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New Phosphorus-Containing Quinone Derivatives

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ABSTRACT: *A variety of new aromatic diols substituted with two (similar and different) phosphorus groups were synthesized via the Michael-type addition of a P—H bond containing reagents to p-benzoquinone, reoxidation and the subsequent addition of a second phosphorus unit. In all studied cases, 2,3-substituted products were obtained exclusively. The resulting hydroquinone derivatives were further investigated regarding rearrangements under basic conditions.* © 2012 Wiley Periodicals, Inc. Heteroatom Chem 00:1–12, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21028

INTRODUCTION

Addition reactions of phosphorus-containing compounds to unsaturated systems have been thoroughly investigated throughout the past decades [1–4]. The phospha-Michael reaction, especially, has been the topic of a great variety of recent studies regarding different types of substrates, different reaction conditions, and diastereoselectivity [4–11]. As such, the reaction behavior of phosphorus-containing reagents toward quinones has been investigated thoroughly due to the significance of quinone derivatives as dyes and biologically active compounds [12–14]. As a relatively new field of use, phosphorus-carrying quinones recently gained importance as flame-retardant additives, for instance, for epoxy resins [15]. P-containing hydroquinones as comonomers for inherent flame-retardant polymers are of special interest in this connection and therefore the subject of current research [16–22].

In general, most phosphorus reagents in a reaction with, e.g., *p*-benzoquinone, undergo the Michael-type addition, resulting in aromatic, *C*-phosphorylated hydroquinone derivatives. Some reagents also perform *O*-phosphorylation [12]. For phosphine- and phosphinoxide-type compounds, di- and trialkyl phosphinoxides are reported to undergo mono-*C*-addition [12], in contrast to primary phosphines (H_2P-R), which directly reduce *p*-benzoquinone to hydroquinone, yielding RPH-HPR [23]. In the case of phosphite-type reagents, mono- and di-*C*-addition takes place as well as *O*-phosphorylation, depending on the conditions [12], whereas phosphate-type compounds normally do not react with *p*-benzoquinone [13].

However, previous work predominantly focuses on monosubstituted phosphorus quinones. This paper presents a novel approach to new quinone derivatives carrying two similar or different phosphorus units.

RESULTS AND DISCUSSION

The reaction of diphenyl phosphite with *p*-benzoquinone resulted in both mono- and

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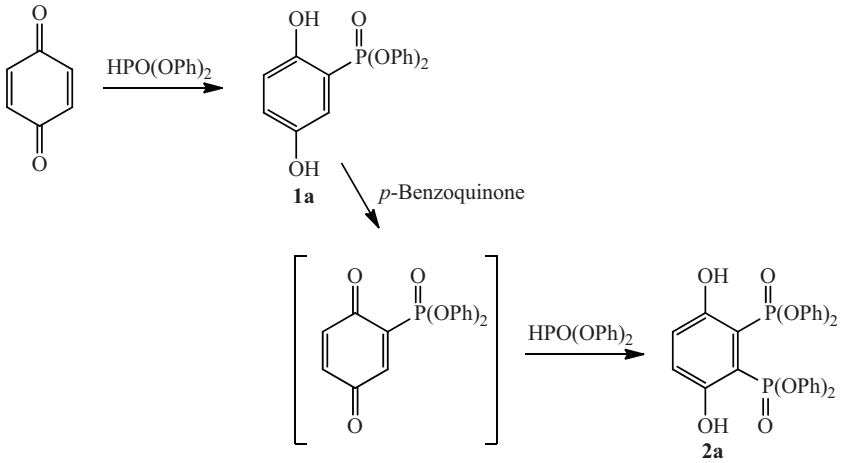


SCHEME 1 Reaction of diphenyl phosphite with *p*-benzoquinone.

disubstituted *p*-hydroquinone derivatives $(PhO)_2PO$-HQ (**1a**) and $(PhO)_2PO$-2-HQ (**2a**) that can be explained by an in situ reoxidation of the former by unreacted *p*-benzoquinone (Scheme 1). This is in agreement with the results published for dimethyl phosphite [24] and 5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan (DDPO; another phosphite-type reactant), which also yielded both products in the reaction with *p*-benzoquinone [20,25]. X-ray analysis of the disubstituted $(PhO)_2PO$-2-HQ (**2a**; Scheme 1) revealed the phosphorus groups in *ortho*-position (Fig. 1).

The reproduction of the procedure described for the reaction of *p*-benzoquinone with DDPO [20,25] also demonstrated formation of both the monoadduct DDPO-HQ (**1b**) and *ortho*-substituted diadduct DDPO-2-HQ (**2b**), as was indicated by NMR spectroscopy. In ^{13}C NMR the carbon directly bound to the phosphorus atom ($\delta = 113.3$ ppm in DMSO-d_6) appears as a doublet of doublets with the coupling constants $^1J_{C\text{-}P} = 174.6$ Hz and $^2J_{C\text{-}P'} = 9.7$ Hz. The aromatic protons of DDPO-2-HQ (**2b**) in the ^1H NMR spectrum represent a triplet at 7.06 ppm with $^4J_{H\text{-}P} = 3.75$ Hz (DMSO-d_6). In the case of the *para*-substitution, a significantly larger coupling constant $^3J_{H\text{-}P}$ (above 10 Hz) for the protons next to the phosphorus units would be expected [26,27]. Furthermore, the *ortho*-structure is confirmed by X-ray analysis (Fig. 1).

It is worth mentioning that the P—C bond formed in the reaction of diphenyl phosphite and *p*-benzoquinone is notably shorter for the monoadduct (**1a**, 1.757 Å) than in the case of the diadduct (**2a**, 1.790–1.800 Å). DDPO-2-HQ (**2b**) shows a corresponding P—C bond length of 1.796–1.798 Å. Furthermore, X-ray structures clearly indicate that in the case of $(PhO)_2POHQ$ (**1a**) and $(PhO)_2PO$-2-HQ (**2a**), all hydroxyl groups form an intramolecular hydrogen bond with the close P=O unit, whereas in DDPO-2-HQ (**2b**), no such intramolecular interaction is observed due to the bulkiness and restricted flexibility of the heterocyclohexane units (Fig. 1). Yet in the latter case, X-ray analysis revealed intermolecular hydrogen bonds with the P=O units of neighboring molecules.

For the reaction of *p*-benzoquinone with phosphinate-type reactants (RHPO-OR′) such as 6-oxido-6*H*-dibenzo[*c*, *e*][1,2]oxaphosphinine (DOPO, a widely used flame retardant by itself and building block for advanced flame retardants) [16–22,28–31], no in situ reoxidation is witnessed and the sole product DOPO-HQ is obtained with a nearly quantitative yield [16,17]. Formation of the diadduct (DOPO-2-HQ, **3**), as described in [32], could not be reproduced. A treatment following of DOPO-HQ with excess *p*-benzoquinone showed no reaction; therefore, a kinetic explanation (an addition of DOPO being much faster than a reoxidation) is unlikely.

To achieve an oxidation of DOPO-HQ, treatment with activated MnO_2 as a quick and easy lab-scale method [33] was applied successfully, yielding DOPO-BQ (**4**) as a bright orange solid (Scheme 2). By a reaction of DOPO-BQ (**4**) with DOPO, DOPO-2-HQ (**3**) was obtained in a good yield. Remarkably, **3** emerged as two diastereomers due to the chirality of the phosphorus atoms. In addition, the bulkiness of the phosphacycles in the *ortho*-position to each other prevents a rotation of the substituents. Isomer **3a** shows a twisted overlapping of the DOPO units, whereas in isomer **3b**, they are congruently staggered. In both cases, they are stabilized via π-stacking, as evident by an X-ray structure analysis

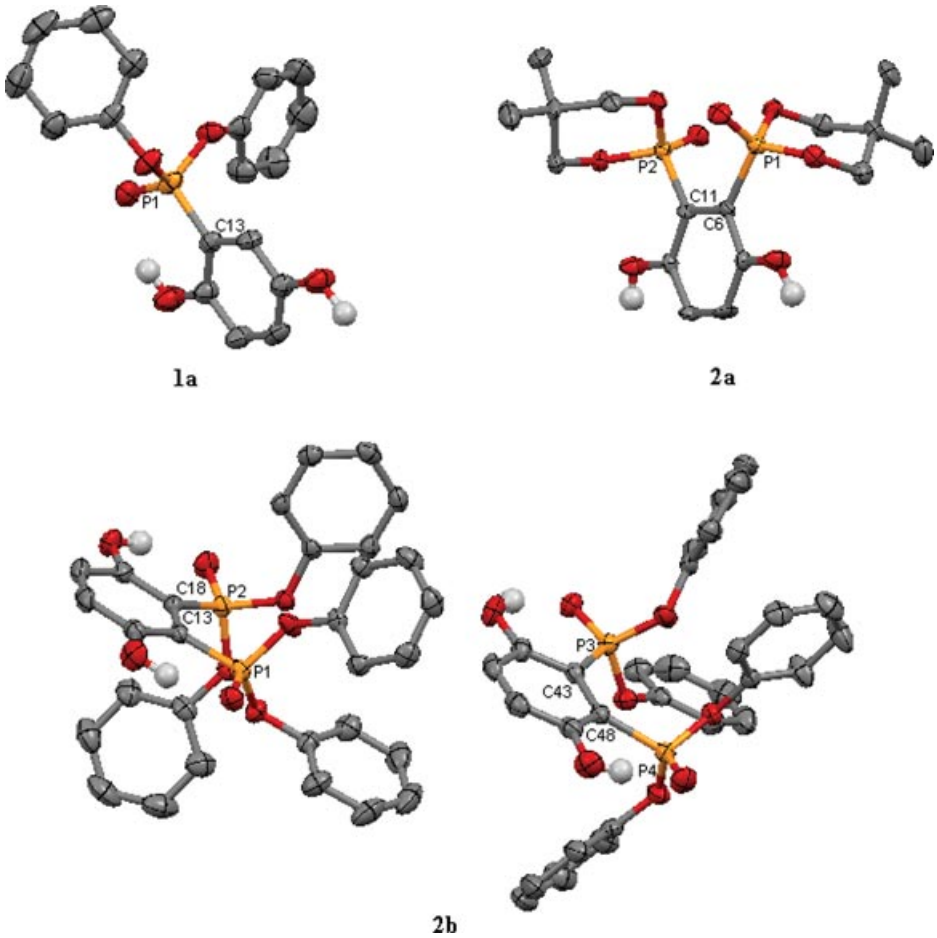
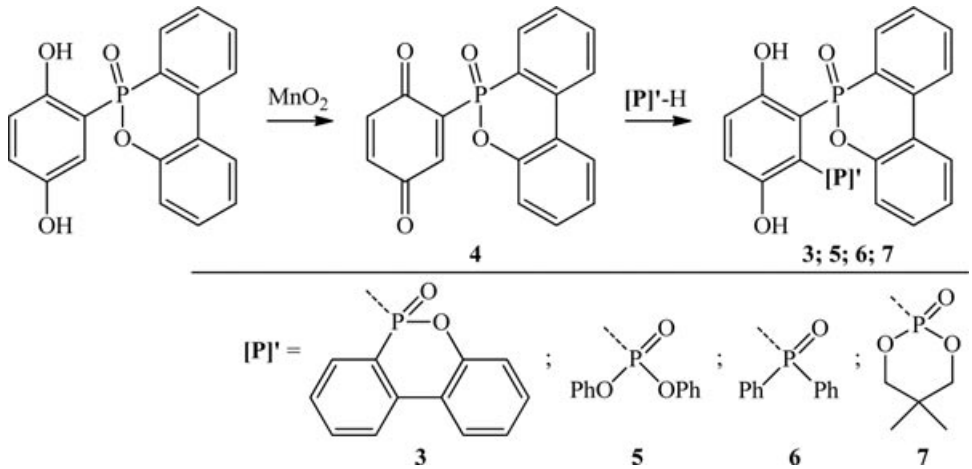
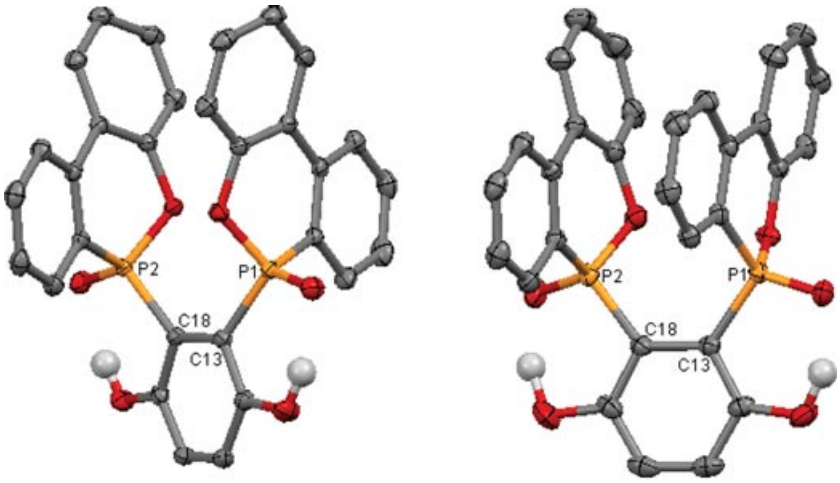


FIGURE 1 Molecular structures of $(PhO)_2PO$-HQ (**1a**), $(PhO)_2PO$-2-HQ (**2a**) (crystallizing as a pair of conformational isomers) and DDPO-2-HQ (**2b**), validated by X-ray analysis (hydrogens omitted except on heteroatoms for reasons of clarity).



SCHEME 2 Syntheses of DOPO-BQ (**4**) and disubstituted *p*-hydroquinones DOPO-2-HQ (**3**), DOPOHQ-$(PhO)_2PO$ (**5**), DOPO-HQ-DPhPO (**6**), and DOPO-HQ-DDPO (**7**).



3a 3b

FIGURE 2 Molecular structures of diastereomers of DOPO-2-HQ (**3**) validated by X-ray analysis (hydrogens omitted except on heteroatoms for reasons of clarity). In isomer a 6-6-π-stacking is present only between the two upper benzo units, whereas isomer b (emerging in higher yield) is stabilized by π-stacking of both benzo units with the opposing ones.

TABLE 1 Lengths of P—C and P—O Bonds between Quinone and Phosphorus Units

Compound	*P—C (DOPO Unit)*	*P—C (Phosphite)*
$(PhPO)_2PO$-HQ (**1a**)	–	1.757
$((PhPO)_2PO)_2$-HQ (**2a**)	–	1.790–1.794
DDPO-2-HQ (**2b**)	–	1.804–1.805
DOPO-2-HQ (**3**)	1.796–1.805	–
DOPO-BQ (**4**)	1.801	–
DOPO-HQ-$(PhO)_2PO$ (**5**)	1.802	1.795
DOPO-HQ-DPhPO (**6**)	1.806	[a]
DOPO-HQ-DDPO (**7**)	1.767–1.749[b]	1.807–1.808[b]
DDPO-2-HQ-rear (**9b**)	–	1.766–1.782

All values are given in Å (standard deviation < 0.005).
[a] P—C Phosphine oxide: 1.808.
[b] standard derivation 0.013.

(Fig. 2). However, the length of the newly formed P—C bond did not significantly differ between the isomers (ranging from 1.796 to 1.805 Å). Furthermore, intramolecular hydrogen bonds between the protons of the hydroquinone hydroxyl groups and the oxygens of the P=O units are present in both cases. The isomers obtained at a 1:1.5 ratio were successfully separated by column chromatography and show slightly different melting points (4–5°C deviation) and chemical shifts in ^{31}P NMR (1.15 ppm deviation).

In addition, a variety of disubstituted *p*-hydroquinones with different phosphorus units were synthesized by the reaction of DOPO-BQ (**4**) with DDPO, diphenyl phosphite and diphenylphosphine oxide (Scheme 2). All products **5–7** turned out to be *ortho*-substituted, according to X-ray and NMR data, as was expected. The P—C bonds of the derivatives with different phosphorus units showed comparable lengths to the corresponding homogeneous disubstituted hydroquinones (Table 1). X-ray analysis (Fig. 3) also revealed the presence of intramolecular hydrogen bonds for both H atoms of DOPO-HQ-$(PhO)_2PO$ (**5**), whereas in DOPO-HQ-DPhPO (**6**), only the hydroxyl group next to the DOPO unit formed an intramolecular hydrogen bond. The other did not due to sterical hindrances, forming rather, intermolecular hydrogen bonds like both H atoms of DOPO-HQ-DDPO (**7**).

Consideration of the distribution of local charges in the mesomeric structures provides an explanation for the formation of 2,3-substituted products from the theoretical point of view. Although unsubstituted *p*-benzoquinone does not favor any position, a negative charge can be localized not only at the carbonyl units but also at the P=O unit (Scheme 3) in the case of the phosphite-functionalized quinone. This leads to an increased positivity of the *ortho*-position and, hence, to a higher probability for nucleophilic addition. The effect is rather significant: although this should preferably, but not exclusively lead to the *ortho*-products, practically no *para*-products were detected in all cases studied.

The reaction of *p*-benzoquinone with diphenyl phosphite or DDPO led to the same products in the presence of acetic acid [20,25] as well as under neutral conditions. Nevertheless, when triethylamine was used as a catalyst, a rearrangement of the monoadduct occurred before reoxidation,

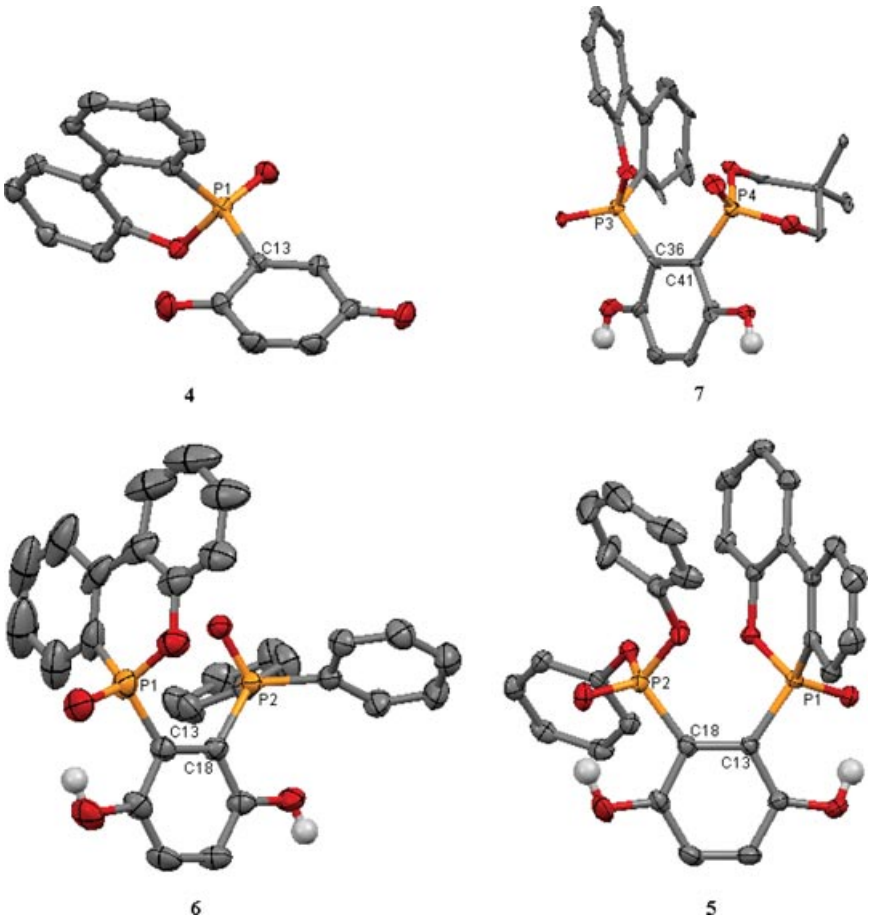
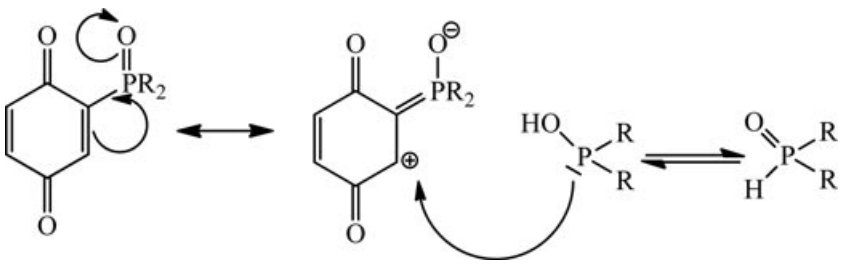


FIGURE 3 Structure of DOPO-BQ (**4**), DOPO-HQ-$(PhO)_2PO$ (**5**), DOPO-HQ-DPhPO (**6**), and DOPO-HQ-DDPO (**7**), validated by X-ray analysis (hydrogens omitted except on heteroatoms for reasons of clarity. **7** shown as one of two conformations).

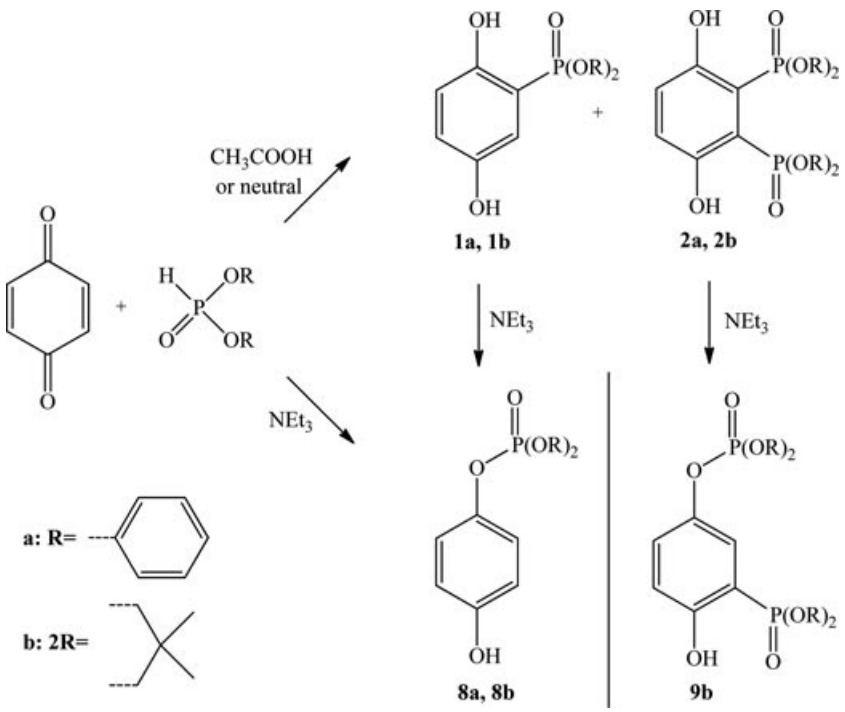


SCHEME 3 Additional mesomeric structure of P=O-functionalized *p*-benzoquinone.

effectively preventing the latter. The resulting oxygen-substituted hydroquinone is unable to undergo reoxidation for obvious reasons. Consequently, no second addition takes place, and $(PhO)_2PO$-HQ-rear (**8a**) or DDPO-HQ-rear (**8b**), respectively, emerged as the only product (Scheme 4). For the reaction of dimethyl phosphite with *p*-benzoquinone, traces of the rearranged product were reported under neutral conditions [24].

In addition, a following treatment of the first isolated monoadducts $(PhO)_2PO$-HQ (**1a**) or DDPO-HQ (**1b**) with triethylamine resulted in the same rearranged compounds **8a** and **8b**. Likewise, a refluxing of DDPO-2-HQ (**2b**) with triethylamine in acetonitrile led to precipitation of DDPO-2-HQ-rear (**9b**) after cooling, with one of two phosphorus units being relocated (Scheme 4 and Fig. 4). The newly formed P—O bonds were significantly shorter (1.561 Å for **8a**, 1.593–1.596 Å for **9b**) than the corresponding P—C bonds (Table 1).

A treatment of DOPO-2-HQ (**3**) with triethylamine resulted in DOPO-2-HQ-rear (**10**), with one



SCHEME 4 Reaction of *p*-benzoquinone with phosphite-type compounds under different conditions.

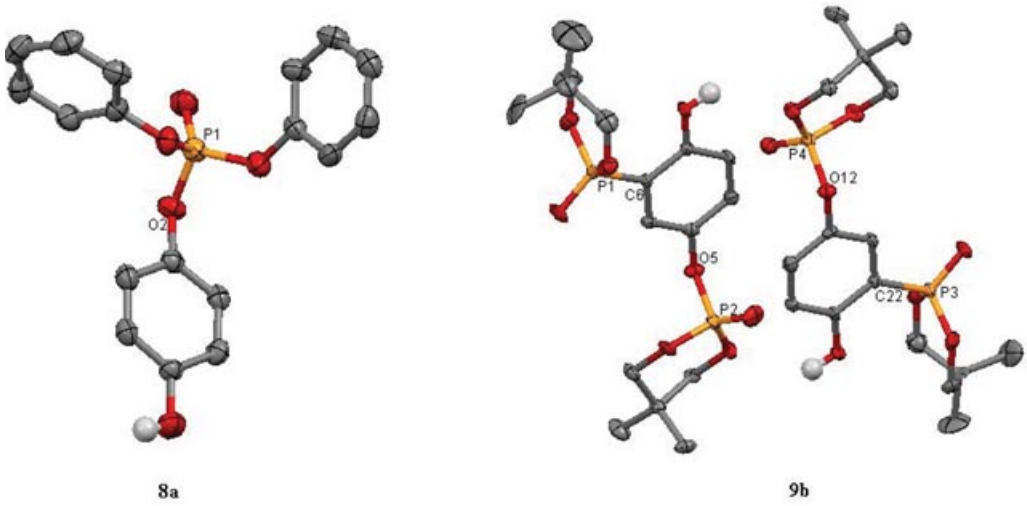


FIGURE 4 Structure of $(PhO)_2PO$-HQ-rear (**8a**) and DDPO-2-HQ-rear (**9b**), validated by X-ray analysis (hydrogens omitted except on heteroatoms for reasons of clarity).

of two DOPO units being relocated (structure similar to **9b**). A rearrangement of the second phosphorus unit did not take place. However, the corresponding compound is known and may easily be synthesized by other means, for example, a reaction of *p*-hydroquinone with 6-chloro-6H-dibenzo[c,e][1,2]oxaphosphinine (DOP-Cl) [34].

Moreover, *O*-phosphorylated *p*-hydroquinones obtained in a similar manner undergo rearrangement by lithium diisopropylamide (LDA) catalysis, resulting in 2,5-substituted derivatives, as described for diethyl phosphite [26] and diphenylphosphine oxide [35].

CONCLUSIONS

A new synthetic approach to difunctional phosphorus-containing quinones and a variety

of correspondent derivatives has been presented. The procedure turned out to lead selectively to 2,3-substituted *p*-hydroquinones. The presented method proved to be convenient and efficient for the synthesis of new aromatic diols suitable as comonomer units of significantly higher phosphorus content that will allow the preparation of polymers with increased flame retardancy or a lower load of additives for the same effect.

EXPERIMENTAL

Materials and Measurements

Unless stated otherwise, solvents and chemicals were obtained from commercial sources and used as received. DDPO was synthesized from neopentyl glycol and dimethyl phosphite as previously described [36].

NMR spectra were recorded with a Bruker (Bellerica, MA) Analytical BZH 250/52 (250 MHz) and a Varian (Palo Alto, CA) INOVA-400 (400 MHz). Chemical shifts are given as δ values with internal standard via solvent. ^{31}P NMR spectra were measured proton decoupled, ^{13}C NMR proton decoupled and phosphorus coupled and ^{1}H NMR phosphorus coupled. IR spectra were recorded with a Varian 660-IR (FT-IR). Melting points were measured with a Büchi (Flawil, Switzerland) B-545 (uncorrected). High-resolution mass spectra were obtained with a MicroMass (Beverly, MA) GCT (EI, 70 eV) and a Bruker microTOF (ESI). Elementary analysis (CHNS) was performed with an Elementar (Hanau, Germany) VarioEL.

Crystallographic Data

XRD measurements were performed using a Siemens SMART CCD 1000 diffractometer with monochromated Mo Kα irradiation collecting a full sphere of data in the θ range from 1.57 to 28.34°. Frames were collected with an irradiation time of 20 or 10 s per frame and ω scan technique with $\Delta\omega$ = 0.45°. Data were corrected to Lorentz and polarization effects, and an empirical adsorption correction with SADABS [37] was applied. The structures were solved by direct methods and refined to an optimum *R*1 value with SHELX-97 [38]. Visualization for evaluation was performed with XPMA [39], and figures were created with Mercury [40].

CCDC numbers 856366–856376 contain 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.

Synthesis

Diphenyl (2,5-dihydroxyphenyl)phosphonate ($(PhO)_2$PO-HQ, **1a***).* Diphenylphosphite (50.0 g, 215 mmol) was dissolved in 100 mL of toluene in a three-necked flask equipped with a condenser and an argon gas inlet. *p*-Benzoquinone (30.0 g, 277 mmol) was added in portions to the reaction mixture over a period of 10 min at room temperature. The reaction mixture was heated using an oil bath to 65°C, stirred at this temperature over a period of 48 h and cooled to room temperature. The solvent was removed at reduced pressure. A solution of the residue in dichlormethane was filtered through a small pad of silica gel, and the filtrate was concentrated by the removal of solvent at reduced pressure. After recrystallization from toluene followed by drying at reduced pressure at 80 °C for 12 h, $(PhO)_2$PO-HQ was obtained as beige crystals (8.9 g, 26 mmol, 12%): mp 149-150°C; ^{31}P NMR (101 MHz, DMSO-d_6) δ 13.0; ^{13}C NMR (63 MHz, DMSO-d_6) δ 152.7 (d, J = 2.0 Hz, 1C), 150.1 (d, J = 6.8 Hz, 1C), 149.4 (d, J = 19.2 Hz, 1C), 129.8 (s, 4C), 125.0 (s, 2C), 122.9 (d, J = 2.5 Hz, 1C), 120.4 (d, J = 4.5 Hz, 4C), 119.6 (d, J = 9.4 Hz, 1C), 117.6 (d, J = 12.9 Hz, 1C), 111.2 (d, J = 186.9 Hz, 1C—P); ^{1}H NMR (250 MHz, DMSO-d_6) δ 9.93 (s, 1H, OH), 9.16 (s, 1H, OH), 7.47–7.29 (m, 4H), 7.29–7.07 (m, 7H), 7.00–6.80 (m, 2H); IR (KBr) ν 3319 (s, O—H), 3065 (w, C_{aryl}—H), 1589 (m, C=C), 1490 (vs, P—C_{aryl}), 1276 (m, C—O), 1236, 1207, 1182 (s, P=O), 1157, 1078, 955, and 943 (vs, P—O), 774 and 747 (s, C—H), 691, 603, 511; HRMS (EI) calcd for $[^{12}C_{18}H_{15}O_5P]^+$ 342.0657, found 342.0609. Anal calcd for $C_{11}H_{15}O_5P$: C 63.16, H 4.42; found: C 63.05, H 4.39.

Tetraphenyl(3, 6 - dihydroxy - 1, 2 - phenylene)bis-(phosphonate) ($(PhO)_2$PO-2-HQ, **2a***).* Diphenyl phosphite (250.0 g, 1068 mmol) and *p*-benzoquinone (150.0 g, 1389 mmol) in 300 mL of toluene were stirred in a round-bottomed flask equipped with a condenser and an argon gas inlet at room temperature over a period of 7 days. The solvent was removed at reduced pressure. A solution of the residue in dichlormethane was filtered through a small pad of silica gel, and the filtrate was concentrated by the removal of solvent at reduced pressure. After recrystallization from acetonitrile, $(PhO)_2$PO-2-HQ was obtained as white crystals (153.3 g, 267 mmol, 25%): mp 93–94°C; ^{31}P NMR (101 MHz, $CDCl_3$) δ 15.0; ^{13}C NMR (63 MHz, $CDCl_3$) δ 158.8 (t, J = 11.3 Hz, 2C), 149.8 (t, J = 3.9 Hz, 4C), 129.7 (s, 8C), 128.7 (t, J = 6.7 Hz, 2C), 125.5 (s, 4C), 120.2 (t, J = 2.4 Hz, 8C), 104.0 (dd, J = 189.4 Hz, J = 7.4 Hz, 2C—P); ^{1}H NMR (250 MHz, $CDCl_3$)

δ11.50 (s, 2H, 2OH), 7.29–7.12 (m, 22H); IR (KBr) ν 3435 (m, O—H), 3015, 2980, and 2928 (m, C_{aryl}—H), 1587 (s, C=C), 1489 and 1437 (vs, P—C_{aryl}), 1263 (s, C—O), 1189 (vs, P=O), 1154, 1135, 1026, 1010, 966, 959, and 941 (vs, P—O), 768 and 749 (s, C—H), 688, 635; HRMS (EI) calcd for $[^{12}C_{30}H_{24}O_8P_2]^+$ 574.0946, found 574.0938. Anal calcd for $C_{30}H_{24}O_8P_2$: C 62.72, H 4.21; found: C 62.71, H 4.21.

*2 - (2, 5 - Dihydroxyphenyl) - 5, 5 - dimethyl - 1, 3, 2 - dioxaphosphinane 2-oxide (DDPO-HQ,***1b***) and 2,2′-(3,6-dihydroxy-1,2-phenylene)bis(5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide) (DDPO-2-HQ,* **2b***).* DDPO (25.02 g, 0.167 mol) was dissolved in 120 mL of dry toluene in a three-necked flask equipped with a condenser and an argon inlet. *p*-Benzoquinone (18.02 g, 0.167 mol) was added in portions during a 2-h period at 75°C. The mixture was refluxed for an additional 2 h and allowed to cool down. The liquid phase was decanted and was kept for isolation of DDPO-1-HQ. The residue was refluxed in 150 mL of 2-ethoxyethanol for 30 min and allowed to cool down to room temperature. A white solid (DDPO-2-HQ, **2b**) was collected by filtration at reduced pressure, washed with ethyl acetate, and air-dried. Yield: 10.23 g (30.15%). mp: 260°C decomp. ^{31}P NMR (101 MHz, DMSO-d_6): 9.69 (s). ^{13}C NMR (63 MHz, DMSO-d_6): 154.4 (t, J = 9.7 Hz, 2C); 123.6 (t, J = 3.5 Hz, 2C); 113.3 (dd, J = 174.6 Hz, J = 9.7 Hz, 2C); 76.9 (s, 4C); 31.6 (t, J = 2.6 Hz, 2C); 21.9 (s, 2C); 20.0 (s, 2C). ^{1}H NMR (250 MHz, DMSO-d_6): 9.87 (s, 2H, arom OH); 7.06 (t, J = 3.75 Hz, 2H, arom.); 3.70 (dd, J_1 = 22.8 Hz, J_2 = 11.25 Hz, 4H, —CH_2— axial), 3.45 (d, J = 11.0 Hz, 4H, —CH_2— equatorial), 1.16 (s, 6H, —CH_3 axial); 0.60 (s, 6H, —CH_3 equatorial). IR (KBr) ν 1477 (m, P—C_{aryl}); 1335 (m); 1244 (s, P=O); 1057 (s, P—O alkyl); 1012 (m); 798 (m); 571 (m); 508 (m). HRMS (ESI) calcd for $[^{12}C_{16}H_{24}O_8P_2]^+$ 406.0946, found 406.0996. Anal calcd for $C_{16}H_{24}O_8P_2$: C 47.30, H 5.95; found: C 47.06, H 5.96.

The filtered 2-ethoxyethanol was completely evaporated, and the residue was refluxed in chloroform for 30 min. After cooling down to room temperature, a white solid (DDPO-1-HQ,**1a**) was collected by filtration at reduced pressure, washed with chloroform, and air-dried. Yield: 12.75 g (35.48%). mp: 185–189°C. ^{31}P NMR (101 MHz, DMSO-d_6): 12.66 (s). ^{13}C NMR (63 MHz, DMSO-d_6): 153.2 (s, 1C); 150.2 (d, J = 11.2 Hz, 1C); 122.3 (s, 1C); 118.9 (d,J = 5.0 Hz, 1C, C—H arom); 118.3 (d, J = 7.7 Hz, 1C); 112.9 (d, J = 113.9 Hz, 1C); 76.6 (s, 1C); 76.5 (s, 1C); 32.7 (d, J = 4.1 Hz, 1C); 22.0 (s, 1C); 21.0 (s, 1C). ^{1}H NMR (250 MHz, DMSO-d_6): 9.63 (s, 1H, arom OH); 9.14 (s, 1H, arom OH); 6.92 (dd,J_1 = 15.75 Hz, J_2 = 2.25 Hz, 1H, arom); 6.85 (dd, J_1 = 12.00 Hz, J_2 = 2.50 Hz, 1H, arom); 6.76 (t, J = 8.00 Hz, 1H, arom); 4.04 (t, J = 10.25 Hz, 2H, —CH_2—); 3.97 (d, J = 3.50 Hz, 2H, —CH_2—); 1.12 (s, 3H, —CH_3); 0.90 (s, 3H, —CH_3). IR (KBr) ν 1453 (s, P—C_{aryl}); 1387 (w); 1225 (vs, P=O);1083 (m); 1059 (s, P—O alkyl); 1008 (m); 833 (m); 778 (m); 531 (w). HRMS (ESI) calcd for $[^{12}C_{11}H_{15}O_5P + H]^+$ 259.0735, found 259.0722. Anal calcd for $C_{11}H_{15}O_5P$: C 51.17, H 5.86; found: C 50.75, H 5.75.

*2-(6-Oxido-6H-dibenzo[c,e][1,2]oxaphosphinine-6-yl)-cyclohexa-2,5-diene-1,4-dione(DOPO-BQ,***4***).* 2-(6-Oxido-6*H*-dibenzo[c,e][1,2]oxaphosphinin-6-yl)-benzene-1,4-diol (DOPO-HQ, 9.73 g, 30 mmol) and manganese dioxide (ca. 25 g) were suspended in 200 mL of acetone and vigorously stirred for 1 h at room temperature. The solid phase was collected by filtration at reduced pressure and thoroughly washed with acetone. To the combined filtrates, 10 g of charcoal was added and stirred for 30 min. After filtration, the liquid phase was diluted with diethyl ether to precipitate the product. The bright orange solid was collected by filtration at reduced pressure, and air-dried. Yield: 6.65 g (68.8%) mp: 195°C decomp. ^{31}P NMR (101 MHz, DMSO-d_6): 16.77 (s). ^{13}C NMR (63 MHz, DMSO-d_6): 186.3 (d, J = 15.9 Hz, 1C); 185.8 (d,J = 8.5 Hz, 1C), 149.0 (d,J = 13.7 Hz, 1C); 144.6 (d, J = 3.3 Hz, 1C); 137.7 (s, 1C); 137.3 (d, J = 7.4 Hz, 1C); 135.9 (d, J = 1.8 Hz, 1C); 135.4 (d, J = 6.2 Hz, 1C); 134.5 (s, 1C); 131.5 (d,J = 13.8 Hz, 1C); 129.1 (d, J = 14.5 Hz, 1C); 126.0 (s, 1C); 125.3 (s, 1C); 124.4 (d, J = 10.1 Hz, 1C), 124.3 (d, J = 168.4 Hz, 1C); 123.1 (d,J = 132.1 Hz, 1C); 121.3 (d, J = 11.5 Hz, 1C); 120.1 (d,J = 6.6 Hz, 1C). ^{1}H NMR (250 MHz, DMSO-d_6): 8.27 (m, 2H, arom.); 8.95–7.78 (m, 2H, arom.); 7.58 (m, 1H, arom.); 7.47 (m, 1H, arom.); 7.32 (m, 2H arom. + 1H quinone); 6.87 (d, J = 40 Hz, 2H, quinone). IR (KBr) ν 3052 (w, C—H aryl); 1664 (s, C=O); 1539 (w, C=C); 1749 (m, P—C_{aryl}); 1325 (m); 1280 (w); 1232 (s, P=O); 1122 (m); 1100 (m); 926 (s, P—O—C_{aryl}); 826 (m); 753 (C—H arom bend.). HRMS (ESI) calcd for $[^{12}C_{18}H_{11}O_4P]^+$ 322.0395, found 322.0466. Anal calcd for $C_{18}H_{11}O_4P$: C 67.09, H 3.44; found C 66.65, H 3.51.

6, 6′ - (3, 6 - Dihydroxy - 1, 2 - phenylene)bis(6H - dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO-2-HQ, **3***).* DOPO-BQ (966 mg, 3 mmol) and DOPO (649 mg, 3 mmol) were fed into a flame-dried flask equipped with a condenser and an argon inlet and refluxed in 25 mL of dry toluene for 3 h until the orange color of the mixture completely faded. The product

was collected by filtration at reduced pressure, washed with toluene and dried at reduced pressure and 100°C for 2 days. Yield: 1380 mg (85.7%). White solid. mp: 240–242°C. ^{31}P NMR (101 MHz, $CDCl_3$): 34.66 (s, isomer **3a**); 33.51 (s, isomer **3b**) in a ratio 1:1.5. ^{1}H NMR (250 MHz, $CDCl_3$): 12.26 (s, 2H, aryl-OH); 7.85–6.75 (m, 16H, arom); 6.67 (s, 1.20 H, C—H quinone isomer **3b**); 5.93 (s, 0.80 H, C—H quinone isomer **3a**). IR (KBr) ν 3065 (w, C—H aryl); 1582 (w, C=C); 1475 (m, P—C_{aryl}); 1446 (s, P—C_{aryl}); 1271 (m, P=O); 1190 (s, P—O aryl); 947 (s, P—O—C_{aryl}); 751 (s, C—H arom bend.); 634 (m). HRMS (ESI) calcd for $[^{12}C_{30}H_{20}O_6P_2]^+$ 538.0735, found 538.0787.

The isomers were separated by column chromatography on silica gel using dichloromethane as an eluent (TLC: isomer **3a**: $R_f = 0.36$; isomer **3b**: $R_f = 0.29$).

Isomer **3a**: Colorless crystals after recrystallization from acetonitrile. mp: 277–279°C ^{31}P-NMR (101 MHz, $CDCl_3$): 34.66 (s). ^{13}C NMR (63 MHz, $CDCl_3$): 161.6 (t, $J = 10.0$ Hz, 2C); 146.5 (t, $J = 4.2$ Hz, 2C); 133.65 (d, $J = 2.6$ Hz, 2C); 132.5 (s, 2C); 129.7 (t, $J = 5.2$ Hz, 2C); 129.3 (s, 2C); 129.2 (t, $J = 7.0$ Hz, 2C); 128.6 (t,$J = 5.1$ Hz, 2C); 126.7 (d, $J = 137.6$ Hz, 2C); 124.8 (s, 2C); 124.0 (t, $J = 5.0$ Hz, 2C); 124.0 (s, 2C); 121.6 (t, $J = 6.4$ Hz, 2C); 120.5 (t, $J = 3.1$ Hz, 2C); 102.6 (dd,$J_1 = 142.5$ Hz,$J_2 = 9.3$ Hz, 2C). ^{1}H NMR (250 MHz, $CDCl_3$): 12.23 (s, 2H, aryl-OH); 7.73 (m, 4H, arom.); 7.52 (m, 3H, arom.); 7.45 (m, 5H, arom.); 6.94 (m, 4H, arom.); 5.93 (d, $J = 8.0$ Hz, 2H, C—H quinone). IR (KBr) ν 3062 (w, C—H aryl); 1583 (w, C=C); 1477 (m, P—C_{aryl}), 1445 (s, P—C_{aryl}); 1269 (m, P=O); 1190 (s, P—O aryl); 942 (s, P—O—C_{aryl}); 748 (s, C—H arom. bend.); 636 (m). Anal calcd for $C_{30}H_{20}O_6P_2$: C 66.92, H 3.74; found: C 66.77, H 3.72.

Isomer **3b**: Colorless crystals after recrystallization from acetonitrile. mp: 272–275°C ^{31}P NMR (101 MHz, $CDCl_3$): 33.51 (s). ^{13}C NMR (63 MHz, $CDCl_3$): 161.7 (t, $J = 9.7$ Hz, 2C); 147.9 (t, $J = 4.2$ Hz, 2C); 133.8 (d, $J = 2.5$ Hz, 2C); 132.3 (s, 2C); 130.2 (s, 2C); 129.6 (t, $J = 5.2$ Hz); 128.9 (t, $J = 6.9$ Hz, 2C); 127.8 (t, $J = 7.8$ Hz, 2C); 124.5 (s, 2C); 124.3 (s, 2C); 123.7 (d, $J = 135.0$ Hz, 2C); 123.2 (t, $J = 5.1$ Hz, 2C); 121.3 (t, $J = 6.1$ Hz; 2C); 120.8 (t,$J = 3.2$ Hz; 2C); 103.3 (dd, $J_1 = 142.5$ Hz, $J_2 = 9.1$ Hz, 2C). ^{1}H NMR (250 MHz, $CDCl_3$): 12.25 (s, 2H, aryl-OH); 7.48 (m, 2H, arom.); 7.42, 2H, arom.); 7.32 (m, 4H, arom.); 7.12 (m, 4H, arom.); 6.90 (m, 4H, arom.); 6.64 (d, $J = 7.5$ Hz, 2H, C—H quinone). IR (KBr) ν 3062 (w, C—H aryl); 1582 (w, C=C); 1475 (m, P—C_{aryl}); 1444 (s, P—C_{aryl}); 1271 (s, P=O); 1190 (s, P—O aryl); 948 (s, P—O—C_{aryl}); 751 (s, C—H arom bend.); 633 (m). Anal calcd for $C_{30}H_{20}O_6P_2$: C 66.92, H 3.74; found: C 67.04, H 3.78.

Diphenyl (3,6-dihydroxy-2-(6-oxido-6H-dibenzo[c, e][1, 2]oxaphosphinin - 6 - yl)phenyl)phosphonate (DOPO-HQ-(PhO)$_2$PO, **5***).* DOPO-BQ (966 mg, 3 mmol) and diphenyl phosphite (703 mg, 3 mmol, 574 μl) were fed into a flame-dried flask equipped with a condenser and an argon inlet and refluxed in 25 mL of dry toluene for 3 h. The hot solution was quickly withdrawn, allowed to cool down to room temperature, and left overnight. The product precipitated as colorless crystals, was collected by filtration at reduced pressure, and air-dried. Yield: 834 mg (50.0%). mp: 181°C. ^{31}P NMR (101 MHz, DMSO-d_6): 32.45 (s, P DOPO); 10.25 (s, P phosphite, isomer a); 10.14 (s, P phosphite, isomer b). ^{13}C NMR (101 MHz, DMSO-d_6): 159.5 (1C); 159.1 (d, $J = 4.9$ Hz, 1C); 156.8 (d, $J = 14.2$ Hz, 1C); 150.3 (dd, $J_1 = 18.1$ Hz, $J_2 = 6.2$ Hz, 2C); 134.9 (d, $J = 4.4$ Hz, 1C), 132.9 (s, 1C); 130.9 (s, 1C); 130.2 (d, $J = 2.6$ Hz, 4C); 128.8 (d, $J = 14.1$ Hz, 1C); 127.8 (d, $J = 12.4$ Hz, 1C); 127.5 (d, $J = 13.1$ Hz, 1C); 125.8 (s, 1C); 125.7 (d, $J = 135$ Hz, 1C); 125,6 (s, 2C); 124.8 (s, 1C); 123.9 (d, $J = 9.8$ Hz, 2C); 121.8 (d, $J = 12.5$ Hz, 1C); 120.9 (s, 4C); 120.5 (d, $J = 6.7$ Hz, 1C); 110.4 (dd, $J_1 = 187.0$ Hz,$J_2 = 9.2$ Hz, 2C), ^{1}H NMR (250 MHz, DMSO-d_6): 12.04 (s, 1H, aryl-OH); 10.88 (s, 1H, aryl-OH); 8.22 (t, $J = 7.5$ Hz, 2H, arom); 7.66 (t, $J = 6.3$ Hz, 1H, arom); 7.50–7.05 (13H, arom); 6.98 (d, $J = 8.0$ Hz, 2H, arom); 6.78 (d,$J = 7.8$ Hz, 2H, arom). IR (KBr) ν 3052 (w, C—H aryl); 1590 (w, C=C); 1490 (m, P—C_{aryl}); 1447 (s, P—C_{aryl}); 1271 (m, P=O DOPO); 1201 (s, P—O aryl); 1180 (s, P=O (PhO)$_2$PO); 965 (s, P—O—C_{aryl}); 953(s, P—O—C_{aryl}); 761 (s, C—H arom. bend.); 633 (m). HRMS (ESI) calcd for $[^{12}C_{30}H_{22}O_7P_2]^+$ 556.0841, found 556.0896. Anal calcd for $C_{30}H_{22}O_7P_2$: C 64.75, H 3.99; found: C 64.75, H 4.09.

*6-(2-(Diphenylphosphoryl)-3,6-dihydroxyphenyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO-HQ-DPhPO,***6***).* DOPO-BQ (1.61 g, 5 mmol) and diphenylphosphine oxide (1.01 g, 5 mmol) were processed in the manner described above for DOPO-2-HQ to obtain a white solid, yield 1.72 g (65.8%). mp: 228–230°C ^{31}P NMR (101 MHz, $CDCl_3$): 47.52 (s); 32.17 (s). ^{13}C NMR (101 MHz, $CDCl_3$): 162.6 (d, $J = 13.8$ Hz, 2C); 145.8 (d,$J = 6.3$ Hz, 1C); 133.1 (d, $J = 3.7$ Hz, 1C); 132.9 (d, $J = 7.5$ Hz, 4C); 132.3 (s, 2C, Ph), 131.7 (d, $J = 113.6$ Hz, 2C); 131.1 (s, 1C); 130.2 (s, 1C); 129.9 (d, $J = 10.8$ Hz, 1C); 128.4–128.1 (m, 5C); 127.5 (d, $J = 12.8$ Hz, 1C); 127.1 (d, $J = 12.8$ Hz); 125.4 (d, $J = 134.3$ Hz, 1C); 125.1 (s, 1C); 124.3 (s, 1C); 124.1 (d, $J = 9.6$, 1C); 122.5 (d, $J = 12.1$ Hz, 1C); 120.2 (d, $J = 5.8$ Hz, 1C); 110.2 (d, $J = 322.6$ Hz, 2C). ^{1}H NMR (250 MHz, $CDCl_3$): 13.02 (s, 1H, OH); 11.18 (s, 1H, OH); 7.92 (dd, $J_1 = 3.1$

Hz, J_2 = 1.8 Hz, 2H arom.); 7.72 (d, J = 1.8 Hz, 1H, arom.); 7.63 (m, 3H, arom.); 7.47 (m, 2H, arom.); 7.34 (m, 3H, arom.); 7.27 (s, 1H arom.); 7.14 (t, J = 0.9 Hz, 2C, arom.); 6.92 (m, 3H, arom.); 6.50 (s, 2H, arom.); 5.86 (s, 1H, arom.). IR (KBr) ν 3052 (w, C—H aryl); 1463 (s, P—C_{aryl}); 1354 (m); 1277 (m, P=O of DOPO unit); 1205 (s, P—O aryl); 1118 (s, P=O of DPhPO unit); 948 (s, P—O—C_{aryl}); 750 (s, C—H arom. bend.); 627 (m). HRMS (ESI) calcd for $[^{12}C_{30}H_{22}O_5P_2]^+$ 524.0943, found 524.0989. Anal calcd for $C_{30}H_{22}O_5P_2$: C 68.71, H 4.23; found: 68.59, H 4.27.

6-(2-(5,5-Dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)-3,6-dihydroxyphenyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO-HQ-DDPO, **7***).* DOPO-BQ (1.61 g, 5 mmol) and DDPO (826 mg, 5.5 mmol) were processed in the manner described above for DOPO-2-HQ to obtain a white solid, yield 1.30 g (55.1%). mp: 133–134°C. ^{31}P NMR (101 MHz, $CDCl_3$): 33.36 (s, P DOPO, isomer a); 33.27 (s, P DOPO, isomer b); 15.11 (s, P DDPO). ^{13}C NMR (101 MHz, $CDCl_3$): 161.1 (s, 1C); 154.7 (d, J = 23.9 Hz, 1C); 149.0 (d, J = 8.0 Hz, 1C); 134.8 (s, 1C); 132.8 (s, 1C); 130.4 (s, 1C); 129.7 (d, J = 13.3 Hz, 1C); 128.1 (d, J = 14.0 Hz, 1C); 127.6 (d, J = 12.1 Hz, 1C); 125.8 (d, J = 153.2 Hz, 1C); 124.7 (s, 1C); 124. 6 (1C); 123.0 (s, 1C); 122.9 (s, 1C); 121.5 (d, J = 12.1 Hz, 1C); 120.8 (d, J = 6.1 Hz, 1C); 114.0 (d, J = 193 Hz, 2C); 75.6 (s, 1C); 75.2 (s, 1C); 32.4 (s, 1C); 21.8 (s, 1C); 21.3 (s, 1C). ^{1}H NMR (250 MHz, $CDCl_3$): 12.13 (s, 1H, OH); 8.61 (s, 1H, OH); 8.09 (t, J = 7.0 Hz, 2H, C—H arom.); 7.68 (t, J = 6.5 Hz, 1H, C—H arom.); 7.57 (d, J = 15.5 Hz, 1C, C—H arom.); 7.43 (m, 2H, C—H arom.); 7.27 (t, J = 7.5 Hz, 2H, C—H arom.); 7.18 (d, J = 6.8 Hz, 2H, C—H quinone); 3.81 (d, J = 39.0 Hz, 2H, —CH_2—); 3.40 (d,J = 38.8 Hz, 2H, —CH_2—); 0.87 (s, 3H, —CH_3); 0.78 (s, 3H, —CH_3). IR (KBr) ν 3064 (w, C—H aryl); 1559 (w, C=C); 1465 (s, P—C_{aryl}); 1359 (m); 1276 (vs, P=O DOPO); 1223 (vs, P=O DDPO); 1195 (vs, P—O aryl); 1071 (vs, P—O alkyl); 943 (P—O—C_{aryl}); 747 (s, C—H arom. bend.); 627 (s). HRMS (ESI) calcd for $[^{12}C_{23}H_{22}O_7P_2]^+$ 472.0841, found 472.0846. Anal calcd for $C_{23}H_{22}O_7P_2$: C 58.48, H 4.69; found: C 58.41, H 4.63.

4-Hydroxyphenyl diphenyl phosphate ($(PhO)_2$PO-HQ-rear, **8a***).* A three-necked flask with a condenser, a thermometer, and an argon gas inlet was flooded with argon and charged with diphenylphosphite (10.0 g, 43 mmol), *p*-benzoquinone (6.0 g, 56 mmol), and 30 mL of toluene. The reaction mixture was cooled with an ice bath to 5°C and triethylamine (2.5 g, 11 mmol) was added. The reaction mixture was stirred at room temperature overnight and concentrated at reduced pressure. A solution of the residue in dichloromethane was filtered through a small pad of silica gel, and the filtrate was concentrated by complete removal of the solvent at reduced pressure. After recrystallization from cyclohexane, $(PhO)_2$PO-HQ-rear was obtained as beige crystals (5.8 g, 17 mmol, 39%): mp 96–97°C; ^{31}P NMR (101 MHz, $CDCl_3$) δ −16.2; ^{13}C NMR (63 MHz, $CDCl_3$) δ 154.3 (s, 1C), 150.2 (d, J = 7.6 Hz, 1C), 142.9 (d, J = 7.6 Hz, 1C), 129.6 (s, 4C), 125.7 (s, 2C), 120.8 (d, J = 4.5 Hz, 2C), 120.0 (d, J = 4.9 Hz, 4C), 116.4 (s, 3C); ^{1}H NMR (250 MHz, CDCl3) 7.67 (s, 1H, OH), 7.42–7.18 (m, 10H, 2Ph), 6.95 (d, J = 8.1 Hz, 2H), 6.62 (d, J = 8.8 Hz, 2H); IR (KBr) ν 3247 (s, O—H), 3057 and 3038 (w, C_{aryl}—H), 1601 and 1587 (m, C=C), 1507, 1488, 1456, 1262 (s, C—O), 1215, 1185 and 1167 (s-vs, P=O), 1152, 1026, 1011, 989 and 972 (vs, P—O), 939, 837, 769, and 757 (s, C—H), 688, 579, 546, 521, 504; HRMS (EI) calcd for $[^{12}C_{18}H_{15}O_5P]^+$ 342.0657, found 342.0605. Anal calcd for $C_{18}H_{15}O_5P$: C 63.16, H 4.42; found: C 63.26, H 4.42.

2-(3-(5,5-Dimethyl-2-oxido-1,3,2-dioxaphosphinane-2-yl)-4-hydroxyphenoxy)-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (DDPO-2-HQ-rear, **9b***).* DDPO-2-HQ (0.50 g, 1.23 mmol) and 3 mL of triethylamine in 20 mL of acetonitrile were refluxed in a round-bottomed flask equipped with a condenser over a period of 3 days. The reaction mixture was cooled with an ice bath. The formed precipitate was collected by filtration at reduced pressure, washed with acetonitrile, and dried at air to give the required product DDPO-2-HQ-rear as an off beige solid (0.35 g, 0.85 mmol, 69%). mp: 218–219°C; ^{31}P NMR (101 MHz, $CDCl_3$) δ 18.4 (s), −12.9 (s); ^{13}C NMR (63 MHz, $CDCl_3$) δ159.3 (d, J = 7.0 Hz, 1C), 142.5 (dd, J = 19.5 Hz, J = 6.7 Hz, 1C), 127.3 (dd, J = 2.6 Hz, J = 5.4 Hz, 1C), 121.6 (dd, J = 7.1 Hz, J = 4.7 Hz, 1C), 119.3 (d, J = 14.4 Hz, 1C), 108.3 (d, J = 194.1 Hz, 1C—P), 78.4 (d, J = 7.0 Hz, 2C), 75.7 (d, J = 6.2 Hz, 2C), 32.6 (d, J = 6.3 Hz, 1C), 32.2 (d, J = 6.0 Hz, 1C), 22.0 (s, 1C), 21.6 (s, 1C), 21.4 (s, 1C), 20.2 (s, 1C); ^{1}H NMR (250 MHz, $CDCl_3$) δ9.98 (s, 1H, OH), 7.43 (d, J = 16.0 Hz, 1H), 7.30 (dd, J = 2.2 Hz, J = 9.0 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 4.41 (dd, J = 4.8 Hz, J = 10.9 Hz, 2H), 4.21 (d, J = 10.3 Hz, 2H), 4.03 (d, J = 11.3 Hz, 2H), 3.95 (d, J = 10.7 Hz, 2H), 1.34 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 0.90 (s, 3H, CH_3); IR (KBr) ν 3431 (m, O-H), 3055 (m, C_{aryl}—H), 2972 (m, C_{alkyl}—H), 1605 (w, C=C), 1497 and 1473 (m, P—C_{aryl}), 1418 (s), 1375, 1295 (vs, C—O), 1216 and 1194 (s-vs, P=O), 1088, 1062 (vs, P—O), 1021, 993, and 954 (s, P—O—C_{aryl}), 880, 853, 836, 567, 490; HRMS (EI) calcd for $[^{12}C_{16}H_{24}O_8P_2]^+$ 406.0946, found 406.1052. Anal.

calcd for $C_{16}H_{24}O_8P_2$: C 47.30, H 5.95; found: C 47.28, H 5.85.

6-(4-Hydroxy-3-(6-oxido-6H-dibenzo[c,e][1,2]-oxaphosphinine-6-yl)phenoxy)-6H-dibenzo[c,e][1,2]-oxaphosphinine 6-oxide (DOPO-2-HQ-rear, **10***).* DOPO-2-HQ (0.20 g, 0.37 mmol) and 3 mL of triethylamine in 20 mL of toluene were refluxed in a round-bottomed flask equipped with a condenser over a period of 5 days. The reaction mixture was cooled to room temperature. The formed precipitate was collected by filtration at reduced pressure, washed with toluene, and dried at air to give the required product DOPO-2-HQ-rear as an off-beige solid (0.11 g, 0.20 mmol, 55%). mp: 251–253°C; ^{31}P NMR (101 MHz, DMSO-d_6) δ 20.4 (s), 7.7 (s); ^{13}C NMR (63 MHz, DMSO-d_6) δ157.5 (d, J = 2.6 Hz, 1C), 149.3 (d, J = 8.5 Hz, 1C), 149.1 (d, J = 8.3 Hz, 1C), 140.7 (dd, J = 17.7 Hz, J = 8.7 Hz, 1C), 136.4 (d, J = 7.0 Hz, 1C), 134.8 (d, J = 5.8 Hz, 1C), 134.3 (s, 1C), 132.7 (s, 1C), 130.9 (s, 1C), 130.2 (s, 1C), 130.2 (d, J = 9.3 Hz, 1C), 129.9 (d, J = 12.8 Hz, 1C), 128.9 (d, J = 15.5 Hz, 1C), 128.3 (d, J = 14.0 Hz, 1C), 127.5 (m, 1C), 125.9 (s, 1C), 125.3 (s, 1C), 125.2 (s, 1C), 124.8 (s, 1C), 124.6 (m, 2C), 124.2 (s, 1C), 123.5 (d, J = 10.0 Hz, 1C), 120.8 (d, J = 133.8 Hz, 1C—P), 120.3 (d, J = 169.9 Hz, 1C—P), 119.1 (dd, J = 210.6 Hz, J = 10.3 Hz, 1C—P), 119.8 (d, J = 6.9 Hz, 1C), 119.6 (d, J = 7.3 Hz, 1C), 116.9 (s, 1C), 114.6 (s, 1C); ^{1}H NMR (250 MHz, DMSO-d_6) δ10.34 (s, 1H, OH), 8.36–8.18 (m, 4H), 7.97–7.82 (m, 2H), 7.81–7.59 (m, 2H), 7.59–7.17 (m, 9H), 7.15–7.04 (m, 1H), 6.74–6.63 (m, 1H); IR (KBr) ν 3434 (m, O—H), 3069 (m, C_{aryl}—H), 1596 and 1584 (m, C=C), 1478 (vs, P—C_{aryl}), 1448, 1431, 1415, 1276 (s, C—O), 1241, 1195 (vs, P=O), 1149, 1119, 960 and 932 (vs, P—O), 864, 755 (vs, C—H), 715, 619, 609, 524, 508; HRMS (EI) calcd for $[^{12}C_{30}H_{20}O_6P_2]^+$ 538.0735, found 538.0736. Anal calcd for $C_{30}H_{20}O_6P_2$: C 66.92, H 3.74; found: C 67.14, H 3.91.

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