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LETTERS TO THE EDITOR

Reaction of (Chloromethyl)phenoxyphosphinothioyl Isothiocyanate with 2-(Methylamino)ethylphosphonates

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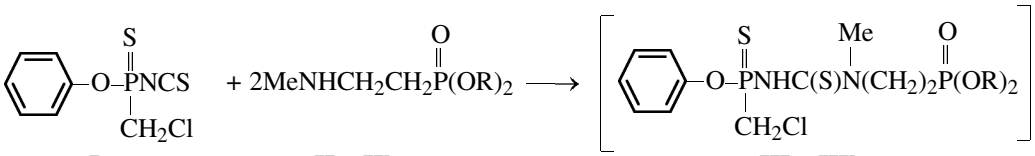
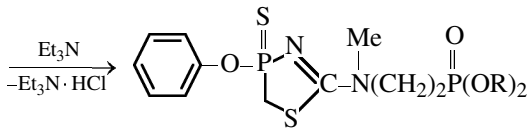
Recently we showed that addition of diphenyl α-(methylamino)benzylphosphonate to phenyl isocyanate or phenyl isothiocyanate proceeds easily in the presence of a catalytic quantity of triethylamine with formation of *N,N'*-substituted heterocycles, viz. diastereomeric 1,3,4-diazaphospholidines [1]. We found that the reaction of *O*-phenyl (chloromethyl)phosphonoisothiocyanatidothioate (**I**) with β-aminoalkylphosphonates provides a different synthetic result. We failed to detect by spectral methods intermediately forming phosphorylated ureas **IIIa** and **IIIb**, because they underwent fast cyclization involving the chloromethyl and thiocarbonyl groups to give 4,5-dihydro-1,3,4λ^5-thiazaphospholes **IVa** and **IVb**. This type of cyclization we observed earlier in the reaction of (chloromethyl)phosphonoisothiocyanatidothioates with primary and secondary amines [2, 3].



I **IIa, IIb** **IIIa, IIIb**



IVa, IVb

II, IV: R= Et (**a**); Ph (**b**).

The IR spectra of compounds **IVa** and **IVb** display an absorption band at 1573 cm^{-1} (C=N). In the ^{31}P NMR spectra, the signal of the endocyclic phosphorus atom is strongly shifted downfield to δ_P 115–116 ppm, which is characteristic of 1,3,4-thiazaphospholine fragments [2, 3]. In the ^{1}H NMR spectra, the PCH_2 proton signals appear as a multiplet consisting of eight lines (*ABX* system) due to the axial and equatorial positions of C–H bonds in the ring [3]: δ_{H^1} 3.52 ppm ($^2J_{H^1H^2}$ 13.0, $^2J_{PH^1}$ 3.8 Hz), δ_{H^2} 3.75 ($^2J_{PH^2}$ 13.6 Hz).

5-[*N*-[2-(Diethoxyphosphinoyl)ethyl]-*N*-methylamino]-2-phenoxy-4,5-dihydro-1,3,4λ^5-thiazaphosphole 2-sulfide (IVa). A mixture of 2.64 g of isothiocyanate **I**, 1.95 g of aminophosphonate **IIa**, and 1.1 g of triethylamine in 20 ml of benzene was kept for

24 h at 20°C. Triethylamine hydrochloride was then filtered off, the solvent was removed, and the residue was reprecipitated to hexane from acetonitrile to obtain 3.46 g (82%) of compound **IVa** as a viscous liquid. ^{31}P NMR spectrum (acetone), δ_P, ppm: 115.48, 26.56. Found, %: N 6.59; P 14.34; S 14.89. $C_{15}H_{24}\cdot N_2O_4P_2S_2$. Calculated, %: N 6.63; P 14.69; S 15.17.

5-[*N*-[2-(Diphenoxyphosphinoyl)ethyl]-*N*-methylamino]-2-phenoxy-4,5-dihydro-1,3,4λ^5-thiazaphosphole 2-sulfide (IVb) was prepared similarly from 2.64 g of isothiocyanate **I**, 2.91 g of aminophosphonate **IIb**, and 1.1 g of triethylamine, yield 79% (4.1 g). ^{31}P NMR spectrum (acetone), δ_P, ppm: 115.88, 20.83. Found, %: N 5.36; P 11.71; S 11.99. $C_{23}H_{24}\cdot N_2O_4P_2S_2$. Calculated, %: N 5.40; P 11.97; S 12.35.

The IR spectrum was registered on a UR-20 spectrometer within the range of 400–3600 cm^{-1} in Vaseline oil. The ^{1}H NMR spectra were measured on a Bruker WM-250 instrument (250.132 MHz) against internal TMS. The ^{31}P NMR spectra were recorded on a Bruker MSL400 Fourier transform NMR spectrometer (100.62 MHz).

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