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One-Pot Atom-Economic Synthesis of Thioselenophosphinates via a New Multicomponent Reaction of Secondary Phosphanes with Elemental Sulfur, Selenium, and Amines

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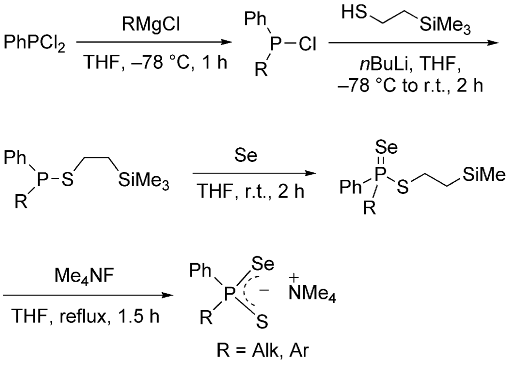
The multicomponent reaction between secondary phosphanes R_2PH (R = Ph, arylalkyl, hetarylalkyl), elemental sulfur, selenium, and primary, secondary, or tertiary amines to afford the corresponding mono-, di-, and trialkylammonium thioselenophosphinates has been discovered. The atom-economic reaction proceeds under mild conditions (ethanol/toluene, 40–70 °C, 40 min) to give the target alkylammonium thioselenophosphinates in high yields (up to 94 %).

Introduction

The chemical and coordinating properties of anionic ligands $R_2PCh_2^-$ with phosphorus and sulfur or selenium donor atoms (Ch = S, Se) are well documented.[1] Dithiophosphinates $R_2PS_2^-$ and diselenophosphinates $R_2PSe_2^-$, where R = alkyl or aryl, are known and widely used as single-source precursors of remarkable nanomaterials,[4,5] ligands for metal complexes,[6,7] lubricant oil additives,[2] extraction agents for the separation of heavy metals,[3] as well as key starting materials for the synthesis of practically important organophosphorus and organochalcogen compounds.[1b,8] At the same time, mixed thioselenophosphinate salts R_2PSeS^- with sulfur and selenium are virtually neglected due to their unavailability.[9–12] For example, the most modern synthesis for ammonium thioselenophosphinates[13] involves utilizing moisture- and air-sensitive phenyldichlorphosphane, Grignard and organolithium reagents, and inaccessible 2-(trimethylsilyl)ethanethiol. A limitation of the above procedure is that it allows only tetraalkylammonium salts to be synthesized (Scheme 1).

Therefore, the development of a direct, mild, and organometallic-free method for the preparation of ammonium thioselenophosphinates is highly desirable. In this paper, we report an original shortcut to alkylammonium salt of thioselenophosphanoic acids on the basis of a novel multicomponent atom-economic reaction of secondary phosphanes with elemental sulfur, selenium, and amines.



Scheme 1. Multistep synthesis of tetraalkylammonium thioselenophosphinates.

Results and Discussion

We have found that secondary phosphanes **1**–**7** readily react with elemental sulfur, selenium, and amines under mild conditions (40–70 °C, 40 min, inert atmosphere) in ethanol/toluene to afford various alkylammonium salts of thioselenophosphanoic acids **8a**–**l** in high yields (76–94%, Table 1).

As seen from Table 1, secondary phosphanes with various substituents as well as primary, secondary, and tertiary amines participate readily in this multicomponent reaction. The generality and preparative efficiency of the method developed have been demonstrated by the synthesis of an earlier unknown series of mono-, di-, and trialkylammonium salts of thioselenophosphanoic acids.

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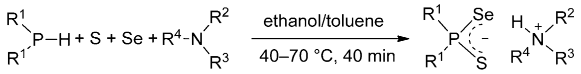
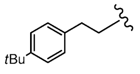
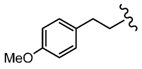
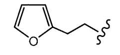
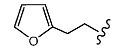
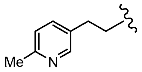
Table 1. One-pot synthesis of thioselenophosphinates from secondary phosphanes, elemental sulfur, selenium, and amines.[a]



1–7 **8a–l**

Entry	Phosphane, $(R^1)_2PH$	R^1	Amine, $R^2R^3R^4N$	Product	Yield[b] [%]
1	**1**	$(CH_2)_2Ph$	$AllNH_2$	**8a**	91
2	**1**	$(CH_2)_2Ph$	$n\text{Pr}_2NH$	**8b**	92
3	**1**	$(CH_2)_2Ph$	Et_3N	**8c**	85
4	**2**[c]	$CH_2CH(Me)Ph$	Et_2NH	**8d**	76
5	**3**		$n\text{Pr}_2NH$	**8e**	79
6	**4**		Et_2NH	**8f**	92
7	**5**		$n\text{Pr}_2NH$	**8g**	89
8	**5**		Et_3N	**8h**	94
9	**6**		$n\text{Pr}_2NH$	**8i**	78
10	**7**	Ph	$AllNH_2$	**8j**	88
11	**7**	Ph	$i\text{Pr}_2NH$	**8k**	82
12	**7**	Ph	Et_3N	**8l**	91

[a] All experiments were carried out at 40–70 °C in ethanol/toluene under an argon blanket; the ratio of secondary phosphane/S/Se/amine was 1.1:1:1:1.1. [b] All yields refer to isolated products. [c] Secondary phosphane **2** was used as a mixture of diastereomers.

The advantages of this method are the following: simple experimental procedure, short reaction time (40 min), and mild reaction conditions (40–70 °C, ethanol/toluene). In addition, the reaction found avoids the use of toxic phosphorus halides and flammable and hazardous organometallic reagents and inaccessible synthons such as 2-(trimethylsilyl)ethanethiol. Taking into account that starting secondary phosphanes **1**–**7** are readily available from red phosphorus and vinylarenes or vinylhetarenes (styrenes,[14] vinylpyridines,[15] or vinylfuranes[14a]), the multicomponent assembly here presented may be considered as one of the most concise and expedient approaches to thioselenophosphinates so far know.

The synthesized alkylammonium thioselenophosphinates **8a**–**l** are white powders, stable at room temperature, soluble in most of organic solvents, and insoluble in diethyl ether and in water (accept for thioselenophosphinate **8i**). Their structure unambiguously follows from the X-ray analysis data and ^{31}P, ^{77}Se, ^{1}H, and ^{13}C NMR spectra.

X-ray crystallographic studies of thioselenophosphinate **8h** have shown that it crystallizes as an ionic salt in the monoclinic $P2_1/n$ space group. Selected bond lengths and angles are presented in the Experimental Section. The molecule of this salt is formed by the anion of bis(2-phenethyl)thioselenophosphanoic acid and the cation of triethylammonium and adopts a monomeric structure in the solid state (Figure 1). The phosphorus atom adopts a slightly distorted tetrahedral structure with the bond angles ranging between 99.8 and 120.0°. The sulfur and selenium atoms are disordered and refined with 50% occupancy for both atoms as observed for the similar structures.[5f,13] The phosphorus–selenium bond length (2.10 Å) within the thioselenophosphinite unit are intermediate between single (P–Se 2.26 Å)[16] and double (P=Se 2.09 Å)[17] bonds, which is indicative of delocalization of the negative charge across the $[PSeS]^-$ moiety. The phosphorus–sulfur distance (2.02 Å) lies between the expected P–S single (2.09 Å) and double (1.95 Å) bond lengths, which also confirms the delocalization over the triade $[PSeS]^-$. This delocalization is observed in solution by using ^{31}P and ^{77}Se NMR spectroscopy. In the ^{31}P NMR spectrum, a singlet (at 43–49 ppm) with one typical satellite pair is present ($^1J_{P,Se}$ = 560–606 Hz). In the ^{77}Se NMR spectrum, the signals (doublet, $^1J_{P,Se}$ = 560–606 Hz) of the selenium atom in the P–Se bond of thioselenophosphinates were observed in the range of –83 to 4 ppm. The $^1J_{P,Se}$ value (560–606 Hz) is intermediate between the coupling constant values for single (200 to 600 Hz) and double (800 to 1200 Hz) P–Se bonds,[18] thus corresponding to the 1.5 order of the phosphorus–selenium bonds. The IR spectra show the absorption bands in the region of 500–600 cm^{-1}, assignable to P–S bond, as well as the bands in the region of 400–500 cm^{-1}, which are typical for P–Se bonds. Elemental analysis of all the compounds isolated corresponds to their structures.

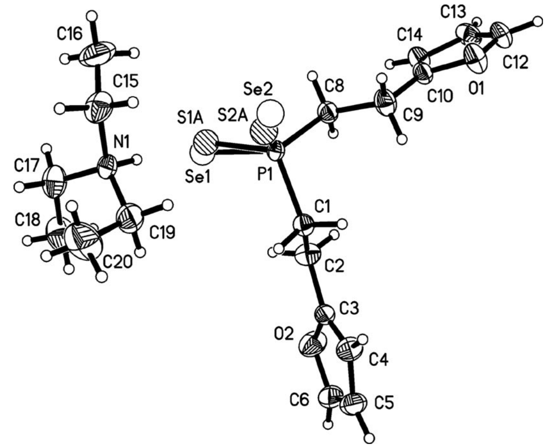
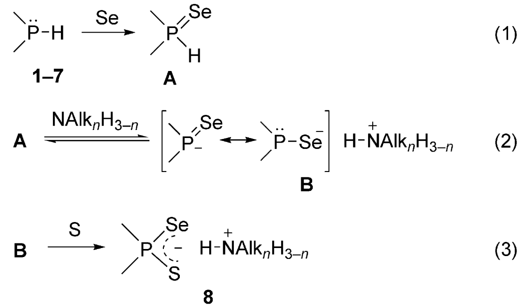


Figure 1. Thermal ellipsoid plot (50% probability) of the structure of **8h** (S1A, S2A, Se1, Se2 atoms are shown as balls because of disorder).

The tentative mechanism of the multicomponent reaction found can be rationalized as follows (Scheme 2). In stage 1, secondary phosphane **1**–**7** reacts with elemental selenium to give secondary phosphane selenide **A**. The latter is deprotonated by the amine to afford selenophosphinite **B** (stage 2), which further reacts with elemental sulfur to provide thioselenophosphinate **8** (stage 3).



Scheme 2. Probable mechanism of alkylammonium thioselenophosphinates formation.

Conclusions

In summary, the efficient one-pot synthesis of alkylammonium thioselenophosphinates has been developed and proceeds through a novel multicomponent atom-economic reaction between secondary phosphanes, elemental sulfur, selenium, and amines. The salts synthesized are promising intermediates to produce single-source precursors of metal chalcogenide nanoparticles, ligands for design of metal complexes and supramolecular structures, prospective extractants of heavy elements, potentially biological active compounds, convenient model compounds for the investigation of SPSe-triade ambident reactivity, as well as the key starting materials for the preparation *S*-alkyl esters and *Se*-alkyl esters of thioselenophosphanoic acids.

Experimental Section

General Procedure for the Preparation of Thioselenophosphinates 8a–l: To a solution of secondary phosphane **1**–**7** (1.1 mmol) in EtOH (7 mL) was added amorphous grey selenium (78.9 mg, 1.00 mmol), and the mixture was stirred for 20 min at 40 °C until dissolution of the residue. To the transparent solution obtained, a solution of elemental sulfur (32.1 mg, 1.00 mmol) in toluene (3 mL) and a solution of amine (1.1 mmol) in EtOH (2 mL) were consecutively added. The resultant solution was stirred for 20 min at 70 °C. The solvents were removed under reduced pressure, and the residue was washed with Et_2O (2×10 mL). The latter was decanted, and the white powder was dried in vacuo (1 Torr, 40–45 °C) to afford corresponding salt **8a**–**l**.

Crystal Data for 8h: $C_{18}H_{30}NO_2PSSe$, M = 434.42, monoclinic, space group $P2_1/n$, a = 10.8883(3) Å, b = 10.4399(3) Å, c = 18.6420(6) Å, β = 91.091(1)°, V = 2118.70(11) Å^3, Z = 4, $D_{\text{calcd.}}$ = 1.362 g cm^{-3}, μ = 1.956 mm^{-1}, $(2\theta)_{\max}$ = 65.3°, data/restraints/parameters: 7692/0/235, R indices [$I = 2\sigma(I)$]: R_1 = 0.0530, wR_2 (all data) = 0.1629. Selected bond lengths [Å]: P1–C1 1.833(3), P1–C8 1.826(3), P1–S1A 2.048(5), P1–S2A 1.994(5), P1–Se1 2.1139(15), P1–Se2 2.0823(10). Selected bond angles [°]: S2A–P1–S1A 114.6(2), S1A–P1–Se2 115.76(15), S2A–P1–Se1 115.09(18), Se2–P1–Se1 117.64(5), C8–P1–C1 105.29(13).

CCDC-789465 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): General Remarks and characterization data for compounds **8a**–**l**.

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