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SHORT COMMUNICATIONS

Terminal Alkynes in Reactions with 2,2,2-Tribromobenzo[*d*]-1,3,2-dioxaphosphol

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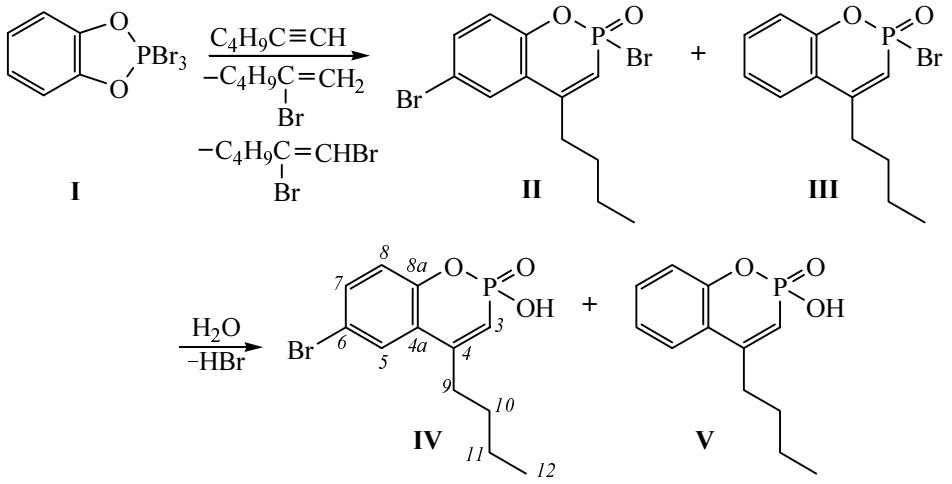
Reactions of 2,2,2-trihalobenzo[*d*]-1,3,2-dioxaphosphols derivatives with arylacetylenes and propargyl chloride that we have formerly investigated [1, 2] is a convenient prepartion method for benzo[*e*]-1,2-oxaphosphorinines, phosphorus-containing analogs of widely occurring natural heterocycles (coumarins and α-chromenes [3, 4].

In this study we for the first time investigated the reaction of 2,2,2-tribromobenzo[*d*]-1,3,2-dioxaphosphol (**I**) [5] with unsubstituted alkylacetylene, 1-hexyne. In contrast to reaction with propargyl chloride 1-hexyne with phosphol **I** at 10–20°C afforded only two phosphorus-containing substances that in the ^{31}P NMR spectrum gave rise to characteristic doublet signals of benzophosphorinines at δ 8–10 ppm ($^{2}J_{PCH}$ 25–27 Hz).

By hydrolysis bromophosphorinines **II** and **III** were converted into the corresponding acids **IV** and **V**. In the ^{1}H NMR spectra of compounds **IV** and **V** in the region of aromatic protons resonances the observed pattern corresponds to 1,2,4- and 1,2-substituted benzene rings. The introduction of a bromine atom into a phenylene fragment in the *para*-position to the endocyclic oxygen (compound **IV**) is confirmed by the multiplicity of H^{7} (d.d.d, $^{3}J_{H^{8}CCH^{7}}$ 8.7, $^{4}J_{H^{5}CCCH^{7}}$ 2.3, $^{4}J_{POCCCH^{7}}$ 2.0 Hz) and H^{5} (d, $^{4}J_{H^{5}CCCH^{7}}$ 2.3 Hz) signals. The structure of hydroxyphosphorinine **IV** was also proved by the data of ^{13}C-{^{1}H} and ^{13}C NMR spectra. In the ^{13}C-{^{1}H} NMR spectrum three carbon atoms (C^{8}, C^{8a}, C^{4a}) of the phenylene fragment among the six are coupled with phosphorus with constants similar to those in the spectrum 6-bromo-2-hydroxy-2-oxo-4-phenylbenzo[*e*]-1,2-oxaphosphorinine [1]. The signal from the atom C^{6} linked to bromine appeared in a stronger field (123.85 ppm).

Thus the reaction of phosphol **I** with hexyne as a representative of terminal acetylenes provided a possibility to prepare in high yield new derivatives of 4-alkylbenzo-



[*e*]phosphorinines and significantly extended the opportunities of the method first described in [1] by an example of reaction between trihalobenzophosphols with arylacetylenes.

Reaction of 2,2,2-tribromobenzo[*d*]-1,3,2-dioxaphosphol (I) with hexyne. To a solution of 31.1 g (0.082 mol) of freshly prepared phosphol **I** [5] in 30 ml of dichloromethane was added at stirring in an argon atmosphere a solution of 18.8 ml (0.164 mol) of 1-hexyne in 15 ml of dichloromethane. The ^{31}P NMR spectrum of the reaction mixture was as follows (36.48 MHz, CH_2Cl_2), δ, ppm: 9.4 d ($^2J_{PCH}$ 26.5 Hz), compound **III**; 8.6 d ($^2J_{PCH}$ 25.1 Hz), compound **II**. A week later the reaction mixture was dried in a vacuum to obtain thick glassy substance that was dissolved in 30 ml of hexane. On storage of the mixture for 3–4 days a crystalline precipitate separated (compound **III**) that was filtered off and hydrolyzed in ethyl ether (30 ml) containing 0.5 ml of HCl. The organic layer was separated and evaporated to a half of volume in a vacuum. The precipitate separated therewith was filtered off and dried in a vacuum to obtain 2.61 g (10%) of **4-butyl-2-hydroxy-2-oxobenzo[*e*]-1,2-oxaphosphorinine (V)**, mp 115°C. IR spectrum, ν, cm^{-1}: 413, 448, 482, 501, 523, 572, 591, 629, 654, 669, 722, 749, 765, 781, 876, 946, 1004, 1042, 1124, 1163, 1197, 1301, 1378, 1421, 1447, 1462, 1486, 1559, 1600, 1673, 2359, 2724, 2854, 2925. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J,* Hz): 0.92 t (3H, $C^{12}H_3$, $^3J_{H^{11}CCH^{12}}$ 7.3), 1.38 t. q (2H, $C^{11}H_2$, $^3J_{HCCH}$ 7.2, $^3J_{HCCH}$ 7.2), 1.53 t.t (2H, $C^{10}H_2$, $^3J_{HCCH}$ 7.9, $^3J_{HCCH}$ 7.9), 2.66 m (2H, C^9H_2, $^3J_{HCCH}$ 7.4), 6.12 br.d (1H, H^3, $^2J_{PCH}$ 17.7), 7.16 d.d (1H, H^8, $^3J_{H^7CCH^8}$ 8.1, $^4J_{H^6CCCH^8}$ 1.2), 7.20 d.d.d (1H, H^6, $^3J_{H^7CCH^6}$ 7.6, $^3J_{H^5CCH^6}$ 7.6, $^4J_{H^8CCCH^6}$ 1.1), 7.40 d.d.d.d (1H, H^7, $^3J_{H^8CCH^7}$ 8.0, $^3J_{H^6CCH^7}$ 8.0, $^4J_{H^5CCCH^7}$ 1.5, $^5J_{POCCCH^7}$ 1.5), 7.62 d.d (1H, H^5, $^3J_{H^6CCH^7}$ 7.9, $^4J_{H^7CCCH^5}$ 1.4). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ, ppm (*J,* Hz) (in parentheses is indicated the appearance of the signal in the ^{13}C-{^{1}H} NMR spectrum): 113.01 d.d.t(d) (C^3, $^1J_{PC^3}$ 172.8, $^1J_{HC^3}$ 161.2, $^3J_{HC^9CC^3}$ 5.6–6.0), 153.26 m(s) (C^4), 122.30 m(d) (C^{4a}, $^3J_{PCCC^{4a}}$ 16.9), 126.79 d.d(s) (C^5, $^1J_{HC^5}$ 159.5, $^2J_{HC^7CC^5}$ 8.5), 123.85 d.d(s) (C^6, $^1J_{HC^6}$ 163.8, $^3J_{HC^8CC^6}$ 8.2), 131.12 d.d(s) (C^7, $^1J_{HC^7}$ 163.0, $^3J_{HC^5CC^7}$ 9.2), 119.68 d.d.d.d(d) (C^8, $^1J_{HC}$ 162.1, $^3J_{POCC^8}$ 7.3, $^3J_{HCCC^8}$ 7.9, $^2J_{HCC^8}$ 1.3–1.8), 152.10 m(d) (C^{8a}, $^2J_{POC^{8a}}$ 7.5), 34.59 t.d.m(d) (C^9, $^3J_{PCCC^9}$ 18.0, $^1J_{HC^9}$ 123.8), 30.81 t.m(s) (C^{10}, $^1J_{HC^{10}}$ 123.0), 22.66 t(s) (C^{11}, $^1J_{HC^{11}}$ 121.7), 13.82 q.t.t(s) (C^{12}, $^1J_{HC^{12}}$ 124.7, $^3J_{HC^{10}CC^{12}}$ 4.0, $^2J_{HC^{11}C^{12}}$ 4.0). ^{31}P NMR spectrum (36.48 MHz, DMSO), δ, ppm: 5.9 d ($^2J_{PCH}$ 17.1 Hz). Found, %: C 60.70; H 6.21; P 12.95. $C_{12}H_{15}O_3P$. Calculated, %: C 60.50; H 6.30; P 13.03.

The hexane filtrate after separation of part of bromophosphorinine **III** was hydrolyzed with water. The precipitate separated therewith was filtered off and dried to obtain 1.82 g (7%) of **6-bromo-4-butyl-2-hydroxy-2-oxobenzo[*e*]-1,2-oxaphosphorinine (IV)**, mp 131°C. IR spectrum, cm^{-1}: 443, 502, 545, 587, 626, 656, 731, 778, 821, 872, 880, 904, 945, 1014, 1083, 1135, 1181, 1235, 1270, 1311, 1351, 1377, 1419, 1466, 1552, 1600, 1896, 1959, 2261, 2359, 2725, 3046. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J,* Hz): 0.98 t (3H, $C^{12}H_3$, $^3J_{H^{11}CCH^{12}}$ 7.3), 1.45 t.q (2H, $C^{11}H_2$, $^3J_{HCCH}$ 7.2, $^3J_{HCCH}$ 7.2), 1.62 t.t (2H, $C^{10}H_2$, $^3J_{HCCH}$ 7.0, $^3J_{HCCH}$ 7.0), 2.63 t (2H, C^9H_2, $^3J_{HCCH}$ 7.7), 6.11 br.d (1H, H^3, $^2J_{PCH}$ 16.6), 7.09 d (1H, H^8, $^3J_{H^7CCH^8}$ 8.7), 7.47 d.d.d (1H, H^7, $^3J_{H^8CCH^7}$ 8.7, $^4J_{H^5CCCH^7}$ 2.3, $^4J_{POCCCH^7}$ 2.0), 7.63 d (1H, H^5, $^4J_{H^7CCCH^5}$ 2.3). ^{31}P NMR spectrum (36.48 MHz, DMSO), δ, ppm: 5.8 d ($^2J_{PCH}$ 17.1 Hz). Mass spectrum, *m*/*z* (peaks of molecular ions are given which contain the most abundant isotopes): 316 $[M]^+$, 274 $[M - C_3H_6]^+$, 256, 237, 212, 209, 196, 178, 144, 131, 115, 102, 77, 63, 43, 41, 27. Found, %: C 45.56; H 4.41; Br 24.85; P 9.84. $C_{12}H_{14}BrO_3P$. Calculated, %: C 45.28; H 4.72; Br 25.16; P 9.75.

IR spectra were recorded on Bruker Vector-22 instrument from mulls in mineral oil.

NMR spectra were registered on a spectrometer MSL-400 with respect to internal reference HMDS (^{1}H), external reference H_3PO_4 (^{31}P), or the solvent signal (^{13}C).

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