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THE CHEMISTRY OF PENTAVALENT ORGANOBISMUTH REAGENTS. PART X[1]. STUDIES ON THE PHENYLATION AND OXIDATION OF PHENOLS

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Abstract — The influence of the substituents on the phenol on the regiochemistry of the arylation reactions with Ph_3BiCl_2 and other bismuth reagents has been studied. O-Phenylation occurs with phenols substituted with electron-withdrawing groups. Electron-donating substituted phenols undergo ortho C-phenylation. Oxidative dimerisation has been observed with 2,6-dialkyl phenols.

Pentavalent organobismuth derivatives are efficient, regioselective O- and C-phenylating reagents of phenols.[2] The regioselectivity of the phenylation relies upon the nature of the bismuth reagent and the reaction conditions. O-Phenylation is observed in the reaction of phenols with tetraphenylbismuth trifluoroacetate 1 under neutral conditions. C-Phenylation, on the other hand, is observed with tetraphenyl and triphenylbismuth derivatives 1-4, under basic conditions or with pentaphenylbismuth 5 under neutral conditions. In the former reaction, we consider that the O-phenylation proceeds by a direct SN-2 type aromatic displacement. In the latter reaction, C-phenylation occurs through intermediacy of a covalent Bi-aryloxide compound, which is decomposed by reductive elimination, in a concerted mechanism.[3] However, in the case of 4-nitrophenol, the regioselectivity of the phenylation was completely different. Only the O-phenyl ether 7 was obtained with pentaphenylbismuth, or with tetraphenylbismuth derivatives under basic conditions[2] (Scheme 1) in spite of the fact that a well characterised pentacovalent derivative of Bi^V could be isolated and fully characterised.

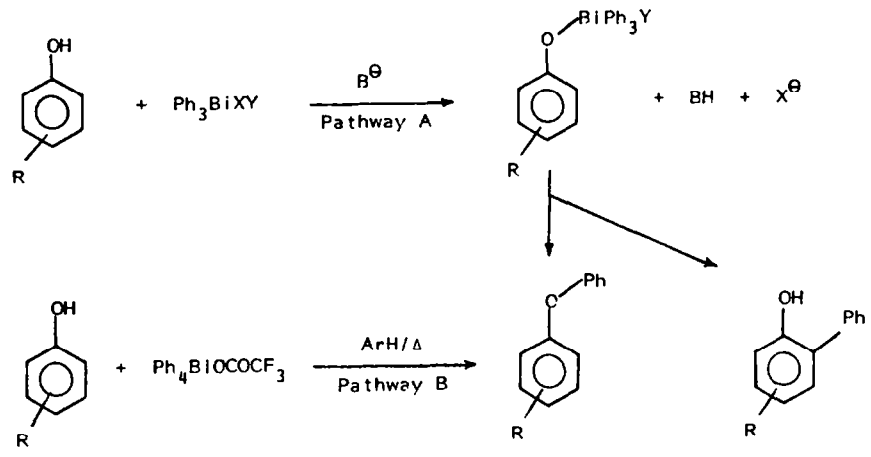
$Ph_4BiOCOCF_3$ 1

$Ph_4BiOTos$ 2

Ph_3BiCl_2 3

$Ph_3Bi(OCOCF_3)_2$ 4

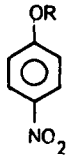
Ph_5Bi 5



Scheme 1

In order to gain a better understanding of the regioselectivity of the phenylation reaction, we turned our attention to the influence of the phenol substituents. We now describe our observations on the phenylation of a series of para, meta, and ortho-substituted phenols with pentavalent organobismuth reagents. Triphenylbismuth dichloride[4] 3 is the most easily prepared pentavalent organobismuth compound[5] and an efficient C-phenylating reagent.[2]

Under basic conditions, 3 reacted with 4-nitrophenol 6 to give the stable aryloxybismuth derivative 8.[2] Thermal degradation of 8 in refluxing benzene gave biphenyl (27%) and only 2% of the O-phenyl ether 7. Similarly, the analogous aryloxybismuth derivative 9[2] afforded biphenyl (69%) and no O-phenyl ether 7. Phenols 10, 12, 14 substituted with other electron-withdrawing groups in the 4-position behaved differently : under basic conditions, an instant coloration appeared, characteristic of a Bi^V intermediate.[8] But upon refluxing the mixture, the coloration slowly disappeared and the O-phenyl ethers 11, 13, 15 were formed in good yields (70-90%). All these reactions are reductive α-elimination processes based on Bi^V intermediates.

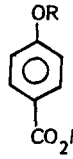


6 R = H

7 R = Ph

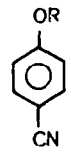
8 R = $BiPh_3Cl$

9 R = $BiPh_3OCOCF_3$



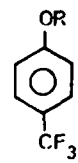
10 R = H

11 R = Ph



12 R = H

13 R = Ph

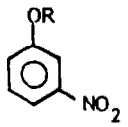


14 R = H

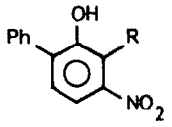
15 R = Ph

Under the same conditions, 3-nitrophenol 16 gave a mixture of the three derivatives 17, 18, 19 with a predominance of the O-phenyl ether 17. 3,5-Disubstituted phenols behaved as expected. 3,5-Di-tert-butyl phenol, as already reported,[2] reacted with 3 to

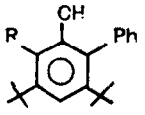
give only the C-phenylated derivatives 20 and 21. The 3,5-dimethoxy analogue 22 gave the C-phenylphenols 24 and 25 with minor amounts of the O-phenyl ether 23.



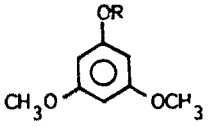
16 R = H
17 R = Ph



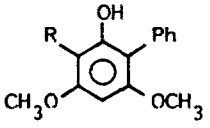
18 R = H
19 R = Ph



20 R = H
21 R = Ph

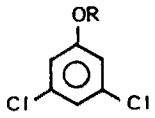


22 R = H
23 R = Ph

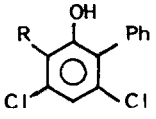


24 R = H
25 R = Ph

3,5-Dichlorophenol 26, on the other hand, gave mostly the O-phenyl ether 27 with only minor amounts of the C-phenyl phenols 28 and 29.

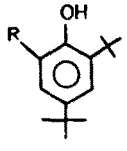


26 R = H
27 R = Ph

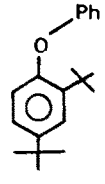


28 R = H
29 R = Ph

It must be noted that in the case of the bulky 2,4-di-tert-butylphenol 30, reaction with triphenylbismuth bistrifluoroacetate, under basic conditions, afforded the 6-phenyl derivative 31 in good yield (81%) together with a small amount of the O-phenyl ether 32 (3%). A lower yield of 31 (65%) was obtained in the reaction of 30 with pentaphenylbismuth.



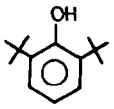
30 R = H
31 R = Ph



32

2,6-Disubstituted phenols showed variable behaviour. For example, 2,6-dimethylphenol reacted with triphenylbismuth carbonate to give the diphenoquinone,[6] with pentaphenylbismuth to give the 6-phenyl cyclohexadienone[7] and with tetraphenylbismuth trifluoroacetate to

afford under neutral conditions the O-phenyl ether.[6] The bulky 2,6-di-tert-butylphenol 33 gave a moderate yield (40-50%) of the diphenoquinone 34 with triphenylbismuth carbonate and with 3 in presence of BTMG (N-tert-butyl-N',N',N",N"-tetramethylguanidine).



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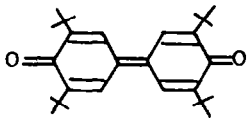
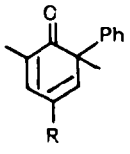


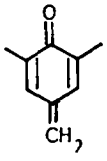
34

We next turned our attention to the related 2,4,6-trisubstituted phenols. The reaction of 3 with 2,4,6-trimethylphenol 35 (mesitol) in the presence of BTMG led to a poor yield (15%) of the cyclohexadienone 36. However, a high yield of 36 (88%) was obtained in the reaction of mesitol with pentaphenylbismuth under mild conditions (3 hours, room temperature). When the reaction of mesitol, 3 and BTMG was performed in the presence of a large excess of methanol, only the α-methoxy p-cresol derivative 37 was formed in high yield (82%). In the reaction of mesitol and 3 in methanol, an unstable p-methylene quinone 38 must be involved. An analogous phenol 39, on treatment with 3 and BTMG for four days at room temperature, gave the 6-phenyldienone 40 (43%) and unreacted phenol 39 (49%). When a solution of 2,6-di-tert-butyl-p-cresol 41 was treated with 3 and BTMG, in benzene-methanol solution, the α-methoxy derivative 42 was formed (74%). When the phenolate anion of 41 was reacted in the presence of acrylonitrile instead of methanol, the adduct 43 was obtained in moderate yield (21%).



36 R = Me

40 R = OMe



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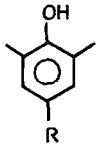
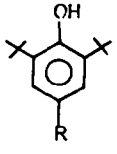


35 R = CH_3

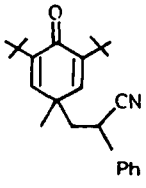
37 R = CH_2OMe

39 R = OMe



41 R = Me

42 R = CH_2OMe



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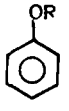
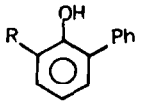


44 R = H

45 R = Ph



46 R = H

47 R = Ph

To complete the range of phenols, we studied in detail the phenylation reaction of phenol itself 44. Its reaction with 3 and BTMG afforded poor yields of phenylated derivatives, as well as a poor recovery of 44. However, upon HCl work-up, the recovery of 44 was significantly improved. Under the best conditions, the two C-phenyl derivatives 46 (30%) and 47 (7%) were obtained, together with the O-phenyl ether 45 (8%) and some biphenyl (8%). HPLC analysis of the crude reaction mixture, under normal or reverse

phase, indicated the absence (limit of detection <1%) of any trace of 4-phenylphenol. When diglyme was added at the end of the reaction, followed by distillation, chlorobenzene was detected in the distillate. Reaction of 44 with tetraphenylbismuth derivatives 1 and 2 under basic conditions gave better yields of phenylated products. The O-phenyl ether was the major isomer (35-42%), the 2,6-diphenylphenol 47 was obtained in a poor yield (3%) and 46 in a moderate yield (29%). Phenylation of 46 gave 47.

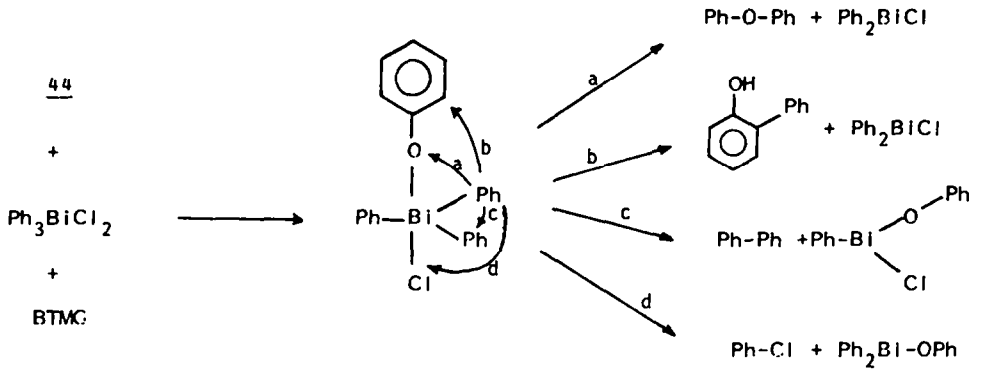
Table. Phenylation and Oxidation of Phenols with Pentavalent Bismuth Reagents.

Substrate	Bi^{V} Reagent[b]	Reaction Condition[a]	Products[c] (%)
10	3	BTMG, toluene, ref., 1.5 h	11 (88)
12	3	BTMG, toluene, ref., 3 h	13 (91)
14	3	BTMG, THF, ref., 3 h	15 (70)
16	3	BTMG, toluene, ref., 16 h	17 (54), 18 (13), 19 (9)
22	3	BTMG, toluene, ref., 4 h	23 (10), 24 (45), 25 (30)
26	3	BTMG, toluene, ref., 16 h	27 (60), 28 (16), 29 (12)
30	4	BTMG, CH_2Cl_2, r.t., 20 h	31 (81), 32 (3)
30	5	benzene, r.t., 24 h	31 (65)
33	3	TMG, THF, r.t., 30 h	34 (40), 48 (28)
33	4	TMG, THF, r.t., 30 h	34 (50), 48 (47)
33	49	TMG, THF, r.t., 30 h	34 (52), 48 (46)
35	5	benzene, r.t., 3 h	36 (88)
35	3	BTMG, CH_2Cl_2-MeOH, r.t., 6.5 h	37 (82), 48 (85)
39	3	BTMG, THF, r.t., 96 h	40 (43)
41	3	BTMG, benzene-MeOH, r.t., 72 h	42 (74), 48 (95)
41	3	BTMG, benzene-CH_2CHCN, ref., 96 h	43 (21)
44	3	BTMG, THF, ref., 48 h	44 (40), 45 (8), 46 (30), 47 (7), 50 (8)
44	1	BTMG, toluene, 80°C, 24 h	44 (22), 45 (42), 46 (29), 47 (3)
46	3	BTMG, THF, ref., 48 h	47 (33)

a) BTMG : N-t-butyl-N',N''-tetramethylguanidine; TMG : N,N'-tetramethylguanidine; ref. : reflux; r.t. : room temperature.

b) 49 : Ph_3BiCO_3. c) 48 : Ph_3Bi; 50 : Ph-Ph.

Apart from the 2,6-dimethyl- and the 2,6-di-tert-butylphenol derivatives, all these results are consistent with the formation of a covalently bonded Bi-O-Ar intermediate, which is reductively cleaved to an array of derivatives, depending upon the structure of the phenolic moiety. The reaction of phenol 44 with 3 which was studied in most detail gives the widest range of products, as four likely decomposition pathways are involved (pathways a-d, Scheme 2).

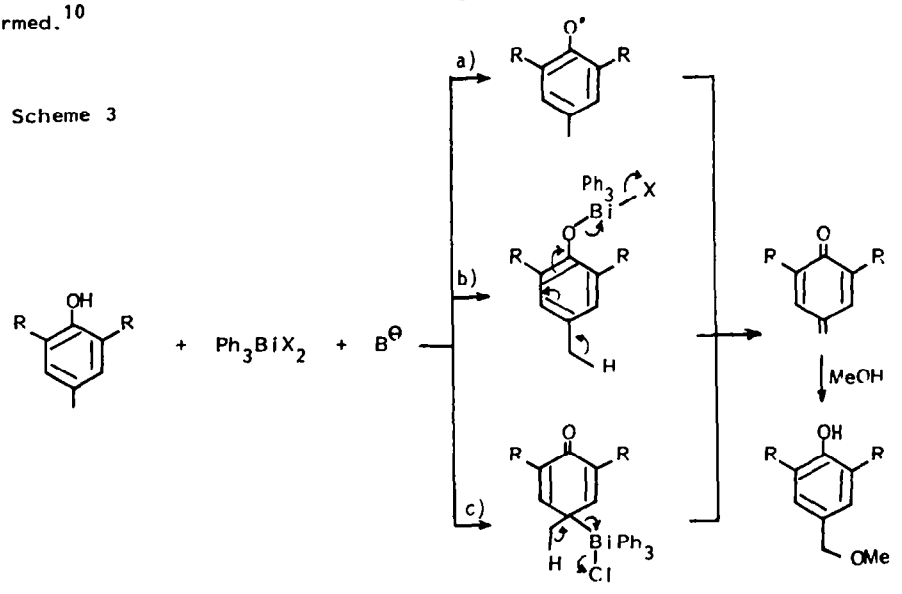


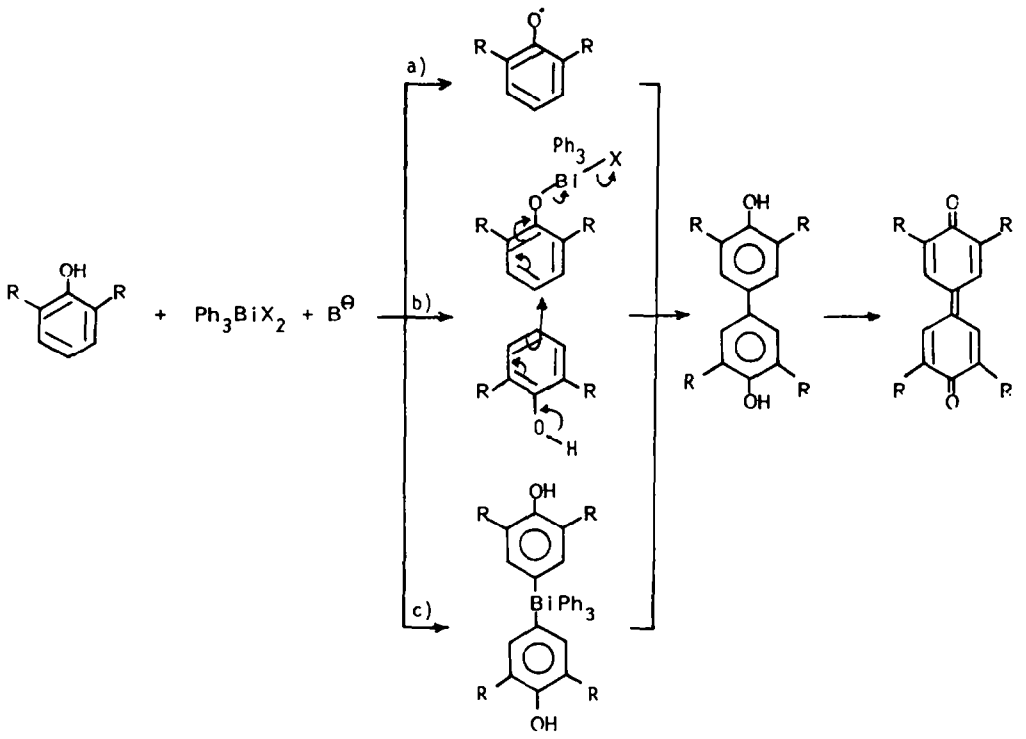
Scheme 2

In the substituted phenols, one pathway is generally favoured. The ortho C-phenyl derivative is the major, if not only isomer in the case of electron-donating substituents. The O-phenyl ether is formed in the case of phenols with electron-withdrawing substituents. The deactivation of the aromatic ring by an electronegative substituent forbids the ortho C-phenylation of p-substituted phenols such as 6, 10, 12 or 14.

In the 2,6-disubstituted series, the reductive elimination follows a different pathway, giving either the diphenoquinone or, in the presence of methanol, the methylenequinone which is then trapped. A covalent aryloxybismuth intermediate is formed in the 2,6-dimethyl series. A radical pathway (Schemes 3 and 4, pathway a) for its decomposition could be considered to explain the oxidative dimerisation, although it is unlikely by analogy to our recently reported radical trapping experiments.[8] However, a covalent aryloxybismuth intermediate is, on the other hand, doubtful with 2,6-di-tert-butylphenol derivatives, and such hypervalent metal alkoxides are, as yet, unknown.[9] Although a radical mechanism again could be invoked in this case, a third pathway can be considered : a C-4 bismuth intermediate (Schemes 3 and 4, pathway c) could be formed and decomposed either by elimination to the methylenequinone (para-methyl series) or to the diphenoquinone (para-hydrogen series). This hypothesis is not contrary to the acrylonitrile experiment, which could result from an anionic Michaël addition, followed by α-arylation of the resulting anion. In the absence of the bismuth reagent the corresponding non-phenylated adduct is formed.[10]

Scheme 3





Scheme 4

Although we favour mechanism c (Schemes 3 and 4), we cannot as yet exclude all the other possibilities. Further studies are in progress and will be reported in due course.[10]

In a recent communication,[11] we reported that a series of phenols were selectively O-phenylated by triphenylbismuth diacetate, triphenylbismuth bis(trifluoroacetate) or by tetraphenylbismuth trifluoroacetate, in the presence of copper salts or copper powder at room temperature. The yields were generally good to high and there was no significant effect of the electronic nature of the substituents on the phenol on the yields, the only limitation being the steric hindrance of the 2 and 6-substituents. The copper catalysed reaction also gives high yields in the N-phenylation of aliphatic and aromatic amines.[11] No ortho C-phenylation is seen in any of these copper catalysed reaction.

As we have already shown the O-arylation of glycols by triphenylbismuth diacetate, studied by David and Thieffry,[12a] is a reaction which has a solvent effect (CH_2Cl_2 only), an induction period and a need for light. As we have reported all restrictions are removed by addition of copper ions and the reaction rate is greatly increased.[12b]

The slow O-phenylation by Bi^V reagents under neutral or slightly acid conditions that we reported earlier[2] requires 80-110° under reflux for some hours and does not show an induction period or solvent or light dependence. Even though the O-phenylation reaction of phenols is dramatically catalysed by copper, this is not an explanation for the ordinary thermal O-phenylation reaction.[2]

Experimental

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. ^{1}H-NMR spectra were determined for solutions in deuteriochloroform with TMS as internal standard on Varian T-60, Varian EM-360, Bruker WP-80 (80 MHz) spectrometers. IR spectra were recorded on a Perkin-Elmer 297 instrument. U.V. spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer. Mass spectra were recorded with AEI MS-9 or MS-50 apparatus. 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.), Merck Kieselgel 60-H (column chromatography at atmospheric pressure or under light pressure). Ether refers to diethyl ether. BTMG is N-tert-butyl-N',N',N'',N''-tetramethylguanidine.

Thermal Decomposition of 4-Nitrophenoxytriphenylbismuth Chloride 8.

A solution of 4-nitrophenoxytriphenylbismuth chloride 8 (0.5 g) in anhydrous benzene (10 ml) was stirred for 43 hrs under reflux, under argon. After distillation of the solvent, the residue was dissolved in methylene dichloride, washed with water, and the solvent distilled. Preparative t.l.c. (eluant: hexane) afforded biphenyl (0.017 g, 27%), triphenylbismuth (0.012 g, 17%), 4-nitrodiphenyl ether (0.004 g, 2%) and 4-nitrophenol (0.022 g, 19%).

Thermal Decomposition of 4-Nitrophenoxytriphenylbismuth Trifluoroacetate 9.

A similar reaction performed on 4-nitrophenoxytriphenylbismuth trifluoroacetate 9 (0.063 g) afforded biphenyl (0.048 g, 69%), triphenylbismuth (0.017 g, 4%) and 4-nitrophenol (0.043 g, 34%).

Phenylation of Phenols with Triphenylbismuth Dichloride under Basic Conditions. - General Procedure.

A solution of the substrate and N-tert-butyl-N',N',N'',N''-tetramethylguanidine (BTMG) (2-2.5 equiv.) in anhydrous THF or toluene was stirred for 15 mins at room temperature under argon. After addition of triphenylbismuth dichloride 3 (1.2-1.5 equiv.) the mixture was stirred at room temperature or under reflux for the time indicated. The reaction was monitored by t.l.c. and stopped when no evolution was noticed or when the substrate had disappeared. Trichloracetic acid (2-3 equiv.) or aqueous HCl (4N) solution was added until acidic pH, and the mixture stirred for 0.5 hr. The mixture was washed with saturated aqueous sodium hydrogencarbonate. The aqueous phase was extracted with methylene dichloride and the combined organic phase distilled under vacuum. The reaction products were isolated after chromatography of the residue.

With methyl 4-hydroxybenzoic acid ester 10 : A solution of methyl 4-hydroxybenzoate 10 (0.076 g), BTMG (0.21 ml) and 3 (0.384 g) in toluene (2 ml) was stirred under reflux for 1.5 hrs. Work-up and preparative t.l.c. (eluant: hexane-ether 9:1) afforded the O-phenyl ether 11 (0.101 g, 88%), m.p. 54-58°C, lit.[13] 60°C.

With 4-cyanophenol 12 : A solution of 4-cyanophenol 12 (0.060 g), BTMG (0.21 ml) and 3 (0.384 g) in toluene (2 ml) was stirred under reflux for 3 hrs. Work-up and preparative t.l.c. of the residue (eluant: hexane-ether 9:1) afforded the O-phenyl ether 13, as a pale yellow oil (0.088 g, 91%), ν_{max} ($CHCl_3$) 2200, 1570, and 1220 cm^{-1}; δ ($CDCl_3$) 7.9-7.1 (9H, m, ArH); m/z 195 (M^+) (Found: C, 80.06; H, 4.77; N, 6.98; O, 8.34. $C_{13}H_9NO$ requires C, 80.00; H, 4.62; N, 7.18; O, 8.20%).

With 4-trifluoromethylphenol 14 : A solution of 4-trifluoromethylphenol 14 (0.163 g), BTMG (0.49 ml) and 3 (0.616 g) in THF (2 ml) was stirred at room temperature for 0.5 hr and under reflux for 3 hrs. Preparative t.l.c. of the residue (eluant: hexane-ether 9:1) afforded the O-phenyl ether 15 (0.146 g, 70%) as an oil, ν_{max} ($CHCl_3$) 1610, 1590, 1310, 1160, 1100, and 1060 cm^{-1}; δ ($CDCl_3$) 7.6-6.8 (9H, m); m/z 238 (M^+), 219 (M^+-F), 169 (M^+-CF_3) (Found: C, 65.42; H, 3.85. $C_{13}H_9F_3O$ requires C, 65.55; H, 3.80%).

With 3-nitrophenol 16 : A solution of 3-nitrophenol 16 (0.139 g), BTMG (0.42 ml) and 3 (0.767 g) in toluene (4 ml) was stirred under reflux for 16 hrs. Work-up and preparative t.l.c. of the residue (eluant: hexane-ether 7:3) afforded the O-phenyl ether 17 as an oil (0.115 g, 54%), ν_{max} ($CHCl_3$) 3100, 1590, 1530, and 1230 cm^{-1}; δ ($CDCl_3$) 7.96-6.76 (8H, m, ArH); m/z 214 (M^+-1), and 168 (M^+-NO_2) (Found: C, 66.90; H, 4.27; O, 22.40; N, 6.21. $C_{12}H_9NO_3$ requires C, 66.98; H, 4.19; O, 22.32; N, 6.51%), 5-nitro-2-phenylphenol 18 (0.026 g, 13%), m.p. 91-95°C (lit.[14] 102°C); ν_{max} ($CHCl_3$) 3600, 1590, 1510, 1340, and 1200 cm^{-1}; δ ($CDCl_3$) 7.64-7.3 (8H, m, ArH) and 5.37 (1H, s, OH); m/z 215 (M^+), and 2,6-diphenyl 3-nitrophenol 19 (0.020 g, 9%), m.p. 107-110°C; ν_{max} ($CHCl_3$) 3600, 1600, 1530, 1260, and 1210 cm^{-1}; δ ($CDCl_3$) 7.52-6.62 (12H, m, ArH) and 5.42 (1H, s, OH); m/z 291 (M^+) (Found: C, 74.42; H, 4.71; O, 16.35. $C_{18}H_{13}NO_3$ requires C,74.23; H, 4.47; O, 16.49%).

With 3,5-dimethoxyphenol 22 : A solution of 3,5-dimethoxyphenol 22 (0.077 g), BTMG (0.21 ml), 3 (0.384 g) in toluene (2 ml) was stirred under reflux for 4 hrs. Work-up and preparative t.l.c. of the residue (eluant: hexane-ethyl acetate 7:3) afforded the O-phenyl ether 23 as an oil (0.01 g, 10%), ν_{max} ($CHCl_3$) 2850, 1590, 1240, 1140, and 1100 cm^{-1}; δ ($CDCl_3$) 7.63 (5H, s, C_6H_5), 6.6-6.5 (3H, m, 2-H, 4-H and 6-H), and 3.85 (6H, s, 2 OCH_3); m/z 230 (M^+) (Found: C, 73.12; H, 6.11; O, 20.81. $C_{14}H_{14}O_3$ requires C, 73.04; H, 6.08; O, 20.86%), the mono-C-phenyl derivative, 3,5-dimethoxy 2-phenylphenol 24, as an oil (0.052 g, 45%), ν_{max} ($CHCl_3$) 3550, 2850, 1620, 1590, 1140, and 1100 cm^{-1}; δ ($CDCl_3$) 7.36 (5H, m, C_6H_5), 6.16 (2H, m, 4-H and 6-H), 5.03 (1H, s, OH), and 3.88 and 3.66 (2x3H, 2s, OCH_3); m/z 230 (M^+) and 3,5-dimethoxy 2,6-diphenylphenol 25 (0.046 g, 30%), m.p. 178-180°C, ν_{max} ($CHCl_3$) 3550, 2850, 1620, 1325, and 1100 cm^{-1}; δ ($CDCl_3$) 7.63 (10H, s, 2xC_6H_5), 6.5 (1H, s, 4-H), 5.23 (1H, s, OH), and 3.87 (6H, s, 2xOCH_3); m/z 306 (M^+), 305 (M^+-1) (Found: C, 78.16; H, 6.00; O, 15.72. $C_{20}H_{18}O_3$ requires C, 78.43; H, 5.88; O, 15.69%).

With 3,5-dichlorophenol 26 : A solution of 3,5-dichlorophenol 26 (0.082 g), BTMG (0.21 ml) and 3 (0.384 g) in toluene (2 ml) was stirred under reflux for 16 hrs. Work-up and preparative t.l.c. of the residue (eluant: hexane-ether 4:1) afforded the O-phenyl ether 27 as an oil (0.071 g, 60%), ν_{max} ($CHCl_3$) 2950, 1590, 1420, 1240, 1160, and 840 cm^{-1}; δ ($CDCl_3$) 7.43-6.79 (m, ArH); m/z 240, 238 (M^+) and 205, 203 (M^+-Cl) (Found: C, 60.68; H, 3.60; O, 6.65; Cl, 29.65. $C_{12}H_8Cl_2O$ requires C, 60.25; H, 3.35; O, 6.69; Cl, 29.71%), 3,5-dichloro 2-phenylphenol 28 as an oil (0.021 g, 16%), ν_{max} ($CHCl_3$) 3550, 1610, 1550, 1410, 1300, 1210, 1150, and 820 cm^{-1}; δ ($CDCl_3$) 7.6-6.8 (7H, m, ArH), 4.93 (1H, s, OH); m/z 240, 238 (M^+) (Found: C, 60.52; H, 3.56; O, 6.74; Cl, 29.47. $C_{12}H_8Cl_2O$ requires C, 60.25; H, 3.35; O, 6.69; Cl, 29.71%) and 3,5-dichloro 2,6-diphenylphenol 29 (0.021 g, 12%), m.p. 120-122°C; ν_{max} ($CHCl_3$) 3550, 1600, 1400, 1300, 1160, and 830 cm^{-1}; δ ($CDCl_3$) 7.27 (10H, s, ArH), 7.13 (1H, s, 4-H), 5.0 (1H, s, OH); m/z 316, 314 (M^+) (Found: C, 68.58; H, 3.79; O, 5.31. $C_{18}H_{12}Cl_2O$ requires C, 68.57; H, 3.81; O, 5.08%).

With 2,4,6-trimethylphenol 35 : A solution of 2,4,6-trimethylphenol 35 (0.275 g), BTMG (1.3 ml) and 3 (1.652 g) in THF (10 ml) was stirred at room temperature for 24 hrs. Preparative t.l.c. of the residue (eluant: hexane-ether 9:1) afforded 2,4,6-trimethyl 6-phenyl 2,4-cyclohexadienone 36 (0.031 g, 15%) as a white solid, m.p. 67-68°C (hexane), ν_{max} ($CHCl_3$) 1660 and 1640 cm^{-1}; δ ($CDCl_3$) 7.28 (5H, s, ArH), 6.70 (1H, m, 3-H), 6.0 (1H, m, 5-H), 1.95 (3H, bs, 2-CH_3), 1.80 (3H, bs, 4-CH_3) and 1.50 (3H, s, 6-CH_3); λ_{max} (CCl_4) 320 (4075)nm; m/z 212 (M^+), 197 (M^+-CH_3), 184 (M^+-CO), and 169 (M^+-$COCH_3$) (Found: C, 84.87; H, 7.65; O, 7.75. $C_{15}H_{16}O$ requires C, 84.86; H, 7.59; O, 7.54%).

With 2,6-dimethyl 4-methoxyphenol 39[15] : A solution of 2,6-dimethyl 4-methoxyphenol 39 (0.106 g), BTMG (0.340 ml) and 3 (0.430 g) in THF (10 ml) was stirred at room temperature for 4 days. Preparative t.l.c. of the residue (eluant: hexane-ether 4:1) afforded 2,6-dimethyl 4-methoxy 6-phenyl 2,4-cyclohexadienone 40 (0.070 g, 43%) as an oil, ν_{max} ($CHCl_3$) 1665 and 1620 cm^{-1}; δ ($CDCl_3$) 7.4-7.12 (5H, m, ArH), 6.7 (1H, m, $W_{\frac{1}{2}}$ 6 Hz, 3-H), 5.2 (1H, d, J 3 Hz, 5-H), 3.57 (3H, s, OCH_3), 1.82 (3H, d, J 1 Hz, 2-CH_3) and 1.55 (3H, s, 6-CH_3); m/z 228 (M^+), 213 (M^+-CH_3), 200 (M^+-CO) and 185 (M^+-$COCH_3$) (Found: C, 79.13; H, 6.81; O, 13.83. $C_{15}H_{16}O_2$ requires C, 78.94; H, 7.01; O, 14.03%), and 39 (0.057 g, 49%).

With phenol 44 : A solution of phenol 44 (0.094 g), BTMG (0.42 ml) and 3 (0.766 g) in THF (3.5 ml) was stirred under reflux for 48 hrs. Work-up and preparative t.l.c. (eluant: hexane-benzene 1:1) yielded 2-phenylphenol 46 (0.050 g, 30%), 2,6-diphenylphenol 47 (0.017 g, 7%), m.p. 100-102°C, lit.[16] 101°C, diphenyl ether 45 (0.013 g, 8%), biphenyl (0.122 g, 8%) and phenol 44 (0.037 g, 40%).

With 2-phenylphenol 46 : A solution of 2-phenylphenol 46 (0.170 g), BTMG (0.42 ml) and 3 (0.768 g) in THF (4 ml) was stirred under reflux for 48 hrs. Work-up and column chromatography afforded 2,6-diphenylphenol 47 (0.082 g, 33%).

Reaction of 2,4-Di-tert-butyl phenol 30 with Triphenylbismuth Bistrifluoroacetate under Basic Conditions.

A solution of 2,4-di-*tert*-butylphenol 30 (0.200 g), BTMG (0.24 ml) and 4 (0.760 g) in methylene dichloride (5 ml) was stirred for 20 hrs under argon. 10% Aqueous HCl solution (3 ml) was added, and the mixture stirred under reflux for 2 hrs. Preparative t.l.c. of the residue (eluant: hexane) afforded 2,4-di-*tert*-butyl 6-phenylphenol 31 (0.220 g, 81%) as a yellow oil, lit.[17] m.p. 57-58°C; ν_{max} ($CHCl_3$) 3550, 2860, 2740, 1600, 1360 cm^{-1}; δ ($CDCl_3$) 7.3-6.9 (7H, m, 3-H, 5-H, Ph), 5.15 (1H, s, OH), 1.4 (9H, s, t-Bu), 1.26 (9H, s, t-Bu); m/z 282 (M^+), 267 (M^+-15) and 77 (Ph), and the O-phenyl ether 32 (0.007 g, 3%), m.p. 48-50°C (hexane), ν_{max} ($CHCl_3$) 2860, 2740, 1600, 1480, 1390 and 1360 cm^{-1}; δ ($CDCl_3$) 7.44-6.68 (8H, m, ArH), 1.48 (9H, s, t-Bu) and 1.35 (9H, s, t-Bu); m/z 282 (M^+), 267 (M^+-15), and 77 (Ph) (Found: C, 84.81; H, 8.91. $C_{20}H_{26}O$ requires C, 85.10; H, 9.21%).

Reaction of Phenol 30 with Ph_5Bi.

When a similar reaction was performed with 30 (0.10 g) and 5 (0.58 g) in benzene (5 ml) for 24 hrs at room temperature under argon, 31 was obtained (0.086 g, 65%).

Reaction of Phenol 44 With Tetraphenylbismuth Trifluoroacetate and BTMG.

A solution of 44 (0.047 g), BTMG (0.171 g) and 1 (0.41 g) in anhydrous toluene (2 ml) was stirred for 24 hrs at 80° under argon in the dark. After work-up with trifluoroacetic acid, preparative t.l.c. afforded 46 (0.025 g, 29%), 47 (0.004 g, 3%), 44 (0.01 g, 22%) and 45 (0.036 g, 42%).

Reaction of 2,4,6-Trimethylphenol with Pentaphenylbismuth.

A solution of 2,4,6-trimethylphenol (0.134 g) and 5 (0.703 g) in benzene (5 ml) was stirred at room temperature for 3 hrs under argon. Distillation of the solvent and preparative t.l.c. of the residue afforded the dienone 36 (0.176 g, 88%).

Dimerisation of 2,6-Di-tert-butyl phenol 33 with 3, 4 and Triphenylbismuth Carbonate.

a) A mixture of 2,6-di-*tert*-butylphenol 33 (0.1 g), TMG (0.2 g) and 3 (0.3 g) in anhydrous THF (10 ml) was stirred for 30 hrs under argon. After the solvent was distilled, the residue was filtered over a short silica column (eluant: ether-hexane 1:1). Preparative t.l.c. of the residue of the filtrate (eluant: hexane) afforded triphenylbismuth (0.060 g,

28%) and 2,6,2',6'-tetra-*tert*-butyldiphenoquinone 34 (0.040 g, 40%), m.p. 245°C (hexane), lit.[19] 245-247°C. *b)* By a similar method 33 (0.050 g), TMG (0.16 g) and 4 (0.166 g) afforded triphenylbismuth (0.050 g, 47%) and 34 (0.025 g, 50%). *c)* By a similar method, 33 (0.116 g), TMG (0.2 g) and triphenylbismuth carbonate (0.3 g) afforded triphenylbismuth (0.114 g, 46%) and 34 (0.060 g, 52%). In the absence of TMG, no reaction occured.

Reaction of Phenols with 3, BTMG and Methanol.

a) Reaction of 2,4,6-Trimethylphenol : A solution of 3 (0.51 g) in methylene dichloride (2 ml) was added dropwise to a solution of 2,4,6-trimethylphenol 35 (0.13 g) and BTMG (0.34 g) in methanol (2 ml). The mixture was stirred for 6.5 hrs under argon at room temperature. The solvents were distilled under reduced pressure and the residue fractionated by column chromatography (eluant: ether gradient in hexane) to afford triphenylbismuth (0.356 g, 85%) and 2,6-dimethyl 4-methoxymethylphenol 37 (0.131 g, 82%) as a colourless oil, lit.[20] m.p. 54-55°C; δ ($CDCl_3$) 6.83 (2H, s, Ar-H), 5.03 (1H, s, OH), 4.27 (2H, s, CH_2), 3.33 (3H, s, OCH_3), and 2.25 (6H, s, $2xCH_3$); m/z 166 (M^+) and 135 (M^+-OMe) (Found: C, 72.4; H, 8.4. Calc. for $C_{10}H_{14}O_2$: C, 72.2; H, 8.5%).

b) Reaction of 2,6-Di-tert-butyl-4-methylphenol 41 : A solution of 3 (0.55 g) in anhydrous benzene (10 ml) was added over 5 mins to a solution of 2,6-di-*tert*-butyl 4-methylphenol 41 (0.22 g) and BTMG (0.4 g) in anhydrous methanol (5 ml). The mixture was stirred at room temperature for 3 days. The solvents were distilled and column chromatography (eluant: ether-hexane 1:13) afforded triphenylbismuth (0.416 g, 95%), 2,6-di-*tert*-butyl 4-methoxymethylphenol 42 (0.185 g, 74%), m.p. 99-100°C (hexane), lit.[21] 98-99°C.

Reaction of 41 with 3, BTMG, and Acrylonitrile.

A solution of 41 (0.44 g), BTMG (1 g), 3 (1.1 g), acrylonitrile (5 ml) and anhydrous benzene (20 ml) was stirred under reflux under argon for 4 hrs. The solvents were distilled and the residue fractionated by column chromatography (eluant: hexane-ether 9:1) to give a mixture of 41 and triphenylbismuth (0.31 g), followed by 43 as a yellow oil (0.144 g, 21%) which crystallised as white plates, m.p. 112°C (ethanol); $\nu_{max.}$ ($CHCl_3$) 1640 cm^{-1}; δ ($CDCl_3$) 7.20-7.06 (5H, m, Ph), 6.56 (1H, d, J 3 Hz, ArH), 6.28 (1H, d, J 3 Hz, ArH), 2.74-2.50 (3H, m, CH_2 + CH), 1.32 (3H, s, CH_3) and 1.28 (18H, s, 2 t-Bu); m/z 349 (M^+) and 219 (M^+ -$CH_2CHPhCN$) (Found: C, 82.6; H, 8.9; N, 4.2. $C_{24}H_{31}NO$ requires C, 82.5; H, 9.0; N, 4.0%).

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