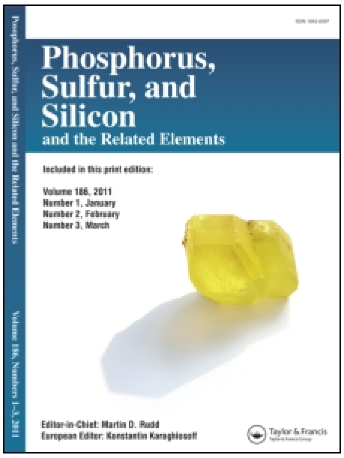

**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# REACTION OF THIOLO AND SELENOLO ESTERS OF PHOSPHORUS ACIDS WITH HALOGENS. 4. HALOGENOLYSIS OF O,O-DINEOPENTYL Se-METHYL (PHENYL) PHOSPHOROSELENOATES

B. Krawiecka[a]
[a] Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Łódź, Poland

**To cite this Article** Krawiecka, B.(1991) 'REACTION OF THIOLO AND SELENOLO ESTERS OF PHOSPHORUS ACIDS WITH HALOGENS. 4. HALOGENOLYSIS OF O,O-DINEOPENTYL Se-METHYL (PHENYL) PHOSPHOROSELENOATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 62: 1, 199 — 210

**To link to this Article: DOI:** 10.1080/10426509108034477

**URL:** http://dx.doi.org/10.1080/10426509108034477

*Phosphorus, Sulfur, and Silicon,* 1991, Vol. 62, pp. 199–210
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# REACTION OF THIOLO AND SELENOLO ESTERS OF PHOSPHORUS ACIDS WITH HALOGENS. 4. HALOGENOLYSIS OF O,O-DINEOPENTYL Se-METHYL (PHENYL) PHOSPHOROSELENOATES

B. KRAWIECKA
*Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies,*
*Sienkiewicza 112, 90-363 Łódź, Poland*

*(Received March 4, 1991; in final form March 26, 1991)*

It has been demonstrated that the reaction of the title phosphoroselenoates with halogens and sulphuryl chloride occurs more readily than that of sulphur analogues. The participation of diphosphorus intermediates, $(NeoO)_2\overset{+}{P}(SeR)OP(O)(ONeo)_2X^-$ has been shown. It was found, that the increased leaving ability of —SeR group strongly influences the decomposition pathways of the latter compounds, leading to the different compositions of the final reaction products from those observed previously for the same reactions of analogous thiolo esters.

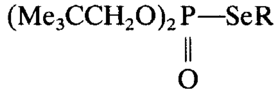
*Key words:* Phosphoroselenoates; halogens; sulphuryl chloride; halogenolysis; phosphorohalogenates; phosphoryloxyphosphonium salts.

## INTRODUCTION

In previous works,[1–6] it was demonstrated that the reaction of thioloesters of phosphorus acids with halogens and sulphuryl chloride involves the transient formation of halo(phosphoryl)sulphonium $>P(O)\overset{+}{S}(X)R\ Y^-$ and phosphoryloxyphosphonium $>\overset{+}{P}(SR)OP(O)<\ X^-$ salts as intermediates. It was observed, that both the reaction of the formation of intermediates and the decomposition of the latter to the reaction products are strongly influenced by the structural factors and the reaction parameters.

Therefore, it was interesting to examine the effect on the reaction course of the replacement of sulphur atom in the studied system by selenium.

The preliminary results[2] showed that generally the reaction of selenolo esters of phosphorus acids with halogens is considerably accelerated and in some cases the reaction intermediates could be observed even in broader range of temperatures than in the case of sulphur analogues. These observations prompted us to undertake a more systematic investigation of the reaction of phosphorus selenolates of varied structure with halogens. This paper presents the full results concerning the reaction of O,O-dineopentyl Se-methyl and Se-phenyl phosphoroselenoates **1a–b**, demonstrating some differences in the reaction course in comparison with sulphur analogues.



$$(Me_3CCH_2O)_2P(=O)—SeR$$

**1a**: R = Me
**1b**: R = Ph

## RESULTS

### *Reaction of Se-methyl O,O-Dineopentyl Phosphoroselenoate* **1a** *with Sulphuryl Chloride and Elemental Halogens*

The reactions of ester **1a** with $SO_2Cl_2$ and halogens were carried out both in methylene chloride and toluene under the same conditions as described previously[1] for sulphur analogue of **1a**. All reactions were followed by $^{31}P$ NMR spectroscopy in the most cases at the variable temperatures. The reaction products were identified by $^{31}P$ NMR spectroscopy and GC or GC/MS analysis. The reaction of ester **1a** with sulphuryl chloride and halogens was expected to proceed faster than that of sulphur analogue for two reasons:

(i) the selenium atom has a stronger donor character[7] towards halogens, so the haloselenonium salt **3** which, according to our previous experience,[5,6] is the obvious reaction intermediate, should be formed more readily than the corresponding sulphonium salt;

(ii) The P—Se bond is weaker than the P—S bond,[8] so the second reaction step, which probably in most cases determines the reaction rate, ought to be facilitated as well.

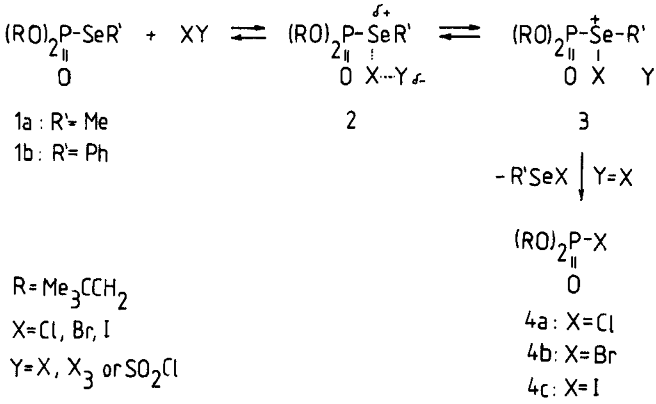
Table I presents the results of the reaction of ester **1a** with sulphuryl chloride in both methylene chloride and toluene in the temperature range 183–293 K. It was found, that the behaviour of the ester **1a** is in agreement with the expectation: ester **1a** disappears from the reaction medium considerably faster than the sulphur analogue under the same condition.[1] It is also observed, that the chemical shift of **1a** in the reaction mixture is at 183 K shifted ca. 7 ppm towards low field in comparison with pure ester **1a** and the coupling constant $J_{P\text{-}Se}$ is increased by 12

TABLE I

$^{31}P$ NMR analysis[a] of the reacting system **1a** + $SO_2Cl_2$ in $CH_2Cl_2$ (toluene)

| Compounds present in the reaction mixture | Temp., K | 183 | 203 | 223 | 243 | 273 | 293 |
|---|---|---|---|---|---|---|---|
| **1a** | | 75(100) | 16(75) | 10(24) | 13(13) | 15(8) | –(–) |
| **5a** | | 16(–) | 33(13) | 16(17) | 6(20) | –(–) | –(–) |
| **4a** | | 4(–) | 7(7) | 5(19) | 10(26) | 9(50)[b] | 5(54) |
| **15** | | 3(–) | 4(–) | 6(–) | 13(–) | 18([b]) | 20(13) |
| **16a** | | –(–) | 12(–) | 15(–) | –(4) | –(–) | –(–) |
| **19** | | –(–) | 20(4) | 38(22) | 51(26) | 51(42) | 65[c](33) |

[a] Relative integrals of $^{31}P$ NMR signals, %.
[b] **4a** + **15** together.
[c] Additionally **18** (2%) and **20** (8%) were present.



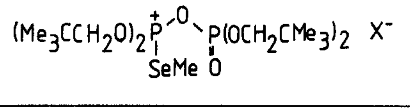
SCHEME I

Hz. Such spectroscopic picture is probably due to the equilibrium **1a** + $SO_2Cl_2 \rightleftarrows$ **2a** $\rightleftarrows$ **3a** (Scheme I). The increase of $J_{P\text{-}Se}$ may be an effect of the presence of the formal positive charge at the selenium atom in **3a**.[9] For the sulphur analogue of **1a** under the similar conditions $\Delta\delta_p$ is only 2.1 ppm. That means that the above equilibrium is shifted in the favour of the selenonium salt **3a** to the greater extent than in the reacting system $(NeoO)_2P(O)SMe + SO_2Cl_2$.

The $^{31}P$ NMR spectrum of the reacting system **1a** + $SO_2Cl_2$ in methylene chloride shows in the temperature range 183–223 K the characteristic doublet of doublets, which is attributed to intermediate **5a** containing two phosphorus atoms. Its chemical shifts (given in Table II) are in the same range as those observed previously for the sulphur analogue.[1] Interestingly, further reaction pathways of salt **5a** differ considerably from those of sulphur analogue. In the reaction of dineopentyl S-methyl phosphorothiolate with sulphuryl chloride dineopentyl phosphorochloridate **4a** is formed practically exclusively; the reacting system **1a** + $SO_2Cl_2$ in $CH_2Cl_2$ at 193 K already shows the presence of several other compounds, among which tetraneopentyl pyrophosphate **19** is the main product. In addition to **4a** and **19**,

TABLE II

$^{31}P$ NMR chemical shifts[a] and coupling constants of phosphonium salt **5a–c**.



$$(Me_3CCH_2O)_2\underset{SeMe}{\overset{+}{P}}{-}O{-}\underset{O}{\overset{\|}{P}}(OCH_2CMe_3)_2\ X^-$$

| No. of compound | $X^-$ | $\delta_{P^+}$, ppm | $\delta_{P(O)}$, ppm | $J_{POP}$, Hz | $J_{P\text{-}Se}$, Hz | Temp.[b], K | Solvent |
|---|---|---|---|---|---|---|---|
| **5a** | $SO_2Cl$ | 38.07 | −14.10 | 29.3 | | 203 | toluene |
| **5a** | $SO_2Cl$ | 37.66 | −12.89 | 26.9 | 627 | 203 | $CH_2Cl_2$ |
| **5b** | $Br(Br_3)$ | 38.12 | −13.04 | 29.3 | | 203 | toluene |
| **5b** | $Br(Br_3)$ | 38.82 | −12.99 | 26.7 | 657 | 213 | $CH_2Cl_2$ |
| **5c** | $I(I_3)$ | 35.25 | −13.65 | 29.3 | | 263 | toluene |

[a] $\delta_P$(24.3 MHz).
[b] Temperature of measurement.

dineopentyl phosphorochloridoselenonate **16a**, and neopentyl phosphorodichloridate **15** are formed. At room temperature, phosphorochloridoselenonate **16a** disappears, and in the reaction mixture in addition to **4a, 15** and **19**, triphosphate **18** and trineopentyl phosphate **20** (8%) are observed. It could be supposed that pyrophosphate **19** would come from the attack of dineopentyl phosphate on the phosphoryl centre of selenonium salt **3**, phosphonium salt **5**, or phosphorochloridate **4a**, while dineopentyl phosphate forms from the same species by an attack of water (either from solvent or from the outside).

However, the careful analysis of the $^{31}P$ NMR spectra of all examined systems and the results of the additional experiments, contradicts such assumption. This problem will be discussed in detail in Discussion.

The spectroscopic picture of the reacting system **1a** + $SO_2Cl_2$ in toluene is generally similar to that observed for the same reactants in methylene chloride (Table 1, data in parenthesis). However, ester **1a** disappears more slowly from the reacting mixture and it is visible up to 273 K. In the temperature range 213–233 K the signal of ester **1a** is splitted into two distinct signals with the chemical shifts $\delta_{P_1}$ +23.17 ($\Delta\delta$ 5.44 ppm) and $\delta_{P_2}$ +20.34 ($\Delta\delta$ 1.61 ppm). It seems plausible that at low temperature the equilibrium **1a** + $SO_2Cl_2 \rightleftarrows$ **2a** $\rightleftarrows$ **3a** is frozen and **2**, or **2** $\rightleftarrows$ **3** is visible in addition to **1**. The $^{31}P$ NMR spectrum of **1a** + $SO_2Cl_2$ in toluene shows the formation of the intermediate **5a** in considerable amount. This picture is different from one observed for sulphur analogue, where only a minute amount of $(NeoO)_2\overset{+}{P}(SR)OP(O)(ONeo)_2\ SO_2Cl^-$ was visible under the same conditions. The course of the reaction of **1a** with $SO_2Cl_2$ in toluene is the same as observed for the reaction in methylene chloride. The formation of phosphorochloridoselenonate **16a** takes place similarly as in the previous experiment, however, the final yield of the dineopentyl phosphorochloridate **4a** is higher (54%) than for the system **1a** + $SO_2Cl_2$ in methylene chloride.

The reaction of **1a** with elemental chlorine in the solvent mixture $CH_2Cl_2$-$CCl_4$ (2.5 : 1.5) is so fast that even at the temperature 193 K only the reaction products: chloride **4a**, pyrophosphate **19** and traces of phosphate **18** are visible. No reaction intermediates could be observed.

The $^{31}P$ NMR spectrum of the reacting system **1a** + $Br_2$ in methylene chloride shows that ester **1a**, in agreement with expectation, reacts with bromine faster than the sulphur analogue. Already at 183 K ester **1a** is absent in the reaction mixture and intermediate **5b** is relatively stable (due to the low nucleophilicity of $Br^-$ and/or $Br_3^-$) (Table III). The salt **5b** disappears above 273 K and the final products are formed: dineopentyl phosphorobromidate **4b** (23%) and tetraneopentyl pyrophosphate **19** (36%) contaminated with dineopentyl phosphate (11%) and unidentified products with chemical shifts $\delta_P$ −22.15 and −36.55.

The reacting system **1a** + $Br_2$ in toluene (Table III, data in parenthesis) transforms slower. At low temperature, the mixture was not homogeneous and only a very low concentration of the intermediate **5b** was observed in the $^{31}P$ NMR spectra. At room temperature, among the reaction products phosphorobromidate **4b** (30%) and pyrophosphate **19** (10%) in addition to the unchanged starting ester **1a** (32%), dineopentyl phosphate (15%) and the unidentified product, $\delta_P$ −40.19 (11%) were found. After the reaction mixture was stored at room temperature for 24 hrs, the signal of the ester **1a** showed to be splitted similarly as it was observed for the

TABLE III

$^{31}$P NMR analysis[a] of the reacting system **1a** + $Br_2$ in $CH_2Cl_2$ (toluene)

| Compounds present in the reaction mixture | Temp., K | 183 | 203 | 223 | 243 | 273 | 293 |
|---|---|---|---|---|---|---|---|
| **1a** (or **1a** ⇄ **2b** ⇄ **3b**) | | −(88) | −(79) | −(64) | −(61)[b] | −(41) | −(32) |
| **5b** | | 79(10) | 77(10) | 18(3) | 6(−) | 4(−) | −(−) |
| **4b** | | −(1) | 8(5) | 14(19) | 22(21) | 23(24) | 23(30) |
| **19** | | −(−) | 4(4) | 22(6) | 26(5) | 26(7) | 36[c](10)[d] |

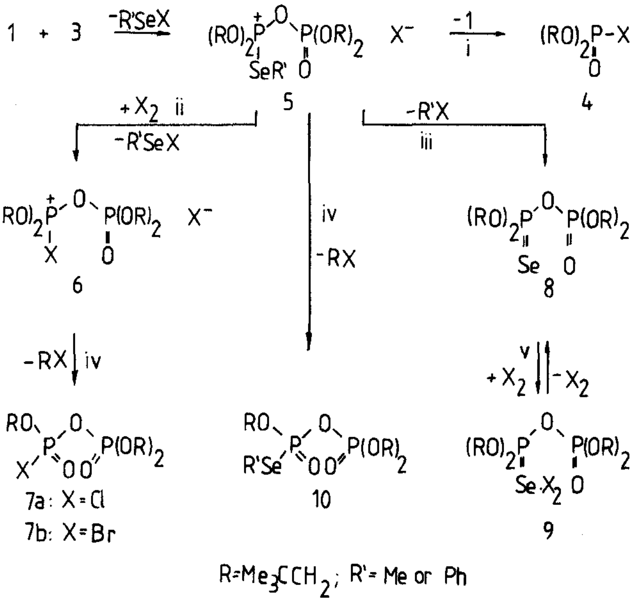
[a] Relative integrals of $^{31}$P NMR signals, %.

[b] $\delta_P$ + 27.39 br. ($\Delta\delta$ 8.66), $J_{P\text{-}Se}$ ca. 535 Hz ($\Delta J$ 69 Hz).

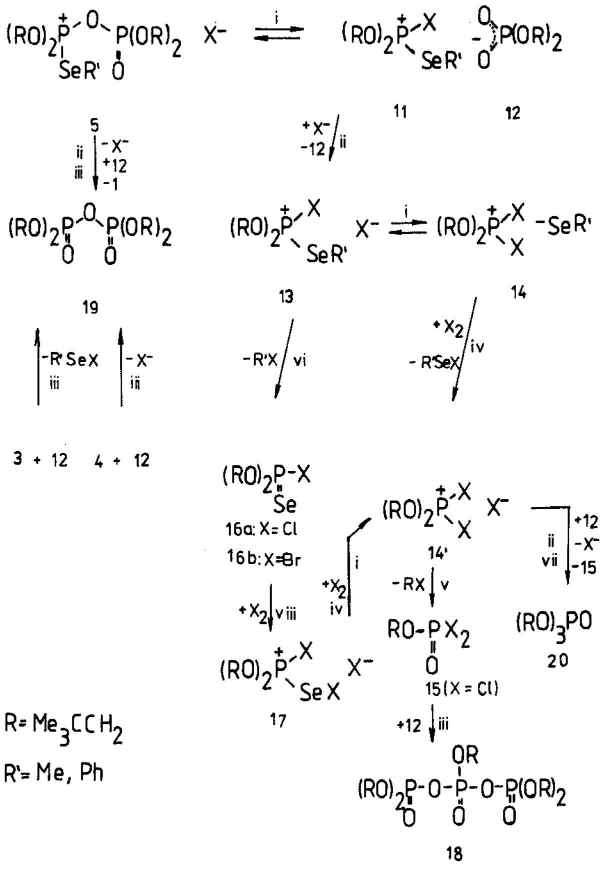
[c] Additionally dineopentyl phosphate (11%) and unidentified product $\delta_P$ −37.61 ppm (23%) were observed.

[d] Additionally dineopentyl phosphate (15%) and $\delta_P$ −40.19 (11%) were found.

reacting system **1a** + $SO_2Cl_2$ in toluene. The chemical shifts of two peaks were: $\delta_{P_1}$ +23.87 ($\Delta\delta$ 5.14 ppm) and $\delta_{P_2}$ +20.24 ($\Delta\delta$ 1.51 ppm). The GC/MS analysis of the reaction mixture showed in addition to the above mentioned reaction products the presence of phosphorobromidoselenonate **16b**, unsymmetrical selenopyrophosphate **8** and probably O-trineopentyl Se-methyl pyrophosphate **10**. The formation of these compounds can be explained assuming that the stabilization of salt **5b** occurs mainly via the pathways iii and iv (Scheme II) and ii, vi (Scheme III). These pathways were observed only when **1a** was caused to react with the higher halogens. The most spectacular difference in the reactivity of ester **1a** and its sulphur analogue was observed in the case of the reaction of **1a** with iodine (Table IV).



SCHEME II Proposed routes of the stabilization of **5**. Paths: i, attack of $X^-$ on phosphoryl P; ii, exchange of anions, followed by halogenation of $R'Se^-$; iii, attack of $X^-$ on carbon attached to Se; iv, attack of $X^-$ on carbon attached to O; v, formation of complex (or salt) with halogen.



SCHEME III Proposed routes to the formation of **15**, **16**, **18**, **19**, and **20**. Paths: i, ligand exchange at phosphonium P, ii, exchange of anions; iii, attack of anion **12** on phosphoryl P; iv, halogenation of $RSe^-$ anion; v, attack of $X^-$ anion on carbon attached to O; vi, attack of $X^-$ anion on carbon attached to Se; vii, attack of anion **12** on carbon attached to O; viii, reaction with halogen.

TABLE IV

$^{31}P$ NMR analysis of the reacting system **1a** + $I_2$ depending on the ratio of $I_2$/**1a**, solvent, time and temperature

| Ratio $I_2$/**1a** | Solvent | Time, min. | Temp., K | Compounds present in the reaction mixture **1a**[a] | **5c** | **4c** | **19** | **8** · $I_2$ |
|---|---|---|---|---|---|---|---|---|
| 1 | benzene | 30 | 293 | 69 | — | 22 | 6 | — |
| | | 2880 | 293 | 5 | — | 15 | 16 | 13 |
| 1 | $CH_2Cl_2$ | 30 | 273 | 98 | — | trace | — | — |
| | | 4320 | 293 | 33[b] | — | 41 | 28 | — |
| 1.8 | toluene | 60 | 263 | 53 | 8 | 35 | 4 | — |
| | | 90 | 283 | 18 | — | 66 | 14 | — |

[a] Or **1a** + $I_2 \rightleftarrows$ **2a** $\rightleftarrows$ **2b**.

[b] $\delta_P$ (24.3 MHz) +29.11 ($\Delta\delta$ 10.38 ppm).

While O,O-dineopentyl S-methyl phosphorothiolate practically does not react with iodine even at room temperature,[1] the reacting system **1a** + $I_2$ in methylene chloride under such conditions gives dineopentyl phosphoroiodidate **4c** (41%) and pyrophosphate **19** (12%) in addition to unreacted ester **1a** (43%). The reaction of the ester **1a** with excess of iodine (1 : 1.8 mol) in toluene leads already at 263 K to the formation of the intermediate **5c** (8%) and phosphoroiodidate **4c** (35%). The $^{31}P$ NMR spectrum shows that the signal corresponding to ester **1a** is shifted towards low field and broadened. At the temperature 283 K **1a** has the chemical shift $\delta_P$ +26.49 ($\Delta\delta$ 7.76 ppm), which confirms that the equilibrium **1a** + $I_2 \rightleftarrows$ **2a** $\rightleftarrows$ **3a** is shifted to some extent in favour of the intermediates **2a** and/or **3a**. At this temperature in the reaction mixture dineopentyl phosphoroiodidate **4c** is the major product (66%) (Table IV). In some of the experiments with the reacting system **1a** + $I_2$, in addition to the above mentioned reaction products, the unsymmetrical tetraneopentyl selenopyrophosphate **8** was found in the $^{31}P$ NMR spectrum and by GC/MS analysis. Such a direction of the stabilization of the salt **5c** was already mentioned in the reaction of **1a** with bromine. The reaction of **1a** with 3 moles of iodine in benzene gives already 0.5 hr after the reactants were mixed, dineopentyl phosphoroiodidate **4c** in the yield 61%. The elongation of the reaction time leads to a decrease in the amount of phosphoroiodidate **4c**, probably due to the hydrolysis and dealkylation of the reaction product.

The behaviour of the ester **1a** towards iodine confirms the affinity of selenium to iodine, which is known[7] to be much higher in comparison to sulphur.

The situation may be changed when instead of the Se-methyl group Se-phenyl will be introduced to phosphorus ester. Such a change in the structure of phosphoro(phosphino)thiolates caused a dramatic decrease of the reactivity.[6] For this reason, the study of the reaction of O,O-dineopentyl Se-phenyl phosphoroselenoate **1b** seemed to be useful.

### *Reaction of O,O-Dineopentyl Se-Phenyl Phosphoroselenolate* **1b** *with Sulphuryl Chloride and Elemental Halogens*

The ester **1b** was prepared in the reaction of dineopentyl phosphonate with benzeneselenenyl chloride. The low temperature $^{31}P$ NMR spectra of the reacting system **1b** + $SO_2Cl_2$ in methylene chloride show that the ester **1b** reacts slower than **1a**: the starting ester **1b** is present in the reaction mixture in the temperature range 183–293 K.

The reaction intermediate **5** could be observed in unmeasurable amount in the temperature range 243–263 K. At room temperature, the same products as those observed for the system **1a** + $SO_2Cl_2$ were found in the reaction mixture. The reacting system **1b** + $SO_2Cl_2$ in $CH_2Cl_2$ contained **4a** (10%), **15** (11%), **19** (70%) and trineopentyl phosphate **20** (8%). The same system in toluene gave **4a** (39%), **15** (11%), **19** (34%), $P^1,P^2$-trineopentyl $P^2$-chloropyrophosphate **7a** (10%) and neopentyl triphosphate **18** (5%).

The reaction of **1b** with elemental chlorine in the solvent mixture $CH_2Cl_2$—$CCl_4$ (1 : 2.5) was found to proceed too fast to observe any intermediate. At the temperature 193 K only the reaction final products were observed: dineopentyl phosphorochloridate, **4a** (32%), **15** (7%), **19** (47%), **7a** (4%), **18** (traces) and trineopentyl phosphate **20** (7%).

The reacting system **1b** + $Br_2$ in $CH_2Cl_2$ gave dineopentyl phosphorobromidate **4b** (31%), **19** (40%), dineopentyl phosphate (10%) and two unidentified products $\delta_P$ −22.145 ppm and −36.546 ppm, in 24% and 3% yield, respectively. The same system in toluene gave **4b** (32%), $P^1$,$P^2$-trineopentyl $P^1$-bromopyrophosphate **7b** (38%), and unidentified products $\delta_P$ −38.825 ppm (4%) and −24.166, −25.377 ppm. When **1b** was caused to react with either elemental chlorine or bromine, benzeneselenenyl chloride and bromide were isolated and characterized as trichloride and tribromide, respectively.

The difference in the reactivity of the esters **1a** and **1b** can be observed, when **1b** is treated with iodine. The ester **1b** reacts slower, although the difference is not very dramatic. The reactants are mixed in equimolar amounts, and after two hours the reaction mixture consisted of the starting ester **1b** (63%), dineopentyl phosphoroiodidate (28%), tetraneopentyl pyrophosphate (6%) and dineopentyl phosphate (3%).

The reacting system **1b** + $I_2$ in toluene after the same time contains the ester **1b** (83%), phosphoroiodidate **4c** (13%) and dineopentyl phosphate (3%). After the reaction mixture was stored for two weeks, only 3% of the ester **1b** remained and the yield of phosphoroiodidate rose to 55%.

## DISCUSSION

On the basis of the presented results and the knowledge about the reaction of phosphorus thioloesters with halogens, there seems to be no doubt that the reaction of the phosphoroselenoates similarly to thio-analogues involves the formation of the two intermediates: the phosphoryl(halo)selenonium salts **3** and the phosphoryloxyphosphonium salts **5**. The formation of the former is assumed to be a crucial reaction step. The formation of the latter is not the obvious step of the reaction, however, the inspection of the results from the presented studies shows that in the case of such esters as **1a**, the reaction pathway leading to the salts **5** is strongly favoured in comparison with the direct attack of the halogenide anion on the electrophilic phosphorus centre of the intermediate **3**. This assumption is confirmed both by the observation of the considerable amounts of **5** at low temperatures in the $^{31}P$ NMR spectra of the reacting systems and by the presence of the reaction products, which could not be formed without the participation of **5** (e.g. compounds **16, 8, 10**). The observation, that for the systems **1b** + $X_2$ the salts **5** are observed in very minute concentration does not exclude the formation of these salts also in this case. Due to the fact that **1b** reacts with a lower rate, at low temperature the salt **5** does not reach a sufficient concentration to be observable, and at higher temperature it probably decomposes as fast as it forms.

The presence of the considerable amount of pyrophosphate **19** in the reacting mixture of **1a** and **1b** with sulphuryl chloride requires some comment.

As it was described above, **19** and dineopentyl phosphate could come from the hydrolysis of reaction intermediates and product **4**. However, in such a case the ratio of these products should be especially high in the reactions where compounds more susceptible to hydrolysis i.e. phosphorobromide and iodide are formed. This is not the case. This fact and the presence in the reacting system **1a** + $SO_2Cl_2$ of a considerable amount of chloride **16** proves, that when compared to the sulphur analogue, different pathways of decomposition of intermediate **5** play here the dominant role (see Scheme III, pathways i–vi). The phosphonium salt **11** · **12** formed as the product of the ligand exchange at the phosphonium centre of **5** (pathway i) leads probably via pathways ii, vi to the formation of dineopentyl phosphorochloridoselenoate **16**, which is observed in the $^{31}P$ NMR spectra below 273 K.

The chlorination of chloride **16** (Scheme III, pathways viii, i, iv, v) gives the dichloride **15**, which can be formed as well from salt **13** by the ligand exchange and transient formation of **14**, followed by chlorination (Scheme III). For the ester **1b** the latter reaction sequence is the only source of dichloride **15** in the reaction with chlorinating agents. The chlorination of **16** to **15** can be observed in the $^{31}P$ NMR spectra by the stepwise disappearance of **16** during the studied reaction. The independent experiment has confirmed such a course of the chlorination of **16**. Pyrophosphate **19** can be formed by the attack of dineopentyl phosphate anion **12** at the phosphoryl centres of **5**, and/or **3** and **4**.

Certainly, the part of pyrophosphate **19** and the whole amount of dineopentyl phosphate come from the hydrolysis, however the analysis of the experiments with higher halogens shows, that the amount of the hydrolysis products should not exceed 10–15%. In the case of the reaction of **1a** with $SO_2Cl_2$ and $Cl_2$, trineopentyl phosphate was found as one of the reaction side products. Its presence may be explained if we assume that anion **12** acts as dealkylating agent competing with $Cl^-$ in the path vi (Scheme III) and/or iv (Scheme II).

The formation of the intermediates similar to **5** has been demonstrated by Uznański[10] who has followed using $^{31}P$ NMR spectroscopy the reaction of three phosphorus compounds containing selenium with sulphuryl chloride: tetraneopentyl selenopyrophosphate **8**, bis-(dineopentoxyphosphoryl)diselenide and triethylammonium O-dineopentyl phosphoroselenoate. In every case at low temperature, the presence of phosphoryloxyphosphonium salt $(Me_3CCH_2O)_2P(O)O\overset{+}{P}(SeCl)(OCH_2CMe_3)_2\ Cl^-$ has been demonstrated. In the present work, the reaction of triethylammonium O-dineopentyl phosphoroselenoate was reinvestigated with excess (3 moles) of sulphuryl chloride and bromine. Following the course of these reactions in the temperature range 193–293 K by $^{31}P$ NMR spectroscopy, the formation of $(Me_3CCH_2O)_2P(O)O\overset{+}{P}(SeX)(OCH_2CMe_3)_2\ X^-$ (X = Cl,Br) was confirmed. The latter salts in the further reaction steps gave exclusively dineopentyl phosphorochloridate and bromidate, respectively.

The final products **4a** and **4b** were rather pure, they were contaminated only with a little amount (below 10%) of pyrophosphate **19**. The above study was carried out in the same solvent, as the previously described investigation of the esters **1a** and **1b** with sulphuryl chloride and halogens. This means, that the side products observed in the latter reactions derive mainly from the nature of the reaction itself, not from the hydrolysis.

It is noteworthy, that the replacement of alkyl group at the selenium atom by chlorine (bromine) in the structure of salt **5** changes the decomposition pathways

**so dramatically. All results described above confirm, that phosphoryl oxygen is a more potent P-nucleophile than halogenide anions. It should be, however, mentioned that under the reaction conditions, the concentration of halogenide anions $X^-$ is rather low, due to the strong tendency of the latter to coordinate with elemental halogens, resulting in the formation of less nucleophilic trihalogenides, $X_3^-$. This fact is probably very important for the course of the reaction under discussion.**

## EXPERIMENTAL

Melting points were measured on a Boëtius PHMK apparatus and are uncorrected. Solvents and commercial reagents were purified by conventional methods before use. NMR spectra were recorded with JEOL JNM-FX 60FT (24.3 MHz, $^{31}P$) and Bruker MSL 300 (121.5 MHz, $^{31}P$); positive chemical shifts are downfield from external 85% $H_3PO_4$. Products were identified with LKB Model 2091 gas-chromatograph-mass spectrometer and/or $^{31}P$ NMR spectroscopy.

Starting materials.—O,O-Dineopentyl Se-methyl phosphoroselenoate **1a** was synthesized from dineopentyl phosphoroselenoate[10,11] following the method described for the sulphur analogue.[1] $^{31}P$ NMR: $\delta_P$ (24.3 MHz, benzene) +18.73, $J_{P\text{-}Se}$ 466.3 Hz; $\delta_P$ (121.5 MHz, $CDCl_3$) +21.183, $J_{P\text{-}Se}$ 475.8 Hz; M.S. m/z (70 eV) 315 ($M^+$, 0.8%), 231(14), 179(14), 177(79), 175(36), 71(79), 70(26), 57(16), 55(42), 43(100), 41(43), 39(14), 29(34), 27(15).

O,O-Dineopentyl Se-phenyl phosphoroselenoate **1b** was obtained by the reaction of benzeneselenenyl chloride[12] with dineopentyl phosphonate.[13] M.p. 53–54°C. $^{31}P$ NMR: $\delta_P$ (24.3 MHz, $CH_2Cl_2$) +15.81; $\delta_P$ (121.5 MHz, $CDCl_3$) +17.993, $J_{P\text{-}Se}$ 479.7 Hz; $\delta_P$ (121.5 MHz, $C_6D_5CD_3$) +16.957, $J_{P\text{-}Se}$ 462.3 Hz. M.S. m/z (70 eV) 378($M^+$ + 1, 11%), 377($M^+$, 1%), 239(15), 238(52), 236(25), 158(11), 157(16), 77(11), 71(61), 57(19), 55(24), 43(100), 41(34), 39(11), 28(25), 26(10).

Benzeneselenenyl chloride[12] was synthesized from the commercial diphenyldiselenide (Aldrich) by chlorination with sulphuryl chloride. The crude product was used in subsequent reactions.

Low Temperature $^{31}P$ NMR Measurements.—The samples were prepared and the spectra recorded as previously[3] described. The concentration of solutions was 0.2–0.3 mol $dm^{-3}$. The composition of the reaction mixtures are presented in Tables I, III, IV. The chemical shifts of the intermediates **5** are given in Table II. Spectral characteristics of the reaction final products are shown in Table V. The experimental details are given below only in the cases when the components in the reaction mixtures were additionally identified by GC/MS method or elemental analysis.

*Reaction of O,O-dineopentyl Se-methyl phosphoroselenoate* **1a** *with sulphuryl chloride.* ($^{31}P$ NMR data are given in Table I). The red reaction mixture at room temperature decolourized spontaneously and elemental selenium precipitated. Selenium was removed by decantation, the solvent evaporated, and the residue was analysed by GC-MS (70 eV). The reaction mixture contained **15**, m/z 139 ($M^+ - 64$, 1.5%), 137($M^+ - 66$, 3%), 135(M − 68, 4%), 57(100); **4a**, m/z 260 ($M^+$, 0.2%), 71(100); **19**, m/z 458 ($M^+$, 0.2%), 192(100).

*Reaction of* **1a** *with bromine in toluene.* ($^{31}P$ NMR data given in Table III). The reaction mixture at room temperature was evaporated and the residue was analysed by GC-MS (70 eV). The reaction mixture contained p-bromotoluene, m/z 172(M + 2, 41%), 170($M^+$, 46%), 91(100); **4b**, m/z 303($M^+ + 3$, 0.5%), 302($M^+ + 2$, 0.2%), 301($M^+ + 1$, 0.4%), 163(11), 161(11), 71(100); **8**, m/z 452($M^+$—$C_5H_9$, 2%), 242(90), 43(100); **16b**, m/z 365($M^+ + 2$, 3%), 363($M^+$, 1%), 226(14), 224(15), 71(100); Se-methyl, O,O,O-trineopentyl selenopyrophosphate, m/z 465($M^+$, 0.5%), 43(100); **19** and **1a**.

*Reaction of O,O-dineopentyl Se-phenyl phosphoroselenoate,* **1b** *with sulphuryl chloride.* Into the cooled (195 K) solution of **1b** (0.2606 g − 0.69 mmol) in $CH_2Cl_2$ (2 ml) placed in NMR tube, sulphuryl chloride (0.0933 g − 0.69 mmol) in $CH_2Cl_2$ (1 ml) was added from a syringe under argon. In the temperature range 195–243 K according to the $^{31}P$ NMR spectroscopy, **1b** was the main product in the reaction mixture. At 283 K a trace amount of $[(Me_3CCH_2O)_2\overset{+}{P}(SePh)OP(O)(OCH_2CMe_3)_2]\ SO_2Cl^-$ in addition to **4a** (2%), **19** (25%) and dineopentyl phosphate (10%) was observed. At room temperature the $^{31}P$ NMR spectrum showed **4a** (10%), **15** (11%), **19** (70%) and trineopentyl phosphate (8%). Chemical shifts of products were in agreement with those given in Table V.

*Reaction of* **1b** *with elemental chlorine.* The reaction was carried out as in the previous experiment, starting from **1b** (0.1741 g − 0.462 mmol) and chlorine (0.096 g − 1.35 mmol) in the solvent mixture

TABLE V

$^{31}$P NMR data (121.5 MHz, $C_6D_5CD_3$) of the reaction products

| Compound | $\delta_P$, ppm | $J_{POP}$, Hz |
|---|---|---|
| **4a** | $+5.404$ | |
| **4b** | $-7.38^{a,b}$ | |
| **4c** | $-39.156^{b}$ | |
| **7a** | $-7.744$(d)<br>$-12.828$(d) | 22 |
| **7b** | $-13.057$(d)<br>$-22.473$(d) | 26 |
| **9(X = I)** | $+54.59$(d)$^{c}$<br>$-13.85$(d) | 44 |
| **15** | $+6.010$ | |
| **16a** | $+62.27^{a,d}$ | |
| **18** | $-12.853$(d)$^{e}$<br>$-24.856$(t) | 14 |
| **19** | $-12.705$ | |
| **20** | $+1.792$ | |

[a] $\delta_P$ (24.3 MHz, $CH_2Cl_2$).

[b] Reference 14 reports for **4b** $\delta_P$ (24.3 MHz, $C_2H_5Cl$) $-9.7$ ppm, and for **4c** $-41.0$ ppm.

[c] $\delta_P$ (24.3 MHz, benzene).

[d] **16a** from the reaction of $(Bu^tCH_2O)_2P(Se)OH$ with $PCl_5$ has $\delta_P$ (121.5 MHz, $CDCl_3$) $+64.703$ ppm, $J_{P\text{-}Se}$ 1052 Hz.

[e] In $CDCl_3$.

$CH_2Cl_2$-$CCl_4$ (1:2.5). In the temperature range 193–293 K only the reaction products were observed by $^{31}$P NMR spectroscopy: **4a** (45%) and **19** (55%). Analysis by GC-MS (70 eV) showed the presence of **4a, 19, 7a**, m/z 334 ($M^+$—$C_5H_9$, 28%), 222(100) and trineopentyl phosphate **20**, m/z 210 ($M^+ -98$, 7%), 180(39), 140(100). The reaction mixture was not homogeneous. The separation of the white precipitate gave a crystalline, hygroscopic product (0.0448 g), m.p. 77–83°C. Anal. Found: C, 28.7%; H, 2.4%; Cl, 32.7% corresponds to a mixture of benzeneselenenyl chloride (ca. 25%) and trichloride (ca. 75%). Literature 12 gives for benzeneselenenyl chloride m.p. 59–60°C, for trichloride 133–134°C.

*Reaction of* **1b** *with bromine.* Reaction was carried out as described above. From **1b** (0.1301–0.345 mmol) and bromine (0.0552–0.345 mmol) in $C_6D_5CD_3$ (3 ml) benzeneselenenyl tribromide (0.0692 g – 42%) was obtained. M.p. 97–100°C (Literature 12 reports 105°C). Anal. Calcd. for $C_6H_5Br_3Se$: C, 18.21%; H, 1.27%; Br, 60.57%. Found: C, 18.39%; H, 1.26%; Br, 59.85%. The $^{31}$P NMR spectrum of the liquid reaction mixture showed the presence of **4b** (31%), **7b** (38%) (chemical shifts are given in Table V) and unidentified products, $\delta_P$ $-24.166$ ppm, $-25.777$ ppm and $-38.825$ ppm.

*Reaction of triethylammonuim O,O-dineopentyl phosphoroselenoate with sulphuryl chloride.* Reaction was carried out as described above. Triethylammonium O,O-dineopentyl phosphoroselenoate (0.3743 g – 0.93 mmol) was treated with sulphuryl chloride (0.0038 g – 2.8 mmol) in $CH_2Cl_2$ (3 ml). In the temp. range 193–283 K the $^{31}$P NMR spectra showed the presence of phosphonium salt $[(Me_3CCH_2O)_2\overset{+}{P}(SeCl)OP(O)(OCH_2CMe_3)_2]SO_2Cl^-$, $\delta_{P+}$ $+24.72$(d), $\delta_{P(O)}$ $-14.93$ (d), $J_{POP}$ 44 Hz (Literature 10 reports $\delta_{P+}$ $+25.0$(d), $\delta_{P(O)}$ $-14.6$(d), $J_{POP}$ 44 Hz, $J_{P\text{-}Se}$ 881 Hz; **4a**; of dineopentoxyoxophosphoranesulphenyl chloride, $\delta_P$ $+19.87$ ppm, $J_{P\text{-}Se}$ 642 Hz (Literature 10 reports $+18.5$ ppm, $J_{P\text{-}Se}$ 514 Hz) and of the diselenide $[(Me_3CCH_2O)_2P(O)Se]_2$, $\delta_P$ $+11.71$, $J_{P\text{-}Se}$ 520 Hz (Literature 10 gives $\delta_P$ $+10.9$ ppm, $J_{P\text{-}Se}$ 496 Hz).

*Reaction of triethylammonium O,O-dineopentyl phosphoroselenoate with bromine.* Triethylammonium O,O-dineopentyl phosphoroselenoate (0.2638 g – 0.655 mmol) was caused to react with bromine

(0.3144 g − 1.96 mmol) in $CH_2Cl_2$ (3 ml). In the temp. range 193–253 K the phosphonium salt, $[(Me_3CCH_2O)_2\overset{+}{P}(SeBr)OP(O)(OCH_2CMe_3)_2]\ Br^-\ (Br_3^-)$ was observed by $^{31}P$ NMR spectroscopy in considerable amounts; $\delta_{P+}$ +19.49(d), $\delta_{P(O)}$ −16.06(d), $J_{POP}$ 46 Hz. Additionally, the presence of the diselenide $[(Me_3CCH_2O)_2P(O)Se]_2$ $\delta_P$ +13.90 ppm (at 203 K) was shown below the temperature 233 K. At room temp. **4b** (90%) was contaminated only with **19** (10%). The same products were found by GC/MS analysis.

## ACKNOWLEDGMENTS

This work was supported by the Polish Academy of Sciences, Research Project CPBP-01.13. The author is grateful to Professor J. Michalski for helpful discussions.

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