Selenothiophosphinic Acid Salts: Efficient Synthesis, Structure and Reactivity

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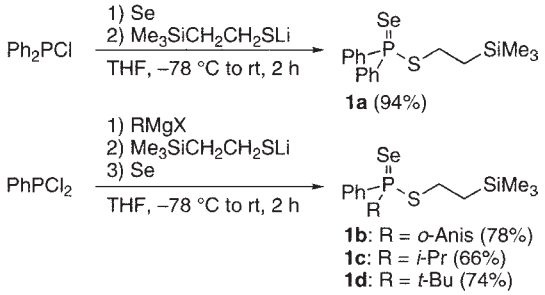
An efficient synthesis of selenothiophosphinic acid salts is achieved by reacting selenothiophosphinic acid *S*-(2-trimethylsilyl)ethyl esters with ammonium or alkali metal fluorides. The X-ray structure analysis of the potassium 18-crown-6 selenothiophosphinic acid salt shows that the salt is monomeric. Alkylation of the salts proceeds at the selenium atom whereas acylation occurs at the sulfur atom.

Dithiophosphinic acids and their esters have been fruitful territory for chemistry.[1] In recent years increasing attention has also been paid to the syntheses of metal complexes of dithiophosphinic acids.[2] In contrast, much less attention has been paid to their selenium isologues, i.e. selenothiophosphinic acids and their salts. The first sodium diethyl selenothiophosphinate was synthesized by reacting thiophosphinyl chloride with sodium hydrogen selenide as early as 1964.[3] The spectroscopic properties of various transition metal complexes of selenothiophosphinic acids were studied in the 1970's.[4] Despite these early reports further progress in the syntheses and properties of metal selenothiophosphinates has not resulted,[5,6] mainly due to the lack of their general synthetic methods. This inspired us to design new synthetic procedure for metal selenothiophosphinates and to disclose their properties. We report here the efficient synthesis of selenothiophosphinic acid alkali metal and ammonium salts and their structure and reactivity.

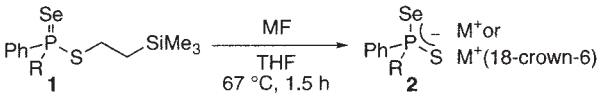
Our approach to the synthesis of the salts utilizes the high affinity of the fluorine atom toward the silicon atom. As a key starting material *S*-2-(trimethylsilyl)ethyl selenothiophosphinate **1a** was prepared by reacting Ph_2PCl with selenium powder and lithium 2-(trimethylsilyl)ethanethiolate (Scheme 1). Alternatively, synthesis of unsymmetrically substituted phosphinates **1b–1d** was attained as follows. To a solution of $PhPCl_2$ in THF (0.1 M) was added a solution of 1 equiv of Grignard reagent in THF (0.1 M) dropwise over a period of 1 h at −78 °C with vigorous stirring. To the resulting solution was added 1 equiv of the lithium thiolate at −78 °C, and the reaction mixture was stirred at that temperature for 15 min. After the addition of selenium powder, the mixture was warmed to room temperature and stirred for an additional 2 h to give **1b–1d** in good to high yields. It is substantially important to control the reaction temperature and the concentration of the reagents. Otherwise, the products, in which two equiv of Grignard reagents were introduced to the phosphorus atom of $PhPCl_2$, were mainly formed.



Scheme 1. Synthesis of *S*-2-(trimethylsilyl)ethyl selenothiophosphinates **1**.

The esters **1** thus obtained were converted to the corresponding metal and ammonium salts **2** by treating with metal and ammonium fluorides. The results are shown in Table 1.[7] For example, the reaction of ester **1a** with RbF in the presence of 18-crown-6 ether under reflux in THF proceeded smoothly to give the salt **2a** in 87% yield (Run 1). Similarly, unsymmetrically substituted Rb salts **2b–2d** were obtained in high yields (Runs 2–4). The 18-crown-6 ether facilitated the reaction and enhanced the solubility of the resulting Rb salts. The reaction with KF, CsF, Me_4NF, and Bu_4NF also took place with high efficiency to give the corresponding salts **2** (Runs 5–9). In all cases the salts **2** were stable, and no appreciable change was observed upon exposure to the air. They were soluble in organic solvents such as CH_2Cl_2 and THF. It should be noted that the salts were also soluble in water, particularly in the case of tetramethylammonium salt **2g**.

Table 1. Synthesis of selenothiophosphinic acid salts **2**



Run	2	R	M	Yield/%	^{31}P NMR[b] /ppm	^{77}Se NMR[b] /ppm	$^{1}J_{P-Se}$[b] /Hz
1[a]	**a**	Ph	Rb	87	44.5	−10.2	624.0
2[a]	**b**	*o*-Anis	Rb	92	38.0	9.1	611.8
3[a]	**c**	*i*-Pr	Rb	92	64.4	−120.6	618.1
4[a]	**d**	*t*-Bu	Rb	94	74.9	−126.6	615.0
5[a]	**e**	*t*-Bu	K	94	74.8	−128.4	607.4
6[a]	**f**	*t*-Bu	Cs	91	74.8	−124.5	610.4
7	**g**	*t*-Bu	Me_4N	92	75.1	– [c]	610.4
					73.3 [d]	−113.2 [d]	635.9 [d]
					76.0 [e]	−125.2 [e]	578.8 [e]
8[f]	**h**	Ph	Bu_4N	93	44.8	−5.2	631.5
9[f]	**i**	*t*-Bu	Bu_4N	94	75.3	−125.0	619.4

[a]18-Crown-6 ether was used as an additive. [b]In $CDCl_3$. [c]Not determined. [d]In DMSO-d_6. [e]In D_2O. [f]The reaction was carried out at 0 °C for 2 h.

The selected NMR spectroscopic data of **2** are also shown in Table 1. The ^{31}P and ^{77}Se NMR signals of **2** were influenced by the substituents on the phosphorus atom, but were independent on the counter cations. In the ^{31}P NMR spectra the signals of **1** were observed in the range of 50.9–86.1 ppm,[8] whereas the signals of the salts **2** showed an upperfield shift by 9.2–12.9 ppm. In the ^{77}Se NMR spectra the signals of the salts **2** were in a lower region than those of the esters **1**[8] by 183.1–233.8 ppm. The coupling constants between the phosphorus atom and the selenium atom were 607.4–631.5 Hz, which were smaller than those of *S*-esters **1**[8] by about

149 Hz. In the case of **2g** the coupling constant changed to 578.8 Hz in D_2O from 610.4 Hz in $CDCl_3$ (Run 7).

The X-ray molecular structure analysis of the potassium 18-crown-6 selenothiophosphinic acid salt **2e** was carried out.[9] Although the quality of the crystal was not high and the position of sulfur and selenium atoms was disordered, the structure of **2e** could be refined. The molecular structure of **2e** is shown in Figure 1 along with selected bond lengths and angles. The salt **2e** adopts a monomeric structure. The K atom resides in the center of the 18-crown-6 ether and is coordinated by the sulfur and selenium atoms.

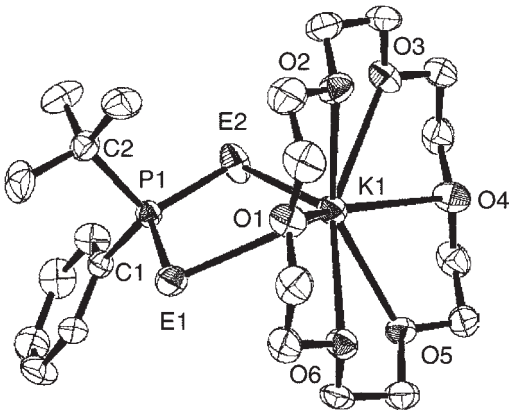
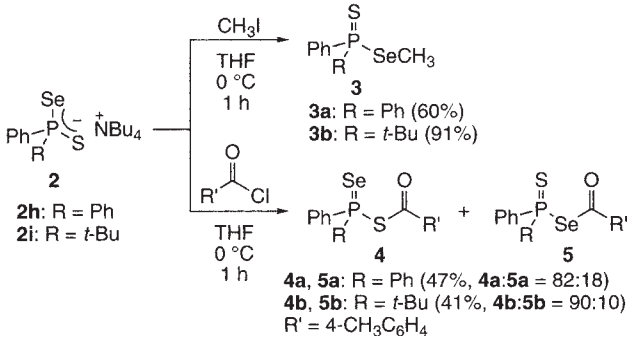


Figure 1. ORTEP drawing of **2e** with thermal ellipsoid plots (50% probability). Hydrogen atoms were omitted for clarity. The atoms E1 and E2 represent selenium or sulfur atom. Selected interatomic distance (Å) and bond angles (deg): P1–E1 2.082(1), P1–E2 2.113(1), P1–C1 1.841(4), P1–C2 1.873(4), E1···K 3.319(1), E2···K 3.4753(9), O···K (ave.) 2.891; E1–P1–E2 117.26(5), E1–P1–C1 109.5(1), E1–P1–C2 106.8(1), E2–P1–C1 107.6(1), E2–P1–C2 109.3(1), C1–P1–C2 105.8(2), P1–E1–K1 90.60(4), P1–E2–K1 85.90(3), E1–K1–E2 63.58(2).

The reactivity of selenothiophosphinates **2** was elucidated (Scheme 2). The reaction of **2h** and **2i** with methyl iodide selectively took place at the selenium atoms of **2h** and **2i** to give *Se*-methyl selenothiophosphinates **3** in high yields within 1 h. In contrast, acylation of the salts **2h** and **2i** preferentially proceeded at the sulfur atom to give mainly the products **4** along with a small amount of the product **5**.[10]



Scheme 2. Reaction of ammonium salts **2** with CH_3I and 4-$CH_3C_6H_4COCl$.

In summary, we successfully synthesized and characterized selenothiophosphinic acid salts. Further studies on their applications as new metal ligands and as key precursors of selenothiophosphinic acids are in progress.

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7 Typical experimental procedure for the synthesis of selenothiophosphinic acid salts: To a suspension of KF (0.116 g, 2.00 mmol) and 18-crown-6 ether (0.264 g, 1.00 mmol) in THF (5 mL) was added a solution of **1d** (0.377 g, 1.00 mmol) in THF (5 mL) at room temperature under Ar atmosphere. The mixture was stirred under reflux in THF for 1.5 h. After the addition of CH_2Cl_2 (20 mL), the insoluble parts were removed by filtration, and the solvent was evaporated under reduced pressure (20 °C, 120 Pa). To the residue was added Et_2O (5 mL), and it was stirred for 10 min. The resulting precipitates were collected by filtration to give 0.544 g (94%) of **2e** as a colorless solid. mp 202–204 °C (dec); ^{1}H NMR ($CDCl_3$): δ 1.21 (d, $^3J_{H-P} = 17.1$ Hz, 9H, CH_3), 3.60 (s, 24H, OCH_2), 7.26–7.48 (m, 3H, Ar), 8.39–8.44 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ 25.4 (d, $^2J_{C-P} = 3.3$ Hz, CH_3), 37.8 (d, $^1J_{C-P} = 44.7$ Hz, *C*CH_3), 70.0 (OCH_2), 126.1 (d, $^3J_{C-P} = 11.6$ Hz, Ar), 128.6 (Ar), 133.7 (d, $^2J_{C-P} = 9.9$ Hz, Ar), 138.4 (d, $^1J_{C-P} = 56.2$ Hz, Ar); ^{31}P NMR ($CDCl_3$): δ 74.8 ($^1J_{P-Se} = 607.4$ Hz); ^{77}Se NMR ($CDCl_3$): δ −128.4 (d, $^1J_{Se-P} = 607.4$ Hz); Anal. Calcd for $C_{22}H_{38}KO_6PSSe$: C, 45.59; H, 6.61. Found: C, 45.31, H, 6.56.

8 Representative spectroscopic data of **1** measured in $CDCl_3$: **1a**: ^{31}P NMR δ 54.0, ^{77}Se NMR δ −217.9, $^1J_{P-Se} = 774.2$ Hz; **1b**: ^{31}P NMR δ 50.9, ^{77}Se NMR δ −209.7, $^1J_{P-Se} = 763.7$ Hz; **1c**: ^{31}P NMR δ 76.0, ^{77}Se NMR δ −354.4, $^1J_{P-Se} = 766.7$ Hz; **1d**: ^{31}P NMR δ 86.1, ^{77}Se NMR δ −311.5, $^1J_{P-Se} = 762.2$ Hz.

9 Crystallographic data for **2e**: $C_{22}H_{38}KO_6PSSe$, fw = 579.63, monoclinic, space group $P2_1/n$, $a = 10.650(4)$, $b = 16.682(6)$, $c = 15.479(6)$ Å, $\beta = 91.973(5)°$, $V = 2748(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.401$ g cm^{-3}, $T = 193$ K, $R = 0.102$, $R_w = 0.141$, 6293 reflections ($I > 3\sigma(I)$). The selenium or sulfur atom appeared at the position [E(1)] or at the position [E(2)] shown in Figure 1. The occupancy of the selenium atom is 0.37 in [E(1)] and 0.63 in [E(2)], respectively, and the reverse results are obtained for the sulfur atom.

10 The starting salts **2** were also recovered, but the reaction at higher temperatures did not necessarily gave the products in better yields mainly because of the decomposition of the products formed.