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SHORT COMMUNICATIONS

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

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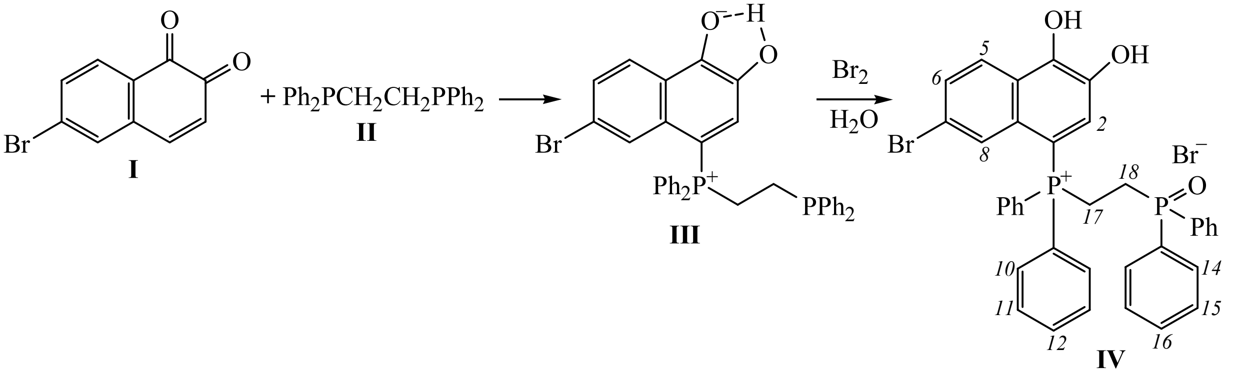
The intense development of the chemistry of quinones and related compounds is due to the wide spread of these compounds in the nature and their versatile biological activity; they play the key part in many biological processes, like respiration or photosynthesis. The presence of a reactive system of multiple bonds C=C and C=O leads to their extensive employment in the organic synthesis as precursors of various heterocyclic and spiro compounds, and the presence in the *o*-qionones of a chelate-forming 1,2-diketone fragment easily transformed into dioxyvinyl moiety makes it possible to use the latter for preparation of a large number of metal complexes [1–7].

o-Quinones fairly easily react with P(III) derivatives giving as a rule phosphoranes [8, 9]. At the same time the phosphorylation of 1,2-naphthoquinone was described in rare publications; it was for instance shown that they reacted with trialkyl phosphites also forming phosphoranes [9]. We showed recently that 1,2-naphthoquinone and its halo derivatives were capable to react with hexaethyltriamidophosphite via regioselective phosphorylation of the position *4* of the naphthalene skeleton with the formation of phosphobetaines containing a bond phosphorus-carbon [10, 11]; reactions with tributyl- [12, 13] and triphenylphosphines proceeded similarly [13, 14].

We extended in this study the discovered approach to more complex phosphorus(III) derivatives, tertiary diphosphines. It turned out that the reaction of 6-bromo-1,2-naphthoquinone (**I**) with 1,2-bis-(diphenylphosphino)-ethane (**II**) in the ratio 1 : 1 resulted in phosphobetaine **III**, product of the reaction involving only one phosphorus atom. In the $^{31}P-\{^1H\}$ NMR spectrum it possesses two signals at δ 19.8 and –12.0 ppm, belonging to phosphorus atoms in coordination P(IV) and P(III) ($^3J_{PCCP}$ 48.1 Hz). By treating with bromine in the presence of air moisture phosphobetaine **III** was converted into a more stable derivative, phosphinoxidophosphonium salt **IV** whose



structure was proved by ^{1}H, ^{31}P–{^{1}H}NMR spectra.

(7-Bromo-3,4-dihydroxy-1-naphthyl)[2-(diphenyl-phosphoryl)ethyl]diphenylphosphonium bromide (IV). To a dispersion of 0.59 g (2.50 mmol) of quinone **I** in 5 ml of CH_2Cl_2 at bubbling argon was added dropwise a solution of 0.5 g (1.25 mmol) of 1,2-bis-(diphenylphosphino)ethane (**II**) in 10 ml of CH_2Cl_2. The reaction mixture turned dark, and a green fine crystalline precipitate separated that within 24 h completely dissolved. The obtained solution of compound **III** [δ 19.8 d (P^+, $^3J_{PCCP}$ 46.2 Hz), –12.0 d (P^{III}, $^3J_{PCCP}$ 48.1 Hz)] was treated with 0.13 ml (2.50 mmol) of bromine. According to the ^{31}P NMR spectrum the content of compound **IV** in the reaction mixture corresponded to the quantitative yield. After 10 days from the solution separated a light-gray precipitate that was filtered off and dried in a vacuum (12 mm Hg). Yield 0.2 g (19%), mp 175–179°C. IR spectrum, ν, cm^{-1}: 3584–3563 (OH), 1712, 1618, 1593, 1559, 1462, 1441, 1377, 1341, 1269 (P=O), 1212, 1177, 1156, 1124, 1106, 1076, 1027, 984, 880, 727, 694, 540, 482. ^{1}H NMR spectrum, δ, ppm: 7.59 d (H^2, $^3J_{PCCH}$ 16.5 Hz), 8.20 d.d (H^5, $^3J_{HCCH}$ 9.2, $^5J_{PCCCCH}$ 1.8 Hz), 7.58 d.d (H^6, $^3J_{HCCH}$ 9.1, $^4J_{HCCCH}$ 1.8 Hz), 7.29 br.s (H^8), 7.83 d.d (H^{10}, $^3J_{PCCH}$ 12.8, $^3J_{HCCH}$ 7.8 Hz), 7.72 d.d.d (H^{11}, $^3J_{HCCH}$ 8.1, $^3J_{HCCH}$ 7.6–7.8, $^4J_{PCCCH}$ 3.4–3.6 Hz), 7.88 d.t (H^{12}, $^3J_{HCCH}$ 7.3–7.8, $^5J_{PCCCCH}$ 0.8–1.0 Hz), 7.68 d.d (H^{14}, $^3J_{PCCH}$ 11.6, $^3J_{HCCH}$ 7.6 Hz), 7.46 d.d.d (H^{15}, $^3J_{HCCH}$ 7.6, $^3J_{HCCH}$ 7.6, $^4J_{PCCCH}$ 2.6 Hz), 7.55 br.d.t (H^{16}, $^3J_{HCCH}$ 7.6, $^5J_{PCCCCH}$ 1.0 Hz), 3.66 m (H^{17}), 2.69 m (H^{18}), 10.93 br.s and 10.36 br.s (2OH). ^{31}P–{^{1}H} NMR spectrum, δ, ppm: 29.7 d (P=O, $^3J_{PCCP}$ 50.8 Hz), 24.2 d (P^+, $^3J_{PCCP}$ 50.8 Hz).

IR spectra were registered on a spectrophotometer Bruker Vector-22 from the mull of the compound in mineral oil. NMR spectra were recorded on spectrometers Bruker Avance-600 (600 MHz, ^{1}H, in DMSO-d_6), Bruker CXP-100 (36.48 MHz, ^{31}P, in $CDCl_3$–DMSO-d_6, 1 : 3).

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