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Synthesis of Tris(organylthioethyl)phosphines and Their Derivatives on the Basis of the Reaction of Phosphine with Vinyl Sulfides

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Abstract—Phosphine generated from the red phosphorus in the system KOH–H₂O–toluene adds regio- and chemoselectively to vinyl sulfides under radical initiation conditions with the formation of tris(2-organylthioethyl)phosphines, which are easily oxidized by elemental sulfur and selenium to the corresponding phosphine sulfides and phosphine selenides in 54–78% yield. The obtained adducts are split when treated with sodium amide in THF to give trivinylphosphine and trivinylphosphine chalcogenides.

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Tertiary phosphines and phosphine chalcogenides containing organylthio groups are efficient polydentate (chemilabile) ligands [1–3]. On their basis, ^{99m}Tc-complexes for myocardial diagnostics [4], as well as the metal complexes for the alkylation [2] and hydro-formylation [3] reactions were obtained. Besides, tertiary organylthiophosphines and phosphine chalcogenides are used as building blocks in organic synthesis (for example, for preparation of vinyl phosphine oxides [5]) and the models for investigation of the fundamental problem of the relative ability of the phosphorus and sulfur atoms of different valence to stabilize the adjacent carbanions [5–7].

One of convenient approaches to the synthesis of these compounds is the reaction of secondary phosphines [7, 8] and phosphine chalcogenides [9] with the available vinyl sulfides [10]. At the same time, the data on the use the simplest representative of the PHaddends, phosphine PH₃, in this reaction are scarce. A short communication [11] reported that phosphine added to vinyl sulfides under radical initiation conditions to form a mixture of primary, secondary, and tertiary phosphines. The conditions for the predominant formation of tris(organylthioethyl)phosphine oxides were found [11].

The goal of the present study was to elaborate an expedient approach to the synthesis of functional tertiary phosphines, phosphine sulfides, and phosphine selenides containing organylthio groups on the basis of the reaction of phosphine with vinyl sulfides, and the investigation of some properties of these compounds.

To this end the initial phosphine was generated in a separate flask from red phosphorus in the system



 $R = C_7 H_{15}$ (I), Ph (II); $R = C_7 H_{15}$, X = S (III); $R = C_7 H_{15}$, X = Se (IV); R = Ph, X = S (V); R = Ph, X = Se (VI).

KOH-H₂O-toluene [12] and passed in the course of 4-6 h at the atmospheric pressure through the solution of vinyl sulfide I, II in dioxane containing catalytic amounts of AIBN heated to 68-80°C. Then the bubbling of phosphine was stopped and the unreacted phosphine was removed by an argon stream. To the reaction mixture a portion of vinyl sulfide (30% of the initial amount) was added, and the heating was continued for another 1.5 h at 68-80°C till the exhaustive sulfinylethylation of phosphine. Under these condition the reaction proceeded regio- and chemoselectively leading to the corresponding tris(2-organylthioethyl)phosphines III-VI. The latter are easily oxidized (without isolation and purification) with elemental sulfur or selenium (20-40°C) to the corresponding phosphine sulfides and phosphine selenides in 54-78% yield.

By the example of the reaction of phosphine with vinyl phenyl sulfide it was shown that the intermediate tris(2-phenylthioethyl)phosphine **VII** can be isolated from the reaction mixture in 73% yield and of up to 90% purity. It contained as an impurity the unreacted vinyl phenyl sulfide identified by the ¹H NMR method.

The individual phosphine **VII** was obtained in 94% yield by the reduction of tris(2-phenylthioethyl)phosphine selenide **VI** with sodium metal in toluene at $108-110^{\circ}$ C.



The synthesized functional tertiary phosphines and phosphine chalcogenides are convenient intermediates for preparation of, for example, trivinylphosphines and trivinylphosphine chalcogenides. Thus, phosphine **VII** and phosphine sulfide **V** when treated with sodium amide in THF ($63-64^{\circ}$ C) form trivinylphosphine **VIII** and trivinylphosphine sulfide **IX** in the yield of 86% and 82%, respectively.



¹ LP is lone electron pair.

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We failed to obtain trivinylphosphine selenide X from phosphine selenide VI and sodium amide under these conditions: a substantial amount of elemental selenium was formed in the reaction mixture. However, compound X is easily obtained by oxidation of trivinylphosphine VIII with elemental selenium (THF, room temperature).



The obtained trivinylphosphine and trivinylphosphine chalcogenides are promising cross-linking agents for noncombustible materials and reactive building blocks for organic synthesis [13]. In particular, trivinylphosphine oxides are used in the metathesis reactions for preparation of P-stereogenic phosphine oxides with three different alkenyl groups [14]. Besides, they are convenient models for physicochemical investigations [15], and for solving a fundamental problem of competitive deprotonation in the vicinal fragment X=PCH₂CH₂S (X = LP, S, Se) [5–7].

Thus, on the basis of the reaction of phosphine and vinylsulfides the earlier unknown representatives of tris (organylthioethyl)phosphines, phosphine sulfides, and phosphine selenides are synthesized. The obtained adducts are convenient intermediates in the synthesis of trivinylphosphine and its chalcogenides, whereas the known methods of their preparation are laborious and based on the reactions of aggressive phosphorus chlorides with organometal compounds [14, 16, 17].

EXPERIMENTAL

¹H, ¹³C, and ³¹P NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.13, 101.62, and 161.98 MHz, respectively), in CDCl₃, internal reference HMDS, external reference 85% H₃PO₄. IR spectra were obtained on a Bruker IFS 25 spectrometer in thin films and KBr pellets.

Tris(organylthioethyl)phosphine chalcogenides (III–VI) (general procedure). The solution of 0.06 g of AIBN in 25 ml of dioxane was flushed with argon and saturated with phosphine in the course of 15 min. To the obtained solution, at 68–80°C, while stirring with a magnetic stirrer and passing the phosphine, the solution of 9.3 mmol of the corresponding vinylorganyl sulfide I, II in 6 ml of hexane was added dropwise during 1 h; the passing of phosphine was continued during 3–5 h, then stopped, the reaction mixture was flushed with argon, and 3.2 mmol of the corresponding vinylorganyl sulfide in 3 ml of dioxane and 0.03 g of AIBN was added. The mixture was stirred for 1.5 h and 4.2 mmol of elemental sulfur was added (at room temperature) or of selenium (at 40–45°C). Dioxane was removed in a vacuum, the residue was crystallized from ethanol.

Tris(2-heptylthioethyl)phosphine sulfide (III). Yield 1.26 g (56%). Light-yellow oil. IR spectrum (film), ν, cm⁻¹: 581 (P=S). ¹H NMR spectrum, δ, ppm: 0.90 t (9H, CH₃ $^{3}J_{HH}$ 6.8 Hz) 1.29 m (24H, C₄H₈), 1.60 m (6H, CH₂C₅H₁₁), 2.19 m (6H, PCH₂), 2.56 t (6H, SCH₂C₆H₁₃ $^{3}J_{HH}$ 7.4 Hz), 2.81 m (6H, SCH₂CH₂P). ³¹P NMR spectrum, δ_P, ppm: 47.03. Found, %: C 59.87; H 10.41; P 5.29; S 23.59. C₂₇H₅₇PS₄. Calculated, %: C 59.94; H 10.62; P 5.73; S 23.71.

Tris(2-heptylthioethyl)phosphine selenide (IV). Yield 1.41 g (58%). Light-yellow oil. IR spectrum (film), v, cm⁻¹: 460 (P=Se). ¹H NMR spectrum, δ, ppm: 0.88 t (9H, CH₃ ${}^{3}J_{\text{HH}}$ 6.8 Hz) 1.28 m (24H, C₄H₈), 1.59 m (6H, CH₂C₅H₁₁), 2.29 m (6H, PCH₂), 2.55 t (6H, SCH₂C₆H₁₃ ${}^{3}J_{\text{HH}}$ 7.3 Hz), 2.79 m (6H, SCH₂CH₂P). ³¹P NMR spectrum, δ_P, ppm: 36.45. Found, %: C 55.39; H 9.80; P 5.06; S 16.52; Se 13.81. C₂₇H₅₇PS₃Se. Calculated, %: C 55.16; H 9.77; P 5.27; S 16.36; Se 13.43.

Tris(2-phenylthioethyl)phosphine sulfide (V). Yield 2.31 g (78%). White needle crystals, mp 71°C (ethanol). IR spectrum (KBr), ν, cm⁻¹: 577 (P=S). ¹H NMR spectrum, δ, ppm: 2.27 m (6H, PCH₂), 3.24 m (6H, SCH₂), 7.41 m (15H, Ph). ³¹P NMR spectrum, δ_P , ppm: 47.15. Found, %: C 61.02; H 5.71; P 6.20; S 27.45. C₂₄H₂₇PS₄. Calculated, %: C 60.72; H 5.73; P 6.52; S 27.02.

Tris(2-phenylthioethyl)phosphine selenide (VI). Yield 1.18 g (54%). White crystals, mp 68°C (ethanol). IR spectrum (KBr), v, cm⁻¹: 482 (P=Se). ¹H NMR spectrum, δ, ppm: 2.21 m (6H, PCH₂), 3.07 m (6H, SCH₂), 7.24 m (15H, Ph). ³¹P NMR spectrum, δ_P , ppm: 36.04. Found, %: C 55.25; H 5.21; P 5.85; S 18.25; Se 15.31. C₂₄H₂₇PS₃Se. Calculated, %: C 55.26; H 5.22; P 5.94; S 18.44; Se 15.14.

Tris(2-phenylthioethyl)phosphine (VII). A threeneck flask equipped with a thermometer, a condenser and an inlet tube for passing argon was charged with 2.09 g (4.0 mmol) of tris(2-phenylthioethyl)phosphine selenide dissolved in 15 ml of anhydrous toluene, flushed with argon, heated to 75–80°C, and a five-fold molar excess of Na (0.46 g) was added. The reaction mixture was vigorously stirred for 2 h 20 min at reflux (108–110°C), cooled, the formed precipitate was filtered off (under argon), washed with toluene, toluene was removed in a vacuum to obtain 1.66 g (94%) of tris(2-phenylthio)phosphine. White paraffin-like mass. ¹H NMR spectrum, δ , ppm: 1.85 m (6H, PCH₂), 3.03 m (6H, SCH₂), 7.32 m (15H, Ph). ³¹P NMR spectrum, δ_P , ppm: –27.01. Found, %: C 65.37; H 6.38; P 6.75; S 21.52. C₂₄H₂₇PS₃. Calculated, %: C 65.12; H 6.15; P 7.00; S 21.73.

Trivinylphosphine (VIII). A three-neck flask equipped with a thermometer, a condenser and an inlet tube for passing argon was charged with the solution of 1.37 g (3.1 mmol) of tris(2-phenylthioethyl)phosphine VII in 25 ml of anhydrous THF, flushed with argon and heated to 40-45°C. Then 0.62 g (16 mmol) of NaNH₂ was added at stirring with a magnetic stirrer, the reaction mixture was heated to 64°C for 5.5 h. The formed precipitate was filtered off, washed with THF, THF was removed under the atmospheric pressure in the stream of argon. 0.3 g (86%) of trivinylphosphine **VIII** was obtained. ¹H NMR spectrum, δ , ppm: 6.26 m $(1H, H_X)$; 5.78 m $(1H, H_A)$; 5.63 m $(1H, H_B)$; ² $J(H_AH_B)$ 1.9 Hz; ${}^{3}J(H_{A}H_{X})$ 11.7 Hz; ${}^{3}J(H_{B}H_{X})$ 18.5 Hz; ${}^{2}J(PH_{X})$ 12.0 Hz; ${}^{3}J(PH_{A})$ 30.8 Hz; ${}^{3}J(PH_{B})$ 14.0 Hz. ${}^{13}C$ NMR spectrum, $\delta_{\rm C}$, ppm: 127.50 (=CH₂, ²J_{PC} 19.7 Hz), 136.55 (=CH, ¹J_{PC} 11.3 Hz). ³¹P NMR spectrum, $\delta_{\rm P}$, ppm: -17.9. Physicochemical characteristics are identical to those described in [17].

Trivinylphosphine sulfide (IX) was prepared similar to phosphine **VIII** from 0.4 g (0.84 mmol) of phosphine sulfide **V** and 0.17 g (4.4 mmol) of NaNH₂. Yield 0.098 g (82%). ¹H NMR spectrum, δ , ppm: 6.36 m (1H, H_X); 6.17 m (1H, H_A); 6.30 m (1H, H_B); ²*J*(H_AH_B) 0.7 Hz; ³*J*(H_AH_X) 11.7 Hz; ³*J*(H_BH_X) 17.8 Hz; ²*J*(PH_X) 24.6 Hz; ³*J*(PH_A) 46.2 Hz; ³*J*(PH_B) 24.8 Hz. ¹³C NMR spectrum, δ_{C} , ppm: 133.67 (=CH₂, ²*J*_{PC} 1.5 Hz), 130.50 (=CH, ¹*J*_{PC} 80.3 Hz). ³¹P NMR spectrum, δ_{P} , ppm: 29.2. Physicochemical characteristics are identical to those described in [17].

Trivinylphosphine selenide (X). To a solution of 0.18 g (1.6 mmol) of trivinylphosphine **VIII** in 10 ml of anhydrous THF at stirring with a magnetic stirrer at room temperature 0.13 g (1.6 mmol) of elemental selenium was added in small portions. The reaction mixture was stirred to complete disappearance of selenium (1 h), THF was removed in vacuum to obtain 0.3 g (97%) of phosphine selenide **X**. ¹H NMR spectrum, δ , ppm: 6.37 m (1H, H_X); 6.16 m (1H, H_A);

6.29 m (1H, H_B); ²*J*(H_AH_B) 1.0 Hz; ³*J*(H_AH_X) 11.8 Hz; ³*J*(H_BH_X) 18.0 Hz; ²*J*(PH_X) 23.9 Hz; ³*J*(PH_A) 47.4 Hz; ³*J*(PH_B) 25.7 Hz. ¹³C NMR spectrum, δ_{C} , ppm: 134.58 (=CH₂, ²*J*_{PC} 1.5 Hz), 129.45 (=CH, ¹*J*_{PC} 71.9 Hz). ³¹P NMR spectrum, δ_{P} , ppm: 22.6. Physicochemical character-istics are identical to those described in [17].

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