REACTION OF 2-TRIMETHYLSILOXY-1,3,2-OXAZAPHOSPHOLANES WITH PHENOL AND ETHANOL

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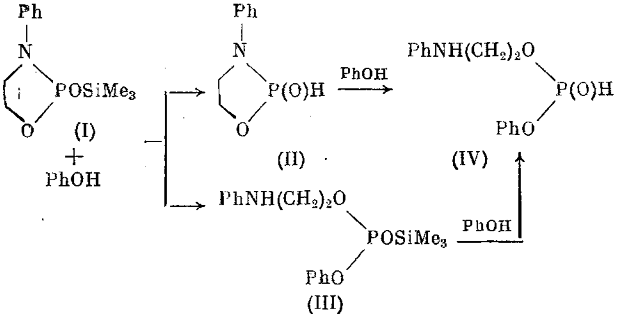
When 2-alkoxy-3-phenyl-1,3,2-oxazaphospholanes are reacted with alcohols, the alcoholysis of the endocyclic P—N bond occurs only on heating, which leads to secondary processes [1]. Phenolysis in the 1,3,2-oxazaphospholane series, and also the siloxy derivatives of trivalent phosphorus, has not been studied up to now.

For phospholanes, which simultaneously contain an endocyclic P—N bond and an exocyclic P—O—Si grouping, the formation of nitrogen-containing heterocycles with a hydrophosphoryl fragment could be expected when they are reacted with proton-donor reagents. However, it proved that the reaction of N-alkylated and N-arylated 2-trimethylsiloxy-1,3,2-oxazaphospholanes with an alcohol or phenol in a 1:1 ratio proceeds ambiguously to give a complex mixture of products. Thus, according to the ^{31}P NMR spectrum, in the reaction mixture of 2-trimethylsiloxy-3-phenyl-1,3,2-oxazaphospholane (I) with phenol are present the starting phospholane (I) (δ −116 ppm), O-phenyl O-(β-anilino)ethyl O-trimethylsilyl phosphite (III) (δ −122 ppm), 2-oxo-2-hydro-3-phenyl-1,3,2-oxazaphospholane (II) (δ −13 ppm, J_{HP} = 650 Hz) [2], and O-phenyl-O-(β-anilino)ethylphosphorous acid (IV) (δ − 4 ppm, J_{PH} = 720 Hz).

The gradual disappearance of (I)-(III) is observed when a second molar equivalent of phenol is added to the reaction mass, and the resulting sole product is the functionally substituted alkylarylphosphorous acid (IV) (δ −4 ppm):



As a result, the reaction of (I) with phenol proceeds simultaneously in two directions, namely via desilylation and with rupture of the P—N bond, in which connection, based on the ^{31}P NMR spectral data, the first direction predominates. Under the conditions of a deficiency of phenol the ratio of the products remains constant when the reaction mixture is kept for a long time.

Acid phosphite (IV) is obtained in high yield if the phospholane and phenol are taken at once in a 1:2 ratio. The reaction of phospholane (I) with p-methoxyphenol proceeds in a similar manner, but the acid that is formed here (δ −6 ppm, J_{PH} = 720 Hz) does not crystallize. Acid phosphites similar to (IV) are also formed in the reaction of 2-trimethylsiloxy-3-methyl-1,3,2-oxazaphospholane with phenol (δ −4 ppm, J_{PH} = 600 Hz) and 2-trimethylsiloxy-3-phenyl-1,3,2-oxazaphospholane with ethanol (δ −8 ppm, J_{PH} = 690 Hz) using a 1:2 ratio of the reactants. The lack of heat stability does not permit isolating them in the pure state.

EXPERIMENTAL

The ^{31}P NMR spectra were taken on a KGU-4 NMR instrument (at 10.2 MHz and using 85% H_3PO_4 as the standard), while the PMR spectra were taken on a Varian T-60 instrument (using TMS as the internal standard).

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O-Phenyl O-(β-Anilino)ethyl Phosphite (IV). To 2.55 g of (I) was added 1.9 g of PhOH, the reaction mixture was kept for 10 h at 20°C, and subsequent vacuum distillation gave 1.28 g (77%) of trimethylphenoxysilane [3], bp 65° (10 mm), n_D^{20} 1.4740. We also obtained 2.1 g (76%) of (IV), mp 44-45°. Found: C 60.46; H 6.20; N 4.80; P 11.04%. $C_{14}H_{16}NO_3P$. Calculated: C 60.64; H 5.77; N 5.05; P 11.29%.

CONCLUSIONS

The reaction of 2-trimethylsiloxy-3-phenyl(methyl)-1,3,2-oxazaphospholanes with phenol or ethanol proceeds in two directions, with rupture of the endocyclic P–N bond and via desilylation of the starting phospholane. The end reaction products are alkylarylphosphorous acids.

LITERATURE CITED

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