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LETTERS TO THE EDITOR

Synthesis of 4-Phenoxytetrahydro-1,3,4λ^5-thiazaphosphol-2-one 4-Sulfide

N. A. Khailova, R. Kh. Bagautdinova, M. A. Pudovik, T. A. Zyablikova,
N. M. Azancheev, R. Z. Musin, and A. N. Pudovik

Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center,
Russian Academy of Sciences, Kazan, Tatarstan, Russia

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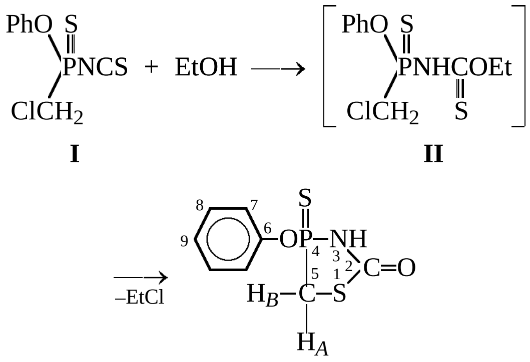
We previously showed that addition of alcohols to bis(chloromethyl)isocyanatophosphine oxide leads to formation of stable phosphorylated carbamates, which undergo heterocyclization in the presence of bases via intramolecular reaction of the chloromethyl and carbonyl groups to give unsaturated heterocycles, dihydro-1,3,4λ^5-oxazaphospholes [1]. The process is accompanied by elimination of hydrogen chloride, the hydrogen atom being abstracted from the secondary amino group which links the phosphinoyl and carbonyl fragments.

We have found that the reaction of chloromethyl(isothiocyanato)phenoxyphosphine sulfide (**I**) with ethanol gives a different synthetic result. The reaction occurs at 20°C in the absence of a base and is likely to involve intermediate formation of thiocarbamate **II** whose intramolecular cyclization yields 4-phenoxytetrahydro-1,3,4λ^5-thiazaphosphol-2-one 4-sulfide (**III**). The product is a representative of a new type of saturated five-membered P,N,S-heterocycles.



I **II**

III

The structure of **III** was proved by the ^{1}H, ^{13}C, and ^{31}P NMR, IR, and high-resolution mass spectra (electron impact). The IR spectrum of **III** contains the following absorption bands, ν, cm^{-1}: 1190 (P–O–Ph), 1590 (C–C$_{arom}$), 1680 (C=O), 3150 (NH). In the ^{1}H NMR spectrum of **III**, protons of the PCH$_2$ group give rise to eight lines (*ABX* system) in the region δ 4.02–4.22 ppm; this pattern is typical of endocyclic methylene group; aromatic protons appear as a multiplet at δ 7.22–7.44 ppm (A_2B_2C system).

4-Phenoxytetrahydro-1,3,4λ^5-thiazaphosphol-2-one 4-sulfide (III). A mixture of 2.0 g of phosphine sulfide **I** and 0.35 g of ethanol was kept for 1 month at 20°C. The precipitate was filtered off and washed with benzene. Yield 0.5 g (27%), mp 163–165°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 4.22 m (1H, H$_A$, $^2J_{PH}$ = 17.2, $^2J_{HH}$ = 14.3), 4.02 m (1H, H$_B$, $^2J_{PH}$ = 5.1), 7.22 m (*o*-H, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.4), 7.44 m (1H, *m*-H, $^3J_{HH}$ 7.4), 7.27 m (1H, *p*-H), 10.02 br.s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ$_C$, ppm (*J*, Hz): 169.54 d (C=O, $^2J_{HC}$ = 23.4), 32.43 m (C^5, $^2J_{PC}$ = 81.2, J_{CH} = 148.0), 149.68 m (C^i, $^2J_{PC}$ = 10.5), 121.36 m (C^o, $^3J_{PC}$ = 4.8, J_{CH} = 166.9, $^3J_{CH}$ = 8.6, $^3J_{CH}$ = 3.3), 128.80 m (C^m, $^4J_{PC}$ = 1.4, $^3J_{CH}$ = 8.0), 125.64 m (C^p, $^5J_{PC}$ = 1.9, $^3J_{CH}$ = 5.2). ^{31}P NMR spectrum: δ$_P$ 81.66 ppm. Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 245 $[M]^+$ (67.9), 202 $[M-\text{NHCO}]^+$ (2.1), 199 $[M-\text{CH}_2\text{S}]^+$ (2.4), 156 $[\text{PhOPS}]^+$ (100.0), 152 $[M-\text{PhO}]^+$ (3.7), 123 $[C_7H_8P]^+$ (70.4), 110 $[C_6H_6S]^+$ (13.5), 94 $[C_6H_6O]^+$ (54.5), 78 $[\text{PSNH}]^+$ (11.3), 77 $[C_6H_5]^+$ (19.6), 63 $[\text{PS}]^+$ (21.7), 47 $[\text{PO}]^+$ (1.2). Found, %: C 39.84; H 3.17; N 5.80; P 12.66; S 26.70. $C_8H_8NO_2PS_2$. Calculated, %: C 39.17; H 3.29; N 5.71; P 12.63; S 26.15.

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The mass spectrum was obtained on an MKh-1310 instrument (R = 15 000, direct sample inlet, 120°C; ion peaks for the most abundant isotopes are given). The IR spectrum was recorded on a UR-20 spectrophotometer in the range from 400 to 3600 cm^{-1}; sample was dispersed in mineral oil. The ^{13}C and ^{31}P NMR spectra were measured on a Bruker MSL-400 instrument (161.97 MHz for ^{31}P). The ^{1}H NMR spectra were obtained on Varian T-60 (relative to TMS) and Bruker WM-250 (250.132 MHz) spectrometers.

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