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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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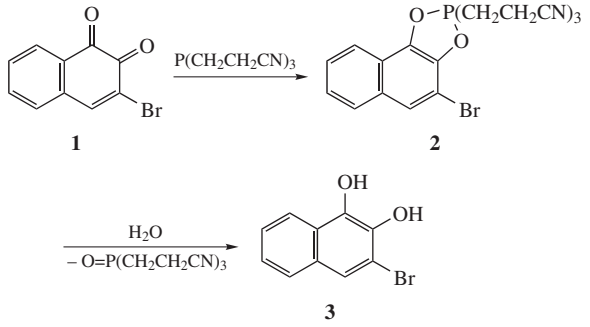
The reaction of 6-bromo-1,2-naphthoquinone with tri(2-cyanoethyl)phosphine or tricyclohexylphosphine leads to the unusual formation of 6,6′-dibromo-1,1′,2,2′-tetrahydroxy-4,4′-binaphthyl; its structure was confirmed by NMR spectroscopy and single crystal X-ray diffraction analysis.

Considerable attention has been devoted to the chemistry of *ortho*-quinones and their derivatives because not only compounds of this type occur in nature and possess many kinds of biological activity but also they find use in syntheses of metal complexes, enantioselective syntheses and syntheses of nitrogen- and oxygen-containing heterocycles.[1–6]

Trivalent phosphorus compounds are generally used to obtain pentacoordinate phosphorus derivatives, such as phosphoranes, or tetracoordinate derivatives, such as quasi-phosphonium salts of betaine nature incorporating a $P^+–OC^-$ bond.[7,8] Of *ortho*-quinones, 1,2-naphthoquinones have been studied least thoroughly in reactions with P^{III} derivatives; they were shown to react with phosphites to give phosphoranes.[9] 1,2-Naphthoquinone[10] and its halo-substituted derivatives[11–13] are regioselectively phosphorylated at the 4-position on treatment with triphenylphosphine, hexaethyltriamidophosphite and tri(*n*-butyl)phosphine under mild conditions to give the corresponding phosphobetaines incorporating a phosphorus–carbon bond. Many derivatives of 1,2-naphthoquinones, particularly 4-substituted 1,2-naphthoquinones, display various types of biological activity and can serve as models of binding of polycyclic carcinogenic hydrocarbons with amino acids.[14]

The synthetic result of the reaction of 1,2-naphthoquinone derivatives depends considerably not only on the nature of the original tertiary phosphine but also on the positions of the substituents in 1,2-naphthoquinone. The reaction with tri(2-cyanoethyl)phosphine containing electron-withdrawing substituents at the phosphorus atom occurs as the classical addition of the P^{III} derivative to 3-bromo-1,2-naphthoquinone **1** in dichloromethane (20 °C) to give hydrolytically unstable phosphorane **2** with a characteristic chemical shift (δ_P –17 ppm) in the $^{31}P-\{^1H\}$ NMR spectrum. Mild hydrolysis of this compound results in 3-bromo-1,2-dihydroxynaphthalene **3**† in a nearly quantitative yield (Scheme 1).



1 **2** **3**

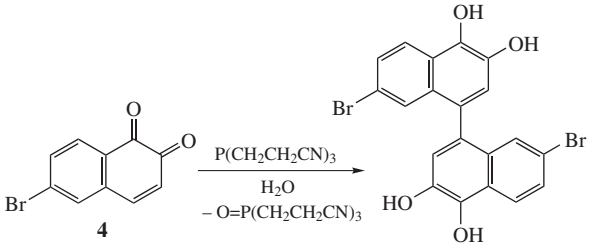
Scheme 1

The reaction of 6-bromo-substituted 1,2-naphthoquinone **4** with tri(2-cyanoethyl)phosphine unexpectedly follows a different route, namely, formation of tri(2-cyanoethyl)phosphine oxide and tetrahydroxy-4,4′-binaphthyl derivative **5**,‡ with one water molecule participating as a reagent (Scheme 2).

The mechanism of the reaction is unclear. It can be proposed that the phosphine molecule is a reducing agent, and the quinone molecule is an oxidant. Water is likely a protons source for a quinone moiety and an oxygen source for the phosphine oxide formation. Taking into account the full oxidation of the used phosphine, the additional participation of oxygen as an oxidizing

† *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 dry argon. During the addition, the reaction mixture turned black. After 24 h, the solution produced a gray crystalline precipitate of tri(2-cyanoethyl)phosphine oxide, which was filtered off and dried *in vacuo* (12 Torr). Yield 0.82 g (92 %), mp 149–150 °C. $^{31}P-\{^1H\}$ NMR (36.48 MHz, $CDCl_3$) δ_P: 43.1. ^1H NMR (600 MHz, $[^2H_6]$DMSO) δ: 2.20 (dt, PCH_2, $^2J_{PCH}$ 3.3 Hz, $^3J_{HCCH}$ 7.8–8.1 Hz), 2.73 (dt, CH_2CN, $^3J_{PCCH}$ 2.5 Hz, $^3J_{HCCH}$ 7.8 Hz). ^{13}C NMR (100.9 MHz, $[^2H_6]$DMSO) (here and further a multiplicity of the signal in $^{13}C-\{^1H\}$ spectrum is given in brackets) δ: 22.84 [dtt (d), PCH_2, $^1J_{PC}$ 64.2 Hz, $^1J_{HC}$ 130.7 Hz, $^2J_{HCC}$ 4.5 Hz], 9.56 [dtt (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]. MS, *m/z*: 209 $[M]^{+\bullet}$ ($C_9H_{12}N_3OP$).

A filtrate was evaporated in a vacuum (12 Torr) to dryness to form compound **3** as a brown solid. Yield 0.82 g (80%), mp 120 °C. IR (Nujol, ν/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, $[^2H_6]$DMSO) δ: 7.70 (s, H^4), 7.71 (d, H^5, $^3J_{HCCH}$ 8.4 Hz), 7.42 (dt, H^6, $^3J_{HCCH}$ 6.8 Hz, $^4J_{HCCCH}$ 1.1 Hz), 7.31 (dt, H^7, $^3J_{HCCH}$ 6.8 Hz, $^4J_{HCCCH}$ 1.0 Hz), 8.04 (d, H^8, $^3J_{HCCH}$ 8.4 Hz), 9.40, 9.19 (2br. s, 2OH). ^{13}C NMR (100.9 MHz, $[^2H_6]$DMSO) δ: 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 [dd (s), C^4, $^1J_{HC}$ 166.8 Hz, $^3J_{HCCC}$ 6.6 Hz], 128.85 [dd (s), C^{4a}, $^3J_{HCCC}$ 6.6 Hz, $^3J_{HCCH}$ 6.6 Hz], 126.60 [dt (s), C^5, $^1J_{HC}$ 154.8 Hz, $^3J_{HCCC}$ 5.4–6.5 Hz], 125.98 [dd (s), C^6, $^1J_{HC}$ 160.3 Hz, $^3J_{HCCC}$ 8.5 Hz], 121.15 [dd (s), C^7, $^1J_{HC}$ 161.3 Hz, $^3J_{HCCC}$ 6.9 Hz], 124.18 [dd (s), C^8, $^1J_{HC}$ 160.6 Hz, $^3J_{HCCH}$ 8.5 Hz], 125.17 [ddd (s), C^{8a}, $^3J_{HCCC}$ 7.2 Hz, $^3J_{HCCC}$ 6.9 Hz, $^3J_{HCCH}$ 9.2 Hz]. MS, *m/z*: 238.0 ($C_{10}H_7BrO_2$).



Scheme 2

agent should be assumed as well (the possible reaction schemes are given in the Online Supplementary Materials).

The structure of this compound was confirmed by ^{1}H and ^{13}C NMR spectra.‡ The carbon signals in the ^{13}C and ^{13}C-{^{1}H} NMR spectra of binaphthyl **5** do not have any additional multiplicity due to coupling with phosphorus. The weak-field region displays four groups of signals of carbon atoms bound with protons and six groups of signals of carbon atoms lacking C–H bonds. The characteristic multiplicity of the signals of C(4) (dd, $^3J_{H^5CCC}$ 4.1 Hz, $^3J_{H^{3'}CCC}$ 4.1 Hz), C(8a) (dd, $^3J_{H^5CCC}$ 6.8 Hz, $^3J_{H^7CCC}$ 6.8 Hz) and C^2 atoms (d, $^2J_{HCC}$ 2.0 Hz) shows that coupling of the two naphthalene rings occurs at the C(4) atoms. The presence of hydroxy groups follows from the intense characteristic absorption in the IR spectrum around 3313 cm^{-1}.

The reaction of quinone **4** with electron-donating tricyclohexylphosphine§ occurs similarly to give binaphthyl derivative **5**. This compound was isolated and crystals suitable for X-ray diffraction analysis¶ were obtained after recrystallization from acetone. The molecule of compound **5** forms a solvate with acetone (Figure 1). The planes of the naphthalene rings are rotated with respect to each other by an angle C(4A)C(4)C(4B)C(4C) of 76.6(4)°.

The following intramolecular hydrogen bonds of O–H···O-type are realized in a crystal: O(1)–H(11)···O(2) *d*(O–H) 0.74(5) Å,

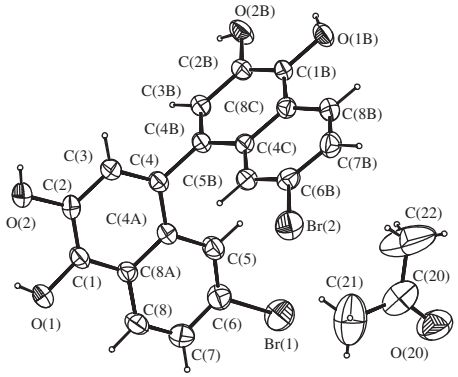


Figure 1 Molecular geometry of compound **5** in a crystal (solvate with acetone). Selected bond lengths (Å): Br(1)–C(6B) 1.904(4), Br(2)–C(6) 1.901(4), C(2)–O(2) 1.379(4), C(1)–O(1) 1.366(4), O(2B)–C(2B) 1.376(4), O(1B)–C(1B) 1.370(4), C(4)–C(4B) 1.495(5).

d(H···O) 2.38(5) Å, *d*(O···O) 2.744(5) Å, ∠ 112(4)°; O(1B)–H(1B)···O(2B) *d*(O–H) 0.79(4) Å, *d*(H···O) 2.24(4) Å, *d*(O···O) 2.703(4) Å, ∠ 118(3)°.

A lot of the intermolecular hydrogen bonds of O–H···O-type between the molecules of 1,1′,2,2′-tetrahydroxy-6,6′-dibromo-4,4′-binaphthyl and acetone are revealed in the crystal of compound **5**. As a result, infinite hydrogen bonded chains are formed along the 0*b* crystal axis. The hydrogen bond parameters are O(1B)–H(1B)···O(2B′) (1 – *x*, –*y*, –*z*) *d*(O–H) 0.79(4) Å, *d*(H···O′) 2.07(4) Å, *d*(O···O′) 2.739(4) Å, ∠ 142(3)°; O(2B)–H(2B)···O(2′) (1 – *x*, –*y*, –*z*) *d*(O–H) 0.86(5) Å, *d*(H···O′) 1.89(5) Å, *d*(O···O′) 2.743(4) Å, ∠ 169(6)°; O(1)–H(11)···O(1B″) (*x*, 1 + *y*, *z*) *d*(O–H) 0.74(5) Å, *d*(H···O″) 2.19(5) Å, *d*(O···O″) 2.858(4) Å ∠ 151(5)°; O(2)–H(10)···O(20‴) (1/2 + *x*, 1/2 + *y*, *z*) *d*(O–H) 0.77(4) Å, *d*(H···O‴) 1.95(4) Å, *d*(O···O‴) 2.707(5) Å, ∠ 168(4)°.

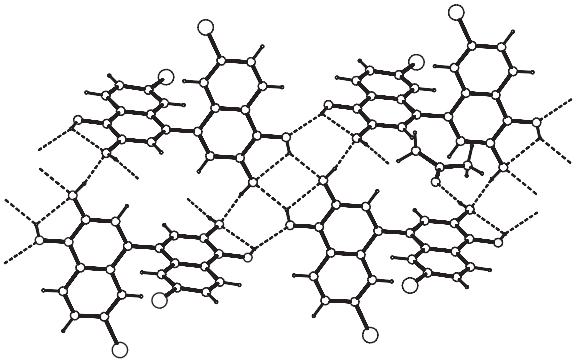


Figure 2 Hydrogen bonds in the molecule of compound **5**.

‡ *6,6′-Dibromo-1,1′,2,2′-tetrahydroxy-4,4′-binaphthyl* **5**. A suspension of tri(2-cyanoethyl)phosphine (0.83 g, 4.3 mmol) in 10 ml of dichloromethane was added dropwise to a suspension of quinone **4** (1 g, 4.3 mmol) in 5 ml of the same solvent at 35 °C with bubbling dry argon. Reaction mixture turned deep brown immediately and gray tri(2-cyanoethyl)-phosphine oxide precipitated, which after 15 min was filtered off. After 24 h, compound **5** precipitated from the filtrate was filtered off and dried in a vacuum (12 Torr) to give a white powder. Yield 0.70 g (71%), mp 122–124 °C. IR (Nujol, ν/cm^{-1}): 3313 (OH), 1624, 1592, 1500, 1330, 1297, 1246, 1156, 1068, 1013, 961, 904, 815, 736, 587, 519, 430. ^{1}H NMR (600 MHz, [^{2}H$_6$]DMSO) δ: 7.12 (s, H^3), 7.20 (d, H^5, $^4J_{HCCCH}$ 1.9 Hz), 7.48 (dd, H^7, $^3J_{HCCH}$ 9.0 Hz, $^4J_{HCCCH}$ 1.9 Hz), 8.08 (d, H^8, $^3J_{HCCH}$ 9.0 Hz), 9.67, 9.31 (2br. s, 2OH). ^{13}C NMR (100.9 MHz, [^{2}H$_6$]DMSO) δ: 137.88 [dd (s), C^1, $^3J_{HCCC}$ 15.6 Hz, $^3J_{HCCC}$ 4.2 Hz], 140.04 [d (s), C^2, $^2J_{HCC}$ 2.0 Hz], 121.64 [d (s), C^3, $^1J_{HC}$ 157.7 Hz], 127.02 [dd (s), C^4, $^3J_{H^5CCC}$ 4.1 Hz, $^3J_{H^{3'}CCC}$ 4.1 Hz], 128.61 [dd (s), C^{4a}, $^3J_{HCCC}$ 7.4 Hz, $^3J_{HCCC}$ 7.3 Hz], 126.84 [dd (s), C^5, $^1J_{HC}$ 164.4 Hz, $^3J_{HCCC}$ 5.1 Hz], 116.41 [ddd (s), C^6, $^3J_{HCCC}$ 12.4 Hz, $^2J_{HCC}$ 2.8–3.1 Hz, $^2J_{HCC}$ 2.8–3.0 Hz], 127.53 [dd (s), C^7, $^1J_{HC}$ 167.6 Hz, $^3J_{HCCC}$ 5.9 Hz], 123.90 [d (s), C^8, $^1J_{HC}$ 163.8 Hz], 124.34 [dd (s), C^{8a}, $^3J_{HCCC}$ 6.8 Hz, $^3J_{HCCC}$ 6.8 Hz]. MS, *m*/*z*: 476 ($C_{20}H_{12}Br_2O_4$).

§ *Reaction of 6-bromo-1,2-naphthoquinone with tricyclohexylphosphine*. To a solution of quinone **4** (0.93 g, 3.9 mmol) in 10 ml of dichloromethane tricyclohexylphosphine (1.10 g, 3.9 mmol) was added dropwise with intense bubbling dry argon. Reaction mixture turned black immediately and slight exothermic effect occurred. After 10 h, the reaction mixture became yellow and solution gradually produced yellow precipitate, which was filtered off and dried in a vacuum (12 Torr). Filtrate was evaporated under reduced pressure in an atmosphere of dry argon. Yellow residue obtained was treated with 10 ml of dry acetone, which gradually produced light brown precipitate, which was filtered off and recrystallized from acetone to give colourless 6,6′-dibromo-1,1′,2,2′-tetrahydroxy-4,4′-binaphthyl **5** as a solvate with acetone, mp 158–160 °C (decomp.). Yield 0.51 g (55%). All data of compound **5** (mp, mass, IR and NMR spectra) were identical to the above except for acetone signals.

¶ *Crystal data*. The X-ray diffraction data for compound **5** were collected at 293 K on a Bruker Smart Apex II CCD diffractometer using graphite monochromated MoKα (0.71073 Å) radiation. Crystals of **5** ($C_{20}H_{12}Br_2O_4{\cdot}C_3H_6O$, M_r = 534.19) are monoclinic, a = 21.824(2), b = 11.9881(9) and c = = 16.859(1) Å, β = 100.186(1)°, V = 4341.2(6) Å^3, d_{calc} = 1.635 g cm^{-3}, Z = 8, space group *C*2/*c*. Cell parameters and intensities of 4265 independent reflections, from which 2682 with $I \geq 2\sigma$ (R_{int} = 0.0502), were measured in the ω-scan mode, 1.95° ≤ θ ≤ 26.00°. Data were corrected for absorption using the SADABS program[15] [μ(MoKα) = 3.766 mm^{-1}]. The structures were solved by direct method using the SHELXS program[16] and refined by the full matrix least-squares using SHELXL97 program[17] on all F^2 data. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and refined as riding atoms except H(1B), H(2B), H(10), H(11) which were located on difference map and refined isotropically. The final residuals were R_{ob} = 0.0433, R_{wob} = 0.0801. Data collection: images were indexed, integrated, and scaled using the APEX2 data reduction package.[18] Figures was made using the program PLATON.[19]

CCDC 713876 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2009.

Thus, the reaction of 6-bromo-1,2-naphthoquinone **4** with tri(2-cyanoethyl)phosphine or tricyclohexylphosphine is a convenient synthetic route to tetrahydroxybinaphthyls **5**, and it can serve as a new facile method of aryl–aryl coupling.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2009.01.016.

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