ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 2, pp. 239–241. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © Yu.I. Blokhin, Yu.V. Volchenkova, K.N. Kornilov, A.V. Akilin, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 2, pp. 213–216.

Impossibility of Macrocyclization of Resorcinol with the Phenylphosphonous Acid Tetraethyldiamide

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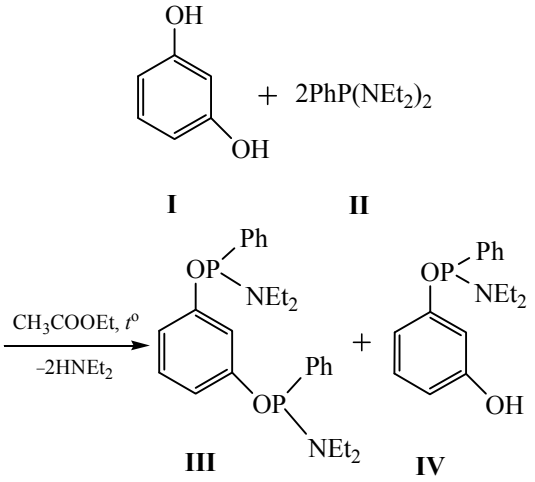
Received June 8, 2009

Abstract—On the basis of resorcinol and phenylphosphonous acid tetraethyldiamide a series of new phosphorylated compounds was prepared for the first time. It was found that on the basis of these products the target macrocycle does not form either under mild or under rigid conditions because instead of macrocyclization oligomerization takes place.

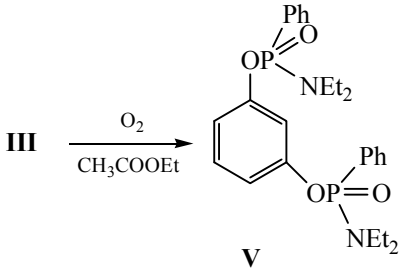
DOI: 10.1134/S1070363210020088

Bis-phosphorylation of resorcinol **I** with the phenylphosphonous acid tetraethyldiamide **II** we carried out recently [1].



Analysis of ^{31}P NMR spectra of the reaction products showed that while performing the reaction at room temperature in ethyl acetate for 24 h (method *1*) bis-phosphorylation is incomplete. Ratio of the signals belonging to the products **III** (δ_P 130.75 ppm) and **II** (δ_P 97.93 ppm) is 1:2.2. Under heating the reaction mixture to 60°C for 2 h and subsequent maintaining at room temperature for 24 h (method *2*) bis-phosphorylation proceeds more eagerly, ratio of signals of the compounds **III** and **II** is 1.1:1 [1]. Refluxing of the reaction mixture in the same solvent for 2 h and maintaining for 24 h at room temperature (method *3*) gives a mixture of bis- and monophosphorylated resorcinols **III** and **IV** (δ_P 129.82 ppm) with the ratio of signals 1.3:1 respectively, and small amount of starting phosphamide **II** remains. Note that we observed the formation of a mixture of mono- and bis-phosphorylated products in the reaction of resorcinol with another phosphorylating agent, hexaethyl phosphorotriamidite at 1:2 ratio in acetonitrile [2].

Considering the obtained ^{31}P NMR data and the reported results [2] we have carried out bis-phosphorylation of resorcinol **I** with molar excess of phosphorylating agent **II** in boiling ethyl acetate for 2 h. After the removing the solvent and the excess of phosphonite **II** we have obtained pure compound **III** without the admixture of the product **IV.** It is capable of oxidation under the above-described conditions to phosphonate **V**.



The oxidation of bis-phosphorylated resorcinol **III** we carried out with the air oxygen according to the procedure [3]. Diphenyl phosphonate **V** (δ_p 10.11 ppm) was obtained for the first time. After crystallization

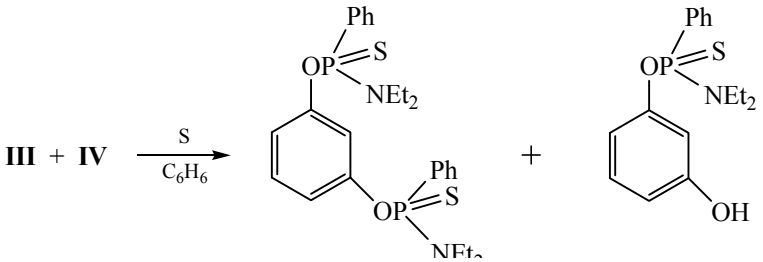
from hexane compound **V** is a glass-like substance with mp 53–54°C. Its composition and molecular mass were confirmed by mass spectrometry.

Compound **III** we also synthesized under the other conditions by the reaction of starting substances **I** and **II** in 1:2 molar ratio at elevated temperature without a solvent. Note that such reaction was carried out recently with hydroquinone [4].

Performing the reaction in a bulk at elevated temperature (145°C) did not lead to the expected results because in this case only the oligomeric and oxidated products are formed. Considering this fact we have carried out this reaction in a water-jet pump vacuum at 90–100°C at the homogenous state of the reaction mixture.

Bis-phosphorylation in a bulk under the established conditions seems to be the most convenient procedure for preparing compound **III** because it permits to avoid the excess of phosphorylating agent, formation of the side product **IV**, and also oxidation of trivalent phosphorus derivatives.

Sulfuration of the reaction mixture containing the compounds **III** and **IV** obtained by means of the third procedure as it was noted already in [1] gave a mixture of thionophosphonates **VI** and **VII** with δp 77.41 and 77.14 ppm respectively.



We managed to separate compound **VI** from the substance **VII** by means of column chromatography. Structure of the product **VI** was confirmed by MALDI mass spectrometry and ^{1}H NMR spectroscopy.

We have established that in all the three above-presented synthetic procedures at the addition of starting bisphenol **I** to the reaction mixture containing the compound **III** no formation of corresponding macrocyclic products on the basis of phenylphosphonic acid tetraethyldiamide takes place.

Instead of that in the presence of residues of the unreacted phenylphosphonite accumulation of monophosphorylated resorcinol **IV** takes place. In the absence of the residual compound **II** no additional interactions were observed. The absence of macrocyclization may be explained firstly by the inertness of the single diethylamino group on phosphorus to the OH group of bisphenol [5]. Besides, inertness of both diethylamido groups of the product **III** in this case is caused by strong stereoelectronic effect of bulky phenyl substituents on phosphorus which impede the reaction of substrate with the molecule of resorcinol.

In extension of [1] where we for the first time mentioned that no macrocyclization took place in the reaction of resorcinol **I** with phenylphosphonous acid tetraethyldiamide **II**, we performed this reaction under rigid conditions. As is known the boiling of phosphonite **II** with 2,2'-di(*p*-hydroxyphenyl)propane in *o*-xylene for 7 h at the 1:1 molar ratio and the concentration no more than 0.2 mol l^{-1} leads to the macrocyclic product [6].

We have found that boiling of a solution of compounds **I** and **II** in *o*-xylene under the above-described conditions [6] for 3 h under argon after removing of solvent in a vacuum yields a light yellow paste. Analysis of its ^{31}P NMR spectrum shows that macrocyclization does not take place. Instead of that oligomeric products (δ_P 157.94 ppm, broad signal) are formed. They are eagerly oxidized in air to give the mixture of substances giving a broad signal with δ_P 14.05 ppm. The formation of such products is explained evidently by the fact that under the conditions described diethylamide group on phosphorus still enters the reaction with the OH groups of bis-phenol. But because of the above-reported stereoelectronic effect of phenyl substituents bis-phosphorylated resorcinol **III** is incapable of the reaction with one more molecule of the starting bis-phenol.

Hence, no formation of the desired macrocycle on the basis of resorcinol **I** and phenylphosphonous acid tetraethyldiamide **II** takes place either under the

$$\mathbf{I} + \mathbf{II} \xrightarrow[t^o]{\text{Xylene}} \text{oligomeric products}$$
$$\xrightarrow{O_2} \text{oxygen products.}$$

conditions of molecular assembly or under direct phosphorylation in ethyl acetate (mild conditions) and in *o*-xylene (rigid conditions).

Product **III** obtained for the first time can be probably used for macrocyclization with other bisphenols to give unsymmetrical macrocycles, the promising substrates for constructing supramolecular systems [7].

EXPERIMENTAL

Mass spectrum was obtained on a Bruker Daltonics Autoflex II instrument equipped with the nitrogen laser (λ 337 nm) under the regime of positive ion registration. ^{31}P NMR spectra of compounds **III** and **VII** in ethyl acetate and of compound **VI** in benzene were taken on a Bruker WP-80GY (32.4 MHz) spectrometer against 85% phosphoric acid. ^{1}H NMR spectrum of compound **V** was obtained on a Bruker AM-400 spectrometer (400 MHz) in deuterated acetone against TMS.

All the operations with trivalent phosphorus compounds were carried out under dry argon. Column chromatography was carried out on the L 100/250 silica gel. TLC was performed on Silufol plates using 1:2 hexane–dioxane (A), 3:1 hexane–dioxane (B), and 5:1 chloroform–ethanol (C) systems, development by the iodine vapor or calcination.

Tetraethyldiamidophenylphosphonite (II) was prepared according to [8].

1,3-bis(Diethylamidophenylphosphonyloxy)benzene (III). Tetraethyldiamidophosphonite **II**, 1.63 g, was added with stirring to 0.36 g of resorcinol. The flask with the reaction mixture was evacuated with a water-jet pump and heated until the formation of the homogenous liquid mass (90–100°C) and kept under these conditions for 2 h. After that it was cooled, and the water-jet pump was disconnected. Crude product **III** was obtained as a thermoplastic glass-like light yellow mass, R_f 0.51(A), δ_P 130.75 ppm, $[M + H]^+$ 469.25.

1,3-bis(Diethylamidophenylphosphonatoxy)benzene (V). A solution of 1.49 g of crude compound **III** in 10 ml of ethyl acetate was refluxed in an open air for 1 h. Solvent was removed in a vacuum, and the obtained viscous paste was heated in boiling hexane, cooled, and the isolated viscous mass was dried in a vacuum (2 h, 50°C, 10 mm Hg). Compound **VII** was obtained as a solid light yellow glass, yield 1.59 g (98% in 2 stages), R_f 0.89 (C), δ_P 10.11 ppm, mp 53–54°C. Found, %: P 12.43. $C_{26}H_{34}N_2O_4P$. Calculated, %: P 12.40. $[M + H]^+$ 500.96.

1,3-bis(Diethylamidophenylthiophosphonatoxy)-benzene (VI). To a solution of 0.51 g of resorcinol **I** in 20 ml of ethyl acetate 2.35 g of tetraethyldiamidophenylphosphonite **II** was added with stirring at room temperature. The reaction mixture was refluxed under argon for 2 h and then left for 24 h. Solvent was removed in a vacuum, and the product containing two signals at 130.75 and 129.82 ppm in ^{31}P NMR spectrum was treated with 0.3 g of sulfur in 20 ml of benzene. The reaction mixture was kept for 24 h at room temperature and then subjected to chromatography on a column, elution with benzene. The product was dried in a vacuum (2 h, 50°C, 10 mm Hg), and compound **V** was obtained as a solid light yellow paste, yield 2.45 g (34% in 2 stages), R_f 0.79 (B), δ_P 74.41 ppm. ^{1}H NMR spectrum: 0.99 t (12H, CH_3), 3.32 m (8H, CH_2, $^{3}J_{HP}$ 10.4 Hz), 7.17 s (1H, CH), 7.36 m (2H, CH_p), 7.50 d (6H, CH_o), 7.96 m (5H, CH_m). Found, %: P 11.73. $C_{26}H_{34}N_2O_2P_2S_2$. Calculated, %: P 11.65. $[M + K]^+$ 572.12.

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