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Unexpected redox reaction of alkali metal diselenophosphinates with elemental iodine

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Redox reaction between alkali metal diselenophosphinates $R_2P(Se)SeM$ (M = Na, K) and elemental iodine in a 2:1 molar ratio (1,4-dioxane, room temperature, 2 min) gives bis(diorganylselenophosphoryl)selenides $[R_2P(Se)]_2Se$ and bis(diorganylselenophosphoryl)triselenides $[R_2P(Se)]_2Se_3$ in 87–90% total yields.

Nowadays the chemistry of diselenophosphinates is intensively studied^{1–3} due to the development of efficient methods for their synthesis *via* novel three-component reactions between secondary phosphines or secondary phosphine selenides, elemental selenium and bases, such as alkali metal hydroxides⁴ or amino compounds.^{5–8} For example, alkali metal diselenophosphinates are useful as precursors of remarkable nanocrystalline materials,^{2,9} ligands for metal complexes¹⁰ and building blocks for organic synthesis.^{3(a),(e)}

In the present work we report on redox reaction of alkali metal diselenophosphinates with elemental iodine.

Alkali metal dithiophosphinates, $R_2P(S)SM$ (R = Alk, Ar; M = Na, K), are known to be readily oxidized by elemental iodine to afford the homocoupling products, disulfides of $R_2P(S)SS(S)PR_2$ type.¹¹ It might be anticipated that alkali metal diselenophosphinates, $R_2P(Se)SeM$ would react with elemental iodine in a similar fashion giving the corresponding diselenides, $R_2P(Se)SeSe(Se)PR_2$.

However, it has been found that this reaction between alkali metal diselenophosphinates **1–3** and elemental iodine in a 2:1 molar ratio unexpectedly furnishes monoselenides $[R_2P(Se)]_2Se$ **4**, **5** and triselenides $[R_2P(Se)]_2Se_3$ **6**, **7** in 87–90% total yields (Scheme 1).^{†,‡} The reaction proceeds in 1,4-dioxane media at room temperature unusually fast (2 min), the expected diselenides $[R_2P(Se)]_2Se_2$ being not formed (³¹P and ⁷⁷Se NMR).

According to ³¹P NMR data, monoselenides **4**, **5** and triselenides **6**, **7** were formed in an equimolar ratio.

The structure of the compounds synthesized unambiguously follows from ³¹P, ⁷⁷Se, ¹³C and ¹H NMR spectra. Monoselenide **4** and triselenide **6** were isolated as molecular (1:1) co-crystals **8**,[†] the structure of which was determined by X-ray diffraction ana-



Scheme 1

lysis.[§] The crystalline structure of the co-crystal **8** is formed by two pair of crystallographically independent molecules **4** and **6** (Figure 1). In selenides **4** and **6**, coordination geometry around the phosphorus atoms is a slightly distorted tetrahedron. The Se=P–Se–P=Se fragment of monoselenide **4** has *cis-trans* (*synanti*, *sp-ap*) conformation. One of close analogues of monoselenide **4**, $[\Pr_2^i P(Se)]_2 Se$,¹² has the same conformation, while other analogue, $[Ph_2P(Se)]_2 Se$,¹² is in *gauche-trans* (*syn-anti*, *sc-ap*) conforma-

[†] The ¹H, ¹³C, ³¹P and ⁷⁷Se NMR spectra were recorded on a Bruker AV-400 spectrometer (400.13, 101.61, 161.98 and 76.31 MHz, respectively) and referenced to H₃PO₄ (³¹P NMR) and Me₂Se (⁷⁷Se NMR). FTIR spectra were run on a Bruker Vertex 70 instrument. All steps of the experiment were carried out in dry argon atmosphere. Absolute 1,4-dioxane was used in the reaction as a solvent. Alkali metal diselenophosphinates **1–3** were prepared according to a published method.⁴

Reaction between alkali metal diselenophosphinates **1**, **2** and elemental iodine. To a solution of alkali metal diselenophosphinate **1**, **2** (1.0 mmol) in 1,4-dioxane (6 ml), a solution of elemental iodine (0.127 g, 0.5 mmol) in 1,4-dioxane (10 ml) was added dropwise with stirring at room temperature over a period of 2 min. The resulting reaction mixture was diluted with water (20 ml) and extracted with toluene (2×20 ml). The extract was dried over K₂CO₃ and concentrated *in vacuo* to one tenth of its volume. Upon addition of hexane (10 ml) and storage at 5–8 °C overnight, co-crystal **8** precipitated as orange-red solid, which was washed with hexane (5 ml) and dried *in vacuo* (1 Torr) to give crystals suitable for X-ray analysis.

Co-crystal 8 {co-crystal of bis[di(2-phenethyl)selenophosphoryl]selenide 4 and bis[di(2-phenethyl)selenophosphoryl]triselenide 6]: orange-red crystals, yield 0.36 g (90%), mp 117-118 °C (hexane-toluene). IR (KBr, v/cm⁻¹): 3060, 3020, 2919, 2888, 2854, 1951, 1878, 1806, 1644, 1590, 1491, 1444, 1387, 1330, 1270, 1210, 1131, 1020, 1005, 939, 906, 825, 745, 670, 570, 507, 458. ¹H NMR (400.13 MHz, CDCl₃) δ: 2.78–2.91 (m, 16H, CH₂P), 3.23–3.33 (m, 16H, CH₂Ph), 7.37–7.48 (m, 40H, Ph). ¹³C NMR (100.62 MHz, CDCl₃) δ: 29.43, 29.56 and 29.74 (CH₂Ph), 37.95, 37.97 and 38.10 (d, CH₂P, ${}^{1}J_{PC}$ 30.1, 30.0 and 32.0 Hz), 126.56 and 126.61 (p-C_{Ph}), 128.29 and 128.64 (o,m-C_{Ph}), 139.25, 139.35 and 139.37 (d, *i*-C_{Ph}, ³J_{PC} 10.35, 10.83 and 10.73 Hz). ³¹P NMR (161.98 MHz, CDCl₃) δ : 50.15 (s + satellites, 1P, triselenide, ¹J_{PSe} 384 Hz, ¹J_{PSe} 740 Hz), 51.94 (br. s, 1P, triselenide), 55.64 (s + satellites, 2P, monoselenide, ${}^{1}J_{PSe}$ 382 Hz, ${}^{1}J_{PSe}$ 726 Hz, ${}^{1}J_{PSe}$ 766 Hz, ${}^{2}J_{PP}$ 19.5 Hz). 77 Se NMR (76.31 MHz, CDCl₃) δ : -195 (d, 2 Se, P=Se of triselenide, ¹J_{PSe} 740 Hz), -142 (d, 2 Se, P=Se of monoselenide, ¹J_{PSe} 741 Hz), 283 (t, 1Se, P-Se-P of monoselenide, ${}^{1}J_{PSe}$ 382 Hz), 364 (d, 2Se, P–Se of triselenide, ${}^{1}J_{PSe}$ 420 Hz), 415 (d, 1Se, P-Se-Se-P of triselenide, ²J_{PSe} 115 Hz). Found (%): C, 48.20; H, 4.56; P, 7.81; Se, 39.46. Calc. for C₆₄H₇₂P₄Se₈ (%): C, 48.14; H, 4.54; P, 7.76; Se, 39.56.



Figure 1 X-ray structures of (*a*) monoselenide 4 (one of two independent molecules) and (*b*) triselenide 6 (one of two independent molecules) in the co-crystal 8. Range of selected bond lengths (Å): P=Se 2.071(4)-2.108(3), P–Se 2.237(3)-2.291(3), P–C 1.79(1)-1.90(1), Se–Se 2.336(2)-2.344(2).

tion. The Se=P–Se–Se–Se–P=Se fragment of both independent molecules of triselenide **6** can be ascribed to *trans-gauche-gauche-trans (anti-syn-syn-anti, ap-sc-sc-ap)* conformation. Close congeners of triselenide **6**, $[Et_2P(Se)]_2Se_3^{13}$ and $[(EtO)_2P(Se)]_2Se_3^{,14}$ have the same conformation. The values of the P–Se and P=Se bond lengths in the molecules of monoselenide and triselenide are similar to literature ones.^{12–14}

Note that Se–Se intermolecular contacts exist between molecules of triselenide in co-crystal 8 (Figure 2) as is evident from

Mixture of bis{di[2-(2-furyl)ethyl]selenophosphoryl}selenide 5 and bis{di[2-(2-furyl)ethyl]selenophosphoryl]triselenide 7: orange-red oil, yield 0.33 g (87%). IR (film, v/cm⁻¹): 3156, 3117, 3104, 2952, 2932, 2895, 2850, 1649, 1593, 1505, 1435, 1390, 1375, 1325, 1276, 1224, 1203, 1194, 1169, 1142, 1120, 1106, 1067, 1031, 1005, 964, 946, 936, 915, 901, 883, 820, 777, 725, 675, 643, 601, 493, 420, 402. ¹H NMR (400.13 MHz, C₆D₆) δ: 2.56–2.69 and 2.71–2.84 (m, 16H, CH₂P), 2.93–3.25 (m, 16H, CH₂Fur), 6.10–7.33 (m, 24 H, Fur). ¹³C NMR (100.62 MHz, C₆D₆) δ: 22.54 (CH₂Fur), 32.80 (d, CH₂P, ${}^{1}J_{PC}$ 35.4 Hz), 106.42 (3-C_{Fur}), 110.45 (4-C_{Fur}), 141.35 (5-C_{Fur}), 152.90 (d, 2-C_{Fur}, ${}^{3}J_{PC}$ 18.6 Hz). ${}^{31}P$ NMR (161.98 MHz, C_6D_6) δ : 49.31 (s + satellites, 1P, triselenide, ¹ J_{PSe} 380 Hz, ${}^{1}J_{\text{PSe}}$ 740 Hz), 50.88 (br. s, 1P, triselenide), 54.95 (s + satellites, 2P, monoselenide, ${}^{1}J_{PSe}$ 376 Hz, ${}^{1}J_{PSe}$ 734 Hz, ${}^{1}J_{PSe}$ 770 Hz, ${}^{2}J_{PP}$ 19.7 Hz). ⁷⁷Se NMR (76.31 MHz, C_6D_6) δ : -193 (d, 2 Se, P=Se of triselenide, ¹J_{PSe} 740 Hz), -147 (d, 2 Se, P=Se of monoselenide, ${}^{1}J_{PSe}$ 752 Hz), 280 (t, 1 Se, P–Se–P of monoselenide, ¹J_{PSe} 376 Hz), 357 (d, 2 Se, P–Se of triselenide, ¹J_{PSe} 424 Hz), 419 (d, 1Se, P-Se-Se-P of triselenide, ²J_{PSe} 120 Hz). Found (%): C, 38.10; H, 3.68; P, 8.11; Se, 41.57. Calc. for C₄₈H₅₆O₈P₄Se₈ (%): C, 38.02; H, 3.72; P, 8.17; Se, 41.65

[§] X-ray diffraction analysis of co-crystal **8** was performed on a Bruker SMART KAPPA APEX-II CCD diffractometer at 150 K [MoKα radiation, λ (MoKα) = 0.71073 Å, φ , ω -scans]. The structure was solved by direct methods and refined by a full matrix least-squares anisotropic procedure using SHELXTL97 programs.¹⁹ The parameters of the hydrogen atoms were given geometrically.

Co-crystals **8** ($C_{64}H_{72}P_4Se_8$, M = 1596.83) are monoclinic, space group $P2_1/n$, a = 26.733(1), b = 10.6037(5) and c = 48.118(2) Å, $\beta = 103.736(2)^\circ$, V = 13250(1) Å³, Z = 8, $d_{calc} = 1.601$ g cm⁻³, μ (MoK α) = 4.546 mm⁻¹, 89 949 reflections were measured, from which 24 246 were independent ($R_{int} = 0.0561$), $R_1 = 0.0829$ for 16480 reflections with $I > 2\sigma(I)$, $wR_2 = 0.2185$, S = 1.155.

CCDC 822761 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2012.



Figure 2 Intermolecular contacts between selenium atoms of triselenide molecules in the lattice of co-crystal 8. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): $Se(1) \cdots Se(1) 3.455(2)$, $Se(4) \cdots Se(9) 3.509(1)$.

the Se(1)…Se(1) and Se(4)…Se(9) distances of 3.455(2) and 3.509(1) Å, respectively, which is less than the sum of the van der Waals radii (3.80 Å).¹⁵

Furthermore, the ³¹P NMR spectra of triselenides **6**, **7** comprise two singlets at 49.31–51.49 ppm which are accompanied by sets of ⁷⁷Se satellites. The presence of the several signals in the ³¹P NMR spectra of the triselenides can be explained by intermolecular interactions between molecules of triselenides in solution. The results of investigation of this phenomenon will be published elsewhere.

To our knowledge, molecular co-crystal **8** is first example of co-crystals of these rare and unstudied mono- and triselenides. Currently, only few representatives of monoselenides and triselenides were prepared (all in the form of monomolecular crystals).^{12–14,16–18}

The mechanism of the discovered redox reaction still needs to be elucidated. At the moment, formation of mono- and triselenides *via* sequence of the following processes seems to be most probable (Scheme 2). Single electron oxidation of diselenophosphinate 1-3 by iodine generates diselenophosphinate radical A (stage 1) which is recombined giving intermediate diselenide B (stage 2). Disproportionation of the latter affords monoselenide 4, 5 and triselenide 6, 7 (stage 3) as the reaction products. The mechanism proposed is in compliance with experimental data indicating that mono- and triselenides are formed in equimolar amounts.

In summary, the unexpected pathway of the redox reaction between alkali metal diselenophosphinates and elemental iodine has been discovered. The reaction proceeds under mild conditions (room temperature, 2 min) to give bis(diorganylselenophosphoryl)selenides and bis(diorganylselenophosphoryl)triselenides in high total yields. The results obtained significantly contribute to basic chemistry of selenophosphorus compounds (including their solid state chemistry).



Scheme 2

[‡] Reaction between sodium diselenophosphinate **3** and elemental iodine. To a solution of sodium bis[2-(2-furyl)ethyl]diselenophosphinate **3** (0.402 g, 1.0 mmol) in 1,4-dioxane (6 ml), a solution of elemental iodine (0.127 g, 0.5 mmol) in 1,4-dioxane (10 ml) was added dropwise with stirring at room temperature over a period of 2 min. The resulting reaction mixture was diluted with water (20 ml) and extracted with toluene (2×20 ml). The extract was dried over K₂CO₃, the toluene was removed *in vacuo*, and the residue was reprecipitated from 1,4-dioxane (4 ml) to hexane (18 ml), dried *in vacuo* (1 Torr) to give mixture of selenides **5** and **7** in a 1:1 molar ratio (³¹P NMR data).

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Online Supplementary Materials

Supplementary data (³¹P NMR spectra of reaction mixtures) associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.01.006.

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