

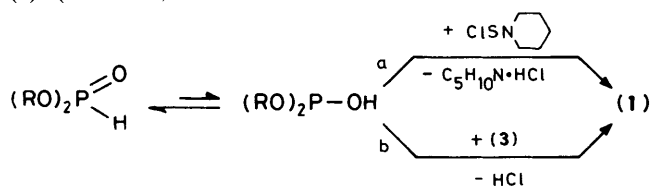
Reaction of Oxophosphorane-sulphenyl and -selenenyl Chlorides with Dialkyl Trimethylsilyl Phosphites. Novel Synthesis of Compounds Containing a Sulphur or Selenium Bridge Between Two Phosphoryl Centres†

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A novel highly efficient synthesis of *sym*-tetra-alkyl monothio- and monoseleno-pyrophosphates $(RO)_2P(O)XP(O)(OR')_2$ ($X = S, Se$) based on the condensation of dialkoxyoxophosphorane-sulphenyl or -selenenyl chlorides $(RO)_2P(O)XCl$ ($X = S, Se$) with dialkyl trimethylsilyl phosphites $(RO)_2POSiMe_3$ (**9**) is described. Remarkably selective reaction of a *O,O'*-dialkyl *O''*-trimethylsilyl selenophosphate $(RO)_2P(Se)OSiMe_3$ (**13**) with sulphuryl dichloride in the presence of an equimolar amount of a phosphite (**9**) leads to the formation of *sym*-monoselenopyrophosphates in excellent yield. A new rearrangement in phosphorus chemistry, *sym*-monoselenopyrophosphates (**11**) to *asym*-monoselenopyrophosphates (**12**), has been observed.

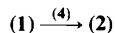
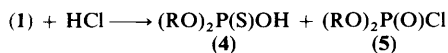
Organic pyrophosphates play a fundamental role in biology. Their thio analogues have been used in stereochemical studies on nucleophilic displacement reactions at tetraco-ordinate phosphorus,² and more recently in enzymatic studies.³

Tetra-alkyl monothiopyrophosphates exist in two isomeric structures: symmetrical $(RO)_2P(O)SP(O)(OR')_2$ (**1**) and asymmetrical $(RO)_2P(S)OP(O)(OR')_2$ (**2**). The monothiopyrophosphates (**2**) are more readily available and thermodynamically more stable than the isomers (**1**). The latter undergo thiothiono rearrangement $(1) \rightarrow (2)$.⁴ This pronounced tendency for isomerization impedes the synthesis of the thioanhydrides (**1**). The only feasible approach towards the synthesis of compounds (**1**) is phosphorylation of dialkyl phosphites with dialkoxyoxophosphoranesulphenyl chlorides $(RO)_2P(O)SCl$ (**3**)⁵ (Scheme 1).



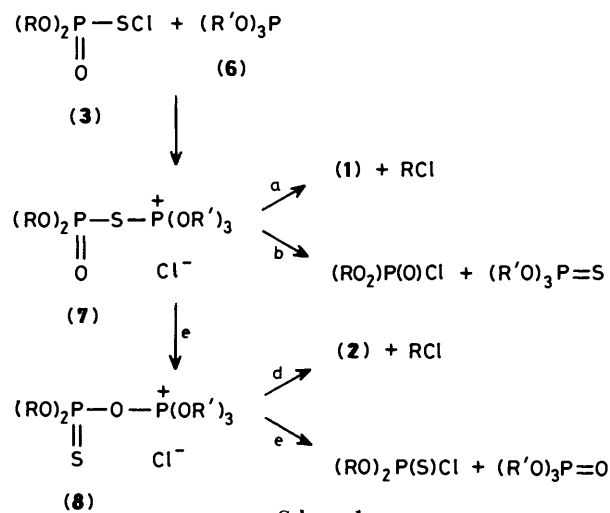
Scheme 1.

Methods a and b are satisfactory for the preparation of the anhydrides (**1**) of relatively high stability. From a preparative point of view method b is more convenient provided that hydrogen chloride is rapidly removed, at below room temperature, from the reaction medium. Even with proper precautions, a certain amount of product (**1**) is lost due to the rearrangement $(1) \rightarrow (2)$ catalysed by dialkyl hydrogen thiophosphate (**4**). The latter and dialkyl phosphorochloridate (**5**) are formed by cleavage of compounds (**1**) with hydrogen chloride (Scheme 2).



Scheme 2.

The reaction between oxophosphoranesulphenyl chlorides (**3**) and trialkyl phosphites (**6**) proceeds in a complex manner. The anhydrides (**1**) are formed in low yield with a number of other products.⁶ Although the phosphonium salt (**7**) containing a phosphorus-sulphur-phosphorus bridge is observed as a first intermediate, its decomposition to thiopyrophosphate (**1**) via dialkylation constitutes a minor pathway (path a) (Scheme 3).



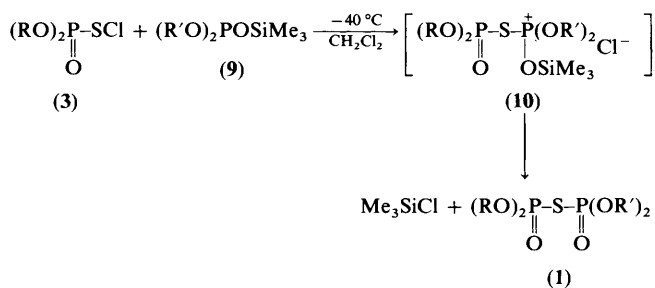
Scheme 3.

Nucleophilic attack of the chloride anion on the phosphoryl centre of intermediate (**7**) (path b), or isomerization of (**7**) into phosphonium salt (**8**) (path c), efficiently competes with dialkylation. The intermediate salt (**8**) also decomposes, usually by dephosphorylation (path e) rather than by dialkylation (path d).

We have found that the course of the reaction could be noticeably changed using dialkyl trimethylsilyl phosphites (**9**). With compounds (**9**), the only phosphorus products observed are the *sym*-monothiopyrophosphates (**1**), resulting from attack of the chloride anion on silicon in the intermediate phosphonium salts (**10**) (Scheme 4).

The reaction between substrates (**3**) and (**9**) can be recommended as the method of choice for the preparation of simple ($R = R'$), mixed ($R \neq R'$), and labelled (^{35}S) thioanhydrides

† Preliminary paper concerning *sym*-monoselenopyrophosphates.¹



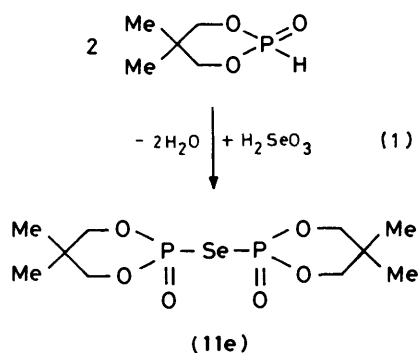
a; R = R' = Me; b; R = R' = Et; c; R = R' = Prⁱ;
 d; R = R' = BuⁱCH₂; e; RR = R'R' = Me₂C<CH₂⁻,
 f; R = BuⁱCH₂, R'R' = Me₂C<CH₂⁻

Scheme 4.

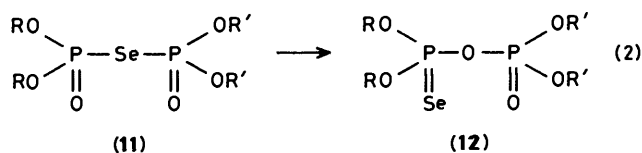
(1). All compounds (1) have n.m.r. and i.r. spectra consistent with the assigned structures.

The reaction is highly exothermic and occurs satisfactorily below -35°C with intensive stirring. In this manner the thioanhydrides (1) can be obtained in almost quantitative yield and high purity. If the esters (9) are sufficiently pure, and nucleophilic catalysis does not operate, the method does not give any by-products. In these conditions the thioanhydrides (1) are relatively stable.

Until recently, access to the seleno analogues of (1) containing the $>\text{P}(\text{O})\text{-Se-P}(\text{O})<$ skeleton has been hampered by the lack of preparative methods. Rycroft and White prepared bis-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphinan-2-yl) selenide (11e)

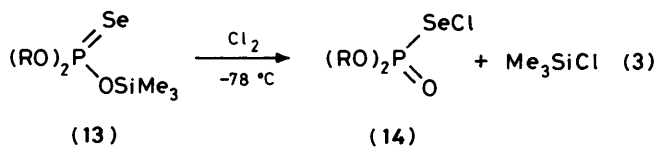


in low yield by condensation of selenious acid with two equivalents of 5,5-dimethyl-2-oxo-1,3,2-dioxaphosphinane⁷ [equation (1)]. We have found that this procedure leads to a complex mixture of phosphorus-containing products. We can confirm, however, that in exceptional cases like the one described above compound (11e) is formed in low yield. This result is not surprising in the light of our present knowledge on the reactivity of compound (11e) and their analogues (11). Water, which is formed in reaction (1), causes hydrolytic splitting of compound (11e). This splitting promotes a variety of secondary reactions including rearrangement (11) \longrightarrow (12) [equation (2)].

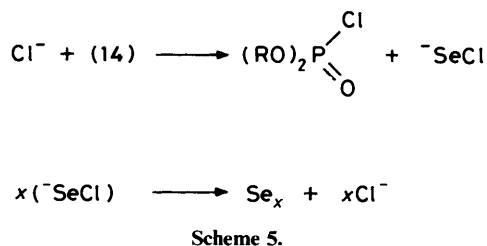


The *sym*-monoselenopyrophosphates (11) are effectively synthesized in a similar manner to their sulphur analogues (1) starting from dialkyl trimethylsilyl phosphites (9) and the

oxophosphoraneselenenyl chlorides (14). The chlorides (14) are extremely unstable, even when prepared from the selenophosphates (13) [equation (3)], and can only be used as reagents if the temperature is sufficiently low.⁸

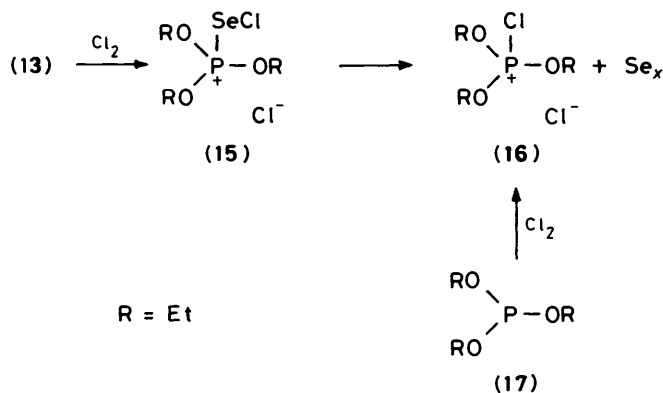


In our experience chlorides (14) decompose rapidly even below -40°C by a chain reaction involving nucleophilic displacement at the phosphoryl centre by chloride anion (Scheme 5).



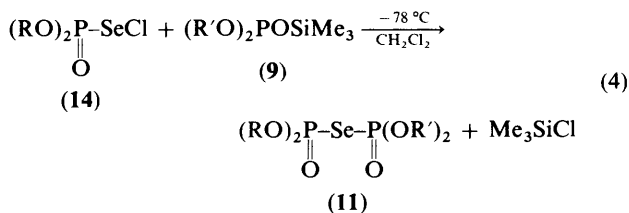
The SeCl group is very readily displaced at both phosphoryl and phosphonium centres. The phosphonium intermediates (15) and (16) are observed at -78°C by ³¹P n.m.r. spectroscopy when elemental chlorine is allowed to react with the silane (13).⁹

The structure of the phosphonium salt (16) has been confirmed by its independent synthesis *via* Arbusov reaction between triethyl phosphite (17) and elemental chlorine¹⁰ (Scheme 6).

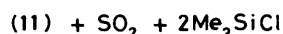
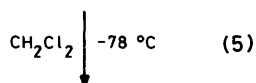
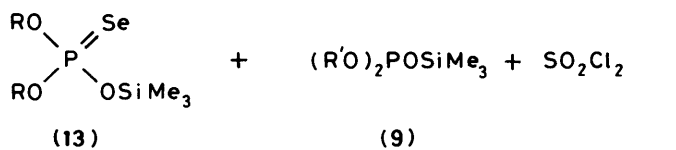


Scheme 6.

The selenenyl chlorides (14) prepared *in situ* by chlorination of silanes (13) were allowed to react immediately at -78°C with the corresponding phosphites (9) to afford the *sym*-monoselenopyrophosphates (11) [equation (4)]. Although this



procedure is quite satisfactory from a preparative point of view, we have improved it. We have discovered a very selective reaction of silanes (13) with sulphuryl dichloride in the presence of an equimolar amount of phosphites (9), leading to the simple ($R = R'$) and mixed ($R \neq R'$) *sym*-monoselenopyrophosphates (11) in excellent yield [equation (5)].



a; $R = R' = \text{Me}$;

b; $R = R' = \text{Et}$;

c; $R = R' = \text{Pr}^i$;

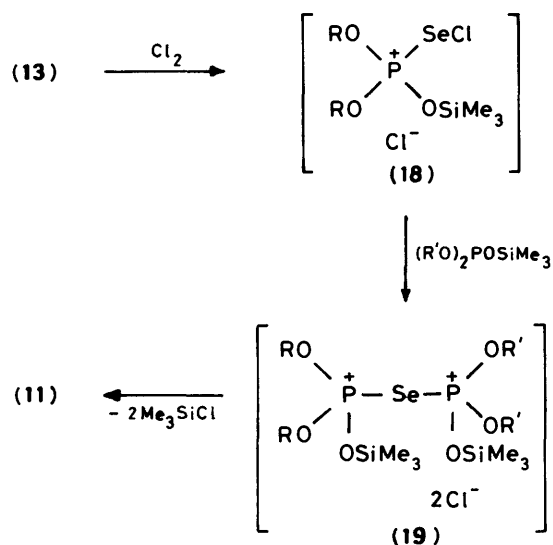
d; $R = R' = \text{Bu}^t\text{CH}_2$;

e; $R R = R' R' = \text{Me}_2\text{C} \begin{array}{l} \diagup \text{CH}_2^- \\ \diagdown \text{CH}_2^- \end{array}$;

f; $R = \text{Bu}^t\text{CH}_2$, $R' R' = \text{Me}_2\text{C} \begin{array}{l} \diagup \text{CH}_2^- \\ \diagdown \text{CH}_2^- \end{array}$

The transformation of silanes (13) into selenopyrophosphates (11) involves two reactions: the formation of selenenyl chlorides (14) from (13) with sulphuryl dichloride [equation (3)] followed by condensation of chlorides (14) with the ester (9) [equation (4)].

The rates of these reactions seem to be significantly higher than the rate of interaction between the trico-ordinate ester (9) and sulphuryl dichloride, and the rate of decomposition of chlorides (14). This result is somewhat surprising because the trico-ordinate phosphorus esters are known to be highly reactive towards elemental chlorine and sulphuryl dichloride.¹⁰ In our opinion, an alternative route (Scheme 7) in which the intermediate phosphonium salt (18) reacts with the phosphite (9) to give the diphosphonium salt (19) and subsequently compound (19) desilylates to afford the selenoanhydrides (11) is less likely.



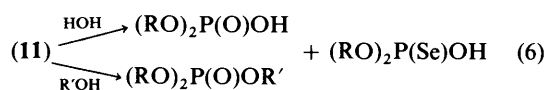
Scheme 7.

Yields of the isolated pure *sym*-monoselenopyrophosphates (11) are very good. Owing to their relative instability com-

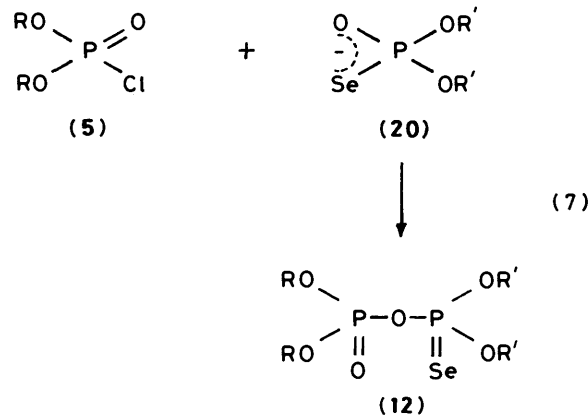
pounds (11) are best purified by crystallization [crude solid (11)] or chromatography on silanized silica gel [crude liquid (11)].

If the required *sym*-selenopyrophosphates (11) contain the same substituents at both phosphorus atoms ($R = R'$), a simplified procedure can be applied. Two mol equiv. of the phosphite (9) were allowed to react with one mol equiv. of elemental selenium. When the exothermic addition was complete the mixture is treated with sulphuryl dichloride. ³¹P N.m.r. spectra of all the anhydrides obtained were in full agreement with their assigned structure (11). The $J_{\text{P-Se}}$ coupling constant values (414–425 Hz) are in the range characteristic for compounds containing a bridging selenium atom.¹¹

Some preliminary observations illustrate the chemical reactivity of *sym*-monoselenopyrophosphates (11). They are very reactive towards nucleophiles and can be considered as potent phosphorylating agents. The phosphorylating properties are demonstrated in reactions with water and alcohols [equation (6)].



sym-Selenopyrophosphates (11) when heated to above 60 °C, isomerize into *asym*-selenopyrophosphates (12) which are identical with the compounds prepared by the condensation of the dialkyl phosphorochloridates (5) with the corresponding salts of dialkyl hydrogen phosphoroselenoates (20) [equation (7)].¹²



The structure of products (12) was evident from their ³¹P n.m.r. spectra which reveal two characteristic doublets, indicating two different phosphorus nuclei, with typical $J_{\text{P-Se}}$ (1 004–1 010 Hz)¹¹ and $^2J_{\text{PP}}$ (23–25 Hz) values.^{5,6}

This new rearrangement (11) → (12) is analogous to that observed for the *sym*-monothio- and -monoseleno-pyrophosphates.⁴

Experimental

Since the *sym*-monothio- and -monoseleno-pyrophosphates are very sensitive to moisture, all reactions were carried out under strictly anhydrous conditions. Solvents and reagents were purified and dried by conventional methods before use. M.p.s were measured on a Boëtius PHMK apparatus and are uncorrected. ¹H N.m.r. spectra were recorded on a Tesla BS B47 (80 MHz) instrument and ³¹P n.m.r. spectra on a JEOL JNM-FX 60 FT spectrometer operating at 24.3 MHz. Positive chemical shift values (p.p.m.) are reported for compounds absorbing at lower field than 85% H₃PO₄ and Me₄Si, respectively. I.r. spectroscopy was carried out on a Perkin-

Elmer Model 325 spectrophotometer. The purity of products were determined from integrated ^{31}P n.m.r. spectra.

Dialkyl trimethylsilyl phosphites (**9**) were prepared from the appropriate dialkyl phosphites and trimethylsilyl chloride in the presence of triethylamine.¹³ *O,O'*-Dialkyl *O'*-trimethylsilyl selenophosphates (**13**) and thiophosphates were obtained by addition of elemental selenium or sulphur to the phosphites (**9**).¹⁴

General Procedure for Preparation of sym-Monothiopyrophosphates.—A solution of sulphuryl dichloride (10 mmol) in methylene dichloride (5 ml) was added dropwise at -10°C to a vigorously stirred solution of the appropriate dialkyl trimethylsilyl thiophosphate (10 mmol) in methylene dichloride (6 ml) at -10°C . After the addition of the sulphuryl dichloride was complete, a solution of the corresponding dialkyl trimethylsilyl phosphite (10 mmol) in methylene dichloride (5 ml) was added dropwise to the mixture at -40°C . The mixture was then allowed to warm slowly to ambient temperature. The solvent was evaporated off under reduced pressure to afford the product. If purification was necessary, the crude liquid product was chromatographed on silanized silica gel 60 with benzene and chloroform as the eluants; the crude solid product was recrystallized from methylene dichloride–benzene (1:1). The following compounds were then prepared.

Thiopyrophosphate (**1a**) ($\text{R} = \text{R}' = \text{Me}$) (95%); δ_{P} + 18.1 p.p.m.; ν_{max} (film) 542 (P–S–P) and 1 289 cm^{-1} (P=O).

Thiopyrophosphate (**1b**) ($\text{R} = \text{R}' = \text{Et}$) (95%); δ_{P} + 14.7 p.p.m.; ν_{max} (film) 542 (P–S–P) and 1 270 cm^{-1} (P=O).

Thiopyrophosphate (**1c**) ($\text{R} = \text{R}' = \text{Pr}^i$) (95%); δ_{P} + 12.4 p.p.m.; ν_{max} (film) 542 (P–S–P) and 1 270 cm^{-1} (P=O).

Thiopyrophosphate (**1d**) ($\text{R} = \text{R}' = \text{Bu}^i\text{CH}_2$) (96%); m.p. 62–63 $^\circ\text{C}$; δ_{P} + 15.2 p.p.m.; ν_{max} (film) 542 (P–S–P) and 1 275 cm^{-1} (P=O).

Thiopyrophosphate (**1e**) ($\text{RR} = \text{R}'\text{R}' = \text{Me}_2\text{C} \begin{smallmatrix} \diagup \text{CH}_2^- \\ \diagdown \text{CH}_2^- \end{smallmatrix}$) (95%); m.p. 113–114 $^\circ\text{C}$; δ_{P} + 5.9 p.p.m.; ν_{max} (film) 542 (P–S–P) and 1 295 cm^{-1} (P=O).

Thiopyrophosphate (**1f**) ($\text{R} = \text{Bu}^i\text{CH}_2$, $\text{R}' = \text{Me}_2\text{C} \begin{smallmatrix} \diagup \text{CH}_2^- \\ \diagdown \text{CH}_2^- \end{smallmatrix}$) (95%); m.p. 186–187 $^\circ\text{C}$; δ_{P} + 6.1 and + 14.3 p.p.m. ($^2J_{\text{PP}}$ 13 Hz); ν_{max} (film) 534 (P–S–P) and 1 297 cm^{-1} (P=O).

General Procedure for Preparation of sym-Monoselenopyrophosphates (11) (R = R') and (R ≠ R').—A solution of sulphuryl dichloride (10 mmol) in methylene dichloride (5 ml) was added dropwise to a vigorously stirred solution of the appropriate dialkyl trimethylsilyl selenophosphate (10 mmol) and dialkyl trimethylsilyl phosphite (10 mmol) in methylene dichloride (10 ml) at -78°C . The mixture was then allowed to warm slowly to ambient temperature. The solvent was evaporated off under reduced pressure to afford the product. If purification was necessary, crude liquid product was chromatographed on silanized silica gel 60 with benzene and chloroform as the eluants; the crude solid product was recrystallized from benzene–light petroleum (b.p. 40–60 $^\circ\text{C}$) (1:1). The following compounds were thus prepared.

Monoselenopyrophosphate (**11a**) ($\text{R} = \text{R}' = \text{Me}$) (80%); δ_{P} + 13.1 p.p.m. (J_{PSe} 425 Hz); ν_{max} (film) 420 (P–Se–P), 1 260 (P=O), and 1 029 cm^{-1} (P–O–C).

Monoselenopyrophosphate (**11b**) ($\text{R} = \text{R}' = \text{Et}$) (78%); δ_{P} + 12.8 p.p.m. (J_{PSe} 425 Hz); ν_{max} (film) 400 (P–Se–P), 1 264 (P=O), and 1 028 (P–O–C).

Monoselenopyrophosphate (**11c**) ($\text{R} = \text{R}' = \text{Pr}^i$) (75%); δ_{P} + 6.9 p.p.m. (J_{PSe} 414 Hz); ν_{max} (film) 480 (P–Se–P), 1 250 (P=O), and 1 030 cm^{-1} (P–O–C).

Monoselenopyrophosphate (**11d**) ($\text{R} = \text{R}' = \text{Bu}^i\text{CH}_2$) (90%); m.p. 46–48 $^\circ\text{C}$; δ_{P} + 10.8 p.p.m. (J_{PSe} 418.7 Hz);

ν_{max} (film) 490 (P–Se–P), 1 245 (P=O), and 1 040 cm^{-1} (P–O–C).

Monoselenopyrophosphate (**11e**) ($\text{RR} = \text{R}'\text{R}' = \text{Me}_2\text{C} \begin{smallmatrix} \diagup \text{CH}_2^- \\ \diagdown \text{CH}_2^- \end{smallmatrix}$) (95%); m.p. 162–164 $^\circ\text{C}$; δ_{P} + 1.1 p.p.m. (J_{PSe} 415 Hz); ν_{max} (film) 495 (P–Se–P), 1 292 (P=O), and 1 040 cm^{-1} (P–O–C).

Monoselenopyrophosphate (**11f**) ($\text{R} = \text{Bu}^i\text{CH}_2$, $\text{R}' = \text{Me}_2\text{C} \begin{smallmatrix} \diagup \text{CH}_2^- \\ \diagdown \text{CH}_2^- \end{smallmatrix}$) (95%); m.p. 100–101 $^\circ\text{C}$; δ_{P} + 1.2 (d) and + 9.8 p.p.m. ($^2J_{\text{PP}}$ 19.5 Hz); ν_{max} (film) 507 (P–Se–P), 1 284 (P=O), and 1 038 cm^{-1} (P–O–C).

Monoselenopyrophosphate (*O,O'*-2,2-dimethyltrimethylene *Se*-phenyl-*t*-butylphosphoryl selenophosphate) (**11g**) [$\text{R} = \text{Me}_2\text{C} \begin{smallmatrix} \diagup \text{CH}_2^- \\ \diagdown \text{CH}_2^- \end{smallmatrix}$, ($\text{R}'\text{O}$)₂ = Buⁱ, Ph] (82%); m.p. 110–112 $^\circ\text{C}$; δ_{P} + 68.3 (d) and + 1.0 (d) p.p.m. ($^2J_{\text{PP}}$ 14.6 Hz); ν_{max} (film) 498 (P–Se–P), 1 284 (P=O), and 995 cm^{-1} (P–O–C).

General Procedure for Preparation of Simple sym-Monoselenopyrophosphates (R = R').—Anhydrous elemental black selenium (5 mmol) was added to stirred dialkyl trimethylsilyl phosphite (10 mmol). The exothermic reaction was complete after several min. The mixture was diluted with methylene dichloride (5 ml), cooled to -78°C , and a solution of sulphuryl dichloride (5 mmol) in methylene dichloride (5 ml) was added dropwise. The reaction mixture was worked up as in the preceding procedure. The following compounds were thus prepared.

Monoselenopyrophosphate (**11a**) ($\text{R} = \text{R}' = \text{Me}$) (80%); δ_{P} + 13.1 p.p.m. (J_{PSe} 425 Hz); ν_{max} (film) 420 (P–Se–P), 1 260 (P=O), and 1 029 cm^{-1} (P–O–C).

Monoselenopyrophosphate (**11b**) ($\text{R} = \text{R}' = \text{Et}$) (79%); δ_{P} + 12.8 p.p.m. (J_{PSe} 425 Hz); ν_{max} (film) 400 (P–Se–P), 1 264 (P=O), and 1 028 cm^{-1} (P–O–C).

Monoselenopyrophosphate (**11c**) ($\text{R} = \text{R}' = \text{Pr}^i$) (78%); δ_{P} + 6.9 p.p.m. (J_{PSe} 414 Hz); ν_{max} (film) 480 (P–Se–P), 1 250 (P=O), and 1 030 cm^{-1} (P–O–C).

Monoselenopyrophosphate (**11d**) ($\text{R} = \text{R}' = \text{Bu}^i\text{CH}_2$) (90%); m.p. 46–48 $^\circ\text{C}$; δ_{P} + 10.8 p.p.m. (J_{PSe} 418.7 Hz); ν_{max} (film) 490 (P–Se–P), 1 245 (P=O), and 1 040 cm^{-1} (P–O–C).

Monoselenopyrophosphate (**11e**) ($\text{RR} = \text{R}'\text{R}' = \text{Me}_2\text{C} \begin{smallmatrix} \diagup \text{CH}_2^- \\ \diagdown \text{CH}_2^- \end{smallmatrix}$) (95%); m.p. 162–164 $^\circ\text{C}$; δ_{P} + 1.1 p.p.m. (J_{PSe} 415 Hz); ν_{max} (film) 495 and 512 (P–Se–P), 1 292 (P=O), and 1 040 cm^{-1} (P–O–C).

*Reaction of Tetra-*O*-neopentyl sym-Selenopyrophosphate (11d) with Water.*—A solution of the selenopyrophosphate (5 mmol) in acetone–water (4:1) (10 ml) was stirred overnight at ambient temperature. The exclusive products were identified (^{31}P n.m.r.) as di-*O*-neopentyl hydrogen phosphoroselenoate (δ_{P} 64.5 p.p.m., J_{PSe} 908 Hz) and dineopentyl hydrogen phosphate (δ_{P} 1.3 p.p.m.).

*Reaction of Tetra-*O*-neopentyl sym-Selenopyrophosphate (11d) with Methanol.*—A solution of the selenopyrophosphate (10 mmol) in methanol (10 ml) was stirred overnight at room temperature. The mixture was shown (^{31}P n.m.r.) to consist only of di-*O*-neopentyl hydrogen phosphoroselenoate and methyl dineopentyl phosphate (δ_{P} – 0.2 p.p.m.).

Acknowledgements

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References

- 1 R. Dembiński, R. Kamiński, J. Michalski, and A. Skowrońska, *J. Chem. Soc., Chem. Commun.*, 1986, 1770.
- 2 J. Michalski, M. Mikołajczyk, B. Młotkowska, and J. Omelańczuk, *Tetrahedron*, 1969, **25**, 1743 and references therein.
- 3 J. A. Gerlt, J. A. Coderre, and S. Mehdi, *Adv. Enzymol.*, 1983, **55**, 291; F. Eckstein, *Annu. Rev. Biochem.*, 1985, **54**, 367.
- 4 J. Michalski, W. Reimschuessel, and R. Kamiński, *Usp. Khim.*, 1978, **47**, 1528; *Russ. Chem. Rev.*, 1978, **47**, 814 and references therein.
- 5 (a) J. Michalski, M. Mikołajczyk, B. Młotkowska, and A. Zwierzak, *Angew. Chem.*, 1967, **79**, 1069; (b) J. Michalski, B. Młotkowska, and A. Skowrońska, *J. Chem. Soc., Perkin Trans. 1*, 1974, 319.
- 6 J. Michalski, and A. Skowrońska, *J. Chem. Soc. C*, 1970, 703; A. Skowrońska, E. Krawczyk, and J. Burski, *Phosphorus Sulfur*, 1983, **18**, 233.
- 7 D. S. Rycroft and R. F. N. White, *J. Chem. Soc., Chem. Commun.*, 1974, 444.
- 8 W. J. Stec and B. Uznański, *Synth. Commun.*, 1978, **8**, 473.
- 9 A. Skowrońska and J. Gwara, unpublished results.
- 10 (a) J. Michalski, J. Mikołajczak, and A. Skowrońska, *J. Am. Chem. Soc.*, 1978, **100**, 5386; (b) J. Michalski, M. Pakulski, and A. Skowrońska, *J. Chem. Soc., Perkin Trans. 1*, 1980, 883.
- 11 W. J. Stec, A. Okruszek, B. Uznański, and J. Michalski, *Phosphorus Sulfur*, 1972, **2**, 97.
- 12 J. Michalski and J. Wieczorkowski, *Rocz. Chem.*, 1954, **29**, 233.
- 13 E. F. Bugerenko, E. A. Chernyshev, and E. M. Popov, *Bull. Acad. Sci. USSR*, 1966, 1334; L. V. Nesterov, N. E. Krepyseva, R. A. Sabirova, and G. N. Romanova, *J. Gen. Chem. USSR (Engl. Transl.)*, 1971, **41**, 2449.
- 14 A. Zwierzak, *Tetrahedron*, 1969, **25**, 5186.

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