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Unusual aryl-aryl coupling of 6-bromo-1,2-naphthoquinone to 6,6'-dibromo-1,1',2,2'-tetrahydroxy-4,4'-binaphthyl in the presence of trialkylphosphine and water

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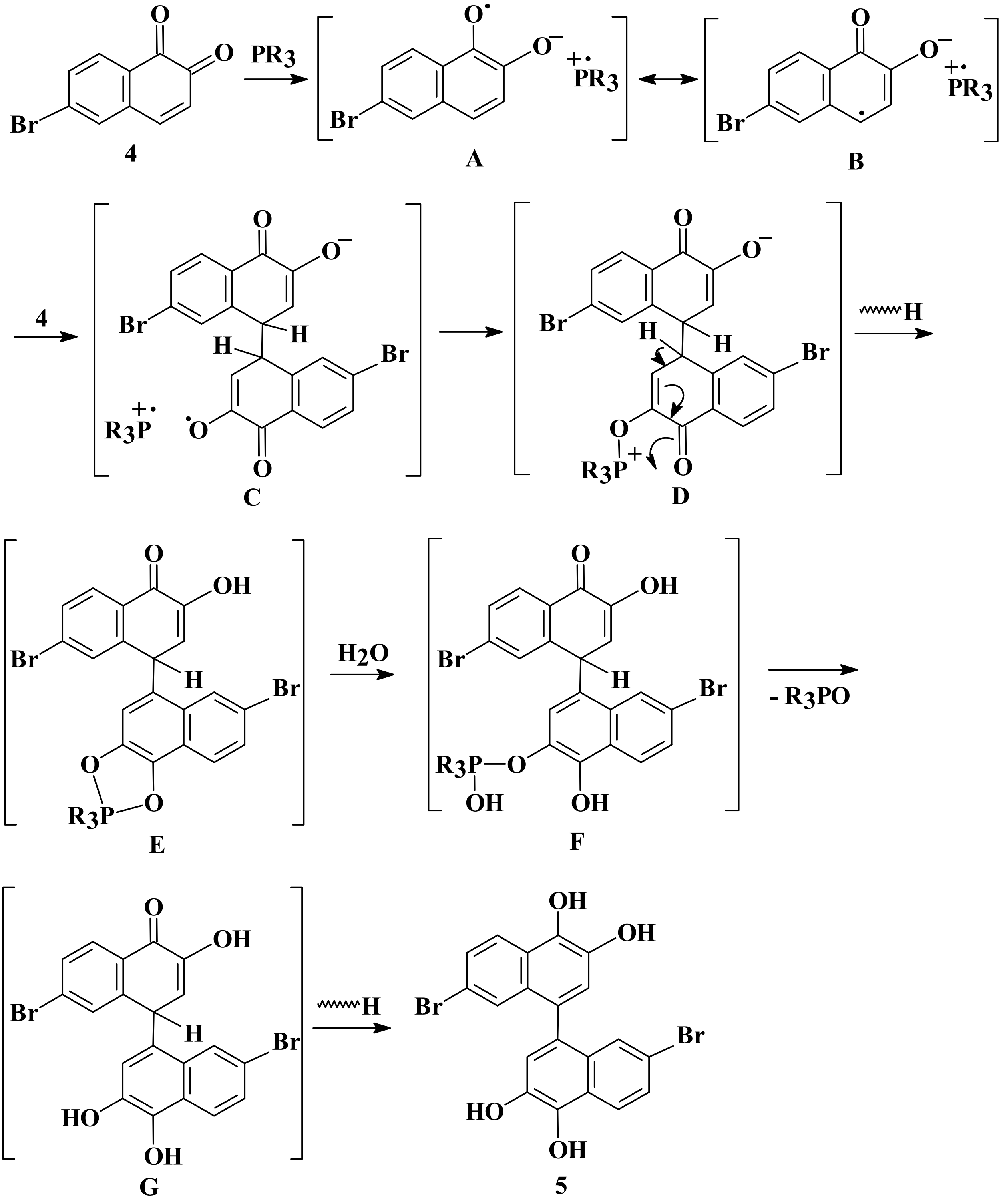
3-Bromo-1,2-dihydroxynaphthalene **3**. A suspension of tri(2-cyanoethyl)phosphine (0.83 g, 4.3 mmol) in 20 ml of dichloromethane was added dropwise to a suspension of quinone **1** (1 g, 4.3 mmol) in 10 ml of the same solvent with bubbling of dry argon. During the addition the reaction mixture turned black. After 24 hours, the solution produced a gray crystalline precipitate of tri(2-cyanoethyl)phosphine oxide, which was filtered off and dried *in vacuo* (12 mmHg). Yield 0.82 g (92 %), m. p. 149-150 °C. Mass-spectrum, *m/z*: 209 $[M]^{+\bullet}$ ($C_9H_{12}N_3OP$). ^{31}P-{^1H} (36.48 MHz, $CDCl_3$), δ_P: 43.1 ppm. ^1H (600 MHz, DMSO-d_6, δ ppm, J Hz): 2.20 d. t (PCH_2, $^2J_{PCH}$ 3.3 Hz, $^3J_{HCCH}$ 7.8-8.1 Hz), 2.73 d. t (CH_2CN, $^3J_{PCCH}$ 2.5 Hz, $^3J_{HCCH}$ 7.8 Hz). ^{13}C (100.9 MHz, DMSO-d_6, δ_C ppm, J Hz) (here and further a multiplicity of the signal in ^{13}C-{^1H} spectrum is given in brackets): 22.84 d. t. t (d), (PCH_2, $^1J_{PC}$ 64.2 Hz, $^1J_{HC}$ 130.7 Hz, $^2J_{HCC}$ 4.5 Hz), 9.56 d. t. t (d) (CH_2, $^2J_{PCC}$ 1.7 Hz, $^1J_{HC}$ 137.7 Hz, $^3J_{HCCC}$ 3.7-4.6 Hz), 120.03 m (d) (CN, $^3J_{PCCC}$ 15.7 Hz, $^2J_{HCC}$ 5.2 Hz). A filtrate was evaporated in vacuum (12 mmHg) to dryness to form compound **3** as a brown solid. Yield 0.82 g (80 %), m. p. 120 °C. Mass-spectrum, *m/z* 238.0 ($C_{10}H_7BrO_2$). IR (nujol, cm^{-1}): 3514-3319 (OH), 1628, 1598, 1506, 1393, 1377, 1355, 1299, 1254, 1222, 1147, 1090, 1022, 973, 954, 890, 830, 743, 578, 555, 447. ^1H NMR (600 MHz, DMSO-d_6, δ ppm, J Hz): 7.70 s (H^4), 7.71 d (H^5, $^3J_{HCCH}$ 8.4 Hz), 7.42 d. t (H^6, $^3J_{HCCH}$ 6.8 Hz, $^4J_{HCCCH}$ 1.1 Hz), 7.31 d. t (H^7, $^3J_{HCCH}$ 6.8 Hz, $^4J_{HCCCH}$ 1.0 Hz), 8.04 d (H^8, $^3J_{HCCH}$ 8.4 Hz), 9.40 br. s (OH), 9.19 br. s (OH). ^{13}C (150.0 MHz, DMSO-d_6, δ_C ppm, J Hz): 139.62 d (s) (C^1, $^3J_{HCCC}$ 3.7 Hz), 137.96 d (s) (C^2, $^3J_{HCCC}$ 8.2 Hz), 113.82 d (s) (C^3, $^2J_{HCC}$ 4.0 Hz), 121.91 d. d (s) (C^4, $^1J_{HC}$ 166.8 Hz, $^3J_{HCCC}$ 6.6 Hz), 128.85 d. d (s) (C^{4a}, $^3J_{HCCC}$ 6.6 Hz, $^3J_{HCCH}$ 6.6 Hz), 126.60 d. t (s) (C^5, $^1J_{HC}$ 154.8 Hz, $^3J_{HCCC}$ 5.4-6.5 Hz), 125.98 d. d (s) (C^6, $^1J_{HC}$ 160.3 Hz, $^3J_{HCCC}$ 8.5 Hz), 121.15 d. d (s) (C^7, $^1J_{HC}$ 161.3 Hz, $^3J_{HCCC}$ 6.9 Hz), 124.18 d. d (s) (C^8, $^1J_{HC}$ 160.6 Hz, $^3J_{HCCH}$ 8.5 Hz), 125.17 d. d. d (s) (C^{8a}, $^3J_{HCCC}$ 7.2 Hz, $^3J_{HCCC}$ 6.9 Hz, $^3J_{HCCH}$ 9.2 Hz).

The mechanism of the reaction of tri(2-cyanoethyl)phosphine with quinone **4** in the presence of water is unclear and additional investigation should be performed. Nevertheless, two possible pathways can be suggested (schemes 1, 2). The starting quinone molecule is an oxidizing reagent and phosphine molecule is a reducing reagent in the both reaction schemes.

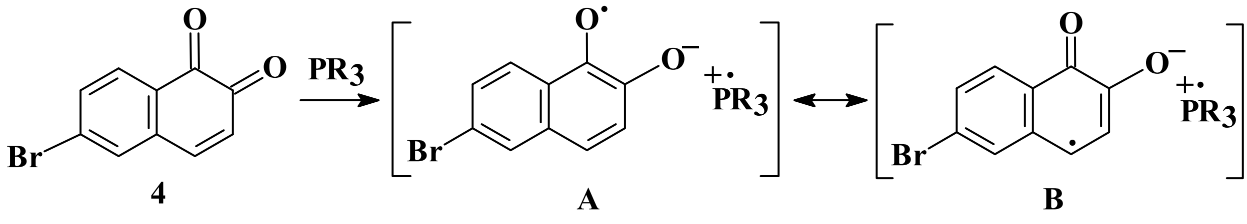


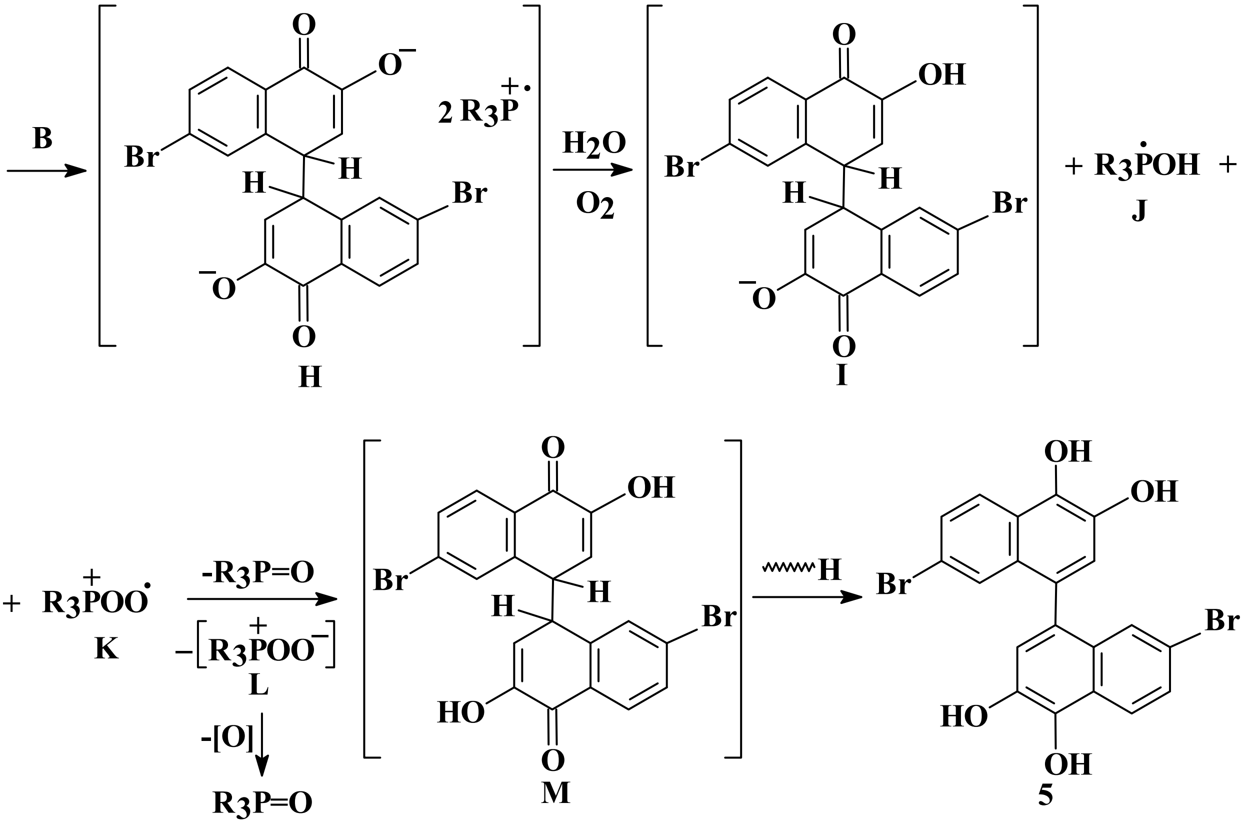
Scheme 1.

The process is likely to begin with the single electron transfer from phosphine molecule to quinone molecule and gives the ion-radical pair **A** (scheme 1). The structure **B**, in which the radical localizes at C^4 atom, is a resonance form of the intermediate **A**. The following electron transfer to the quinone molecule leads to the formation of intermediate **C**, which accepts a further electron from phosphorus and turns into betaine **D** with separated charges. The phosphorane **E** is formed in the result of the following electron density transfer from a C–H σ-bond to the oxygen atom and simultaneous attack of the last on the phosphorus atom in the betaine **D**. The process is accompanied by the proton transition to the alkoxide-anione. The hydrolysis of phosphorane **E** via intermediate hydroxyphosphorane **F** occurs with a phosphine oxide evolving and a formation of the quinone-methyde structure **G**, which is easily aromaticized in the result of prototropic shift. The considered reactions are the typical ones for the aromatic systems and quinones.

The proposed pathway does not explain the full oxidation of phosphine (according to this mechanism only 0.5 mole of phosphine is needed for the reaction). In view of the fact that phosphine is completely utilized the other directions of the further transformations for the ion-radical pair **B** can be proposed (scheme 2). The most probable pathway includes the ion-radical pair **B** dimerization to the intermediate **H** instead of the attack on starting quinone molecule. The protonation of ion-radical pair **H** with the formation of the intermediates **I** and then **J** takes place in this case. The last structure is easily aromaticized in the result of prototropic shifts.

The oxidation of the cation-radical $R_3P^{+\bullet}$ (the formation of $R_3P^{\bullet}OH$ and $R_3P^{+}OO^{\bullet}$) is likely to proceed by two pathways in the result of the attack of hydroxide-anion and oxygen, which may be both in water and in the solvent. The further transformation of the intermediates **J** and **K** (or **L**) to phosphine oxide is possible by various pathways. The chemistry of cation-radical $R_3P^{+\bullet}$ is considered in detail in works of Yu.M.Kargin and H.Ohmori [(1) N.P.Tomilov, Yu. M.Kargin, I. N. Chernykh. Electrochemistry of Elementoorganic Compounds (Elements of IV, V, VI Groups of Periodic System), Moscow, Nauka, 1986, 94-177; (2) H. Maeda, H. Ohmori, Acc. Chem. Res., 1999, Vol. 32, 72-80]. ½ Mole of O_2 is needed for the realization of the pathway, shown in the scheme 2.





Scheme 2.