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LETTERS TO THE EDITOR

First Example of Alkylation of Secondary Phosphine Selenides

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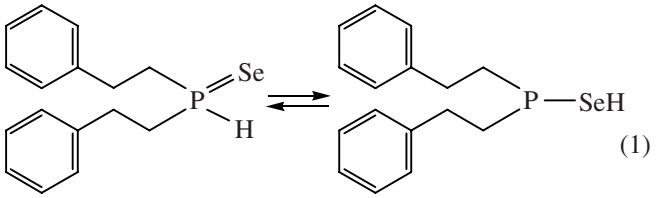
The secondary phosphine selenides **I** that recently has become available [1] are promising synthons for the synthesis of various organophosphorus-selenium compounds [2–7]. For example, their alkylation may result in derivatives of three- or four-coordinated phosphorus since they, similar to the corresponding phosphine oxides [8–10] and phosphine sulfides [10–12], might exist in the two tautomeric forms **A** and **B**.



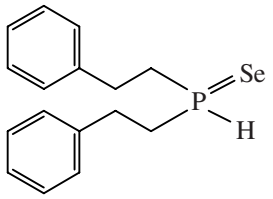
(1)

A **B**

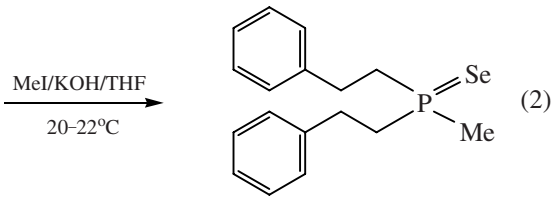
However, to the best of our knowledge, there are no published data on the alkylation of secondary phosphine selenides under basic conditions. At the same time, investigation of this reaction promises to open not only a new general preparative route to synthesis of unsymmetrical tertiary phosphine selenides but also to throw the light on the problem of their tautomerism.

Our experiments showed that phosphine selenide **I** when treated with methyl iodide in the presence of equimolar amount of KOH (room temperature, THF) afforded tertiary phosphine selenide **II** in 74% yield.

No products of methylation of the possible tautomeric form **B** were found. The obtained result suggests that alkylation of secondary phosphine selenides provides a possibility to synthesize dificultly available unsymmetrical phosphine selenides under mild conditions in a satisfactory preparative yield.



I



(2)

II

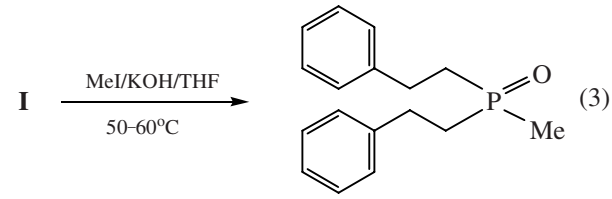
Molar ratio of phosphine selenides **I** : MeI:KOH = 1:1:1

Apparently, the contribution of tautomer **B** in Eq. (1) is negligible since the nucleophilicity of its anion must exceed that of the *P*-centered anion of the tautomeric form **A** and, therefore, it would have reacted with methyl iodide with a higher rate.

Semiempirical quantum chemical calculations of the conjugate anion of dimethylphosphine selenide by PM3 method have shown that the HOMO is localized mainly on the selenium atom. Calculations of the relative energies of the products of methylation of this anion suggest the thermodynamic preference of trimethylphosphine selenide (0 kcal mol^{-1}) whereas the methyl ester of dimethylselenophosphinous acid is by 15 kcal mol^{-1} more endothermic.

Carrying out the methylation of phosphine selenide **I** with molar excess of methyl iodide and KOH at

heating (50–60°C) led to a complete replacement of the selenium atom by oxygen, namely, to the formation of the corresponding tertiary phosphine oxide **III**.



(3)

III

Molar ratio of phosphine selenides **I** : MeI:KOH = 1:5:4

Methyl[di(2-phenethyl)]phosphine selenide (II). To the suspension of 0.056 g of ground KOH in 0.5 ml of THF the solution of 0.321 g of phosphine selenide **I** in 1 ml of THF was added, dry argon was bubbled through the mixture, and the solution of 0.141 g of MeI in 0.5 ml of THF was added dropwise in the course of 3 min. The reaction mixture was stirred for 3.5 h at room temperature, diluted with 2.5 ml of water and extracted with chloroform (2.5×3 ml). The chloroform extract was dried with sodium sulfate, the solvent was removed, the residue was washed with hexane and dried in a vacuum to afford 0.25 g (74%) of phosphine selenide **II**, yellowish oil. ^{1}H NMR, δ, ppm: 1.78 d (3H, CH_3, $^{2}J_{HP}$ 12.6 Hz), 2.23–2.29 m (4H, PCH_2), 2.95–3.00 m (4H, $PhCH_2$), 7.21–7.29 m (10H, Ph). ^{13}C NMR, δ_C, ppm: 18.85 d (CH_3, $^{1}J_{CP}$ 45.9 Hz), 29.09 CH_2Ph, 34.16 d (PCH_2, $^{1}J_{CP}$ 43.1 Hz), 126.38 C_p, 128.09 C_o, 128.50 C_m, 140.08 d (C_i, $^{3}J_{CP}$ 14.4 Hz). ^{31}P NMR, δ_P, ppm: 28.55 ($^{1}J_{PSe}$ 693.8 Hz). ^{77}Se NMR, δ_{Se}, ppm: –341.62 d ($^{1}J_{SeP}$ 694.9 Hz). Mass spectrum, *m/z*: 336 $[M]^+$.

Methyl[di(2-phenethyl)]phosphine oxide (III). To the suspension of 0.21 g of ground KOH in 0.5 ml of THF the solution of 0.30 g of phosphine selenide **I** in 2 ml of THF was added, dry argon was bubbled through the mixture, and it was heated at 50–60°C, then the solution of 0.66 g of MeI in 0.5 ml of THF was added in the course of 5 min. The reaction mixture was stirred for 1.5 h at 60°C and for another 5 h at room temperature, diluted with water (3 ml), extracted with chloroform (2.5×3 ml), the extract was dried over sodium sulfate, the solvent was removed, the residue was washed with 2 ml of diethyl ether and dried in a vacuum. 0.2 g (80%) of phosphine oxide **III** was obtained as a sandy powder, mp 58–60°C. ^{1}H NMR, δ, ppm: 1.47 d (3H, CH_3, $^{2}J_{HP}$ 12.2 Hz), 2.03–2.12 m (4H, PCH_2), 2.93–3.00 m (4H, $PhCH_2$), 7.22–7.35 m (10H, Ph). ^{13}C NMR, δ_C, ppm: 14.39 d (CH_3, $^{1}J_{CP}$ 65.8 Hz), 27.77 CH_2Ph, 31.96 d (PCH_2, $^{1}J_{CP}$ 65.1 Hz), 126.44 C_p, 127.99 C_o, 128.66 C_m, 140.79 d (C_i, $^{3}J_{CP}$ 13.1 Hz). ^{31}P NMR, δ_P, ppm: 44.45. IR spectrum (KBr), cm^{-1}: 3103, 3079, 3060, 3026, 3000 [ν(=CH)]; 2978, 2923, 2900, 2861 [ν(CH)]; 1603, 1584, 1508, 1497 [ν(C=C)]; 1454, 1418 [δ(CH_2)]; 1296 [δ(CH_3)]; 1166, 1134 [ν (P=O)]; 1071, 1030, 968, 957, 943, 915, 895, 871 [δ(CH–Ph)]; 767, 753 [δ(P–C)]. Mass spectrum, *m/z*: 272 $[M]^+$.

IR spectra were recorded on a Bruker IFS-25 spectrometer in KBr. ^{1}H, ^{13}C, ^{31}P and ^{77}Se were taken on a Bruker DPX-400 spectrometer (400.13, 101.61, 161.98 and 76.31 MHz, respectively) in $CDCl_3$, internal reference HMDS, external reference 85% H_3PO_4 (^{31}P NMR), and internal reference Me_2Se (^{77}Se NMR). Electron impact mass spectra (70 eV) were obtained on a GCMS-QP5050A SHIMADZU instrument (quadrupole mass analyzer, range of detected masses 34-450 D, capillary column, phase SPB-5). The reaction was monitored by ^{31}P NMR spectroscopy.

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