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LETTERS
TO THE EDITOR

Reaction of 1,6-Bis(diphenylphosphino)hexane with 6-Bromo-1,2-naphthoquinone

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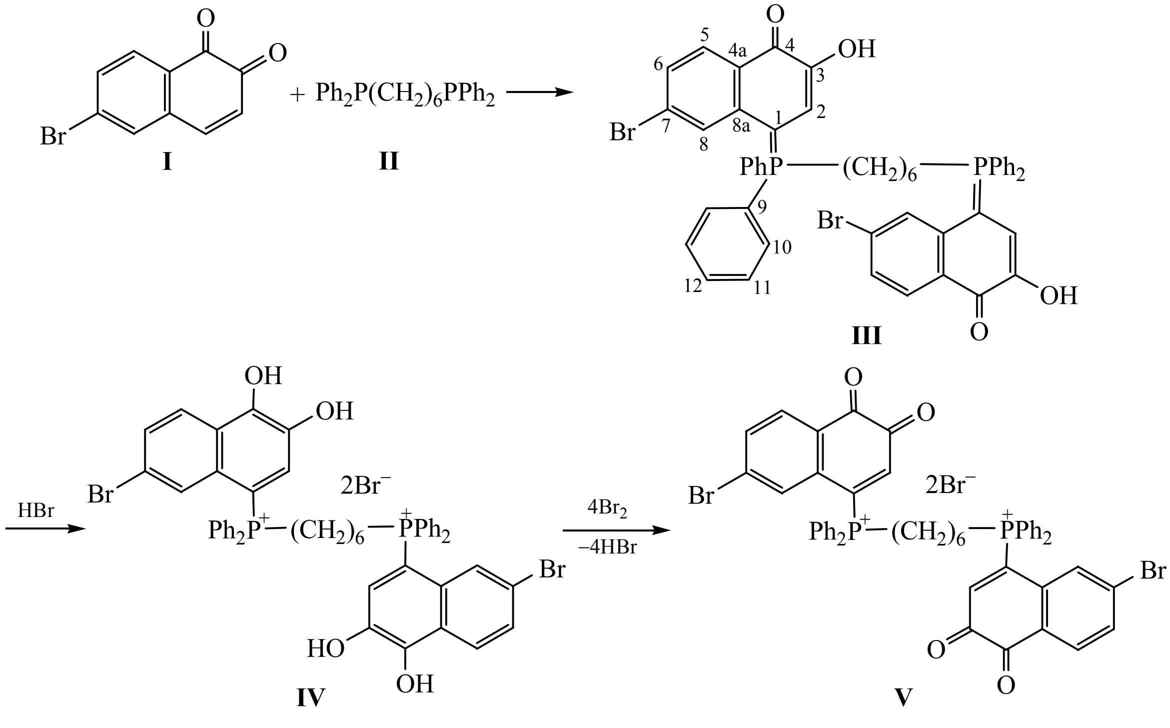
The phosphonium salts with a wide range of practically useful properties are of a considerable interest [1]. Among them biologically active compounds were found capable of the preferential accumulation in mitochondria that causes inhibiting tumor cell growth owing to antioxidant effect [2], antibacterial substances [3], ionic liquids [4], phase-transfer catalysts [5] and organocatalysts [6]. Previously, we developed a new synthetic approach to phosphonium salts on the basis of the reaction of triphenylphosphine with 6-bromo-1,2-naphthoquinone **I**, in which the phosphorylation of naphthalene fragment occurs in the position *4* to form phosphorus ylide followed by its treating with hydrogen halides [7]. An attempt to extend this approach to 1,2-bis(diphenylphosphino)ethane led to the formation of phosphonium salts with only one phosphorus atom [8]. It may probably be due to steric hindrances to the double phosphorylation of the naphthalene ring. In this report we show that lengthening the spacer connecting two phosphine centers in 1,6-bis(diphenylphosphino)hexane **II** makes it possible to obtain the bis-phosphorylated derivative **III** in almost the quantitative yield in the reaction with quinone **I**.



The reaction of bis-ylide **III** with dry hydrogen bromide results in a more stable bis(1,2-dihydroxynaphthylphosphonium) salt **IV**.

In the ^{13}C NMR spectra of compound **IV** the signal of C^{1} is shifted upfield (from 122.55 in **III** to 97.90 ppm) that indicates a change in the electron density on the phosphorus atom and the salt formation from ylide **III**. The signals of carbons C^{3} and C^{4} are observed in the stronger field at δ_C 140.68 and 146.86 ppm in comparison with the signals of ylide **III** (δ_C 143.89 and 164.30 ppm). The broad absorption band in the region of 3458 cm^{-1} in the IR spectrum of bisphosphonium salt **IV** corresponds to the stretching vibrations of hydroxy groups.

The bis-phosphonium salt **IV** is oxidized with bromine under the mild conditions (20°C) to give the corresponding phosphorus diquinone in high yield. The reaction progress was monitored by the disappearance of a broad absorption band of hydroxy groups at of 3458 cm^{-1} and the appearance of a narrow intense absorption band at 1671 cm^{-1} belonging to the *ortho*-quinone moiety in the IR spectrum of the resulting salt.

1,6-Bis-(diphenylphosphonium 6-bromo-2-hydroxynaphth-4-yl-1-ate)hexane (III). To a boiling suspen-sion of 0.62 g (2.62 mmol) of naphthoquinone **I** in 15 ml of benzene was added dropwise 0.59 g (1.30 mmol) of diphosphine **II** under argon atmosphere. The reaction mixture became black, and the light green precipitate was formed. After 10 min the color of reaction mixture was changed to brown-green. The precipitate was filtered off, washed with 10 ml of diethyl ether, and dried in a vacuum (12 mm Hg). Yield 0.98 g (81%), mp 190–191°C (decomp.). IR spectrum, ν, cm^{-1}: 1596, 1536, 1343, 1284, 1222, 1154, 1110, 1072, 966, 817, 722, 689, 478. ^{1}H NMR spectrum (DMF-d_7), δ, ppm (*J*, Hz): 7.18 d (H^{2}, $^{3}J_{PCCH}$ 14.9), 7.22 d (H^{5}, $^{3}J_{HCCH}$ 8.9–9.1, $^{4}J_{PCCCH}$ 1.3–1.5), 8.36 d.d (H^{6}, $^{3}J_{HCCH}$ 8.6, $^{4}J_{HCCCH}$ 1.0), 7.31 br.s (H^{8}), 7.86 m (H^{10}, H^{12}), 7.74 d.d (H^{11}, $^{3}J_{HCCH}$ 7.5, $^{5}J_{PCCCCH}$ 2.8), 3.40 m (H^{13}), 1.54 m (H^{14}, H^{15}). ^{13}C–{^{1}H}/DEPT NMR spectrum (DMF-d_7), δ_C, ppm (*J*, Hz): 122.55 d (C^{1}, $^{1}J_{PC}$ 85.5), 128.74 d (C^{2}, $^{2}J_{PCC}$ 11.4), 143.89 d (C^{3}, $^{3}J_{PCCC}$ 20.2), 164.30 br.s (C^{4}), 123.98 br.s (C^{4a}, overlapped with the signal of C^{5}), 123.98 br.s (C^{5}), 128.39 s (C^{6}), 119.24 s (C^{7}), 125.99 d (C^{8}, $^{3}J_{PCCC}$ 6.2), 127.65 d (C^{8a}, $^{2}J_{PCC}$ 12.1), 122.55 d (C^{9}, $^{1}J_{PC}$ 85.5), 133.19 d (C^{10}, $^{2}J_{PCC}$ 9.9), 130.09 d (C^{11}, $^{3}J_{PCCC}$ 12.1), 134.02 br.s (C^{12}), 23.83 d (C^{13}, $^{1}J_{PC}$ 54.3), 22.79 d (C^{15}, $^{3}J_{PCCC}$ 3.3), the signal of C^{14} was not identified due to the overlapping with the DMF signal. ^{31}P–{^{1}H} (^{31}P) NMR spectrum (DMF-d_7, 162.0 MHz): δ_P 20.3 ppm [s (m)]. Found, %: C 64.31; H 4.41; Br 17.41; P 6.37. $C_{50}H_{42}Br_2O_4P_2$. Calculated, %: C 64.65; H 4.52; Br 17.24; P 6.68.

1,6-Bis-(6-bromo-1,2-dihydroxynaphth-4-yldiphenylphosphoniumbromido)hexane (IV). Through a suspension of 0.50 g (0.54 mmol) of compound **III** in 15 ml of $CHCl_3$ was passed hydrogen bromide until the solution became pale yellow. After 2 h the reaction mixture was evaporated to dryness under vacuum (14 mm Hg). The dry glassy residue was triturated with 15 ml of anhydrous diethyl ether. The resulting white precipitate was filtered off, washed with 5 ml of diethyl ether, and dried in a vacuum (12 mm Hg). Yield 0.50 g (85%), mp 186°C. IR spectrum, ν, cm^{-1}: 3458 (OH), 1620, 1592, 1563, 1339, 1318, 1211, 1162, 1111, 1079, 979, 961, 818, 744, 722, 691. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.59 d (H^{2}, $^{3}J_{PCCH}$ 16.4, $^{5}J_{HCCCCH}$ 0.5), 7.44 d.d (H^{5}, $^{3}J_{HCCH}$ 8.9–9.1, $^{5}J_{PCCCCH}$ 1.1–1.3), 8.17 d.d (H^{6}, $^{3}J_{HCCH}$ 8.7, $^{4}J_{HCCCH}$ 1.2), 7.28 br.s (H^{8}, $^{5}J_{HCCCCH}$ 0.6), 7.74 m (H^{10}, H^{11}), 3.34 br. d. t (H^{13}, $^{2}J_{PCH}$ 11.9, $^{3}J_{HCCH}$ 3.7), 1.65–1.75 m (H^{14}, H^{15}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz) (the signal form in the ^{13}C–{^{1}H} NMR spectrum is given in parentheses): 97.90 d (d) (C^{1}, $^{1}J_{PC}$ 92.8), 129.33 d.d (d) (C^{2}, $^{1}J_{HC}$ 161.2, $^{2}J_{PCC}$ 12.1, overlapped with the signal of C^{8a}), 140.68 d.d (d) (C^{3}, $^{3}J_{PCCC}$ 17.9, $^{2}J_{HCC}$ 3.3), 146.86 d (d) (C^{4}, $^{4}J_{PCCCC}$ 2.2), 124.75 m (d) (C^{4a}, $^{3}J_{PCCC}$ 11.7, overlapped with the signal of C^{5}), 125.39 d (s) (C^{5}, $^{1}J_{HC}$ 166.9), 129.07 d.d (s) (C^{6}, $^{1}J_{HC}$ 169.1, $^{3}J_{HCCC}$ 5.1–5.5, overlapped with the signal of C^{8a}), 120.22 d.d (s) (C^{7}, $^{3}J_{HCCC}$ 12.8, $^{2}J_{HCC}$ 5.1), 126.54 d.d. (d) (C^{8}, $^{1}J_{HC}$ 161.7, $^{3}J_{PCCC}$ 5.9, $^{3}J_{HCCC}$ 4.8), 129.98 m (d) (C^{8a}, $^{2}J_{PCC}$ 8.1, overlapped with the signals of C^{2} and C^{6}), 119.11 d.t (d) (C^{9}, $^{1}J_{PC}$ 85.1, $^{3}J_{HCCC}$ 7.3–7.7), 133.05 d.d.d (d) (C^{10}, $^{1}J_{HC}$ 163.9, $^{2}J_{PCC}$ 9.9, $^{3}J_{HCCC}$ 7.3), 130.50 d.d (d) (C^{11}, $^{1}J_{HC}$ 165.8, $^{3}J_{PCCC}$ 12.5), 134.77 br.d.d (d) (C^{12}, $^{1}J_{HC}$ 163.2, $^{3}J_{HCCC}$ 7.3, $^{4}J_{PCCCC}$ 2.2), 25.42 t.d (d) (C^{13}, $^{1}J_{HC}$ 131.6, $^{1}J_{PC}$ 53.6, $^{3}J_{HCCC}$ 3.7), 29.15 br.t.d (d) (C^{14}, $^{1}J_{HC}$ 129.6, $^{2}J_{PCC}$ 17.2), 22.53 t. d (d) (C^{15}, $^{1}J_{HC}$ 128.4, $^{3}J_{PCCC}$ 3.3). ^{31}P–{^{1}H} (^{31}P) NMR spectrum (DMF-d_7, 162.0 MHz): δ_P 21.6 ppm [s (m)]. Found, %: C 55.01; H 4.09; Br 29.65; P 5.15. $C_{50}H_{44}Br_4O_4P_2$. Calculated, %: C 55.04; H 4.03; Br 29.35; P 5.68.

1,6-Bis-(6-bromo-1,2-dioxonaphth-4-yldiphenylphosphoniumbromido)hexane (V). To a solution of 0.3 g (0.27 mmol) of compound **IV** in 20 ml of trichloromethane was added dropwise 0.06 ml (1.08 mmol) of bromine. The dark red reaction mixture was poured into 30 ml of hot (70°C) water. The red precipitate was filtered off, washed with 10 ml of diethyl ether, and dried in a vacuum (12 mm Hg) at room temperature. Yield 0.25 g (86%), mp 180–182°C. IR spectrum, ν, cm^{-1}: 1671 (C=O), 1620, 1580, 1341, 1310, 1273, 1161, 1110, 108, 963, 932, 746, 723, 692, 515, 488. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (J, Hz): 7.44 m (H^2, H^{11}), 7.69 d.d (H^5, $^3J_{HCCH}$ 8.2, $^4J_{PCCCH}$ 1.7), 7.92 d (H^6, $^3J_{HCCH}$ 8.2), 7.23 s (H^8), 7.65 m (H^{10}, H^{12}), 1.56 m (H^{13}, H^{14}), 1.37 m (H^{15}). ^{31}P–{^{1}H} (^{31}P) NMR spectrum (DMF-d_7, 162.0 MHz): δ_P 26.2 ppm [s (m)]. Found, %: C 54.45; H 3.25; Br 30.70; P 5.60. $C_{50}H_{40}Br_4O_4P_2$. Calculated, %: C 55.24; H 3.68; Br 29.46; P 5.71.

The ^{1}H, ^{13}C, ^{13}C–{^{1}H}, ^{31}P, and ^{31}P–{^{1}H} NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 MHz, ^{1}H; 162.0 MHz, ^{31}P; 100.6 MHz, ^{13}C) relative to the signal of residual protons or carbon atoms in the solvent (^{1}H and ^{13}C) or to an external H_3PO_4 (^{31}P). The IR spectra were recorded on a Bruker Vector-22 spectrometer from the mulls in mineral oil. The elemental analysis was performed on an EuroVector-3000 (C, H) instrument and by the sample pyrolysis in an oxygen stream (Br, P).

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