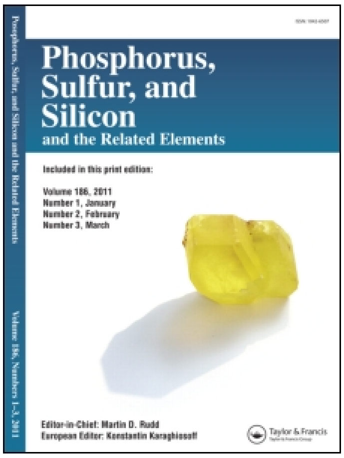

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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Roman Dembinski[a]; Ewa Krawczyk[a]; Aleksandra Skowronska[a]
[a] Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Lódz, Boczna, Poland

To cite this Article Dembinski, Roman , Krawczyk, Ewa and Skowronska, Aleksandra(1988) 'REACTION OF DIPHOSPHORYL DISELENIDES WITH DIALKYLTRIMETHYLSILYL PHOSPHITES. A NEW ROUTE TO SYMMETRICAL MONOSELENOPYROPHOSPHATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 35: 3, 345 — 348

To link to this Article: DOI: 10.1080/03086648808074339

URL: http://dx.doi.org/10.1080/03086648808074339

Phosphorus and Sulfur, 1988, Vol. 35, pp. 345–348
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REACTION OF DIPHOSPHORYL DISELENIDES WITH DIALKYLTRIMETHYLSILYL PHOSPHITES. A NEW ROUTE TO SYMMETRICAL MONO-SELENOPYROPHOSPHATES

ROMAN DEMBIŃSKI, EWA KRAWCZYK and
ALEKSANDRA SKOWROŃSKA*

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

(Received June 5, 1987; in final form July 20, 1987)

A novel efficient synthesis of sym-monoselenopyrophosphates **3** based on the reaction of diphosphoryl diselenides **1** with dialkyltrimethylsilyl phosphites **2** is described.

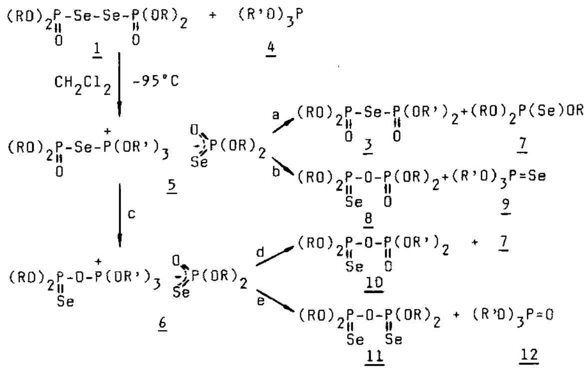
INTRODUCTION

Organic pyrophosphates and thiopyrophosphates play an important role in biochemistry and biology.[1] Until recently an access to seleno-analoques of these compounds sym-monoselenopyrophosphates **3** has been hampered by lack of preparative method.[2] In the proceeding paper we have reported a first general synthesis of anhydrides **3**.[4] They are formed in high yield in remarkably selective reaction of O,O,O-dialkyltrimethylsilylselenophosphates $(RO)_2P(Se)OSiMe_3$ with sulphuryl chloride in the presence of equimolar amounts of dialkyltrimethylsilyl phosphites $(RO)_2POSiMe_3$.

We now wish to report an alternative method for preparation of **3** developed during the course of our studies on the reaction of phosphorus pseudohalogens with tricoordinate phosphorus compounds.

RESULTS AND DISCUSSION

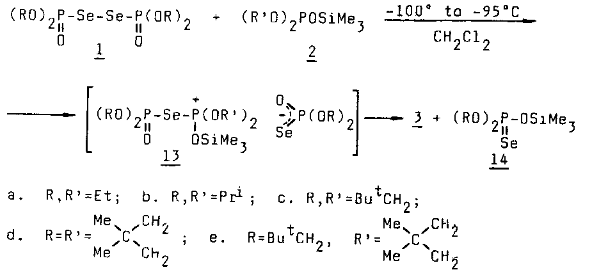
We have observed that phosphorus pseudohalogens diphosphoryl diselenides **1** react with trialkyl phosphites **4** in a complex way. The desired sym-monoselenopyrophosphates were formed in addition to other products. Using F.T. ^{31}P NMR spectroscopy at low temperatures we have demonstrated that the key intermediates in all reactions involved are the phosphonium salts **5**.[5] Further transformation of the salt **5** involving nucleophilic attack of phosphoroselenoic anion on each of the phosphorus and carbon atoms of the phosphonium counter-ion depends on the electronic and steric nature of substituents around the particular reactive centers. Consequently the ratio of the products **3**, **8**, **10** and **11** (Scheme 1) can vary over a large range. For example when $R = C_2H_5$ and $R' = CH_3$, sym-monoselenopyrophosphates **3** are formed in 80%, while the $R = R' = C_2H_5$ **3** is obtained only in 20%. A known fact that nucleophilic



SCHEME 1

displacement at ethoxyl carbon occurs approximately 2000 times slower than that at methoxyl carbon,[6] may explain the poor yield of **3** in the latter reaction.

We have found that the course of the reaction is strikingly changed by replacing trialkyl phosphites **4** by dialkyltrimethylsilyl phosphites **2**. In this new reaction the completely selective attack of phosphoroselenoic anion on silicon in the intermediate phosphonium salt **13** produces exclusively the anhydrides **3**.



SCHEME 2

The starting materials **1** and **2** are readily available. Diselenides **1** are prepared by oxidation of phosphoroselenoic acids salts in aqueous medium with elemental iodine.[7] Dialkyltrimethylsilyl phosphites are synthesized by silylation of dialkyl phosphites.[8]

The reaction between **1** and **2** is extremely exothermic and in order to secure a pure product **3** in high yield it must be carried out between −100° and −95°C under strictly anhydrous conditions. The monoselenopyrophosphates **3** were readily isolated and purified by crystallization or by column chromatography on silanised silica gel 60 when **3** are liquids.

The procedure described here is well suited for the synthesis of simple R = R′ and mixed R ≠ R′ sym-monoselenopyrophosphates **3** in good yields. Elemental analysis, infrared and NMR spectra of all obtained **3** are in agreement with the expected structure.

When moisture is present in the reaction medium the products of hydrolysis and subsequent formation of tetra-alkyl pyrophosphates and unsymmetrical tetra-alkyl monoselenopyrophosphates are observed (Scheme 3).

$$\underline{3} + H_2O \longrightarrow (RO)_2P(O)OH + (RO)_2P(Se)OH$$

$$\underline{3} + (RO)_2P(O)OH \longrightarrow (RO)_2P(O)OP(O)(OR)_2 + (RO)_2P(Se)OH$$

$$\underline{3} + (RO)_2P(Se)OH \longrightarrow (RO)_2P(Se)OP(O)(OR)_2 + (RO)_2P(Se)OH$$

SCHEME 3

EXPERIMENTAL

Since the sym-monoselenopyrophosphates are very sensitive to moisture, all reactions were carried out under strictly anhydrous conditions. Solvents and reagents were purified and dried by conventional method before use. M.ps. are uncorrected, ^{1}H NMR spectra were recorded on a Tesla BS 847 (80 MHz) instrument and ^{31}P NMR spectra on a JEOL JNM-FX 60 FT spectrometer operating at 24.3 MHz. Positive chemical shift values (ppm) were reported for compounds absorbing at lower field than 85% H_3PO_4 and Me_4Si, respectively. Infrared spectroscopy was carried out on a Perkin–Elmer Model 325 spectrophotometer. The purity of products were determined from integrated ^{31}P NMR spectra.

Starting materials and preparations. Dialkyltrimethylsilyl phosphites **2** were prepared from appropriate dialkyl phosphites and trimethylsilyl chloride in the presence of triethylamine.[8] Diphosphoryl diselenides **1** were synthesized by the oxydation of the corresponding phosphoroselenoic acids salts with elemental iodine in aqueous medium.[7]

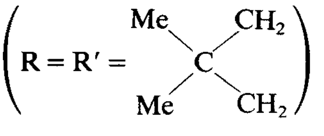
Reactions of diselenides with dialkyltrimethylsilyl phosphites. General procedure. The selenide (1.5 m mol) in methylene chloride (5 ml) was added at −100°C to −95°C to a solution of the corresponding dialkyltrimethylsilyl phosphite (1.5 m mol) in methylene chloride solution (5 ml). After addition was completed, the reaction mixture was then slowly warmed to room temperature. ^{31}P NMR spectra of the reaction mixture showed complete conversion of starting materials to sym-monoselenopyrophosphates **3** and O,O,O-dialkyltrimethylsilylselenophosphates **14**. After addition of petroleum ether, ethyl ether (1:1) (10 ml) the solid **3** crystallize on standing for a few days in the refrigerator. An analytical sample is prepared by two successive recrystallizations from petroleum ether-ethyl ether (1:1). In the case of liquid **3**, the mixture of crude **3** and **14** were separated by column chromatography on silanised silica gel 60, using benzene, chloroform (1:1) as the eluents.

Monoselenopyrophosphate **3a**: (R = R′ = Et). Yield 60% (Found: C, 27.17; H, 5.8; P, 17.9; $C_8H_{20}O_6P_2Se$ requires: C, 27.21; H, 5.7; P, 17.5); δ_P + 11.8, J_{PSe} 425 Hz; IR (film): ν_{PSeP} 400, $\nu_{P=O}$ 1264, ν_{POC} 1028 cm^{-1}.

Monoselenopyrophosphate **3b**: (R = R′ = Pr^i). Yield 70% (Found: C, 34.9; H, 5.95; P, 15.3; $C_{12}H_{28}O_6P_2Se$ requires: C, 35.05; H, 6.02; P, 15.5); δ_P + 6.9; J_{PSe} 414 Hz; IR(film): ν_{PSe} 480; $\nu_{P=O}$ 1250; ν_{POC} 1030 cm^{-1}.

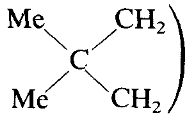
Monoselenopyrophosphate **3c**: (R = R′ = Bu^{t}CH$_2$). Yield 75% (Found: C, 46.5; H, 9.1; P, 12.3, $C_{20}H_{44}O_6P_2Se$ requires: C, 46.1; H, 8.9; P, 11.9); δ_P +10.8; J_{PSe} 418.7 Hz; IR(KBr/disc): ν_{P-Se-P} 490; $\nu_{P=O}$ 1245; ν_{POC} 1040 cm^{-1}.

Monoselenopyrophosphate **3d**:



Yield 75% (Found: C, 31.7; H, 5.6; P, 16.0; $C_{10}H_{20}O_6P_2Se$ requires: C, 31.6; H, 5.3; P, 16.4); m.p. 162–4°C, δ_P +1.1; J_{PSe} 414 Hz; IR(KBr/disc); ν_{PSeP} 495, 512; $\nu_{P=O}$ 1292; ν_{POC} 1040 cm^{-1}.

Monoselenopyrophosphate **3e**: $\left(R = Bu^{t}CH_2;\ R' = \right.$



$$\left(R = Bu^{t}CH_2;\ R' = \begin{matrix} Me & & CH_2 \\ & C & \\ Me & & CH_2 \end{matrix}\right)$$

Yield 70% (Found: C, 39.4; H, 7.2; P, 14.1; $C_{15}H_{32}O_6P_2Se$ requires: C, 39.8; H, 7.2; P, 13.8); m.p. 100–1°C; δ_P +1.2 d + 9.8 d, $^2J_{PP}$ 19.5 Hz; IR(KBr/disc): ν_{PSeP} 507; $\nu_{P=O}$ 1284; ν_{POC} 1038 cm^{-1}.

ACKNOWLEDGEMENT

This work was supported by the Polish Academy of Sciences, Research Project-CPBP 01.13.

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