Russian Journal of General Chemistry, Vol. 75, No. 3, 2005, pp. 379–380. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 3, 2005, pp. 415–416.

Synthesis and Properties of Phosphorylated 4-Methylpyrocatechol Derivatives

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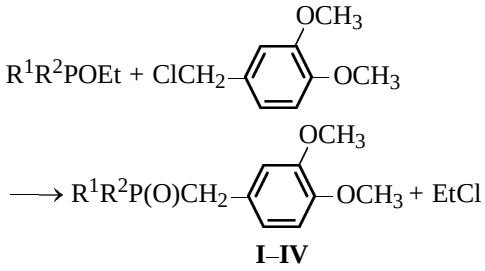
Received July 9, 2003

Abstract — Procedures for preparing α-phosphorylated 4-methylpyrocatechols were developed. Diphenyl-(3,4-dimethoxybenzyl)phosphine oxide yields diphenyl(3,4-dihydroxybenzyl)phosphine oxide under the action of hydrobromic acid.

Alkylphenols form an important class of modern antioxidants and biologically active compounds [1–3]. Proceeding with studies in the field of phosphorylated phenol derivatives [4–6], we examined dimethyl ethers of α-phosphorylated 4-methylpyrocatechols. Compounds of this type were prepared following the scheme of the Arbuzov reaction by treating 3,4-dimethoxybenzyl chloride with P(III) acid esters.



I–**IV**

$R^1 = R^2 =$ EtO (**I**), Et (**III**), Ph (**IV**); $R^1 =$ EtO, $R^2 =$ Et (**II**).

The reaction proceeds at 90–160°C; the temperature of the reaction onset decreases in going from triethyl phosphite to diethyl ethylphosphonite and then to ethyl diethyl- and ethyl diphenylphosphinites. The compounds prepared are colorless liquids (**I**, **II**) or crystalline compounds (**III**, **IV**) readily soluble in organic solvents. Compound **III** is soluble in water.

With the aim of preparing phosphorylated pyrocatechols, compounds **I**, **III**, and **IV** were treated with hydrobromic acid in acetic acid [7]. Only in **IV** the hydrolysis of the ether bonds yielded the desired product, diphenyl(3,4-dihydroxybenzyl)phosphine oxide **V**. In all the other cases, we obtained intractable tars.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil were recorded on a Specord M-80 spectrometer. The ^{1}H and ^{31}P NMR spectra were taken on Tesla BS-567A (100 MHz) and Bruker WP-80 (32.4 MHz) spectrometers, respectively, against TMS (^{1}H) and 85% H_3PO_4 (^{31}P).

3,4-Dimethoxybenzyl chloride was prepared according to [8].

Compounds **I**–**IV** *(general procedure).* A mixture of 0.02 mol of ethyl ester of P(III) phosphorus acid and 0.02 mol of 3,4-dimethoxybenzyl chloride was heated with stirring for 1.5–3 h until the evolution of ethyl chloride was complete. Compounds **I**–**III** were isolated by vacuum distillation, and compound **IV** crystallizes in the course of the reaction.

Diethyl 3,4-dimethoxybenzylphosphonate I. Yield 43%, bp 153–156°C (0.1 mm), n_D^{20} 1.5140, d_4^{20} 1.1707. IR spectrum, ν, cm^{-1}: 1600 (C_6H_3), 1270 (P=O), 1070, 1050 (POC). ^{1}H NMR spectrum (CCl_4 + $CDCl_3$), δ, ppm: 1.25 t (6H, CH_3-ethyl, $^3J_{HH}$ 7 Hz), 3.15 d (2H, CH_2P, $^2J_{PH}$ 23 Hz), 3.9 s (6H, CH_3O), 4.0 q (4H, CH_2OP, $^3J_{HH}$ 7 Hz), 6.9 d (3H, C_6H_3, $^4J_{HH}$ 2 Hz). ^{31}P NMR spectrum: δ_P 26.7 ppm. Found P, %: 10.25, 10.10. $C_{13}H_{21}O_5P$. Calculated P, %: 10.74.

Ethyl ethyl(3,4-dimethoxybenzyl)phosphinate II. Yield 51%, bp 157–158°C (0.1 mm), n_D^{20} 1.5270, d_4^{20} 1.1730. IR spectrum, ν, cm^{-1}: 1590 (C_6H_3), 1260 (P=O), 1030 (POC). Found P, %: 10.53, 10.90. $C_{13}H_{21}O_4P$. Calculated P, %: 11.38.

Diethyl 3,4-dimethoxybenzylphosphine oxide III. Yield 57%, bp 178–179°C (0.1 mm), n_D^{20} 1.5469, mp 59–60°C (heptane). IR spectrum, ν, cm^{-1}: 1600 (C_6H_3), 1250 (P=O). ^{31}P NMR spectrum: δ_P 45.6 ppm.

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Found P, %: 11.45, 11.35. $C_{13}H_{21}O_3P$. Calculated P, %: 12.10.

Diphenyl 3,4-dimethoxybenzylphosphine oxide IV. Yield 91%, mp 164–167°C (5:1 heptane–benzene). Found, %: P 8.80, 8.85. $C_{21}H_{21}O_3P$. Calculated, %: P 8.81.

Diphenyl 3,4-dihydroxybenzylphosphine oxide V. A mixture of 3.52 g of **IV** and 5 ml of 48% hydrobromic acid was refluxed in 10 ml of acetic acid for 2 h. The solid residue obtained after removing the volatile products in a vacuum was washed with water to give 2.72 g (83%) of **V**, mp 207–209°C (5:1 acetic acid–water). IR spectrum, ν, cm^{-1}: 3310 br (OH assoc.), 1600, 1520 (C_6H_5), 1150 (P=O). ^1H NMR spectrum (acetone-d_6), δ, ppm: 3.75 d (2H, CH_2P, $^3J_{PH}$ 10 Hz), 6.50 s (2H, OH), 6.95 d (3H, C_6H_3, $^4J_{HH}$ 2 Hz), 7.70 s, 7.75 m (10H, C_6H_5). Found P, %: 9.23, 9.46. $C_{19}H_{17}O_3P$. Calculated P, %: 9.57.

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