REACTION OF BIS(HYDROXYMETHYL)PHENYLPHOSPHINE SULFIDE AND BIS(HYDROXYMETHYL)PHENYLPHOSPHINE SELENIDE WITH THE DIMETHYLACETAL OF DIMETHYLFORMAMIDE

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In our previous work [1], we showed that the reaction of $bis(\alpha-hydroalkyl)$ phenylphosphine sulfides with acetals of aldehydes and ketones leads to transacetalization products, namely, 5-phenyl-5-thio-1,3,5-dioxaphosphorinanes. However, 0-dimethylphenylthiophosphinate (I) was isolated in the case of bis(hydroxymethyl)phenylphosphine sulfide and the dimethylacetal of dimethylformamide, which presupposes attack of the acetal at the sulfur atom of the thiophosphoryl group. The structure of (I) was established by IR and PMR spectroscopy, mass spectrometry and comparison of the ³¹P NMR spectra with spectra of model compounds [2, 3]. Bis(hydroxymethyl)phenylphosphine selenide and dimethylformamide dimethylacetal react analogously to give 0-dimethylphenylselenophosphinate (II).

 $\begin{array}{c} X \\ PhP(CH_2OH)_2 \xrightarrow{(MeO)_2CHNMe_2} PhP(CH_2OH)_2 \\ \downarrow \\ XCH(OM_{\theta})NMe_2 \end{array} \xrightarrow{(MeOH, CH_2O, Me_2)} PhP(Me)OMe \\ \downarrow \\ XCH(OM_{\theta})NMe_2 \xrightarrow{(MeOH, CH_2O, Me_2)} PhP(Me)OMe \\ \downarrow \\ (I)-(II) \end{array}$

The synthesis of (I) by the methylation of methylphenylphosphonic acid has been described by Snatzke et al. [4].

A sample of 4.12 g (0.0346 mole) DMF dimethylacetal was added to 6.98 g (0.0346 mole) bis(hydroxymethyl)phenylphosphine sulfide, heated at reflux for 30 min and then subjected to chromatography on silica gel using 1:1 benzene-petroleum ether to give 2.06 g (32%) (I), nD²⁰ 1.5758, δ^{31} P 89 ppm. PMR spectrum (δ , ppm): 1.88 ($^{2}J_{PH} = 14$ Hz) and 3.45 ($^{3}J_{PH} = 14$ Hz). Found: C, 51.70; H, 5.64; P, 16.67%. Calculated for C₈H₁₁PSO: C, 51.61; H, 5.91; P, 16.67%. m/z 186.02 (theor.), 186.02 (exp.).

A sample of 3.69 g (0.031 mole) DMF dimethylacetal was added to 7.70 g (0.031 mole) bis(hydroxymethyl)phosphine selenide, heated at reflux for 30 min and then subjected to chromatography on silica gel using 1:1 benzene-petroleum ether as eluant to give 1.15 g (16%) (II), $\delta^{31}P$ 90 ppm. PMR spectrum (δ , ppm): 1.91 ($^{2}J_{PH} = 14$ Hz) and 3.28 ($^{3}J_{PH} = 14$ Hz). Found: P, 12.24%. Calculated for C₈H₁₁PSe0: P, 13.31%. m/z 233.97 (exp.), 233.97 (theor.). The IR spectra of (I) and (II) lack absorption at 3100-3600 cm⁻¹.

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