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Studies on the interaction of phosphine selenides and their structural analogues wth dihalogens and sulfuryl chloride†

Ewa Krawczyk, Aleksandra Skowrońska * and Jan Michalski

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences,
Sienkiewicza 112, 90–363 Łódź, Poland. E-mail: askow@bilbo.cbmm.lodz.pl

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The phosphine selenides, tris(dimethylamino)phosphine selenide, esters of selenophosphoric acid, and esters of selenophosphonic acid react with dihalogens and sulfuryl chloride to form halogenoselenophosphonium salts $(\equiv P–SeX)^+X^-$. The latter undergo deselenization *via* ligand exchange to form phosphonium salts $(\equiv P–X)^+X^-$ and elemental selenium. The stability of these salts depends on the substituents at the phosphorus atom and the type of counter ion. It is likely that the phosphonium salts are in equilibrium with the corresponding phosphoranes, and this is demonstrated for esters containing an *o*-phenylene ligand. The structures of phosphonium salts, phosphoranes and other phosphorus compounds are supported by ^{31}P NMR spectroscopy data and electrical conductivity. Additional evidence comes from addition reactions of halogenoselenophosphonium salts to cyclohexene.

Introduction

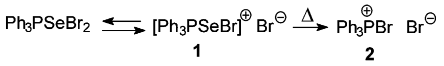
Interest in phosphorus–selenium compounds is growing. Derivatives of monoselenophosphoric acid $P(Se)(OH)_3$ are of special interest. Monoselenophosphate has been shown to be the key intermediate in selenoprotein synthesis.[1] Monoselenophosphate has been chemically synthesized and shown to be identical with the biological selenium donor.[2] Organic pyrophosphates play a fundamental role in biology: their selenium analogues may be of interest for biological studies. The first rational synthesis of tetraalkyl selenopyrophosphates containing a selenium atom bridging two phosphoryl centers has been previously described by us.[3] These compounds are very reactive towards nucleophiles and can be considered as potent phosphorylation reagents. *sym*-Selenopyrophosphates when heated to above 60 °C isomerize into *asym*-selenopyrophosphates, which are identical with compounds previously prepared.[3d] *sym*-Selenopyrophosphates have been prepared by interaction of selenophosphates $(RO)_3P{=}Se$ with dihalogens or sulfuryl chloride.[3c] Also interaction of tertiary phosphine selenides $R_3P{=}Se$ with dihalogens has attracted the attention of several authors.[4] The most meticulous studies have concerned the interaction between tertiary phosphine selenide and elemental iodine.[4a,d,f,h] However, there is very little information about the behavior and structure of compounds obtained in solution and some results are confusing.

In this paper we describe our studies on the interaction of compounds $R^1R^2R^3P{=}Se$ (R^1, R^2, R^3 = alkyl, aryl, dialkylamino, alkoxy, aryloxy) with dichlorine, dibromine and sulfuryl chloride providing a rationale for earlier observations. The most significant part of this paper deals with esters of selenophosphoric acid and similar structures. Finally we describe the behavior of $[\equiv PSe–X]^+X^-$ structures towards olefins.

Results and discussion

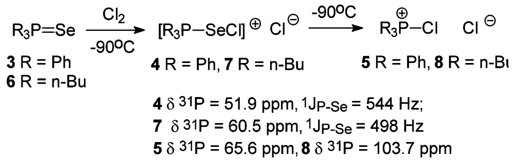
Reaction of triphenyl and tri-n-butyl phosphine selenides with dihalogens

Williams and Wynne have examined the adduct of elemental bromine with triphenylphosphine selenide.[4b] On the basis of IR and Raman spectra they assigned to Ar_3PSeBr_2 a non-ionic structure with a linear arrangement of the Br–Se–Br group. We repeated this procedure and the yellow solid obtained was examined by ^{31}P NMR spectroscopy in dichloromethane solution. At room temperature a single signal δ_P = 50.7 ppm was observed with an absence of satellite peaks derived from ^{77}Se. Glidewell and Leslie have also examined this adduct in $CDCl_3$ solution and observed only one signal by ^{31}P NMR spectroscopy.[5] In our opinion the solid Ph_3PSeBr_2 adduct undergoes deselenization in CH_2Cl_2 or $CDCl_3$ solution, probably *via* the phosphonium intermediate **1**, to give the adduct **2**. We observed the signal δ_P = 50.6 ppm for the adduct of triphenylphosphine with elemental bromine prepared independently from triphenylphosphine and elemental bromine [eqn. (1)].



$$Ph_3PSeBr_2 \rightleftarrows \underset{\mathbf{1}}{[Ph_3PSeBr]^{\oplus}Br^{\ominus}} \xrightarrow{\Delta} \underset{\mathbf{2}}{Ph_3\overset{\oplus}{P}Br\ Br^{\ominus}} + Se_x \qquad (1)$$

This deselenization course involves ligand exchange and decomposition of the transient anion $SeBr^- \longrightarrow Se_x + Br^-$. We did not observe the hypothetical structure **1** at −90 °C by ^{31}P NMR spectroscopy. In contrast the reaction of triphenylphosphine selenide **3** and tri-n-butylphosphine selenide **6** with dichlorine proceeds at −90 °C *via* formation of the ionic intermediates **4** and **7**. These phosphonium salts decompose into the corresponding chlorophosphonium chlorides **5** and **8**, which are observed at −90 °C [eqn. (2)].



$$\underset{\substack{\mathbf{3}\ R = Ph\\ \mathbf{6}\ R = n\text{-}Bu}}{R_3P{=}Se} \xrightarrow[-90^oC]{Cl_2} \underset{\mathbf{4}\ R = Ph,\ \mathbf{7}\ R = n\text{-}Bu}{[R_3P{-}SeCl]^{\oplus}\ Cl^{\ominus}} \xrightarrow{-90^oC} \underset{\mathbf{5}\ R = Ph,\ \mathbf{8}\ R = n\text{-}Bu}{R_3\overset{\oplus}{P}{-}Cl\quad Cl^{\ominus}} \qquad (2)$$

4 $\delta\ ^{31}P$ = 51.9 ppm, $^1J_{P\text{-}Se}$ = 544 Hz;
7 $\delta\ ^{31}P$ = 60.5 ppm, $^1J_{P\text{-}Se}$ = 498 Hz
5 $\delta\ ^{31}P$ = 65.6 ppm, **8** $\delta\ ^{31}P$ = 103.7 ppm

The phosphonium salt structure is in agreement with ^{31}P NMR spectroscopic data on chemical shift and $^1J_{PSe}$ coupling constants indicating the presence of a selenium atom linked by a single bond to a phosphorus center.[6]

Interestingly we observed a similar phosphonium structure **4a** when triphenylphosphine was allowed to react with selenium chloride Se_2Cl_2 at −90 °C in dichloromethane solution [eqn. (3)].

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† This paper is dedicated to Professor Reinhard Schmutzler on the occasion of his retirement.

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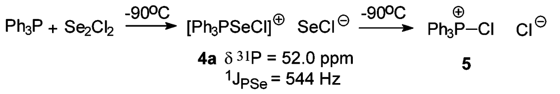
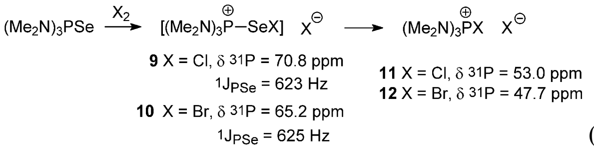


$$\mathrm{Ph_3P + Se_2Cl_2 \xrightarrow{-90^oC} [Ph_3PSeCl]^{\oplus}\ SeCl^{\ominus} \xrightarrow{-90^oC} Ph_3\overset{\oplus}{P}{-}Cl\ \ Cl^{\ominus}} \qquad (3)$$

4a $\delta\,^{31}$P = 52.0 ppm, $^1J_{\rm PSe}$ = 544 Hz; **5**

Reaction of tris(dimethylamino)phosphine selenide with elemental chlorine and bromine

This interaction is represented by eqn. (4). Halogenoselenophosphonium salts **9** and **10** exhibit greater stability than the analogous compounds derived from phosphine selenides: **4** and **7**. They undergo transformation into phosphonium salts **11** and **12** after being kept for 3 days at room temperature. Chemical shifts δ^{31}P and coupling constants $^1J_{\rm PSe}$ correlate well with those known for the corresponding alkylselenophosphonium salts **13**[7] and **14**.[8]



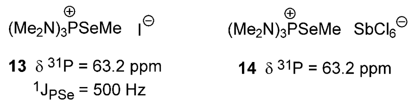
$$\mathrm{(Me_2N)_3PSe \xrightarrow{X_2} [(Me_2N)_3\overset{\oplus}{P}{-}SeX]\ X^{\ominus} \longrightarrow (Me_2N)_3\overset{\oplus}{P}X\ \ X^{\ominus}} \qquad (4)$$

9 X = Cl, $\delta\,^{31}$P = 70.8 ppm, $^1J_{\rm PSe}$ = 623 Hz

10 X = Br, $\delta\,^{31}$P = 65.2 ppm, $^1J_{\rm PSe}$ = 625 Hz

11 X = Cl, $\delta\,^{31}$P = 53.0 ppm

12 X = Br, $\delta\,^{31}$P = 47.7 ppm



$$\mathrm{(Me_2N)_3\overset{\oplus}{P}SeMe\ \ I^{\ominus}} \qquad \mathrm{(Me_2N)_3\overset{\oplus}{P}SeMe\ \ SbCl_6^{\ominus}}$$

13 $\delta\,^{31}$P = 63.2 ppm, $^1J_{\rm PSe}$ = 500 Hz

14 $\delta\,^{31}$P = 63.2 ppm

In the solid state a non-ionic structure was established, on the basis of X-ray analysis, for the (Me$_2$N)$_3$PSeBr$_2$ adduct.[4e]

Reaction of *O,O,O*-triethylselenophosphate with dichlorine and sulfuryl chloride

These studies have been undertaken with the aim of finding a route to the synthesis of oxophosphoraneselenyl halides >P(O)SeX. The reaction of *O,O,O*-triethylselenophosphate with dichlorine differs from the analogous reaction with triethylthionophosphate, which was studied earlier in this laboratory.[9] The former reaction when performed at room temperature gives diethylphosphorochloridate along with precipitation of elemental selenium [eqn. (5)].

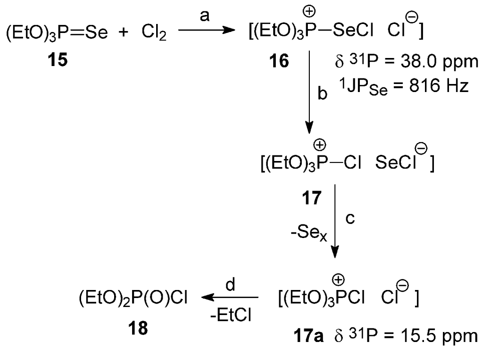
$$\mathrm{(EtO)_3P{=}Se + Cl_2 \longrightarrow (EtO)_2P(O)Cl + EtCl + Se_x} \qquad (5)$$

Reaction of dichlorine with thionophosphate leads to diethoxyoxophosphoranesulfenyl chloride [eqn. (6)].

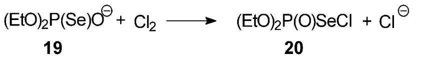
$$\mathrm{(EtO)_3P{=}S + Cl_2 \longrightarrow (EtO)_2P(O)SCl + EtCl} \qquad (6)$$

To rationalize this difference variable-temperature ^{31}P NMR studies were undertaken. In the range from −100 °C to −80 °C two peaks were observed corresponding to the starting triethylselenophosphate **15** ($\delta_{\rm P}$ = 70 ppm, $^1J_{\rm PSe}$ = 905 Hz) and the salt like compound **16** ($\delta_{\rm P}$ = 38 ppm, $^1J_{\rm PSe}$ = 816 Hz). At −70 °C the starting material **15** disappeared and a new peak corresponding to the triethoxychlorophosphonium salt (EtO)$_3$P$^+$ClCl$^-$ **17a** was observed. This salt was identical with that obtained earlier when triethylphosphite was allowed to react with elemental chlorine at −100 °C in C$_2$H$_5$Cl solution.[9] Subsequently at −60 °C a peak derived from diethylphosphorochloridate **18** ($\delta_{\rm P}$ = 3 ppm) appeared . At −30 °C the salt **17a** disappeared and this is in agreement with our earlier observations.[9] Above −30 °C the salt **16** is gradually transformed into diethylphosphorochloridate **18** and other minor unidentified products. The interaction of *O,O,O*-triethylselenophosphate **15** with elemental chlorine is represented in Scheme 1.

The transformation of salt **16** into **18** probably proceeds by ligand exchange (path b). There is no spectral indication for the formation of diethoxyoxophosphoraneselenyl chloride **20**. This unstable compound with chemical shift $\delta_{\rm P}$ = 23.5 ppm and coupling constant $^1J_{\rm PSe}$ = 644 Hz is formed when diethylphosphoroselenoic acid **19** is allowed to react with elemental chlorine at a temperature below −20 °C in ethyl chloride solution [eqn. (7)].



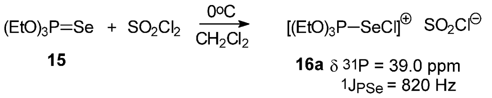
Scheme 1



$$\mathrm{(EtO)_2P(Se)O^{\ominus} + Cl_2 \longrightarrow (EtO)_2P(O)SeCl + Cl^{\ominus}} \qquad (7)$$

19; **20**

A surprising difference was observed when *O,O,O*-triethylselenophosphate was allowed to react with sulfuryl chloride SO$_2$Cl$_2$ at 0 °C. The salt **16a** was formed and is stable for several hours in solvents like dichloromethane or benzene at room temperature [eqn. (8)].



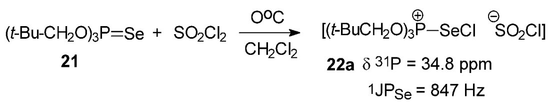
$$\mathrm{(EtO)_3P{=}Se + SO_2Cl_2 \xrightarrow[CH_2Cl_2]{0^oC} [(EtO)_3P{-}SeCl]^{\oplus}\ SO_2Cl^{\ominus}} \qquad (8)$$

15; **16a** $\delta\,^{31}$P = 39.0 ppm, $^1J_{\rm PSe}$ = 820 Hz

Salt **16a** undergoes slow decomposition into the diethylphosphorochloridate **18** by steps analogous to those indicated in Scheme 1. In earlier studies in this laboratory the salt **16a** was misidentified as the selenyl chloride **20**.[10] The easy accessibility of the salt **16a** and its relative stability have led to its successful use in organic synthesis.[11]

Reaction of *O,O,O*-trineopentylselenophosphate with sulfuryl chloride

Another object of our studies was *O,O,O*-trineopentylselenophosphate **21**. We hoped to obtain crystalline compounds useful for X-ray studies, but this was not achieved. *O,O,O*-Trineopentylselenophosphate (Bu^{t}CH$_2$O)$_3$P=Se **21** reacts with sulfuryl chloride to afford the phosphonium salt **22a** [eqn. (9)].



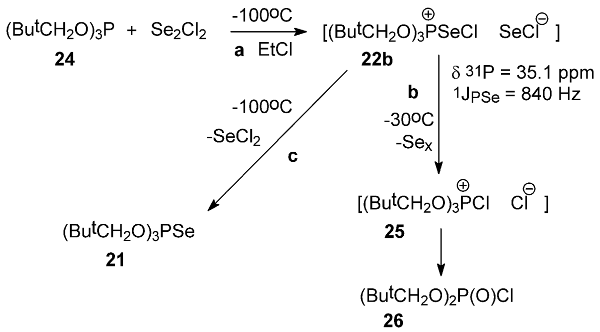
$$\mathrm{(\mathit{t}\text{-}Bu\text{-}CH_2O)_3P{=}Se + SO_2Cl_2 \xrightarrow[CH_2Cl_2]{0^oC} [(\mathit{t}\text{-}BuCH_2O)_3\overset{\oplus}{P}{-}SeCl\ \ \overset{\ominus}{S}O_2Cl]} \qquad (9)$$

21; **22a** $\delta\,^{31}$P = 34.8 ppm, $^1J_{\rm PSe}$ = 847 Hz

Compound **22a** is more stable than salt **16a** containing the ethoxy ligand. As expected a similar reaction with elemental chlorine led to compound **22** [(Bu^{t}CHO)$_3$P$^+$–SeClCl$^-$] ($\delta_{\rm P}$ = 35 ppm, $^1J_{\rm PSe}$ = 838 Hz) which decomposed even at −20 °C. We did not observe formation of the corresponding selenyl chloride (Bu^{t}CH$_2$O)$_2$P(O)SeCl **23**. However the unstable **23** was prepared from *O,O*-dineopentyl-*O*-trimethylsilylselenophosphate.[12]

Additional experiments involving ligand exchange at the phosphorus center and independent synthesis of these systems supported the phosphonium structure of the products obtained from the reaction of *O,O,O*-trialkylselenophosphates with dihalogens.

Formation of the phosphonium salt **22b** was observed at −100 °C in ethyl chloride solution when trineopentyl phosphite **24** was allowed to react with selenium monochloride Se_2Cl_2. In addition to the salt corresponding to the salt **22b** (δ_P = 35.1 ppm, ${}^1J_{PSe}$ = 840 Hz) another signal was noted belonging to *O,O,O*-trineopentylselenophosphate **21**. The latter compound is presumably formed *via* pathway c (Scheme 2).



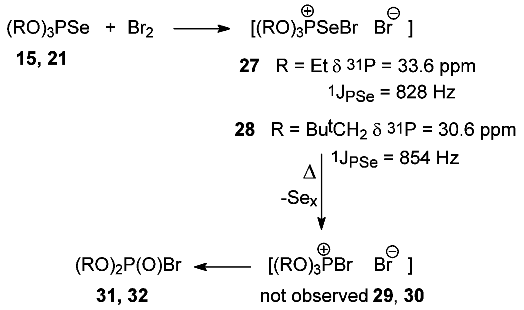
Scheme 2

At −30 °C the product of oxidative addition of Se_2Cl_2 to trineopentylphosphite, **22b** was decomposed into the phosphonium compound **25**. The spectral properties of both salts are in good agreement with analogous phosphonium structures formed when elemental chlorine or sulfuryl chloride are reacted with *O,O,O*-trialkylselenophosphates. Path b in Scheme 2 is likely to involve deselenization of the $SeCl^-$ anion and ligand exchange.

The reaction of *O,O,O*-trialkylselenophosphates with elemental bromine

Interaction of elemental bromine with *O,O,O*-trialkylselenophosphates $(RO)_3P{=}Se$ was investigated in two cases (R = Et, Bu^tCH_2). The corresponding bromoselenophosphonium salts **27**, **28** are formed at 20 °C in dichloromethane solution.

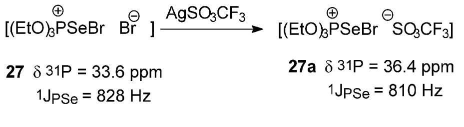
The reactions described in Scheme 3 proceed at temperature as low as −85 °C to give bromoselenophosphonium salts **27** and **28**. However, we were not able to observe the intermediates **29** and **30**.



Scheme 3

The crystalline salt **28** precipitates from dichloromethane solution. Its elemental analysis was in agreement with the proposed structure. Unfortunately under X-ray irradiation **28** underwent decomposition with the precipitation of elemental selenium.

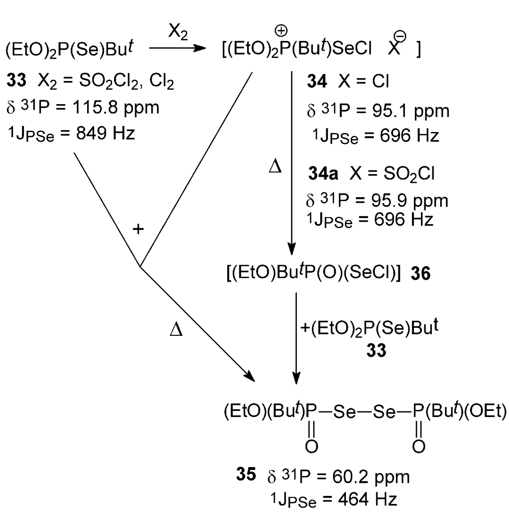
The bromide anion was readily exchanged by the reaction of salt **27** with silver trifluoromethanesulfonate. Salt **27a** is stable at temperatures below −20 °C. Its spectral properties are in agreement with the proposed structure **27a** [eqn. (10)].


$$[(EtO)_3\overset{\oplus}{P}SeBr\ \overset{\ominus}{Br}] \xrightarrow{AgSO_3CF_3} [(EtO)_3\overset{\oplus}{P}SeBr\ \overset{\ominus}{S}O_3CF_3] \quad (10)$$

In all reactions described above concerning interaction of elemental halogens and sulfuryl chloride with $(RO)_3P{=}Se$ compounds we were not able to observe selenyl halides $(RO)_2P(O)$-SeX which could be formed by the dealkylation of intermediate salts **16**, **16a**, **22a** and **27**, **28**.

The reaction of *O,O*-diethyl-*P*-*tert*-butylselenophosphonate with elemental chlorine and sulfuryl chloride

To explain the results presented above, one option is to assume that $(RO)_2P(O)SeX$ structures are exceptionally unstable and undergo rapid deselenization leading to the corresponding halogenoanhydrides $(RO)_2P(O)X$. Another option is that ligand exchange at the phosphonium centers is faster than dealkylation. Ligand exchange is facilitated by higher electrophilicity at the phosphonium center compared with the corresponding sulfur structures due to lower participation of d_π–p_π coupling in P–Se bonding and the presence of a better leaving group –SeX in comparison with –SX. We anticipated that steric hindrance at the phosphorus center would suppress exchange of ligands and not interfere with dealkylation. For this reason *O,O*-diethyl-*P*-*tert*-butylselenophosphonate **33** was employed as a model compound. Salts **34** and **34a** (see Scheme 4) are stable up 0 °C and **34a** transforms at room temperature into bis(phosphinoyl) diselenide among other products. The diselenide **35** is probably formed *via* the reaction of the substrate **33** with the salt **34a** or the $(EtO)Bu^tP(O)SeCl$ **36**.



Scheme 4

The reaction of *O,O*-dimethyl-*P*-phenylselenophosphonate and *O*-methyl-*P,P*-diphenylselenophosphinate with elemental halogens

The interaction of compounds *O,O*-dimethyl-*P*-phenylselenophosphonate **37** and *O*-methyl-*P,P*-diphenylselenophosphinate **38** with elemental chlorine, bromine and sulfuryl chloride led at −100 °C to the halogenoselenophosphonium salts **39**, **40**, **41** and **42** which decompose at 0 °C to the corresponding halogenoanhydrides **43**, **44** and **45**, **46**. We did not observe halogenophosphonium salts $(\equiv PX)^+X^-$ which are formed by ligand exchange. These reactions proceed in a similar manner to those of other types of ≡P=Se compounds. The spectral data for salts **39**, **40** and **41**, **42** are given in Table 1.

The data shown are in agreement with those observed by others [8] for R_3P^+–$SeMeSbCl_6^-$ salts.

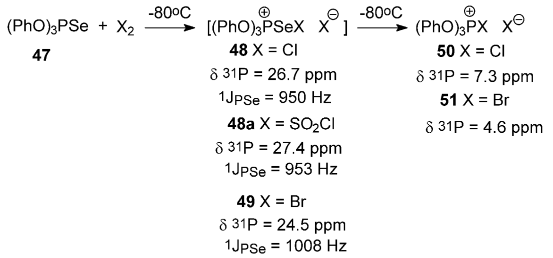
The reaction of *O,O,O*-triphenylselenophosphate with elemental halogens

Halogenoselenophosphonium salts **48**, **48a**, **49** are formed when *O,O,O*-triphenylselenophosphate **47** is allowed to react

Table 1 ^{31}P NMR data collection for compounds **37**–**46**

≡P=Se	=P$^+$SeCl X$^-$	>P(O)X
(MeO)$_2$PhP=Se (**37**)	(MeO)$_2$PhP$^+$SeClX$^-$ (**39**) X$^-$ = SO$_2$Cl$^-$, Cl$^-$	(MeO)PhP(O)Cl (**43**)
δ_P = 98.5	δ_P = 72.7	δ_P = 30.0
$^1J_{PSe}$ = 881 Hz	$^1J_{PSe}$ = 701 Hz	—
	(MeO)$_2$PhP$^+$SeBrBr$^-$ (**40**)	(MeO)PhP(O)Br (**44**)
	δ_P = 69	δ_P = 11.3
	$^1J_{PSe}$ = 696 Hz	—
(MeO)Ph$_2$P=Se (**38**)	(MeO)Ph$_2$P$^+$SeClX$^-$ (**41**) X$^-$ = SO$_2$Cl$^-$, Cl$^-$	Ph$_2$P(O)Cl (**45**)
δ_P = 88	δ_P = 85	δ_P = 45.2
$^1J_{PSe}$ = 788 Hz	$^1J_{PSe}$ = 605 Hz	—
	(MeO)Ph$_2$P$^+$SeBrBr$^-$ (**42**)	Ph$_2$P(O)Br (**46**)
	δ_P = 82.4	δ_P = 71.2
	$^1J_{PSe}$ = 592 Hz	—

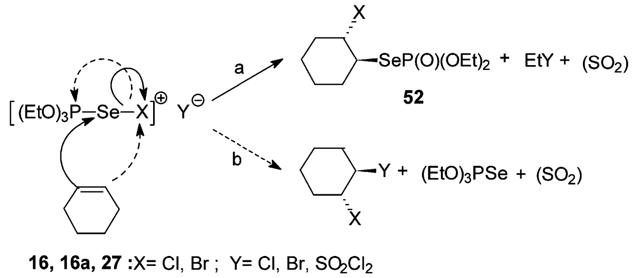
with elemental chlorine, bromine and sulfuryl chloride. They are visibly less stable than the salts derived from *O,O,O*-trialkylselenophosphates and are predisposed to easy ligand exchange due to a higher positive charge at the phosphonium center caused by electronegative ligands [eqn. (11)].



(11)

The reaction of halogenoselenophosphonium salts with cyclohexene

Additional evidence for the structure of salts **16**, **16a** and **27** is their reaction with cyclohexene. Two sets of products are formed indicating the ambident electrophilic character of compounds **16**, **16a** and **27**. This behavior is presented in Scheme 5, disregarding hypothetical unstable intermediates. The addition leads to compounds of *trans* configuration.

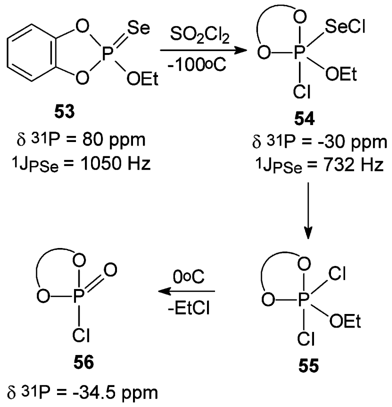


Scheme 5

The total yield of products formed by pathways a and b is high. Low temperatures favor path a. These and similar reactions of selenium containing ambident electrophiles are the subject of our current studies.

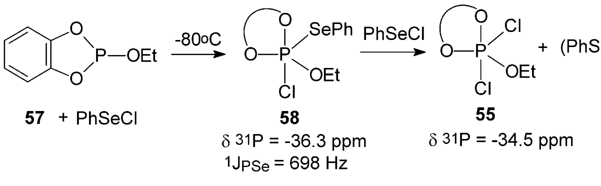
The reaction of *O,O*-phenylene-*O*-ethylselenophosphate with sulfuryl chloride

A significant observation was made when *O,O*-phenylene-*O*-ethylselenophosphate **53** was allowed to react with sulfuryl chloride at −100 °C in ethyl chloride solution. Monitoring of this reaction by ^{31}P NMR showed formation of the pentacoordinate structure **54** containing an SeCl ligand. The phosphorane **54** was gradually transformed into the dichlorophosphorane **55** and finally, after warming to 0 °C, into the chloroanhydride **56** (Scheme 6).



Scheme 6

Transformation of the phosphorane **54** (containing a chloroseleno ligand) into the dichlorophosphorane **55** probably proceeds *via* corresponding phosphonium salts. A similar pentacoordinate structure was obtained in the reaction of ethyl-*O*-phenylene phosphite **57** and phenylselenyl chloride PhSeCl (Scheme 7).



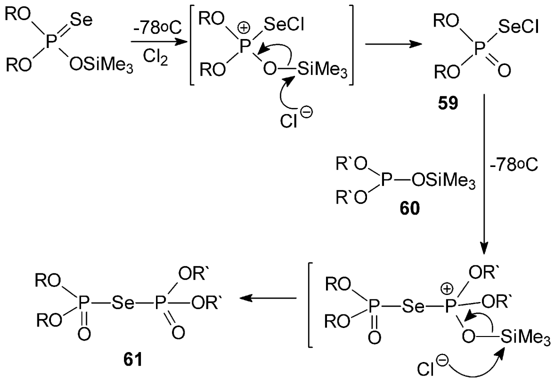
Scheme 7

It is well known that the ligand derived from 1,2-dihydroxybenzene contributes towards the stability of phosphorane pentacoordinate structures. It is also well established that they are in equilibrium with their corresponding tetracoordinate phosphorus salt structures, which are involved in ligand exchange.[13]

Presumably fast equilibrium with the corresponding pentacoordinate structure takes place in all reactions leading to the halogenoselenophosphonium structures described in this paper. However their concentration is too low to be detected by ^{31}P NMR spectroscopy.

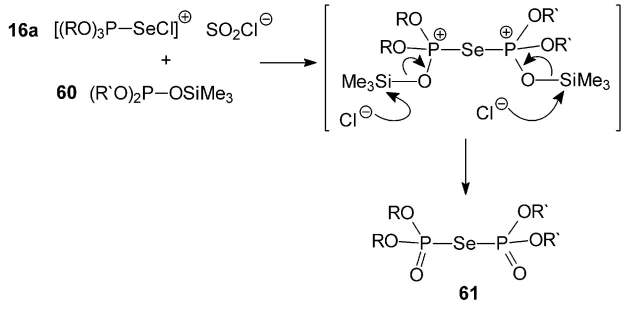
Reaction of *O,O*-dialkyl-*O*-trimethylsilylselenophosphate with elemental chlorine and sulfuryl chloride

This is the only rational approach towards synthesis of compounds $(RO)_2P(O)SeCl$ **59** which are formed at −78 °C almost quantitatively. Because of their high instability they must be used *in situ*. A good illustration of this situation is the synthesis of *sym*-tetraalkyl selenopyrophosphates. The selenyl chloride **59** formed at −78 °C reacts very rapidly with dialkyl trimethylsilylphosphite **60** to give the *sym*-selenopyrophosphates **61** in very high yield[3c] (Scheme 8).



Scheme 8

In the synthesis of selenopyrophosphate **61** however it is more convenient to use a relatively stable phosphonium salt *e.g.* **16a**, which reacts at room temperature to give the desired compound (Scheme 9).



Scheme 9

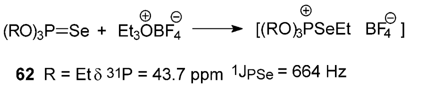
Coupling constants $^1J_{PSe}$ in halogenoselenophosphonium salts

In all halogenoselenophosphonium salts described in this paper $^1J_{PSe}$ values were up to 800 Hz and therefore close to those assigned earlier for seleno compounds ≡P=Se ($^1J_{PSe}$ = 745–1100 Hz).[6] It is known that the presence of positive charge at the phosphorus center leads to higher values of $^1J_{PSe}$.[14] This can be explained by contraction of phosphorus d-orbitals.[15] One can expect that the real structure of halogenoselenophosphonium salts can be described by two resonance forms **A** and **B**.

$$\overset{\oplus}{(RO)_3P{-}SeCl} \longleftrightarrow \overset{\oplus}{(RO)_3P{=}SeCl}$$

A **B**

For comparison we obtained ethylselenophosphonium salts by the alkylation of *O,O,O*-trialkylselenophosphates employing the Meerweine salt [eqn. (12)].



$$(RO)_3P{=}Se + Et_3\overset{\oplus}{O}\overset{\ominus}{BF_4} \longrightarrow [(RO)_3\overset{\oplus}{P}SeEt\ \overset{\ominus}{BF_4}] \qquad (12)$$

62 R = Et δ ^{31}P = 43.7 ppm $^1J_{PSe}$ = 664 Hz

63 R = Bu^tCH_2 δ ^{31}P = 44 ppm $^1J_{PSe}$ = 646.6 Hz

Both $^1J_{PSe}$ coupling constants observed exceeded the values reported for >P(O)–SeR compounds. The high value of $^1J_{PSe}$ has also been noted by other authors for the salts $(EtO)_2P^+(OSiMe_3)SeRX^-$.[15]

It is also known that $^1J_{PSe}$ rises when electronegative substituents are attached to the phosphorus center.[6,16,17] In our case the difference in $^1J_{PSe}$ can be seen when $(RO)_2P(O)SeCl$ (R = Et, $^1J_{PSe}$ = 644 Hz; R = Bu^tCH_2,[12] $^1J_{PSe}$ = 514 Hz) are compared with *O,O*-diethyl-*Se*-ethylphosphate ($^1J_{PSe}$ = 468).[6]

Electrical conductivity of halogenoselenophosphonium salts

Measurements of conductivity provide more strong evidence for the ionic character of halogenoselenophosphonium salts described in this study.

Two solvents of different polarity were used: dichloromethane (ε = 9.08) and 1-nitropropane (ε = 23.2). Conductivity calculated according to the equation $\Lambda_o' = 1/c \times p \times G_o'$ for the concentration 10^{-1} mol is presented in Table 2.

These data indicate that we are dealing with ion pairs whose degree of separation depends on the polarity of the solvent. Our observations of conductivity are analogous to those described for alkyltriphenoxyphosphonium salts described by Hudson and co-workers.[18]

Conclusion

We have examined the interaction of $R^1R^2R^3P{=}Se$ compounds with dihalogens and sulfuryl chloride in solution. We have demonstrated that, in contrast to the structures observed in the solid state, halogenoselenophosphonium salts $[R^1R^2R^3P{-}SeX]^+X^-$ (C) are formed. They undergo deselenization *via* ligand exchange to form phosphonium salts $[R^1R^2R^3P{-}X]^+X^-$ (D) and elemental selenium. Salts (C) derived from *O,O,O*-trialkylselenophosphate are stable enough to be used as convenient electrophilic selenophosphorylating reagents in synthetic procedures.

In the case of reaction between *O,O*-phenylene-*O*-ethylselenophosphates and sulfuryl chloride we observed the formation of pentacoordinate species containing SeCl and Cl ligands which were transformed into dichlorophosphorane. It seems most likely that the phosphonium salts are in dynamic equilibria with the corresponding phosphoranes. The equilibria favour the phosphonium form except when phosphorus bears a ligand, which stabilizes P^V species. But in every case reactions of selenophosphates with dihalogens and sulfuryl chloride proceed with formation of phosphonium salts.

Experimental

Glassware was flame-dried and cooled under a stream of nitrogen and all reactions were performed under a dry argon atmosphere. Solvents were dried by conventional methods and distilled under nitrogen. Triphenylphosphine (Lab BDH Reagent), phenylselenenyl chloride (Aldrich) and dichlorodiselenide (Alfa Product) were used as received. ^1H, ^{13}C NMR spectra were run on a Bruker AC-200 at 200.1 (^1H), 50.32 (^{13}C) using internal $SiMe_4$ (^1H, ^{13}C). ^{31}P NMR spectra were recorded on a FT JEOL FX-60H at 24.3 MHz and on a Bruker AC-200 at 81.02 MHz. Positive chemical shifts were reported in parts per million (ppm) downfield from 85% H_3PO_4 as external standard. $CDCl_3$, CH_2Cl_2, C_6D_6 were used as solvents. IR spectra were taken with ATI MATTSON INFINITY FTIR 60 spectrometer and Carl Zeiss UR-10 spectrometer and Beckman IR-11 spectrometer. Mass spectra were registered on LKB 2091 and Finnigan MAT 95. Microanalyses were obtained on a Carlo Erba CH NS-OEA 1108 Elemental Analyzer. Melting and boiling points were uncorrected.

Table 2 Conductivity of $[(RO)_3P{-}SeX]^+X^-$ species in CH_2Cl_2 (ε = 9.08) and 1-nitropropane (ε = 23.2) ($\Lambda_o{}' = 1/c \times p \times G_o{}'$)

$[(RO)_3P{-}SeX]^+X^-$	Solvent	T/°C	$\Lambda_0\ 10^{-1}/\Omega^{-1}\ cm^2\ mol^{-1}$
$[(EtO)_3P{-}SeCl]^+SO_2Cl^-$ (**16a**)	CH_2Cl_2	+20.2	0.255
$[(Bu^tCH_2O)_3P{-}SeCl]^+SO_2Cl^-$ (**22a**)	CH_2Cl_2	+20.2	0.639
$[(EtO)_3P{-}SeBr]^+Br^-$ (**27**)	CH_2Cl_2	+20.2	0.163
$[(Bu^tCH_2O)_3P{-}SeBr]^+Br^-$ (**28**)	CH_2Cl_2	+20.2	0.1746
$[(Me_2N)_3P{-}SeMe]^+I^-$ (**13**)	CH_2Cl_2	+20.2	49.47
$[(Bu^tCH_2O)_3P{-}SeCl]^+SO_2Cl^-$ (**22a**)	CH_2Cl_2	−30.0	0.995
$[(Bu^tCH_2O)_3P{-}SeCl]^+SO_3CF_3{}^-$ (**22c**)	CH_2Cl_2	−30.0	1.392
$[(Bu^tCH_2O)_3P{-}SeCl]^+SO_2Cl^-$ (**22a**)	$C_3H_7NO_2$	−30.0	2.05
$[(EtO)_3P{-}SeCl]^+SO_2Cl^-$ (**16a**)	$C_3H_7NO_2$	−30.0	7.56
$[(EtO)_3P{-}SeBr]^+Br^-$ (**27**)	$C_3H_7NO_2$	+20.2	25.88
$[(Me_2N)_3P{-}SeMe]^+I^-$ (**13**)	$C_3H_7NO_2$	+20.2	282.98

Table 3 Physical data for the halogenoselenophosphonium salts

Phosphonium compounds	Yield[a] (%)	Stability in solution (rt)	ν(P=Se)/cm^{-1}	δ_P (ppm)	$^1J_{PSe}$/Hz
9 $(Me_2N)_3PSeCl^+Cl^-$	100	3 days	—	70.8	623
10$(Me_2N)_3PSeBr^+Br^-$	100	2 days	—	65.2[f]	652
16a $(EtO)_3PSeCl^+SO_2Cl^-$	100	2 h	513m,522m[c]	39.0	820
22a $(Bu^tCH_2O)_3PSeCl^+SO_2Cl^-$	100	6 h	—	34.8	847
27 $(EtO)_3PSeBr^+Br^-$	100	1 h	510m,545m[c]	33.6	828
28 $(Bu^tCH_2O)_3PSeBr^+Br^-$	100	[b]	519w,579s[d] 550w,570s[e]	30.0	854

[a] From ^{31}P NMR. [b] Precipitate from CH_2Cl_2 solution during evaporation. [c] Carl Zeiss UR-10 (−60 °C, film). [d] ATI MATTSON INFINITY FTIR 60 (CsI, rt). [e] Beckman IR-11 (film, rt). [f] Lit.,[4e] δ_P 66.1.

Materials

1,2-Dichlorocyclohexane,[19a] triethyloxotetrafluoroborate,[20] trineopentyl phosphite,[19b] diethyl trimethylsilyl phosphite,[21] dineopentyl trimethylsilyl phosphite,[21] ethyl-*ortho*-phenylene phosphite,[22] *O,O*-diethyl hydrogen phosphoroselenoate[23] were prepared by literature procedures. *O,O,O*-Triethylselenophosphate,[6] *O,O,O*-triphenylselenophosphate,[24] *O,O*-dimethyl-*P*-phenylselenophosphonate,[8] *O*-methyl-*P,P*-diphenylselenophosphinate,[8] tris(dimethylamino)phosphine selenide,[4d] triphenylphosphine selenide,[4b] tributylphosphine selenide,[6] *O,O,O*-trineopentylselenophosphate [80%, mp 41–43 °C (Found: C, 48.3; H, 8.6; P, 7.98.%. $C_{15}H_{33}O_3PSe$ requires C, 48.5; H, 8.9; P, 8.3%); δ_P 72.6 ($^1J_{PSe}$ 955 Hz)], *O,O*-diethyl-*P*-*tert*-butylselenophosphonate[32] [70%, bp 48–50 °C/0.2 Torr (Found: C, 37.4; H, 7.4; P, 12.0%. Calcd for $C_8H_{19}O_2PSe$: C, 37.2; H, 7.1; P, 12.6%); δ_P 115.8 ($^1J_{PSe}$ 849 Hz)], *O*-ethyl-*O,O*-*ortho*-phenyleneselenophosphate [75%, bp 56–58 °C/0.05 Torr, (Found C, 36.1; H, 3.41; P, 12.01%. $C_8H_9O_3PSe$ requires C, 36.5; H, 3.45; P, 11.77%); δ_P 80.1 ($^1J_{PSe}$ 1050 Hz)], were obtained by addition of dry elemental selenium to the corresponding trivalent phosphorus compounds at 5 °C or 40 °C in dry diethyl ether or benzene.

Conductivity

Specific conductivity at 10^{-1}M was measured utilizing a Radelkis conductometer OK-102, equipped with a standard conductivity cell (p = 0.582 cm^{-1}). Measurements were made in dichloromethane and 1-nitropropane, which were purified according to described procedures.[25] Manipulations involving air-sensitive compounds were performed in a polyethylene glovebag under a dry argon atmosphere. The specific conductivity of solvents and substrates was negligible.

Preparations

General procedure. A solution of sulfuryl chloride or bromine (10 mmol) in dichloromethane (10 cm^3) was added dropwise to a stirred solution of the appropriate selenonophosphate (10 mmol) in CH_2Cl_2 (25 cm^3) at 0 °C. Stirring was continued at the same temperature for 15 min. Crude halogenoselenophosphonium compounds (besides **28**) were not isolated owing to their instability, and were characterized by ^{31}P NMR and in few cases by IR spectra. Their yield, stability and spectral data were collected in Table 3.

$(Bu^tCH_2O)_3PSeBr^+Br^-$ **28** brown solid (88%); mp 43–47 °C (decomp., diethyl ether–benzene) (Found: C, 34.3; H, 6.28; P, 6.1; Br, 29.4%. requires C, 33.9; H, 6.21; P, 5.8; Br, 30.1%); ν_{max}/cm^{-1}(Br–Se–Br) 190 (vs), 157 (w); *m*/*z* (CI, isobutane) 532 [M$^+$ (^{80}Se), 100%], 530 [M$^+$ (^{78}Se), 48.3%].

The reaction of *O,O*-diethyl-*P*-*tert*-butylselenophosphonate 33 with sulfuryl chloride. The reaction of **33** with sulfuryl chloride was performed at −20 °C. ^{31}P NMR spectrum recorded at that temperature revealed the presence of $Bu^t(EtO)_2PSeCl^+SO_2Cl^-$ **34a** (60%) and unchanged substrate **33** (40%). Raising the temperature to 20 °C resulted in the formation of bis(*O*-ethyl-*tert*-butylphosphonyl)diselenide **35** (80%). **33** δ_P (24.3 MHz, $CDCl_3$) 115.8 ($^1J_{PSe}$ 849 Hz); **34a** δ_P (24.3 MHz, $CDCl_3$) 95.9 ($^1J_{PSe}$ 690 Hz); **35** red viscous oil (Found: C, 31.2; H, 6.43; P, 13.4%; $C_{12}H_{28}O_4P_2Se_2$ requires C, 31.6; H, 6.18; P, 13.6%); δ_P (24.3 MHz, $CDCl_3$) 60.2 ($^1J_{PSe}$ 464 Hz); δ_H $CDCl_3$ (200 MHz) 1.21, 1.24 (2 × d, $^3J_{PH}$ 15 Hz, 18 H), 1.34, 1.36 (2 × t, $^3J_{HH}$ 7.0 Hz, 6H), 4.04–4.31 (m, 4H); *m*/*z* (EI, 70 eV) 456 [M$^+$ (^{80}Se),2.6%], 454 [M$^+$ (^{80}Se), 1.2%].

The reaction of bromoselenotriethoxyphosphonium bromide 27 with silver triflate. A solution of silver trifluoromethanosulfonate (3.08 g, 12 mmol) in dry diethyl ether (15 cm^3) was added dropwise at −70 °C to a stirred solution of **27** (freshly prepared) (4.86 g, 12 mmol) in dichloromethane/acetonitrile (1 : 1) (30 cm^3). Stirring was continued at −70 °C and progress of the reaction was monitored by ^{31}P NMR (24.3 MHz, $CDCl_3$) spectroscopy. Complete conversion of **27** into bromoselenotriethoxyphosphonium trifluorosulfonate **27a** was achieved after 10 h. The precipitated silver bromide was filtered off at −30 °C under anhydrous conditions (glovebag), (2.07 g, 92%) and the crude reaction mixture, analysed by ^{31}P NMR spectroscopy at −30°, showed the presence of **27a** (90%), δ_P 36.4 ($^1J_{PSe}$ 810 Hz). The compound **27a** was stable in solution below −20 °C. ^{31}P NMR spectrum recorded at that temperature revealed the presence of a number of unidentified compounds.

The reaction of $(EtO)_3PSeCl^+SO_2Cl^-$ 16a with cyclohexene. A solution of freshly prepared **16a** (1.9 g, 5 mmol) in dichloromethane (15 cm^3) was added by cannula to a stirred solution of cyclohexene (0.45 g, 5.5 mmol) in the same solvent (30 cm^3) at −78 °C. Stirring was continued at −78 °C for 5 h and the reaction mixture was then allowed to warm slowly to ambient temperature. After evaporation of solvent the crude reaction mixture was analysed and was found to contain, by ^{31}P NMR (CDCl$_3$, 81.02 MHz) spectroscopy, selenophosphoric acid *Se*-(2-chlorocyclohexyl)ester *O,O*-diethyl ester **52** (90%) together with *O,O,O*-triethylselenophosphate **15** (10%). Column chromatography (silica gel, eluent C$_6$H$_6$–EtOAc in ratio 1 : 1 v/v) afforded: **52**[10a] (1.3 g, 78%), R*f* 0.5 (C$_6$H$_6$–EtOAc 1 : 1 v/v); δ_P 19.9 ppm ($^1J_{PSe}$ 484 Hz); δ_H (CDCl$_3$, 200 MHz) 1.34 (t, $^3J_{HH}$ 7 Hz, 6H, OCH$_2$C*H*$_3$), 1.71–2.30 (m, 5H), 2.58–2.68 (m, 2H), 2.79 (s, 1H), 3.32 (dt, $^3J_{HH}$ 10.1, 4.4 Hz, *H*C–Cl), 3.61 (ddt, $^3J_{HH}$ 9.8, 4.3 Hz, $^3J_{PH}$ 13.4 Hz, *H*C–SeP), 4.06–4.31 (m, 4H, OC*H*$_2$CH$_3$); δ_C (CDCl$_3$, 50.32 MHz) 15.63, 15.87 (OCH$_2$*C*H$_3$), 22.52 (CH$_2$), 24.22 (CH$_2$), 31.85 (CH$_2$), 33.85 (CH$_2$), 49.41 (s, H*C*–SeP), 62.54 (d, $^3J_{PC}$ 4.3 Hz, H*C*–Cl), 63.51 (d, $^3J_{PC}$ 5.5 Hz, O*C*H$_2$CH$_3$), 65.71 (d, $^3J_{PC}$ 6 Hz, O*C*H$_2$CH$_3$); *m*/*z* (CI, isobutane) 335 [M$^+$ (^{80}Se) +H, 100%], 333 [M$^+$ (^{78}Se) +H, 46.5,%], 297/299 [M$^+$ − Cl], 219 [(M$^+$ − Cl − Se]. **15** (0.068 g, 5.5%), R*f* 0.8 (C$_6$H$_6$–EtOAc 1 : 1 v/v); δ_P 70.8 ($^1J_{PSe}$ 942 Hz); GCMS *m*/*z* 246 [M$^+$ (^{80}Se), 16.6%], 244 [M$^+$ (^{78}Se), 8.5%] [lit.,[6] δ_P 71.8]. *trans*-1,2-dichlorocyclohexane (0.03 g, 4%), R*f* 0.7 (C$_6$H$_6$–EtOAc 1 : 1 v/v); GCMS *m*/*z* 152 [M$^+$ 0.9%], retention time 379 s (compared with authentic sample: retention time 370 s).

Preparation of ethylselenotriethoxyphosphonium tetrafluoroborate 62. To a solution of triethyloxonium tetrafluoroborate (0.95 g, 5 mmol) in 1-nitropropane (20 cm^3) a solution of *O,O,O*-triethylselenophosphate **15** (1.2 g, 20 mmol) in CH$_2$Cl$_2$ (5 cm^3) was added dropwise at −80 °C. Stirring was continued at that temperature for 48 h. The reaction was monitored and the reaction mixture was found by ^{31}P NMR spectroscopy, to contain **62** (30%) together with unchanged substrate (70%). The reaction mixture was then allowed to warm to 0 °C and stirred at that temperature for 48 h. ^{31}P NMR spectrum recorded at 0 °C revealed of the presence of **62** (70%) and **15** (30%). **62** δ_P 43.7 ($^1J_{PSe}$ 664 Hz) (stable for 5 h in CH$_2$Cl$_2$–1-nitropropane solution). All attempts to obtain pure **62** failed because of its instability.

Preparation of *O,O,O,O*-tetraethyl-*sym*-monoselenopyrophosphate 61. A solution of freshly prepared **16a** (0.42 g, 1.1 mmol) in dichloromethane (5 cm^3) was added by cannula to a stirred solution of diethyl trimethylsilyl phosphite **60** (0.23 g, 1.1 mmol) in CH$_2$Cl$_2$ (2 cm^3) at 0 °C and stirring was continued for 24 h at that temperature. Solvent was evaporated under reduced pressure to afford crude **61** (0.34 g, 88%), δ_P 11.5 ($^1J_{PSe}$ 427 Hz) [lit.,[3c] δ_P 11.8 ($^1J_{PSe}$ 425 Hz)]; ν_{max}/cm^{-1} (film) (P=O) 1230 (s), (POC) 1030 (s), (P=Se) 420 (w); *m*/*z* (CI, isobutane) 355 [M$^+$ (^{80}Se) + H, 100%], 353 [M$^+$ (^{78}Se) + H, 49.2%], 217/219 [C$_4$H$_{11}$O$_3$PSe, 5.3/11.2%].

Preparation of dibromo(triphenylphosphine)selenium(II), Ph$_3$PSeBr$_2$. From triphenylphosphine selenide **3** (0.55 g, 1.6 mmol) and bromine (0.23 g, 1.4 mmol) Ph$_3$PSeBr$_2$ was obtained as a yellow powder, according to the procedure of Williams and Wynne.[4b] Ph$_3$PSeBr$_2$: (0.53 g, 75%) mp 90 °C (decomp.); δ_P (CDCl$_3$, 81.02 MHz) 50.7 (br s), δ_P (C$_6$D$_6$, 81.02 MHz) 42.0 (br s); CP/MAS solid state ^{31}P NMR spectrum was recorded at 121.46 MHz (Bruker 300 DSX) δ_P 42.13 (br s) [lit.,[5] δ_P 51.96]. Ph$_3$P$^+$BrBr$^-$ δ_P (CDCl$_3$, 81.02 MHz) 50.6 (br s).

Low-temperature ^{31}P NMR measurements

A 10 mm NMR tube (cooled in liquid N$_2$ or acetone–solid CO$_2$) was charged with the compounds (0.5–1 mmol) in dichloromethane or ethyl chloride. All operations were carried out in a dry argon atmosphere. The tubes were closed tightly with rubber septa. Variable-temperature spectra were recorded on a JEOL-60H spectrometer at 24.3 MHz, and monitored usually at intervals of 10 °C and 10 min. Phosphoric acid (85%) was run prior to all samples where the chemical shift was to be determined.

Reactions of tributylphosphine selenide 6 [run (1)], triphenylphosphine selenide 3 [run (2)] with elemental chlorine and a triphenyl phosphine with selenium chloride [run (3)]. ^{31}P NMR (C$_2$H$_5$Cl, 24.3 MHz) spectra recorded at −90 °C reveals the presence of:

1) [Bu$_3$PSeCl]$^+$Cl$^-$ **7** (40%) and Bu$_3$P$^+$ClCl$^-$ **8** (60%). **7** δ_P 60.5 ($^1J_{PSe}$ 498 Hz); **58** δ_P 103.7 [lit.,[26] δ_P 105].

2) [Ph$_3$PSeCl]$^+$Cl$^-$ **4** (70%) and Ph$_3$P$^+$ClCl$^-$ **5** (30%). **4** δ_P 51.9 ($^1J_{PSe}$ 544 Hz); **5** δ_P 65.6 [lit.,[26] δ_P 63].

3) [Ph$_3$PSeCl]$^+$SeCl$^-$ **4a** (40%), triphenylphosphine selenide **3** (40%) and Ph$_3$P$^+$ClCl$^-$ **5** (20%). **4a** δ_P 52 ($^1J_{PSe}$ 544 Hz); **3** δ_P 34 ($^1J_{PSe}$ 761 Hz) [lit.,[6] δ_P 36]; **5** δ_P 65.

Raising the temperature to −40 °C resulted in the formation of:

1) Bu$_3$P$^+$ClCl$^-$ **8** (100%).

3) **3** (40%) and Ph$_3$P$^+$ClCl$^-$ **5** (60%) and after raising the temperature to 0 °C:

2) Ph$_3$P$^+$ClCl$^-$ **5** (100%) was found by means ^{31}P NMR spectroscopy.

Reactions of *O,O*-dimethyl-*P*-phenylselenophosphonate 37 and *O*-methyl-*P,P*-diphenylselenophosphinate 38 with sulfuryl chloride, elemental chlorine and elemental bromine. From **37** and surfuryl chloride and elemental chlorine a crude reaction mixture was obtained at −90 °C and found by means of its ^{31}P NMR (C$_2$H$_5$Cl, 24.3MHz) spectrum to contain **39** (100%). **39** (MeO)$_2$PhPSeCl$^+$SO$_2$Cl$^-$ (Cl)$^-$ δ_P 72.7 ($^1J_{PSe}$ 701 Hz). After raising the temperature to −10 °C ^{31}P NMR spectrum recorded at that temperature reveals the presence of methyl phenyl chlorophosphonate **43** δ_P 30.0 [lit.,[27] δ_P 29.5].

From **37** and elemental bromine the crude **40** (MeO)$_2$PhPSeBr$^+$Br$^-$ (100%) was obtained at −90 °C. **40** δ_P 69 ($^1J_{PSe}$ 696 Hz). Raising the temperature to −30 °C resulted in the formation of methyl phenyl bromophosphonate **44** δ_P 11.3.

From **38** and sulfuryl chloride and elemental chlorine (MeO)Ph$_2$PSeCl$^+$SO$_2$Cl$^-$ (Cl)$^-$ **41** (100%) was obtained at −80 °C, δ_P 85 ($^1J_{PSe}$ 605 Hz). Complete conversion of **41** into diphenyl phosphinoyl chloride **45** was achieved after raising the temperature to −20 °C. **45** δ_P 45.2 [lit.,[28] δ_P 42.7].

From the reaction of **38** and elemental bromine, performed at −85 °C the crude (MeO)Ph$_2$PSeBr$^+$Br$^-$ **42** (100%) was obtained and after raising the temperature to −40 °C was found by means ^{31}P NMR (C$_2$H$_5$Cl, 24.3MHz) recorded at that temperature to have converted completely (100%) into diphenyloxybromophosphine **46**. **42** δ_P 82.4 ($^1J_{PSe}$ 592 Hz). **46** δ_P 71.2 [lit.,[29] δ_P 78.4].

Reactions of *O,O,O*-triphenylselenophosphate 47 with sulfuryl chloride [run (1)], and elemental chlorine [run (2)] and bromine [run (3)]. ^{31}P NMR (CH$_2$Cl$_2$, 24.3MHz) spectra recorded at −80 °C reveals the presence of:

1) (PhO)$_3$PSeCl$^+$SO$_2$Cl$^-$ **48a** (60%) and (PhO)$_3$P$^+$ClCl$^-$ **50** (40%). At −20 °C the only product is **50**. **48a** δ_P 27.4 ($^1J_{PSe}$ 953 Hz), **50** δ_P 7.3 [lit.,[30] δ_P 7.0].

2) (PhO)$_3$PSeCl$^+$Cl$^-$ **48** (35%) and (PhO)$_3$P$^+$ClCl$^-$ **50** (65%). At −50 °C the only product is **50**. **48** δ_P 26.7 ($^1J_{PSe}$ 950 Hz), **50** δ_P 7.3.

3) (PhO)$_3$PSeBr$^+$Br$^-$ **49** (80%) and (PhO)$_3$P$^+$BrBr$^-$ **51** (20%). Raising the temperature to −60 °C resulted in the formation of **51** (100%). **49** δ_P 24.5 ($^1J_{PSe}$ 1008 Hz), **51** δ_P 4.6 [lit.,[30] δ_P 3.6].

Reaction of ethyl *ortho*-phenylene phosphite 57 with phenylselenyl chloride. The reaction of **57** with PhSeCl was performed at −80 °C. The reaction mixture, analysed by ^{31}P NMR (CH_2Cl_2, 24.3MHz) spectroscopy, showed the presence of unchanged substrate **57** (30%) and the phosphorane **58** (70%) δ_P −36.3 ($^1J_{PSe}$ 698 Hz). Raising the temperature to −50 °C resulted in the formation of 2,2-dichloro-2-ethoxy-1,3,2λ^5-benzodioxaphosphole **55** (80%) δ_P −34.6 [lit.,[31] δ_P −34.5 ppm] and diphenyl diselenide, identified by GC (analysis of crude reaction mixture at rt), by comparison with authentic samples.

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