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LETTERS TO THE EDITOR

2-Phenylselenoethylphosphine, the First Representative of Primary Organylchalcoalkylphosphines

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It is known that the phosphoryl group in phosphonates and phosphinates is reduced with lithium aluminum hydride to primary and secondary phosphines, respectively [1, 2]. However, with organylchalco-substituted alkylphosphonates this result was not evident, because, at least in the case of organic sulfides, lithium aluminum hydride is capable of cleaving the C–S bond with the formation of the thiol and the corresponding protonated organic fragment [3, 4].

We have found that diethyl 2-phenylselenoethylphosphonate **I** is reduced with lithium aluminum hydride in diethyl ether with the selective formation of 2-phenylselenoethylphosphine **II**.

$$\underset{\mathbf{I}}{PhSe(CH_2)_2PO(OEt)_2} \xrightarrow{LiAlH_4} \underset{\mathbf{II}}{PhSe(CH_2)_2PH_2}.$$

Formation of the primary phosphine was proved by ^{1}H and ^{31}P NMR spectra and by gas chromatography–mass spectrometry. The PH_2 group in the ^{31}P NMR spectrum recorded without proton decoupling gives a triplet at –133 ppm with the coupling constant $^1J_{PH}$ 195 Hz. In the ^{1}H NMR spectrum, the phosphine protons give a doublet of triplets with the same constant $^1J_{PH}$.

A solution of phosphine **II** in chloroform is fairly stable to oxidation. After 1 day, the content of **II** in the mixture with oxidation products was 87%, after 5 days, 81%, and only after 2 weeks it decreased to 57%. In the ^{31}P NMR spectrum, these oxidized products give signals with δ_P 5.15, 23.80, 24.33, 36.74, and 50.77 ppm appearing only after storage of the phosphine for 2 weeks. These data suggest that the primary phosphine is successively oxidized to phosphine oxide, phosphonous acid, and phosphonic acid.

Our results suggest that the reduction of organylchalcoalkylphosphonates with lithium aluminum hydride should also yield organylchalco-substituted primary phosphines.

2-(Phenylseleno)ethylphosphine II. To a solution of 2.24 g of phosphonate **I** in 20 ml of diethyl ether, we added lithium aluminum hydride in small portions with stirring under argon, until the vigorous reaction was complete. The resulting mixture was stirred for 10 h. The reaction completion was judged by disappearance of the peak of phosphonate **I** (GLC). The solvent was distilled off, the residue was diluted with chloroform, and the precipitate consisting of excess lithium aluminum hydride and lithium and aluminum hydroxides was filtered off. The solvent was removed in a vacuum to leave 0.78 g (51.5%) of phosphine **II**. ^{1}H NMR spectrum, δ, ppm: 7.59–7.42 m, 7.28–7.23 m (5H, C_6H_5), 3.05 t, 3.03 t ($SeCH_2$, $^3J_{HH}$ 8, $^3J_{PH}$ 5.6 Hz), 1.89–1.79 m (2H, PCH_2), 2.98 t, 2.49 t (2H, PH_2, $^1J_{PH}$ 195, $^3J_{HH}$ 7.4 Hz). ^{31}P NMR spectrum, δ_P, ppm: –133.4 d.t ($^1J_{PH}$ 195, $^3J_{PH}$ 5.6 Hz). GC–MS data, *m/z*: 218 $[M]^{+\cdot}$, 190 $[PhSePH_2]^{+\cdot}$, 157 $[PhSe]^+$, 141 $[M - Ph]^+$, 109 $[CH_2CH_2SeH]^+$.

The chromatograms were obtained on a Chrom-5 chromatograph (2000 × 3-mm column; stationary phase 30% SE-30 on Chromaton N-AW-DMCS, 0.200–0.250 mm; thermal conductivity detector; carrier gas helium). The ^{1}H and ^{31}P NMR spectra were taken on a Bruker DPX-400 spectrometer from 5-10% solutions in $CDCl_3$ relative to internal HMDS (^{1}H) and external 85% phosphoric acid (^{31}P).

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