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Straightforward Solvent-Free Synthesis of Tertiary Phosphine Chalcogenides from Secondary Phosphines, Electron-Rich Alkenes, and Elemental Sulfur or Selenium

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ABSTRACT: *A series of tertiary phosphine sulfides and selenides have been synthesized in excellent yields (88-99%) via a three-component reaction between secondary phosphines, electron-rich alkenes (styrene, vinyl chalcogenides), and elemental sulfur or selenium, proceeding under solvent-free conditions (80-82°C, 4–44 h). The interaction occurs via initial oxidation of secondary phosphines with elemental sulfur or selenium followed by noncatalyzed anti-Markovnikov addition of the generated $R_2P(E)H$ (E = S, Se) species to alkenes to afford the corresponding adducts with high chemo- and regioselectivity.* © 2015 Wiley Periodicals, Inc. Heteroatom Chem. 27:48–53, 2016; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21300

INTRODUCTION

Tertiary phosphine sulfides and selenides constitute an important class of organophosphorus compounds [1]. They are widely used as popular precursors and stabilizing agents for semiconductive nanoparticles [2–4], extractants of noble metal ions [5,6], versatile ligands for metal complexes [7,8] (including catalysts [9, 10]) as well as reagents for organic synthesis [11, 12]. In addition, tertiary phosphine sulfides are offered as additives to electrolytes [13], modifiers for rubbers [14], and sensitizers in photographic materials [15].

Although a number of synthetic approaches to tertiary phosphine sulfides and selenides were described [1, 16], most of them are environmentally hazardous or require application of hardly available materials. Therefore, the development of more efficient and environmentally benign routes to the phosphine chalcogenides (especially, functionalized ones), starting from accessible compounds, still represents a certain challenge and remains a subject of steadily growing investigations.

In this line, it was reported a radical and nucleophilic addition [17] of secondary phosphine sulfides

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and selenides to various alkenes and alkynes [18–24] leading to the corresponding anti-Markovnikov adducts, tertiary phosphine chalcogenides. Later, a noncatalyzed version of this reaction was implemented [25–27]. α-Hydroxylated tertiary phosphine chalcogenides were synthesized by catalyst-free addition of $R_2P(E)H$ ($E = S$, Se) species to the C=O bond of aldehydes under solvent-free conditions [28]. In the last year [29], the noncatalyzed three-component synthesis of functionalized phosphine sulfides was published from diphenylphosphine, sulfur, and enones in the absence of solvent. Recently [30], a series of tris[2-(aryl)ethyl]phosphine sulfides was prepared directly from red phosphorus, sulfur, and aromatic alkenes under microwave-assisted superbasic conditions.

Following the approach in [29], herein we report a straightforward synthesis of tertiary phosphine sulfides and selenides via the three-component reaction between secondary phosphines, electron-rich alkenes, and elemental chalcogens (S or Se).

RESULTS AND DISCUSSION

We have found that the secondary phosphines **1**, **2** react with electron-rich alkenes **3–5** and elemental sulfur or selenium in equimolar ratio to deliver the corresponding tertiary phosphine chalcogenides **6a–l** in almost quantitative yields (Table 1). Notably, the reaction successfully occurs without any solvents under moderate heating (80–82°C). The order of the reactants mixing affects chemo- and regioselectively of the three-component reaction just negligibly because both main and possible side reactions (vide infra) do not take place at room temperature.

Table 1 reveals that the three-component reaction (earlier exemplified only by Ph_2PH, sulfur, and enones [29]) tolerates also electron-rich alkenes (such as **3–5**) and elemental selenium as well as other secondary phosphines (for instance, **2**). As for reactivity within the alkene series, vinyl sulfides and selenides appear to be more reactive than styrene. Interestingly, the phenyl vinyl ether (an oxygen analogue of alkenes **3** and **4**) under similar conditions reacted with phosphine **2** and sulfur (or selenium) nonselectively to give a complex mixture of products (conversion of **2** being 100%), among which the expected tertiary phosphine chalcogenides were identified by ^{31}P NMR. Apparently, such behavior of phenyl vinyl ether is due to its high tendency to the hydrolysis under the action of acids (e.g., $R_2P(S)SH$), which can be formed in trace amounts from secondary phosphines and elemental chalcogens (in 1:2 mol ratio).

Generally, the tertiary phosphine selenides are formed faster than the phosphine sulfides, probably due to the lower dissociation energy of the P–H bond in the secondary phosphine selenides (actual reaction intermediates, vide infra), as compared with that in the secondary phosphine sulfides.

Common side products of the reaction, according to ^{31}P NMR monitoring, are dichalcogenophosphinates, $R^1{}_2P(E)ECH(Me)R^2$ ($E = S$, Se), forming in up to 10 mol% via previously reported a three-component reaction [31,32], in which 2 equiv of elemental chalcogen is employed (Scheme 1). In this reaction, in situ generation of dichalcogenophosphinic acids $R^1{}_2P(E)EH$ (from secondary phosphines and elemental S or Se) takes place; the further addition of which to alkenes gives the esters of dichalcogenophosphinic acids [31,32].

The selective formation of the tertiary phosphine chalcogenides (under the solvent-free conditions studied) is likely due to the higher rate of the addition of the intermediate secondary phosphine chalcogenides (vide infra) to alkenes compared to the rate of competitive reaction of these intermediates with elemental chalcogen.

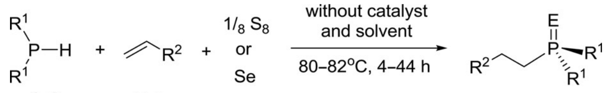
The products **6a–l** were characterized by X-ray diffraction (for **6h**, Fig. 1), NMR (^1H, ^{13}C, ^{31}P, and, if appropriate, ^{77}Se) and FT-IR spectroscopy, which proved their structures.

The ^{31}P NMR monitoring of the three-component reaction shows that the secondary phosphine sulfides and selenides are its actual intermediates. These species are formed by well-known oxidation of phosphines **1** and **2** with elemental chalcogens. As anticipated, elemental sulfur reacts faster than selenium: its full dissolution is observed within 10–20 min, whereas 1–1.5 h is necessary for 100% conversion of selenium. Moreover, in the reactions with sulfur, a self-heating (up to 40–45°C for 1 mmol loading) of the reaction mixture is observed under the stirring at room temperature.

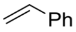
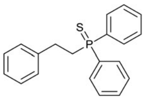
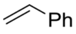
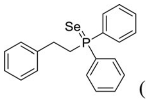
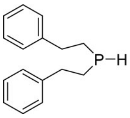
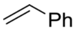
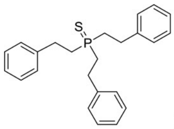
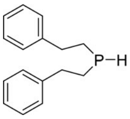
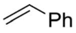
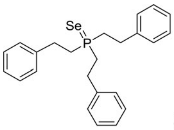
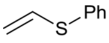
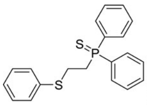
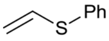
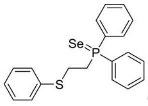
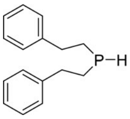
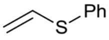
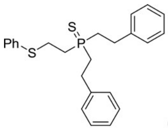
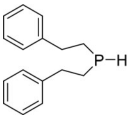
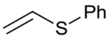
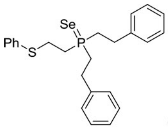
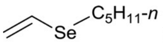
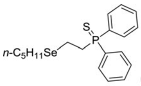
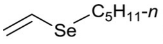
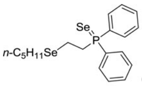
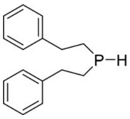
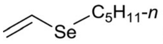
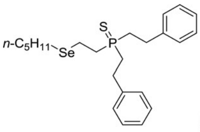
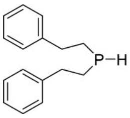
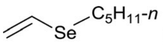
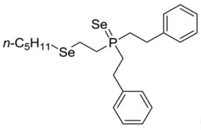
Therefore, formation of products **6a–l** in the three-component reaction can be rationalized as anti-Markovnikov addition of secondary phosphine chalcogenides **A**, generated from secondary phosphines **1**, **2** and elemental sulfur or selenium, to the double bond of alkenes **3–5** (Scheme 2).

Noteworthy, although noncatalytic addition of diphenylphosphine to alkenes is known [33], the possible formation of products **6a–l** in the three-component reaction via initial addition of secondary phosphines **1**, **2** to alkenes **3–5** is less probable, since, as demonstrated in [29], the secondary phosphines at the beginning of reaction are rapidly and completely converted into the secondary phosphine chalcogenides.

TABLE 1 Three-Component Synthesis of Tertiary Phosphine Sulfides, and Selenides[a]

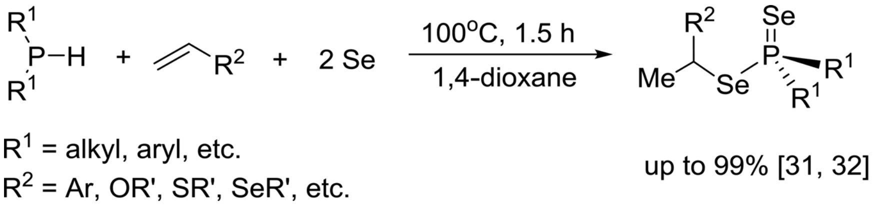


1, **2** **3-5** **6a–l**, 88–99%

Entry	*Phosphine*	*Alkene*	*Chalcogen*	*Reaction Time (h)*	*Product*	*Yield (%)*[b]
1	Ph_2PH	 **(3)**	S	20.5	 **(6a)**	94
2	Ph_2PH	 **(3)**	Se	13	 **(6b)**	98
3		 **(3)**	S	44	 **(6c)**	88
4		 **(3)**	Se	36	 **(6d)**	96
5	Ph_2PH	 **(4)**	S	15	 **(6e)**	97
6	Ph_2PH	 **(4)**	Se	11	 **(6f)**	95
7		 **(4)**	S	5	 **(6g)**	96
8		 **(4)**	Se	8	 **(6h)**	99
9	Ph_2PH	 **(5)**	S	15	 **(6i)**	92
10	Ph_2PH	 **(5)**	Se	11	 **(6j)**	95
11		 **(5)**	S	21	 **(6k)**	88
12		 **(4)**	Se	4.5	 **(6l)**	90

[a] Reaction conditions: secondary phosphine **1**,**2** (1.0 mmol), alkene **3–5** (1.0 mmol), elemental sulfur or selenium (1.0 mmol), inert atmosphere, stirring, 80–82°C, 4–44 h

[b] Isolated yield.



SCHEME 1 Three-component reaction between secondary phosphines, alkenes, and elemental selenium.

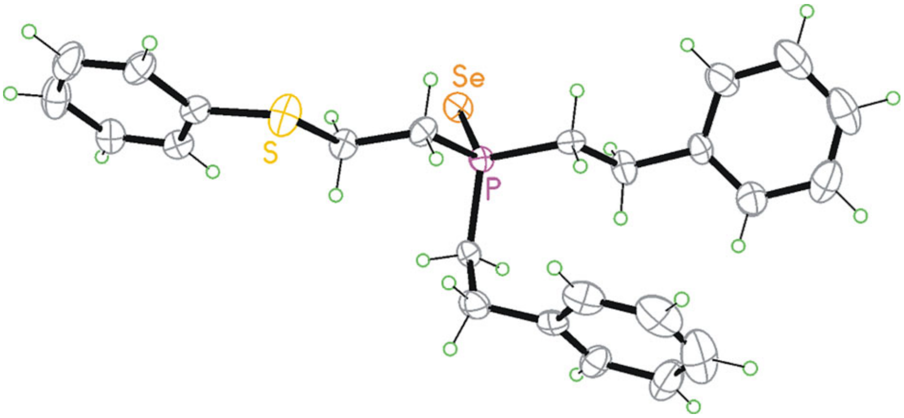
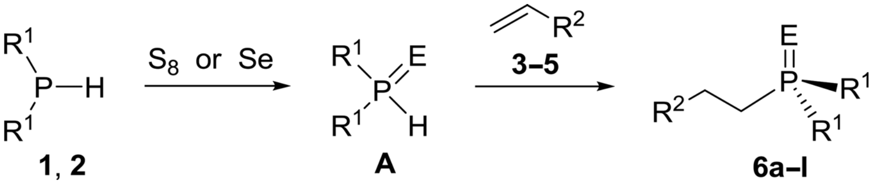


FIGURE 1 ORTEP drawing (30% thermal ellipsoid) of phosphine selenide **6h** (one of the two crystallographically independent molecules is shown).



SCHEME 2 A tentative reaction pathway.

CONCLUSIONS

Thus, we have developed a straightforward atom-economic synthesis of tertiary phosphine sulfides and selenides based on the three-component reaction between secondary phosphines, electron-rich alkenes, and elemental chalcogens, proceeding under mild solvent-free conditions. The actual intermediates of this reaction are secondary phosphine chalcogenides [29]; the noncatalytic addition of which to the alkenes leads to tertiary phosphine chalcogenides. The accessibility of the starting materials and their potential structural diversity as well as excellent isolated yields and high chemo- and regioselectivity of this reaction allow it to be considered as one of the most efficient methods for preparation of various tertiary phosphine chaclogenides. The latter are useful precursors and stabilizing agents for nanoparticles [2–4], prospective extractants of noble metal ions [5, 6], and ligands for metal complexes [7, 8].

EXPERIMENTAL

General

The ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra were recorded on a Bruker AV-400 spectrometer (400.13, 100.62, 161.98, and 76.31 MHz, respectively). Eighty-five percent H_3PO_4/H_2O was employed as external standard for ^{31}P NMR, HMDS was used for ^{1}H and ^{13}C NMR, and Me_2Se was the external standard for ^{77}Se NMR. FT-IR spectra were run on a Bruker Vertex 70 instrument. The C and H microanalyses were performed on a Flash EA 1112 elemental analyzer, whereas P, S, and Se contents were determined by combustion and spectrophotometric methods.

All experiments were carried out in an inert atmosphere (dry argon). Bis(2-phenethyl)phosphine (**1**) was prepared from red phosphorus and styrene [34]. Vinyl sulfide **4** and vinyl selenide **5** were synthesized as published in [35] and [36], respectively. Diphenylphosphine (**2**), styrene, elemental sulfur, and selenium are commercial products.

Synthesis of Tertiary Phosphine Chalcogenides **6a-l** *(General Procedure)*

A mixture of secondary phosphine **1**, **2** (1.0 mmol), alkene **3–5** (1.0 mmol), and elemental sulfur (S_8) or selenium (1.0 mmol) was stirred at 80–82°C for 4–44 h. After the reaction completion, the crude product was purified by flash chromatography (neutral alumina, hexane/Et_2O 1:1 mixture as an eluent) to give pure products **6a–l** in 88–99% yields.

X-Ray Crystallography of **6h**

The XRD data were obtained on a Bruker Kappa Apex II CCD diffractometer using φ, ω scans of narrow (0.5°) frames with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. The structures were solved by direct methods and refined by the full-matrix least-squares method against all F^2 in anisotropic approximation using the SHELX-97 programs set [37]. The H atoms positions were calculated with the riding model. Absorption corrections were applied empirically using SADABS programs. Compound **6h** is triclinic, space group P-1, a = 7.6775(7), b = 18.006(2), c = 18.281(2) Å, α = 63.802(4), β = 89.779(4), γ = 82.341(4)°, V = 2243.0(4) Å^3, Z = 4, $C_{24}H_{27}PSSe$, D_c = 1.355 g/cm^3, μ = 1.845 mm^{-1}, F(0 0 0) = 944, crystal size 0.8 × 0.60 × 0.04 mm^3, independent reflections 8050, wR_2 = 0.1860, S = 1.02 for all reflections (R = 0.0754 for 4859 $F > 4\sigma$). Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles are available as CCDC 1404950 from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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