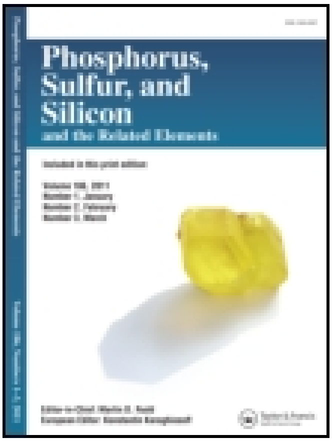

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On the Redox Reaction of 1,2-Bis(diphenylphosphino) Alkanes Toward o-, and p-Quinones

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ON THE REDOX REACTION OF 1,2-BIS(DIPHENYLPHOSPHINO) ALKANES TOWARD *O*-, AND *P*-QUINONES

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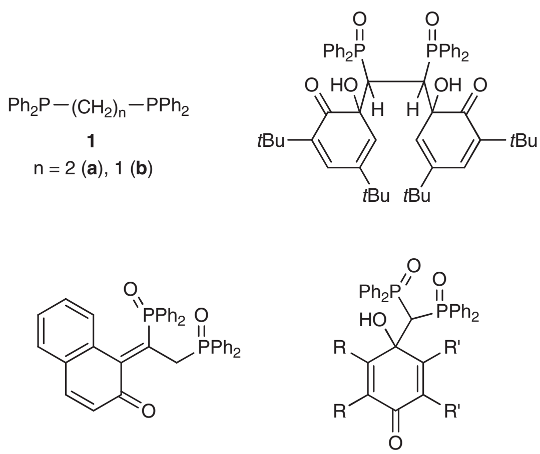
GRAPHICAL ABSTRACT



Abstract *The reaction of 1,2-bis(diphenylphosphino)ethane with substituted o-benzoquinones afforded new bis(6-hydroxycyclohexa-2,4-dienone) derivatives. Treatment of the same reagent with o-naphthoquinone, phenanthrenequinone, and acenaphthenequinone gave the respective bis(diphenylphosphoryl)ethylidenes or diacenaphthylenone derivatives. On the other hand, p-quinones react with 1,2-bis(diphenylphosphino)methane to yield the corresponding 4-hydroxycyclohexa-2,5-dien-1-ones. Possible reaction mechanisms are considered and the structural assignments are based on compatible analytical and spectroscopic data.*

Keywords 1,2-Bis(diphenylphosphino)alkanes; *o*-quinones; *p*-quinones; bis(6-hydroxycyclohexa-2,4-dienone); hydroquinones

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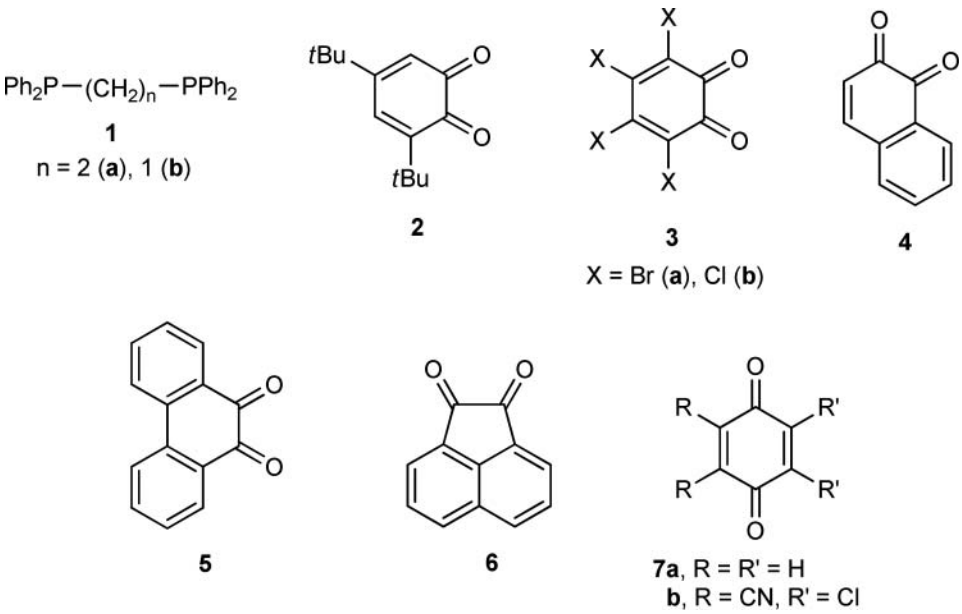


Figure 1 Reactants used in the present study.

INTRODUCTION

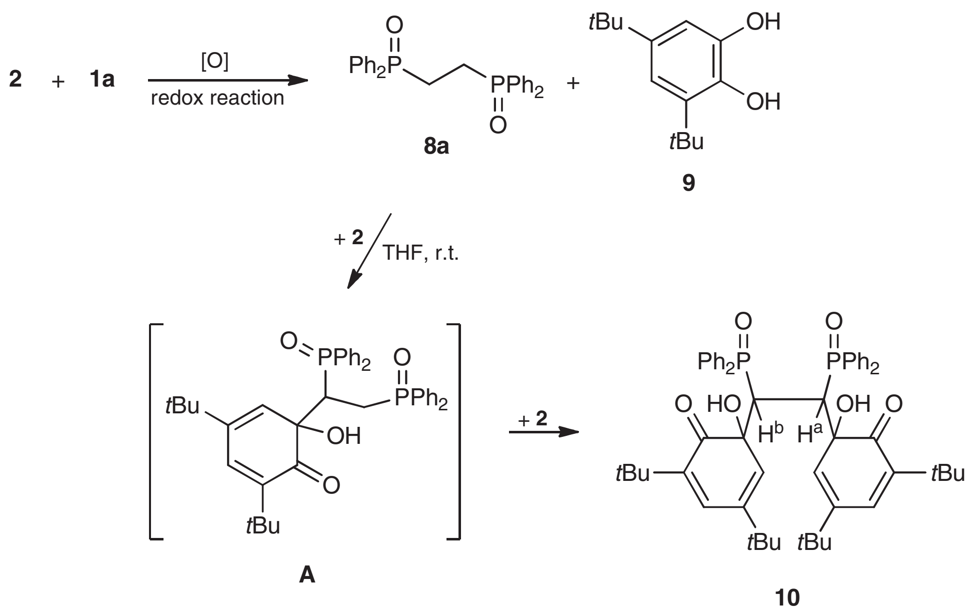
The intense development of the chemistry of quinones and related compounds is due to the wide occurrence of these compounds in nature and their versatile biological activity; they play the key part in many biological processes, such as respiration and photosynthesis.[1,2] Meanwhile, considerable interest has also been focused on the reaction of trivalent phosphorus compounds with mono- and polycyclic-quinones.[1,2]

The presence of a reactive system of multiple bonds (C=C and C=O) in quinones leads to an extensive employment of these compounds in organic synthesis as precursors of various heterocyclic and spirocyclic compounds.[3–9] Coordination complexes of 1,2-bis(diphenyl-phosphino)ethane (dppe) and bisphosphine ligands in general are almost entirely used as homogenous catalysts in a wide range of reactions. The reactions of trivalent phosphorus compounds with *ortho*- and *para*-quinones have been studied in considerable detail by Ramirez and his coworkers.[10] In view of this and in continuation of our work in organophosphorus chemistry[11–17], it was of considerable interest to study the reactivity of bis(diphenylphosphino)alkanes **1a**,**b** toward quinones (**2**–**7**) (Figure 1).

RESULTS AND DISCUSSION

Chemistry

1,2-Bis(diphenylphosphino)ethane **1a** was treated with two molar equivalents of 3,5-di-*tert*-butyl-*o*-benzoquinone (**2**) and the mixture was kept under stirring in tetrahydrofuran at room temperature (r.t.) for 5 h. Column chromatography of the



Scheme 1

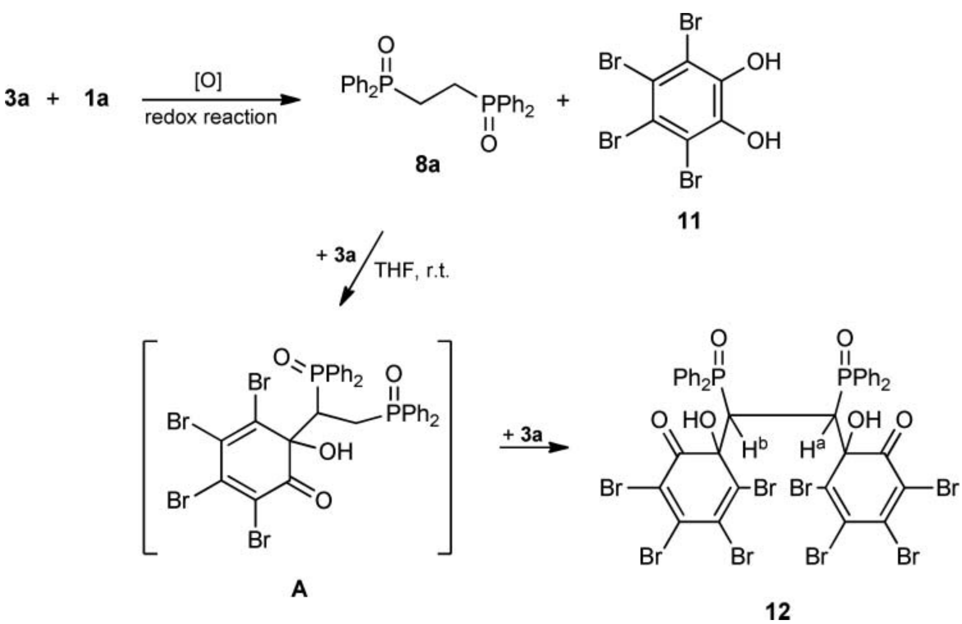
crude product yielded 2,2′-4,4′-di-*tert*-butyl-6,6′-[1,2-bis(diphenylphosphoryl)ethane-1,2-diyl-]bis(6-hydroxycyclohexa-2,4-dien-1-one) (**10**, 65%) and ethane 1,2-diylbis(diphenylphosphane)dioxide (**8a**, 15%) (Scheme 1). Moreover, 3,5-di-*tert*-butyl-catechol (**9**, 10%) was also isolated and identified by comparing its melting point (mp) and Infrared (IR) spectrum with those of an authentic sample.[18]

The most important feature of structure **10** is the presence of one signal at $\delta_P = 36.1$ ppm (s) in its ^{31}P NMR spectrum. Moreover, the ^{1}H NMR spectrum of compound **10** (at 500 MHz) revealed signals at $\delta_H = 1.25$ (s, 18H, *tert*-butyl), 1.27 ppm (s, 18H, *tert*-butyl), and 2.41 (ddd, $J_{HH} = 6.8$ Hz, $^2J_{PH} = 25.3$ Hz, $^3J_{PH} = 11.0$ Hz, 2H, $Ph_2P(O)CH\text{-}CH\text{-}P(O)Ph_2$), corresponding to the two methine protons attached to the two phosphorus atoms. It is worth mentioning that only one isomer of compound **10**, most probably the *(RRRR/SSSS)* isomer, is formed. The assignment *(RRRR/SSSS)* for this product, although not established with certainty, is supported by an inspection of the Newman projections[19] as well as by the ^{1}H NMR chemical shifts and coupling constant of the two *ortho* methine protons near the phosphorus atom. The observed $^3J_{HH}$ coupling constant of 6.8 Hz indicates a *cis* configuration, rather than a *trans* configuration, which would give rise to larger coupling constants ranging from 9 to 15 Hz. Moreover, the presence of one singlet in the ^{31}P NMR spectrum indicates the presence of only one stereoisomer. The structure of compound **10** has also been assigned on the basis of ^{13}C NMR data, elemental analysis, and mass spectral data (FAB$^+$, *cf*. Experimental Section).

Compound **8a** (minor product, 15% yield) was identified as ethane-1,2-diylbis-(diphenylphosphane)dioxide on the basis of the IR, ^{1}H, ^{13}C, ^{31}P NMR, and mass spectral data (*cf*. Experimental Section).

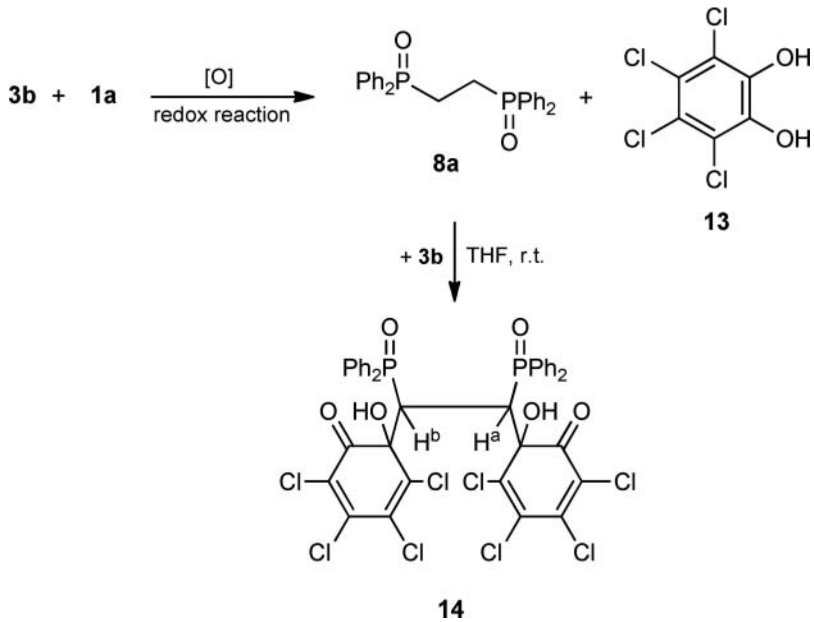
A possible explanation of the course of the reaction of the bisphosphine **1a** with *o*-quinone **2** is depicted in Scheme 1. Apparently, this reaction is redox in nature leading to oxidation of the tertiary phosphine **1a** to the respective dioxide **8a**, whereby the *o*-quinone **2** is partially reduced to the respective catechol derivative **9**. It is worth mentioning that **1a** was recovered practically unchanged (according to mp and mixed mp) upon long boiling alone in THF (or dry toluene) even for 10 h. Concurrent with the aforementioned transformations, the methylene group in the resulting bisphosphoryl compound **8a** can add to the carbonyl function in **2** to give intermediate **A**. The same process can be repeated through the other methylene function in **8a** to yield **10** (Scheme 1).

The reaction of 1,2-bis(diphenylphosphino)ethane **1a** with tetrabromo-*o*-benzoquinone **3a** was also investigated. The reaction of **1a** with **3a** in dry tetrahydrofuran was almost completed at r.t.. The crude product was purified by column chromatography to give 6,6′-[1,2-bis(diphenylphosphoryl)ethane-1,2-diyl]bis(2,3,4,5-tetrabromo-6-hydroxy-cyclohexa-2,4-dien-1-one) (**12**) as the major product (65% yield), and ethane-1,2-diylbis-(diphenylphosphane)dioxide (**8a**, 15% yield). 3,4,5,6-Tetrabromobenzene-1,2-diol (**11**) was also isolated from the reaction mixture and identified by comparing its mp and IR spectrum with those of an authentic sample (Scheme 2). Elemental analysis and molecular weight determination (MS) for compound **12** are related to $C_{38}H_{24}Br_8O_6P_2$. The IR spectrum of compound **12** (in KBr) shows absorption bands at $\upsilon = 1185$ (P=O), 3252(OH), and 1677 (C=O) cm^{-1}. The ^{1}H NMR spectrum of compound **12** (at 500 MHz) displays signals at $\delta_H = 2.35$ ppm (ddd, $J_{HH} = 5.6$ Hz, $^2J_{PH} = 30.0$ Hz, $^3J_{PH} = 18.0$ Hz, 2H, $Ph_2P(O)CH\text{-}CH\text{-}P(O)Ph_2$) corresponding to the two methine protons next to the two phosphorus atoms. The D_2O exchangeable protons (OH) appear as a broad singlet at $\delta = 2.80$ ppm. The aromatic protons fall in the region $\delta = 7.06$–7.18 ppm as a multiplet. The structure of compound **12** has also been confirmed by its ^{13}C and ^{31}P NMR as well as mass spectral data (*cf*. Experimental Section).



Scheme 2

On the other hand, when two mole equivalents of tetrachloro-*o*-benzoquinone **3b** were treated with one mole of 1,2-bis(diphenylphosphino)ethane **1a** in dry tetrahydrofuran



Scheme 3

at r.t. for 3 h, products **14** (70%) and **8a** (15%) were isolated together with 3,4,5,6-tetrachlorobenzene-1,2-diol (**13**, 5%) (Scheme 3).

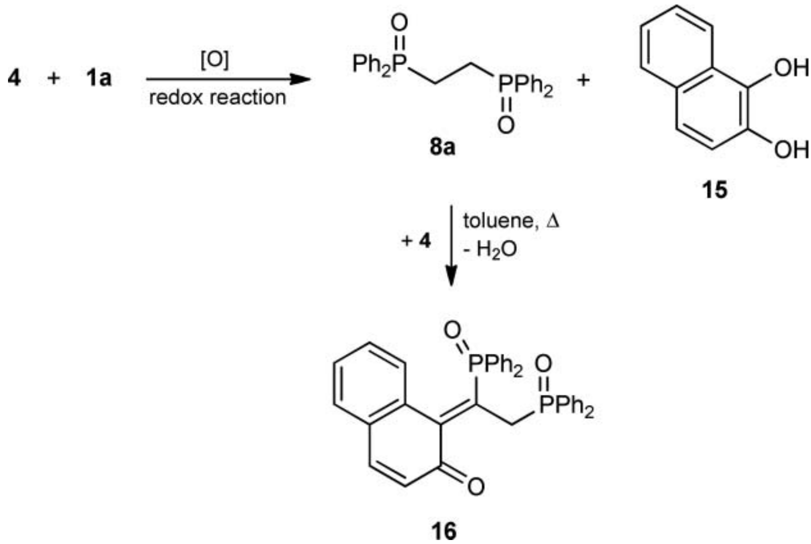
Structural assignments for compound **14** are based upon elemental analysis and spectroscopic (IR, ^{1}H, ^{13}C, ^{31}P NMR, and MS) data (*cf*. Experimental Section).

We have found that one mole of 1,2-bis(diphenylphosphino)ethane **1a** reacts with two equivalents of *o*-naphthoquinone **4** in refluxing dry toluene to give a yellow crystalline compound identified as 1-[1,2-bis(diphenylphosphoryl)ethylidene]naphthalene-2(1*H*)-one (**16**) as the major product and compound **8a** as a minor product (Scheme 4). Naphthalene-1,2-diol (**15**) was also isolated from the reaction mixture and identified (mp and mixed mp). Structural assignment for compound **16** is based upon elemental analysis and spectroscopic (IR, ^{1}H, ^{13}C, ^{31}P NMR, as well as MS) data (*cf*. Experimental Section).

Similarly, when one mole of phenanthrenequinone **5** is allowed to react with one equivalent of 1,2-bis(diphenylphosphino)ethane (**1a**) in refluxing dry toluene for 8 h, 10-[1,2-bis(diphenylphosphoryl)ethylidene]phenantherene-9-(10*H*)-one **18**, compound **8a,** and phenanthrene-9,10-diol (**17**) are obtained (Scheme 5). The structure of compound **18** results from its spectral data (*cf*. Experimental Section).

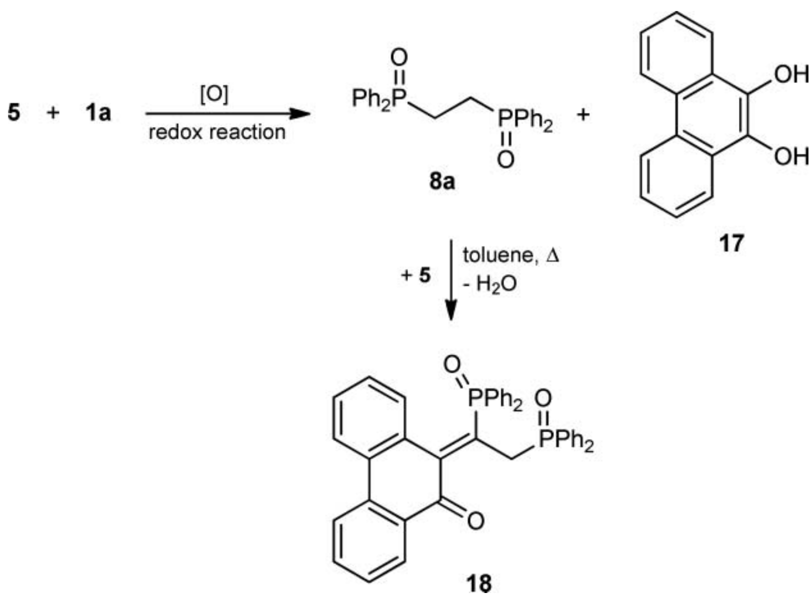
Performing the reaction of **1a** with acenaphthenequinone **6** in refluxing dry toluene for 7 h leads to the formation of 2,2′-[1,2-bis(diphenylphosphoryl)ethane-1,2-diylidene]diacenaphthylenone **20** as the main product (65% yield), ethane-1,2-diylbis(diphenylphosphane)-dioxide (**8a**, 15% yield), and acenaphthene-1,2-diol (**19**) (Scheme 6). The structural assignment for compound **20** is based upon elemental analysis and spectroscopic (IR, ^{1}H, ^{13}C, ^{31}P NMR) as well as MS data (*cf*. Experimental Section).

The study was extended to also include the behavior of *p*-quinones **7a**,**b** toward 1,2-bis(diphenylphosphino)methane (**1b**) in order to determine the preferential site of attack. We have found that when **7a** was allowed to react with 1,2-bis(diphenylphosphino)methane

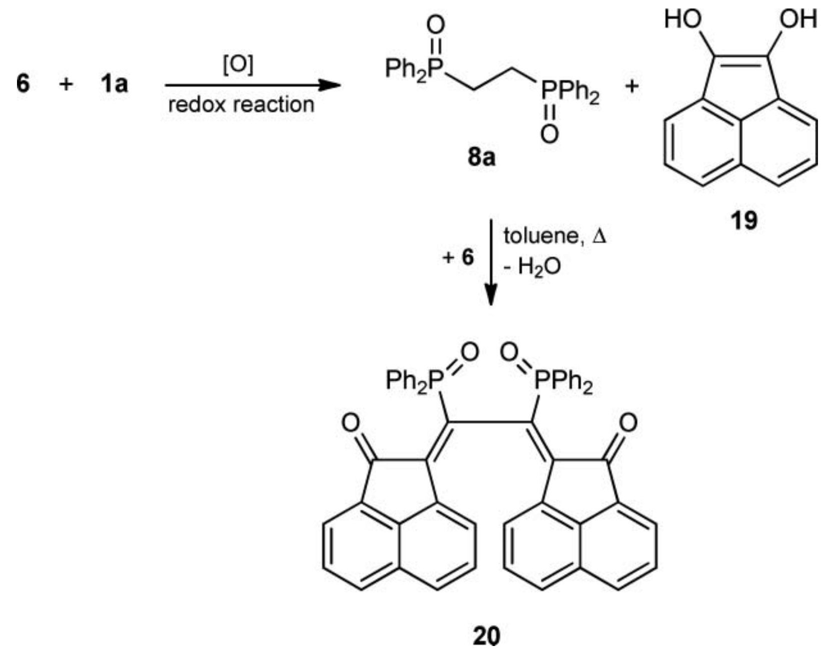


Scheme 4

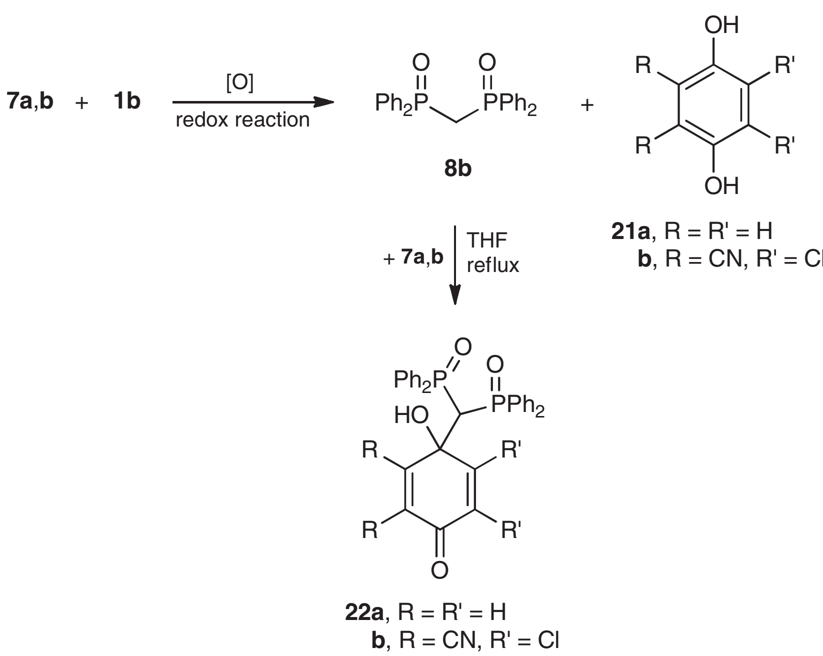
(**1b**) in refluxing dry THF for 20 h, the corresponding 4-[bis(diphenylphosphonyl)methyl]-4-hydroxycyclohexa-2,5-dien-1-one (**22a**) was isolated as the major product (65% yield). Methane-1,2-diylbis(diphenylphosphane)dioxide (**8b**) was also isolated as a minor product (15%). Hydroquinone **21a,b** was also isolated (5%) from the reaction mixture and identified by comparing its mp and IR spectrum with those of an authentic sample (Scheme 7).



Scheme 5



Scheme 6



Scheme 7

Similarly, 3,4-dichloro-6,7-dicyano-*o*-benzoquinone **7b** reacts with **1b** to give **22b** (major product), **8b** (minor product), and 4,5-dichloro-3,6-dihydroxybenzene-1,2-dinitrile (**21**, 3%). Structures of **22a**,**b** and **8b** have been confirmed on the basis of full sets of their spectral data (*cf*. Experimental Section).

A possible explanation of the course of the reaction of the bisphosphine **1b** with *p*-quinones **7a**,**b** is depicted in Scheme 7. Apparently, this reaction is redox in nature leading to oxidation of the tertiary phosphine **1b** to the respective dioxide **8b** whereby, the *p*-quinones **7a,b** are reduced to the respective hydroquinone derivatives **21a,b**. The methylene group in the resulting dioxide **8b** can add to one of the carbonyl functions in **7a,b** to yield **22a,b** (Scheme 7).

CONCLUSION

Results of the present investigation allow for certain interesting conclusions to be drawn. Thus, 1,2-bis(diphenylphosphino)ethane (**1a**) and 1,2-bis(diphenylphosphino)methane (**1b**) showed marked stability toward auto-oxidation even upon prolonged heating solely in the presence of a solvent. On the other hand, the same tertiary phosphines (**1a**,**b**) undergo redox reaction with *ortho*-quinones (e.g. **3b**, **4**, **5**, or **6**) or *para*-quinones (**7a**,**b**) leading to bisphosphine dioxides (**10**, **12**, **14**) together with the corresponding hydroquinone (*cf*. **9**, **11**, **13**, **15**, **17**, **19**, **21a**,**b**). This process is accompanied by addition or condensation reaction of **8a** or **8b** with another molecule of the respective quinone. These mechanisms represent a new approach for the synthesis of a variety of phosphorylated aryl compounds. The fast oxidation of the tertiary phosphines **1a**,**b** prevents the lone pair at the phosphorus atom to attack the carbonyl carbon atom in quinones **2**–**7** according to the conventional reactions.[1,2,10]

EXPERIMENTAL

Melting points were determined in open glass capillaries using Electrothermal IA 9000 series digital mp apparatus and are uncorrected. The IR spectra were measured in KBr pellets with a Perkin-Elmer Infracord Spectrophotometer model 157(Grating). The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO as solvent with a JEOL-500 MHz spectrometer and the chemical shifts are reported relative to TMS. The ^{31}P NMR spectra were obtained with a Varian CFT-20 spectrometer. ^{31}P chemical shifts are refered to 85% H_3PO_4 as external standard. The mass spectra were recorded at 70 eV with a Shimada GCS-OP 1000 Ex Spectrometer equipped with a data system. Elemental analyses were performed using Elmenter Varu EL Germany Instrument. The reported yields refer to pure materials isolated by column chromatography. Solvents were dried/purified according to conventional procedures.

Reaction of 1,2-Bis(diphenylphosphino)ethane (1a) with 3,5-di-tert-butyl-o-benzo-quinone (2)

(0.44 g, 2 mmol) 3,5-di-*tert*-butyl-*o*-benzoquinone (**2**) and (0.39 g, 1 mmol) 1,2-bis(diphenyl-phosphino)ethane (**1a**) were stirred in 30 mL dry THF at r.t. for 5 h. The course of the reaction was monitored by TLC. The volatile materials were evaporated under reduced pressure. The residue was chromatographed on silica gel column to give two products: 2,2′-4,4′-di-*tert*-butyl-6,6′-[1,2-bis(diphenylphosphoryl)ethane-1,2-diyl-]bis(6-hydroxycyclohexa-2,4-dien-1-one) (**10**) and ethane 1,2-diylbis(diphenylphosphane)dioxide (**8a**).

When 1,2-bis(diphenylphosphino)ethane (**1a**) was boiled in dry THF or dry toluene for more than 10 h, the same reagent **1a** was isolated unchanged (mp and mixed mp).

2,2′-4,4′-Di-*tert*-butyl-6,6′-[1,2-bis(diphenylphosphoryl)ethane-1,2-diyl-]bis(6-hydroxy-cyclohexa-2,4-dien-1-one) (10)

Eluent: petroleum ether/acetone (90/10, v/v). Product **10** was separated as colorless crystals, yield 0.53 g (65%), mp 192 °C. IR (KBr): ν = 1182 (P=O), 1435 (P-Ph), 1677 (C=O), 3262 (OH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.25$ (s, 18H, *tert*-butyl), 1.27 (s, 18H, *tert*-butyl), 2.41 (ddd, $J_{HH} = 6.8$ Hz, $^2J_{PH} = 25.3$ Hz, $^3J_{PH} = 11.0$ Hz, 2H, $Ph_2P(O)CH$-CH-$P(O)Ph_2$), 2.80 (s, 2H, OH, exchangeable with D_2O), 6.59 (s, 2H, cyclohexadienone), 6.64 (s, 2H, cyclohexadienone), 7.46-7.71 (m, 20H, arom-H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.8$ (d, $J_{PC} = 130.0$ Hz, C-P=O), 30.0 (s, *tert*-butyl), 32.0 (s, *tert*-butyl), 34.3 (s, *tert*-butyl), 35.0 (s, *tert*-butyl), 82.6 (d, $^2J_{PC} = 40.1$ Hz, cyclic $\underline{C}$-OH), 113.6 (arom-CH), 129.3 (arom-C), 131.0 (arom-C), 132.4 (arom-C), 135.0 (arom-C), 140.4 (arom-C), 141.8 (arom-C), 144.8 (arom-C), 189.5 (C=O). ^{31}P NMR ($CDCl_3$): $\delta = 36.1$. MS (FAB$^+$): *m/z* (%) = 871 (M^+, 10), 670 (M^+-(O=PPh_2), 25), 428 ($Ph_2P(O)CH$-CH-$P(O)Ph_2$, 55). Anal. Calcd. for $C_{54}H_{64}O_6P_2$ (871.03): C, 74.46; H, 7.41; P, 7.11. Found: C, 74.41; H, 7.42; P, 7.12%.

Ethane 1,2-Diylbis(diphenylphosphane)dioxide (8a)

Eluent: petroleum ether/acetone (50/50, v/v). Product **8a** was separated as colorless crystals, yield 0.09 g (15%), mp 276 °C. IR (KBr): ν = 1183 (P=O), 1437 (P-Ph) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.41$ (s, $J_{PH} = 6.8$ Hz, 4H, $Ph_2P(O)\underline{CH_2\text{-}CH_2}$-$P(O)Ph_2$), 7.36-7.63 (m, 20H, arom-H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.4$ (C-P=O), 128.7 (arom-C), 130.4 (arom-C), 131.8 (arom-C), 132.5 (arom-C). ^{31}P NMR ($CDCl_3$): $\delta = 33.2$. MS (EI): *m/z* (%) = 430 (M^+, 60). Anal. Calcd. for $C_{26}H_{24}O_2P_2$ (430.42): C, 72.55; H, 5.62; P, 14.39. Found: C, 72.50; H, 5.63; P, 14.38.

Reaction of 1,2-Bis(diphenylphosphino)ethane (1a) with 3,4,5,6-Tetrabromo-*o*-benzo-quinone (3a)

3,4,5,6-Tetrabromo-*o*-benzoquinone (**3a**, 0.84 g, 2 mmol) and 1,2-bis(diphenylphosphino)-ethane (**1a**, 0.39 g, 1 mmol) were stirred in 30 mL dry THF. The reaction was almost completed at r.t.; the course of the reaction was monitored by TLC. The volatile materials were evaporated under reduced pressure. The residue was chromatographed on silica gel column to give the 6,6′-[1,2-bis(diphenylphosphoryl)ethane-1,2-diyl]bis(2,3,4,5-tetrabromo-6-hydroxycyclohexa-2,4-dien-1-one) (**12**) and compound **8a**.

6,6′-[1,2-Bis(diphenylphosphoryl)ethane-1,2-diyl]bis(2,3,4,5-tetrabromo-6-hydroxycyclo-hexa-2,4-dien-1-one) (12)

Eluent: petroleum ether/ethyl acetate (75/25, v/v). Product **12** was separated as colorless crystals, yield 0.79 g (65%), mp 130 °C. IR (KBr): ν = 1185 (P=O), 1435 (P-Ph), 1677 (C=O), 3252 (OH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.35$ (ddd, $J_{HH} = 5.6$ Hz,

$^2J_{PH} = 30.0$ Hz, $^3J_{PH} = 18.0$ Hz, 2H, $Ph_2P(O)CH\text{-}CH\text{-}P(O)Ph_2$), 2.80 (s, 2H, OH, exchangeable with D_2O), 7.06-7.18 (m, 20H, arom-H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.8$ (d, $J_{PC} = 130.0$ Hz, C-P=O), 86.5 (d, $^2J_{PC} = 40.1$ Hz, cyclic C-OH), 113.8 (arom-C), 118.1 (arom-C), 125.3 (arom-C), 128.3 (arom-C), 129.3 (arom-C), 129.6 (arom-C), 131.2 (arom-C), 133.5 (arom-C), 142.9 (arom-C), 185.6 (C=O). ^{31}P NMR ($CDCl_3$): $\delta = 33.3$. MS (FAB$^+$): *m/z* (%) = 1278 (M^+, 5), 1076 (M^+-(O=PPh_2), 25), 852 (M^+-($C_6HBr_4O_2$), 70), 428 ($Ph_2P(O)CH\text{-}CH\text{-}P(O)Ph_2$, 85). Anal. Calcd. for $C_{38}H_{24}Br_8O_6P_2$ (1277.77): C, 35.72; H, 1.89; Br, 50.03; P, 4.85. Found: C, 35.70; H, 1.86; Br, 50.04; P, 4.85%.

Reaction of 1,2-Bis(diphenylphosphino)ethane (1a) With 3,4,5,6-Tetrachloro-*o*-benzo-quinone (3b)

3,4,5,6-Tetrachloro-*o*-benzoquinone (**3b**, 0.48 g, 2 mmol) and 1,2-bis(diphenylphosphino)-ethane (**1a**, 0.39 g, 1 mmol) were stirred in 30 mL dry THF at r.t. for 3 h. The course of the reaction was monitored by TLC. The volatile materials were evaporated under reduced pressure. The residue was chromatographed on silica gel to give three products: 6,6′-[1,2-bis(diphenylphosphoryl)ethane-1,2-diyl]bis(2,3,4,5-tetrachloro-6-hydroxycyclohexa-2,4-diene-1-one) (**14**), compound **8a**, and 3,4,5,6-tetrachlorobenzene-1,2-diol (**13**, 5%).

6,6′-[1,2-Bis(diphenylphosphoryl)ethane-1,2-diyl]bis(2,3,4,5-tetrachloro-6-hydroxycyclo-hexa-2,4-diene-1-one) (14)

Eluent: petroleum ether/ethyl acetate (85/15, v/v). Compound **14** was separated as colorless crystals, yield 0.60 g (70%), mp 185 °C. IR (KBr): $\nu = 1186$ (P=O), 1435 (P-Ph), 1677 (C=O), 3252 (OH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.31$ (ddd, $J_{HH} = 6.8$ Hz, $^2J_{PH} = 25.3$ Hz, $^3J_{PH} = 11.0$ Hz, 2H, $Ph_2P(O)CH\text{-}CH\text{-}P(O)Ph_2$), 2.80 (s, 2H, OH, exchangeable with D_2O), 7.42-7.68 (m, 20H, arom-H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.8$ (d, $J_{PC} = 130.0$ Hz, C-P=O), 86.5 (d, $^2J_{PC} = 40.1$ Hz, cyclic C-OH), 119.3 (arom-C), 121.0 (arom-C), 125.2 (arom-C), 128.1 (arom-C), 130.4 (arom-C), 131.8 (arom-C), 137.3 (arom-C), 143.4 (arom-C), 195.6 (C=O). ^{31}P NMR ($CDCl_3$): $\delta = 30.8$. MS (EI): *m/z* (%) = 922 (M^+, 15). Anal. Calcd. for $C_{38}H_{24}Cl_8O_6P_2$ (922.17): C, 49.49; H, 2.62; Cl, 30.76; P, 6.72. Found: C, 49.45; H, 2.64; Cl, 30.73; P, 6.75%.

Reaction of 1,2-Bis(diphenylphosphino)ethane (1a) With *o*-Naphthoquinone (4)

o-Naphthoquinone (**4**, 0.15 g, 1 mmol) and 1,2-bis(diphenylphosphino)ethane (**1a**, 0.39 g, 1 mmol) were refluxed in 30 mL dry toluene for 7 h. The course of the reaction was monitored by TLC. The volatile materials were evaporated under reduced pressure. The residue was chromatographed on silica gel column to give the products: naphthalene-1,2-diol (**15**), 1-[bis(diphenylphosphoryl)methylidene]naphthalen-2(1*H*)-one (**16**), and compound **8a**.

1-[Bis(diphenylphosphoryl)methylidene]naphthalen-2(1H)-one (16)

Eluent: petroleum ether/ethyl acetate (80/20, v/v). Product **16** was separated as yellow crystals, yield 0.27 g (50%), mp 150 °C. IR (KBr): $\nu = 1187$, 1190 (P=O), 1698

(C=O), 1644 (C=C) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.46$ (dd, $^{2}J_{PH} = 35.3$ Hz, $^{3}J_{PH} = 10.5$ Hz, 2H, CH_2), 6.56-7.78 (m, 26H, arom-H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.7$ (dd, $^{1}J_{PC} = 135.6$ Hz, $^{2}J_{PC} = 55.4$ Hz, CH_2-P), 128.8 (arom-C), 128.9 (arom-C), 130.8 (arom-C), 131.3 (arom-C), 131.4 (arom-C), 131.8 (arom-C), 132.1 (arom-C), 132.2 (arom-C), 132.4 (arom-C), 140.3 (dd, $^{1}J_{PC} = 135.6$ Hz, $^{2}J_{PC} = 55.4$ Hz, P-C=C), 175.6 (C=O). ^{31}P NMR ($CDCl_3$): $\delta = 33.2$ (d), 33.3 (d), $^{3}J_{PP} = 50.8$ Hz. MS (EI): *m/z* (%) = 570 (M^+, 15), 369 (M^+- (O=PPh_2), 25), 201 (O=PPh_2, 75). Anal. Calcd. for $C_{36}H_{28}O_3P_2$ (570.55): C, 75.78; H, 4.95; P, 10.86. Found: C, 75.74; H, 4.92; P, 10.84%.

Reaction of 1,2-Bis(diphenylphosphino)ethane (1a) with Phenanthrene-9,10-dione (5)

Phenanthrene-9,10-dione (**5**, 0.20 g, 1 mmol) and 1,2-bis(diphenylphosphino)ethane (**1a**, 0.39 g, 1 mmol) were refluxed in 30 mL dry toluene for 8 h. The course of the reaction was monitored by TLC. The volatile materials were evaporated under reduced pressure. The residue was chromatographed on silica gel column to give the products: phenanthrene-9,10-diol (**17**), 10-[1,2-bis(diphenylphosphoryl)ethylidene]phenanthren-9(10*H*)-one (**18**), and compound **8a**.

10-[1,2-Bis(diphenylphosphoryl)ethylidene]phenanthren-9(10*H*)-one (18)

Eluent: petroleum ether/ethyl acetate (80/20, v/v). Compound **18** was separated as yellow crystals, yield 0.29 g (50%), mp 170 °C. IR (KBr): $\nu = 1180$, 1185 (P=O), 1445 (P-Ph), 1697 (C=O), 1623 (C=C) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.35$ (dd, $^{2}J_{PH} = 43.2$ Hz, $^{3}J_{PH} = 11.5$ Hz, 2H, CH_2), 7.25-7.78 (m, 28H, arom-H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.7$ (dd, $^{1}J_{PC} = 135.6$ Hz, $^{2}J_{PC} = 55.4$ Hz, CH_2-P), 128.8 (arom-C), 128.9 (arom-C), 130.8 (arom-C), 131.3 (arom-C), 131.4 (arom-C), 131.8 (arom-C), 132.1 (arom-C), 132.2 (arom-C), 132.7 (arom-C), 136.3 (dd, $^{1}J_{PC} = 135.6$ Hz, $^{2}J_{PC} = 55.4$ Hz, P-C=C), 175.8 (C=O). ^{31}P NMR ($CDCl_3$): $\delta = 33.3$(d), 33.4 (d), $^{3}J_{PP} = 50.8$ Hz. MS (EI): *m/z* (%) = 620 (M^+, 15), 420 (M^+-(O=PPh_2), 25), 201 (O=PPh_2, 50), 192 (phenantherene, 35). Anal. Calcd. for $C_{40}H_{30}O_3P_2$ (620.61): C, 77.41; H, 4.87; P, 9.98. Found: C, 77.44; H, 4.85; P, 9.95%.

Reaction of 1,2-Bis(diphenylphosphino)ethane (1a) with Acenaphthenequinone (6)

Acenaphthenequinone (**6**, 0.40 g, 2 mmol) and 1,2-bis(diphenylphosphino)ethane (**1a**, 0.39 g, 1 mmol) were refluxed in 30 mL dry toluene for 7 h. The course of the reaction was monitored by TLC. The volatile materials were evaporated under reduced pressure. The residue was chromatographed on silica gel column to give the products: acenaphthene-1,2-diol (**19**), 2,2′-[1,2-bis(diphenylphosphoryl)ethane-1,2-diylidene]diacenaphthylenone (**20**), and compound **8a**.

2,2′-[1,2-Bis(diphenylphosphoryl)ethane-1,2-diylidene]diacenaphthylenone (20)

Eluent: petroleum ether/ethyl acetate (85/15, v/v). Compound **20** was separated as brown crystals, yield 0.51 g (65%), mp 165 °C. IR (KBr): $\nu = 1180$ (P=O), 1447

(P-Ph), 1695 (C=O), 1628 (C=C) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41–7.67 (m, 32H, arom-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 127.6 (arom-C), 128.5 (arom-C), 130.4 (arom-C), 131.8 (arom-C), 132.6 (arom-C), 134.6 (arom-C), 135.1 (arom-C), 150.3 (arom-C), 140.7 (d, J_{PC} = 135.6 Hz, C-P), 189.8 (C=O). ^{31}P NMR ($CDCl_3$): δ = 33.3. MS (EI): *m/z* (%) = 758 (M^+, 15), 557 (M^+-(O=PPh_2), 25), 201 (O=PPh_2, 80). Anal. Calcd. for $C_{50}H_{32}O_4P_2$ (758.73): C, 79.15; H, 4.25; P, 8.16. Found: C, 79.19; H, 4.21; P, 8.13%.

Reaction of 1,2-Bis(diphenylphosphino)methane (1b) with *p*-Quinones (7a,b)

The respective *p*-quinone (**7a** or 7**b**, 1 mmol) and 1,2-bis(diphenylphosphino)methane (**1a**) (0.38 g, 1 mmol) were refluxed in 30 mL dry THF for 20 h. The course of the reaction was monitored by TLC. The volatile materials were evaporated under reduced pressure. The residue was chromatographed on silica gel column to give the products: hydroquinones **21a**,**b**, 4-[bis(diphenylphosphoryl)methyl]-4-hydroxycyclohexa-2,5-dien-1-one (**22a**) or 3-[bis(di-phenylphosphoryl)methyl]-4,5-dichloro-3-hydroxy-6-oxocyclohexa-1,4-diene-1,2-dicarbo-nitrile (**22b**), and methane-1,2-diylbis(diphenylphosphane)dioxide (**8b**).

4-[Bis(diphenylphosphoryl)methyl]-4-hydroxycyclohexa-2,5-dien-1-one (22a)

Eluent: petroleum ether/ethyl acetate (85/15, v/v). Product **22a** was separated as brown crystals, yield 0.31 g (65%), mp 200 °C. IR (KBr): ν = 1180 (P=O), 1447 (P-Ph), 1665 (C = O), 1628 (C = C), 3245 (OH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.98 (t, $^{2}J_{PH}$ = 43.2 Hz, 1H, CH), 2.86 (s, 1H, OH, exchangeable with D_2O), 6.48-7.68 (m, 24H, arom-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 40.5 (t, $^{1}J_{PC}$ = 135.6 Hz, C-P), 54.2 (d, $^{2}J_{PC}$ = 55.4 Hz, cyclic C-OH), 116.1 (arom-C), 128.7 (arom-C), 129.7 (arom-C), 131.0 (arom-C), 131.1 (arom-C), 131.8 (arom-C), 150.3 (d, $^{2}J_{PC}$ = 33.4 Hz, cyclic C-OH), 185.8 (C = O). ^{31}P NMR ($CDCl_3$): δ = 24.2. MS (EI): *m/z* (%) = 524 (M^+, 15), 323 (M^+-(O = PPh_2), 25), 201 (O = PPh_2, 80). Anal. Calcd. for $C_{31}H_{26}O_4P_2$ (524): C, 70.99; H, 5.00; P, 11.81. Found: C, 70.98; H, 5.01; P, 11.83%.

3-[Bis(diphenylphosphoryl)methyl]-4,5-dichloro-3-hydroxy-6-oxocyclohexa-1,4-diene-1,2-dicarbonitrile (22b)

Eluent: petroleum ether/ethyl acetate (85/15, v/v). Product **22b** was separated as brown crystals, yield 0.39 g (65%), mp 211 °C. IR (KBr): ν = 1180 (P=O), 1445 (P-Ph), 1665 (C = O), 1628 (C = C), 2225 (CN), 3245 (OH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.50 (t, $^{2}J_{PH}$ = 43.2 Hz, 1H, CH), 2.06 (s, 1H, OH, exchangeable with D_2O), 7.37-7.75 (m, 20H, arom-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 40.5 (t, $^{1}J_{PC}$ = 135.6 Hz, C-P), 61.3 (t, $^{2}J_{PC}$ = 55.4 Hz, cyclic C-OH), 102.2 (CN), 114.3 (CN), 128.6 (arom-C), 129.7 (arom-C), 131.0 (arom-C), 131.1 (arom-C), 131.8 (arom-C), 151.3 (arom-C), 170.2 (C = O). ^{31}P NMR ($CDCl_3$): δ = 24.3. MS (EI): *m/z* (%) = 643 (M^+, 15), 442 (M^+-(O = PPh_2), 25), 201 (O = PPh_2, 80). Anal. Calcd. for $C_{33}H_{22}Cl_2N_2O_4P_2$ (643.39): C, 61.60; H, 3.45; Cl, 11.02; N, 4.35; P, 9.63. Found: C, 61.62; H, 3.45; Cl, 11.04; N, 4.32; P, 9.64%.

Methane-1,2-diylbis(diphenylphosphane)dioxide (8b)

Eluent: petroleum ether/ethyl acetate (50/50, v/v). Product **8b** was separated as colorless crystals, yield 0.09 g (15%), mp 156 °C. IR (KBr): $\nu = 1183$ (P=O), 1435 (P-Ph) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.41$ (d, $J_{HH} = 6.8$ Hz, 2H, $Ph_2P(O)$-CH_2-$P(O)Ph_2$), 7.36-7.63 (m, 20H, arom-H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.5$ (t, $^{1}J_{PC} = 135.6$ Hz, O=P-C-P=O), 128.8 (arom-C), 131.3 (arom-C), 132.5 (arom-C). ^{31}P NMR ($CDCl_3$): $\delta = 25.5$. MS (EI): *m/z* (%) = 416 (M^+, 60). Anal. Calcd. for $C_{26}H_{24}O_2P_2$ (416.38): C, 72.11; H, 5.33; P, 14.88. Found: C, 72.10; H, 5.33; P, 14.87%.

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