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> LETTERS TO THE EDITOR

## Features of Phenolysis of Phenylphosphonous Acid Tetraethydiamide

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Previously we reported that alcohols and phenols react with trivalent phosphorus acid amides by similar schemes, that is, both alcohols and phenols in the reaction with equivalent amount of a phosphorus amide substitute completely its >P-N bonds [1]:

 $>P-NR_2 + HOR' \longrightarrow >P-OR' + HNR_2.$ 

Here we report that phenylphosphonous tetraethyldiamide I reacts with phenols and alcohols quite differently. With hexane-1-ol at 110°C, phosphorylating agent I reacts in 1:2 molar ratio in a closed system to give the diester of phenylphosphonous acid II:

$$PhP(NEt_{2})_{2} + 2CH_{3}(CH_{2})_{4}CH_{2}OH$$

$$I$$

$$\longrightarrow PhP[O(CH_{2})_{5}CH_{3}]_{2} + 2HNEt_{2}.$$
(1)

On the contrary, reaction of phosphonous amide I with phenol in 1:2 molar ratio in a closed system

yields diester **III** and phenyl *N*,*N*-diethylphenylphosphonamidite **IV**. The ratio of the formed diester **III** and monoester **IV**, according to <sup>31</sup>P NMR spectra, depends on the reaction temperature. Actually, an equilibrium is attained:

$$\begin{array}{ccc} PhP(NEt_2)_2 + 2PhOH \longrightarrow PhP(NEt_2)OPh + [Et_2NH_2]OPh \\ \mathbf{I} & \mathbf{IV} \\ \stackrel{\rightarrow}{\leftarrow} PhP(OPh)_2 + 2HNEt_2. \end{array} (2)$$

Similar results were obtained in the reactions of equimolar amounts of phosphonous amide I with hexane-1,6-diol [complete phosphorylation, reaction (1)] and 4,4'-dihydroxybiphenyl or hydroquinone [partial phosphorylation, equilibrium, reaction (2)].

## REFERENCES

1. Nifantiev, E.E., Gratchev, M.K., and Burmistrov, Yu.V., *Chem. Rev.*, 2000, vol. 100, no. 10, p. 3755.

In all the cases reagent **I** contained small amounts of diethylamine hydrochloride which catalyzes phosphorylation [1].