

CHEMISTRY

Novel Method for the Synthesis of Diselenophosphinates

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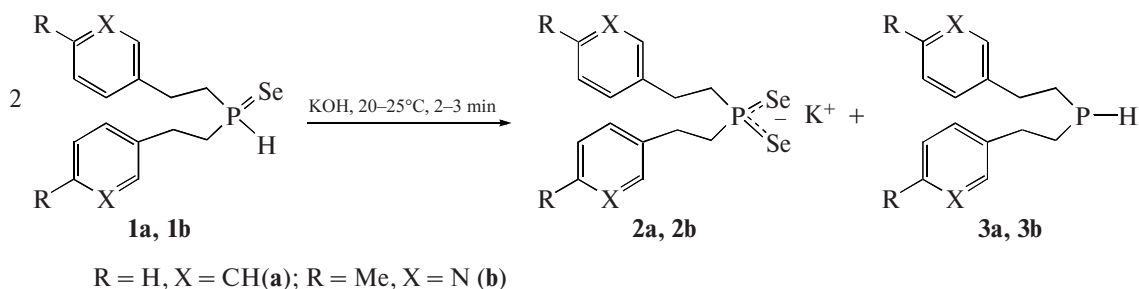
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Alkali metal and organylammonium diselenophosphinates are convenient precursors for semi-conducting [1] and magneto-optical [2] nanomaterials, ligands for designing metal complexes [3], promising extractants of rare and transuranium elements [4], potential biologically active compounds [5], and building blocks for organic synthesis [6]. At the same time, the known methods for their preparation are multistep and laborious and based on the use of toxic, corrosive, and not readily available compounds [1, 7–9]. For example, sodium diphenyldiselenophosphinate was obtained as a solvate $[\text{Na}(\text{Se}_2\text{PPh}_2) \cdot \text{THF} \cdot 5\text{H}_2\text{O}]$ in low yield from chlorodiphenylphosphine, sodium metal, and elemental selenium in liquid ammonia [9]. Similar potassium salt results as a monohydrate $[\text{K}(\text{Se}_2\text{PPh}_2) \cdot \text{H}_2\text{O}]$ from the reaction of potassium diphenylphosphide (obtained by the cleavage of

Ph_3P with potassium metal K) with elemental selenium [2]. Triethylammonium diphenyldiselenophosphinate $[\text{Ph}_2\text{PSe}_2][\text{HNEt}_3]$ was isolated from a complex reaction mixture resulting from the treatment of chlorodiphenylphosphine with a triethylsilane–triethylamine system (ambient temperature, 6 h) followed by refluxing the reaction products with elemental selenium (toluene, 20 h) [1].

In this work, we report a new convenient approach to the synthesis of alkali metal and organylammonium diselenophosphinates, as exemplified by the reaction of available secondary phosphine selenides (**1a**, **1b**) (prepared from red phosphorus, selenium, and styrene or 2-methyl-5-vinylpyridine [10, 11]) with KOH and diisopropylamine (Scheme 1).



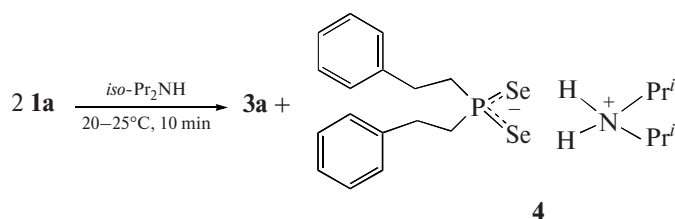
Scheme 1.

Secondary phosphine selenides (**1a**, **1b**) react instantly with KOH at ambient temperature to give potassium diselenophosphinates (**2a**, **2b**) in preparative yields of 87 and 81%, respectively (calculated toward the taken amount of the secondary phosphine

selenide). Along with the diselenophosphinates, equimolar amounts of the corresponding secondary phosphines (**3a**, **3b**) are also formed in quantitative yield according to ^{31}P NMR.

Even weak bases, such as secondary amines, readily react according to this scheme. Thus, diisopropylammonium diselenophosphinate (**4**) was obtained in 86% yield by the reaction of bis(2-phenylethyl)phosphine selenide (**1a**) and diisopropylamine (Scheme 2).

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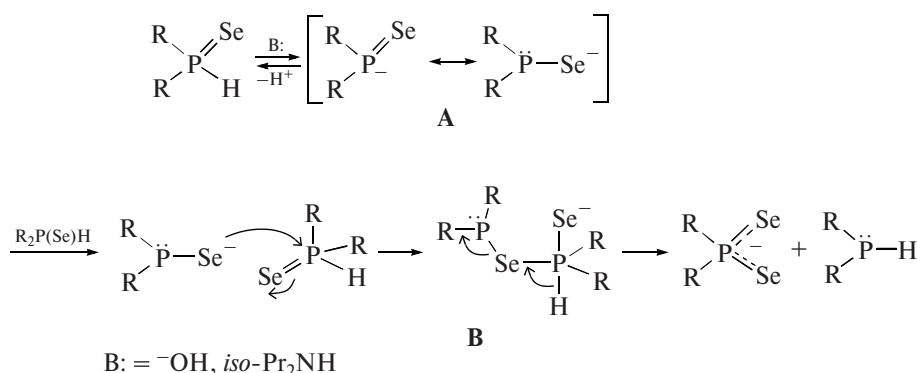
Scheme 2.

The developed method for the synthesis of diselenophosphinates **2a**, **2b**, and **4** may be considered as waste free since the resulting secondary phosphines (**3a**, **3b**) can be readily and quantitatively oxidized with elemental selenium to the initial secondary phosphine selenides (**1a**, **1b**) [10, 11].

The structure of the obtained compounds was proved by multinuclear (^1H , ^{13}C , ^{31}P , and ^{77}Se) NMR and IR spectroscopy, while the composition was confirmed by elemental analysis data. Thus, the ^{77}Se NMR spectra of the diselenophosphinates show one doublet ($^1J_{\text{SeP}} = 556\text{--}569\text{ Hz}$), while ^{31}P NMR spectra display a singlet with one pair of satellites ($^1J_{\text{SeP}} = 556\text{--}569\text{ Hz}$), which is convincing evidence of the chemical equivalence of the selenium atoms in the obtained diselenophosphinates. The IR spectra show

strong absorption bands in the region of $476\text{--}496\text{ cm}^{-1}$ responsible for the symmetric stretching vibrations (ν_s) of the PSe_2 group and weak bands at $521\text{--}567\text{ cm}^{-1}$ due to the antisymmetric stretching vibrations (ν_{as}) of the PSe_2 group [9].

The reaction of secondary phosphine selenides with bases may be represented by the following scheme (Scheme 3). An ambident selenophosphinite anion **A** (a product of deprotonation of the initial H-phosphine selenide under the action of KOH or *iso*- Pr_2NH) undergoes addition to the polarized $\text{P}=\text{Se}$ bond of another molecule of the secondary phosphine selenide to form an intermediate **B** followed by the fragmentation of the latter to give the reaction products.



Scheme 3.

Thus, the reaction of secondary phosphine selenides with bases opens a new convenient approach to the synthesis of alkali metal and organylammonium diselenophosphinates, which are promising precursors of nanosized metal selenides, extractants for radioactive waste partitioning, potential biologically active compounds, and reactive building blocks for organic and organoelement synthesis.

EXPERIMENTAL

IR spectra were recorded on a Bruker IFS 25 spectrometer as KBr pellets. ^1H , ^{13}C , ^{31}P , and ^{77}Se NMR spectra were obtained on a Bruker DPX 400 spectro-

meter operating at 400.13, 101.61, 161.98, and 76.31 MHz, respectively, using hexamethyldisiloxane as an internal reference, 85% H_3PO_4 as an external standard (^{31}P NMR), and Me_2Se as an internal reference (^{77}Se NMR). All experiments were carried out in an inert atmosphere (argon). Secondary phosphine selenides (**1a**, **1b**) were obtained according to procedures [10, 11].

Potassium bis(2-phenylethyl)diselenophosphinate (2a). A solution of 0.033 g (0.50 mmol) of $\text{KOH} \cdot 0.5\text{H}_2\text{O}$ in 2 mL of EtOH was added to a solution of 0.321 g (1.00 mmol) of bis(2-phenylethyl)phosphine selenide **1a** in 5 mL of ether. The mixture was stirred at ambient

temperature for 2–3 min. The ^{31}P NMR spectrum of the reaction mixture showed two signals: a singlet at 26.50 ppm and a doublet at 69.70 ppm ($^1J_{\text{PH}} = 199.5$ Hz) due to salt **2a** and secondary phosphine **3a**, respectively. The solvent was removed, and the residue was washed with anhydrous ether (2×5 mL) and dried in vacuum to give 0.191 g (87% yield) of potassium bis(2-phenylethyl)diselenophosphinate **2a** as colorless crystals, mp 208–210°C. IR (KBr, ν , cm^{-1}): 564, 521 (ν_{as} PSe_2), 496, 484 (ν_{s} PSe_2). ^1H NMR (D_2O , δ], ppm): 2.13–2.19 (m, 4H, CH_2P), 2.61–2.68 (m, 4H, CH_2Ph), 6.80–6.88 (m, 10H, Ph). ^{13}C NMR (D_2O , δ], ppm): 30.92 (CH_2Ph), 42.99 (d, $^1J_{\text{CP}} = 35.4$ Hz, CH_2P), 126.27 (*p*-C), 128.45 (*o*-C), 128.71 (*m*-C), 141.32 (d, $^3J_{\text{CP}} = 15.9$ Hz, *ipso*-C). ^{31}P NMR (D_2O , δ], ppm): 26.45 (+ doublet of satellites, $^1J_{\text{SeP}} = 557.4$ Hz). ^{77}Se NMR (D_2O , δ], ppm): –63.09 (d, $^1J_{\text{SeP}} = 557.4$ Hz).

For $\text{C}_{16}\text{H}_{18}\text{KPSe}_2$ anal. calcd. (%): C, 43.84; H, 4.14; P, 7.07; Se, 36.03.

Found (%): C, 43.90; H, 4.17; P, 7.19; Se, 36.10.

Potassium bis[2-(2-methyl-1-pyridyl-5)ethyl]diselenophosphinate (2b). A solution of 0.033 g (0.50 mmol) of $\text{KOH} \cdot 0.5\text{H}_2\text{O}$ in 2 mL of EtOH was added to a solution of 0.351 g (1.00 mmol) of bis[2-(2-methyl-1-pyridyl-5)ethyl]phosphine selenide **1b** in 5 mL of EtOH. The mixture was stirred at 20–25°C for 2–3 min. The ^{31}P NMR spectrum of the reaction mixture showed the presence of secondary phosphine **3b** (d, –72.50 ppm, $^1J_{\text{PH}} = 200$ Hz) and salt **2b** (s, 25.74 ppm). The solvent was removed, the residue was washed with anhydrous ether (2×5 mL) and dried in vacuum to give 0.190 g (81% yield) of potassium bis[2-(2-methyl-1-pyridyl-5)ethyl]diselenophosphinate **2b** as colorless crystals, mp 199–202°C. IR (KBr, ν , cm^{-1}): 549, 538 (ν_{as} PSe_2), 483 (ν_{s} PSe_2). ^1H NMR (D_2O , δ], ppm): 2.13–2.31 (m, 10H, CH_2P , Me), 2.63–2.69 (m, 4H, CH_2Py), 6.84 (d, 2H, $\text{CH}=\text{C}-\text{Me}$, $^3J_{\text{HH}} = 7.8$ Hz), 7.22–7.24 (m, 2H, $\text{CH}=\text{C}$), 7.94 (d, 2H, $\text{CH}=\text{N}$, $^4J_{\text{HH}} = 1.6$ Hz). ^{13}C NMR (D_2O , δ], ppm): 22.76 (Me), 27.73 (CH_2Py), 42.70 (d, $^1J_{\text{CP}} = 36.2$ Hz, CH_2P), 124.08 (s, $\text{HC}=\text{CMe}$), 134.30 (d, $\text{CCH}_2\text{CH}_2\text{P}$, $^3J_{\text{CP}} = 15.8$ Hz), 137.87 (s, $\text{CH}=\text{C}$), 147.83 (s, $\text{HC}=\text{N}$), 155.75 (CMe). ^{31}P NMR (D_2O , δ], ppm): 25.71 (+ doublet of satellites, $^1J_{\text{SeP}} = 556.7$ Hz). ^{77}Se NMR (D_2O , δ], ppm): –58.18 (d, $^1J_{\text{SeP}} = 556.7$ Hz).

For $\text{C}_{16}\text{H}_{20}\text{KN}_2\text{PSe}_2$ anal. calcd. (%): C, 41.03; H, 4.30; P, 6.61; Se, 33.72.

Found (%): C, 40.90; H, 4.17; P, 6.19; Se, 33.10.

Diisopropylammonium bis(2-phenylethyl)diselenophosphinate (4). Diisopropylamine (0.051 g, 0.50 mmol)

was added to a solution of 0.321 g (1.00 mmol) of bis(2-phenylethyl)phosphine selenide **1a** in 5 mL of ether. A colorless crystalline precipitate formed (20–25°C, 10 min). The supernatant solution (containing secondary phosphine **3a** according to ^{31}P NMR) was decanted, the precipitate was washed with ether (1×5 mL) and dried in vacuum to give 0.216 g (86% yield) of diisopropylammonium bis(2-phenylethyl)diselenophosphinate **4** as colorless crystals, mp 190–192°C. IR (KBr, ν , cm^{-1}): 2755, 2706 (ν NH), 567 (ν_{as} PSe_2), 476 (ν_{s} PSe_2). ^1H NMR (CDCl_3 , δ], ppm, J , Hz): 1.55 (d, 6H, $^3J_{\text{HH}} = 6.5$ Hz, Me), 2.51–2.58 (m, 4H, CH_2P), 3.06–3.13 (m, 4H, CH_2Ph), 3.43–3.50 (m, 2H, CH), 7.16–7.27 (m, 10H, Ph), 8.63 (s, 2H, NH). ^{13}C NMR (CDCl_3 , δ], ppm): 20.13 (Me), 30.42 (CH_2Ph), 43.71 (d, $^1J_{\text{CP}} = 37.1$ Hz, CH_2P), 48.31 (CH), 125.59 (*p*-C), 128.11 (*o*-C), 128.18 (*m*-C), 141.52 (d, $^3J_{\text{CP}} = 17.3$ Hz, *ipso*-C). ^{31}P NMR (CDCl_3 , δ], ppm): 21.02 (+ doublet of satellites, $^1J_{\text{SeP}} = 569.1$ Hz). ^{77}Se NMR (CDCl_3 , δ], ppm): –63.09 (d, $^1J_{\text{SeP}} = 569.1$ Hz).

For $\text{C}_{22}\text{H}_{34}\text{NPSe}_2$ anal. calcd. (%): C, 52.70; H, 6.83; P, 6.18; Se, 31.50.

Found (%): C, 52.76; H, 6.87; P, 6.60; Se, 32.05.

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