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LETTERS TO THE EDITOR

Dedicated to the 90th Anniversary of Corresponding Member of the Russian Academy of Sciences A.N. Pudovik Reaction of 2H-1,2,3-Diazaphosphole with Ethanolamine

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Reactions of cyclic derivatives of two-coordinate phosphorus, containing a P=C bond, with difunctional nucleophilic reagents have scarcely been studied. We previously found that a mixture of 1,2,3-diazaphospholene and β -hydroxybutoxyhydrospirophosphorane containing a diazaphospholene and a dioxaphospholane ring, formed by the reaction of 2-acetyl-5-methyl-2*H*-1,2,3-diazaphosphole (**I**) with butane-2,3-diol at -10 to 0°C undergoes fragmentation into a symmetrical hydroslirotetraoxaphosphorane, its tautomeric hydrogen phosphite, and acetone hydrazone, as the temperature increases [1].

In the present communication we report on the results of the reaction of diazaphosphole **I** with ethanolamine (**II**) at 0°C. Analysis of the ³¹P NMR spectrum of the reaction mixture, measured after mixing of equimolar reagent amounts, established that the reaction involves preferential attack of the P=C bond of diazaphosphole **I** with the β -aminoethoxy group of compound **II**, as evidenced by the appearance of strong signals at $\delta_{\rm P}$ 111 (1) (²J_{PH} 29.8 Hz)

and 112.5 ppm (0.5) (${}^{2}J_{\rm PH}$ 30.7 Hz); figures in parentheses relate to the integral intensity of the signal. The observation of several signals from 2-acetyl-3-(2-aminoethoxy)-5-methyl-3,4-dihydro-2*H*-1,2,3-diazaphosphole (**III**) is explained by the presence of geometric isomers: The OC₂H₄NH₂ substituent can be *syn* and *anti* with respect to the electronic pair of the P^{III} atom of compound **III** [2]. In addition, the following signals are observed, $\delta_{\rm P}$, ppm: 236 (0.08) (diazaphosphole **I**), 220 (0.4) (${}^{2}J_{\rm PH}$ 44.5 Hz), 57.7 and 57.4 (0.1), -57.6 (0.24) and -52.8 (0.04).

To establish the chemical shift of the P^{III} atom bearing the amino group in a diazaphospholene, we reacted diazaphosphole **I** with diethylamine. The ³¹P NMR spectrum acquired a signal at δ_P 59 ppm. We assigned the signal at δ_P 57 ppm to the P^{III} nucleus in 2-acetyl-3-[2-(hydroxyethylamino)-5-methyl-3,4-dihydro-2*H*-1,2,3-diazaphosphole (**IV**). The presence of a weak signal at δ_P 220 ppm points to formation of a 2*H*-1,2,3-diazaphosphole bearing no substituents on N² [3]. The signals at -57.6 (¹J_{PH} 705 Hz) and



-52.8 ppm (${}^{1}J_{PH}$ 737 Hz) relate to 1-acetyl-3-methyl-1,2,6-triaza-9-oxa-5 λ^{5} -phosphaspiro[4.4]non-2-ene (**V**) and 1,6-diaza-4,9-dioxa-5 λ^{5} -phosphoaspiro[4.4]nonane (**VI**) [4]. The reaction mixture was left to stand for 1 week at 5–7°C, after which the 31 P NMR spectrum acquired a signal at δ_{p} 140 ppm (0.10), that we assign to the P^{III} atom in 2-(2-aminoethoxy)-1,3,2oxazaphospholane (**VII**). Phospholane **VII** is formed by partial fragmentation of compounds **III** and **V**, accompanied by elimination of acetone hydrazone **VIII** [1, 5].

Thus, the reaction of diazaphosphole **I** with aminoethanol **II** involves both protic functions of reagent **II**, resulting in O-, N-, and O,N-fuctionalization of the P center (compounds **II**–**V**, respectively), the O-functionalization products prevailing.

The ${}^{31}P$ NMR spectra were obtained on a Varian Unity-300 spectrometer (121.42 MHz) in CH₂Cl₂, external reference 85% H₃PO₄.

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