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LETTERS TO THE EDITOR

Reaction of Secondary Phosphines with Elemental Sulfur and Hydrazine: Atom-Economic Synthesis of Dithiophosphinates

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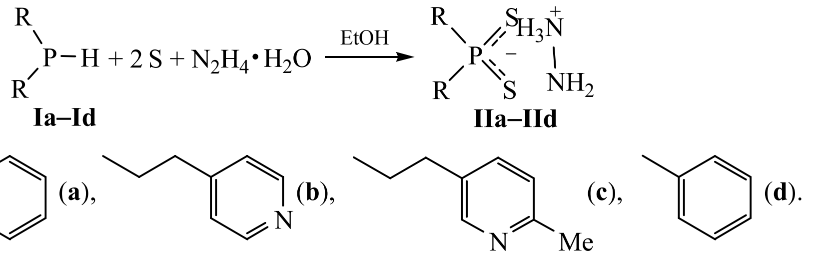
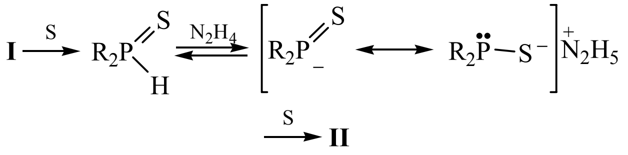
Here we for the first time report on the three-component reaction of the secondary phosphines with elemental sulfur and hydrazine. By the example of the readily available [1–2] secondary phosphines **Ia–Id** it was shown that heating of the reagents (molar ratio $R_2PH : S : N_2H_4 = 1 : 2 : 1.1$) at 70–75°C for 20 min in ethanol led to hydrazinium dithiophosphinates **IIa–IId** in 84–92% yield.

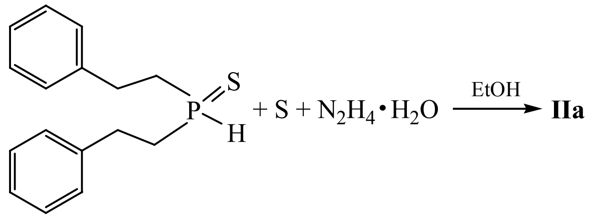


The reaction is highly selective. No side products, in particular, the expected polysulfides (the products of the known reaction of elemental sulfur with hydrazine [3]) were found in the studied three-component reaction.

The dicovered three-component reaction, apparently proceeds via the stage of formation of the secondary phosphine sulfides from the secondary phosphines **I** and one equivalent of elemental sulfur. Further hydrazine, acting as a base, deprotonates the secondary phosphine sulfides. The generated *P,S*-ambident thiophosphinites enter the reaction with the second equivalent of sulfur to afford hydrazinium dithiophosphinates **II**.



The above scheme is indirectly proved by the fact of formation of hydrazinium dithiophosphinate **IIa** in the reaction of equivalent amounts of bis(2-phenylethyl)phosphine sulfide (**III**), elemental sulfur, and hydrazine hydrate (EtOH, 70–75°C, 20 min).



III

Thus, it is shown for the first time that the reaction of the secondary phosphines with elemental sulfur and hydrazine is an effective atom-economic route to hydrazinium dithiophosphinates, promising ligands for designing metal complexes [4], antioxidants [5], potentially biologically active compounds [6], and reactive building blocks for organic and organoelemental synthesis [7].

Synthesis of hydrazinium dithiophosphinates (IIa-IId) (*general procedure*). To the solution of a secondary phosphine **I** (1.0 mmol) and hydrazine hydrate (0.055 g, 1.1 mmol) in 10 ml of ethanol rhombic sulfur (0.064 g, 2.0 mmol) was added at room temperature. The mixture was stirred at 70–75°C for 20 min, filtered, the solvent was removed, the residue was washed with ether (2×10 ml), and dried in a vacuum (35–40°C, 1 mm Hg) to obtain salt **II**.

Reaction of bis(2-phenylethyl)phosphine sulfide (III) with elemental sulfur and hydrazine. To the solution of phosphine sulfide **III** (0.274 g, 1.0 mmol) and hydrazine hydrate (0.055 g, 1.1 mmol) in 10 ml of ethanol rhombic sulfur (0.032 g, 1.0 mmol) was added at room temperature. The mixture was stirred at 70–75°C for 20 min, filtered, the solvent was removed, the residue was washed with ether (2×10 ml), and dried in a vacuum (35–40°C, 1 mm Hg) to obtain 0.30 g (89%) of dithiophosphinate **IIa**.

Hydrazinium bis(2-phenylethyl)dithiophosphinate (IIa), 0.30 g (89%), white powder, mp 146–148°C (ethanol). IR (KBr), cm^{-1}: 3305, 3234, 3187, 3161, 3081, 3059, 3023, 2973, 2931, 2811, 2676, 2642, 2559, 1600, 1583, 1562, 1494, 1479, 1454, 1441, 1392, 1266, 1229, 1213, 1198, 1179, 1162, 1147, 1127, 1091, 1028, 1018, 1009, 1000, 989, 973, 948, 938, 910, 896, 852, 828, 769, 756, 743, 730, 695, 666, 606, 577, 551, 508, 490, 479. ^{1}H NMR, δ, ppm: 2.00–2.07 m (4H, CH_2P), 2.90-2.97 m (4H, CH_2Ph), 6.93 s (5H, NH), 7.12–7.27 m (10H, Ph). ^{13}C NMR, δ_C, ppm: 29.79 (CH_2Ph), 44.47 d (CH_2P, $^1J_{CP}$ = 50.8 Hz), 125.51 (C-*p*), 128.10 (C-*o*), 128.29 (C-*m*), 143.0 d (C-*i*, $^3J_{CP}$ = 16.2 Hz). ^{31}P NMR, δ_P, ppm: 67.32. Found, %: C 56.70; H 6.81; N, 8.30; P 9.01; S 19.05. $C_{16}H_{23}N_2PS_2$. Calculated, %: C 56.78; H 6.85; N, 8.28; P 9.15; S 18.95.

Hydrazinium bis[2-(4-pyridyl)lethyl]dithiophosphinate (IIb), 0.31 g (91%), white powder, mp 193–196ºC (ethanol). IR (KBr), cm^{-1}: 3263, 3134, 3070, 3036, 2899, 2581, 2089, 1603, 1556, 1499, 1448, 1418, 1316, 1280, 1238, 1214, 1202, 1137, 1128, 1081, 1070, 1003, 965, 947, 924, 828, 800, 772, 758, 742, 726, 714, 614, 603, 582, 512, 490. ^{1}H NMR, δ, ppm: 2.03–2.10 m (4H, CH_2P), 2.95–3.01 m (4H, CH_2Py), 7.10 s (5H, NH), 7.22 and 8.42 m (8H, Py). ^{13}C NMR, δ_C, ppm: 29.27 (CH_2Py), 43.17 d (CH_2P, $^1J_{CP}$ = 50.8 Hz), 123.86 (C-3, Py), 149.50 (C-2, Py), 152.06 d (C-4, Py, $^3J_{CP}$ = 17.3 Hz). ^{31}P NMR, δ_P, ppm: 67.46. Found, %: C 49.45; H 6.20; N, 16.34; P 8.87; S 19.02. $C_{14}H_{21}N_4PS_2$. Calculated, %: C 49.39; H 6.22; N, 16.46; P 9.10; S 18.84.

Hydrazinium bis[2-(2-methylpyrid-5-yl)lethyl]dithiophosphinate (IIc), 0.31 g (84%), white powder, mp 149–151ºC (ethanol). IR (KBr), cm^{-1}: 3238, 3142, 3076, 3035, 2918, 2766, 2694, 2605, 2106, 1604, 1567, 1515, 1491, 1446, 1393, 1331, 1300, 1278, 1245, 1202, 1138, 1099, 1037, 1013, 970, 943, 930, 858, 827, 782, 734, 727, 709, 700, 655, 611, 557, 543, 494. ^{1}H NMR, δ, ppm: 2.60–2.67 m (4H, CH_2P), 3.04 s (6H, Me), 3.51–3.57 m (4H, CH_2Py), 7.70 s (5H, NH), 7.76 and 8.11 m (4H, Py), 8.90 s (2H, Py). ^{13}C NMR, δ_C, ppm: 24.69 (Me), 27.76 (CH_2Py), 45.30 d (CH_2P, $^1J_{CP}$ = 49.8 Hz), 123.81 (C-3, Py), 136.23 d (C-5, Py, $^3J_{CP}$ = 15.2 Hz), 137.10 (C-4, Py), 149.69 (C-6, Py), 156.06 (C-2, Py). ^{31}P NMR, δ_P, ppm: 67.68. Found, %: C 52.18; H 6.87; N, 8.71; P 8.32; S 17.65. $C_{16}H_{25}N_4PS_2$. Calculated, %: C 52.15; H 6.84; N, 15.20; P 8.41; S 17.40.

Hydrazinium diphenyldithiophosphinate (IId), 0.26 g (92%), white powder, mp 96–98°C (ethanol). IR (KBr), cm^{-1}: 3302, 3245, 3140, 302, 2869, 2697, 2643, 2564, 1569, 1496, 1481, 1472, 1434, 1387, 1303, 1224, 1173, 1158, 1094, 1067, 1024, 998, 932, 851, 752, 743, 702, 692, 653, 644, 628, 612, 607, 560, 526, 488. ^{1}H NMR, δ, ppm: 6.61 s (5H, NH), 7.19–7.27 and 7.96–8.01 m (10H, Ph). ^{13}C NMR, δ_C, ppm: 126.81 d (C-*o*, $^2J_{CP}$ = 12.2 Hz), 128.14 (C-*p*), 130.24 d (C-*m*, $^3J_{CP}$ =10.2 Hz), 145.77 d (C-*i*, $^1J_{CP}$ = 77.2 Hz). ^{31}P NMR, δ_P, ppm: 61.61. Found, %: C 51.08; H 5.39; N, 9.71; P 10.69; S 22.84. $C_{12}H_{15}N_2PS_2$. Calculated, %: C 51.04; H 5.35; N, 9.92; P 10.97; S 22.71.

IR spectra were recorded on a Bruker IFS-25 spectrometer in KBr pellets. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained on a Bruker DPX-400 spectrometer (400.13, 101.61 and 161.98 MHz, respecttively) in DMSO-d_6, external standard 85% H_3PO_4 (^{31}P). Secondary phosphines **Ia**, **Ib**, and **Ic** were synthesized from red phosphorus, styrene [1], 4-vinylpyridine [2] or 2-methyl-5-vinylpyridine [2], respectively. Bis(2-phenylethyl)phosphine sulfide (**III**) was obtained by oxidation of phosphine **Ia** with elemental sulfur by the known procedure [8].

Diphenylphosphine was a commercial product (Aldrich, 2009). Commercial 96% ethanol was used as a solvent. All experiments were run in an inert atmosphere (argon).

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