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## LETTERS TO THE EDITOR

# Reaction of 3-(4-Bromophenyl)-2-ethoxy-4,4-bis(2,2,3,3-tetrafluoropropoxy)-2,3,4,5-tetrahydro-1,2$\lambda^5$-benzoxaphosphepine-2,4-dione with Phenylhydrazine

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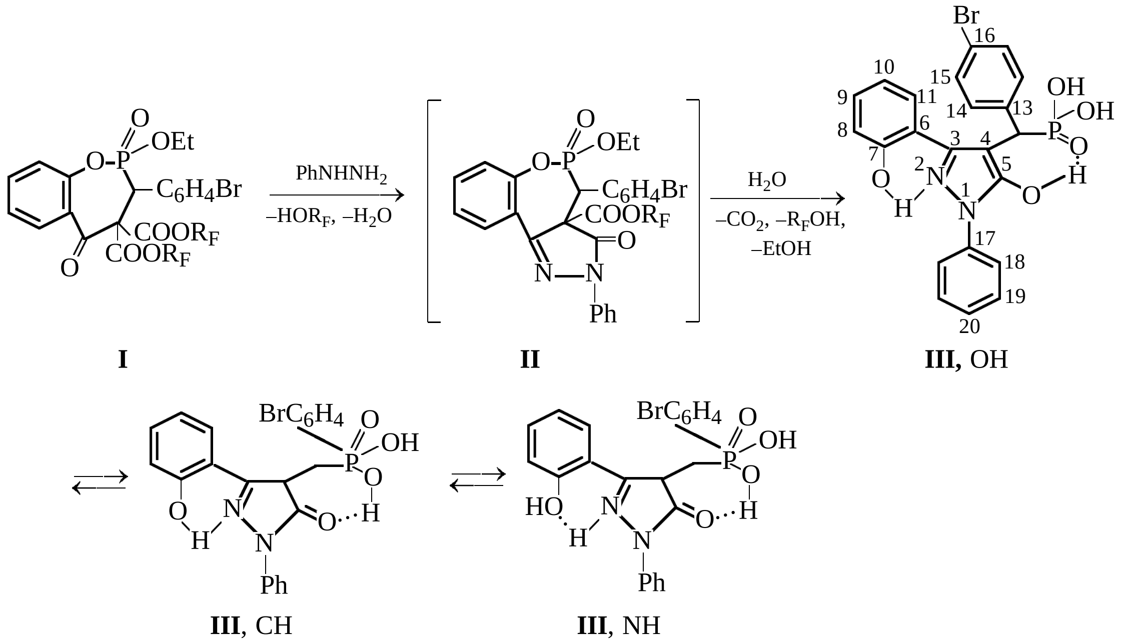
Previously we showed that 2-R-1,3,2-benzodioxaphosphinin-4-ones highly regio- and stereoselectively react with ethyl and bis(2,2,3,3-tetrafluoropropyl) esters of arylidenemalonic acids in mild conditions to form 1,2-benzoxaphosphepines [1, 2].

In the present paper we report for the first time on the reaction of 3-(4-bromophenyl)-2-ethoxy4,4-bis-(2,2,3,3-tetrafluoropropoxy)-2,3,4,5-tetrahydro-1,2$\lambda^5$-benzoxaphosphepine-2,4-dione with phenylhydrazine. It is known that reactions of carbonyl compounds with hydrazines form one of the principal synthetic approaches to pyrazolones that have found wide application in pharmacology and medicine, and also serve as convenient extractants and chelating agents for metal ions [3].

The reaction of compound **I** with phenylhydrazine (benzene, 80°C, 8 h) gave pyrazolone **III** instead of expected pyrazolone **II**. The IR spectrum of the resulting compound contains absorption bands belonging to strongly hydrogen-bonded OH and P–OH groups (3200–3000, 2580–2290 cm$^{-1}$), as well as strong absorption bands of the multiple bonds C=N (1680 cm$^{-1}$) and C=C (1612–1615, 1575–1580, 1500–1510 cm$^{-1}$). The $^{31}$P–{$^1$H} spectrum contains a single signal at $\delta_P$ 27.4 ppm, corresponding to a four-coordinate phosphorus atom bound with carbon, which transforms into a doublet with $^2J_{PCH}$ 27.1 Hz in the $^{31}$P NMR spectrum. A doublet with the same constant is present in the $^1$H NMR spectrum of the product in low fields ($\delta$ 5.00 ppm). The spectrum lacks signals of both tetrafluoropropyl groups that are eliminated as tetrafluoropropanol in the course of the reaction. Moreover, elimination of $CO_2$ and the acyclic substituent at the phosphorus atom (probably, as $C_2H_5OH$) take place. The structure of compound **III** was also confirmed by 1H, $^{13}$C, and $^{13}$C–{$^1$H} NMR using 2D-COSY, 2D-HSQC, and 2D-HMBC. Based on the resulting data, we assigned to compound **III** the structure of the OH(NH) tautomer of 4-[(4-bromophenyl)phosphonomethyl]-3-(2-hydroxyphenyl)-1-phenylpyrazol-5-one. It should be noted that the $^{13}$C NMR spectrum of compound **III** lacks carbonyl carbon signal. At the same time, there are two downfield doublets ($\delta_C$ 162–165 ppm) from C$^3$ and C$^5$. These signals were identified on the basis of their multiplicities and the 2D-HMBC spectrum that shows cross peaks between H$^{11}$ and C$^3$ and H$^{12}$ and C$^5$. The $^{13}$C NMR spectrum shows only one signal in a region characteristic of the $sp^3$ carbon atom, assigned to C$^{12}$ (doublet, $\delta_C$ 42.81 ppm); this finding points to the absence of the CH form. The OH and NH forms are impossible to decide between at this stage of the work because of the intricate IR spectral pattern. This problem requires special investigation.

**Compound III.** A mixture of 2.31 g of compound **I** and 0.35 g of phenylhydrazine was heated in 25 ml of benzene with a Dean–Stark trap for 8 h. Compound **III** precipitated as a light gray powder. It was filtered off, washed with pentane, and dried in a vacuum (0.02 mm Hg), yield 73%, mp 107–108°C. IR spectrum, cm$^{-1}$: 2920, 1680, 1616, 1560, 1492, 1460, 1376, 1248, 1136, 1072, 1060, 1044, 764. $^1$H NMR spectrum, $\delta$, ppm ($J$, Hz): 7.27 d.d (1H, H$^9$, $^3J_{H^9CCH^8}$



$R_F = CH_2CF_2CHF_2$.

8.5, ${}^4J_{\mathrm{H^{10}CCCH^8}}$ 0.9), 7.60 d.d.d (1H, H$^9$, ${}^3J_{\mathrm{H^8CCH^9}}$ 8.5, ${}^3J_{\mathrm{H^{10}CCH^9}}$ 7.3, ${}^4J_{\mathrm{H^{11}CCCH^9}}$ 1.6), 7.35 d.d.d (1H, H$^{10}$, ${}^3J_{\mathrm{H^{11}CCH^{10}}}$ 8.0, ${}^3J_{\mathrm{H^9CCH^{10}}}$ 7.3, ${}^4J_{\mathrm{H^8CCCH^{10}}}$ 0.9), 7.97 d.d (1H, H$^{11}$, ${}^3J_{\mathrm{H^{10}CCH^{11}}}$ 8.0, ${}^4J_{\mathrm{H^9CCCH^{11}}}$ 1.6), 5.00 d (1H, PCH, ${}^2J_{\mathrm{PCH}}$ 27.1), 7.47 m (4H, H$^{14}$, H$^{15}$), 7.07 d.d (1H, H$^{18}$, ${}^3J_{\mathrm{H^{19}CCH^{18}}}$ 8.6, ${}^4J_{\mathrm{H^{20}CCCH^{18}}}$ 1.0), 7.16 d.d (1H, H$^{19}$, ${}^3J_{\mathrm{H^{18}CCH^{19}}}$ 8.6, ${}^3J_{\mathrm{H^{20}CCH^{19}}}$ 7.3), 6.74 t.t (1H, H$^{20}$, ${}^3J_{\mathrm{H^{19}CCH^{20}}}$ 7.3, ${}^4J_{\mathrm{H^{18}CCCH^{20}}}$ 1.0). $^{13}$C NMR spectrum, $\delta_C$, ppm ($J$, Hz): 162.88 d.d.d (d) (C$^3$, ${}^3J_{\mathrm{PCCC^3}}$ 5.8, ${}^3J_{\mathrm{HC^{12}CC^3}}$ 4.6–5.8, ${}^3J_{\mathrm{HC^{11}CC^3}}$ 4.6–4.8), 101.31 br.d (br.s) (C$^4$, ${}^2J_{\mathrm{HC^{12}C^4}}$ 8.1), 163.32 d.d (d) (C$^5$, ${}^3J_{\mathrm{PCCC^5}}$ 12.3, ${}^3J_{\mathrm{HC^{12}CC^5}}$ 5.6–5.7), 117.49 d.d (s) (C$^6$, ${}^3J_{\mathrm{HC^{10}CC^6}}$ 7.0, ${}^3J_{\mathrm{HC^8CC^6}}$ 6.2), 152.47 m (s) (C$^7$), 115.86 d.d (s) (C$^8$, ${}^1J_{\mathrm{HC^8}}$ 164.3, ${}^3J_{\mathrm{HC^{10}CC^8}}$ 7.7–7.8), 132.18 d.d.d (s) (C$^9$, ${}^1J_{\mathrm{HC^9}}$ 161.7, ${}^3J_{\mathrm{HC^{11}CC^9}}$ 9.2, ${}^2J_{\mathrm{HCC^9}}$ 1.8), 124.03 d.d.d (s) (C$^{10}$, ${}^1J_{\mathrm{HC^{10}}}$ 165.2, ${}^3J_{\mathrm{HC^8CC^{10}}}$ 8.4, ${}^3J_{\mathrm{HCC^{10}}}$ 1.2–1.5), 123.87 d.d (s) (C$^{11}$, ${}^1J_{\mathrm{HC^{11}}}$ 163.1, ${}^3J_{\mathrm{HC^9CC^{11}}}$ 7.9), 42.81 d.d.t (d) (C$^{12}$, ${}^1J_{\mathrm{PC^{12}}}$ 133.1, ${}^1J_{\mathrm{HC^{12}}}$ 126.0, ${}^3J_{\mathrm{HC^{14}CC^{12}}}$ 2.4), 136.80 m (d) (C$^{13}$, ${}^2J_{\mathrm{PCC^{13}}}$ 3.8), 131.23 d.d.d.d (d) (C$^{14}$, ${}^1J_{\mathrm{HC^{14}}}$ 161.1, ${}^3J_{\mathrm{PCCC^{14}}}$ 6.2, ${}^3J_{\mathrm{HC^{12}CC^{14}}}$ 5.8–6.4, ${}^3J_{\mathrm{HC^{14'}CC^{14}}}$ 5.8–6.4), 131.37 d.m (d) (C$^{15}$, ${}^1J_{\mathrm{HC^{15}}}$ 168.4, ${}^4J_{\mathrm{PCCCC^{15}}}$ 1.8), 120.48 m (d) (C$^{16}$, ${}^5J_{\mathrm{PCCCCC^{16}}}$ 3.0), 146.33 m (s) (C$^{17}$); 112.94 d.d.d (s) (C$^{18}$, ${}^1J_{\mathrm{HC^{18}}}$ 160.2, ${}^3J_{\mathrm{HCCC^{18}}}$ 7.7.37.8, ${}^3J_{\mathrm{HCCC^{18}}}$ 5.3.35.4), 128.74 d.d (s) (C$^{19}$, ${}^1J_{\mathrm{HC^{19}}}$ 158.8, ${}^3J_{\mathrm{HC^{19'}CC^{19}}}$ 8.5), 119.01 d.t (s) (C$^{20}$, ${}^1J_{\mathrm{HC^{20}}}$ 160.1, ${}^3J_{\mathrm{HC^{18,18'}CC^{20}}}$ 8.4–8.5). $^{31}$P–{$^1$H} NMR spectrum (acetone-$d_6$): $\delta_P$ 27.4 ppm. Found, %: C 52.33; H 3.78; N 5.64; P 6.03. $C_{22}H_{18}BrN_2O_5P$. Calculated, %: C 52.69; H 3.59; N 5.59; P 6.19.

The IR spectrum was measured on a Specord M-80 instrument in mineral oil between KBr plates. The NMR spectra were obtained on Bruker Avance-600 (1H, 600 MHz; $^{13}$C, $^{13}$C–{$^1$H}, 150.9 MHz, 2D-COSY, 2D-HSQC, and 2D-HMBC) and Varian Unity-300 instruments ($^{31}$P, $^{31}$P–{$^1$H}, 121.42 MHz) in acetone-$d_6$ against internal HMDS and external $H_3PO_4$.

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