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Influence of the Steric Hindrance of the Aryl Group of Pentavalent Triarylbismuth Derivatives in Ligand Coupling Reactions

Alexey Fedorov, Sébastien Combes and Jean-Pierre Finet*

Laboratoire "Chimie, Biologie et Radicaux Libres" UMR 6517 CNRS-Universités d'Aix-Marseille 1 et 3
Faculté des Sciences Saint-Jérôme, 13397 Marseille Cedex 20 France

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Abstract: Tris(*ortho*-tolyl)bismuth dichloride derivatives react with nucleophiles under basic conditions to give good to high yields of the *C*-arylated substrates. Under the same conditions, trimesitylbismuth dichloride affords only poor yields of the *C*-mesitylated substrates. Similar influence of the substitution pattern of tris(*ortho*-tolyl)bismuth diacetate derivatives was observed in the copper-catalysed arylation of hydroxyl or amino groups. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Arylation; Bismuth; Ligand coupling; Regioselectivity

Formation of carbon-carbon or carbon-heteroatom bonds by reaction of an organoheteroatomic compound, acting as a carbocation synthetic equivalent, with a nucleophile is now well documented.[1] These reactions, taking place by a ligand coupling mechanism, involve a number of organic derivatives of main group p-block elements, such as iodine, sulfur, selenium, tellurium, phosphorus, antimony, bismuth, lead and thallium. The arylation reaction is the most common reaction observed with all these elements, although other groups have also been transferred (alkenyl, alkynyl or perfluoroalkyl groups). In the reactions of diaryliodonium salts with nucleophiles, preferential bonding of the more hindered aryl group with the incoming nucleophile was observed and attributed to an "α-effect".[2] For example, thermolysis of phenyl *ortho*-tolyliodonium tetrafluoroborate in the presence of chloride ion as the nucleophile afforded 84% of *ortho*-chlorotoluene and 16% of *ortho*-iodotoluene. In ligand coupling reactions implying organolead triacetates, very high yields of arylated derivatives were obtained with highly substituted electron-rich aryllead triacetate derivatives.[3] By contrast, in a recent report, we observed a small detrimental influence of the introduction of an *ortho*-substituent in arylation reactions involving organobismuth reagents.[4] We therefore decided to investigate the steric influence of *ortho* substitutions on the outcome of arylation reactions with pentavalent triarylbismuth derivatives.

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* Fax : 33 4 91 98 85 12; E-mail : finet@srepir1.univ-mrs.fr

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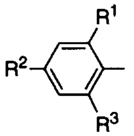
Triarylbismuth diacetates are useful reagents as they exhibit the widest range of reactivity, depending on the reaction conditions.[5] Under basic conditions, they lead to the products of *C*- or *O*-arylation. In the presence of a copper catalyst, they lead to the products of *O*- and *N*-arylation. Triphenylbismuth diacetate **(9)** and the mono-*ortho*-tolyl derivatives **(10)**-**(11)** can be easily prepared by the sodium perborate in acetic acid oxidation.[6] However, when trimesitylbismuthane **(8)** was treated under these conditions, the expected trimesitylbismuth diacetate **(12)** was not obtained. Instead, the reaction afforded an ill-defined compound **(12a)**, containing acetoxy ligands. To study the arylation reactions under basic conditions, we therefore turned our attention to the triarylbismuth dichlorides,[7] as the three compounds **(13)**, **(14)** and **(16)** have been described.[8,9] The more hindered tris(2,4,6-trimethylphenyl)bismuth dichloride **(16)** can be conveniently prepared by reaction of trimesitylbismuthane with thionyl chloride.[9] In the case of the reagents **(13)**-**(15)**, classical methods of oxidative chlorination can be used. However, we found that ligand exchange takes place during the treatment of triarylbismuth diacetate with an aqueous saturated sodium chloride solution.

$$\mathrm{Ar_3Bi(OAc)_2} + \mathrm{NaCl} \longrightarrow \mathrm{Ar_3BiCl_2}$$

These dichlorides were therefore easily obtained by a modification of our synthesis of triarylbismuth diacetates.[6] When triarylbismuthanes were treated with sodium perborate in acetic acid, aqueous work-up followed by treatment of the organic phase with brine led directly to good yields of the chlorides **(13)**-**(15)**.

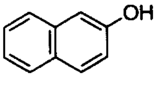
	Ar	Ar_3Bi	$Ar_3Bi(OAc)_2$	Ar_3BiCl_2
R^1, R^2, R^3 = H	**1**	**5**	**9**	**13**
R^1 = Me, R^2, R^3 = H	**2**	**6**	**10**	**14**
R^1, R^2 = Me, R^3 = H	**3**	**7**	**11**	**15**
R^1, R^2, R^3 = Me	**4**	**8**	**12**	**16**

Reactions under basic conditions:

The reactions of a variety of substrates **(17)**, **(22)**, **(29)**, **(34)** and **(39)** with the dichlorides **(13)**-**(16)** in the presence of *N,N,N',N'*-tetramethylguanidine (TMG) led usually to the expected products of α-arylation (Table 1). The presence of one methyl group on the *ortho* position reduces the rate of the reactions with **(14)** and **(15)**, which required longer reaction times and/or higher temperatures. The yields of the α-arylated products were not significantly reduced by comparison with the reactions with **(13)**. In the case of the reaction with the phenol **(22)**, the mono-aryl derivatives **(24)** and **(25)** were obtained in good to high yields. A small amount of the *O*-aryl ether **(26)** was also isolated in the reaction of **(22)** with the bismuth reagent **(15)**. By contrast, the reactions of the mesityl derivative **(16)** with the various substrates always led to modest yields of the α-mesityl derivatives. The more reactive 2-naphthol afforded a relatively good yield of 1-mesityl-2-naphthol (61%) and the more bulky phenol **(22)** afforded an equimolecular mixture of the *ortho*-*C*-aryl and *O*-aryl ether. A number of substrates failed to react with the mesityl reagent **(16)** under basic conditions: acetophenone, 4-*tert*-butylcyclohexanone, 1,3-indandione, 2-phenyl-1,3-indandione and 2-nitropropane.

Table 1: Arylation reactions under basic conditions

$$\mathrm{NuH + TMG + Ar_3BiCl_2 \longrightarrow NuAr}$$



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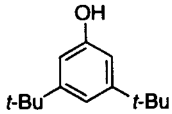

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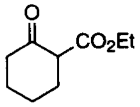

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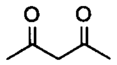

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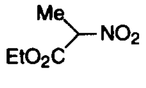

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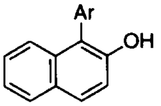
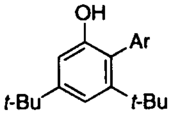
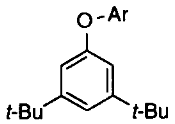


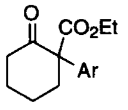
(18), Ar = **(1)**
(19), Ar = **(2)**
(20), Ar = **(3)**
(21), Ar = **(4)**



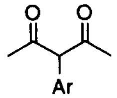
(23), Ar = **(1)**
(24), Ar = **(2)**
(25), Ar = **(3)**
(27), Ar = **(4)**



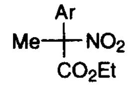
(26), Ar = **(3)**
(28), Ar = **(4)**



(30), Ar = **(1)**
(31), Ar = **(2)**
(32), Ar = **(3)**
(33), Ar = **(4)**



(35), Ar = **(1)**
(36), Ar = **(2)**
(37), Ar = **(3)**
(38), Ar = **(4)**



(40), Ar = **(1)**
(41), Ar = **(2)**
(42), Ar = **(3)**
(43), Ar = **(4)**

Substrate	Reagent	Reaction conditions*	Products (%)	Ref
(17)	**(13)**	C_6H_6, RT, 4.5 h	**(18)** 90	10
	(14)	RT, 15 h	**(19)** 86	
	(15)	RT, 15 h	**(20)** 94	
	(16)	RT, 17 h, then 10 h at 50°C under N_2	**(21)** 61	
(22)	**(13)**	C_6H_6, NaH, reflux, 3.5 h	**(23)** 26, **(23a)** 2**	10
	(14)	18 h, 50°C	**(24)** 80	
	(15)	15 h, 50°C	**(25)** 57, **(26)** 10	
	(16)	15 h, 60°C under N_2	**(27)** 24, **(28)** 25	
(29)	**(13)**	C_6H_6, 80°C, 2 h	**(30)** 75	11
	(14)	RT, 4 d	**(31)** 64	
	(15)	RT, 4 d	**(32)** 63	
	(16)	RT, 5 d under N_2	**(33)** 25	
(34)	**(13)**	C_6H_6, 80°C, 2 h	**(35a)** 74***	11
	(14)	RT, 20 h	**(36)** 76	
	(15)	RT, 2 d	**(37)** 53	
	(16)	RT, 15 h, then 3 h at 60°C under N_2	**(38)** 31	
(39)	**(13)**	RT, 3 h	**(40)** 81	12
	(14)	RT, 4 d	**(41)** 79	
	(15)	RT, 4 d	**(42)** 72	
	(16)	RT, 50 h, then 30 h at 60°C under N_2	**(43)** 7****	

* All reactions performed in THF in the presence of TMG, unless otherwise indicated.

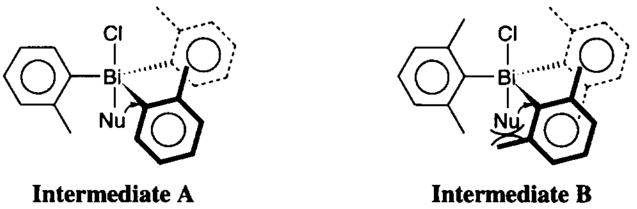
** **(23a)** is 2,6-diphenyl-3,5-di-*tert*-butylphenol. When two equivalents of the bismuth reagent **(13)** were used, **(23a)** was obtained in a 77% yield.

*** **(35a)** is 3,3-diphenyl-2,4-pentanedione; 2 equivalents of bismuth reagent were used.

**** Compound **(43)** could not be isolated pure.

Comparison of these results with the known examples of mesitylation reactions with iodine or lead reagents shows that the bismuth reagent is as susceptible to steric hindrance as the corresponding reagents.[13,14] However, as only mesitylation of 1,3-indandione derivatives was reported for the iodonium reagent[13] and one example of arylation of a β-ketoester with the mesityllead triacetate was reported,[14] comparison of the relative reactivity patterns is not significant. The difference in the yields between the two series of reactions (arylbismuth reagents with only one *ortho*-methyl group and arylbismuth reagents with two *ortho*-methyl groups) is likely to result from the difference in the overlap between the π-systems of the aryl group and the nucleophilic ligand. The presence of the *ortho*-methyl group is likely to induce a reduced topological mobility of the intermediates, the dihedral angle between the planes of the aryl group and the plane containing the bismuth atom and the three *ipso*-carbon atoms becomes more important with the presence of one methyl group and even more in the case of two *ortho*-methyl groups. In the case of the 2-naphthol, the flatness of the naphthyl ligand allows an easier overlap between the two π-systems, which can take a parallel arrangement favourable for the ligand coupling. Ligand coupling takes place also to give a relatively good overall yield of coupled products in the base-catalysed reaction of the more bulky 3,5-di-*tert*-butylphenol (**22**). However, the steric bulk of the two *tert*-butyl groups leads to a less favourable overlap between the two π-systems. Therefore, the ligand coupling occurs between the *ipso* carbon of the mesityl group with the C-2 carbon of the phenol as well as with the oxygen center to afford equivalent amounts of the *C*-aryl derivative (**27**) and of the *O*-aryl ether (**28**).

In the mono *ortho*-methyl series, the nucleophile may occupy the less hindered apical position, that is on the side possessing only one or no methyl group. The overlap between the nucleophile and the π-system of an equatorial aryl ligand can be reasonably reached (Scheme 1, intermediate A). In the case of the mesityl series, the two apical positions of the covalent bismuth-nucleophile intermediate are equally hindered and the overlap is strongly impeded (Scheme 1, intermediate B).



Scheme 1: Possible structures of the covalent bismuth-nucleophile intermediates

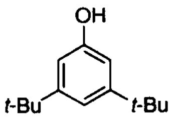
Copper-catalysed reactions:

In the presence of a catalytic copper species, triarylbismuth diacetates react with hydroxyl or amino groups to afford the corresponding *O*-aryl ethers or aniline derivatives.[5] A similar behaviour is observed in the reaction of triarylbismuthanes Ar_3Bi with a stoichiometric amount of copper (II) diacetate, acting both as an oxidant and as the catalyst. In this study as well as in our related work on mono *ortho*-substituted organobismuth reagents, the influence of the substitution pattern of the aryl groups of the triarylbismuth diacetates appeared clear-cut.[4]

In the case of the aniline (**51**), the introduction of an *ortho*-methyl group on the aryl group of the bismuth reagent had no effect on the yield of the derived diarylamines (**53**) and (**54**) (84-88%). However, the reaction rate appeared again slower than in the case of the unsubstituted reagent. Even an attractive yield of

Table 2: Copper-catalysed arylation reactions

$$R\text{-}Z\text{-}H + Ar_3Bi(OAc)_2 \xrightarrow[Z\ =\ O\text{ or }N]{Cu(OAc)_2} R\text{-}Z\text{-}Ar$$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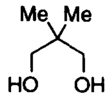
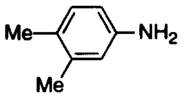
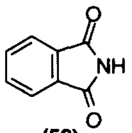
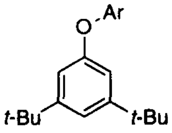
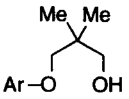
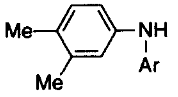

(46)

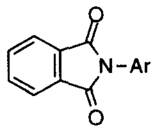

(51)


(56)









(44), Ar = **(1)**
(45), Ar = **(2)**
(26), Ar = **(3)**
(28), Ar = **(4)**

(47), Ar = **(1)**
(48), Ar = **(2)**
(49), Ar = **(3)**
(50), Ar = **(4)**

(52), Ar = **(1)**
(53), Ar = **(2)**
(54), Ar = **(3)**
(55), Ar = **(4)**

(57), Ar = **(1)**
(58), Ar = **(2)**
(59), Ar = **(3)**
(60), Ar = **(4)**

Substrate	Reagent	Reaction conditions	Products (%)	Ref
(22)	**(9)**	$Cu(OAc)_2$ (0.1 equiv.), RT, 1 h	**(44)** 80	15
	(10)	$Cu(OAc)_2$ (0.1 equiv.), RT, 3 d	**(45)** 16	4
	(11)	$Cu(OAc)_2$ (0.1 equiv.), 50°C, 10 h	**(26)** 19	
	(12a)	$Cu(OAc)_2$ (0.1 equiv.), 50°C, 10 h	**(28)** <5	
(46)	**(9)**	$Cu(OAc)_2$ (0.1 equiv.), RT, 1 h	**(47)** 82	16
	(10)	$Cu(OAc)_2$ (0.1 equiv.), RT, 32 h	**(48)** 65	
	(11)	$Cu(OAc)_2$ (0.1 equiv.), RT, 3 h	**(49)** 51	
	(8)	$Cu(OAc)_2$ (1 equiv.), pyridine (3 equiv.), 50°C, 3 d	**(50)** 16	
(51)	**(9)**	$Cu(OAc)_2$ (0.1 equiv.), RT, 2 h	**(52)** 86	17
	(10)	$Cu(OAc)_2$ (0.1 equiv.), RT, 16 h	**(53)** 84	
	(11)	$Cu(OAc)_2$ (0.1 equiv.), RT, 1 d	**(54)** 88	
	(8)	$Cu(OAc)_2$ (1 equiv.), 50°C, 2 d	**(55)** 51	
(56)	**(5)**	$Cu(OAc)_2$ (1 equiv.), pyridine (1 equiv.), RT, 24 h	**(57)** 98	18
	(10)	$Cu(OAc)_2$ (0.1 equiv.), pyridine (1 equiv.), RT, 3 d	**(58)** 18	
	(6)	$Cu(OAc)_2$ (1 equiv.), pyridine (1 equiv.), RT, 2 d	**(58)** 31	
	(11)	$Cu(OAc)_2$ (0.1 equiv.), pyridine (3 equiv.), RT, 3 d	**(59)** 19	
	(8)	*a*) $NaBO_3$, AcOH; *b*) $Cu(OAc)_2$ (0.1 equiv.), pyridine (3 equiv.), RT, 35 h	**(60)** 18	

the mesitylamine **(55)** was observed in the reaction of **(51)** with trimesitylbismuthane **(8)** and stoichiometric copper (II) diacetate. With less reactive substrates, such as the glycol **(46)**, a significant drop was already observed with the mono *ortho*-methyl derivatives. With the least reactive substrates, phenol **(22)** and phthalimide **(56)**, the reactions were so slow that decomposition of the reagent became predominant and the *O*- or *N*-arylation products were obtained in very modest yields (< 20%).

In these various copper-catalysed reactions, the steric hindrance of the organobismuth reagent plays a significant role, probably at the stage of the transmetallation bismuth --> copper. When this transfer is very easy (by coordination of the copper species with an aniline), the steric effect induces less important consequences.

Conclusion:

In the base-catalysed type of reactions, the steric hindrance plays an inhibitory role which is more pronounced in the mesityl series. This behaviour is similar to the reactivity of dimesityliodonium salts with nucleophiles, although a limited number of reactions were described at the time.[13] As this effect is likely to result from steric interactions during the ligand coupling step, dissymetric reagents, such as mixed phenylmesitylbismuth derivatives, should offer an attractive alternative to obtain higher yields of coupled products. It should also be useful to improve the efficiency of the copper-catalysed reactions with very hindered reagents. Work in this direction is now underway and will be reported in due course.

Experimental

Melting points were taken on a Büchi capillary apparatus and are uncorrected. NMR spectra were obtained on a Bruker AC200 spectrometer: ^{1}H-NMR at 200.13 MHz and ^{13}C-NMR at 50.32 MHz. Chemical shifts (δ) are reported in ppm for solution of the compounds in $CDCl_3$ with internal Me_4Si and J values in Hertz. TMG refers to N,N,N',N'-tetramethylguanidine and ether refers to diethyl ether. CC refers to column chromatography on silicagel and PLC refers to preparative layer chromatography on silicagel.

Tris(2,4,6-trimethylphenyl)bismuth dichloride **(16)** was prepared by treatment of **(8)** with thionyl chloride.[8] Tris(2-methylphenyl)bismuth diacetate **(10)** was prepared by oxidation of the triarylbismuthane with sodium perborate monohydrate in acetic acid.[6,17]

Tris(2,4-dimethylphenyl)bismuth diacetate (11): prepared from **(7)** by the same procedure as for **(10)**; colourless plates from dichloromethane-pentane (1:3), 72%, m.p. 135-136°C; δ_H 1.72 (6H, s, CH_3CO), 2.34 (9H, s, 4-Me), 2.55 (9H, s, 2-Me), 7.15-7.33 (6H, m, 5-H and 6-H) and 8.14 (3H, d, *J* 8, 3-H); δ_C 21.3 (4-Me), 22.9 ($\underline{C}H_3CO$), 23.4 (2-Me), 128.9, 133.9, 134.3 (C-3, C-5 and C-6), 140.8 and 141.7 (C-2 and C-4), 159.8 (C-Bi) and 176 ($CH_3\underline{C}O$) (Found: C, 52.14; H, 5.23. $C_{28}H_{33}BiO_4$ requires: C, 52.34; H, 5.18%).

Synthesis of triarylbismuth dichloride by ligand exchange: A mixture of sodium perborate monohydrate (6 mmol) and triarylbismuthane (2 mmol) in acetic acid (20 mL) was stirred at room temperature for 1 h. The resulting solution was poured into brine (60 mL) and then vigorously shaken for 15 minutes. The mixture was extracted with dichloromethane (3 x 20 mL). The organic extracts were combined, washed with water, dried over $MgSO_4$. The solvent was distilled under reduced pressure and the solid residue was recrystallised from dichloromethane-ethanol (1:2) at -15°C.

Triphenylbismuth dichloride (13): 91%, m.p. 156-157°C, lit.[8] 156°C.

Tris(2-methylphenyl)bismuth dichloride (14): 87%, m.p. 172°C, lit.[8] 169-171°C; δ_H 2.73 (9H, s, Me), 7.35-7.55 (9H, m, 3-H, 4-H and 5-H) and 8.02 (3H, dd, $J_{H6\text{-}H5}$ 6.8, d, $J_{H6\text{-}H4}$ 2.3, 6-H); δ_C 24.2 (Me), 128.9, 131.5, 133.5, 134.5 (C-3, C-4, C-5 and C-6), 141.9 (C-2) and 161.6 (C-Bi).

Tris(2,4-dimethylphenyl)bismuth dichloride (15): colourless plates, 65%, m.p. 169°C; δ_H 2.37 (9H, s, 4-Me), 2.68 (9H, s, 2-Me), 7.20-7.35 (6H, m, 3-H and 5-H) and 7.90 (3H, d, *J* 8.1, 6-H); δ_C 21.3 (4-Me), 24 (2-Me), 129.4, 134, 134.4 (C-3, C-5 and C-6), 141.2 and 141.9 (C-2 and C-4) and 158.6 (C-Bi) (Found: C, 48.42; H, 4.57. $C_{24}H_{27}BiCl_2$ requires: C, 48.42; H, 4.57%).

Arylation reactions with triarylbismuth derivatives in the presence of *N,N,N',N'*-tetramethylguanidine (TMG): General procedure: A mixture of the substrate (0.25-0.5 mmol, 1 equiv.) and TMG (1.2 equiv.) in distilled THF (5 mL/ mmol of substrate) was stirred for 10 min at room temperature. The triarylbismuth dichloride reagent (1.2 equiv) was added and the mixture stirred as indicated below. The solvent was distilled off and the residue was purified by chromatography as described below to afford the reaction products.

With 2-Naphthol (17):

1-(2'-Methylphenyl)-2-naphthol (19): CC (eluent: pentane-ether 7:3); colourless plates, m.p. 79°C; δ_H 2.07 (3H, s, 2'-Me), 5.04 (1H, s, OH), 7.15-7.49 (8H, m, ArH) and 7.79-7.91 (2H, m, ArH); δ_C 19.6 (2'-Me), 117.4 (C-3), 120.3 (C-1), 123.3, 124.5, 126.6, 126.9, 128.2, 129, 129.5, 131, 131.6 (C-4, C-5, C-6, C-7, C-8, C-3', C-4', C-5' and C-6'), 133.1 and 133.2 (C-9 and C-10), 139 (C-1' and C-2') and 150.1 (C-2) (Found: C, 87.05; H, 6.06. $C_{17}H_{14}O$ requires: C, 87.15; H, 6.02%).

1-(2',4'-Dimethylphenyl)-2-naphthol (20): CC (eluent: pentane-ether 7:3); colourless gum; δ_H 2.04 (3H, s, 2'-Me), 2.47 (3H, s, 4'-Me), 7.18-7.40 (7H, m, ArH) and 7.79-7.91 (2H, m, ArH); δ_C 19.5 (2'-Me), 21.3 (4'-Me), 117.3 (C-3), 120.3 (C-1), 123.2, 126.5, 127.7, 128.1, 129.3, 131.5 and 131.8 (C-4, C-5, C-6, C-7, C-8, C-3', C-5' and C-6'), 129 (C-10), 130 (C-9), 133.3 (C-1'), 138.7 (C-2' and C-4') and 150.2 (C-2) (Found: C, 86.98; H, 6.52. $C_{18}H_{16}O$ requires: C, 87.06; H, 6.49%).

1-(2',4',6'-Trimethylphenyl)-2-naphthol (21): CC (eluent: pentane-ether 7:3) and PLC (eluent: pentane-ether 7:3); colourless plates, m.p. 97°C (pentane-ether 8:2); δ_H 1.93 (6H, s, 2'-Me and 6'-Me), 2.42 (3H, s, 4'-Me), 4.95 (1H, s, OH), 7.09 (2H, s, 3'-H and 5'-H), 7.12-7.41 (4H, m, ArH) and 7.80-7.91 (2H, m, ArH); δ_C 19.9 (2'-Me and 6'-Me), 21.3 (4'-Me), 117.2 (C-3), 119.6 (C-1), 123.3, 124, 126.7, 128.3, 129, 129.1 (C-4, C-5, C-6, C-7, C-8, C-3' and C-5'), 129 and 132.8 (C-9 and C-10), 138.5 (C-4'), 138.9 (C-2' and C-6') and 150.2 (C-2) (Found: C, 86.93; H, 6.87. $C_{19}H_{18}O$ requires: C, 86.99; H, 6.92%).

With 3,5-di-*tert*-butylphenol (22):

3,5-Di-*tert*-butyl-2-(2'-methylphenyl)phenol (24): CC (eluent: pentane-ether 5:1) and PLC (eluent: pentane-ether 5:1); colourless plates, m.p. 72°C (pentane); δ_H 1.21 (9H, s, 5-CMe₃), 1.33 (9H, s, 3-CMe₃), 2.06 (3H, s, 2'-Me), 4.30 (1H, s, OH), 6.88 (1H, d, *J* 1.9, 6-H), 7.14 (1H, d, *J* 1.9, 4-H) and 7.20-7.37 (4H, m, 3'-H, 4'-H, 5'-H and 6'-H); δ_C 19.9 (2'-Me), 31.1 ($3\text{-C}\underline{\text{Me}_3}$), 31.8 ($5\text{-C}\underline{\text{Me}_3}$), 34.6 ($3\text{-}\underline{\text{C}}\text{Me}_3$), 36.7 ($5\text{-}\underline{\text{C}}\text{Me}_3$), 109.5 (C-6), 116.1 (C-4), 123 (C-1'), 126 (C-3'), 128.4 (C-5'), 130.4, 132.2 (C-4' and C-6'), 136.2 (C-2), 138.7 (C-2'), 147.5 (C-3), 151.1 (C-5) and 152.3 (C-1) (Found: C, 85.04; H, 9.54. $C_{21}H_{28}O$ requires: C, 85.08; H, 9.52%).

3,5-Di-*tert*-butyl-2-(2',4'-dimethylphenyl)phenol (25): CC (eluent: pentane-ether 19:1); colourless amorphous solid, m.p. 107-108°C (pentane); δ_H 1.13 (9H, s, 5-CMe_3), 1.33 (9H, s, 3-CMe_3), 2.02 (3H, s, 2'-Me), 2.38 (3H, s, 4'-Me), 4.36 (1H, s, OH), 6.87 (1H, d, *J* 2, 6-H) and 7.01-7.13 (4H, m, 4-H, 3'-H, 5'-H and 6'-H); δ_C 20.2 (2'-Me), 21.3 (4'-Me), 31.5 (3-$C\underline{Me}_3$), 32.1 (5-$C\underline{Me}_3$), 34.9 (3-$\underline{C}Me_3$), 37 (5-$\underline{C}Me_3$), 109.6 (C-6), 116.3 (C-4), 123.2 (C-1' and C-3'), 131.5 (C-5'), 132.4 (C-6'), 133.2 (C-2), 138.3 (C-4'), 138.7 (C-2'), 148 (C-3), 151.3 (C-5) and 152.8 (C-1) (Found: C, 84.92; H, 9.68. $C_{22}H_{30}O$ requires: C, 85.11; H, 9.74%).

(3,5-Di-*tert*-butylphenyl)(2',4'-dimethylphenyl)ether (26): colourless oil; δ_H 1.26 (18H, s, 3-CMe_3 and 5-CMe_3), 2.21 (3H, s, 2'-Me), 2.29 (3H, s, 4'-Me), 6.70-6.81 (3H, m, 2-H, 6-H and 6'-H), 6.82-6.95 (1H, m, 5'-H), 7.03 (1H, s, 3'-H) and 7.08 (1H, t, *J* 1.6, 4-H); δ_C 16 (2'-Me), 20.5 (4'-Me), 29.5 ($C\underline{Me}_3$), 34.7 ($\underline{C}Me_3$), 111.8 (C-2 and C-6), 116.2 (C-4), 118.4 (C-6'), 127.1 (C-3'), 128.9 (C-4'), 131.6 (C-5'), 132.4 (C-2'), 152.2 (C-3 and C-5), 152.4 (C-1) and 157.1 (C-1') (Found: C, 85.09; H, 9.72. $C_{22}H_{30}O$ requires: C, 85.11; H, 9.74%).

3,5-Di-*tert*-butyl-2-(2',4',6'-trimethylphenyl)phenol (27): CC (eluent: pentane-ether 97:3) followed by PLC (eluent: pentane-ether 97:3); colourless plates, m.p. 87°C (pentane); δ_H 1.09 (9H, s, 5-CMe_3), 1.31 (9H, s, 3-CMe_3), 1.96 (6H, s, 2'-Me and 6'-Me), 2.31 (3H, s, 4'-Me), 4.36 (1H, s, OH), 6.85 (1H, d, *J* 1.9, 6-H), 6.94 (2H, s, 3'-H and 5'-H) and 7.11 (1H, d, *J* 1.9, 4-H); δ_C 20.9 (2'-Me and 6'-Me), 21.3 (4'-Me), 31.6 (3-$C\underline{Me}_3$), 32.4 (5-$C\underline{Me}_3$), 35 (3-$\underline{C}Me_3$), 37.3 (5-$\underline{C}Me_3$), 109.5 (C-6), 117.6 (C-4), 121.7 (C-1'), 129.1 (C-3' and C-5'), 133.1 (C-2), 138.1 (C-4'), 138.8 (C-2' and C-6'), 147.4 (C-3), 151.2 (C-5) and 152 (C-1) (Found: C, 85.35; H, 9.77. $C_{23}H_{32}O$ requires: C, 85.13; H, 9.94%).

(3,5-Di-*tert*-butylphenyl)(2,4,6-trimethylphenyl)ether (28): colourless oil; δ_H 1.25 (18H, s, 3-CMe_3 and 5-CMe_3), 2.08 (6H, s, 2'-Me and 6'-Me), 2.30 (3H, s, 4'-Me), 6.58 (2H, d, *J* 1.7, 2-H and 6-H), 6.88 (2H, s, 3'-H and 5'-H) and 7 (1H, t, *J* 1.7, 4-H); δ_C 16.5 (2'-Me and 6'-Me), 20.9 (4'-Me), 31.5 ($C\underline{Me}_3$), 35 ($\underline{C}Me_3$), 109 (C-2 and C-6), 115.1 (C-4), 129.5 (C-3' and C-5'), 131.1 (C-2' and C-6'), 134.2 (C-4'), 148.8 (C-1'), 152.3 (C-3 and C-5) and 157.7 (C-1) (Found: C, 84.92; H, 9.94. $C_{23}H_{32}O$ requires: C, 85.13; H, 9.94%).

With ethyl 2-oxocyclohexanecarboxylate (29):

Ethyl 1-(2'-methylphenyl)-2-oxocyclohexanecarboxylate (31): CC (eluent: pentane-ether 7:3); colourless oil; δ_H 1.21 (3H, t, *J* 7.1, $C\underline{H}_3CH_2O$), 1.65-1.97 (4H, m, 4-H and 5-H), 2.18 (3H, s, 2'-Me), 2.41-2.75 (4H, m, 3-H and 6-H), 4.19 (1H, q, *J* 7.1, $CH_3C\underline{H}_2O$), 4.20 (1H, q, *J* 7.2, $CH_3C\underline{H}_2O$) and 7.09-7.25 (3H, m, Ar-H); δ_C 13.8 ($\underline{C}H_3CH_2O$), 21.5 (2'-Me), 21.7, 27.8, 36.5 and 40.8 (cyclic CH_2), 61.4 ($CH_3\underline{C}H_2O$), 66.8 (C-1), 125.7 (C-3'), 126.8 (C-5'), 127.3, 132 (C-4' and C-6'), 136.1 (C-2'), 137.8 (C-1'), 171.4 ($\underline{C}O_2CH_2$) and 207.4 (C-2) (Found: C, 73.75; H, 7.74. $C_{16}H_{20}O_3$ requires: C, 73.82; H, 7.74%).

Ethyl 1-(2',4'-dimethylphenyl)-2-oxocyclohexanecarboxylate (32): CC (eluent: pentane-ether 7:3); colourless oil; δ_H 1.21 (3H, t, *J* 7.2, $C\underline{H}_3CH_2O$), 1.64-2.03 (4H, m, 4-H and 5-H), 2.14 (3H, s, 2'-Me), 2.28 (3H, s, 4'-Me), 2.48-2.81 (4H, m, 3-H and 6-H), 4.19 (1H, q, *J* 7.1, $CH_3C\underline{H}_2O$), 4.20 (1H, q, *J* 7.1, $CH_3C\underline{H}_2O$) and 6.85-7.09 (3H, m, 3'-H, 5'-H, 6'-H); δ_C 14 ($\underline{C}H_3CH_2O$), 20.8 (4'-Me), 21.5 (2'-Me), 22, 28.1, 36.8 and 40.9 (cyclic CH_2), 61.5 ($CH_3\underline{C}H_2O$), 66.7 (C-1), 126.7 (C-3'), 127 (C-5'), 133.3 (C-6'), 133.4 (C-1'), 137.2 (C-2'), 137.8 (C-4'), 171.8 ($\underline{C}O_2CH_2$) and 207.9 (C-2) (Found: C, 74.39; H, 8.11. $C_{17}H_{22}O_3$ requires: C, 74.42; H, 8.08%).

Ethyl 1-(2',4',6'-trimethylphenyl)-2-oxocyclohexanecarboxylate (33): CC (eluent: pentane-ether 3:1) and PLC (eluent: pentane-ether 7:3); colourless oil; δ_H 1.21 (3H, t, *J* 7.2, $C\underline{H}_3CH_2O$), 1.58-1.73 (1H, m, cyclic

CH_2), 1.84-1.98 (3H, m, cyclic CH_2), 2.16 (6H, s, 2'-Me and 6'-Me), 2.21 (3H, s, 4'-Me), 2.30-2.51 (3H, m, cyclic CH_2), 2.60-2.75 (1H, m, cyclic CH_2), 4.19 (1H, q, *J* 7.2, $CH_3C\underline{H}_2O$), 4.20 (1H, q, *J* 7.2, $CH_3C\underline{H}_2O$) and 6.80 (2H, s, 3'-H and 5'-H); δ_C 13.8 ($\underline{C}H_3CH_2O$), 20.5 (4'-Me), 21.7 and 26 (C-4 and C-5), 23.4 (2'-Me and 6'-Me), 36.9 and 40.8 (C-3 and C-6), 61.8 ($CH_3\underline{C}H_2O$), 68 (C-1), 131.3 (C-3' and C-5'), 135.2 and 136.3 (C-1' and C-4'), 137.1 (C-2' and C-6'), 171.5 ($\underline{C}O_2CH_2$) and 207.8 (C-2) (Found: C, 74.81; H, 8.36. $C_{18}H_{24}O_3$ requires: C, 74.97; H, 8.39%).

With 2,4-pentanedione (34):

3-(2'-Methylphenyl)-2,4-pentanedione (36): CC (eluent: pentane-ether 7:3); pale yellow gum; δ_H 1.79 (6H, s, 1-H and 5-H), 2.16 (3H, s, 2'-Me), 6.95-7.31 (4H, m, Ar-H) and 9.97 (1H, s, 3-H); δ_C 19.6 (2'-Me), 23.5 (C-1 and C-5), 113.4 (C-3), 126.2 (C-3'), 127.8 (C-5'), 130.2, 131.2, 137.7 (C-4' and C-6'), 135.8 (C-2'), 137.5 (C-1') and 190.5 (C-2 and C-4) (Found: C, 75.53; H, 7.31. $C_{12}H_{14}O_2$ requires: C, 75.76; H, 7.42%).

3-(2',4'-Dimethylphenyl)-2,4-pentanedione (37): CC (eluent: pentane-ether 5:1); colourless plates, m.p. 49°C (ether-pentane 1:19); δ_H 1.78 (6H, s, 1-H and 5-H), 2.11 (3H, s, 2'-Me), 2.32 (3H, s, 4'-Me), 6.85-7.15 (3H, m, Ar-H) and 9.99 (1H, s, 3-H); δ_C 19.8 (2'-Me), 21.2 (4'-Me), 23.8 (C-1 and C-5), 113.5 (C-3), 127.2 (C-6'), 131.2 (C-3'), 131.4 (C-5'), 133.1, 137.5, 137.7 (C-1', C-2' and C-4') and 190.9 (C-2 and C-4) (Found: C, 76.60; H, 7.93. $C_{13}H_{16}O_2$ requires: C, 76.44; H, 7.90%).

3-(2',4',6'-Trimethylphenyl)-2,4-pentanedione (38): CC (eluent: pentane-ether 3:1); colourless solid, m.p. 83-84°C (pentane), lit.[19] 83°C.

With ethyl 2-nitropropionate (39):

Ethyl 2-(2'-methylphenyl)-2-nitropropionate (41): CC (eluent: pentane-ether 7:3); pale yellow oil; δ_H 1.30 (3H, t, *J* 7.1, $C\underline{H}_3CH_2O$), 2.25 (3H, s, 3-H or 2'-Me), 2.28 (3H, s, 2'-Me or 3-H), 4.33 (1H, q, *J* 7.1, $CH_3C\underline{H}_2O$), 4.34 (1H, q, *J* 7.2, $CH_3C\underline{H}_2O$) and 7.10-7.35 (4H, m, Ar-H); δ_C 13.6 ($\underline{C}H_3CH_2O$), 20.6 (2'-Me), 24.1 (C-3), 63.2 ($CH_3\underline{C}H_2O$), 95.9 (C-2), 126 (C-3'), 126.7 (C-5'), 129.3, 132.5 (C-4' and C-6'), 133.5 (C-2'), 137.2 (C-1') and 167.3 ($\underline{C}O_2CH_2$) (Found: C, 60.62; H, 6.38; N, 5.83. $C_{12}H_{15}NO_4$ requires: C, 60.75; H, 6.37; N, 5.90%).

Ethyl 2-(2',4'-dimethylphenyl)-2-nitropropionate (42): CC (eluent: pentane-ether 5:1); pale yellow oil; δ_H 1.30 (3H, t, *J* 7.2, $C\underline{H}_3CH_2O$), 2.24 (6H, s, 3-H and 2'-Me), 2.31 (3H, s, 4'-Me), 4.33 (1H, q, *J* 7, $CH_3C\underline{H}_2O$), 4.34 (1H, q, *J* 7.1, $CH_3C\underline{H}_2O$) and 7.02-7.06 (3H, m, 3'-H, 5'-H, 6'-H); δ_C 13.9 ($\underline{C}H_3CH_2O$), 20.8 (2'-Me), 20.9 (4'-Me), 24.4 (C-3), 63.3 ($CH_3\underline{C}H_2O$), 96 (C-2), 126.9 (C-3'), 127.1 (C-5'), 130.9 (C-1'), 133.6 (C-6'), 137.4 (C-2'), 139.7 (C-4') and 167.8 ($\underline{C}O_2CH_2$) (Found: C, 62.08; H, 6.99; N, 5.55. $C_{13}H_{17}NO_4$ requires: C, 62.14; H, 6.82; N, 5.57%).

Ethyl 2-(2',4',6'-trimethylphenyl)-2-nitropropionate (43): CC (eluent: pentane-ether 7:3) followed by PLC (pentane-ether 7:3); impure pale yellow oil; δ_H 1.35 (3H, t, *J* 7, $C\underline{H}_3CH_2O$), 2.19 (3H, s, 3-H), 2.26 (3H, s, 4'-Me), 2.57 (6H, s, 2'-Me and 7'-Me), 4.12 (1H, q, *J* 7, $CH_3C\underline{H}_2O$), 4.13 (1H, q, *J* 7.1, $CH_3C\underline{H}_2O$) and 6.83 (2H, s, 3'-H and 5'-H).

Copper-catalysed arylation reactions with triarylbismuth diacetates: General procedure: A mixture of the substrate (1 equiv.), copper diacetate (0.1 equiv.) and the triarylbismuth diacetate (1.1 equiv.) in THF (5 mL/mmol of substrate) was stirred at room temperature for the time indicated (Table 2). The solvent was distilled off and the residue was purified by column chromatography on silicagel (eluent indicated below) to afford the reaction products.

With 2,2-dimethyl-1,3-propanediol (46):

3-(2'-Methylphenoxy)-2,2-dimethylpropan-1-ol (48): (eluent: pentane-ether 7:3); colourless oil; δ_H 1.05 (6H, s, CMe_2), 2.19 (1H, s, OH), 2.24 (3H, s, 2'-Me), 3.57 (2H, s, 1-H), 3.77 (2H, s, 3-H), 6.75-6.95 (2H, m, Ar-H) and 7.10-7.21 (2H, m, Ar-H); δ_C 16.7 (2'-Me), 21.5 ($C\underline{Me}_2$), 36.3 (C-2), 69.9 (C-1), 74.5 (C-3), 110.5 (C-6'), 120.2 (C-4'), 126.3 (C-2'), 126.7, 130.4 (C-3' and C-5') and 156.7 (C-1') (Found: C, 74.18; H, 9.30. $C_{12}H_{18}O_2$ requires: C, 74.19; H, 9.34%).

3-(2',4'-Dimethylphenoxy)-2,2-dimethylpropan-1-ol (49): (eluent: pentane-ether 7:3); pale yellow oil; δ_H 1.04 (6H, s, CMe_2), 2.20 (3H, s, 2'-Me), 2.25 (3H, s, 4'-Me), 3.56 (2H, s, 1-H), 3.74 (2H, s, 3-H) and 6.69-6.95 (3H, m, Ar-H); δ_C 16.2 (2'-Me), 20.5 (4'-Me), 21.8 ($C\underline{Me}_2$), 70.4 (C-1), 75.3 (C-3), 110.9 (C-6'), 126.4 (C-2'), 127 (C-3'), 129.7 (C-4'), 131.5 (C-5') and 154.9 (C-1') (Found: C, 74.92; H, 9.68. $C_{13}H_{20}O_2$ requires: C, 74.96; H, 9.68%).

With 3,4-dimethylaniline (51):

***N*-(3,4-Dimethylphenyl)-*N*-(2'-methylphenyl)amine (53)**: CC (eluent: pentane-ether 95:5) and PLC (eluent: pentane-ether 19:1); yellow oil; δ_H 2.22 (6H, s, 3-Me and 4-Me), 2.25 (3H, s, 2'-Me), 5.27 (1H, s, N-H), 6.59-6.70 (3H, m, Ar-H) and 7.01-7.28 (4H, m, Ar-H); δ_C 17.6, 18.7, 19.7 ($C\underline{Me}$), 115.7, 117.1, 119.8, 120.7, 126.5, 130.1, 130.6 (C-2, C-5, C-6, C-3', C-4', C-5' and C-6'), 126.8, 128.9, 137.2 (C-3, C-4 and C-2'), 141.2 and 141.9 (C-1 and C-1') (Found: C, 85.21; H, 8.20; N, 6.58. $C_{15}H_{17}N$ requires: C, 85.26; H, 8.11; N, 6.63%).

***N*-(2',4'-Dimethylphenyl)-*N*-(3,4-dimethylphenyl)amine (54)**: CC (eluent: pentane-ether); yellow oil; δ_H 2.32 (9H, s, 3-Me, 4-Me and 4'-Me), 2.41 (3H, s, 2'-Me), 5.25 (1H, s, N-H), 6.70-6.89 (2H, m, Ar-H) and 7.03-7.25 (4H, m, Ar-H); δ_C 17.7, 18.8, 19.8, 20.6 ($C\underline{Me}$), 114.5, 118.7, 119.3 (C-2, C-6 and C-6'), 127.1, 130.2, 131.5 (C-5, C-3' and C-5'), 128.1, 128.5, 131.1, 137.3 (C-3, C-4, C-2', C-4') and 139, 142.3 (C-1 and C-1') (Found: C, 85.20; H, 8.49; N, 6.14. $C_{16}H_{19}N$ requires: C, 85.29; H, 8.50; N, 6.22%).

With phtalimide (56):

***N*-(2'-Methylphenyl)phtalimide (58)**: CC (eluent: pentane-ether 65:35) and PLC (eluent: pentane-ether 65:25); colourless powder, m.p. 181°C, lit.[20] 182°C.

***N*-(2',4'-Dimethylphenyl)phtalimide (59)**: CC (eluent: pentane-ether 65:35) and PLC (eluent: pentane-ether 60:40); colourless powder, m.p. 152°C (pentane-dichloromethane 7:3), lit.[20] 153°C.

Reaction of tris(2,4,6-trimethylphenyl)bismuth and stoichiometric copper diacetate:

With 2,2-dimethyl-1,3-propanediol (46): 3-(2',4',6'-Trimethylphenoxy)-2,2-dimethylpropan-1-ol (50): PLC (eluent: pentane-ether 3:1); colourless oil; δ_H 1.05 (6H, s, CMe_2), 2.21 and 2.22 (9H, s, Ar-Me), 3.55 (2H, s, 1-H), 3.62 (2H, s, 3-H) and 6.78 (2H, s, 3'-H and 5'-H); δ_C 15.8 (2'-Me and 6'-Me), 20.4 (4'-Me), 21.5 ($C\underline{Me}_2$), 36.4 (C-2), 71.2, 79.9 (C-1 and C-3), 129.3 (C-3' and C-5'), 130, 130.2 (C-2', C-4' and C-6') and 152.4 (C-1') (Found: C, 75.57; H, 9.99. $C_{14}H_{22}O_2$ requires: C, 75.63; H, 9.97%).

With 3,4-dimethylaniline: *N*-(3,4-Dimethylphenyl)-*N*-(2',4,'6'-trimethylphenyl)amine (55): CC (eluent: pentane-ether 24:1) and PLC (eluent: pentane-ether 19:1); yellow oil; δ_H 2.19, 2.21 and 2.34 (15H, s, Ar-Me), 5 (1H, s, N-H), 6.27 (1H, dd, $J_{H6\text{-}H5}$ 8 and $J_{H6\text{-}H2}$ 2.5, 6-H), 6.39 (1H, d, J 2.4, 2-H), 6.9 (1H, d, J 8, 5-H) and 7 (2H, s, 3'-H and 5'-H); δ_C 18.3 (2'-Me and 6'-Me), 18.8, 20, 20.9, (3-Me, 4-Me and 4'-Me), 110.8 (C-2), 115.1 (C-6), 129.2 (C-3' and C-5'), 130.3 (C-5), 125.9, 135, 135.6, 136 (C-3, C-4, C-2', C-4' and C-6'), 137.4 and 144.6 (C-1 and C-1') (Found: C, 85.28; H, 8.82; N, 5.85. $C_{17}H_{21}N$ requires: C, 85.31; H, 8.84; N, 5.85%).

Oxidation of tris(2,4,6-trimethylphenyl)bismuth with sodium perborate and copper-catalysed reaction with phtalimide: A mixture of tris(2,4,6-trimethylphenyl)bismuth (1 g) in acetic acid (20 mL) was treated with sodium perborate monohydrate (0.55 g) for 1 hour at room temperature. After aqueous work-up, extraction with dichloromethane, the crude product was crystallised from dichloromethane-ether-pentane to afford **(12a)** (0.55 g) which was directly used in the arylation reaction. A mixture of copper diacetate (0.010 g), phtalimide **(56)** (0.07 g), **(12a)** (0.39 g) and pyridine (0.11 g) in THF (5 mL) was stirred for 35 h at room temperature. The solvent was distilled and the residue was purified by column chromatography on silicagel (eluent: pentane-ether 7:3) to afford *N*-(2',4',6'-trimethylphenyl)phtalimide **(60)** (0.023 g, 18%), as a colourless amorphous solid, m.p. 177-178°C, lit.[21] 178-179°C.

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