

Synthesis of Symmetrical Tetra-alkyl Monoselenopyrophosphates: Compounds containing a Selenium Bridge between Two Phosphoryl Centres

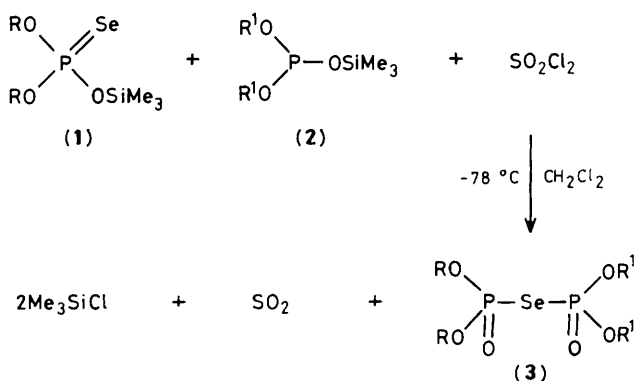
R. Dembiński, R. Kamiński, J. Michalski,* and A. Skowrońska*

Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, 90-362 Łódź, Boczna 5, Poland

The remarkably selective reaction of *O,O,O*-dialkyltrimethylsilylselenophosphates (1) in the presence of equimolar amounts of dialkyltrimethylsilyl phosphites (2) with sulphuryl chloride leading to tetra-alkyl symmetrical selenopyrophosphates (3) in excellent yields is reported.

Organic pyrophosphates and thiophosphates are of importance in bio-organic phosphorus chemistry.¹ Until recently, however, access to the seleno analogues has been hampered by a lack of preparative methods.†

We have recently discovered a remarkably selective reaction of *O,O,O*-dialkyltrimethylsilylselenophosphates (1) in the presence of equimolar amounts of *O,O,O*-dialkyltrimethylsilyl phosphites (2) with sulphuryl chloride leading to the symmetrical selenopyrophosphates (3) in excellent yields. In this way general access to compounds containing a selenium bridge between two phosphoryl centres is achieved. In the case of symmetrically substituted selenopyrophosphates (3a–e) ($R = R^1$) this procedure can be simplified because the selenophosphate (1) is prepared *in situ* by addition of a suitable amount of elemental selenium to the phosphite (2). The method is based on readily accessible starting materials.



- a; $R, R^1 = \text{Me}$
 b; $R, R^1 = \text{Et}$
 c; $R, R^1 = \text{Pr}^i\text{O}$
 d; $R, R^1 = \text{Bu}^t\text{CH}_2\text{O}$
 e; $R, R^1 = \begin{array}{c} \text{Me} \quad \text{CH}_2\text{-O} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{CH}_2\text{-O} \end{array}$
 f; $R = \begin{array}{c} \text{Me} \quad \text{CH}_2\text{-O} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{CH}_2\text{-O} \end{array}$
 $R^1 = \text{Bu}^t\text{CH}_2\text{O}$

The trimethylsilylselenophosphates (1) are readily available either by addition of elemental selenium to the trimethylsilyl phosphites (2) or by silylation of the corresponding selenoacid anion $(\text{RO})_2\text{P}(\text{Se})\text{O}^-$.³ The trimethylsilyl phosphites (2) are equally accessible by silylation of dialkyl phosphites.⁴

During the synthesis the following reactions take place. First the dialkoxyoxophosphoranyl selenyl chloride (4) is formed by reaction of the selenophosphate (1) with sulphuryl chloride and then (4) condenses with compound (2) leading to the selenopyrophosphate (3). The rates of these reactions were monitored by ³¹P n.m.r. spectroscopy and found to be significantly higher than the rate of interaction between the phosphite (2) and sulphuryl chloride and the rate of decomposition of (4). This result is somewhat surprising because trico-ordinate phosphorus esters are known to be highly reactive towards elemental chlorine and sulphuryl chloride.⁶ The intermediate selenyl chlorides (4) are very unstable;^{3a} they decompose above -40°C *via* a chain reaction involving nucleophilic displacement by the chloride anion at the phosphorus centre.

The symmetrical selenopyrophosphates (3a–e) are very reactive towards nucleophiles. They are potent phosphorylating agents owing to the excellence of the leaving group present [the anion $(\text{RO})_2\text{P}(\text{Se})\text{O}^-$ is very stable and the P–Se bond is of low energy]. The symmetrical selenopyrophosphates (3a–e) on warming above 60°C isomerise into the selenopy-

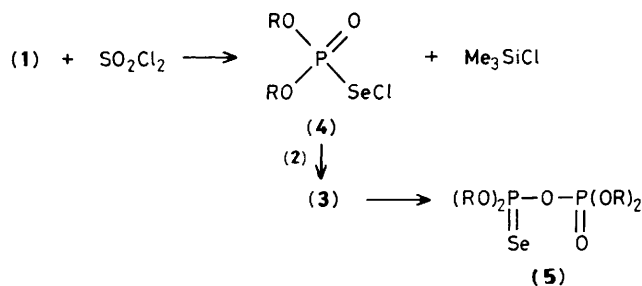


Table 1. Yields and properties of selenopyrophosphates (3).^a

	% Yield ^b	M.p./°C	³¹ P N.m.r. δ/p.p.m.	¹ J _{P–Se} /Hz
a;	80		+13.1	425
b;	78		+10.7	425
c;	75		+ 6.9	414
d;	90	46–8	+10.4	416
e;	95	162–4	+ 0.9	414
f;	85	99–101	+1.2(d), +9.5(d)	² J _{PP} 19.5

^a All products have i.r. and mass spectra and elemental analyses consistent with the assigned structures. ^b Yields of (3a–c) are based on chromatographically isolated products (silica gel 60 silanised, benzene–chloroform). ^c These coupling constant values are in the range characteristic of compounds containing a bridging selenium atom (ref. 5).

† Rycroft and White reported preparation of the bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl) selenide (3e) in low yield by condensation of selenous acids with two equivalents of 5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane (ref. 2). Our attempts to generalize this method to give other tetra-alkyl symmetrical selenopyrophosphates failed. We have found that this procedure leads to complex mixtures of phosphorus-containing products. However, we can confirm that in exceptional cases like the one described above, compound (3e) is formed in low yield.

rophosphates (5). This new rearrangement is analogous to that observed for the symmetrical tetra-alkyl thiopyrophosphates.⁷

This work was supported by the Polish Academy of Sciences.

Received, 1st August 1986; Com. 1099

References

- 1 J. A. Gerlt, J. A. Coderre, and S. Mehdi, *Adv. Enzymol.*, 1983, **55**, 291; F. Eckstein, *Ann. Rev. Biochem.*, 1985, **54**, 367.
 - 2 D. S. Rycroft and R. F. M. White, *J. Chem. Soc., Chem. Commun.*, 1974, 444.
 - 3 (a) W. J. Stec and B. Uznański, *Synth. Commun.*, 1978, **B(7)**, 473; (b) B. Borecka, J. Chojnowski, M. Cypryk, J. Michalski, and J. Zielińska, *J. Organomet. Chem.*, 1979, **171**, 17.
 - 4 E. F. Bugerenko, E. A. Chernyshev, and E. M. Popov, *Bull. Acad. Sci. USSR*, 1966, 1334; L. V. Nesterov, N. E. Kvepysheva, R. A. Sabirova, and G. N. Romanova, *J. Gen. Chem. USSR (Engl. Transl.)*, 1971, **41**, 2449.
 - 5 W. J. Stec, A. Okruszek, B. Uznański, and J. Michalski, *Phosphorus Sulfur*, 1972, **2**, 97.
 - 6 J. Michalski, J. Mikołajczak and A. Skowrońska, *J. Am. Chem. Soc.*, 1978, **100**, 5386; J. Michalski, M. Pakulski, and A. Skowrońska, *J. Chem. Soc., Perkin Trans. I*, 1980, 833.
 - 7 J. Michalski, B. Młotkowska, and A. Skowrońska, *J. Chem. Soc., Perkin Trans. I*, 1974, 319.
-