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LETTERS TO THE EDITOR

Synthesis of 1,3,4-Thiazaphosphols by Reaction of *O*-Phenylchloromethylisothiocyanatothiophosphonate with 1,2-Diaminocyclohexane

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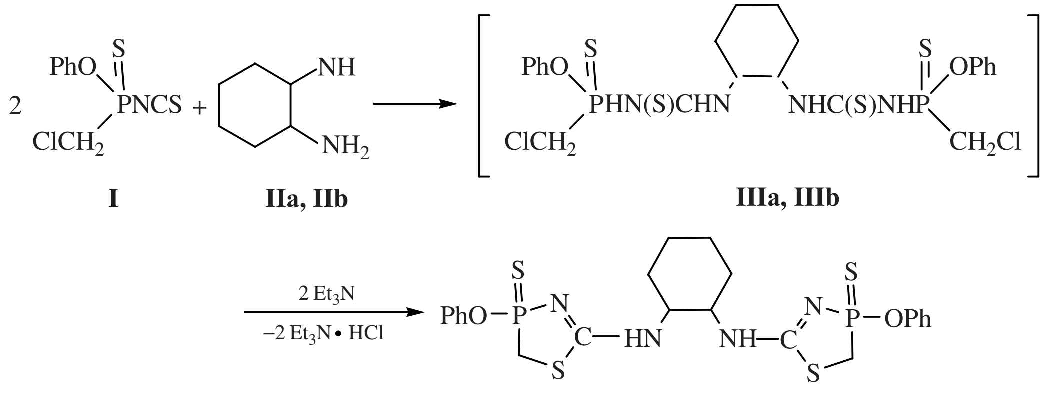
Primary and secondary amines were found earlier to add readily to chloromethylisothiocyanatothiophosphonates (-phosphinates) yielding initially phosphorylated thioureas, that underwent fast cyclization to form 1,3,4-thiazaphosphols [1, 2]. We found that the involvement of 1,2-diaminocyclohexanes **IIa** and **IIb** into the reaction with *O*-phenylchloromethylisothiocyanatothiophosphones **I** gives rise to compounds **IVa** and **IVb** with two phosphorus-containing five-membered heterocycles. The intermediately forming phosphorylated thioureas **IIIa** and **IIIb** we failed to register spectrally due to their rapid cyclization. Chemical shifts of the endocyclic phosphorus nuclei of compounds **IVa** and **IVb** resonate in the region of 116–118 ppm characteristic of compounds of this type [1, 2].



I **IIa, IIb** **IIIa, IIIb** **IVa, IVb**

II, III, IV 1,2-diaminocyclohexane (isomers mixture) (**a**); (1*R*,2*R*)-(–)-1,2-diaminocyclohexane (**b**).

It should be noted that compounds **IVa** and **IVb** have four chiral centers and therefore form complex mixture of diastereomers. The ^{31}P NMR spectrum of **IVa** contains two broad signals at 118.77 and 118.34 ppm (in the ratio 81 : 19), and spectrum of **IVb** has three signals at 116.09, 116.64, and 117.21 ppm (in the ratio 21 : 34 : 45). These results demonstrate that stereoselectivity of the studied processes is low. In the ^{1}H NMR spectra there are complex multiple signals assigned to methyl and methine protons of cyclohexane ring (1.15–2.16 ppm), methyl protons at the phosphorus atom (3.77–3.98 ppm), and protons of phenyl fragments (7.22–7.49 ppm).

***N,N'*-Bis(4-phenoxy-4-thioxo-1,3,4-thiazaphosphol)-1,2-diaminocyclohexane (IVa).** To a mixture of 0.22 g of 1,2-diaminocyclohexane **IIa** and 0.49 g of triethylamine in 50 ml of anhydrous benzene at stirring and cooling to 5°C was added 1.3 g of isothiocyanate **I**. After 24 h triethylamine hydrochloride was separated, and benzene was removed. To the residue was added 10 ml of anhydrous hexane. Precipitate formed was filtered off and washed with hexane. Yield 0.61 g (44%), mp 271–273°C. IR spectrum (KBr), ν, cm^{-1}: 1568 (C=N). ^{31}P NMR spectrum, δ_P, ppm (DMSO-*d*$_6$): 118.77, 118.34. Mass spectrum, *m*/*z* 566 [*M*]$^+$. Found, %: C 46.46; H 4.32; N 9.74; P 10.87; S 22.14. $C_{22}H_{24}N_4O_2P_2S_4$. Calculated, %: C 46.65; H 4.27; N 9.89; P 10.94; S 22.60.

***N,N'*-Bis(4-phenoxy-4-thioxo-1,3,4-thiazaphosphol)-1,2-diaminocyclohexane (IVb)** was prepared similarly from 0.32 g of diamine **IIb**, 0.60 g of triethylamine and 1.50 g of isothiocyanate **I**. Yield 0.51 g (32%), 97–100°C. IR spectrum (KBr), ν, cm^{-1}: 1571 (C=N). ^{31}P NMR spectrum, δ_P, ppm (C_6D_6): 116.09, 116.64, 117.21 (ratio 21 : 34 : 45). Found, %: C 46.39; H 4.19; N 9.77; P 10.66; S 22.31. $C_{22}H_{24}N_4O_2P_2S_4$. Calculated, %: C 46.65; H 4.27; N 9.89; P 10.94; S 22.60.

IR spectra were recorded on a UR-20 spectrometer in the range of 400–3600 cm^{-1} (mineral oil). ^{31}P NMR spectra were measured on a Bruker MSL-400 Fourier-spectrometer (100.62 MHz). The mass spectrum was taken on a TRACE–MS Finnigan–MAT device.

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