Selective synthesis of hydrazinium diselenophosphinates from secondary phosphines, elementary selenium, and hydrazine

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A three-component reaction of secondary phosphines, elementary selenium, and hydrazine hydrate (the molar ratio 1 : 2 : 1.1) selectively proceeds under mild conditions (EtOH, 70—75 °C, 0.5 h) to form earlier unknown hydrazinium diselenophosphinates (81—95%).

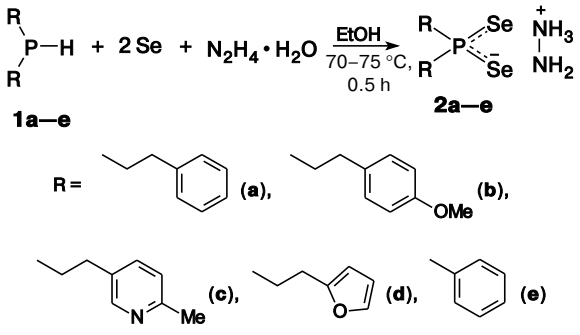
Key words: secondary phosphines, elementary selenium, hydrazine, diselenophosphinates.

At present, salts of diselenophosphine acids[1—7] are actively used as convenient "single-source" precursors of nanomaterials,[8,9] ligands for the design of metal complexes,[10] key intermediates in the synthesis of esters $R_2P(Se)SeAlk$,[11,12] prospective binary extragents of heavy metals,[13] and potential antimicrobal drugs.[14] Recently, a convenient approach to the synthesis of alkali metal,[15,16] ammonium,[17] and alkylammonium[18] diselenophosphinates has been suggested from secondary phosphines (or secondary phosphine selenides), elementary selenium, and bases (alkali metal hydroxides,[15,16] ammonia,[17] or amines[18,19]).

In the present work, we for the first time report on a three-component reaction of secondary phosphines **1a—e** with elementary selenium and hydrazine hydrate.

Experiments showed that heating (70—75 °C, 0.5 h) reagents (the molar ratio $R_2PH : Se : N_2H_4 \cdot H_2O = 1 : 2 : 1.1$) in ethanol leads to hydrazinium diselenophosphinates **2a—e** in 81—95% yields (Scheme 1).

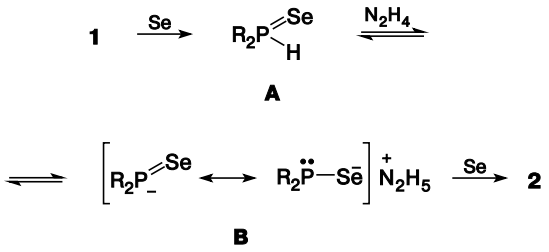
Scheme 1



The reaction proceeds with high degree of selectivity. No side compounds, in particular, expected bis(diorganoselenophosphoryl)selenides $(R_2P{=}Se)_2Se$ (the oxidation products of secondary phosphines with 2 equiv. of selenium[20]) or hydrazinium polyselenides (the reduction products of elementary selenium with hydrazine[21]), in the three-component reaction studied were found.

Formation of diselenophosphinates **2** can be represented as follows (Scheme 2). The intermediate secondary phosphine selenide (**A**) (the product of the known[22] reaction of secondary phosphine **1** with 1 equiv. of elementary selenium) is deprotonated upon the action of hydrazine, forming the *P*,*Se*-ambident selenophosphinite (**B**). The reaction of the latter with 1 equiv. of selenium leads to diselenophosphinate **2**.

Scheme 2



The fact of formation of hydrazinium diselenophosphinate **2a** by the reaction (EtOH, 70—75 °C, 0.5 h) of equivalent amounts of bis(2-phenylethyl)phosphine selenide (**3**), elementary selenium, and hydrazine hydrate is an (Scheme 3) indirect evidence of involvement of secondary phosphine selenides as reactive intermediates into the reaction found (see Scheme 2).

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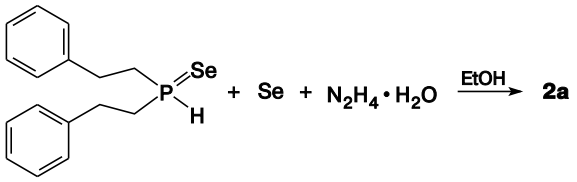
Scheme 3



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In conclusion, a selective and efficient synthesis of the earlier unknown hydrazinium diselenophosphinates has been developed based on a three-component atom-saving reaction of secondary phosphines with elementary selenium and hydrazine. It can be expected that these compounds will exhibit properties characteristic of both the alkali metal and alkylammonium[10–12] diselenophosphinates, and salts containing hydrazinium pharmacophore cation. For example, hydrazinium sulfate possesses anticancer activity[23] (pharmaceutical drug Sigrazine), as well as antioxidative and fungicide activity.[24]

Experimental

IR spectra were recorded on a Bruker IFS-25 spectrometer in KBr pellets. ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.13, 101.61, 161.98, and 76.31 MHz, respectively), with 85% H_3PO_4 (^{31}P NMR) and Me_2Se (^{77}Se NMR) being external standards. Secondary phosphines **1a**, **1b**, **1c**, and **1d** were synthesized from red phosphorus and styrene[25], 4-methoxystyrene, 2-methyl-5-vinylpyridine,[26] or 2-vinylfuran,[25] respectively. Bis(2-phenylethyl)phosphine selenide (**3**) was obtained by oxidation of phosphine **1a** with elementary selenium according to the procedure described earlier.[22] Diphenylphosphine (**1e**) was purchased from Aldrich. Commercial ethanol (96%) was used as the solvent. All the experimental steps were carried out under inert atmosphere (argon).

Synthesis of hydrazinium diselenophosphinates 2a—e (general procedure). Amorphous selenium (0.158 g, 2.0 mmol) was added to a solution of secondary phosphine **1** (1.0 mmol) and hydrazine hydrate (0.055 g, 1.1 mmol) in ethanol (10 mL) at ~20 °C. The reaction mixture was stirred for 0.5 h at 70—75 °C and filtered, the solvent was evaporated, the residue was washed with diethyl ether (2×10 mL) and dried *in vacuo* (40—45 °C, 1 Torr) to give salt **2**.

Reaction of phosphine selenide 3 with elementary selenium and hydrazine hydrate. Amorphous selenium (0.079 g, 1.0 mmol) was added to a solution of phosphine selenide **3** (0.321 g, 1.0 mmol) and hydrazine hydrate (0.051 g, 1.0 mmol) in ethanol (10 mL) at ~20 °C. The reaction mixture was stirred for 0.5 h at 70—75 °C and filtered, the solvent was evaporated, the residue was washed with diethyl ether (2×10 mL) and dried *in vacuo* (40—45 °C, 1 Torr) to obtain diselenophosphinate **2a**.

Hydrazinium bis(2-phenylethyl)diselenophosphinate (2a). The yield was 0.38 g (88%), white powder, m.p. 95—97 °C (EtOH). ^{1}H NMR (DMSO-d_6), δ: 2.25—2.32 (m, 4 H, CH_2P); 2.95—3.01 (m, 4 H, CH_2Ph); 5.37 (br.s, 5 H, NH); 7.14—7.29 (m, 10 H, Ph). ^{13}C NMR (DMSO-d_6), δ: 31.00 (CH_2Ph); 45.26 (d, CH_2P, $^1J_{P,C}$ = 36.6 Hz); 125.88 (*p*-C_{Ph}); 128.49 (*o*-C_{Ph}); 128.64 (*m*-C_{Ph}); 142.93 (d, *ipso*-C_{Ph}, $^3J_{P,C}$ = 17.3 Hz). ^{31}P NMR (DMSO-d_6), δ: 25.41 (+ d of satellites: $^1J_{P,Se}$ = 610 Hz). ^{77}Se NMR (DMSO-d_6), δ: –40 (d, $^1J_{P,Se}$ = 610 Hz). IR, ν/cm^{-1}: 3297, 3265, 3227, 3146, 3081, 3060, 3000, 2918, 2846, 2796, 2660, 2633, 2547, 1600, 1558, 1539, 1493, 1471, 1453, 1439, 1392, 1340, 1313, 1261, 1212, 1197, 1160, 1128, 1084, 1061, 1029, 1009, 972, 944, 933, 902, 851, 766, 749, 743, 728, 711, 696, 650, 572, 554, 509, 480, 471, 418. Found (%): C, 44.31; H, 5.28; N, 6.40; P, 6.98; Se, 36.42. $C_{16}H_{23}N_2PSe_2$. Calculated (%): C, 44.46; H, 5.36; N, 6.48; P, 7.17; Se, 36.53.

Hydrazinium bis[2-(4-methoxyphenyl)ethyl]diselenophosphinate (2b). The yield was 0.40 g (81%), white powder, m.p. 140—142 °C (EtOH). ^{1}H NMR (DMSO-d_6), δ: 2.19—2.26 (m, 4 H, CH_2P); 2.86—2.92 (m, 4 H, $CH_2C_6H_4$); 3.71 (s, 6 H, MeO); 6.82, 7.10 (m, 8 H, C_6H_4). ^{13}C NMR (DMSO-d_6), δ: 29.68 ($CH_2C_6H_4$); 45.07 (d, CH_2P, $^1J_{P,C}$ = 36.6 Hz); 54.94 (MeO); 113.71 (*o*-$C_{C_6H_4}$); 129.01 (*m*-$C_{C_6H_4}$); 134.31 (d, *ipso*-$C_{C_6H_4}$, $^3J_{P,C}$ = 17.3 Hz); 157.26 (*p*-$C_{C_6H_4}$). ^{31}P NMR (DMSO-d_6), δ: 24.02 (+ d of satellites: $^1J_{P,Se}$ = 611 Hz). ^{77}Se NMR (DMSO-d_6), δ: –76 (d, $^1J_{P,Se}$ = 611 Hz). IR, ν/cm^{-1}: 3489, 3279, 3160, 3059, 3005, 2935, 2917, 2839, 2800, 2663, 2551, 1610, 1581, 1513, 1468, 1443, 1397, 1391, 1374, 1323, 1301, 1249, 1178, 1127, 1088, 1032, 946, 933, 913, 868, 850, 818, 776, 727, 710, 696, 658, 644, 545, 504, 450. Found (%): C, 43.88; H, 5.61; N, 5.76; P, 6.07; Se, 32.19. $C_{18}H_{27}N_2O_2PSe_2$. Calculated (%): C, 43.91; H, 5.53; N, 5.69; P, 6.29; Se, 32.08.

Hydrazinium bis[2-(2-methylpyrid-5-yl)ethyl]diselenophosphinate (2c). The yield was 0.43 g (93%), white powder, m.p. 156—159 °C (Et_2O). ^{1}H NMR (D_2O), δ: 2.12—2.18 (m, 10 H, CH_2P, Me); 2.61—2.68 (m, 4 H, CH_2Py); 6.86, 7.27 (m, 4 H, Py); 7.93 (s, 2 H, Py). ^{13}C NMR (D_2O), δ: 21.56 (Me); 27.79 (CH_2Py); 41.60 (d, CH_2P, $^1J_{P,C}$ = 36.6 Hz); 123.46 (3-C_{Py}); 133.73 (d, 5-C_{Py}, $^3J_{P,C}$ = 16.2 Hz); 137.65 (4-C_{Py}); 146.36 (6-C_{Py}); 154.58 (2-C_{Py}). ^{31}P NMR (D_2O), δ: 23.60 (+ d of satellites: $^1J_{P,Se}$ = 567 Hz). ^{77}Se NMR (D_2O), δ: –62 (d, $^1J_{P,Se}$ = 567 Hz). IR, ν/cm^{-1}: 3279, 3205, 3143, 3034, 3003, 2922, 2639, 2525, 1643, 1603, 1569, 1491, 1444, 1398, 1390, 1327, 1309, 1298, 1277, 1244, 1212, 1207, 1189, 1137, 1115, 1099, 1040, 1004, 979, 948, 939, 934, 919, 865, 855, 844, 834, 826, 793, 774, 739, 725, 716, 709, 653, 547, 515, 481, 418, 402. Found (%): C, 41.55; H, 5.53; N, 12.16; P, 6.52; Se, 34.35. $C_{16}H_{25}N_4PSe_2$. Calculated (%): C, 41.57; H, 5.45; N, 12.12; P, 6.70; Se, 34.16.

Hydrazinium bis[2-(2-furyl)ethyl]diselenophosphinate (2d). The yield was 0.39 g (95%), white powder, m.p. 59—61 °C (Et_2O). ^{1}H NMR (DMSO-d_6), δ: 2.23—2.30 (m, 4 H, CH_2P); 2.97—3.03 (m, 4 H, CH_2Fur); 5.63 (br.s, 5 H, NH); 6.08, 6.23, 7.48 (m, 6 H, Fur). ^{13}C NMR (DMSO-d_6), δ: 23.27 (CH_2Fur); 41.06 (d, CH_2P, $^1J_{P,C}$ = 38.2 Hz); 104.74 (3-C_{Fur}); 110.31 (4-C_{Fur}); 141.14 (5-C_{Fur}); 155.55 (d, 2-C_{Fur}, $^3J_{P,C}$ = 20.3 Hz). ^{31}P NMR (DMSO-d_6), δ: 22.61 (+ d of satellites: $^1J_{P,Se}$ = 615 Hz). ^{77}Se NMR (DMSO-d_6), δ: –54 (d, $^1J_{P,Se}$ = 615 Hz). IR, ν/cm^{-1}: 3263, 3149, 3107, 2992, 2877, 2778, 2677, 2657, 2568, 2552, 1614, 1589, 1504, 1477, 1444, 1425, 1401, 1325, 1286, 1228, 1212, 1177, 1146, 1101, 1080, 1068, 1004, 953, 929, 921, 902, 884, 855, 837, 816, 799, 779, 764, 738, 726, 702, 665, 636, 612, 600, 509, 451, 420. Found (%): C, 34.88; H, 4.71; N, 6.76; P, 7.38; Se, 38.42. $C_{12}H_{19}N_2O_2PSe_2$. Calculated (%): C, 34.97; H, 4.65; N, 6.80; P, 7.51; Se, 38.31.

Hydrazinium diphenyldiselenophosphinate (2e). The yield was 0.33 g (88%), white powder, m.p. 101—103 °C (EtOH). ^{1}H NMR (DMSO-d_6), δ: 7.21—7.30, 8.00—8.05 (m, 10 H, Ph); 7.49 (br.s, 5 H, NH). ^{13}C NMR (DMSO-d_6), δ: 126.71 (d, *o*-C_{Ph}, $^2J_{P,C}$ = 11.6 Hz); 128.40 (d, *p*-C_{Ph}, $^4J_{P,C}$ = 2.3 Hz); 130.75 (d, *m*-C_{Ph}, $^3J_{P,C}$ = 11.2 Hz); 142.93 (d, *ipso*-C_{Ph}, $^1J_{P,C}$ = 59.3 Hz). ^{31}P NMR (DMSO-d_6), δ: 23.60 (+ d of satellites: $^1J_{P,Se}$ = 644 Hz). ^{77}Se NMR (DMSO-d_6), δ: –10 (d, $^1J_{P,Se}$ = 644 Hz). IR, ν/cm^{-1}: 3182, 3102, 2910, 2869, 1723, 1690, 1658, 1640, 1629, 1585, 1547, 1528, 1512, 1500, 1476, 1433, 1373, 1344, 1331, 1302, 1229, 1037, 1026, 996, 920, 803, 757, 745, 693, 670, 618, 587, 539, 516, 468. Found (%): C, 38.25; H, 4.07; N, 7.51; P, 8.09; Se, 41.90. $C_{12}H_{15}N_2PSe_2$. Calculated (%): C, 38.32; H, 4.02; N, 7.45; P, 8.23; Se, 41.98.

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