The authors are grateful to M. M. Buzlanova, I. V. Karandi, and L. N. Bulatnikova for the quantitative determination of formaldehyde.

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Received May 16, 1996

# Phosphorylation of dihydric phenols with amides of phosphorous acid

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> Phosphorylation of dihydric phenols with triamides of phosphorous acid was performed under different reaction conditions and using reactants taken in various ratios. The selectivity of the reaction depends on the presence of the solvent, its polarity, and, to a lesser degree, on the temperature.

Key words: phenol, phosphamide, phosphorylation; <sup>31</sup>P NMR spectra.

Amides of trivalent phosphorus acids are convenient reagents for phosphorylating alcohols and phenols.<sup>1</sup> It is known that phenols react with phosphamides more readily in aromatic solvents due to the formation of associates.<sup>2</sup> However, the role of the polarity of the solvent in these reactions remains unclear. In this connection, we studied the reactions of 2,2-di(*p*-hydroxyphenyl)propane (1) with hexaethyltriamide of phosphorous acid (2) under different reaction conditions and taking the reagents in various ratios (Scheme 1) by <sup>31</sup>P NMR spectroscopy and mass spectrometry.

The spectral characteristics of the products of the reactions studied are given in Table 1. The values of the  $^{31}$ P chemical shifts (118, 132, 141, and 128 ppm) correspond to the signals of the P atoms of compounds 2, 3,

and 4 (see Scheme 1) and of the triester of phosphorous acid 5, respectively.



In the mass spectra,  $[M]^+ = 576$  and 557 for the molecular ions of 3 and 4, respectively.

The data in Table 1 indicate that the highest selectivity of phosphorylation is observed when the reaction is performed in dioxane, which is the most polar solvent used. When other solvents were used, a polymeric com-

1066-5285/96/4509-2250 \$15.00 © 1997 Plenum Publishing Corporation

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 9, pp. 2369-2370, September, 1996.

#### Scheme 1



**Table 1.** Dependence of the spectral characteristics of the products on the reaction conditions

1	2	Solvent	Dilu-	<i>∙ T/</i> °C	t/h	<sup>31</sup> P NMR*	
mol			tion		-	δ	/ (%)**
1	2	_	_	115	2	141	26
						132	74
1	2	Benzene	1:5	20-25	48	141	18
						132	82
2	1	Benzene	1:5	20-25	48	141	100
2	I		_	20-25	24	141	100
2	ł	Toluene	1:5	20-25	48	141	100
2	ł	Benzene	1:5	80	4	141	93
						128	7
2	1	Benzene	1:20	20-25	48	141	100
2	1	Dioxane	1:5	20-25	48	141	2
						132	98
2	1	Dioxane	1:5	20-25	196	141	4
						132	96
2	1	Dioxane	1:5	80	2.5	141	97
						132	3
2	I	Dioxane	1:5	100	1.5	141	100

\* The <sup>31</sup>P NMR spectra for the solutions were recorded in the same solvents in which the reactions were performed; for the reactions proceeding without a solvent, the <sup>31</sup>P NMR spectra were recorded in benzene or toluene. \*\* Concentrations (%) of the corresponding products were calculated based on the intensities of the signals of these products in the <sup>31</sup>P NMR spectra.

pound along with the desired product 4 was found based on the data of TLC. Note that the selectivity of the reaction is less affected by the temperature.

## Experimental

The <sup>31</sup>P NMR spectra were recorded on a Bruker WP-80 SY instrument (32.4 MHz). Chemical shifts were measured relative to 85% H<sub>3</sub>PO<sub>4</sub> (external standard). The mass spectra were obtained on a MKh-1321A instrument with direct introduction of the sample and on a MSBKh instrument (the

Elektron Joint-Stock Company, Sumy, Ukraine) using ionization by the products of the decomposition of <sup>252</sup>Cf.

The TLC was carried out on Silufol UV-254 plates in a 5:1 benzene-dioxane mixture. The chromatograms were developed in an iodine chamber or were calcinated at 200-250 °C.

All syntheses involving compounds of trivalent phosphorus were carried out under an atmosphere of dry argon or nitrogen purified from oxygen.

**Phosphamides 3 and 4.** The corresponding amounts of the solvent and tris(diethylamino)phosphine (2) were added to 2,2-di(2-hydroxyphenyl)propane (1) (0.228 g, 1 mmol). The reaction mixture was stirred and studied.

**4,4'-[Bis(diethylamino)phosphineoxy]-2,2-diphenylpropane** (3). A mixture of 2,2-di(*p*-hydroxyphenyl)propane (1) (5.2 g, 22.8 mmol) and tris(diethylamino)phosphine (2) (11.26 g, 45.6 mmol) in anhydrous benzene (82 mL) was kept at ~20 °C for 48 h with periodic shaking (5–6 times). The solvent was removed by evaporation on a water bath at atmospheric pressure, and then the residue was kept at 50 °C *in vacuo* (10 Torr) for 1 h. The oily product was distilled *in vacuo* (1 Torr), and the fraction that boiled at 310–320 °C, was taken. An oily pale yellow compound was obtained in a yield of 7.1 g (54%). <sup>31</sup>P NMR (benzene),  $\delta$ : 132. Found (%): C, 64.77; H, 9.69; P, 10.66. C<sub>31</sub>H<sub>54</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>. Calculated (%): C, 64.58; H, 9.37; P, 10.76.

**Bis(2-***p*-hydroxyphenylprop-2-ylphenyl)(diethylamino)phosphite (4). A mixture of 2,2-di(*p*-hydroxyphenyl)propane (1) (2.28 g, 10 mmol) and tris(diethylamino)phosphine (2) (1.24 g, 5 mmol) in anhydrous dioxane (18 mL) was boiled for 1.5 h. The solvent was removed *in vacuo* (10 Torr) at 50 °C. A viscous colorless product was obtained. <sup>31</sup>P NMR (dioxane),  $\delta$ : 141. Found (%): C, 74.17; H, 8.09; P, 5.76. C<sub>34</sub>H<sub>40</sub>NO<sub>4</sub>P. Calculated (%): C, 73.25; H, 7.18; P, 5.56.

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Received July 11, 1996