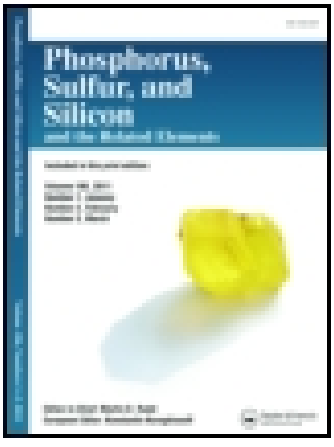

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REACTIONS OF ASYMMETRICALLY SUBSTITUTED O-QUINONES: 3,5-DI-TERT-BUTYL-1,2-BENZOQUINONE WITH TRIPHENYL-PHOSPHINE, -ARSINE, -STIBINE, THEIR OXIDES AND TRIALKYL PHOSPHATES

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REACTIONS OF ASYMMETRICALLY SUBSTITUTED O-QUINONES: 3,5-DI-TERT-BUTYL-1,2-BENZOQUINONE WITH TRIPHENYL-PHOSPHINE, -ARSINE, -STIBINE, THEIR OXIDES AND TRIALKYL PHOSPHATES

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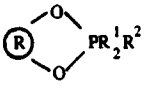
(Received 2 July, 1996; In final form 25 January, 1997)

The entitled quinone **4** reacts with triphenylphosphine **(3a)** and triphenylarsine **(3b)** to give the cyclic products **12a** and **12b,** respectively. The same quinone reacts with triphenylstibine **(3c)** to yield the stibine-methylene **17.** The reaction of oxides of **3a-c (5a-c)** and trialkyl phosphates **6a-c** with the same quinone **4** affords hydrogen bonded complexes **13a-c** and o-quinol monophosphates **23a-c,** respectively. In both cases compound **22** is the other product. Possible reaction mechanisms are proposed to explain the formation of the new adducts.

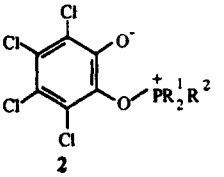
Keywords: Asymmetrically o-quinones; (dioxy)phosphorane; (dioxy)arsinane; stibine- methylene; hydrogen-bonded formulation; aryl dealkylation

INTRODUCTION

Previous work has established[1-5] that tertiary phosphines react with o-quinones to yield either (dioxy)-phospholene **1** or an open-dipolar structure **2.**



1, R = C_6H_4, $C_{10}H_6$, Phenanthrene



2

1, 2 R^1, R^2 = alkyl, aryl

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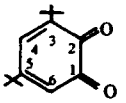
As part of our extended study[6-9] of the behavior of asymmetrically substituted o- quinones, specifically, 3,5-di-tert-butyl-1,2-benzoquinone **(4)** toward different nucleophilic phosphorus reagents, in the current paper we have investigated the reaction of triphenylphosphine (TPP, **3a)** and **4.** Since arsenic and antimony are present like phosphorus in the 15th group of the periodic table, a comparative study of the reactivity of compound **4** toward triphenylarsine (TPAs, **3b)** and triphenylstibine (TPSb, **3c)** was undertaken. Moreover, the action of their oxides **5a-c** as well as some trialkyl phosphates of type **6a, 6b** and **6c** on **4** has, also, been reported.

$(C_6H_5)_3X$
3a, X = P
3b, X = As
3c, X = Sb



4

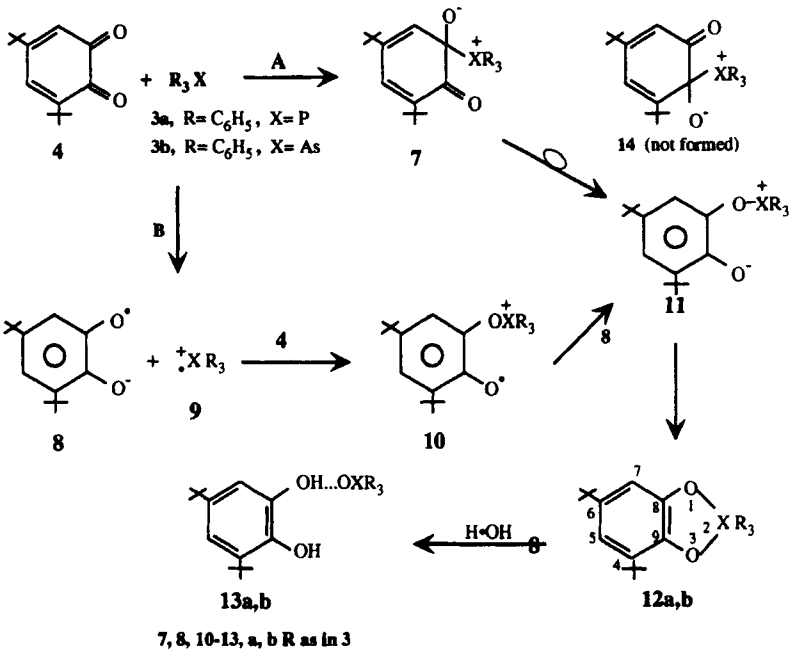
$(C_6H_5)_3X = O$
5ac
,X as in **3**

$O = P(OR)_3$
6a, R = CH_3
6b, R = C_2H_5
6c, R = Bu-.t

RESULTS AND DISCUSSION

I. *Action of 3a-c on* 4

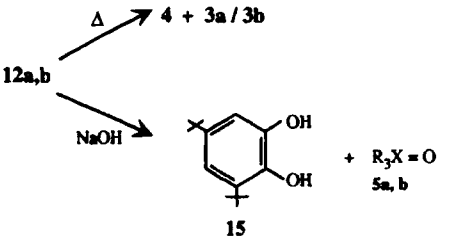
When a solution of one equivalent of 3,5-di-tert-butyl-1,2-benzoquinone **(4)** in dry dioxane (no reaction was observed in anhydrous benzene) was added to that of triphenylphosphine **(3a),** the reaction was completed at room temperature after 24 h as judged from the disappearance of the green color of the o-quinone. The product was isolated in 82% yield and formulated as 2,2,2-triphenyl-1,3,2-dioxaphospholene **(12a)** (Scheme 1). The (dioxy)phosphorane **12a** is moderately stable, only for few days, toward atmospheric moisture and its spectral data vary considerably according to the sample history. The ^{31}p NMR spectrum of freshly prepared sample of **12a** showed a single resonance at δp -15.8 ppm which is that expected of a ring (dioxy)phosphorane structure **12a**.[4,10] Its ^{1}H.NMR spectrum revealed the protons of the tert-butyl groups as two singlets at 1.3 (9H) and 1.44 (9H) and the aromatic protons in the 6.8-7.8 ppm region. The IR and the ^{13}C NMR spectra lack any absorption of a carbonyl group. In the ^{13}C NMR[11,12] spectrum of **12a**, signals were absorbed at: δ 31.6 and 32.3 [-$C(CH_3)$], 35.13 and 35.57 (C-CH_3). The dioxaphospholene ring was attested by the presence of signals at 143.47 and 144.35 [P-O- **C** (aryl)] in its ^{13}C NMR spectrum. Its mass spectrum yielded a prominent ion peak at m/ z= 482 (M^+, 23%). Suplementary evidence for the assigned structure **12a** has been gained from degradative experiments. The quinone-triphenylphosphine adduct **12a,** read- ily, dissociates into its original components **(4 + 3a)** at 260 °C and 0.2 mm/Hg. The regeneration of the



SCHEME 1

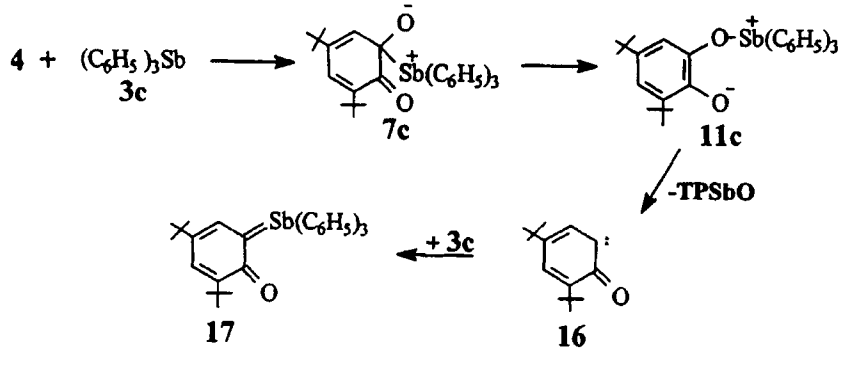
starting quinone **4** upon the pyrolysis of **12a** is in agreement with what is known regarding the facile elimination of phosphorus from cyclic compounds.[13] Hydrolysis of **12a** with aqueous sodium hydroxide solution afforded 3,5-di-tert-butyl-pyrocatechol **(15)** and triphenylphosphine oxide **(5a)** (Scheme 2). Treatment of **12a** with water, yielded brown substance assigned **13a** (Scheme 1). Adduct **13a** possessed a hydrogen-bonded structure since it exhibited a postive shift in its ^{31}P NMR spectrum at δ 17.4 ppm. Other spectral data are fully in accord with the proposed structure (see experimental).

In the same way, 3,5-di-tert-butyl-1,2-benzoquinone **(4)** reacts with triphenylarsine **(3b)** in dry dioxane at reflux temperature to give the first reported 1,3,2-benzodioxarsole structure **12b** (Scheme 1). This adduct is a colorless crystalline substance with a sharp melting point and is remarkably stable. Upon thermolysis, the (dioxy)arsinane **12b** regenerates the quinone **4** and triphenylarsine **(3b)** (Scheme 2). Spectral investigations for **12b** were also performed and by analogy with the product **12a,** the data were in agreement with the assigned structure. Its IR spectrum, for example, revealed the absence of absorption in the 1400-1480 cm^{-1} region (enolate) and in the 1660-1700 cm^{-1} region (carbonyl).



SCHEME 2

On the other hand, when quinone **4** was allowed to react with two moles of triphenylstibine (**3c**) in dioxane, triphenylstibine[3,5-di-tert-butyl-2-oxo-benzylidene(1)] (**17**) and triphenylstibine oxide (**5c**) were the reaction products (Scheme 3). Carrying out the reaction using equimolar amounts of **4** and **3c** led to the isolation of **17, 5c** and unchanged quinone. The structure of the stiboranylidene **17** has been elucidated as follows: the microanalysis of **17** corresponds to an empirical formula of $C_{32}H_{35}OSb$. Strong bands at 1240 (Sb=C, aryl.), 1437, 1010 (Sb-C, aryl)[11] and at 1670 cm^{-1} (C – 2 = O)[14] are the distinguishing features of its IR spectrum. Structure **17** was, also, attested by signals at 178.5 and 158.83 ppm in its ^{13}C NMR spectrum attributed to the aryl-carbonyl group[14] and the stibine-methylene linkage, respectively. Meanwhile, the tert-butyl groups appeared as two singlets at 1.33 (9H) and 1.43 (9H)[14] in the ^{1}H NMR spectrum and were observed in its ^{13}C NMR spectrum at 31.84, 32.15 [-C-$(CH_3)_3$] and 34.3, 35.82 [**C**-$(CH_3)_3$].[12]The mass spectrum of **17** exhibits a prominent-ion peak at m/z= 557 (M^+, 10%). Moreover, fusion of the stiboranylidene **17** with sulfur afforded triphenylstibine sulfide. There seems to be great tendency for triphenylstibine to form stibine-methylenes with ortho[15] and para-quinones.[16]



SCHEME 3

Formally, the reaction of **4** with **3a,b** leads to the 1:1 addition outcome **12a** and **12b**, while it reacts with **3c** to give the substituted product **17.** We, therefore, propose the first stages of the reaction resembles those postulated for the reaction of tertiary phosphines (or phosphites) with o-quinones. For these reactions, two mechanisms have been discussed (Scheme 1). Ogata et al[1] postulated primary nucleophilic attack of phosphorus in phosphines on the carbonyl-C atom of the o-quinone **4** to give **7** (route **A**) which subsequently rearranges to the zwitterionic intermediate **11.** Alternatively, Buck et al[2] proposed a single electron transfer producing the semiquinone anion **8,** and the cation radical **9** (route **B**). **9** adds to **4**, and the cation radical **10** is reduced by **8** to **11**, at which point the two mechanisms merge. The intermediate **11** closes ring at the heteroatom (P or As)) under formation of the (dioxy)phosphorane **12a** or (dioxy)arsinane **12b.**

Considering the reaction of **4** and **3c,** contrary to **11,** the corresponding **11c** (Scheme 3) collapses to form triphenylstibine oxide **(5c)** and the carbene **16** which could be trapped by another molecule of **3c** to furnish the stibine-methylene **17.** Obviously, the intermediates corresponding to **7c** or **11c** (X = Sb) should not be long lived due to the increase of the size of the electron clouds and no product comparable to **12a,b** should be expected. Moreover, the basicity of antimony, i.e. the weakening of non-metallic character as being in the order P< As<Sb series,[17] also, evoked the collapse of **11c** and formation of **17.**

Even though our results do not permit a clear distinction between the nucleophilic and the electron transfer mechanism in the first stage (Scheme 1), an indication in favor of the nucleophilic pathway may be derived from the reaction of **4** and **3c,** in which the triphenylstibine oxide is formed and can be interpreted as Wittig type process. Therefore, our results slightly favor the nucleophilic mechanism for **3a-c.** Moreover, both mechanisms would on steric reasons, predict preferential attack at the C_1=O group in **4,** under formation of **7** or **8,** respectively. The effect of the neighbouring t-Bu group in **14** would be expected to be quite unfavorable compared to the relatively unhindered **7.** A similar preference of C atom 1 was observed in other substitution or addition reactions of **4.**[8,9,18]

II. *Action of* 5a-c *on* 4

The behavior of polyphenols toward derivatives of **Group 15** elements in their pentavalent state constitutes a phase of the more general problem of the interaction between electron acceptors and electron donors.[19] Thus, the sharp-melting substances of compostion [R_3PO, HX] formed upon fusion of phenols and triarylphosphine oxides have been regarded [19b] either as true quasiphosphonium compounds [$R_3P(OH)X$][5] with pentacovalent phosphorus, or as hydrogen-bonded complexes [R_3PO...HX],[20] a phosphonium hydroxide, but experi-

mental data to decide among the alternatives have been lacking. This led us to investigate the reaction of our quinone **4** with these reagents, e.g., **5a-c** and **6a-c** and to evaluate the synthetic potential of this reaction pathway.

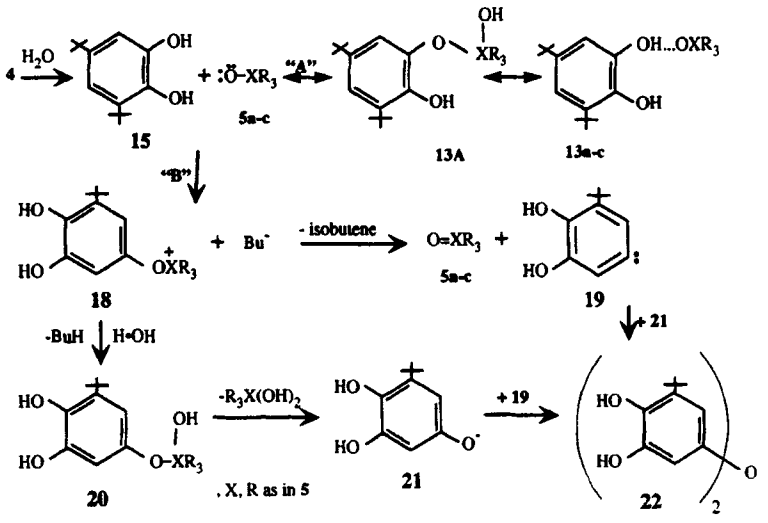
3,5-Di-tert-butyl-1,2-benzoquinone **(4)** was found to react with triphenylphosphine oxide **(5a)** in dilute methanol at reflux temperature for ~18 h to give a mixture of two main products **(A + B),** which could be separated by chromatography. The first product **(A,** 55%) was assigned the hydrogen-bonded complex **13a** from its molecular weight, IR, PMR measurements. The data are consistent with that previously ascribed *(see supra).* Moreover, both thermolysis and alkali hydrolysis of **13a** regenerated its components **(15 + 5a).** This behavior, i.e., formation of H-bonded complexes, is parallel to the reaction course of other *ortho* and *para*-quinones with triphenylphosphine oxide and trialkyl phosphates.[16,20,21]

The second product **(B,** ~ 9%) has been found to be devoid of phosphorus, as is inferred from its elemental analysis and ^{31}P NMR spectrum. It was identified as 5,5-di [3-tert-butyl-pyrocatechol] ether **(22)** for the following reasons : its elemental analysis and molecular weight determination (MS) agreed with the molecular formula ($C_{20}H_{26}O_5$). In the IR spectrum of **22** the most characteristic absorptions are bands at 1075 cm^{-1} attributed to the symmetrical C-O-C stretching (vinyl ether) and a broad band due to the hydroxyl groups at 3435 cm^{-1}. The NMR spectra showed a feature of one unit of the diaryl ether **22.** Thus, its ^1H NMR revealed the presence of one tert-butyl group at 1.32 (C_3-Bu-t). The aromatic protons gave two doublets (each with J_{HH} = 4.2 Hz) at 6.33 (C_6-H) and 6.99 (C_4-H), respectively. Moreover, the broad signal presented at 8.55 ppm (exchangeable with D_2O) accounted for two phenolic OH groups; the ^{13}C NMR spectrum showed signals at δ_c 29.35 (C-CH_3); 37.84 (**C**-CH_3), 151.4 (**C**-O-**C**, aryl), 153.6, 157.5 (OH-**C**, aryl).

The reaction products of **4** with **5b,c** were assigned analogous structures on the basis of comparable spectroscopic arguments and degradative experiments.

A rationalization for the formation of **13a-c** and **22** from the reaction of **(4+5)** is presented in Scheme 4. It starts with reduction of the quinone with traces of water to yield 3,5-di-tert-butyl-pyrocatechol **(15),** followed by addition of the oxide **5,** pathway **"A",** through hydrogen-bonding to yield the complex **13** *via* the rearrangement of the intermediate **13A.** The proposed mechanism is in accordance with the mechanisms previously reported in similar occasions.[20,21]

The diaryl ether **22,** is remarkable because it was not foreseen, but may be explained by poor reactivity of **4** toward compounds **5** compared to that quinones, previously, reported,[20,21] e.g. tetrachlorobenzoquinone toward the same reagents. In our reaction, the long time of heating (~ 18 h) allowed the phosphorylation (taken **5a** as a representative example) of the aromatic nucleus by splitting off a tert-butyl group as isobutene or tert-butane and formation of

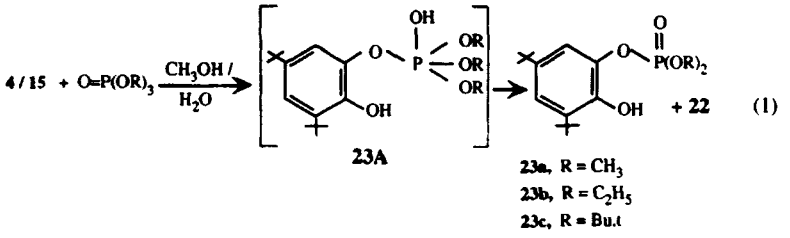


SCHEME 4

O-phosphonium form **18.** This unexpected reaction probably proceeds according to C-phosphorylation of benzoquinone with triphenylphosphine[22] or aryl phosphorylation of quinone-methides involving aryl dealkylation, as proved by Gross et al.[23]The intermediate **18** in which phosphorus can act as good leaving group decomposes to give the carbene **19** and TPPO, or reacts with water to give **20** which collapses then to the anion **21.** The negative charge on oxygen is neutralized by adding the carbene moiety, yielding the diaryl ether **22.**

III. *Action of 6a-c on 4*

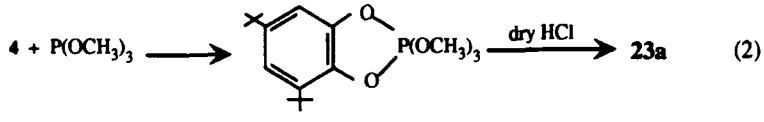
We have extended our observations to include certain phosphate esters, i.e. trimethyl-, triethyl- and tributyl (t) phosphates **(6a-c),** respectively, with the aforementioned quinone **4** under the conditions previously reported with the oxides **5.** In a systematic study, the reaction proceeds, smoothly, to lead to the formation of diaryl ether (**22,** major, ~35%) and o-quinol monophosphates (**23,** minor, ~ 15%). The latter can be viewed as in the case with the oxides, the corresponding primary addition products **23A** (eq. 1) seem to be highly instable. However, a stabilization of **23A** just by rearrangement, as in the former case (Scheme 4, route **"A")** is not possible for **23A,** instead these transient intermediates undergo partial hydrolysis to yield the o-quinol monophosphates **23.** In contrast, it was reported[20] that the reaction of phosphate esters of type **6a** or **6b** with o-benzoqui-



(1)

none or symmetrically substituted o-quinones leads to the formation of complexes with hydrogen-bonded formulation.

The structure of compound **23a** is unambigously verified, mixed m.ps. and comparative IR and MS spectra, with that prepared by partial hydrolysis of the reaction product of trimethyl phosphite and quinone **4,** (eq. 2).[8] **23b** and **23c** were established on comparable analytical and spectral grounds (experimental).



(2)

CONCLUSION

As a consequence following from the data reported above for the reactions of quinone **4** with **3, 5** and **6,** although quinone **4** reacts with triphenylphosphine **(3a)** to give (dioxy)phosphorane, as frequently observed with o-quniones,[1,2] it reacts with triphenylphosphine oxide **(5a)** and phosphate esters **6** in a manner rather different from the already known.[5,20] Thus, it reacts with **5a** to yield the diaryl ether **22** in addition to the expected hydrogen-bonded complex **13a.** While it reacts with **6** to give o-quinol monophosphates **23** and **22.** Furthermore, although this anomalous behavior, formulation of diaryl ether, is a new reaction for phosphorus - reagents of type [R_3P=O], it lends a support for the already known fact that tert-butyl group could be substituted by phosphorus reagents in substituted quinones.[23] Furthermore, the fact that greater amounts of **22** were formed in eq. 1 than in scheme 4, can be explained in terms of the poorer reactivity of trialkyl phosphates toward phosphorylation and the longer heating of the reaction than with **5a-c.**

EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer spectrophotometer model 197 (Grating) using KBr disc. ^{1}H NMR spectra were recorded with a Varian spectrometer at 90 MHz, using TMS as an internal reference. ^{31}P and ^{13}C NMR spectra were recorded with a Varian FT-80 spectrometer. ^{31}P NMR spectra were recorded relative to external H_3PO_4 (85%). ^{13}C NMR spectra were recorded relative to internal TMS. The mass spectra were performed at 70 eV on MS-50 Kratos (A.E.I.) spectrometer provided with data system. The appropriate precautions in handling moisture-senstive compounds were observed. Materials and reagents were purchased from Aldrish company.

I. *Reaction of 3,5-Di-tert-butyl-1,2-benzoquinone (4) with triphenylphosphine (3a).*

To a stirred solution of (0.2 g, 9 mmol) of the quinone **4** in 10 ml of dry dioxane at r. t. was added a solution of (0.32 g, 9 mmol) of TPP **(3a)** in the same solvent (10 ml), then it was further stirred at r. t. for 24 h. After evaporation of the solvent, *in vacuo,* the residual material was collected (0.35 g, 82%) and recrystallised from cyclohexane to give **12a** as colorless crystals, m.p. 143-145 °C Anal. Calcd. for: $C_{32}H_{35}O_2P$ (482.61), C, 79.64; H, 7.3; P, 6.42. Found: C, 79.57; H, 7.25; P, 6.3%. MS: m/z= 482 (M^+, 23%). NMR ($CDCl_3$): ^{1}H δ_H 1.3, 1.44 (18H, t-Bu, 2s); 6.8-7.8 ppm (17H, aryl-**H**, m); ^{31}P, δp: -15.8 ppm; ^{13}C, δc: 31.6, 32.6 (C-$\mathbf{C}H_3$); 35.13, 35.57 (**C**-CH_3), 143.47, 144.35 (P-O-**C**, aryl).

No reaction was observed, however, in a parallel experiment when the reactants were stirred in anhydrous benzene even after 60 h.

I. a. Action of Heat on 12a.

Dioxaphospholene **12a** (0.2 g) was heated in a cold finger sublimator at 260 °C for 30 min. under reduced pressure (10 mm/Hg). The substance that sublimed was triturated with pentane (20 ml). The pentane solution was concentrated to half its volume and cooled. The crystals that separated were filtered off and proved to be quinone **4** (50 mg, 53%). Evaporation of the filtrate and triturating the residual substance with light petroleum (40-60 °C) afforded triphenylphosphine **(3a).** The products **4** and **3a** were identified by comparison with authentic samples.

I. b. Action ofAlkali on 12a.

A mixture **of 12a** (0.2 g) and 10% NaOH aq. (30 ml) was refluxed for 2 h. After cooling, the solution was acidified with 15% HC1, then directly extracted twice

with chloroform. The combined extracts (60 ml) were dried over $CaCl_2$ (anhydrous). The solvent evaporated and the residue extracted with light petroleum (40-60 °C). The undissolved material was, then recrystallised from benzene to give colorless crystals, proved to be triphenylphosphine oxide **(5a).**

The light petroleum solution was concentrated to half its volume and cooled. The crystals that separated was collected and proved to be catechol **15** (32 mg, 35%), whose identity was established by comparison with authentic sample.

I. c. Action of Water on 12a.

Compound **12a** (0.2 g) in 25 ml benzene containing water (2 ml) was refluxed for 3 h. After evaporation of the volatile materials under reduced pressure, the oily residue was treated with acetone (8 ml), then left for 12 h, at room temperature. Recrystallisation of the resulting solid material **13a** (0.18 g, 90%) from ethyl alcohol afforded brown crystals, m.p. 229 - 231°C. Anal. Calcd. for $C_{32}H_{37}O_3P$ (500.65), C, 76.77; H, 7.45; P, 6.19. Found: C, 76.54; H, 7.32; P, 6.07% : MS: m/z = 222 (catechol, 43%) and 278 (TPPO, 100%). IR cm^{-1} (KBr): 3433 (OH), 1230 (P=O), 1090 (P-C, aryl). NMR ($CDCl_3$): ^1H δ_H 1.32, 1.45 (18 H, t-Bu, 2s); 6.8 - 7.8 (17 H, aryl-**H**, m); 8.5 (2H, **OH**, br., exchangeable with D_2O), ^{31}P, δp : 17.4 ppm.

II. *Reaction of 3,5-Di-tert-butyl-1,2-benzoquinone (4) with Triphenylarsine (3b).*

A mixture of quinone **4** (0.2 g, 9 mmol) and triphenylarsine (0.27 g, 9 mmol) in dry dioxane (25 ml) was refluxed for 3 h. After evaporating the solvent, *in vacuo,* the precipitated material (0.3 g, 68.5%), recrystallised from chloroform - ether (1:1) to give 1,3,2-benzodioxarsole **12b** as colorless crystals, m.p. 125-127.°C. Anal. Calcd. for : $C_{32}H_{35}AsO_2$ (526.55), C, 72.99; H, 6.7. found : C, 72.94; H, 5.88%. MS: m/z= 526 (M^+, 12%). NMR ($CDCl_3$): ^1H δ_H 1.31, 1.45 (18 H, t-Bu, 2s), 6.8-7.8 ppm (17H, aryl-**H**, m); ^{13}C, δc : 31.65, 33.17 (C-CH_3); 34.3, 35.7 (**C**-CH_3), 142.5, 144.6 (As-O-**C**, aryl).

II. a. Action of Heat on 12b.

(Dioxy)arsinane **12b** (0.2 g) was heated in a cold finger sublimator at 260 °C for 30 min. under reduced pressure (10 mm/Hg). Working up as described before in **I-a** yielded quinone **4** (37 mg, 45%) and triphenylarsine **(3b).** The products **4** and **3b** were identified by comparison with authentic samples.

II. b. Action ofAlkali on 12b.

A mixture of **12b** (0.2 g) and 10% NaOH aq. (30 ml) was refluxed for 2 h. Working up as described in **I-b** yielded triphenylarsine oxide **(5b)** and catechol **15** (28 mg, 33%). **5b** and **15** were identified by comparison with authentic samples.

II. c. Action of Water on 12b.

Compound **12b** (0.2 g) in 25 ml benzene containing water (2 ml) was refluxed for 3 h. working up as described above in **I-c** yielded the complex **13b** as brown crystals (0.17 g, 87%) from benzene-light petroleum (40-60 °C) m.p. 211-213 °C. Anal. Calcd. for: $C_{32}H_{37}AsO_3$ (544.57), C, 70.58; H, 6.85. Found: C, 70.42; H, 6.77%. MS: m/z= 544 (M^+, < 5%). NMR ($CDCl_3$): ^1H δ_H 1.35, 1.4 (18 H, t-Bu, 2 s); 6.8 - 7.8 ppm (17 H, aryl-**H**, m); 8.55 (2H, **OH**, br., exchangeable with D_2O). IR cm^{-1} (KBr): 3455 (OH), 1100 - 980 (As-C, aryl).

III. *Reaction of 3,5-Di-tert-butyl-1,2-benzoquinone (4) with triphenylstibine (3c).*

To a stirred solution of (0.2 g, 9 mmol) of the quinone **4** in (10 ml) of dry dioxane at r. t. was added a solution of (0.64 g, 18 mmol) of TPSb **(3c)** in the same solvent (20 ml), then it was further stirred at r. t. for 24 h. After evaporating the solvent, the residual substance was taken up in methylene chloride, leaving behind a colorless material, (0.26 g, 78%) which proved to be triphenylstibine oxide **(5c)** (comparative m.ps. and IR spectra).

The methylene chloride soluble portion was precipitated by light petroleum, upon filteration, it yielded **17** as colorless crystals (0.3 g, 60%), m.p. 246-248°C. Anal. Calcd. for : $C_{32}H_{35}OSb$ (557.38), C, 68.96; **H,** 6.33. Found : C, 68.78; H, 6.29. MS: m/z = 557 (M^+, 18%). NMR ($CDCl_3$): ^1H δ_H 1.33, 1.43 (18 H, t-Bu, 2 s), 6.68 - 7.7 ppm (17 H, aryl-**H**, m); ^{13}C δc: 31.84, 32.15 (C-**C**H_3), 34.3, 35.82 (**C**-CH_3), 158.83 (d, J_{CSb} = 85.6 Hz, Sb = **C**, aryl), 178.5 (**C**$_2$ = O). IR cm^{-1} (KBr): 1670 (C_2=O), 1240 (C=Sb), 1437, 1010 (Sb-C, aryl).

When the reaction was performed using equimolar amounts from quinone **4** and triphenylstibine **(3c),** the stibine-methylene **17** and triphenylstibine oxide **(5c)** were obtained together with some unchanged **4.**

III. a. Action of Sulfur on 17.

Compound **17** (0.2 g) and sulfur *(ca.* 0.1 g) were fused together at 270-280 °C (bath temperature) for 30 min. and the residue was extracted with hot ethanol. The solid material that crystallised out upon cooling, was collected and proved to be TPSbS (comparative m.ps. and MS spectra).

IV. *Reaction of 4 or 15 with 5a-c.*

A solution of **4** (0.6 g, 22 mmol) and triphenylphosphine oxide **(5a),** triphenylarsine oxide **(5b,** 24 mmol) in methanol-H_2O (30 ml, 1:1) or triphenylstibine oxide **(5c,** 24 mmol) in benzene -H_2O (30 ml, 1:1) was refluxed for ~ 18 h (TLC). After evaporation of the solvent, the remainder was subjected to column chromatography [silica gel, light pet. (60-80 °C) / chloroform (9:1 v/v) with increasing amounts of chloroform].

The fraction up to 7:3 v/v gave compound **13a, 13b** or **13c,** respectively. The complexes **13a** (0.75 g, 55%) and **13b** (0.7g, 48%) were identified by m.p., mixed mps. and comparative IR and MS spectra).

13c was obtained as brown crystals (1 g, 63%), m.p. 202 - 204 °C (benzene). Anal. Calcd. for : $C_{32}H_{37}O_3Sb$ (591.38), C, 64.99; H, 6.31. Found: C, 64.63; H, 6.1. MS: m/z= 222 **(15,** 50%), 368 **(5c,** 100%). IR cm^{-1}: 3455 (OH), 1100, 1020 (Sb-C, phenyl). ^1H NMR ($CDCl_3$): δ_H: 1.33, 1.42 (18 H, t-Bu, 2s); 6.8-7.8 (17H, aryl - **H,** m); 8.55 (2H, O**H**, br., exchangeable with D_2O).

The fraction 6:4 v/v afforded triphenylphosphine oxide **(5a),** triphenylarsine oxide **(5b),** or triphenylstibine oxide **(5c),** proved by TLC, m.p. and mixed m.ps.

The fraction up to 3:7 yielded in each case diaryl ether **22** as dark red crystals (~ 0,14 g, ~ 11%) m.p. 123-125 °C (ethyl alcohol). Anal. Calcd. for $C_{20}H_{26}O_5$ (346.41), C, 69.34; H, 7.57. Found: C, 68.26; H, 7.24. MS: m/z = 346 (M^+, 38%). IR cm^{-1}: 3435 (br., OH), 1075 (C-O-C, aryl). NMR ($CDCl_3$): ^1H, δH 1.32 (9H, t-Bu, s), 6.23, 6.99 (2H, aryl-**H**, 2d, J_{HH}= 4.2 Hz), 8.55 (2H, O**H**, br.); ^{13}C, δ_c 29.35 (C-CH_3), 37.84 (**C**-CH_3); 151.4 (**C**-O-**C**, aryl); 153.6, 157.5 (OH-**C**, aryl).

Alternatively, carrying out the above experiments, using the pyrocatechol **15** instead of **4** led, also, to the formation of **13a-c** and **22.**

IV-a. Action of Heat on 13a-c.

Complex **13a** (0.5 g) was heated in a cold finger sublimator at 250 °C (bath temp.) for about 15 min. Under reduced pressure (10 mm/Hg). The substance that sublimed was triturated with pentane. The undissolved material was then recrystallised from ethyl alcohol and proved to be TPPO **(5a).** The pentane solution was concentrated and cooled in the refrigerator. The aggregated crystals were filtered off and proved to be pyrocatechol **15** (0.1 g, 40%). Adducts **5a** and **15** were identified by comparison with authentic samples.

In the same way, pyrolysis of **13b** or **13c** (as above) led to the isolation of **15** (~ 40%) and **5b** or **5c,** respectively.

IV-b. Action of Alkali on 13a-c.

When a solution **of 13a, 13b** or **13c** (0.5 g) in 20 ml (ethanol) was shaken with alcoholic sodium hydroxide [prepared by adding ethyl-alcohol (5 ml) to NaOH (15 ml, 10%)] for about 2 h, a quantitative separation of alkali-insoluble of TPXO **(5a-c)** as a hydrate and alkali-soluble quinol (obtained by acidification of the alkaline solution) was effected.

VI. *Reaction of 4 or 15 with 6a-c.*

A mixture of **4** (0.6 g, 22 mmol) and trimethyl-, triethyl- or tri-t-butyl phosphate **(6a-c),** respectively, (25 mmol) in methanol-H_2O (30 ml, 1:1) was refluxed for ~30 h (TLC). After cooling, dark red substance was separated, recrystallised from ethyl alcohol to give the diaryl ether **(22)** (~33%) **22** was identical (m.p., mixed mps, comparative IR and MS spectra) with that obtained from reaction **IV.**

The mother liquors were evaporated to dryness, the residue, so obtained, was crystallised from the suitable solvent to give **23a-c.**

2-Hydroxy-3,5-di-tert-butylbenzene-1-dimethyl phosphate **(23a)** (0. 1 g, 10%), m.p. 66-68 °C (cyclohexane), authentic m.p. 67 °C,[8] superimposable IR spectra.

2-Hydroxy-3,5-di-tert-butylbenzene-1-diethyl phosphate **(23b)** (0.14 g, 15%), m.p. 60-62 °C (pentane). Anal. Calcd. $C_{18}H_{31}O_5P$ (358.42): C, 60.32; H, 8.72; P, 8.64. Found: C, 60.08; H, 8.65; P, 8.43%. MS: m/z= 358 (M^+, 12%), IR cm^{-1}: 3530 (OH), 1245 (P = O), 1040 (P-O-CH_2). NMR ($CDCl_3$): ^1H δ_H 1.35 - 1.53 (24 H, t-Bu & CH_3, m), 4.32 (4H, - CH_2, d of q, J_{HH} = 11.5 Hz), 6.7 - 7.8 ppm (2H, aryl-**H**, 2d, J_{HH} = 4.2 Hz), ^{31}P: δp = -4.37 ppm.

2-Hydroxy-3,5-di-tert-butylbenzene-1-di-tert-butyl phosphate **(23c)** (0.14 g, 13%), m.p. 47-48.°C (light petroleum). Anal. Calcd. $C_{22}H_{39}O_5P$ (414.53): C, 63.74; H, 9.48; P, 7.47. Found: C, 63.52; H, 9.36; P, 8.05%. MS: m/z= 414 (M^+, 17%). NMR ($CDCl_3$): ^1H δ_H: 1.35-1.62 (36H, 4t-Bu, m), 6.8-7.8 ppm (2H, aryl-**H**, 2d, J_{HH} = 4.2 Hz).

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