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# THE REACTION OF A PHOSPHAALKENE WITH ORTHOQUINONES

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**Abstract**—The reaction of (2,6-dimethylphenyl)diphenylmethylenephosphine (**1**) with tetrachloro-o-benzoquinone (**2**), 3,5-di-t-butyl-o-benzoquinone (**3**) and phenanthrenequinone (**4**) yielded the formal [2 + 4] cycloaddition products **5**, **14** and **19**, respectively. In the given order, the rate of reaction and the formation of 1:2 adducts decreased. With 2 equivalents of the orthoquinones, the 1:2 adducts were the only products observed. The mechanism of the addition reactions is discussed against the background of current proposals for the reaction of tervalent phosphorus compounds with orthoquinones.

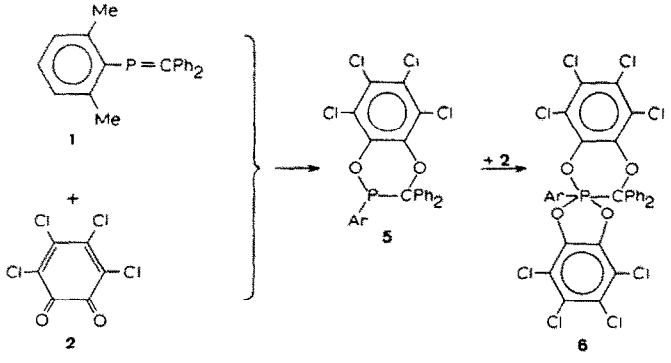
Intensive studies on the chemical behaviour of the recently accessible phosphaalkenes are beginning to reveal a broad range of reactivity of this class of compounds.[1] Cycloadditions have so far not been investigated systematically. In one case, an intramolecular Diels–Alder reaction involving attack on a benzene ring has been invoked.[2] In our hands, 2,4,6-trimethylphenyl(diphenylmethylene)phosphine yielded no well-defined products with a variety of dienes,[3] but it did undergo 1,3-dipolar addition reactions.[4] 1,3-Dipolar additions are also known for heterosubstituted[5] and heterocyclic[6] phosphaalkenes. We now wish to report formal [2 + 4] reactions of 2,6-dimethylphenyl-(diphenylmethylene)phosphine (**1**)[7] with the three orthoquinones **2**, **3**, and **4**.

## RESULTS AND DISCUSSION

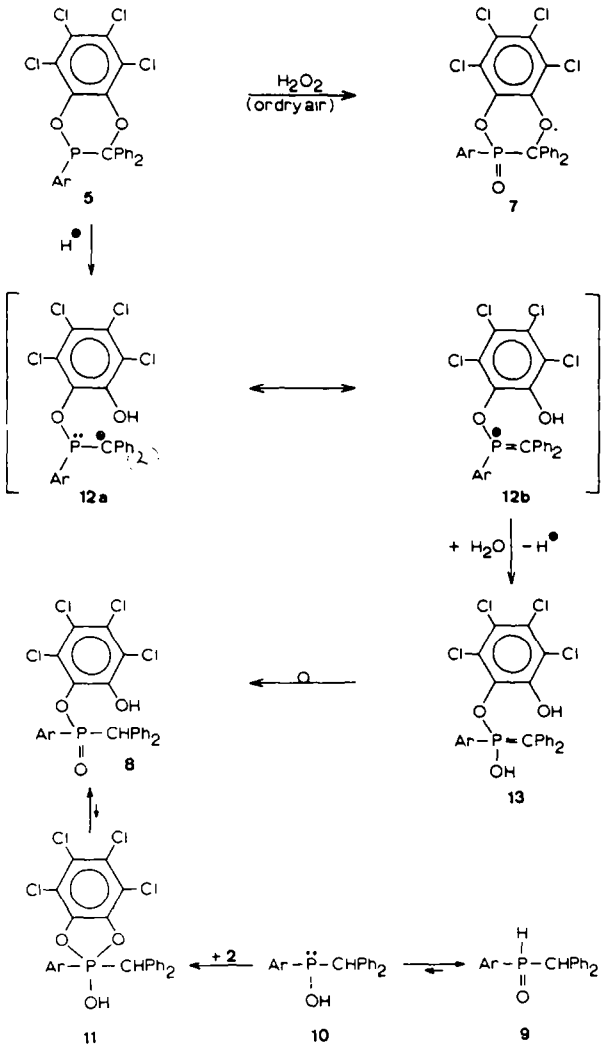
All reactions were performed under argon in benzene. When a solution of 1 equivalent of tetrachloro-o-benzoquinone (**2**) was added to that of **1**, the reaction was instantaneous at room temperature as judged from the disappearance of the red colour of the orthoquinone. Besides the 1:1 adduct **5** (68%), the 1:2 adduct **6** (23%) was formed according to $^{31}$P NMR spectroscopy. Apparently, **2** is so reactive that it adds to **1** and to **5** with comparable rate. With 2 equivalents of **2**, **1** gave **6** (73% isolated yield) as the only identifiable product (Scheme 1).

The structures of **5** and **6** were in accord with the spectral data. Compound **5** was further characterized by oxidation with hydrogen peroxide to **7** (42%). Similarly, **5** in benzene solution was oxidized to **7** by dry oxygen during 3 days at room temperature (*ca* 50% yield). However, in $CDCl_3$ solution, exposure of **5** to air resulted in a remarkable conversion to **8** (Scheme 2). According to the elemental analyses, **8** had the composition of water addition product of **5**; its structure was elucidated from its NMR data (Experimental) and from its independent synthesis from **9**[8] and **2**; the latter reaction probably proceeds via the tautomeric phosphinous acid **10** derived from **9** (for a discussion of such tautomeric equilibria, see ref. 9). It is well known that quinones add to trivalent P compounds under formation of oxyphosphoranes;[10] in analogy, we assume that additional of **2** to **10** furnishes **11** which isomerizes to the more stable aryl phosphinate **8**. The only plausible mechanism for the formation of **8** from **5** is the acid catalyzed pathway indicated in Scheme 2. Cleavage of the aryloxy ether in **5** under the influence of acid leads to the formation of the relatively stable (substituted) diphenylmethyl cation **12a**. Another resonance structure of **12** is that of an aryloxyphosphoniaalkene **12b**, which explains[7,8] the addition of water to form the hydroxyaryloxphosphorane **13** which in turn tautomerizes to **8**. This rationalization finds experimental support in the transformation of **5**–**8** with acid. A solution of **5** in tetrahydrofuran containing 9% water was stable for 19 h; on addition of 25 mol% 2 N $H_2SO_4$, no change occurred at room temperature, but on heating under reflux for 3.5 hr, a 1:2 mixture of **5** and **8** was obtained ($^{31}$P NMR).

The 1:2 adduct **6**, a trioxyphosphorane, is remarkable because it is a mixture of two stereoisomers (ratio *ca* 1:4) which are in a rapid dynamic equilibrium. At 0°, the $^{31}$P NMR signals at $\delta = -2.7$ and $-17.3$ ppm were sharp; at room temperature, the signals broaden considerably



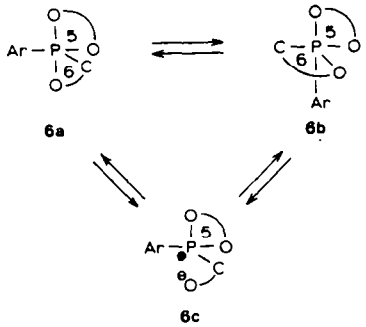

Scheme 1. (Ar = 2,6-dimethylphenyl).



Scheme 2.

without changing position; they disappear at higher temperature without coalescence below 100°. These phenomena are fully reversible. They may be explained in terms of a rapid equilibrium between two trigonal bipyramids (TBP) **6a** and **6b** (assignment arbitrary). Based on the apicophilicity rules,[11] we assume that in both TBP's the 5-membered ring has an apical-equatorial arrangement. The 6-membered ring apparently switches between a diequatorial and an apical-equatorial arrangement. None of these arrangements fulfills all the requirements of the apicophilicity order. The diequatorial arrangement of the 6-membered ring (**6b**) is usually the preferred one, but it forces the O atom into the less favourable equatorial position and the xylyl group into the apical position; the bulk of the xylyl group will make this violation of the electronegativity order even more severe. On the other hand, the apical-equatorial arrangement of the 6-membered ring (**6a**) allows the O to occupy the apical position and the two C substituents on P the equatorial position, but is less favourable for geometric reasons.

It is not clear whether this isomerization occurs by pseudorotation or via a ring-opened, zwitterionic intermediate like **6c**. The latter is expected to have a much lower $^{31}P$ chemical shift. As the observable $^{31}P$ signals have a temperature-independant position, pseudorotation appears to be more likely. The nearly complete disappearance of the signals over a large temperature range, which also holds for the $^{13}C$ NMR spectra, must be a consequence of the occurrence of several different



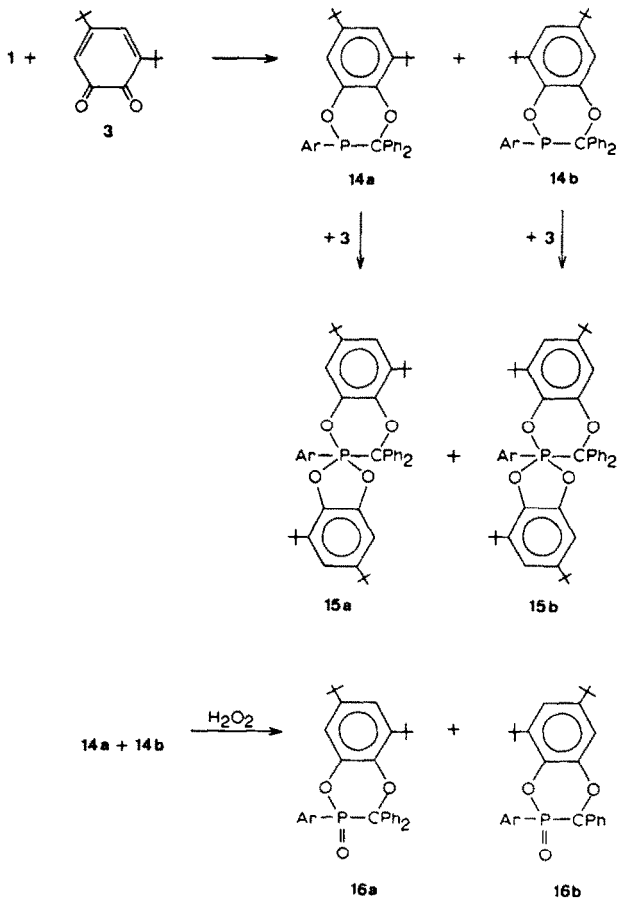
Scheme 3.

dynamic processes. Hindered rotation of the xylyl group is probably one of them, as indicated by two distinct Me signals of equal intensity at −20° ($\delta$ = 23.0 and 21.7 ppm), which disappear at 50°. An estimate of the activation barrier was possible from the 250 MHz $^1$H NMR spectrum which has broad signals at $\delta$ = 2.58 and 2.95 ppm for the two ortho-Me groups. They coalesce at 51°, which corresponds to a barrier of $\Delta G^{\neq}$ 15.4 kcal/mol for the xylyl group. Similarly, two broad singlets in the aromatic region (one proton each) at $\delta$ = *ca* 7.5 and 7.9 ppm coalesce at 45–50° ($\Delta G^{\neq}$ approx. 15 kcal/mol) and from a relatively sharp signal at $\delta$ = 7.62 ppm at 106° (this signal has a half-width of 12 Hz and is flattened at the top). The typical low field shift identifies these protons as the two ortho-protons of one of the phenyl rings, so that hindered rotation is also proven for this substituent.

The reaction of **1** with 3,5-di-t-butyl-o-benzoquinone (**3**) was, expectedly, not quite so rapid as that with **2**; after complete addition of **3**, the green colour remained for *ca* 15 min. Besides the 1:1 adducts **14a** (63%) and **14b** (13%), only 6% of the 1:2 adducts **15** was formed ($^{31}$P NMR). **14a** and **14b** were not separated, but the mixture was oxidized with aqueous $H_2O_2$ in acetone to furnish a 4:1 mixture of **16a** and **16b**. The reaction of **1** with 2 equivalents of **3** in boiling benzene gave only a mixture of **15a** and **15b** (ratio 3:1; total isolated yield 83%) (Scheme 4).

As the isomeric mixtures of **14–16** could not be separated, their characterization posed some problems. However, their composition is established by determination of the exact mass (**14**, **16**) or by elemental analysis (**15**), while the assigned structure is in agreement with the expected course of the reaction and with the $^{31}$P chemical shifts and $^1$H NMR data of the major isomer (**a** series; Experimental). The assignment of the regiochemistry (i.e. major isomer = **a** series) is tentative and based on mechanistic considerations (Conclusion).

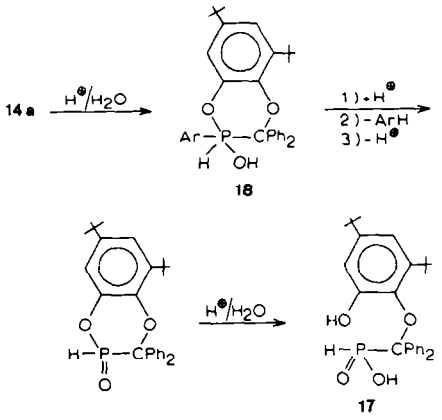
For a further chemical corroboration of the structure of **14** it was treated with aqueous $H_4SO_4$ in THF in the expectation to observe a reaction similar to the conversion of **5–8**. However, the reaction took a different and not fully understood course. The reaction product **17** was formed in 41% yield, m.p. 150–160°, but could not be purified and fully characterized. Its NMR spectra (Experimental) indicate that the xylyl group has been cleaved off, while the 3,5-di-t-butylcatechol moiety is retained with one free OH group ($\delta$($^1$H) = 8.55 ppm); the diphenylmethyl C atom bears no H; the $^{31}$P chemical shift ($\delta$ = 32.6 ppm) is in accord with that of a phosphinic acid; the presence of a P–H group follows from the $^1$H NMR spectrum ($\delta$ = 8.10 ppm, $^1J_{PH}$ = 484 Hz, which is also observed in the proton-coupled $^{31}$P NMR spectrum). A mass spectrum could only be obtained by the field desorption technique and showed $m/z$ = 386 (corresponding to [17–$H_3O_2P$]$^+$ as the highest mass peak). A rationalization for the formation of **17** is presented in




Scheme 4.

Scheme 5. It starts with protonation of **14a** at phosphorus, followed by addition of water to yield the hydroxyaryloxyphosphorane **18**. Protonation of **18** at the ipso C atom of the 2,6-dimethylphenyl group leads to the extrusion of *m*-xylene. The resulting phosphinous ester is hydrolyzed to yield **17** (which, under the conditions of work-up, may be in part transformed to the Na-salt; Experimental). The different behavior of **5** and **14** (*cf* also the behavior of **19**, *vide infra*) was not forseen, but may be explained by the stronger electron withdrawing capacity of the tetrachlorobenzene system in **5**, compared to that of the di-t-butylbenzene system in **14**. In **5**, the aryloxy-carbon bond may cleave in a $S_N1$-type fashion; after the negative charge on oxygen is neutralized by protonation, the reaction will proceed via **12** as described (Scheme 2). In contrast, the reaction of **14** is initiated by protonation at phosphorus which is more basic in **14** than in **5**.

Following the trend of decreasing reactivity[12], **4** was the least reactive of the three orthoquinones investigated. The reaction hardly proceeded at room temperature; in boiling benzene, it was completed within a few minutes under formation of **19** (90%). No 1:2 adduct was observed in this case. **19** was fully characterized by its spectral data (Experimental) and by oxidation with hydrogen peroxide in acetone to **20** (Scheme 6). The acid-catalyzed reaction of **19** ($H_2SO_4/H_2O$/THF) gave two compounds **21** (30%: $\delta$ ($^{31}P$) = 57.0 ppm) and **22** (70%, $\delta(^{31}P)$ = 33.4 ppm) which, although not fully characterized (Experimental) appear to indicate a double pathway reflecting an intermediate behavior of **19** compared to **5** and **14**: **5** yields **8** (corresponding to **21**), and **14** yields **17** (corresponding to **22**). Qualitatively, one would indeed expect that the electron withdrawing power of the phenanthrene moiety in **19** is intermediate between that of the tetrachlorobenzene moiety of **5** and that of the di-t-butylbenzene moiety in **14**.

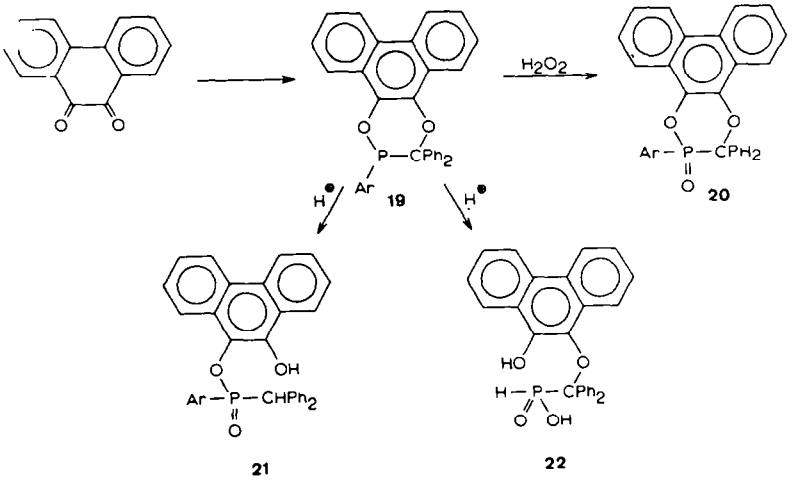



Scheme 5.

In an attempt to correlate the reactivity of **1** with that of trimethylphosphite, the two compounds were reacted with **4** in boiling benzene in a competition experiment, the molar ratio being 1:1:1. After a few minutes, the reaction was complete. The mixture was analyzed by NMR spectroscopy. The ratio of **19** to the pentaoxyphosphorane adduct derived from trimethylphosphite was 5.5:1, showing **1** to be more reactive towards **4** than trimethylphosphite.

## CONCLUSION

Formally, the reaction of **1** with the three orthoquinones leads to the 1:1 adducts **5**, **14** and **19** in a [2+4] addition which might proceed in a symmetry-allowed, concerted fashion analogous to the Diels–Alder reaction. However, we feel that a multistep mechanism is more likely for several reasons. In the first place, phosphaalkenes have so far not proven to be particularly reactive dienophiles in attempted Diels–Alder reactions with a variety of dienes.[3] On the other hand, it has been shown that formal Diels–Alder adducts from orthoquinones and furans are formed by a two-step, ionic mechanism.[13] Finally, the lone pair at phosphorus has been calculated to be the HOMO.[14] We therefore propose that the first stages of the reaction resembles those postulated for the reaction of tertiary phosphines (or phosphites) with orthoquinones. For these addition reactions, two mechanisms have been discussed. Ogata *et al.*[15] postulate primary nucleophilic attack of phosphorus on a carbonyl C atom of the orthoquinone **23** to give **24**, which subsequently rearranges to the zwitterionic intermediate **28**. Alternatively, Buck *et al.*[16] proposed a

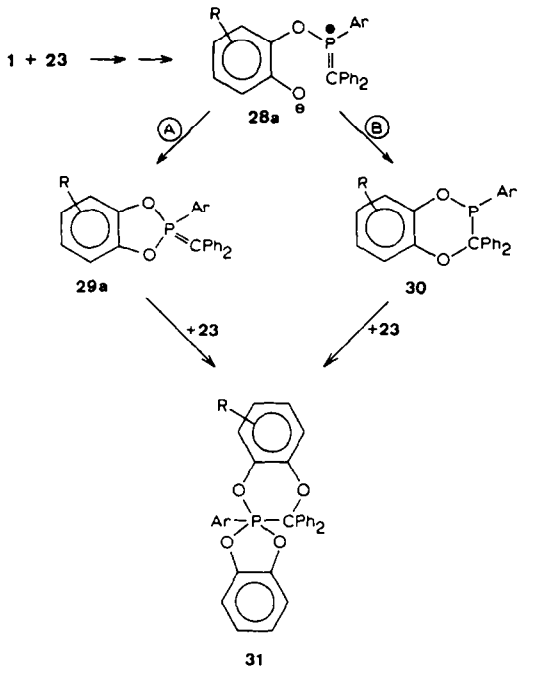



Scheme 6.

single electron transfer producing the semiquinone anion **25** and the cation radical **26**; **26** adds to **23**, and the cation radical **27** is reduced by **25** to **28**, at which point the two mechanisms merge. Intermediate **28** closes ring at phosphorus under formation of the (dioxy)phosphorane **29** (Scheme 7).

Contrary to **28**, the corresponding intermediate **28a** (Scheme 8) has two options: pathway A involving ring closure at phosphorus to form the phosphorane **29a**, or pathway B involving ring closure at carbon to form the cyclic phosphinites **30** (e.g. **5**, **14** and **19**). Both **29a** and **30** can add a second molecule of orthoquinone **23** to form trioxyphosphoranes of type **31** (e.g. **6** and **15**). In our reactions, only compounds of type **30** and **31**, but not of type **29a** were encountered. Moreover, **29a** is a methylenephosphorane; this class of compounds reacts with quinones to give Wittig-reactions which may or may not be followed by consecutive reactions.[17] Products of such reactions were not observed in our case. Thus we conclude that pathway B is the only one actually occuring.

Our results do not permit a clear distinction between the nucleophilic and the electron transfer mechanism in the first stage (Scheme 7). An indication in favour of the electron transfer pathway may be derived from the reaction of **1** with **3**, in which the two stereoisomeric 1:1 adducts **14a** and **14b** are formed in a ratio of approx. 5:1; this corresponds with a difference in transition state free energy of about 1 kcal/mol. Both mechanisms would, on steric reasons, predict preferential attack at the CO group 1 of **3**, under formation of **32a** and **33a**, respectively (Scheme 9): both would eventually furnish **14a**. For this reason, the structure of **14a** was assigned to the major isomer (*vide supra*).. However, the effect of the neighbouring t-Bu group in **32b** would be expected to be quite unfavorable compared to the relatively unhindered **32a**; a similar preference of C atom 1 was observed in other additions reactions of **3**.[18] Thus, if this mechanism were operating, a product ratio of $\gg 5:1$ should apply. For **33b** and **33a**, the energy difference must be less dramatic and may easily explain the observed ratio of **14a**:**14b**. We therefore feel that our results slightly favour the electron transfer mechanism for **1**.




Scheme 8.

## EXPERIMENTAL

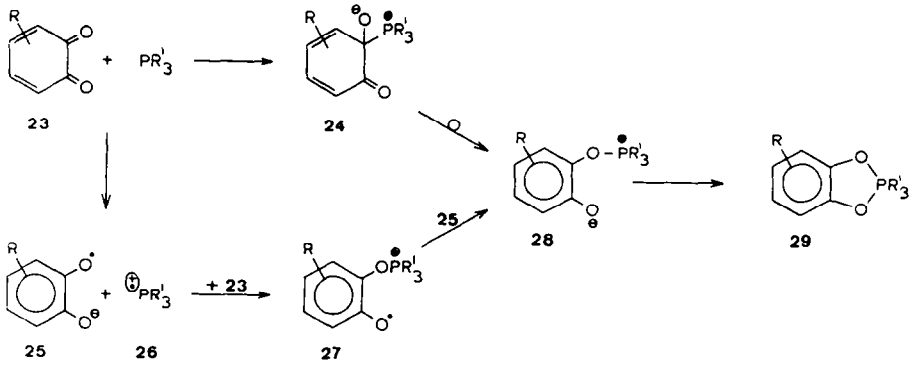
NMR spectra were recorded on a Burker WH-90 or a WM-250 spectrometer. Mass spectra were recorded on a Varian CH5DF (EI) or a Varian MAT 771 (Field Desorption). Reactions of **1** were performed under argon or $N_2$. M.p. are uncorrected. Elemental analyses were performed by Organisch Chemisch Instituut TNO, Zeist.

*Reaction of 2,6-dimethylphenyl(diphenylmethylene)phosphine(**1**) with 1 equivalent of tetrachloro-o-quinone (**2**)*

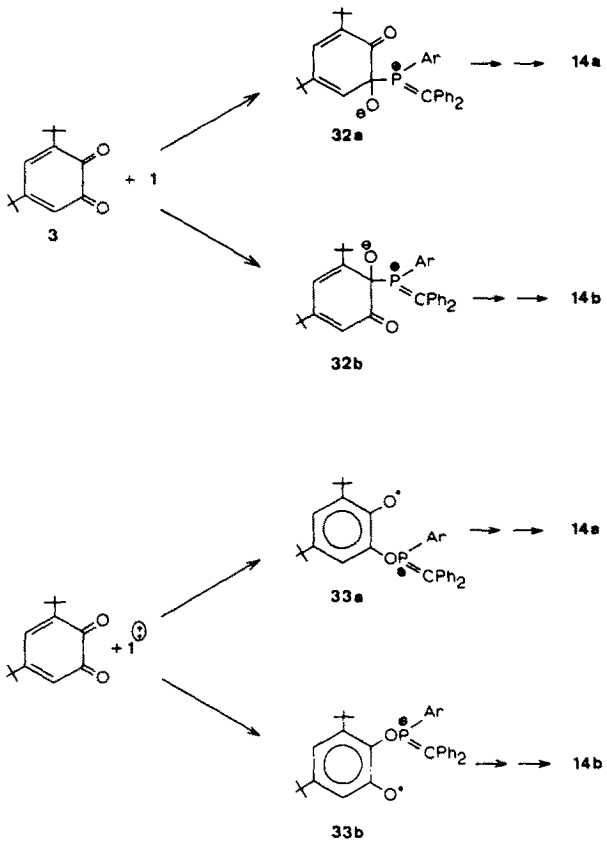
Compound **1** (136 mg, 0.45 mmol) was dissolved in benzene (2 ml) and a soln of **2** (110 mg, 0.45 mmol) in benzene (2 mL) was added under intensive stirring. The typical red colour of the quinone disappeared instantaneously on mixing; evaporation yielded a white foamy residue. A $^{31}P$ NMR spectrum of this residue indicated the presence of **5** (68%), **6** (23%) and some minor products. Then the NMR solution was exposed to air for 24 hr. MeOH (2 mL) was added and the soln was heated to reflux, and $CHCl_3$ was added until the residue had completely dissolved. After cooling to toom temp., crystals of **6** separated (49.9 mg, 14%), m.p. 226–230°.

Partial evaporation of the mother liquor yielded crystals of **8** (92.0 mg, 36%), m.p. 155–178°. One crystallization from MeOH/$CHCl_3$ raised the m.p. to 187–189°. $^1H$ NMR ($CDCl_3$): $\delta = 2.58$ (d, $^4J_{PH} = 1$ Hz, 6H, o-$CH_3$), 4.87 (d, $^2J_{PH} = 15$ Hz, 1H, methine H), 6.91–7.40 (m, 11H, aryl H), 7.51–7.69 (m, 2H, aryl H) 10.7 ppm (d, $^5J_{PH} = < 0.5$ Hz 1H, OH). $^{31}P$ NMR ($CDCl_3$): $\delta = 57.0$ ppm. (Found: C, 57.17; H, 3.72; Cl, 25.21; P, 5.41. $C_{27}H_{21}Cl_4O_3P$ (M = 566.21) requires: C, 57.17; H, 3.74; Cl, 25.04; P, 5.47%).

In a separate experiment the reaction residue (obtained from **1** (162.5 mg, 0.54 mmol) and **2**'(130 mg, 0.53 mmol)) was dissolved




Scheme 7.




Scheme 9.

in acetone, whereupon **5** crystallized (155.5 mg, 54%), m.p. 157–159°. A second fraction could be obtained (33.8 mg), m.p. 185–227°, which consisted of 40% **5** and 60% **6** according to a $^1$H NMR spectrum. One crystallization from acetone raised the m.p. of **5** to 163–164°. $^1$H NMR ($CDCl_3$): $\delta$ = 1.99 (d, $^4J_{PH}$ = 2.4 Hz, 6H, o-$CH_3$), 6.80–7.44 (m, 11H, aryl H), 7.79–7.95 ppm (m, 2H, aryl H). $^{31}$P NMR ($CDCl_3$): $\delta$ = 129.6 ppm. Mass spectrum *m/z* (%): 550(4) $[C_{27}H_{19}{}^{37}Cl_2{}^{35}Cl_2O_2]^+$, 548(10) $[C_{27}H_{19}{}^{37}Cl{}^{35}Cl_3O_2P]^+$, 546(7) $[C_{27}H_{19}{}^{35}Cl_4O_4P]^+$, 381(8) $[M-\phi_2CH]^+$, 167(100) $[\phi_2CH]^+$; $[C_{27}H_{19}{}^{35}Cl_4O_2P]^+$. Calcd.: 545.9877. Found: 545.9870. (Found C, 59.10; H, 3.57; Cl, 25.48; P, 5.59. $C_{27}H_{19}Cl_4O_2P$ (M = 548.19), requires: C, 59.15; H, 3.49; Cl, 25.87; P, 5.65%.)

*Reaction of* **1** *with* 2 *equivalents of* **2**

Compound **1** (138 mg, 0.457 mmol) was dissolved in benzene (1 mL). **2** (225 mg, 0.918 mmol), dissolved in benzene (1 mL), was added dropwise; the red colour of **2** disappeared on mixing. A $^1$H NMR spectrum showed broad signals of **6** and unidentified signals accounting for less than 10% of the material. After evaporation and crystallization from MeOH/$CHCl_3$, colourless crystals of **6** (190 mg) m.p. 226.5–228° could be obtained. Partial evaporation gave a second fraction, m.p. 223.5–225° (74 mg; total yield 73%). $^1$H NMR (toluene, $d_8$, broad signals): $\delta$ = 2.58 (s, 3H, o-$CH_3$), 2.95 (s, 3H, o-$CH_3$), 6.50–7.10 (m, 11H, aryl H), 7.32–7.52 (m, 1H, aryl H), 7.76–8.10 ppm (m, 1H, aryl H). $^{13}$C NMR of one isomer at −20° ($CDCl_3$): $\delta$ = 23.0 (d, $^3J_{PC}$ = 4 Hz, o-$CH_3$), 27.1 (d, $^3J_{PC}$ = 6 Hz, o-$CH_3$), 97.8 ppm (d, $^1J_{PC}$ = 133 Hz, $CPh_2$). $^{31}$P NMR ($CDCl_3$, broad signals): $\delta$ = −2.1 (18%), −17.3 ppm (82%). Mass spectrum *m/z* (%): 794(15) $[C_{33}H_{19}{}^{37}Cl_2{}^{35}Cl_6O_4P]^+$ with isotope pattern expected for **8**$^+$, 575(60), 377(39), 167(100) $[Ph_2CH]^+$. (Found C, 49.51; H, 2.52; Cl, 35.81; P, 4.03. $C_{33}H_{19}Cl_8O_4P$ (M = 794.05) requires: C, 49.91; H, 2.41; Cl, 35.72; P, 3.90%.)

*2-Hydroxy-3,4,5,6-tetrachlorophenyl 2,6-dimethylphenyl(diphenylmethyl)phosphinate* (**8**)

Compound **9**[8] (149 mg, 0.47 mmol) was dissolved in benzene (4 mL) and **2** (114.5 mg, 0.47 mmol) was added. The soln was heated for 1 min. According to the $^1$H NMR spectrum of a sample, 44% of **8** (determined by the integral of the o-Me signal) was present; **9** was completely consumed. The soln was evaporated, and the residue dissolved in MeOH; **8** crystallized (73.1 mg, 28%) m.p. 184–188.5°. $^1$H NMR and $^{31}$P NMR spectra were identical with those of **8** from the reaction of **5** and air (*vide supra*).

*Reaction of* **5** *with* $H_2O_2$

Compound **5** (obtained from the reaction of 86 mg **1** with 63 mg **2**, *vide supra*) was dissolved in acetone (5 mL), and 30% aqueous $H_2O_2$ (200 $\mu$L) was added dropwise. After evaporation, the solid residue was dissolved in $CHCl_3$/water. The organic layer was dried with $CaCl_2$ and evaporated. The residue was crystallized from MeOH/$CHCl_3$ yielding **7** (61.9 mg, 42%) m.p. 230–250°. Three additional crystallizations raised the m.p. to 253.5–255°. $^1$H NMR ($CDCl_3$): $\delta$ = 2.09 (d, $^4J_{PH}$ = 1.5 Hz, 6H, o-$CH_3$) 6.82–7.38 (m, 11H, aryl H), 7.82–7.98 ppm (m, 2H, aryl H). $^{31}$P NMR ($CDCl_3$): $\delta$ = 34.9 ppm. (Found: C, 57.34; H, 3.44; Cl, 25.16; P, 5.67. $C_{27}H_{19}Cl_4O_3P$ (M = 564.19) requires: C, 57.48; H, 3.39; Cl, 25.13; P, 5.49%.)

*Reaction of* **5** *with* $O_2$

Compound **5** (29.4 mg, 0.54 mmol) was dissolved in benzene (3 mL) under an atmosphere of dry $O_2$. After heating at 80° for 2 hr, a $^1$H NMR spectrum showed unchanged **5**, a trace of **7** and broad signals from unidentified material. Therefore the reaction was continued at room temp. for 72 hr. A $^1$H and $^{31}$P NMR spectrum showed that **5** had completely disappeared, and **7** was formed in about 50% yield.

*Reaction of* **5** *with water and* $H_2SO_4$

Under argon, **5** (110 mg of a mixture prepared from **1** (149.5 mg, 0.495 mmol) and **2** (110 mg, 0.447 mmol)) was dissolved in THF (4 mL) and water (300 μL) was added. After 19 hr a $^1H$ NMR spectrum showed unchanged **5** and **1**. Then $H_2SO_4$ (50 μL 2N $H_2SO_4$, 0.1 mmol) was added. After 24 hr at room temp., no reaction could be observed by $^1H$ NMR. Then the mixture was boiled for 3.5 hr. After evaporation, $^1H$ and $^{31}P$ NMR spectroscopy showed that a mixture of **5** and **8** (1:2) was formed.

*Reaction of* **1** *with* 1 *equivalent of* **3**

Compound **1** (91 mg, 0.30 mmol) was dissolved in benzene (2 mL). Then **3** (69 mg, 0.30 mmol) dissolved in benzene (2 mL) was added dropwise at room temp. under vigorous stirring. Initially, the red colour of **3** disappeared within 5 s, while after complete addition of **3** the colour remained for about 15 min. A $^{31}P$ NMR spectrum showed signals of **14a** (63%), **14b** (13%), **15** (6%) besides small signals of unidentified products. $^1H$ NMR ($CDCl_3$): (**14a**) δ = 1.22 (s, 9H, t-Bu), 1.36 (s, 9H, t-Bu), 1.98 (d, $^4J_{PH}$ = 2 Hz, 6H, o-$CH_3$), 6.67–7.46 (m, 13H, aryl H), 7.64–7.87 ppm (m, 2H, aryl H). $^{31}P$ NMR ($CDCl_3$): δ = 130.7 (**14b**), 127.5 (**14a**), −6.4 ppm (**15**). Mass spectrum *m/z* (%): 522 (100) [14]$^+$, 431 (22) $[M-C_7H_7]^+$, 373 (23), 355 (35), $[M-Ph_2CH]^+$ 167 (51) $[Ph_2CH]^+$ $C_{35}H_{39}O_2P^+$. Calc 522.2687. Found: 522.2653. Then the mixture was evaporated and dissolved in acetone (5 mL): 30% aqueous $H_2O_2$ (50 μL) was added, the solvent evaporated and the residue extracted with $CHCl_3$/water. The organic layer was dried with $CaCl_2$ and evaporated. Attempted crystallization from EtOH/water gave an oil which solidified on standing, yielding 102 mg **16a** + **16b** (63%) m.p. 108–140°. $^1H$ NMR ($CDCl_3$): (**16a**) δ = 1.20 (s, 9H, t-Bu) 1.28 (s, 9H, t-Bu) 2.27 (d, $^4J_{PH}$ = 1 Hz, 6H, o-$CH_3$) 6.64–7.69 ppm (m, 15H, aryl H). $^{31}P$ NMR ($CDCl_3$): δ = 38.3 (**16b**, 20%) 36.2 (**16a**, 80%). Mass spectrum *m/z* (%): 538 (21) $[M]^+$ 356 (100) $[M-Ph_2C=O]^+$ 341 (20) 224 (15) 167 (33) $[Ph_2CH]^+$ $C_{35}H_{39}O_2P^+$. Calc 538.2586. Found: 538.2590.

*Reaction of* **1** *with* 2 *equivalents of* **3**

Compound **1** (136 mg, 0.45 mmol) was dissolved in benzene (4 mL) and heated to 80°. Subsequently **3** (207 mg, 0.90 mmol), dissolved in benzene (5 mL), was added dropwise. The mixture was evaporated and the residue crystallized from MeOH/$CHCl_3$. A mixture of crystals of **15a** and **15b** was obtained; (223 mg), m.p. 232–233.5°; recrystallization did not raise the m.p. A second fraction (54 mg, total yield 83%), m.p. 225–229°, crystallized after partial evaporation of the mother liquor. $^1H$ NMR ($CDCl_3$): (**15a**, broad signals) δ = 1.06 (s, 9H, t-Bu-H), 1.13 (s, 18H, t-Bu-H), 1.33 (s, 9H, t-Bu-H), 2.19 (s, 6H, o-$CH_3$), 5.93 (s, 1H, aryl H of catechol moiety), 6.41 (s, 1H, aryl H of catechol moiety), 6.51–7.38 (m, 13H, aryl H), 8.04 ppm (s, 2H, aryl H). $^{31}P$ NMR ($CDCl_3$): (broad signals) δ = −6.4 (75%, **15a**), −28.4 ppm (25%, **15b**). (Found: C, 77.93; H, 7.84; P, 4.09. $C_{49}H_{69}O_4P$ (M=742.93) requires: C, 79.21; H, 8.00; P, 4.17%.)

*Reaction of* **14** *with* $H_2SO_4/H_2O$

Compound **14** as obtained from **1** (142 mg, 0.47 mmol) and **3** (93 mg, 0.42 mmol) was dissolved in THF (3 mL). Then 2 N $H_2SO_4$ was added (100 μl, 0.2 meq) and the soln was heated to 65°. After cooling to room temp. the soln was neutralized with $NaHCO_3$, filtered and evaporated. The residue was dissolved in EtOH and a ppt (4.5 mg) was filtered off. After partial evaporation and addition of water, crystals of **17** were obtained (87.0 mg, 41%, relative to **1**) m.p. 150–160°. 2 Crystallizations from boiling aqueous EtOH did not raise the purity of **17** due to slight decomposition (yellow colour). $^1H$ NMR ($CDCl_3$): δ = 0.98 (s, 9H, o-t-Bu), 1.31 (s, *p*-t-Bu, 9H), 5.88 (d, $^4J_{HH}$ = 2 Hz, 1H, H(4) of the 3,5-di-t-butylcatechol moiety), 6.71 (d, $^4J_{HH}$ = 2 Hz, 1H, H(6) of the 3,5-di-t-butylcatechol moiety), 7.02–7.24 (m, 6H, aryl H), 7.40–7.57 (m, 4H, aryl H), 8.10 (d, $^1J_{PH}$ = 483 Hz, PH), 8.55 ppm (s, 1H, phenolic OH). $^{31}P$ NMR ($CDCl_3$): δ = 32.6 ppm (d, $^1J_{PH}$ = 485 ± 1 Hz. Mass spectrum (FD): *m/z*: 386 $[17-H_2O_2P]^+$.

*Reaction of* **1** *with* **4**

Compound **1** (149 mg, 0.49 mmol) was dissolved in benzene (2 mL), **4** was partially dissolved and partially suspended in benzene (3 mL) and added dropwise at 80°. After addition, a residual brown colour of **4** remained. Subsequently, the solvent was evaporated and the residue was dissolved in acetone (1 mL). After 10 min crystals of **19** appeared (143.4 mg, 57%), m.p.: 166–169°. The supernatant liquid contained another 33% of **19**, according to a $^1H$ NMR spectrum (total yield 90%).$^1H$ NMR ($CDCl_3$): δ = 2.00 (d, $^4J_{PH}$ = 2 Hz, 6H, o-$CH_3$), 6.67–6.87 (m, 2H, aryl H), 6.93–7.09 (m, 9H, aryl H), 7.42–7.69 (m, 4H, aryl H), 7.82–8.02 (m, 2H, aryl H), 8.40–8.42 (m, 2H, aryl H), 8.42–8.67 ppm (m, 2H, aryl H). $^{31}P$ NMR ($CDCl_3$): δ = 125.8 ppm. $^{13}C$ NMR ($CDCl_3$): δ = 21.9 (d, $^3J_{PC}$ = 21 Hz, o-$CH_3$), 87.5 (d, $^1J_{PC}$ = 42 Hz, $Ph_2\underline{C}$–O), 121.1–103.3 (m, aryl C), 140.2 (d, $^3J_{PC}$ = 5 Hz, P–O–C–$\underline{C}$–O), 142.5 (d, $^2J_{PC}$ = 19 Hz, P–O–$\underline{C}$) (possibly, the assignment for 140.2 and 142.5 ppm must be reversed), 143.0 ppm (d, $^3J_{PC}$ = 20 Hz, 2 × P–C–$\underline{C}$–$CH_3$). Mass spectrum *m/z* (%): 510 (100), $M^+$, 419 (22), 360 (20), 344 (23) $[M-Ph_2C]^+$, 343 (54) $[M-Ph_2CH]^+$, 167 (59), $Ph_2CH^+$·$C_{35}H_{27}O_2P^+$. Calc 510.1748 Found: 510.1724. (Found: C, 81.77; H, 5.53; P, 5.81. $C_{35}H_{27}O_2P$ (M=510.54) requires: C, 82.34; H, 5.33; P, 6.07%.)

*Reaction of* **19** *with* $H_2O_2$

Compound **19** (343 mg, 0.67 mmol) was dissolved in acetone (5 mL) and $H_2O_2$ (200 μL, 30% $H_2O_2$) was added dropwise. The soln was heated to reflux and then evaporated. Crystallization from MeOH/$CHCl_3$ gave **20** (134 mg, 38%), m.p. 245–250°. 3 Crystallizations raised the m.p. to 259–260.5°. $^1H$ NMR ($CDCl_3$): δ = 2.16 (s, 6H, o-$CH_3$), 6.72–8.72 ppm (m, 21H, aryl H). $^{31}P$ NMR ($CDCl_3$): δ = 35.6 ppm. (Found: C, 79.19; H, 5.30; p, 5.79. $C_{35}H_{27}O_3P$ (M=526.54) requires: C, 79.83; H, 5.17; P, 5.88%.)

*Reaction of* **19** *with* $H_2SO_4/H_2O$

Compound **19** (88 mg, 0.215 mmol) was dissolved in THF (4 mL) and 2 N $H_2SO_4$ (50 μL, 0.1 meq.) was added. After heating under reflux for 2.5 hr, the soln was neutralized with $NaHCO_3$, filtered and evaporated. The residue was dissolved in $CDCl_3$ and NMR spectra were recorded. $^1H$ NMR ($CDCl_3$, aromatic signals omitted )**22**, δ = 8.16 (d, $^1J_{PH}$ = 487 Hz, 1H, P–H), 12.35 (brs, Ph–OH + P–OH ; **21**, 2.57 (s, 6H, o-$CH_3$), 4.87 ppm (d, $^2J_{PH}$ = 15 Hz, 1H, PH). $^{31}P$ NMR: δ = 33.4 (d, $^1J_{PH}$ = 496 Hz, **22**, 70%) 57.0 ppm (d, $J_{PH}$ = 16 Hz, **21**, 30%).

*Reaction of* **4** *with* **1** *and trimethyl phosphite in a ratio* 1:1:1

Compound **1** (50 mg, 0.17 mmol) and trimethyl phosphite (21 mg, 0.17 mmol) were dissolved in benzene (4 mL). **4** (35 mg, 0.17 mmol) was added at 80° under stirring. After 1 min the decrease of the brown colour of **4** indicated at the end of the reaction. The mixture was evaporated to dryness, and $^1H$ and $^{31}P$ NMR spectra ($CDCl_3$) were recorded. From the integrals of the o-Me protons of **19** (δ = 2.00) and of the OMe protons of trimethoxy-9,10-phenanthrylenedioxylphosphorane (δ = 3.82), a ratio of 5.5:1 was determined. Integration of the $^{31}P$ NMR signals (δ = 125.9 and −44.0, respectively) gave a ratio of 9:1. As the $^1H$ NMR signal is less subject to relaxation effects, the ratio of 5.5:1 is considered to be more reliable.

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