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LETTERS TO THE EDITOR

Atom-Economic Synthesis of Ammonium Diselenophosphinates from Secondary Phosphine Selenides, Elemental Selenium, and Ammonia

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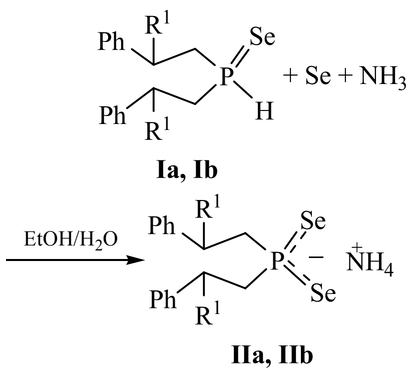
There are no data in the literature on ammonium diselenophosphinates. At the same time, alkylammonium diselenophosphinates are now actively studied as convenient "single-source" precursors of nanodimensional metal phosphides [1] or selenides [2-3] possessing unique semiconducting [4], magneto-optical [5–6] and electric properties [2]. Alkylammonium diselenophosphinates are also ligands of interest for the design of metal complexes [7], promising extragents for rare, noble, and transuranium elements [8], potential biologically active compounds [9] and precursors for synthesis, for example, of esters $R^1_2P(Se)\cdot SeR^2$ [10–12]. Conventional methods of the synthesis of alkylammonium diselenophosphinates are multistep, labor-consuming, and require the use of aggressive phosphine halides and organometal compounds [4]. Recently, we have suggested a new convenient approach to the synthesis of mono-, di-, and trialkylammonium diselenophosphinates based on the reaction of secondary phosphine selenides with elemental selenium and amines [13].

In the present work we report on the atom-economic synthesis of the first representatives of ammonium diselenophosphinates by the reaction of the available [14, 15] bis(2-phenylalkyl)-phosphine-selenides (**Ia, Ib**) with elemental selenium and ammonia.

The experiments showed that the three-component reaction readily proceeds in water–ethanol medium (22–24°C, 0.5 h) to afford ammonium diselenophosphinates (**IIa, IIb**) in 92 and 85% yield, respectively.

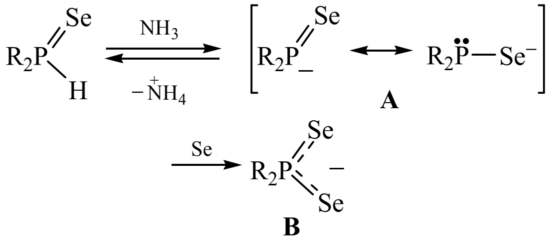


Ia, Ib

IIa, IIb

R^1 = H (**a**), Me (**b**).

The reaction can be represented by the following scheme: the ambident selenophosphinite anion **A** formed by deprotonation of the secondary phosphine selenide by ammonia, reacts with elemental selenium to give diselenophosphinate anion **B**.



Therefore, the three-component reaction between the secondary phosphine selenides, elemental selenium, and ammonia is the effective atom-economic method of synthesis of the earlier unknown ammonium diselenophosphinates, promising intermediates for the design of semiconducting and magneto-optical nanomaterials and highly reactive precursors for the synthesis of organoelemental compounds and coordination structures.

Ammonium bis(2-phenylethyl)diselenophosphinate (IIa). To the solution of bis(2-phenylethyl)phosphineselenide (**Ia**) (0.32 g, 1.0 mmol) in 8 ml of ethanol amorphous selenium (0.08 g, 1.0 mmol) and 25% aqueous ammonia (0.12 ml, ~1.6 mmol) were added at room temperature, the mixture was stirred for 0.5 h, filtered, the solvent was removed in a vacuum, the residue was ground in hexane (2×10 ml), hexane was decanted, the residue was dried (35–40°C, 1 h, 0.5 mm Hg). 0.38 g (92%) of salt **IIa** was obtained as white fine-crystalline powder, mp 217–219°C (ether). IR spectrum (KBr), cm^{-1}: 3060, 3023, 2944, 2789, 1949, 1876, 1810, 1752, 1633, 1601,1495, 1453, 1397, 1265, 1208, 1193, 1156, 1137, 1126, 1068, 1028, 1008, 958, 938, 909, 832, 810, 751, 736, 697, 620, 566, 517, 506, 481, 413. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.26–2.31 m (4H, CH_2P), 2.95–3.02 m (4H, CH_2Ph), 7.15–7.28 m (14H, Ph, NH_4). ^{13}C NMR spectrum, δ_C, ppm: 30.58 d (CH_2Ph, $^2J_{PC}$ 1.8 Hz), 44.84 d (CH_2P, $^1J_{PC}$ 36.9 Hz), 125.50 (C_p), 128.09 (C_o), 128.25 (C_m), 142.50 d (C_i, $^3J_{CP}$ 16.4 Hz). ^{31}P NMR spectrum, δ_P, ppm: 24.29 (plus doublet of satellites with $^1J_{PSe}$ 610 Hz). ^{77}Se NMR spectrum, δ_{Se}, ppm: –36 d ($^1J_{PSe}$ 616 Hz). Found, %: C 46.10; H 5.29; N 3.31; P 7.31; Se 37.75. $C_{16}H_{22}NPSe_2$. Calculated, %: C 46.06; H 5.31; N 3.36; P 7.42; Se 37.85.

Ammonium bis(2-phenylpropyl)diselenophosphinate (IIb) was prepared similarly from bis(2-phenylpropyl)phosphineselenide (**Ib**).Yield 0.38 g (85%), white powder, mp 154–156°C (ether). IR spectrum (KBr), cm^{-1}: 3250, 3080, 3060, 2957, 2867, 2765, 1947, 1880, 1806, 1638, 1601, 1582, 1493, 1451, 1392, 1306, 1283, 1234, 1196, 1182, 1148, 1086, 1075, 1047, 1027, 1005, 995, 911, 847, 829, 763, 747, 732, 699, 584, 562, 544, 532, 488, 462, 404. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.27–1.35 m (6H, Me), 2.04-2.24 m (4H, CH_2P), 3.36–3.52 m (2H, CH), 7.08–7.22 m (14H, Ph, NH_4). ^{13}C NMR spectrum, δ_C, ppm: 23.98 and 24.37 d (Me $^2J_{PC}$ 5.2 Hz), 37.02 and 37.40 (*C*HPh), 52.22 and 52.63 d (CH_2P, $^1J_{PC}$ 34.0 and 35.0 Hz), 125.01 (C_p), 127.52 and 127.54 (C_o), 128.30 (C_m), 149.49 and 149.60 d (C_i, $^3J_{PC}$ 12.9 Hz). ^{31}P NMR spectrum, δ_P, ppm: 22.94 and 24.14 (plus doublet of satellites with $^1J_{PSe}$ 607 and 612 Hz), the ratio of intensities 52 : 48. ^{77}Se NMR spectrum, δ_{Se}, ppm: –23.2 and 23 d ($^1J_{PSe}$ 607 Hz). Found, %: C 48.50; H 5.77; N 3.11; P 6.69; Se 35.43. $C_{18}H_{26}NPSe_2$. Calculated, %: C 48.55; H 5.89; N 3.15; P 6.96; Se 35.46.

IR spectra were recorded on a Bruker IFS-25 spectrometer. ^{1}H, ^{13}C, ^{31}P, ^{77}Se NMR spectra were registered on a Bruker DPX-400 spectrometer (400, 100, 162, 76.3 MHz, respectively) in DMSO-d_6, external standards 85% H_3PO_4 (for ^{31}P) and Me_2Se (for ^{77}Se). All experiments were run in an inert atmosphere (argon) in commercial ethanol.

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