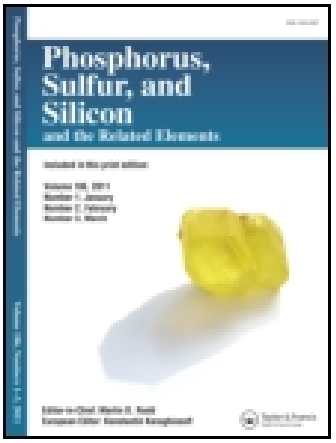

Phosphorus, Sulfur, and Silicon and the Related Elements

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Reaction of 1,1-Bis(Diphenylphosphino)Methane with O-Quinones and Naphtho[2,1-B]Furan-1,2-Dione. Novel Synthesis of Bis(Diphenylphosphoryl) Derivatives and their Antimicrobial Activity

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REACTION OF 1,1-BIS(DIPHENYLPHOSPHINO) METHANE WITH *O*-QUINONES AND NAPHTHO [2,1-B]FURAN-1,2-DIONE. NOVEL SYNTHESIS OF BIS(DIPHENYLPHOSPHORYL) DERIVATIVES AND THEIR ANTIMICROBIAL ACTIVITY

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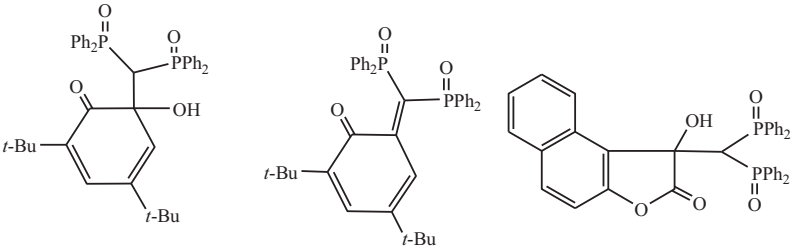
GRAPHICAL ABSTRACT



Abstract *The reaction of 1,1-bis(diphenylphosphino)methane with substituted o-quinones afforded the novel 6-[bis(diphenylphosphoryl)methyl]- and 6-bis(diphenyl phosphoryl)methylidene derivatives. Moreover, 1,1-bis(diphenylphosphino)methane reacts with 3,4,5,6-tetrabromo-o-benzoquinone to give only the new 6-[bis(diphenylphosphoryl)methyl] derivative. Mechanisms accounting for the formation of the new products are discussed. The antimicrobial activity of some of the newly synthesized compounds was also examined.*

Keywords 1,1-Bis(diphenylphosphino)methane; *o*-quinones; bis(diphenyl phosphoryl) derivatives; antimicrobial activity

INTRODUCTION

o-Quinones and their derivatives are of great interest due to their significance in nature. They play an important role in electron transport and possess various kinds of biological

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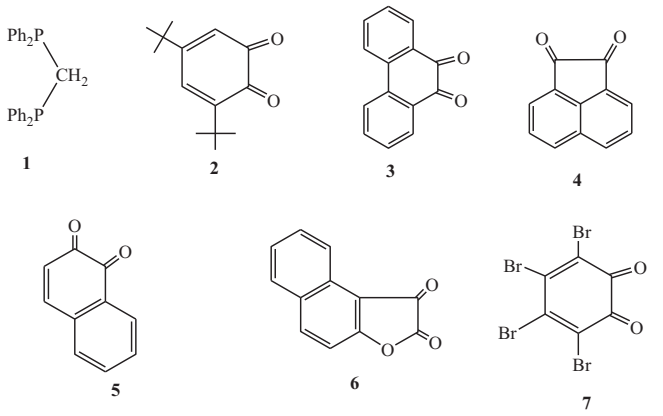


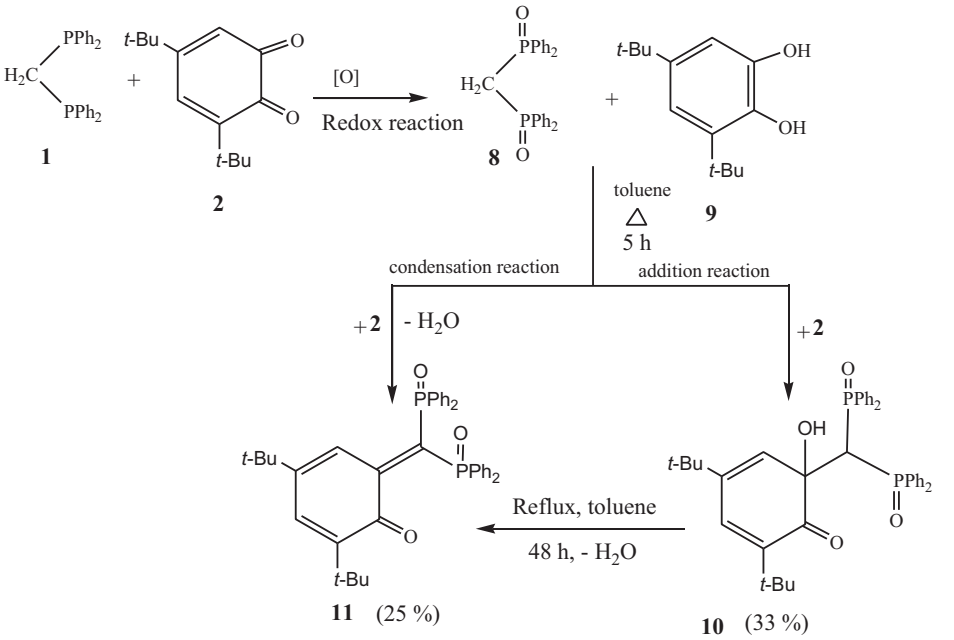
Figure 1 Starting materials (1–7).

activities. They are also used in the synthesis of metal complexes, nitrogen- or oxygen-containing heterocycles, and in enantioselective synthesis.[1–6] Trivalent phosphorus compounds are widely used in *o*-quinone chemistry, as a rule, for the preparation of pentacoordinated phosphorus derivatives (phosphoranes) or tetracoordinated ones (quasi-phosphonium salts having a betaine structure with the P^+–OC bond), which are used in organic synthesis.[7,8] Recently, we have reported that the reaction of 1,2-bis(diphenylphosphino) ethane with substituted *o*-benzoquinones afforded the new bis(6-hydroxycyclohexa-2,4-dienone) derivatives.[9] In view of this and in continuation of our work in the reaction of organophosphorus chemistry,[10–13] it was of considerable interest to investigate the behavior of 1,1-bis(diphenylphosphino) methane (**1**) toward *o*-quinones (**2**–**5**, **7**) and naphtha[2,1-*b*] furan-1,2-dione (**6**) (Figure 1).

RESULTS AND DISCUSSION

Chemistry

1,1-Bis(diphenylphosphino)methane (**1**) was treated with two mole equivalents of 3,5-di-*tert*-butyl-*o*-benzoquinone (**2**) in dry toluene at reflux temperature for 7 h. Column chromatography of the crude product yielded 6-[bis(diphenylphosphoryl) methyl]-2,4-di-*tert*-butyl-6-hydroxycyclohexa-2,4-dien-1-one (**10**, 33%), 6-[bis(diphenylphosphoryl)methylidene]-2,4-di-*tert*-butylcyclohexa-2,4-dien-1-one (**11**, 25%), and methane-1,2-diylbis(diphenylphosphane)dioxide (**8**, 10%). 3,5-Di-*tert*-butyl-catechol (**9**, 5%) was also isolated and identified by comparing its melting point (mp 97°C; Lit. 97–100°C) and IR spectrum with those of an authentic specimen.[14] The most important feature of structure **10** is the presence of one signal at $\delta_P = 24.2$ ppm(s) in its ^{31}P NMR spectrum. Moreover, the ^1H NMR spectrum of compound **10** (at 500 MHz) revealed signals at $\delta_H =$ 1.13 (s, 18H, *t*-Bu), 2.08 (dd, $^2J_{HP} = 25.27$ Hz, 1H, $Ph_2P(O)$-CH-$P(O)Ph_2$) corresponding to the methine proton attached to the two phosphorus atoms. The structure of compound **10** has also been assigned on the basis of ^{13}C NMR data, elemental analysis, and mass spectral data (FAB^+, see Experimental section). Compound **8** (minor product, 10%) was identified as methane-1,1-diylbis(diphenylphosphane)dioxide on the basis of the IR, ^1H, ^{13}C, ^{31}P NMR, and mass spectral data,[9,15] as well as by comparing its mp with that of



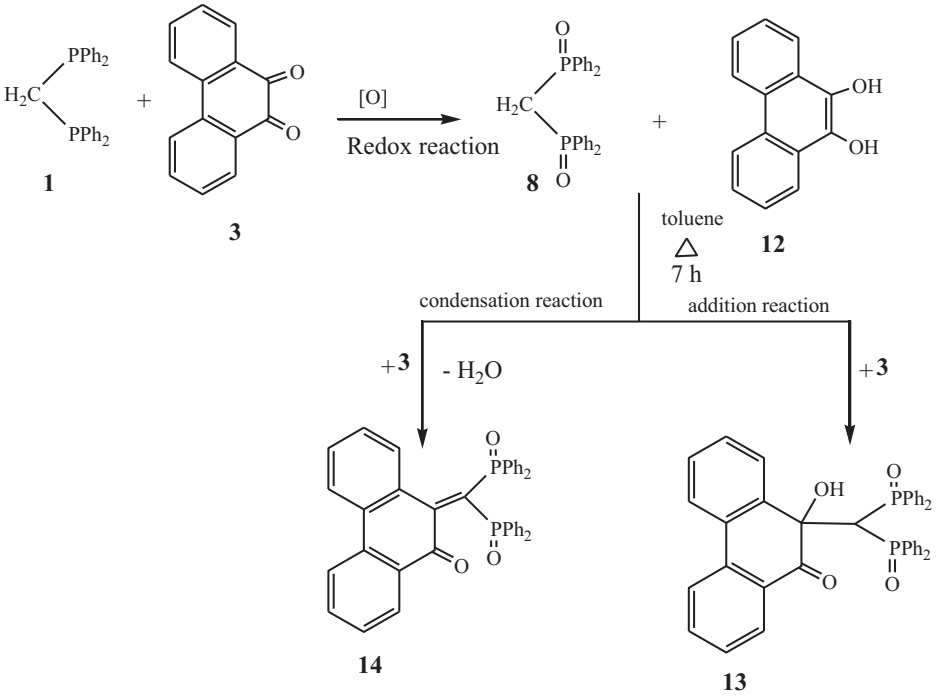
Scheme 1

a reference sample prepared by oxidation of **1** with hydrogen peroxide.[15] It is worthy to mention that refluxing equimolar amounts of **2** and **8** in dry toluene for 7 h also yielded a mixture of the same phosphorylated products **10** (35%) and **11** (40%).

A possible explanation of the reaction course of bisphosphine **1** with *o*-quinone **2** is depicted in Scheme 1. Apparently, this reaction is redox in nature leading to oxidation of the tertiary phosphine **1** to the respective diphosphoryl species **8**, whereby the *o*-quinone **2** is partially reduced to the respective dihydroxy derivative **9**. Compounds **10** and **11** were probably obtained through the methylene group in the resulting bisphosphoryl compound **8** by addition or condensation reaction with another molecule of quinone **2** (Scheme 1).[9] Upon refluxing **10** alone in dry toluene for a long period (48 h), it yields **11** almost quantitatively (see Experimental section).

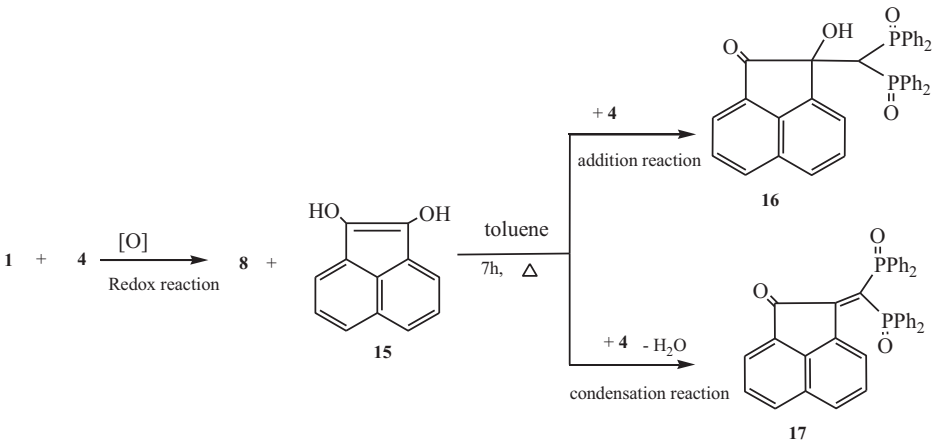
In accord with the mechanistic proposal, one equivalent of the corresponding catechol should be formed during the oxidative conversion of **1** to diphosphoryl species **8** due to the presence of unavoidable moisture that acts as the source of hydrogen and oxygen during the reaction course.

The reaction of 1,1-bis(diphenylphosphino)methane (**1**) with phenanthrene-9,10-dione (**3**) was also investigated. When two mole equivalents of **3** were treated with one mole of 1,1-bis(diphenylphosphino)methane (**1**) in boiling toluene for 7 h, products **13** (34%), **14** (50%), and **8** (10%) were isolated together with phenanthrene-9,10-diol **12** (5%) (Scheme 2). Structural assignments for compounds **13** and **14** are based upon elemental analysis and spectroscopic (IR, ^{1}H, ^{13}C, ^{31}P NMR, and mass spectrum (MS)) data (see Experimental section).

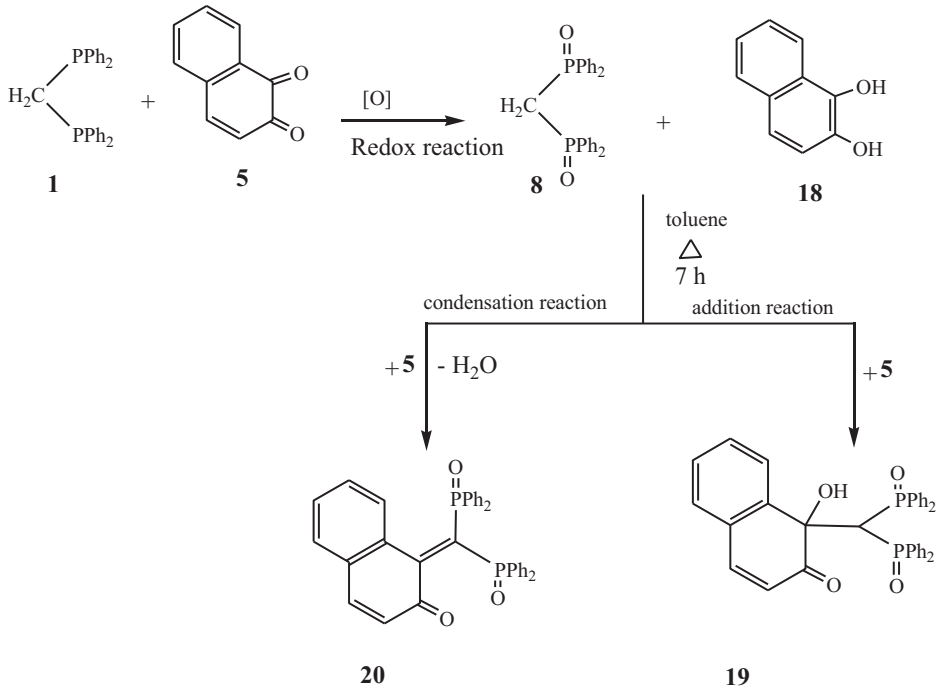


Scheme 2

Similarly, when two moles of acenaphthenequinone (**4**) are allowed to react with one mole equivalent of **1** in refluxing toluene for 7 h, 2-[bis(diphenylphosphoryl)methyl]-2-hydroxyacenaphthylen-1(2*H*)-one (**16**), 2-[bis(diphenylphosphoryl)methylidene] acenaphthylen-1(2*H*)-one (**17**), compound **8**, and acenaphthylene-1,2-diol (**15**) are obtained[14] (Scheme 3). The structures assigned for compounds **16**, **17** are gained from their spectroscopic data (see Experimental section).



Scheme 3

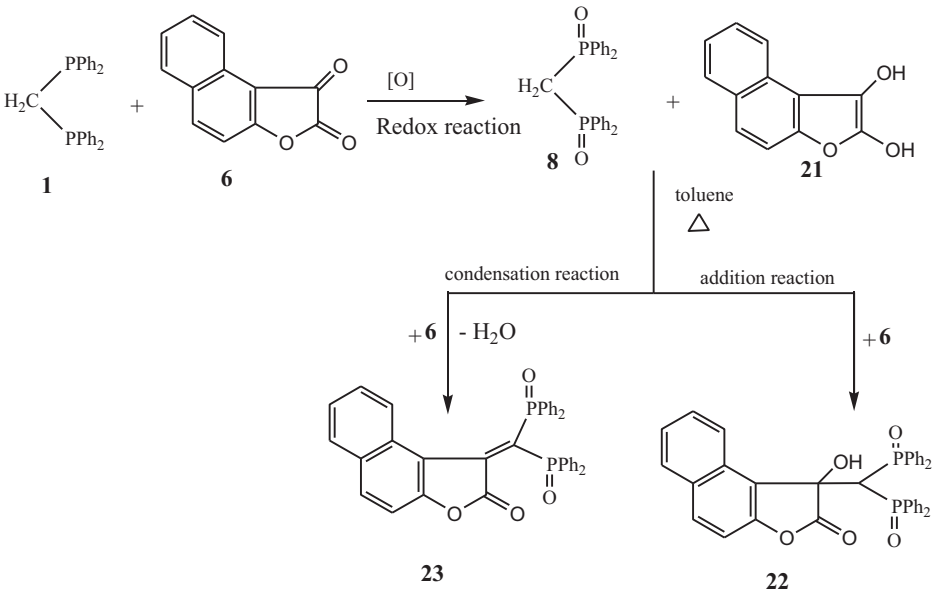


Scheme 4

Similarly, *o*-naphthoquinone (**5**) reacts with **1** to give both the addition product **19** in a 32% yield and the condensation product **20** in a 28% yield as the major products. Methane-1,1-diylbis(diphenylphosphane)dioxide (**8**) (10%) and benzocatechol **18** (5%) were also isolated (Scheme 4). Structural assignments for compounds **19** and **20** are based upon elemental analysis and spectroscopic (IR, ^{1}H, ^{13}C, ^{31}P NMR, and MS) data (see Experimental section).

Also, the study was extended to include the behavior of naphtho[2,1-*b*]furan-1,2-dione (**6**) towards 1,1-bis(diphenylphosphino)methane (**1**) in order to determine the preferential site of attack. We have found that when **6** was allowed to react with 1,1-bis(diphenylphosphino)methane (**1**) in refluxing toluene for 7 h, the corresponding 1-[bis(diphenylphosphoryl)methyl]-1-hydroxynaphtho[2,1-*b*]furan-2(1*H*)-one (**22**) and 1-[bis(diphenylphosphoryl)methylidene]naphtho[2,1-*b*]furan-2(1*H*)-one (**23**) were isolated as major products. Compound **8** and naphtho[2,1-*b*]furan-1,2-diol (**21**) were also isolated and identified by comparing their mps and IR spectra with those of authentic specimens.[14] Structural assignments for compounds **22** and **23** are based upon elemental analysis and spectroscopic (IR, ^{1}H, ^{13}C, ^{31}P NMR, and MS) data (see Experimental section).

On the other hand, when one mole equivalent of tetrabromo-*o*-benzoquinone (**7**) was treated with one mole of 1,1-bis(diphenylphosphino)methane (**1**) in dry toluene at room temperature for 3 h, the corresponding 6-[bis(diphenylphosphoryl)methyl]-2,3,4,5-tetrabromo-6-hydroxycyclohexa-2,4-dien-1-one (**25**) was isolated as the major product (61% yield). Methane-1,1-diylbis(diphenylphosphane) dioxide (**8**) was also isolated as a minor product (10%). Tetrabromocatechol (**24**) was also isolated (5%) from the reaction

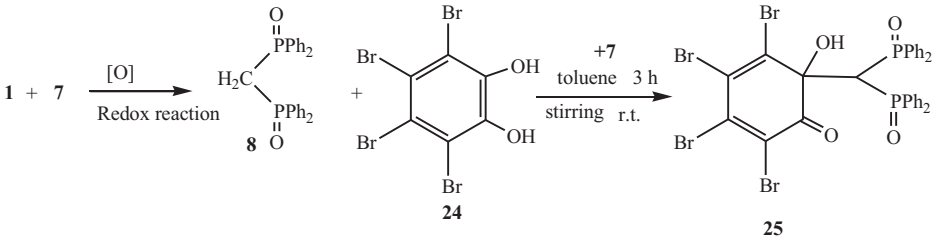


Scheme 5

mixture and identified by comparing its mp and IR spectra with those of an authentic sample[14] (Scheme 6).

ANTIMICROBIAL ACTIVITY

The antibacterial and antifungal activities[16–20] were carried out in the Microbial Chemistry Department, National Research Centre, using the diffusion plate method. A filter paper sterilized disk saturated with the measured quantity (25 μL) of the sample (1 mg/mL) was placed on a plate (9 cm diameter) containing a solid bacterial medium (nutrient agar) or a fungal medium (potato dextrose agar) that was seeded with the spore suspension of the test organism. After incubation at 37°C for 24 h for bacteria (in case of fungi, at 25°C for 72 h), the diameter of the clear zone of inhibition surrounding the sample is taken as a measure of the inhibitory power of the sample against the particular test organism (% inhibition = sample inhibition zone (cm)/plate diameter × 100). All measurements were done in methanol as a solvent that has zero inhibition activity. The antimicrobial activity



Scheme 6

of the new compounds was examined against Gram positive bacteria *Bacillus subtilis*, *Bacillus cereus*, and *Staphylococcus aureus*, as well as Gram negative bacteria *Escherichia coli*, *Pseudomonas aeruginose* and fungus *Candida albicans*. The obtained results are compared with the reference antibiotics that were purchased from Egyptian markets.[16–20] Tables S1 and S2 (supplemental materials) contain data of the antibacterial and antifungal testing.

CONCLUSION

From the results of the present investigation, it can be concluded that although 1,1-bis(diphenylphosphino)methane (**1**) shows marked stability toward auto-oxidation even upon prolonged heating solely in the presence of a solvent,[9] it undergoes redox reaction with *o*-quinones **2**–**5**, **7**, and naphtho[2,1-*b*]furan-1,2-dione (**6**) leading to bisphosphine dioxide **8** together with the corresponding hydroquinones (**9**, **12**, **15**, **18**, **21**, **24**). This process is accompanied by addition or condensation reaction of **8** with another molecule of the starting quinone.[9] This mechanism represents a new model for phosphorylated aryl compounds. Moreover, we noted that fast oxidation of the tertiary phosphine **1** in the redox reaction with *o*-quinone prevents the lone pair on phosphorus in **1** to attack the carbonyl carbon in *o*-quinones **2**–**5**, **7**, and in **6** according to the convention reaction.[8b,21–23]

EXPERIMENTAL

General Procedures for the Reaction of 1,1-Bis(diphenylphosphino) methane (1) With *o*-Quinone 2–6

o-Quinones (**2**–**6**, 2 mmol) and 1,1-bis(diphenylphosphino)methane (**1**, 1 mmol) were refluxed in dry toluene (30 mL) for 7 h and the reaction was followed by TLC (thin layer chromatography). The volatile materials were evaporated under reduced pressure. The residue was chromatographed on silica gel column to give two products: addition hydroxyl derivatives (**10**, **13**, **16**, **19**, or **22**) and condensation derivatives (**11**, **14**, **17**, **20**, or **23**) together with methane-1,1-diylbis(diphenylphosphane)dioxide (**8**, data in supplemental materials). Catechol (**9**, **12**, **15**, **18**, or **21**) was also isolated and identified by comparing its melting point and IR spectrum with those of an authentic specimen.[14] The supplemental materials file contains sample ^{1}H, ^{13}C, and ^{31}P NMR spectra for compounds **17** and **23** (Figures S1–S6).

Worthy of mention is that when 1,1-bis(diphenylphosphino)methane (**1**) was boiled in dry tetrahydrofuran (THF) or dry toluene for more than 10 h, the same reagent **1** was isolated unchanged (mp, mix mp).

Reaction of 3,5-Di-*tert*-butyl-*o*-benzoquinone (2) With Methane-1, 1-diylbis(diphenylphosphane)dioxide (8)

3,5-Di-*tert*-butyl-*o*-benzoquinone (**2**, 1 mmol) and methane-1,1-diylbis(diphenylpho sphane)dioxide (**8**, 1 mmol) were refluxed in dry toluene (30 mL) for 7 h and the reaction was followed by TLC. The volatile materials were evaporated under reduced pressure. The residue was chromatographed on silica gel column to give the same phosphorylated products **10** (35%) and **11** (40%).

Conversion of Addition Hydroxyl Derivative (10) and Condensation Derivatives (11)

1 mmol of 6-[bis(diphenylphosphoryl)methyl]-2,4-di-*tert*-butyl-6-hydroxycyclohexa-2,4-dien-1-one (**10**) was refluxed alone in dry toluene (30 mL) for 48 h and the reaction was followed by TLC. The volatile materials were evaporated under reduced pressure. The residue was washed by ethyl acetate (3*20 mL) and recrystalized by ethyl acetate to give 6-[bis(diphenylphosphoryl)methylidene]-2,4-di-*tert*-butylcyclohexa-2,4-dien-1-one (**11**).

6-[Bis(diphenylphosphoryl)methyl]-2,4-di-*tert*-butyl-6-hydroxycyclohexa-2,4-dien-1-one (10)

Eluent: petroleum ether/acetone (90/10, v/v). Product **10** was separated as colorless crystals, yield 0.27 g (33%). mp 182–184°C. IR (KBr): $\tilde{\nu}$ = 1182 (P=O), 1435 (P-Ph), 1677 (C=O), 3262 (OH) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.13 (s, 18H, *tert*-butyl), 2.08 (dd, $^2J_{HP}$ = 25.27 Hz, 1H, $Ph_2P(O)$-*CH*-$P(O)Ph_2$), 2.55 (s, 1H, OH, exchangeable with D_2O), 5.54, 7.28 (s, 2H, cyclohexadienone), 7.35–8.50 (m, 20H, $H_{arom.}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.1 (d, J_{CP} = 130 Hz, C—P=O), 30.2, 30.7, 31.3, 34.9 (4 s, *tert*-butyl), 64.8 (cyclic C-OH, $^2J_{CP}$ = 40.1 Hz), 113.6, 129.3, 131.32, 132.4, 135.0, 140.4, 141.8, 144.8 (aromatic, C—H), 162.50 (C=O) ppm. ^{31}P NMR ($CDCl_3$): δ = 24.2 ppm. MS (EI 70 eV): *m/z* (%) = 636 (10) $[M]^+$, 435 (25) $[M\text{-}201]^+$, 415(55) $[Ph_2P(O)\text{-}CH\text{-}P(O)Ph_2]^+$. Anal. Calcd. for $C_{39}H_{42}O_4P_2$ (636.7): C, 73.57; H, 6.65; P, 9.73. Found: C, 73.42; H, 6.60; P, 9.64.

6-[Bis(diphenylphosphoryl)methylidene]-2,4-di-*tert*-butylcyclohexa-2,4-dien-1-one (11)

Eluent: petroleum ether/acetone (10/90, v/v). Product **11** was separated as yellow crystals, yield 0.20 g (24%). mp > 320°C. IR (KBr): $\tilde{\nu}$ = 1190 (P=O), 1644 (C=C), 1698 (C=O) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.02 (s, 18H, *tert*-butyl), 6.59, 7.28 (s, 2H, cyclohexadienone), 7.35–7.73 (m, 20H, $H_{arom.}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.5, 27.4, 29.5, 30.9 (4 s, *tert*-butyl), 130.1 (d, J_{CP} = 130 Hz, C—P=O), 150.1 (cyclic C = C—P, $^2J_{CP}$ = 40.1 Hz), 113.6, 129.3, 131.32, 132.4, 135.0, 140.4, 141.8, 144.8 (aromatic, C—H), 166.23 (C=O) ppm. ^{31}P NMR ($CDCl_3$): δ = 30.9 ppm. MS (EI 70 eV): *m/z* (%) = 618 (10) $[M]^+$, 415 (65) $[Ph_2P(O)\text{-}CH\text{-}P(O)Ph_2]^+$, 417 (20) $[M\text{-}201]^+$. Anal. Calcd. for $C_{39}H_{40}O_3P_2$ (618.25): C, 75.71; H, 6.52; P, 10.01. Found: C, 75.69; H, 6.60; P, 10.11.

10-[Bis(diphenylphosphoryl)methyl]-10-hydroxyphenanthren-9(10*H*)-one (13)

Eluent: petroleum ether/ethyl acetate (93/7, v/v). Product **13** was separated as yellow crystals, yield 0.26 g (34%). mp 178–180°C. IR (KBr): $\tilde{\nu}$ = 1185 (P=O), 1693 (C=O), 3260 (OH) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.04 (s, 1H, OH, exchangeable with D_2O), 4.03 (dd, $^2J_{HP}$ = 27.27 Hz, 1H, $Ph_2P(O)$-CH-$P(O)Ph_2$), 7.20–7.74 (m, 28H, $H_{arom.}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7 (dd, J_{CP} = 135.57 Hz, C—P), 76.7 (d, $^2J_{CP}$ = 55.38 Hz, cyclic C—OH), 128.8, 128.9, 130.8, 131.3, 131.4, 131.8, 132.1, 132.2, 132.7 (aromatic C—H), 175.75 (C=O) ppm. ^{31}P NMR ($CDCl_3$): δ = 24.4 ppm. MS (EI 70 eV):

m/z (%) = 624 (15) $[M]^+$, 423 (25) [M-(201)]$^+$, 201 (50) [O=PPh_2]. Anal. Calcd. for $C_{39}H_{30}O_4P_2$ (624.16): C, 74.99; H, 4.84; P, 9.92. Found: C, 74.95; H, 3.99; P, 9.89.

10-[Bis(diphenylphosphoryl)methylidene]phenanthren-9(10*H*)-one (14)

Eluent: petroleum ether/ethyl acetate (80/20, v/v). Product **14** was separated as yellow crystals, yield 0.39 g (50%). mp 128–130°C. IR (KBr): $\tilde{\nu}$ = 1180, 1185 (P=O), 1445 (P-Ph), 1628 (C=C) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52–8.72 (m, 28H, $H_{arom.}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 122.8, 127.0, 129.4, 131.5, 132.1, 132.2, 132.7, 133.4 (aromatic C−H), 131.5 (dd, J_{CP} = 135.57 Hz, C−P), 164.6 (dd, $^2J_{CP}$ = 55.38 Hz, C=C−P), 178.7 (C=O) ppm. ^{31}P NMR ($CDCl_3$): δ = 38.3 ppm. MS (EI 70 eV): *m/z* (%) = 606 (15) $[M]^+$, 405 (25) [M^+-(201)]. Anal. Calcd. for $C_{39}H_{28}O_3P_2$ (606.59): C, 77.22; H, 4.65; P, 10.21. Found: C, 77.24; H, 4.61; P, 10.23.

2-[Bis(diphenylphosphoryl)methyl]-2-hydroxyacenaphthylen-1(2*H*)-one (16)

Eluent: petroleum ether/ethyl acetate (85/15, v/v). Product **16** was separated as yellow crystals, yield 0.28 g (36%). mp 148–150°C. IR (KBr): $\tilde{\nu}$ = 1180 (P=O), 1447 (P-Ph), 1695 (C=O), 3250 (OH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.02 (s, 1H, OH, exchangeable with D_2O), 7.32–8.54 (m, J_{HH} = 8.37 Hz, 26H, H_{arom}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 32.5 (dd, J_{CP} = 135.57 Hz, C−P), 128.1, 128.5, 130.4, 131.8, 132.6, 134.6, 135.1, 140.3 (aromatic C−H), 189.7 (C=O) ppm. ^{31}P NMR ($CDCl_3$): δ = 24.3 ppm. MS (EI 70 eV): *m/z* (%) = 598 (15) $[M]^+$, (80) 201 [O = PPh_2]$^+$. Anal. Calcd. for $C_{37}H_{28}O_4P_2$ (598.56): C, 74.24; H, 4.72; P, 10.35. Found: C, 74.22; H, 4.75; P, 10.31.

2-[Bis(diphenylphosphoryl)methylidene]acenaphthylen-1(2*H*)-one (17)

Eluent: petroleum ether/ethyl acetate (10/90, v/v). Product **17** was separated as brown crystals, yield 0.34 g (44%). mp 243–245°C. IR (KBr): $\tilde{\nu}$ = 1185 (P=O), 1445 (P-Ph), 1628 (C=C), 1678 (C=C) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88–8.41 (m, J_{HH} = 8.37 Hz, 26H, $H_{arom.}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 121.7, 128.1, 129.1, 129.3, 131.0, 132.8 (aromatic C−H), 144.8 (d, J_{CP} = 135.57 Hz, C = P), 188.1 (C=O) ppm. ^{31}P NMR = 33.3 ppm. MS (EI 70 eV): *m/z* (%) = 580 (15) $[M]^+$, 201(80) [O = PPh_2]$^+$. Anal. Calcd. for $C_{37}H_{26}O_3P_2$ (580.55): C, 76.55; H, 4.51; P, 10.67. Found: C, 76.51; H, 4.53; P, 10.69.

2-[Bis(diphenylphosphoryl)methyl]-2-hydroxynaphthalen-1(2*H*)-one (19)

Eluent: petroleum ether/ethyl acetate (80/20, v/v). Product **19** was separated as colorless crystals, yield 0.22 g (32%). mp 138–140°C. IR (KBr): $\tilde{\nu}$ = 1187, 1190 (P=O), 1698 (C=O), 3265 (OH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.03 (dd, $^2J_{HP}$ = 35.27 Hz, 1H, CH), 2.4 (s, 1H, OH, exchangeable with D_2O), 7.32–7.87 (m, 26H, $H_{arom.}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.7 (dd, J_{CP} = 135.57 Hz, $^2J_{CP}$ = 55.38 Hz, CH-P), 52.3 (dd, $^2J_{CP}$ = 55.38 Hz, cyclic C−OH), 128.8, 128.9, 130.8, 131.3, 131.4, 131.8, 132.1, 132.2, 132.4, 134.3, 135.1, 136.9 (aromatic C−H), 172.6 (C=O) ppm. ^{31}P NMR ($CDCl_3$): δ = 24.1 ppm. MS (EI 70 eV): *m/z* (%) = 574(15) $[M]^+$, 373 (25) [M^+-201]$^+$, 201 (75)

$[O{=}PPh_2]^+$. Anal. Calcd. for $C_{37}H_{28}O_4P_2$ (574.54): C, 73.17; H, 4.91; P, 10.78; found: C, 73.20; H, 4.90; P, 10.75.

2-[Bis(diphenylphosphoryl)methylidene]naphthalen-1(2*H*)-one (20)

Eluent: petroleum ether/ethyl acetate (20/80, v/v). Product **20** was separated as black crystals, yield 0.19 g (28%). mp 238–240°C. IR (KBr): $\tilde{\nu}$ = IR (KBr): $\tilde{\nu}$ = 1180, 1185 (P=O), 1444 (P-Ph), 1626 (C=C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.52–8.72 (m, 26H, $H_{arom.}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 130.5 (dd, J_{CP} = 135.57 Hz, C−P), 122.6, 125.1, 127.7, 128.9, 130.8, 131.3, 131.4, 131.8, 132.1, 132.2, 132.4, 133.2, 134.3, 135.1 (aromatic C−H), 163.2 (dd, $^2J_{CP}$ = 55.38 Hz, C=C−P), 175.6 (C=O) ppm. ^{31}P NMR ($CDCl_3$): δ = 21.3 ppm. MS (EI 70 eV): *m/z* (%) = 556 (15) $[M]^+$, 201 (75) $[O{=}PPh_2]^+$. Anal. Calcd. for $C_{37}H_{26}O_3P_2$ (556.53): C, 75.54; H, 4.71; P, 11.13. Found: C, 75.55; H, 4.61; P, 11.15.

1-[Bis(diphenylphosphoryl)methyl]-1-hydroxynaphtho [2,1-*b*]furan-2(1*H*)-one (22)

Eluent: petroleum ether/ethyl acetate (80/20, v/v). Product **22** was separated as yellow crystals, yield 0.19 g (25%). mp < 300°C. IR (KBr): $\tilde{\nu}$ = 1185, 1195 (P=O), 1672 (C=O), 3250 (OH) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.98–4.06 (dd, $^2J_{HP}$ = 35.27 Hz, 1H, CH), 7.04–7.87 (m, 26H, $H_{arom.}$) 8.02 (s, 1H, OH, exchangeable with D_2O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 30.1 (dd, J_{CP} = 135.57 Hz, $^2J_{CP}$ = 55.38 Hz, CH-P), 45.6 (dd, $^2J_{CP}$ = 55.38 Hz, cyclic C−OH), 128.7, 128.9, 130.8, 131.3, 131.4, 131.8, 132.1, 132.2, 132.4, 133.2, 134.3, 135.1 (aromatic C−H), 172.6 (C=O) ppm. ^{31}P NMR ($CDCl_3$): δ = 26.3 ppm. MS (EI 70 eV): *m/z* (%) = 614 (15) $[M]^+$, 413 (25) $[M\text{-}201]^+$. Anal. Calcd. for $C_{37}H_{28}O_5P_2$ (614.56): C, 72.31; H, 4.59; P, 10.08. Found: C, 72.21; H, 4.60; P, 10.10.

1-[Bis(diphenylphosphoryl)methylidene]naphtho[2,1-b]furan-2(1*H*)-one (23)

Eluent: petroleum ether/ethyl acetate (20/80, v/v). Product **23** was separated as colorless crystals, yield 0.16 g (21%). mp 238–240°C. IR (KBr): $\tilde{\nu}$ = IR (KBr): $\tilde{\nu}$ = 1180, 1190 (P=O), 1634 (C=C), 1726 (C=O lactone) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): 6.22–8.01 (m, 26H, $H_{arom.}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.5 (dd, J_{CP} = 135.57 Hz, $^2J_{CP}$ = 55.38 Hz, C=P), 122.6, 125.1, 127.7, 128.9, 130.8, 131.3, 131.4, 131.8, 132.1, 132.2, 132.4, 133.2 (aromatic C−H), 162.2 (dd, $^2J_{CP}$ = 55.38 Hz, cyclic C=C), 169.5 (C=O) ppm. ^{31}P NMR ($CDCl_3$): δ = 25.1 ppm. MS (EI 70 eV): *m/z* (%) = 596 (15) $[M]^+$, 201 (75) $[O{=}PPh_2]^+$. Anal. Calcd. for $C_{37}H_{26}O_4P_2$ (596.13): C, 74.49; H, 4.39; P, 10.38. Found: C, 74.45; H, 4.41; P, 10.35.

Reaction of 1,1-Bis(diphenylphosphino)methane (1) with 3,4,5,6-Tetrabromo-*o*-benzoquinone (7)

0.42 g (1 mmol) 3,4,5,6-tetrabromo-*o*-benzoquinone (**7**) and 0.38 g (1 mmol) 1,1-bis(diphenylphosphino)methane (**1**) were stirred in dry toluene (30 mL) at room temperature for 3 h and the reaction was followed by TLC. The volatile materials were evaporated under reduced pressure. The residue was chromatographed on silica gel column to give two

products 6-[bis(diphenylphosphoryl)methyl]-2,3,4,5-tetrabromo-6-hydroxycyclohexa-2,4-dien-1-one (**25**) and methane-1,1-diylbis(diphenylphosphane)dioxide (**8**). Tetrabromocatechol (**24**) was also isolated and identified by comparing its mp 188–190°C (Lit. 189–193°C) and IR spectra with those of an authentic specimen.

6-[Bis(diphenylphosphoryl)methyl]-2,3,4,5-tetrabromo-6-hydroxycyclohexa-2,4-dien-1-one (25)

Eluent: petroleum ether/ethyl acetate (75/25, v/v). Product **25** was separated as green crystals, yield 0.49 g (61%). mp 223–225°C. IR (KBr): $\tilde{\nu} = 1185$ (P=O), 1435 (P-Ph), 1677 (C=O), 3252 (OH) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.80$ (s, 1H, OH, exchangeable with D_2O), 4.02 (dd, $J_{HH} = 5.6$ Hz, $^2J_{HP} = 30$ Hz, 1H, $Ph_2P(O)$-CH-$P(O)Ph_2$), 7.37–7.84 (m, 20H, $H_{arom.}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 30.7$ (d, $J_{CP} = 130$ Hz, C−P=O), 76.5 (cyclic C-OH, $^2J_{CP} = 40.1$ Hz), 118.1, 125.3, 128.3, 129.3, 129.6, 131.2, 133.5, 142.9 (aromatic C−H), 185.6 (C=O) ppm. ^{31}P NMR ($CDCl_3$): $\delta = 24.3$ ppm. MS (EI 70 eV): *m/z* (%) = 840 (5) $[M^+]$, 638 (25) $[M\text{-}201]^+$, 415 (85) $[Ph_2P(O)CH\text{-}P(O)Ph_2]^+$. Anal. Calcd. for $C_{31}H_{22}Br_4O_4P_2$ (840.07): C, 44.32; H, 2.64; Br, 38.05; P, 7.37; found: C, 44.30; H, 2.65; Br, 38.15; P, 7.35.

SUPPLEMENTAL MATERIAL

Supplementary data for this article can be accessed on the publisher's website, www.tandfonline.com/gpss

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