (3) Finally, abstraction of the alkyl group from sulfur or selenium produces the thionate or selenonate, IIb. Although this reaction plays scarcely any role in the case of thio derivatives, it does contribute in the reaction of seleno derivatives. Thiolates or selenolates Ib react analogously.

The mechanism of the reactions of thionates and their selenium analogues is not so straightforward. We cannot reject at the moment the possibility of the attack of the phosphorus-alkyl bridging oxygen of the esters IIa, b, c at silicon. However, this formally simple mechanism of reactions C′, C″ and C‴ would require the assumption that the mechanistic pathways in the series of the homomorphic esters with $\geqslant$P=O, $\geqslant$P=S and $\geqslant$P=Se groups are not the same, whereas all the foregoing results can be satisfactorily explained in terms of a single mechanism, involving nucleophilic attack on silicon exclusively by the chalcogen atom occupying the terminal position, i.e. phosphoryl, thiophosphoryl and selenophosphoryl. This nucleophilic attack of IIa on the halosilane lead to formation of the unstable *S*-silyl or *Se*-silyl substituted phosphonium salt IV. Again desilylation leading to the regeneration of the substrate is strongly favoured, but abstraction of the alkyl group may occur concurrently to produce the *O*,*O*-dialkyl-*S*-trimethylsilyl phosphorothiolate or its selenium analogue VI. This ester cannot be detected in the reaction system because of the high reactivity of thiolates towards trimethyliodosilane under the conditions in which the thionate or selenonate IIa can be brought into reaction, (i.e. the temperature must be above 60° C). Hence VI must be considered as an unstable intermediate, which immediately gives the disilylphosphonium salt VII, and this undergoes fast desilylation. If the silyl group is taken from the oxygen, the intermediate ester VI is reformed. On the other hand, the abstraction of the silyl group from the sulfur or selenium leads to thionates or their selenium analogues, IIb, as the first stable product in the foregoing sequence of reactions. In the presence of the halosilane it is subjected to an analogous sequence of processes leading to IIc, which than gives IId.

It is noteworthy that compounds of structures similar to the intermediate VI, containing the $>$P(O)SSiR$_3$ grouping, were recently found as thermodynamically unstable products in reactions between phosphorochloridates and silanothiolates [20].

The reluctance shown by the thiolates and selenolates to react with trialkylhalosilanes constitutes a good example of low philicity of P=S and P=Se groups towards silicon, which contrasts with an exceptionally high philicity exhibited by the P=O group. The equilibria for the thiono—thiolo and selenono—selenolo rearrangements lie over to opposite sides for alkyl and silyl esters (Scheme 5), which is an agreement with recent observations [20].

SCHEME 5



6. *Synthesis of some O,O-trimethylsilyl substituted thio and seleno esters of phosphorus*

The reactions of *S*-organyl-*O*-alkyl substituted thiophosphates with trialkylbromosilane and trialkyliodosilane, because of their selectivity, offer a convenient method of synthesizing the corresponding *O*-silyl-*S*-organyl thiophosphates, which are of interest as precursors of the corresponding *S*-organyl thiophosphoric acids. Some new thiolates were prepared by this route (Table 3). The reaction with iodosilanes at room temperature usually proceeds violently and less selectively, but it can lead to a fairly high yield of the *O*,*O*-disilyl substituted product if carried out at low temperatures with a 1/2 molar ratio of the thiophosphate to the silane. The rates of both steps A' and A'' are comparable, so mixed *O*-silyl-*O*-alkyl derivatives may be obtained in fairly good yields starting with a 1/1 molar ratio of the thiophosphate to bromo- or iodo-silane (Table 1).

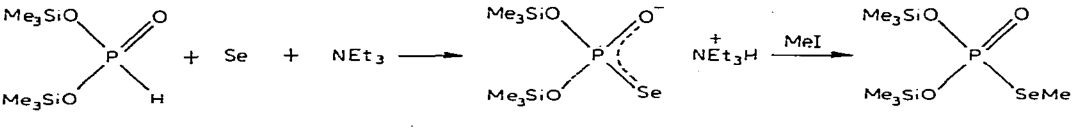
Analogous reactions involving *O*-alkyl-*S*-organyl organylphosphonothiolates may be used for the synthesis of *O*-trialkylsilyl-*S*-organyl organylphosphonothiolates.

In principle the yields of *O*-silyl-*S*-organyl substituted thiophosphates of thiophosphonates are smaller when the *S*-organyl group is more labile. This is the case in reactions of *S*-allyl and *S*-benzyl derivatives, for which competitive dealkylation involving S—C bond cleavage leads to substantial yields of thiono by-products.

The dealkylation involving Se—C cleavage occurs more readily than that involving S—C cleavage, and so the reaction of *Se*-organyl-*O*-alkyl selenophosphate is less selective in favour of *Se*-organyl substituted products. The reaction leads to many products, the isolation of which is difficult because of their high boiling points and poor stability. In the case of *Se*-allyl derivatives the dealkylation involving Se—C cleavage is so fast that monosubstituted *O*-silyl phosphoroselenonate can be obtained in good yield. This reaction was used to obtain *O*-trimethylsilyl-*O*,*O*-diethyl phosphoroselenonate.

Some model *O*-trimethylsilyl esters of phosphoroselenoic acids were prepared by other routes. *O*,*O*-Bis(trimethylsilyl)-*Se*-methyl phosphorothiolate was synthesized by the reaction of triethylammonium *O*,*O*-bis(trimethylsilyl) phosphoroselenoate with methyl iodide according to scheme 6.

SCHEME 6



The salt can be used as a general reagent for introducing the *O*,*O*-bis(trimethylsilyl)phosphoroselenolate group into organic compounds. *O*,*O*,*O*-Tris(trimethylsilyl) selenophosphate was obtained from tris(trimethylsilyl) phosphite and selenium by a procedure similar to that used [21] for the preparation of its sulfur analogue.

$(Me_3SiO)_3P + Se \rightarrow (Me_3SiO)_3P{=}Se$

TABLE 3

O-TRIMETHYLSILYL ESTERS OF THIO AND SELENO ACIDS OF PHOSPHORUS [a]

No	Compound	B.p. (°C/mmHg)	n_D^{20}	^{1}H NMR (ppm)	^{31}P NMR (ppm)	Elemental analysis (Found (calcd.) (%))			
						C	H	P	S
2b	$(Me_3SiO)_2P(O)SCH_2$-$CH=CH_2$	62—68/0,05	1.4513	0,23 (s, 18H, $Si\underline{CH_3})_3$); 3.0—3.7 (m, 2H, $SC\underline{H}_2$); 4.8—6,1 (m, 3H, $C\underline{H}_2=C\underline{H}$)	4.8 (t) J(PSCH) 15 Hz	35,8 (36,3)	7,9 (8,0)	11.0 (10,5)	10,3 (10,7)
2c	$(Me_3SiO)_2P(O)SPh$	100/0,05	1.4890	0,2 (s, 18H, $Si(C\underline{H}_3)_3$); 7.1—7.6 (m, 5H, $SC_6\underline{H}_5$)	0.8 (s)	42,9 (43,1)	6.8 (6,9)	9,8 (9,3)	9,7 (9,6)
2e	$(Me_3SiO)_2P(O)SCH_2$-C_6H_4Br-*p*	120—124/ 0.05	1.5085	0,26 (s, 18H, $Si(C\underline{H}_3)_3$; 3.9 (d, 2H, $SC\underline{H}_2$, J(PSCH) 16 Hz); 7,0—7.5 (m, 4H, $C_6\underline{H}_4Br$)	4.4 (t) J(PSCH) 16 Hz	35,5 (36,6)	5,8 (5,6)	7,5 (7,3)	7,1 (7,5)
3a	$(Et_3SiO)(MeO)P(O)SMe$	60—65/0,3	1.4638	0,5—1,3 (m, 15H, $Si(C_2\underline{H}_5)_3$); 2,3 (d, 3H, $SC\underline{H}_3$, J(PSCH) 16 Hz); 3,8 (d, 3H, $OC\underline{H}_3$, J(POCH) 15 Hz)	17.6 (sept)	37,2 (37,5)	8,2 (8,2)	13,6 (12,7)	12,7 (12,5)
4a	$(Me_3SiO)EtP(O)SMe$	90—95/10	1.4400	0,3 (s, 9H, $Si(C\underline{H}_3)_3$); 0,9—2,0 (m, 5H, $C_2\underline{H}_5$); 2,2 (d, 3H, $SC\underline{H}_3$, J(PSCH) 15 Hz)	50,3 (m)				
5a	$(Me_3SiO)_2P(O)SeMe$	65—67/0,2	1.4608	0,33 (s, 18H, $Si(C\underline{H}_3)_3$), 2,15 (d, 3H, $SeC\underline{H}_3$, J(PSeCH) 15 Hz)	−7 (q) J(PSeCH) 15 Hz J(PSe) 472 Hz	27,8 (26,4)	7,0 (6,6)	10,3 (9.7)	
6a	$(Me_3SiO)_2P(O)Se^-H\overset{+}{N}Et_3$				20 (s) J(PSe) 797 Hz				
7a	$(Me_3SiO)(EtO)_2P=Se$	52—54/0,2	1.4643	0,33 (s, 9H, $Si(C\underline{H}_3)_3$); 1,25 (t, 6H, $CH_2C\underline{H}_3$); 4,05 (oct, 2H, $C\underline{H}_2CH_3$, J(POCH) 10 Hz)	55 (quint) J(POCH) 10 Hz J(PSe) 940 Hz	28,3 (29,1)	6,8 (6,6)	11,0 (10,7)	
7b	$(Me_3SiO)_3P=Se$	65—67/0,4	1.4484	0,33 (s, 27H, $Si(C\underline{H}_3)_3$)	21,4 (s) J(PSe) 942 Hz	28,5 (28,6)	7.2 (7.2)	8,8 (8,2)	

[a] Other esters of phosphorus used were known compounds.

Experimental

Synthesis of trialkylsilyl esters of thio and seleno acids of phosphorus

General

Trimethylbromosilane (**1a**), trimethyliodosilane (**1b**), and triethylbromosilane (**1c**) and the more common esters of phosphorothioic and phosphoroselenoic acids used were synthesized by standard methods and purified by distillation through a Vigreux column. In all the syntheses described below atmospheric moisture was excluded.

Preparation of O,O-bis(trimethylsilyl)-S-allyl phosphorothiolate (2b) and some other esters of phosphorothioic and phosphonothioic acids

O,O-Dimethyl-*S*-allyl phosphorothiolate (4.8 g; 0.026 mol) was placed in a 10 ml round-bottom flask equipped with a magnetic stirrer, a micro dropping funnel, and a reflux condenser. 8 g (0.052 mol) of **1a** was introduced with stirring and a slight generation effect was observed. The mixture was kept for about 10 h at room temperature. Distillation at 0.05 mmHg gave 5.5 g (0.018 mol, 71% yield) of **2b**. The yield of **2b** in the product mixture was 87% as indicated by ^{31}P NMR spectroscopy.

The following products were obtained analogously from 1a and the appropriate *O,O*-dimethyl-*S*-organyl phosphorothiolate (in brackets are given the yield of isolated product and the yield of the product in the reaction mixture, respectively): *O,O*-bis(trimethylsilyl)-*S*-methyl phosphorothiolate (2a) (77%, 97%), *O,O*-bis(trimethylsilyl)-*S*-phenyl phosphorothiolate (2c) (69%, 100%), *O,O*-bis(trimethylsilyl)-*S*-β-chloroethyl phosphorothiolate (2d) (60%, 97%), *O,O*-bis(trimethylsilyl)-*S*-*p*-bromobenzyl phosphorothiolate (2e) (70%, 83%). All these compounds except 2e were obtained previously by other methods [22].

Similarly from 2.9 g (0.018 mol) of **1c** and 2.8 g (0.018 mol) of *O,O,S*-trimethyl phosphorothiolate, was obtained *O*-methyl-*O*-triethylsilyl-*S*-methyl phosphorothiolate 3a (1.5 g, 0.006 mol, 30% yield). The yield in the product mixture as indicated by ^{31}P NMR spectroscopy was 50%.

Similarly from *O*-methyl-*S*-methyl ethylphosphonothiolate (2.9 g, 0.018 mol) and **1a** (2.35 g, 0.018 mol), was obtained *O*-trimethylsilyl-*S*-methyl ethylphosphonothiolate 4a (2.4 g, 0.011 mol, 61% yield) was obtained. The yield in the product mixture was 97% (^{31}P NMR spectroscopy).

The reaction of trimethyliodosilane (1b) with O,O-dimethyl-S-phenyl phosphorothiolate

The same apparatus was used as in the synthesis of **2b**. A mixture of *O,O*-dimethyl-*S*-phenyl phosphorothiolate (3.1 g, 0.014 mol) and 3.0 ml of dry benzene was stirred in the flask while 5.6 g (0.028 mol) of **1b** was added during several minutes. A strong exothermic effect was observed. Distillation gave 2c (3.8 g, 0.011 mol, 81% yield). The yield in the product mixture was 100% (^{31}P NMR spectroscopy).

Preparation of O,O-bis(trimethylsilyl)-Se-methyl phosphoroselenolate (5a)

A 0.25 litre, two-necked, round-bottom flask equipped with a mechanical stirrer, a thermometer and a reflux condenser was charged with bis(trimethylsilyl) phosphite (25 g, 0.1 mol), dry benzene (100 ml) and triethylamine (10 g, 0.1 mol). The mixture was stirred, and powdered dried selenium (8 g, 0.11 mol) was slowly introduced. The mixture was then stirred for another 10 h at 80° C. The ^{31}P NMR spectrum showed the conversion of bis(trimethylsilyl) phosphite into the triethylammonium salt of *O,O*-bis(trimethylsilyl) phosphoroselenoic acid **6a**. Methyl iodide (14.2 g, 0.1 mol) was introduced, and generation of heat and precipitation of trimethylammonium iodide were observed. Vacuum distillation of the filtrate gave **5a** (12.7 g, 0.4 mol, 40% yield).

Preparation of O,O-diethyl-O-trimethylsilyl phosphoroselenonate (7a)

In an analogous procedure to that used in the synthesis of **5a**, *O,O*-diethyl-*Se*-allyl phosphoroselenonate (**7c**) was obtained in 86% yield. The **7c** (13 g, 0.05 mol) together with 15 ml of dry benzene was placed in a two necked, round-bottom 100 ml flask, equipped with a magnetic stirrer, a thermometer, and a reflux condenser. The mixture was stirred and **1b** (10 g, 0.05 mol) was added slowly while the temperature was kept at 30—35° C. The mixture was stirred for a further hour. After removal of the solvent vacuum distillation gave **7a** (11.6 g, 0.04 mol, 80% yield).

Preparation of O,O,O-tris(trimethylsilyl) phosphoroselenonate (7b)

A 100 ml round-bottom, two necked flask equipped with a magnetic stirrer, thermometer, and reflux condenser was charged with tris(trimethylsilyl) phosphite (12 g, 0.04 mol). The mixture was stirred while powdered, dried selenium (3.22 g, 0.042 mol) was introduced. The temperature was kept at 50° C during the addition, and stirring was continued at this temperature for a further hour. The excess of selenium was filtered off and vacuum distillation of the filtrate gave **7b** (9.1 g, 0.024 mol, 60% yield).

^{31}P NMR studies of the silylation reactions

^{31}P NMR spectra were recorded on a Jeol JNM-FX-60 FT-NMR instrument at 24.2 MHz. The computer resolution was 1.95 Hz.

In a typical procedure an alkyl ester of phosphorothioic or phosphoroselenoic acid in methylene chloride or benzene solution or without any solvent was placed in a 10 mm O.D. NMR tube, which had been thoroughly flushed with an inert gas. In some cases the ^{31}P NMR spectrum of the ester solution was recorded. Then the given amount of the halosilane was introduced with a hypodermic syringe. The tube was kept under the appropriate conditions for the relevant time, and the ^{31}P NMR spectrum was then recorded.

In a low temperature experiments the tube containing the solution of the ester which was connected through a teflon needle to a reservoir of inert gas for leveling the pressure, was immersed in liquid nitrogen. The halosilane was introduced through the needle into the frozen ester solution, and the tube was warmed cautiously to about —100° C to give a uniform solution then put into the NMR probe.

^{31}P NMR chemical shifts of substrates and products of the silylation reactions including phosphonium salts are listed in Fig. 4. The spectra of the following esters were recorded to confirm ^{31}P NMR assignments: $(Me_3SiO)_n(EtO)_{2-n}P(O)$-

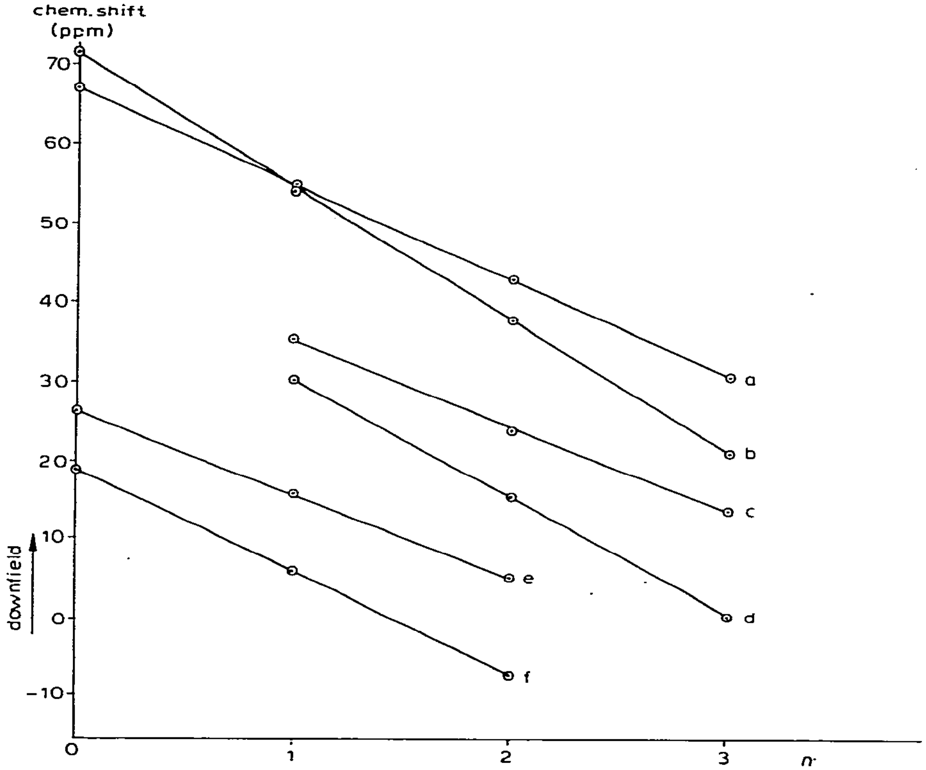


Fig. 4. Chemical shifts of substrates, products, and intermediates in the process of silylation of thio and seleno esters of phosphorus. (a) $(Me_3SiO)_n(EtO)_{3-n}PS$; (b) $(Me_3SiO)_n(EtO)_{3-n}PSe$; (c) $[(Me_3SiO)_n(EtO)_{3-n}\overset{+}{P}SMe]$ (d) $[(Me_3SiO)_n(EtO)_{3-n}PSeMe]$; (e) $(Me_3SiO)_n(EtO)_{2-n}P(O)SMe$ and (f) $(MeSiO)_n(EtO)_{2-n}P(O)SeMe$.

YMe (Y = S, n = 0—2; Y = Se, n = 0—2); $(Me_3SiO)_n(EtO)_{3-n}P = Y$ (Y = S, n = 0—3; Y = Se, n = 0—3). The additive effect of the introduction of subsequent trimethylsilyl groups shown in Fig. 4 helped in the assignments.

Conductometric studies

Conductivity measurements were carried out with a Radelkis conductometer OK 102/1 with the conductivity cell described in [23].

Optical rotation

Optical rotations were measured at λ 498 nm with a Perkin—Elmer 291 MC polarimeter.

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