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LETTERS TO THE EDITOR

Regiochemistry of Reactions of 2-Chloro-4(5)-dichlorophosphinyloxybenzo-1,3,2-dioxophospholes with Phosphorus Pentachloride and Chlorine

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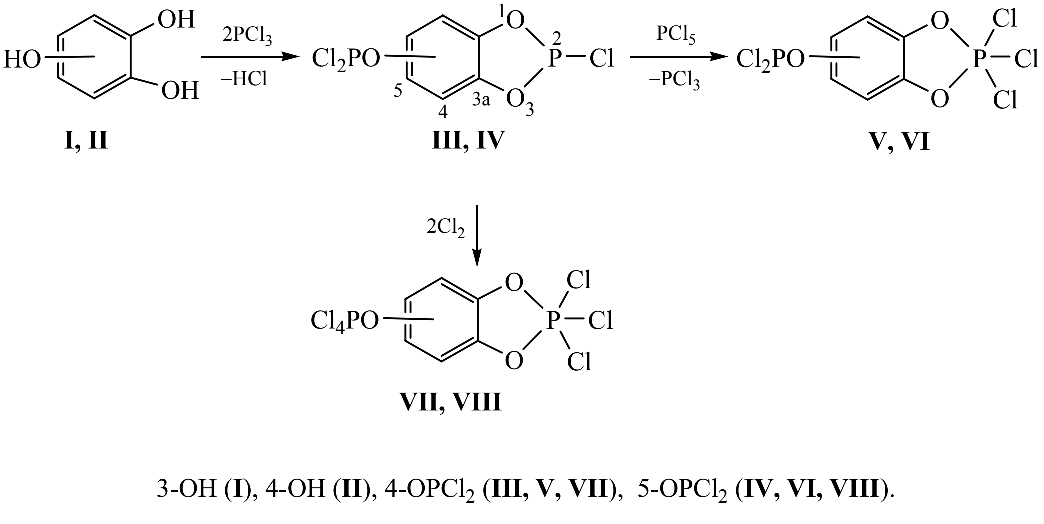
Polyphenols are widely used in various fields of chemistry as scaffolds of supramolecular systems [1], for preparation of polydentate ligands, as additives in polymer composites [2], etc. Inclusion of phosphorus fragments into such compounds provides for their fire resistance [3–5]. Simple polyphenols, such as pyrogallol **I** and oxyhydroquinone **II**, are convenient models to study phosphorylation of more complex natural systems. Nevertheless, we have not come across any systematic study of phosphorylation reactions of polyphenols with most common phosphorylating agents such as phosphorus halides.

In this work we first investigated reactions of compounds **I** and **II** with PCl_3 as well as regioselectivity of chlorination of the obtained P(III) derivatives with phosphorus pentachloride and chlorine. Phosphorylation of **I** and **II** with PCl_3 resulted in 2-chloro-4(5)-dichlorophosphinyloxybenzo-1,3,2-dioxaphospholes **III** and **IV** with yields of 60–85%. Chlorination of phospholes **III** and **IV** with equimolar amount of PCl_5 occurred selectively at endocyclic phosphorus atom. The latter was more reactive towards PCl_5 as compared to acyclic phosphorus. That reaction yielded phospholes **V** and **VI**, their content in the

Scheme 1.



I, II **III, IV** **V, VI** **VII, VIII**

3-OH (**I**), 4-OH (**II**), 4-$OPCl_2$ (**III, V, VII**), 5-$OPCl_2$ (**IV, VI, VIII**).

reaction mixture after drying in vacuum being over 95%. The molecules of **V** and **VI** contained phosphorus atoms of various coordination and oxidation states (Scheme 1).

In order to explicitly identify the obtained derivatives **V** and **VI**, we treated the phospholes **III** and **IV** with molecular chlorine at –20°C. The reaction resulted in 2,2,2-trichloro-4-(tetrachlorophosphoranyloxy)- and 2,2,2-trichloro-5-(tetrachlorophosphoranyloxy)benzo-1,3,2-dioxyphospholes **VII** and **VIII**, respectively, containing two pentacoordinated phosphorus atoms. Content of **VII** and **VIII** in the reaction mixtures was of 95%.

Compound III. Yield 60%, colorless liquid, bp 98°C (0.1 mmHg), d_4^{20} 2.2044 g cm^{-3}, n_D^{20} 1.5990. IR spectrum, ν, cm^{-1} (film): 466, 504, 553, 594, 666, 712, 746, 777, 794, 849, 922, 956, 1027, 1171, 1238, 1253, 1333, 1455, 1481, 1614, 1692, 1835, 1908, 2017, 2099, 2194, 2274, 2406, 2587, 2660, 2854, 2925, 3044, 3101, 3630, 3650, 3691. ^{13}C NMR spectrum, δ_C, ppm, (*J*, Hz): 136.19 br.m (d.d) (C^{3a}, $^2J_{PC3a}$ 7.7, $^3J_{PC3a}$ 2.9), 137.4 m (d.d) (C^4, $^2J_{PC4}$ 11.4, $^3J_{PC4}$ 2.6), 118.7 d.d.d (d) (C^5, $^3J_{PC5}$ 5.1, $^1J_{HC5}$ 166.9, $^3J_{HC5}$ 6.6), 124.22 d (s) (C^6, $^1J_{HC6}$ 166.2), 111.86 d.d (s) (C^7, $^1J_{HC7}$ 168, $^3J_{HC7}$ 5.5), 146.48 br.m (d.d) (C^{7a}, $^2J_{PC7a}$ 7.7, $^4J_{PC7a}$ 1.1). ^{31}P NMR spectrum (CH_2Cl_2), δ_P, ppm: 182.3, 176.5.

Compound IV. Yield 85%, colorless liquid, bp 110–111°C (0.9 mmHg), d_4^{20} 1.6270 g cm^{-3}, n_D^{20} 1.6002. IR spectrum, ν, cm^{-1} (film): 434, 473, 511, 554, 577, 598, 628, 690, 711, 750, 773, 813, 849, 886, 967, 1005, 1097, 1130, 1169, 1229, 1300, 1325, 1365, 1438, 1484, 1504, 1517, 1606, 1853, 2152, 2472, 2683, 2853, 2924, 3085, 3109. ^{13}C NMR spectrum, δ_C, ppm, (*J*, Hz): 144.84 br.d.d.d (d) (C^{3a}, $^2J_{PC}$3a 7.3, $^3J_{HC3a}$ 7.2, $^2J_{HC3a}$ 5.1), 117.58 d.d.d (d) (C^4, $^3J_{PC4}$ 5.1, $^1J_{HC4}$ 170.2, $^3J_{HC4}$ 4.5), 146.46 br.d.d (d) (C^5, $^2J_{PC5}$ 11.7, $^3J_{HC5}$ 11.7, $^2J_{HC5}$ 4.3–4.4, $^2J_{HC5}$ 4.4), 108.88 d.d.d (d) (C^6, $^3J_{PC6}$ 4.8, $^1J_{HC6}$ 170.9, $^3J_{HC6}$ 4.5), 113.78 br.d (s) (C^7, $^1J_{HC7}$ 168.0), 142.47 d.d.d.d (d.d) (C^{7a}, $^2J_{PC7a}$ 7.3, $^5J_{PC7a}$ 1.1, $^3J_{HC7a}$ 11.4–11.6, $^3J_{HC7a}$ 7.1–7.2, $^2J_{HC7a}$ 3.4). ^{31}P NMR spectrum (CH_2Cl_2), δ_P, ppm: 179.2, 178.6.

Compound V. Compound **III** (2.69 g, 9.0 mmol) was added to suspension of 1.9 g (9.0 mmol) of PCl_5 in 10 mL of CH_2Cl_2 at room temperature. The mixture was stirred during 1 h under argon atmosphere. After, the solvent and PCl_3 were removed. Yield 96%, viscous pale yellow liquid. ^{13}C NMR spectrum, δ_C, ppm, (*J*, Hz): 135.37 br.m (br.d.d) (C^{3a}, $^2J_{PC3a}$ 2.8, $^3J_{PC3a}$ 2.8), 132.32 m (d.d) (C^4, $^2J_{PC4}$ 11.7, $^3J_{PC4}$ 20.9), 118.60 d.d.d (d) (C^5, $^3J_{PC5}$ 4.8, $^1J_{HC5}$ 166.5, $^3J_{HC5}$ 4.8), 122.55 d (s) (C^6, $^1J_{HC6}$ 166.5), 109.07 d.d.d (d) (C^7, $^3J_{PC7}$ 18.7, $^1J_{HC7}$ 170.9, $^3J_{HC7}$ 8.1), 143.24 br.m (br.s) (C^{7a}). ^{31}P NMR spectrum (162 MHz, CH_2Cl_2), δ_P, ppm: 183.2, –23.3.

Compound VI was prepared similarly from 1.64 g (7.9 mmol) of PCl_5 and 2.32 g (7.9 mmol) of **IV**. Yield 97%, viscous pale yellow liquid. ^{13}C NMR spectrum, δ_C, ppm, (*J*, Hz): 143.11 d.d (s) (C^{3a}, $^3J_{HC3a}$ 5.1, $^3J_{HC3a}$ 4.7), 105.89 d.d.d.d (d.d) (C^4, $^3J_{PC4}$ 18.0, $^1J_{HC4}$ 170.2, $^3J_{PC4}$ 4.8, $^3J_{HC4}$ 4.8), 145.64 d.d.d.d (d) (C^5, $^2J_{PC5}$ 11.7, $^3J_{HC5}$ 11.0, $^2J_{HC5}$ 5.1, $^2J_{HC5}$ 5.1), 116.68 d.d.d (d) (C^6, $^3J_{PC6}$ 5.1, $^1J_{HC6}$ 166.5, $^3J_{HC6}$ 5.1), 111.38 d.d (d) (C^7, $^3J_{PC7}$ 17.6, $^1J_{HC7}$ 168.0), 140.20 d.d.d (s) (C^{7a}, $^3J_{HC7a}$ 10.6, $^3J_{HC7a}$ 5.1, $^2J_{HC7a}$ 4.7). ^{31}P NMR spectrum (CH_2Cl_2), δ_P, ppm: 179.0, –22.5.

Compound VII. Chlorine dissolved in 10 mL of CCl_4 was added dropwise to a solution of 1.3 g (4.4 mmol) of compound **III** in 5 mL of CCl_4 under argon upon stirring and cooling (–20°C). Then the solvent and excess of chlorine were removed in vacuum at 12 and 0.1 mmHg, respectively. Yield 97%, viscous pale yellow liquid. ^{13}C NMR spectrum, δ_C, ppm, (*J*, Hz): 136.39 d.d.d.d (d.d) (C^{3a}, $^2J_{PC3a}$ 3.3, $^3J_{PC3a}$ 8.4, $^3J_{HC3a}$ 8.2–8.4, $^3J_{HC3a}$ 8.3), 134.93 d.d.d.d (d.d) (C^4, $^2J_{PC4}$ 25.0, $^3J_{PC4}$ 21.7, $^3J_{HC4}$ 11.0, $^2J_{HC4}$ 3.7), 118.38 d.d.d (d) (C^5, $^3J_{PC5}$ 8.8, $^1J_{HC5}$ 166.5, $^3J_{HC5}$ 8.8), 122.77 d.d (d) (C^6, $^4J_{PC6}$ 5.9, $^1J_{HC6}$ 167.3), 110.19 d.d.d.d (d.d) (C^7, $^3J_{PC7}$ 18.7, $^4J_{PC7}$ 7.3, $^1J_{HC7}$ 169.5, $^3J_{HC7}$ 7.3), 143.17 d.d (br.s) (C^{7a}, $^3J_{HC7a}$ 8.8, $^2J_{HC7a}$ 2.2). ^{31}P NMR spectrum (CCl_4), δ_P, ppm: –23.1, –62.7.

Compound VIII was prepared similarly from 1.3 g (4.4 mmol) of **IV** and 0.63 g (8.9 mmol) of chlorine. Yield 96%, white powder. ^{13}C NMR spectrum, δ_C, ppm, (*J*, Hz): 143.33 m (d.d) (C^{3a}, $^2J_{PC3a}$ 5.5, $^4J_{PC3a}$ 1.1), 106.25 d.d.d (d.d) (C^4, $^3J_{PC4}$ 18.3, $^1J_{HC4}$ 169.8, $^3J_{PC4}$ 8.4), 146.46 m (d) (C^5, $^2J_{PC5}$ 24.9), 117.17 d.d.d (d) (C^6, $^3J_{PC6}$ 9.9, $^1J_{HC6}$ 170.1), 111.59 d.d.d (d.d) (C^7, $^3J_{PC7}$ 17.6, $^4J_{PC7}$ 6.2, $^1J_{HC7}$ 170.3), 141.06 m (d) (C^{7a}, $^2J_{PC7a}$ 7.7). ^{31}P NMR spectrum (162 MHz, CCl_4), δ_P, ppm, (*J*, Hz): –22.6. –63.6.

The NMR spectra ($CDCl_3$) were recorded using the Avance-400 spectrometer [400.0 (^{1}H), 162.0 (^{31}P), 100.6 MHz (^{13}C)] relative to internal HMDS (^{1}H, ^{13}C) or external H_3PO_4 (^{31}P) references. IR spectra were registered with the Bruker Vector-22 instrument.

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