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LETTERS TO THE EDITOR

Facile Exchange of Phosphoryl Oxygen by Sulfur and Selenium in Teriary Phosphine Oxides

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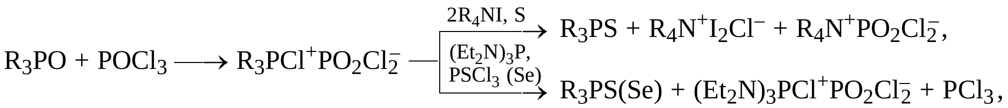
It is known that tertiary phoshine oxides can be converted into their sulfides by heating either with silver sulfide [1] or with phosphorus pentasulfide [2] at 110–150°C. Tertiary phosphine selenides can be prepared by treatment of phosphine oxides with selenium in the presence of potassium dihydrophosphate at 270–370°C [3].

We found that such transformations can easily be accomplished by treatment of triorganylchlorophosphonium dichlorophosphates, formed by reactions of tertiary phosphine oxides with phosphorus oxychloride first with tetraalkylammonium iodide or hexaethylphosphoric triamide and then with elemental sulfur, thiophosphoryl chloride, or selenium. In both cases, no heating of the reaction mixtures is required. Evidently, the first stage involves halophilic reduction of chlorophosphonium salt with the easily polarizable nucleophiles: phosphorous triamide or iodide ion. The same transformation can also occur under the action of a mixture of red phosphorus and a catalytic amount of white phosphorus. In the second stage, the resulting tertiary phosphine with chalcogen donor by known schemes.



$$R_3PO + POCl_3 \longrightarrow R_3PCl^+PO_2Cl_2^- \begin{cases} \xrightarrow{2R_4NI,\ S} R_3PS + R_4N^+I_2Cl^- + R_4N^+PO_2Cl_2^-, \\ \xrightarrow[PSCl_3\ (Se)]{(Et_2N)_3P,} R_3PS(Se) + (Et_2N)_3PCl^+PO_2Cl_2^- + PCl_3, \end{cases}$$

R = Et, CH_2Ph, Ph.

To a solution of 1.5 g of Ph_3P in 20 ml of dry benzene, 1.2 g of $POCl_3$ was added, and the mixture was stirred for 4 h. The oily substance that formed was separated, the solution was diluted with 20 ml of benzene, and 3.7 g of $Bu_3EtN^+I^-$ and 0.9 g of $PSCl_3$ were added to it one after another. After 4-h stirring, an oil formed and was separated and washed with benzene (3 × 20 ml). The combined benzene solutions were evaporated. Recrystallization from ethanol gave 1 g (63%) of triphenylphosphine sulfide was obtained, mp 160–162°C, δ_P 40.5 ppm. Triethylphosphine sulfide was obtained analogously, yield 35%, mp 96–97°C, δ_P 53.5 ppm (chloroform). Found, %: C 47.83; H 10.39; P 19.67. $C_6H_{15}PS$. Calculated, %: C 48.0; H 10.0; P 20.66.

To a suspension of 2.3 g of tribenzylphosphine oxide in 20 ml of toluene, 1.1 g of $POCl_3$ was added. A day after, 1.8 g of $(Et_2N)_3P$ was added. The mixture was stirred for 1 h, and then 0.23 g of sulfur was added. After 2-h stirring, a precipitate formed and was separated and recrystallized from chloroform to obtain 1.3 g (54%) of tribenzylphosphine sulfide, mp 269–271°C, δ_P 47.1 ppm. Found, %: P 9.23; S 9.44. $C_{21}H_{21}PS$. Calculated, %: P 9.22; H 9.52.

To a suspension of 2.2 g of Ph_3PO in 20 ml of dry toluene, 1.2 g of phosphorus oxychloride was added, and the reaction mixture was stirred for 4 h. After that, 1.95 g of $(Et_2N)_3P$ was added, and after 2 h the reaction mixture was treated with 0.63 g of selenium powder. When the selenium had dissolved completely, the precipitate that formed was separated and recrystallized from ethanol to obtain 2.3 g (85%) of triphenylphosphine selenide, mp 184–185°C, δ_P 34.7. Found, %: C 63.5; H 4.25; P 23.0; Se 23.0. $C_{18}H_{15} \cdot PSe$. Calculated, %: C 63.34; H 4.39; P 9.09; Se

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23.16. Tribenzylphosphine selenide was obtained analogously, mp 258–260°C (from CH_3COOH), δ_P 39.15 (CH_3COOH). Found, %: P 7.71. $C_{21}H_{21}PSe$. Calculated, %: P 8.08.

The ^{31}P NMR spectra were measured on a Varian VXR-500S spectrometer (202 MHz) against external 85% phosphoric acid.

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