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LETTERS TO THE EDITOR

Chlorination of Secondary Phosphine Selenides with the System CCl_4/NEt_3

S. F. Malysheva, A. V. Artem'ev, N. K. Gusarova, L. V. Klyba, A. A. Tatarinova, and B. A. Trofimov

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: mal@irioch.irk.ru

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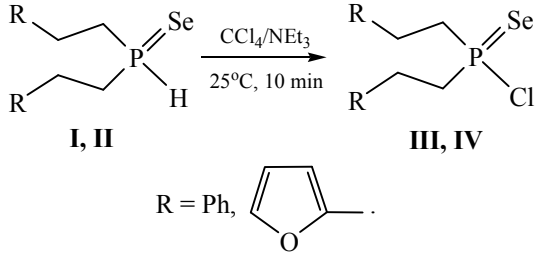
Selenophosphoryl chlorides $R_2P(Se)Cl$ are highly reactive selenophosphorylating reagents widely used in the synthesis of organoelement compounds [1–5]. They readily react with alkylmagnesium halides [1], al-cohols [2], amines [3] and other compounds [4, 5] to form tertiary phosphine selenides as well as esters, amides, and salts of selenophosphinic acids: ligands for the design of single-source precursors of nano-materials [6, 7], efficient iniferters [8], prospective extragents of the rare-earth elements [9] and coor-dination media for synthesis of semiconducting nano-materials [10].

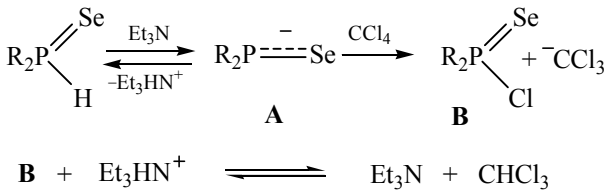
Traditional method of preparation of seleno-phosphoryl chlorides based on the reaction of hardly accessible diorganylchlorophosphines with elemental selenium (reflux in benzene for 3 h) [3, 11] is labor-consuming and does not meet modern ecological requirements.

Here, we report on a novel and convenient method of synthesis of selenophosphoryl chlorides by the reaction of secondary phosphine selenides with carbon tetrachloride in the presence of triethylamine. Chlorination of bis(2-phenylethyl)phosphine selenide (**I**) and bis[2-(2-furyl)ethyl]phosphine selenide (**II**) prepared from red phosphorus, styrene or 2-vinylfuran and elemental selenium [12-14] proceeds under mild conditions (25°C, 10 min, CCl_4, molar ratio phosphine selenide : Et_3N = 1 : 1) with the formation of selenophosphoryl chlorides **III, IV** in quantitative yield.



It should be mentioned that the reaction occurs also in the presence of catalytic amounts of triethylamine (10 mol %) but in this case more time is required for completing the reaction (1 h). The reaction does not proceed without triethylamine.

The elaborated reaction can be represented by the following scheme described in the literature on the example of hydrophosphoryl compounds and their thio analogs [15–17]: P,Se-ambident selenophosphinite anion **A** formed by deprotonation of the secondary phosphine selenide by NEt_3 react with carbon tetra-chloride to form selenophosphoryl chlorides and tri-chloromethyl carbanion **B**. Protonation of the latter with the triethylammonium cation leads to recovery of triethylamine and formation of chloroform (identified in the reaction mixture by chromato-mass spectro-metry).



Therefore, the reaction of chlorination of secondary phosphine selenides with the system CCl_4/NEt_3 provides a new and convenient approach to the synthesis of

selenophosphoryl chlorides, reactive intermediates and synthons for organic and organoelement synthesis.

Bis(2-phenylethyl)selenophosphoryl chloride (III). To the solution of bis(2-phenylethyl)phosphine selenide **I** (0.32 g, 1 mmol) in 7 ml of CCl_4 triethylamine (0.10 g, 1 mmol) was added and stirred for 10 min at room temperature. Formation of chloroform in the reaction mixture was proved by chromato-mass spectrometry (peak of molecular ion $[M]^+$ with *m/z* 118). The solvent was removed, the residue washed with 5 ml of cold hexane, dried in vacuum. Obtained 0.35 g (98%) of compound **III** as colorless needles deliquescing in the air. ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 3.01–3.22 m (4H, CH_2P), 3.49–3.59 m (4H, CH_2Ph), 7.73–7.86 m (10H, Ph). ^{13}C NMR, δ_C, ppm: 29.53 (CH_2Ph), 42.76 d (CH_2P, $^1J_{CP}$ 43.0 Hz), 126.75 (C_p), 128.29 (C_o), 128.75 (C_m), 139.23 d (C_i, $^3J_{CP}$ 17.2 Hz). ^{31}P NMR, δ_P, ppm: 102.35 (satellites: $^1J_{PSe}$ 782.6 Hz, $^1J_{PSe}$ 870.0 Hz). ^{77}Se NMR, δ_{Se}, ppm: –171.2 d ($^1J_{PSe}$ 825.3 Hz). Mass spectrum, *m/z* (for ^{80}Se, ^{35}Cl): 356 $[M]^+$. Found, %: C 54.10; H 5.19; P 9.77; Se 21.96. $C_{16}H_{18}ClPSe$. Calculated, %: C 54.03; H 5.10; P 9.97; Se 22.20.

Bis[2-(2-furyl)ethyl]selenophosphoryl chloride (IV). Prepared similarly by chlorination of bis[2-(2-furyl) ethyl]phosphine selenide **II**. Yield 0.33 g (98%), colorless needles deliquescing in the air. ^{1}H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 2.56–2.67 m (4H, CH_2P), 2.94–3.96 m (4H, CH_2-furan), 6.05–7.30 m (6H, H^{3-5} furan). ^{13}C NMR, δ_C, ppm: 21.72 (CH_2-furan), 38.60 d (CH_2P, $^1J_{CP}$ 45.4 Hz), 106.76 (C-3, furan), 110.01 (C-4, furan), 141.08 (C-5, furan), 151.70 d (C-2, furan, $^3J_{PC}$ 18.2 Hz). ^{31}P NMR, δ_P, ppm: 101.67 (satellites: $^1J_{PSe}$ 793.0 Hz, $^1J_{PSe}$ 872.0 Hz). ^{77}Se NMR, δ_{Se}, ppm: –183.0 ($^1J_{PSe}$ 832.2 Hz). Mass spectrum, *m/z* (for ^{80}Se, ^{35}Cl): 336 $[M]^+$. Found, %: C 42.85; H 4.31; P 9.01; Se 23.40. $C_{12}H_{14}ClO_2PSe$. Calculated, %: C 42.94; H 4.20; P 9.23; Se 23.53.

^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR spectra were registered on a Bruker DPX-400 spectrometer (400.13, 101.61, 161.98, and 76.31 MHz, respectively) in $CDCl_3$, internal standard HMDS, ^{31}P and ^{77}Se chemical shifts were measure relative to 85% H_3PO_4 and Me_2Se, respectively. Mass spectra of electron ionization (70 eV) were obtained on a Shimadzu GCMS–QP5050*A* instrument (quadruple mass analyzer, the range of detected mass was from 34 to 650 Da). Chromatograph with capillary column SPB–5ms (60 m × 0.25 mm × 0.25 μm), gas carrier helium, flow rate 0.7 ml min^{-1}, temperature of injector and ion source 250°C, pressure 300 kPa; temperature programming from 70 to 250°C, 10 deg min^{-1}. All experiments were run in an inert atmosphere (argon). The reactions were followed by the ^{31}P NMR spectroscopy.

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