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THE CHEMISTRY OF PENTAVALENT ORGANOBISMUTH REAGENTS. PART XI. REACTIONS WITH STERICALLY HINDERED PHENOLS

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Abstract - The reactivity of Bi^V reagents towards very hindered phenols with *tert.*-butyl groups at 2 and 6 under basic conditions has been studied. Unexpected phenylation at the 4-position and, in several cases, replacement of a *tert.*-butyl group by phenyl have been observed. The mechanism of these unexpected reactions has been discussed.

Numerous studies have been devoted to the oxidative coupling of phenols.[1,2] A wide range of oxidants has been used, and among them, metallic oxides and salts play a proeminent role.[3] In the case of sterically hindered phenols, particularly the 2,6-di-*tert.*-butylphenol derivatives, the coupling step involves an aryloxyl radical.[4] Sodium bismuthate behaves as a one-electron oxidant towards phenols to give various types of coupling products.[5] In the case of organobismuth reagents, the first example of phenolic oxidative coupling was observed in the reaction of 2,6-dimethylphenol 7 with triphenylbismuth carbonate 1. With other bismuth reagents, phenylation occurred.[6] *Ortho* C-phenylation to the cyclohexadienone 13 is realized with pentaphenylbismuth 3 or with tetraphenylbismuth esters 4 or 5 under basic conditions.[7] The *O*-phenyl ether is obtained with 4 under neutral conditions[8] or with triphenylbismuth diacylates 6 under copper catalysis.[9] During our investigations on the regioselectivity of the phenylation of phenols by pentavalent organo-bismuth reagents, we discovered that 2,6-di-*tert.*-butylphenol 8 is oxidized to the diphenoquinone 12 by Ph_3BiCO_3 in the presence of *N-tert.*-butyl-*N',N',N'',N''*-tetramethylguanidine (BTMG). No reaction occurred in absence of BTMG. Similarly, reaction of 8 with Ph_3BiCl_2 2 and BTMG led also to the diphenoquinone 12. Reaction of 2,4,6-trisubstituted phenols afforded various products. Mesitol 9 yielded the *O*- or *C*-phenylation products under the same conditions as for its congener 7. However, treatment of 9 with Ph_3BiCl_2 and BTMG yielded the *ortho* C-phenyl product 14 in benzene in poor yield, and the 4α-methoxylated derivative 15 in good yield in methanol. 2,6-Di-*tert.*-butyl-4-methylphenol 10 gave also the 4α-methoxylated derivative 16 and the cyclohexadienone 17 in the presence of acrylonitrile[10]. Various pathways are involved in these reactions. *C*-phenylation and some *O*-phenylation reactions were explained by the formation of

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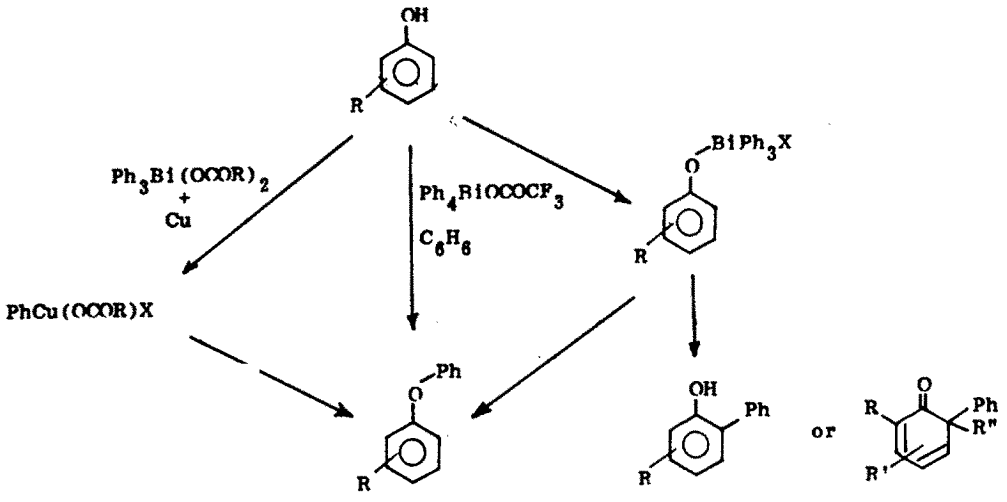
covalent intermediates (some of which were isolated), followed by reductive elimination.[7] *O*-phenylation occurs through an aromatic S_N2 like pathway or through trivalent aryl-copper species[7,11] (Scheme 1). No free radicals were considered to be involved in these phenylations.[12]



Scheme 1. Pathways involved in Earlier Experiments on the *O*- and *C*-Phenylation of Phenols.

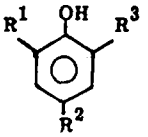
In the case of the oxidative coupling to diphenoquinones, three possible pathways were suggested : through an aryloxyl radical or through two types of covalent bismuth-substituted intermediates, the Bi-O and the Bi-C(4) derivatives.[10] In the 4-methyl series, a methylenequinone can be formed and trapped by methanol to yield the 4-methoxymethyl derivatives. Although monoaryloxy derivatives of Li, Na[13], K and diaryloxy derivatives of Zn[14] and Pb[15] are known for the bulky 2,6-di-*tert*.-butyl substituted phenols, a similar Bi-O intermediate seems questionable.

Following our recently described studies on the possible occurrence of free radical mechanisms in various phenylation reactions[12], we decided to investigate the mechanistic aspects of these oxidative coupling reactions of hindered phenols. We now report our results.

Bismuth Compounds :

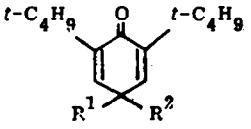
Ph_3BiCO_3	Ph_3BiCl_2	Ph_5Bi
1	2	3
$Ph_4BiOCOCF_3$	$Ph_4BiOTos$	$Ph_3Bi(OCOR)_2$
4	5	6

Phenolic Compounds :



N°	R^1	R^2	R^3
7	CH_3	H	CH_3
8	t-C_4H_9	H	t-C_4H_9
9	CH_3	CH_3	CH_3
10	t-C_4H_9	CH_3	t-C_4H_9
15	CH_3	CH_3-O-CH_2	CH_3
16	t-C_4H_9	CH_3-O-CH_2	t-C_4H_9
22	t-C_4H_9	Ph_4Bi	t-C_4H_9
23	t-C_4H_9	C_6H_5	t-C_4H_9
24	t-C_4H_9	CH_3	C_6H_5
26	t-C_4H_9	Ph_3ClBi	t-C_4H_9
27	t-C_4H_9	t-C_4H_9	t-C_4H_9
28	t-C_4H_9	t-C_4H_9	C_6H_5
29	t-C_4H_9	C_6H_5	t-C_4H_9
30	t-C_4H_9	ClHg	t-C_4H_9

Substituted 2,5-Cyclohexadienones :



N°	R^1	R^2
17	CH_3	C_6H_5-CH(CN)-CH_2
19	$R^1 + R^2 = O$	
25	CH_3	C_6H_5
31	CH_3	NC-$(CH_2)_2$-

In view of the importance of the aryloxyl radicals pathway in other oxidative systems, we first attempted to trap the aryloxy radical, which might play the major role in the reactions of 2,6-di-*tert.*-butylphenol 8. Oxygen is an efficient trap for aryloxyl radicals, leading to stable peroxides.[1] However, in the reaction of 8 with Ph_3BiCl_2 and BTMG, oxygen cannot be used as it oxidizes the Na anion of 8 to the diphenoquinone 12 by a radical mechanism.[16] Nitroxides also trap aryloxyl radicals to yield the *p*-quinone, whereas phenols are not affected by highly hindered nitroxides such as 2,2,6,6-tetramethylpiperidin-4-on-1-yloxy.[17] No reaction was detected between 2,2,6,6-tetramethyl 1-piperidinyloxy 18 (TEMPO) and phenol 8, as

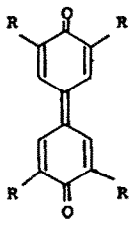
after 48 hrs 87% of 8 was recovered. When the reaction of phenol 8 with Ph_3BiCl_2 and BTMG was performed in the presence of TEMPO (2 equiv.), a new product was also formed, the *p*-quinone 19, resulting from the trapping of the aryloxyl radical by TEMPO. The ratio 12:19 appeared dependent upon the amounts of bismuth reagent and base (Table 1). In absence of 2, the oxidation product 19 was nevertheless formed in high yield (85%). Therefore, although inert towards phenols, TEMPO oxidized phenol 8 under basic conditions.

Table 1. Effect of TEMPO 18 on the Oxidative Coupling of Phenol 8 with Ph_3BiCl_2 2 and BTMG.[a]

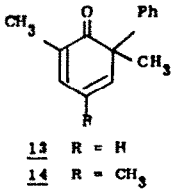
BTMG (eq.)	2 (eq.)	18 (eq.)	12 (%)	19 (%)
5	2	0	87	0
5	1	5	traces	76
5	2	5	7	64
5	3	5	17	36
3	2	5	14	21
2	2	5	12	51
1	2	5	5	51
5	0	5	1	85

[a] All reactions performed in THF at room temperature for 17 hrs. Nb. of equivalents relative to 8.

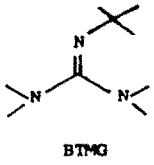
When 1,1-diphenylethylene was used as a radical trap, the yield of 12 dropped significantly : only 6% was obtained. However, 1,1-diphenylethylene (DPE) is a poor trap for aryloxyl radicals. Indeed, in the Kharash (alkali-oxygen)[16] oxidation of 8, addition of DPE did not inhibit the reaction much : 12 was obtained in 83% yield, instead of 98%.



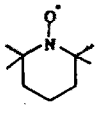
11 R = CH_3
12 R = t-C_4H_9



13 R = H
14 R = CH_3



BTMG



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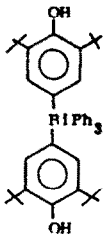

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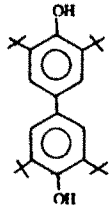

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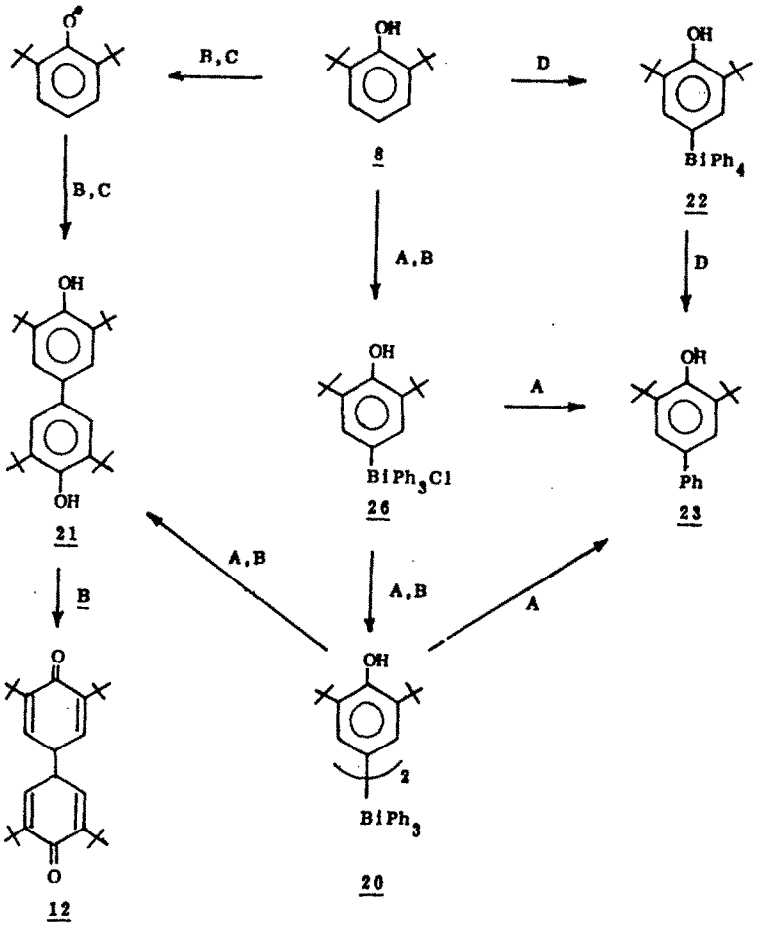
The results (Table 1) suggest that TEMPO and bismuth reagent 2 are in competition for phenol 8. One explanation would be that TEMPO, under basic conditions, forms and traps phenolate radicals to give quinone 19, whereas 2 produces coupling from an intermediate 20 (see below, Scheme 2).

In agreement with the latter, the use of pyridine instead of the strong organic base BTMG produced no oxidation at all. This is in keeping with the formation of an intermediate like 20 (Scheme 2) giving the hydroquinone 21 easily oxidised to the quinone 12 in the medium used for the coupling[10] (Scheme 2).



A : 2 and KH ; B : 2 and BTMG ; C : effect of oxygen traces:
D : 5 and BTMG or KH.

Scheme 2. Pathways involved in the Reactions of Phenol 8.

A logical inference from the above is that the use of a tetraphylbismuth reagent would give a different intermediate 22 which by reductive elimination would afford the 4-phenyl derivative 23. Indeed use of reagent 5 gave only traces of the diphenoquinone 12 and

4-phenyl derivative 23 was isolated (33%) instead. This is the first example of the 4-phenylation of a phenol. Diligent search[10] has given no indication of 4-phenylation in phenols where the phenolic hydroxyl is less hindered and can form a Bi-O intermediate.

The 4-methyl analogue 10 of phenol 8 was studied next. Oxidation with reagent 2 and BTMG in the presence of methanol afforded the methoxymethylene derivative 16 in reasonable yield (45%). This reaction is analogous to the similar reaction with mesitol[10] and involves formation of a methylenequinone.

In a similar way, when tetraphenylbismuth reagent 5 was used, the 4-phenylcyclohexadienone 25 was isolated (22%), together with another unexpected product phenol 24, in which one of the *tert.*-butyl of 10 had been replaced by phenyl.

The formation of the methoxymethylene derivative 16 and of the 4-phenyl derivative 25 are compatible with a 4-substituted Bi-C intermediate analogous to 22 (Scheme 2). This could eliminate to give the postulated methylenequinone or reductively eliminate to 25. However, the replacement of *tert.*-butyl by phenyl to give 24 would require the formation of an intermediate dienone analogous to 14 with loss of the *tert.*-butyl group as a *tert.*-butyl radical or as isobutylene. All this would suggest the formation of the customary Bi-O intermediate, which we had regarded (see above) as questionable.

In order to make the formation of a Bi-O bond more probable, we decided to make the phenolate anion unambiguously before adding the bismuth reagent. Thus phenol 8 in anhydrous THF was treated with potassium hydride (evolution of hydrogen) and then with reagent 2. The reaction was faster and after 1 hour only 15% of starting material 8 was unconsumed. The 4-phenyl derivative 23 was obtained in better yield (37%) as well as 21 (15%). No diphenoquinone 12 was detected. These results are not incompatible, therefore, with Scheme 2 (26 -> 23 and 26 -> 20 -> 21).

In a similar fashion, the 4-methylphenol 10 afforded the 4-phenylcyclohexadienone 25 (17%) and the 2-phenylphenol 24 (12%) after 1 hour. The yields were not improved by using the tetraphenylbismuth compound 5. Reaction of 8 and 10 with 5 and KH gave 23 (21%) and 24 (12%), 25 (14%) respectively.

Eventually, 2,4,6-tri-*tert.*-butylphenol 27 was treated with 2 and KH. After 1 hour a non resolved mixture of mono-*C*-phenylated di-*tert.*-butylated phenols 28 and 29 was isolated (22%) in a NMR ratio of 28:29 = 1.5, as well as unreacted phenol (46%).

A comparison of these phenylation reactions shows that overall yields of *ortho*- and *para*-phenylated products ranging between 22% and 37% in one hour are obtained. The relative p-phenylation rates are : 8 (4-H) : 1; 10 (4-CH_3) : 0.5; 27 (4-*t*-C_4H_9) : 0.24. All the results for very hindered phenols are summarised in Table 2.

Mercury-bismuth exchange[18] was attempted as an alternative approach to intermediates 20 and 26. However treatment of the 4-chloromercurio derivative[19] 30 with 2 in THF under reflux for 15 hrs failed to give any coupled products. Reaction of this mercury derivative with triphenylbismuth afforded only the reduced phenol 8 (82%) together with diphenylmercury (63%).

This work on the arylation reactions of very hindered phenols has turned up two reactions which are unexpected in relation to the considerable body of work already accomplished.[7-10] In particular, we have proven that almost all the prior results are incompatible with radical chemistry.[12] Thus, the abnormal 2- and 4-phenylation reactions can be accommodated into prior ideas by supposing the formation of Bi-O and Bi-C intermediates respectively. However, we have also considered the hypothesis that extreme steric hindrance has finally produced a new mechanism in which electron transfer between B.T.M.G. (or other base) and a Bi^V reagent leads to the latter fragmenting to aryl, in this context phenyl, radicals. Such a mechanism has already been detected and shown not to play a role with normal substrates.[12]

Table 2. Oxidation and Phenylation of Sterically Hindered Phenols with Bi^V Reagents.

Phenol	Bi Reagent	Reaction Conditions	Products (%)
7	1 (1.5)	THF, 15 h	11 (30)
7	1 (1.5)	THF, BTMG (3), 3 h	7 (39)
7	1 (1.5)	CH_2Cl_2, 4.5 h	11 (33), 7 (64)
7	1 (1.5)	CH_2Cl_2, PhNO (2), 4.5 h	11 (60), 7 (39)
8	2 (2)	THF, BTMG (5), 17 h	12 (37)
8	5 (1.2)	THF, BTMG (1.2), 15 h	12 (traces), 23 (33)
8	2 (2.2)	THF, KH (1.5), 1 h	8 (15), 21 (15), 23 (37)
8	5 (1.1)	THF, KH (3), 1 h	23 (21)
10	5 (1.2)	THF, BTMG (1.2), 15 h	24 (20), 25 (22)
10	2 (1.2)	THF, KH (2), 1 h	10 (40), 24 (12), 25 (17)
10	5 (1.2)	THF, KH (3), 1 h	24 (12), 25 (14)
27	2 (1.2)	THF, KH (2), 1h	27 (46), 28+29 (22)

All reactions performed at room temperature.

We have, therefore, examined the effect of 1,1-diphenylethylene (DPE), a good trap for phenyl radicals, on the reactions concerned (Table 3). This olefin had little effect on the formation of the methoxymethyl derivative 16 from phenol 10. This is in keeping with earlier discussion (see above). In the other examples in Table 2, the radical trap DPE had little effect on yields of products formed. The exception was the reaction of phenol 8 to give the coupled product 12. This reaction needs further study.

Table 3. Effect of the Addition of 1,1-Diphenylethylene (DPE) on Various Oxidation Reactions.

Phenol	2 (eq.)	DPE	Reaction Conditions	Products
8	2	0	THF, BTMG (5), 17 h	12 (37)
8	2	2	THF, BTMG (5), 17 h	12 (6)
8	0	0	t-BuOH, NaOH, O_2, 15 h	12 (98)
8	0	5	t-BuOH, NaOH, O_2, 15 h	12 (83)
9	1	0	MeOH, BTMG (2), 15 h	15 (65)
9	1	2	MeOH, BTMG (2), 15 h	15 (67)
10	1	0	MeOH-CH_2Cl_2, BTMG (4), 3 days	16 (45)
10	1	2	MeOH-CH_2Cl_2, BTMG (4), 3 days	16 (46)

All reactions performed at room temperature.

As noted before,[10] when acrylonitrile was added to the reaction of phenol 10 with bismuth reagent 2 in benzene in the presence of BTMG, the addition-phenylation product 17 was obtained. We now report that when the reagent 2 is omitted, a normal Michael reaction takes place to give 31. We conclude that 17 was formed by a similar reaction followed by *C*-phenylation via a Bi-C bonded intermediate. Radicals are not involved.

The reaction of mesitol 9 with reagent 2 in the presence of BTMG in methanol produced immediately a deep red colouration, characteristic of the formation of a covalent Bi-O compound.[12,21] This was in contrast to phenols 8 and 10 which do not give a similar colouration. Base-catalysed reductive elimination afforded, through the elusive methylene-quinone, the adduct 15 (65% without DPE and 67% in the presence of DPE).

The presence of aryloxyl species was detected by e.s.r. study of these reactions. A signal was already detected in a solution of 2,6-di-*tert.*-butyl 4-methylphenol. Its intensity was increased upon addition of BTMG, but no significant modification occurred after addition of Ph_3BiCl_2. The signal was a quadruplet of triplets, g = 2.0057±0.0004, a_{CH_3} = 11.29±0.05G and a_{Hm} = 1.67±0.05G, characteristic of the aryloxyl radical.[22] Spin density studies were not possible because of the coupling reactions to quino-ethers or the dismutation reaction.[1] The e.s.r. spectrum of a solution of 2,4,6-tri-*tert.*-butylphenol 27, BTMG and 2 showed the presence of the corresponding aryloxyl radical, g = 2.0043±0.0004 and a_{Hm} = 1.82±0.05G[30]. As this radical is stable and gives colored solutions ($\lambda_{max.}$ 625 nm, ε 410), the concentration was easily measured by UV-vis spectroscopy. An equimolar solution of 27, BTMG and 2 contained 1.8% of aryloxyl radical after 2 hrs. When oxygen was bubbled through the solution, the phenol was completely consumed in 5 hrs. In blank experiments, 27 remained unaffected by Ph_3BiCl_2 alone or by BTMG alone.

Oxidation of 2,6-dimethylphenol 7 by Ph_3BiCO_3 was also monitored by e.s.r. A poorly resolved signal which can be attributed to the aryloxyl radical was observed : g_{iso} = 2.0043±0.004, a_{H4} = 10.92±0.05G, $a_{CH_3(2,6)}$ = 5.83±0.05G and $a_{H(3,5)}$ = 1.09±0.05 G. Further chemical experiments, however, excluded the radical pathway in this case. The oxidative coupling of 7 with 1 gave the diphenoquinone 11 in 30-35%. Addition of BTMG inhibited the reaction : from the mixture, 11 was not present and 7 was recovered in 39% yield. Eventually, the yield of 11 increased in the presence of nitrosobenzene (60% yield). Therefore, the ionic mechanism[10] with formation of a covalent Bi-O intermediate is more consistent with these observations.

The observation of small concentrations of aryloxyl radicals does not, of course,[12] mean that they necessarily play a role in the reactions leading to isolated products.

The conclusion to be drawn from this work is that the mechanisms of the type already used in the chemistry of Bi^V can be extended to explain the present results. However, the possibility of phenylation by phenyl radicals and eventual displacement of a *tert.*-butyl group for very hindered phenols needs to be studied further.

Experimental

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 257 instrument. N.m.r. spectra were determined for solutions in deuteriochloroform with $SiMe_4$ as internal standard on Varian T-60 and Varian EM-360 instruments. Mass spectra were recorded with an AEI MS-9 or MS-50 apparatus. E.s.r. spectra were recorded on Bruker ER-420 and ER-100D apparatus equipped with Bruker ER-400X-RL or TR-4102 cavities. Deaerated solutions of the samples were maintained under argon in a quartz tube. All solvents and reagents were purified and dried by standard techniques. Chromatographic separations were performed using Merck Kieselgel 60 GF-254 (preparative t.l.c.) and Merck Kieselgel 60H (column chromatography). BTMG refers to *N-tert.*-butyl-*N'*,*N'*,*N''*,*N''*-tetramethylguanidine, and ether to diethyl ether.

Oxidation of 2,6-Di-*tert.*-butylphenol 8 by 2 and BTMG.

A solution of 2,6-di-*tert.*-butylphenol 8 (0.103 g) and BTMG (0.5 ml) in anhydrous THF (3 ml) was stirred for 10 mins at room temperature under an atmosphere of argon. 2 (0.511 g)

was added and the mixture stirred for 17 hrs. After addition of 1M aqueous HCl (a few drops) and extraction with ether, the organic phase was washed with water, dried ($MgSO_4$) and distilled under reduced pressure. Preparative t.l.c. of the residue (eluant: hexane) gave 2,6,2',6'-tetra-*tert.*-butyldiphenoquinone 12 (0.037 g, 37%), m.p. 245°C (hexane), lit.[24] 245-247°C.

Oxidation of 2,6-Di-*tert.*-butylphenol 8 by 2 and BTMG in the Presence of 2,2,6,6-Tetramethyl-1-piperidinyloxy 18 (TEMPO).

A reaction as above performed in the presence of TEMPO (0.39 g) yielded 12 (0.007 g, 7%) and 2,6-di-*tert.*-butyl-1,4-benzoquinone 19 (0.070 g, 64%), m.p. 64-67°C (ethanol), lit.[25] 65-66°C.

Oxidation of 8 by BTMG and 18.

When the previous experiment was performed in absence of 2, 12 (0.001 g, 1%) and 19 (0.094 g, 85%) were obtained.

Reaction of 8 and 18.

A mixture of 8 (0.103 g) and 18 (0.16 g) in anhydrous THF (3 ml), stirred for 48 hrs at room temperature under an atmosphere of argon, yielded after usual work-up 8 (0.91 g, 83%).

Oxidation of 8 by 2 and BTMG in the Presence of 1,1-Diphenylethylene.

A mixture of 8 (0.103 g), BTMG (0.5 ml), 1,1-diphenylethylene (0.18 ml) and 2 (0.511 g) in anhydrous THF (3 ml) was stirred for 17 hrs at room temperature under an atmosphere of argon. The usual work-up and column chromatography (eluant: hexane, followed by hexane-ether 95:5) afforded 12 (0.006 g, 6%) and 1,1-diphenylethylene (0.112 g, 65%).

Oxidation of 8 by O_2 and NaOH in the Presence of 1,1-Diphenylethylene.

Oxygen was bubbled through a stirred mixture of 8 (0.188 g), NaOH (0.2 g) and 1,1-diphenylethylene (0.8 ml) in 2-methyl-2-propanol (5 ml) and water (0.5 ml) for 15 hrs at room temperature. After addition of water, the diphenoquinone 12 was filtered and dried (0.154 g, 83%).

A similar reaction performed in absence of 1,1-diphenylethylene afforded 12 (0.182 g, 98%).

Oxidation of Diphenohydroquinone 21 by 2 and BTMG.

A solution of 3,3',5,5'-tetra-*tert.*-butyldiphenohydroquinone 21 [obtained by reduction of 12 with H_2 and PtO_2 (10%) of a methanol-methylene dichloride solution, m.p. 179-184°C, lit.[16] 185°C], BTMG (0.2 ml) and 2 (0.256 g) in anhydrous THF (5 ml) was stirred for 48 hrs at room temperature under an atmosphere of argon. The usual work-up and preparative t.l.c. afforded 12 (0.073 g,71%).

Reaction of Phenol 8 with 5 and BTMG.

A mixture of 8 (0.103 g), BTMG (0.12 ml) and tetraphenylbismuth p-toluenesulphonate 5 (0.412 g) in anhydrous THF (5 ml) was stirred for 15 hrs at room temperature under argon. The usual work-up and preparative t.l.c. (eluant: hexane) yielded 2,6-di-*tert.*-butyl-4-phenylphenol 23 (0.047 g, 33%), m.p. 102-103°C (pentane), lit.[26] 100-101°C.

Reaction of Phenol 8 with 2 and Potassium Hydride.

A mixture of 8 (0.103 g) and potassium hydride (300 mg, 20% suspension in oil) in anhydrous THF (5 ml) was stirred for 1 hr at 5°C under an atmosphere of argon. After addition of 2 (0.562 g), the mixture was stirred for 1 hr at room temperature. A concentrated aqueous HCl solution (1 ml) was added and the stirring was maintained for 1 hr. The organic phase

was then washed with water, dried ($MgSO_4$) and distilled off under reduced pressure. Preparative t.l.c. of the residue afforded 8 (0.015 g, 15%), 23 (0.052 g, 87%) and 21 (0.014 g, 15%), m.p. 183-185°C (pentane), lit.[16] 185°C.

Reaction of 2,6-di-*tert.*-butyl-4-methylphenol 10 with Acrylonitrile and BTMG.

A solution of 10 (0.22 g), BTMG (0.4 ml) and acrylonitrile (5 ml) in benzene (5 ml) was stirred for 5 days under reflux under an atmosphere of argon. Every 24 hrs, 1 ml of acrylonitrile was added. After addition of 1M aqueous HCl (a few drops), the organic phase was washed with water, dried ($MgSO_4$) and distilled under reduced pressure. Preparative t.l.c. of the residue (eluant: hexane-ether 4:1) afforded 10 (0.027 g, 12%) and 4-(2-cyanoethyl) 2,6-di-*tert.*-butyl-4-methylcyclohexa-2,5-dien-1-one 31 (0.053 g, 22%), m.p. 72-75°C (pentane), $\nu_{max.}$ ($CHCl_3$) 2900, 2225, 1650 and 1630 cm^{-1}; $\lambda_{max.}$ (EtOH) 239.9 (ε 10000) nm; δ ($CDCl_3$) 6.3 (2H, s, 3-H, 5-H), 2.0 (4H, s, CH_2), and 1.3 (21H, s, CH_3); m/z 273 (M^+) (Found: C, 78.93; H, 9.94; N, 5.05. $C_{18}H_{27}NO$ requires C, 79.07; H, 9.96; N, 5.12%).

Reaction of Phenol 10 with 2 and BTMG in Methanol.

A mixture of 10 (0.110 g), BTMG (0.2 ml) and 2 (0.255 g) in methanol (5 ml) and methylene dichloride (5 ml) was stirred for 3 days at room temperature under an atmosphere of argon. The usual work-up and preparative t.l.c. (eluant: hexane) yielded 2,6 di-*tert.*-butyl-4-methoxymethylphenol 16 (0.056 g, 45%), m.p. 98-101°C (hexane), lit.[27] 98-99°C.

Reaction of Phenol 10 with 2, BTMG, Methanol and 1,1-Diphenylethylene.

A reaction as above performed in the presence of 1,1-diphenylethylene (0.18 ml) afforded 16 (0.057 g, 46%).

Reaction of Phenol 10 with 5 and BTMG.

A mixture of 10 (0.110 g), BTMG (0.12 ml) and 5 (0.412 g) in anhydrous THF (5 ml) was stirred for 15 hrs at room temperature under an atmosphere of argon. Work-up and preparative t.l.c. gave 2-*tert.*-butyl-4-methyl-6-phenylphenol 24 (0.024 g, 20%) as an oil, $\nu_{max.}$ ($CHCl_3$) 3550, 2900, 1600, 1420, and 1320 cm^{-1}; δ ($CDCl_3$) 7.53-6.83 (7H, m, ArH), 5.25 (1H, s, OH), 2.33 (3H, s, CH_3), and 1.50 (9H, s, C_4H_9); m/z 240 (M^+) (Found: C, 84.79; H, 8.51. $C_{17}H_{20}O$ requires C, 84.95; H, 8.39%) and 2,6-di-*tert.*-butyl-4-methyl-4-phenylcyclohexa-2,5-dien-1-one 25 (0.033 g, 22%) as an oil, $\nu_{max.}$ ($CHCl_3$) 2900, 1660, 1640, 1360, and 900 cm^{-1}; δ ($CDCl_3$) 7.43-7.17 (5H, s, ArH), 6.60 (2H, s, 3-H, 5-H), 1.63 (3H, s, CH_3), and 1.27 (18H, s, 2xC_4H_9); m/z 296 (M^+) (Found: C, 85.01; H, 9.64. $C_{21}H_{28}O$ requires C,85.08; H, 9.52%).

Reaction of Phenol 10 with 2 and Potassium Hydride.

A mixture of 10 (0.110 g) and potassium hydride (200 mg, 20% suspension in oil) in anhydrous THF (5 ml) was stirred for 1 hr at 5°C under an atmosphere of argon. After addition of 2 (0.562 g), the mixture was stirred for 1 hr at room temperature.

A concentrated aqueous HCl solution (1 ml) was added and the stirring maintained for 1 hr. Usual work-up and preparative t.l.c. (eluant: hexane) afforded 10 (0.044 g, 40%), 24 (0.018 g, 12%), and 25 (0.025 g, 17%).

Reaction of Phenol 10 with 2 and Potassium Hydride in Methanol.

A mixture of 10 (0.110 g) and potassium hydride (100 mg, 20% suspension in oil) in methanol (5 ml) was stirred for 1 hr at 5°C under an atmosphere of argon. 2 (0.511 g) was added and the mixture stirred for 3 days at room temperature. After work-up, only 10 was obtained (0.10 g, 91%).

Reaction of 2,4,6-Trimethylphenol 9 with 2 and BTMG in Methanol.

A mixture of 9 (0.136 g), BTMG (0.4 ml) and 2 (0.511 g) in methanol (5 ml) was stirred for 15 hrs at room temperature under an atmosphere of argon. Work-up and preparative t.l.c. afforded 2,6-dimethyl-4-methoxymethylphenol 15 (0.108 g, 65%), m.p. 50-54°C (pentane), lit.[28] 54-55°C.

Reaction of Phenol 9 with 2, BTMG in Methanol in the Presence of 1,1-Diphenylethylene.

A reaction as above performed in the presence of 1,1-diphenylethylene (0.36 ml) gave 15 (0.112 g, 67%).

Reaction of 2,4,6-Tri-*tert.*-butylphenol 27 with 2 and Potassium Hydride.

A mixture of 27 (0.131 g) and potassium hydride (200 mg, 20% suspension in oil) in anhydrous THF (5 ml) was stirred for 1 hr at 5°C under an atmosphere of argon. After addition of 2 (0.306 g) the reaction was stirred for 1 hr at room temperature. The usual work-up and preparative t.l.c. afforded 27 (0.060 g, 46%) and an unresolved mixture of *ortho*- and *para*-phenyl-di-*tert.*-butylphenol 28 and 29 (0.031 g, 22%), m.p. 80-101°C (pentane), lit. 28[26]: 57-58°C, 29[29]: 101-102°C, $\nu_{max.}$ ($CHCl_3$) 3650, 3550, 2900, 1600, 1420, and 1360 cm^{-1}; δ ($CDCl_3$) 7.60-7.13 (7H, m, ArH), 5.17-5.03 (1H, s, OH); 1.51-1.33 (18H, 3s, C_4H_9); m/z 282 (M^+) (Found: C, 85.19; H, 9.09; O, 5.70. Calc. for $C_{20}H_{26}O$: C, 85.05; H, 9.28; O, 5.67%).

Reaction of 2,6-Dimethylphenol 7 with Ph_3BiCO_3 1.

a) A mixture of phenol 7 (0.12 g) and triphenylbismuth carbonate 1 (0.75 g) in anhydrous THF (5 ml) was stirred overnight at room temperature. The solvent was distilled off and preparative t.l.c. of the residue (eluant: hexane) afforded the diphenoquinone 11 (0.035 g, 30%), m.p. 210-212°C, lit.[30] 211°C.

b) When BTMG (0.6 ml) was added to the same reaction and the mixture stirred for 3 hrs at room temperature, only 7 was recovered (0.048 g, 40%).

c) When reaction a was performed in CH_2Cl_2 (5 ml) for 4.5 hrs, diphenoquinone 11 (0.039 g, 33%) and 7 (0.077 g, 64%) were obtained.

d) When nitrosobenzene (0.215 g) was added to reaction c, 11 (0.070 g, 60%) and phenol 7 (0.046 g, 39%) were obtained after stirring for 4.5 hrs at room temperature.

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