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On the Exclusion of Radical Species in the Ligand Coupling Reactions with Pentavalent Triarylbismuth Derivatives

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In Memoriam Professor Sir Derek Barton

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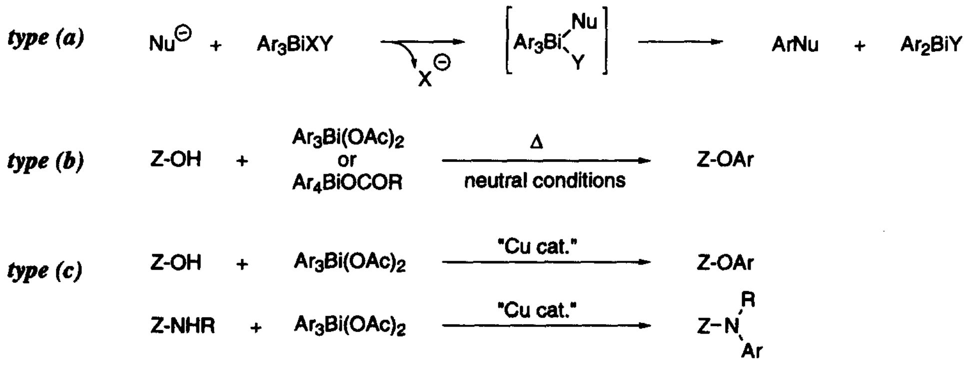
Abstract: The presence of aryl radical species in the course of arylation reactions with tri and pentavalent organobismuth compounds has been studied by the use of an internal-trap containing reagent: tris(2-allyloxyphenyl)bismuth and its diacetate. The intervention of radical species can be excluded in *C*- and *O*-arylation under basic conditions as well as in copper catalyzed *O*- and *N*-arylation, as cyclized products were never detected in any of these reactions. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords : Arylation; Bismuth; Ligand coupling; Radicals

Organobismuth reagents allow three major types of arylation reactions: a) *C*- and *O*-arylation *via* a covalent intermediate b) *O*-arylation under neutral conditions c) *O*- and *N*-arylation under copper catalysis.[1-3]



The reactions of type (a) involve the formation of an unstable organobismuth intermediate undergoing a ligand coupling process, which is a non-synchronous concerted mechanism. The reactions of type (c) can be viewed as a variety of ligand coupling occurring on a copper (III) intermediate, itself resulting from oxidative

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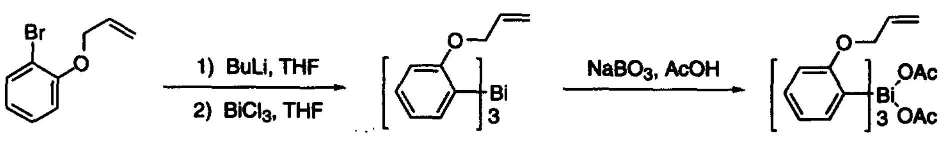
addition of ligands from the bismuth reagent on the catalytic copper species. These type (c) reactions are sometimes presumed to be one-electron transfer reactions. The mechanism of the reactions of type (b) still remains a matter of debate.

Qualitative ESR studies of a number of reactions belonging to types (a) and (c) led to the detection of free radical species by way of their spin adducts.[3-5] However, quantitative studies showed these processes to be minor pathways. Moreover, when a number of *C*-, *N*- and *O*-arylation reactions were performed in the presence of 1,1-diphenylethylene, an efficient free radical scavenger inhibiting chain mechanisms, the yields of the arylation products were not affected.[4] However, radical species can be involved in these reactions. Indeed, if the coupling reaction takes place within the sphere of coordination of the bismuth center before diffusion in the solvent, an alternative method has to be used to study the nature of the reactive species. To detect the intervention of radical species, the substrate or the reagent should be able to react selectively under different pathways: arylation without rearrangement if radical species are not involved, internal trapping if radical species are formed. The reaction of a phenol containing a disulfide group in the vicinity of the reactive center seemed in favor of the absence of radical species.[2c] We now describe the results of the alternative more general approach: the use of an organobismuth reagent containing an internal trap. As the rate of cyclization of 2-(prop-2-enyloxy)phenyl radicals (k_c = 5.2 to 6.3 . 10^9 s^{-1})[6a-c] is nearly ten times higher than those of the closely related systems: 2-(but-3-enyl)phenyl radicals (k_c = 4 . 10^8 s^{-1})[6a] and 2-(but-3-enyloxy)phenyl radicals (k_c = 4.9 . 10^8 s^{-1}),[6b] we selected the tris[2-(prop-2-enyloxy)phenyl]bismuth derivatives as the reagent of choice to probe the radical character of arylation reactions of type (a) and type (c). We hoped that the introduction of an *ortho* substituent would not interfere too significantly with the outcome of the reactions, as the major part of the reactions of arylation with arylbismuth reagents have used aryl groups substituted only on the *meta* or *para* positions.

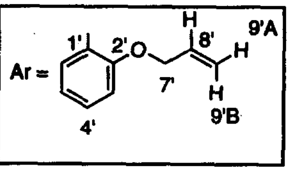
Results and Discussion:

The trivalent organobismuth compound (**1**) was easily prepared from 2-bromophenol. Allylation of the phenolic group, metallation with butyllithium followed by treatment with bismuth chloride afforded the trivalent compound (**1**). Although tris(2-methoxyphenyl)bismuth is oxidized to the corresponding diacetate in relatively good yields by iodobenzene diacetate under neutral conditions,[7] compound (**1**) was recovered unaffected. Oxidation of the trivalent bismuth compound (**1**) was done by reaction with sodium perborate in acetic acid,[8] which led to the diacetate (**2**) in 63% yield.

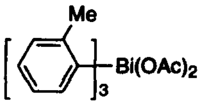


(1), 61% **(2)**, 63%

In the figures of tables 1 and 2, the group Ar corresponds to the 2'-allyloxyphenyl structure, unless otherwise stated. In the NMR descriptions of the products, the following numbering system has been used throughout.



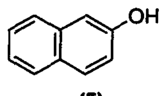
$Ph_3Bi(OAc)_2$ **(3)**


(4)

In pentavalent triarylbismuth derivatives, the nature of the two extra ligands determine the type of reactivity.[2,3] Only the diacetate derivatives show the different types of behaviour: (a), (b) and (c).[9] Under basic conditions, triarylbismuth diacetates react with a number of soft nucleophiles to lead to the products of *C*- or *O*-arylation. As a detrimental influence due to the steric effect of the 2-allyloxy group was possible, we selected four types of substrates, in which the reactive center is not significantly sterically hindered, as representative of the major classes of arylation reaction: 2-naphthol **(5)** leading to 1-aryl-2-naphthol, ethyl 2-oxocyclohexanecarboxylate **(7)** giving the corresponding 1-aryl derivative, 2-nitropropane **(10)** giving the 2-aryl-2-nitropropane derivative and 4-nitrophenol **(12)** giving the *O*-aryl ether.

C-Arylation of 2-naphthol **(5)** and of the β-ketoester **(7)** with the diacetate **(2)** under basic conditions afforded high yields of **(6)** and **(8)** respectively. In the reaction of **(7)**, small amounts of by-products were also isolated. The reaction of 2-nitropropane **(10)** afforded moderate yields of the *C*-arylation product **(11)** at room temperature. Only a slight increase of the yield was noted when the reaction was performed under reflux. In the case of the reaction of the 4-nitrophenol **(12)**, the influence of the leaving group on the outcome of the ligand coupling is remarkable. Reaction of triphenylbismuth dichloride or bistrifluoroacetate with the anion of **(12)** does not afford the diaryl ether.[10] In contrast, the reaction of **(12)** with triphenylbismuth diacetate **(3)** in the presence of TMG (*N,N,N',N'*-tetramethylguanidine) led to the diaryl ether **(13)** in 33%. When the reaction of **(12)** was performed with **(2)**, a high yield of the diaryl ether **(14)** was isolated (77%).

Table 1 : Arylation reactions under basic conditions: type (a)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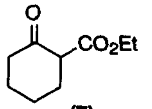
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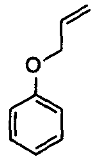
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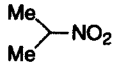
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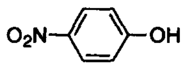
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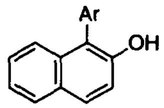
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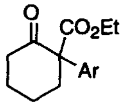
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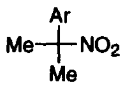
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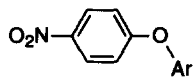
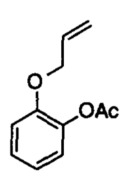

(13), Ar = Phenyl
(14), Ar = 2'-Allyloxyphenyl

Substrate	Reaction conditions	Products (%)
(5)	**(2)**, TMG, THF, RT, overnight	**(6)** (91), **(1)** (11)
(7)	**(2)**, TMG, THF, RT, 3 d	**(8)** (80), **(1)** (18), **(7)** (14), **(9)** (10)
(10)	**(2)**, TMG, THF, RT, 20 h	**(11)** (50), **(1)** (32), **(9)** (8)
(10)	**(2)**, TMG, THF, reflux, 48 h	**(11)** (60), **(1)** (38), **(9)** (19)
(12)	**(3)**, TMG, THF, reflux, 24 h	**(13)** (33), **(12)** (60)
(12)	**(2)**, TMG, toluene, reflux, 24 h	**(14)** (77), **(12)** (18)

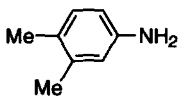
The moderate to high yields of non-rearranged arylation products in these four types of reactions is a strong evidence against the involvement of radical species in the ligand coupling mechanism of pentavalent organobismuth intermediates. Moreover, ^{1}H NMR examination of the crude product mixtures did not reveal the presence of rearranged products.

In the reactions of type (c), a glycol, a phenol or an amine undergoes *O*- or *N*-arylation upon treatment with an appropriate triarylbismuth diacetate in the presence of a copper catalyst.[9] Barton *et al.* suggested that these reactions involve an oxidative addition of two ligands of the bismuth reagent on a copper(I) catalytic species, leading to a copper(III) intermediate.[11] After the substrate is present in the sphere of coordination of the copper metal center, reductive elimination effects the aryl ligand transfer. However, when the reaction was performed in the cavity of an ESR spectrometer, the presence of free radicals was detected by way of their spin trap adducts with 2-methyl-2-nitrosopropane and with 2,4,6-tribromonitrosobenzene.[5] Dodonov *et al.* therefore concluded that one-electron transfer reactions were taking place at least in one elementary step of the whole mechanism.[5] On the other hand, addition of 1,1-diphenylethylene did not alter the overall yield of these copper-catalyzed reactions.[12] To determine the real weight of radical species, the internal trap containing reagents (1) and (2) were therefore tested in copper catalyzed *O*- and *N*-arylation reactions.

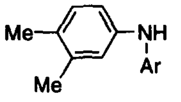
Table 2 : Copper-catalyzed arylation reactions: type (c)



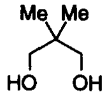
(15)



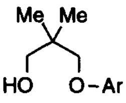
(16)



(17)



(18)



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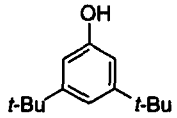

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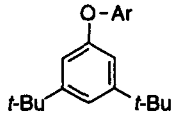

(21), Ar = 2-Methylphenyl
(22), Ar = Phenyl

Substrate	Reagent	Reaction conditions	Products (%)
(2)	-	Cu(OAc)$_2$ (0.4 equiv.), reflux, 48 h	(1) (7), (9) (62)*, (15) (57)
(16)	(2)	Cu(OAc)$_2$ (0.1 equiv.), RT, 2 h	(17) (91)
(16)	(1)	Cu(OAc)$_2$ (2 equiv.), reflux, 1.5 h	(16) (33), (17) (64), (9) (73)*
(18)	(2)	Cu(OAc)$_2$ (0.1 equiv.), reflux, 2 h	(19) (68), (18) (29), (1) (5), (9) (48)*, (15) (12)
(20)	(2)	Cu(OAc)$_2$ (0.1 equiv.), RT, 20 h	(20) (97), (1) (33)
(20)	(4)	Cu(OAc)$_2$ (0.1 equiv.), RT, 72 h	(20) (78), (21) (16)
(20)	(3)	Cu(OAc)$_2$ (0.1 equiv.), RT, 3 h	(20) (22), (22) (76)
(20)	(2)	Cu(OAc)$_2$ (0.1 equiv.), reflux, 18 h	(1) (38), (9) (27)*, (15) (33), (20) (23)

* All yields are based on the molar-equivalent of the substrate or of the reagent, except in the case of (9) for which the yields are based on the three aryl groups present in the organobismuth reagent

As copper diacetate increases the rate of decomposition of triarylbismuth diacetate,[9b] the diacetate **(2)** was heated for 2 days under reflux in the presence of copper diacetate. The main products were allyloxybenzene **(9)** and 2-allyloxyphenyl acetate **(15)**. Reaction of the aniline **(16)** with the diacetate **(2)** in the presence of a catalytic amount of copper diacetate afforded a high yield (91%) of the diarylamine **(17)**. When the arylation of the aniline **(16)** was performed with **(1)** and stoichiometric copper diacetate acting as the oxidant, no reaction was observed at room temperature, but upon reflux in methylene dichloride for only 1.5 h, three products were isolated: unreacted **(16)** in a 33% yield, the diarylamine **(17)** in 64%, and **(9)** in 73% yield based on three aryl ligands present in the bismuth reagent **(1)**. Compound **(9)** is likely to be formed by acidolysis of **(1)** in the presence of acetic acid which can be formed from the interaction of copper diacetate with the amine. The mass balance shows a 97% overall recovery of the aniline and its derivative, and 94% recovery of the aryl ligands of **(1)** as non-rearranged products. The reaction of the glycol **(18)** with **(2)** in the presence of a catalytic amount of copper diacetate led to a good yield of the monoaryl ether **(19)** (68%). The other isolated products were the unreacted glycol **(18)** (29%) and the thermal decomposition products of the reagent: **(1)** in 5%, **(9)** in 48% and **(15)** in 12% yields. In the case of the 3,5-di-*tert*-butylphenol **(20)**, reaction with **(2)** in the presence of copper diacetate did not give any diaryl ether. This can be attributed to a detrimental effect of the *ortho* substituent. Under the same conditions, reaction of **(20)** with triphenylbismuth diacetate **(3)** led to the diaryl ether **(22)** in 76% yield. However, reaction of **(20)** with the tris(*ortho* -methylphenyl)bismuth diacetate reagent **(4)** led to a dramatic decrease of the yield as only 16% of the diarylether **(21)** was obtained after 3 days. Finally, when the reaction of **(20)** with **(2)** was attempted under reflux, decomposition products of the reagent were observed, but again rearranged products were not detected by ^{1}H NMR and after chromatographic resolution.

The good yields of the products of *O*-arylation **(19)** and *N*-arylation **(17)** without rearrangement are good evidence of the absence of one-electron transfer as an elementary step in these copper-catalyzed reactions. Moreover, it must be noted that an *ortho* substituent has a generally detrimental effect on the reactivity. This is particularly noticeable in the case of the less reactive substrates such as monohydric phenols. But this effect is also significant with the glycol, as it required reflux temperature as well as the triarylbismuth-stoichiometric copper diacetate reaction with the aniline.

In conclusion, the use of the internal-trap containing organobismuth reagents **(1)** and **(2)** has shown that aryl radical species are not involved in the *C*- and *O*-arylation reactions under basic conditions as well as in the copper-catalyzed *O*- and *N*-arylation reactions. These results lend strong support to the previously observed dichotomy in the mechanism of reaction of organobismuth reagents. The observation of free radical adducts is only a minor decomposition pathway, competing with the arylation reaction. The reactions under basic conditions follow a typical ligand coupling mechanism, a non-synchronous concerted process and the copper-catalyzed *O*- and *N*-arylation reactions follow an oxidative addition - reductive elimination sequence, the reductive elimination step being the transition metal chemistry equivalent of the ligand coupling.[13]

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 $CDCl_3$ solutions with internal Me_4Si and J values in Hertz. TMG refers to N,N,N',N'-tetramethylguanidine.

Tris(2-allyloxyphenyl)bismuthane (1) : Butyllithium (16.2 mL of a 1.6M solution in hexane) was added to a solution of allyl 2-bromophenyl ether[14] (5 g) in freshly distilled anhydrous THF (50 mL) at -78 °C and the mixture was stirred for 1 h. Bismuth trichloride (2.44 g) was added by portions over 10 min. The mixture was stirred at -78 °C for 1.5 h, then stirred overnight at room temperature. A 10% ammonium chloride solution in brine (50 mL) was added. The aqueous phase was extracted with diethyl ether (4 x 20 mL). The combined organic extracts were washed with a 10% ammonium chloride solution in brine, then with brine. After distillation of the solvents under reduced pressure, the residue was filtered through a short path silicagel column (eluant: ethyl acetate-pentane 1:19). The crude product was crystallized from chloroform-ethyl alcohol at -15 °C to afford (1) as thin white needles (8.68 g, 61%), m.p. 60 °C; δ_H 4.48 (6H, d, J 4.8, 7-H), 5.18 (3H, dd, J_{H8-H9A} 10.6 and $J_{H9A-H9B}$ 1.4, 9A-H), 5.33 (3H, dd, J_{H8-H9B} 17.3 and $J_{H9A-H9B}$ 1.4, 9B-H), 5.93 (3H, ddt, J_{H7-H8} 4.8, J_{H8-H9A} 10.6 and J_{H8-H9B} 17.3, 8-H), 6.91 (3H, t, J 7.2, 5-H), 7.00 (3H, d, J 7.2, 3-H), 7.32 (3H, td, J 7.2 and J 1.5, 4-H) and 7.58 (3H, dd, J 7.2 and J 1.5, 6-H); δ_C 69.0 (C-7), 111.2 (C-3), 116.9 (C-9), 124.2 (C-5), 129.1 (C-4), 133.5 (C-8), 139.3 (C-6), 143.5 (CBi) and 161.2 (C-2) (Found: C, 53.30; H, 4.63. $C_{27}H_{27}BiO_3$ requires: C, 53.30; H, 4.47%).

Bis(acetato)tris(2-allyloxyphenyl)bismuth (2) : A mixture of sodium perborate monohydrate (0.6 g) and tris(2-allyloxyphenyl)bismuthane (1) (1.21 g) in acetic acid (20 mL) was stirred at room temperature for 50 min. The resulting solution was poured into water (40 mL) and the mixture was extracted with CH_2Cl_2 (2 x 20 mL). The organic extracts were combined, washed with water, dried over $MgSO_4$ and reduced under vacuum to a small volume. Diethyl ether (20 mL) was then added and the solution was maintained overnight at -15 °C. The solid was filtered and recrystallized from pentane-acetone (1:1) to afford the title compound (2) as colorless plates (0.915 g, 63%), m.p. 121-124 °C; δ_H 1.65 (6H, s, CH_3CO), 4.57 (6H, d, J 5.1, 7-H), 5.07 (3H, dd, J_{H8-H9A} 10.6 and $J_{H9A-H9B}$ 1.4, 9A-H), 5.26 (3H, dd, J_{H8-H9B} 17.3 and $J_{H9A-H9B}$ 1.4, 9B-H), 5.80 (3H, ddt, J_{H7-H8} 5.1, J_{H8-H9A} 10.6 and J_{H8-H9B} 17.3, 8-H), 7.09-7.17 (6H, m, 3-H and 5-H), 7.36 (3H, td, J 7.7 and J 1.4, 4-H) and 8.27 (3H, dd, J 8.1 and J 1.4, 6-H); δ_C 22.6 ($\underline{C}H_3CO$), 70.0 (C-7), 113.7 (C-3), 117.4 (C-9), 122.9 (C-5), 131.5 (C-4), 132.6 (C-8), 134.4 (C-6), 151.0 (CBi), 157.7 (C-2) and 175.7 ($CH_3\underline{C}O$) (Found: C, 51.24; H, 4.58. $C_{31}H_{33}BiO_7$ requires: C, 51.25; H, 4.58%).

Reaction of (2) with 2-naphthol (5) : Under an atmosphere of argon, a mixture of 2-naphthol (5) (0.144 g) and TMG (0.138 g) in freshly distilled anhydrous THF (5 mL) was stirred for 10 min at room temperature. A solution of (2) (0.798 g) in THF (5 mL) was added and the mixture stirred overnight at room temperature. The solvent was distilled off and the residue purified by column chromatography on silicagel (eluant: pentane-ether 7:3) to afford 1-(2'-allyloxyphenyl)-2-naphthol (6) (0.250 g, 91%) as colorless plates, m.p. 74 °C (CH_2Cl_2-pentane 1:25); δ_H 4.46-4.51 (2H, m, 7'-H), 5.02-5.12 (2H, m, 9'-H), 5.37 (1H, s, OH), 5.78 (1H, ddt, $J_{H7'-H8'}$ 5.0, $J_{H8'-H9'A}$ 10.1 and $J_{H8'-H9'B}$ 17.4, 8'-H), 7.09-7.50 (8H, m, ArH) and 7.79 (2H, d, J 9.0, ArH); δ_C 69.3 (C-7'), 113.9 (C-3'), 117.3 (C-9'), 117.9 (C-3), 118.0 (C-1), 121.8 (C-5'), 123.2 (C-6), 123.3 (C-1'), 125.0 (C-7), 126.2 (C-5), 128.0 (C-4), 129.2 (C-10), 129.5 (C-8), 130.1 (C-4'), 132.8 (C-6'), 133.5 (C-8' and C-9), 150.7 (C-2) and 156.7 (C-2') (Found: C, 82.61; H, 5.95. $C_{19}H_{16}O_2$ requires: C, 82.58; H, 5.84%). Tris(2-allyloxyphenyl)bismuthane (1) (0.072 g, 11%) was also obtained.

Reaction of (2) with ethyl 2-oxocyclohexanecarboxylate (7) : A mixture of ethyl 2-oxocyclohexanecarboxylate (7) (0.085 g) and TMG (0.096 g) in distilled THF (10 mL) was stirred for 10 min at room temperature. The reagent **(2)** (0.520 g) was added and the mixture stirred for 3 days at room temperature. The solvent was distilled off and the residue was purified by column chromatography on silicagel (pentane-ethyl acetate 17:3) to afford ethyl 1-(2'-allyloxyphenyl)-2-oxocyclohexanecarboxylate **(8)** (0.121 g, 80%) as a colorless oil; δ_H 1.19 (3H, t, J 7.1, $C\underline{H}_3CH_2O$), 1.59-1.98 (4H, m, 4-H and 5-H), 2.48-2.66 (4H, m, 3-H and 6-H), 4.16 (1H, q, J 7.1, $CH_3C\underline{H}_2O$), 4.20 (1H, q, J 7.1, $CH_3C\underline{H}_2O$), 4.47 (2H, q, J 5.3, 7'-H), 5.22 (1H, dd, $J_{H8'\text{-}H9'A}$ 10.5 and $J_{H9'\text{-}H9'B}$ 1.4, 9'A-H), 5.33 (1H, dd, $J_{H8'\text{-}H9'B}$ 17.4 and $J_{H9'A\text{-}H9'B}$ 1.4, 9'B-H), 5.96 (1H, ddt, $J_{H7'\text{-}H8'}$ 5.3, $J_{H8'\text{-}H9'A}$ 10.5 and $J_{H8'\text{-}H9'B}$ 17.4, 8'-H), 6.90 (1H, dd, J 7.6 and J 1.1, 3'-H), 6.94 (1H, td, J 7.6 and J 1.1, 5'-H), 7.08 (1H, dd, J 7.6 and J 1.7, 6'-H) and 7.25 (1H, dd, J 7.6 and J 1.7, 4'-H); δ_C 14.0 ($\underline{C}H_3CH_2O$), 21.9 (cyclic CH_2), 27.1 (cyclic CH_2), 35.2 (cyclic CH_2), 40.7 (cyclic CH_2), 61.3 ($CH_3\underline{C}H_2O$), 64.8 (C-1), 69.7 (CH_2O), 113.2 (C-3'), 117.4 (C-9'), 120.9 (C-5'), 127.4 (C-4'), 128.2 (C-1'), 128.7 (C-6'), 133.0 (C-8'), 156.5 (C-2'), 171.3 ($\underline{C}O_2CH_2$) and 205.8 (C-2) (Found: C, 71.41; H, 7.32. $C_{18}H_{22}O_4$ requires: C, 71.50; H, 7.33%). Tris(2-allyloxyphenyl)bismuthane **(1)** (0.077 g, 18%), allyloxybenzene **(9)** (0.028 g, 10%) and unreacted 2-ethyl 2-oxocyclohexanecarboxylate **(7)** (0.012 g, 14%) were also recovered.

Reaction of (2) with 2-nitropropane (10) : A mixture of 2-nitropropane **(10)** (0.089 g) and TMG (0.127 g) in distilled THF (5 mL) was stirred for 10 min at room temperature. The reagent **(2)** (0.798 g) was added and the mixture stirred for 20 h at room temperature. The solvent was distilled off and the residue was resolved by column chromatography on silicagel (eluant: pentane-ether 19:1) to afford allyloxybenzene **(9)** (0.035 g, 8%) and a unseparable mixture (0.321 g) of tris(2-allyloxyphenyl)bismuthane **(1)** and 2-(2'-allyloxyphenyl)-2-nitropropane **(11)**. After addition of a drop of 35% aqueous HCl, the solution of the two unseparable products in acetone (5 mL) was stirred for a few minutes. After distillation of the solvent, purification of the residue by preparative chromatography (eluant: pentane-ether 19:1) afforded 2-(2'-allyloxyphenyl)-2-nitropropane **(11)** (0.110 g, 50%) as a light yellow oil; δ_H 1.94 (6H, s, Me), 4.49 (2H, d, J 5.1, CH_2O), 5.23 (1H, dd, $J_{H8'\text{-}H9'A}$ 10.6 and $J_{H9'A\text{-}H9'B}$ 1.4, 9'A-H), 5.30 (1H, dd, $J_{H8'\text{-}H9'B}$ 17.7 and $J_{H9'A\text{-}H9'B}$ 1.4, 9'B-H), 5.93 (1H, ddt, $J_{H7'\text{-}H8'}$ 5.1, $J_{H8'\text{-}H9'A}$ 10.6 and $J_{H8'\text{-}H9'B}$ 17.7, 8'-H), 6.89 (1H, d, J 7.8, 3'-H), 6.98 (1H, t, J 7.8, 5'-H), 7.29 (1H, d, J 7.8, 6'-H) and 7.32 (1H, t, J 7.8, 4'-H); δ_C 27.0 (Me), 69.2 (CH_2O), 88.3 (C-2), 112.7 (C-3'), 117.6 (C-9'), 120.7 (C-5'), 126.4 (C-4'), 129.5 (C-1'), 130.1 (C-6'), 132.4 (C-8') and 155.8 (C-2') (Found: C 65.11; H, 6.88; N, 6.30. $C_{12}H_{15}NO_3$ requires: C, 65.14; H, 6.83; N, 6.33%). The amount of tris(2-allyloxyphenyl) bismuthane **(1)** was deduced by substraction (0.211 g, 32%).

When the same reaction was performed under reflux for 2 days, allyloxybenzene **(9)** (0.085 g, 19%), tris(2-allyloxyphenyl)bismuthane **(1)** (0.251 g, 38%) and 2-(2'-allyloxyphenyl)-2-nitropropane **(11)** (0.131 g, 60%) were obtained.

Reaction of (3) with 4-nitrophenol (12) : Under an atmosphere of argon, a solution of **(3)** (0.558 g) in anhydrous THF (10 mL) was added dropwise to a stirred solution of 4-nitrophenol **(12)** (0.139 g) and TMG (0.130 g) in freshly distilled anhydrous THF (10 mL). The mixture was stirred under reflux for 24 h and the solvent was then distilled under reduced pressure. The residue was purified by column chromatography on silicagel (eluant: pentane-ether 97:3) to afford (4-nitrophenyl)phenylether **(13)** (0.070 g, 33%) as fine white needles, m.p. 55 °C (ethanol), lit.[15] 56-58 °C. Unreacted **(12)** (0.084 g, 60%) was also recovered.

Reaction of (2) with 4-nitrophenol (12) : By a similar procedure as above, **(2)** (0.725 g) in anhydrous toluene (15 mL) was added to a stirred solution of 4-nitrophenol **(12)** (0.139 g) and TMG (0.130 g) in anhydrous toluene (15 mL). After 24 h under reflux, work-up and purification by column chromatography on silicagel (eluant: pentane-ether 17:3) followed by preparative layer chromatography (eluant: pentane-ether) afforded (2-allyloxyphenyl)(4-nitrophenyl)ether **(14)** (0.209 g, 77%) as colorless plates, m.p. 58 °C (ether-pentane); δ_H 4.49 (2H, dt, $J_{H7'-H8'}$ 5.0 and $J_{H7'-H9'}$ 1.5, 7'-H), 5.13 (1H, dq, $J_{H8-H9'A}$ 10.5 and $J_{H7'-H9'A}$ = $J_{H9'A-H9'B}$ = 1.5, 9'A-H), 5.16 (1H, dq, $J_{H8-H9'B}$ 17.3 and $J_{H7'-H9'B}$ = $J_{H9'A-H9'B}$ = 1.5, 9'B-H), 5.82 (1H, ddt, $J_{H7'-H8'}$ 5.0, $J_{H8'-H9'A}$ 10.5 and $J_{H8'-H9'B}$ 17.3, 8'-H), 6.92 (2H, d, J 9.2, 2-H and 6-H), 7.02 (2H, d, J 7.6, 3'-H and 6'-H), 7.10-7.26 (2H, m, 4'-H and 5'-H) and 8.15 (2H, d, J 9.2, 3-H and 5-H); δ_C 69.3 (C-7'), 114.7 (C-3'), 115.8 (C-2 and C-6), 117.5 (C-9'), 121.8 (C-6'), 122.8 (C-5'), 125.8 (C-3 and C-5), 126.8 (C-4'), 132.5 (C-8'), 142.3 (C-4), 142.9 (C-1'), 150.5 (C-2') and 163.7 (C-1) (Found: C, 66.37; H, 4.91; N, 5.08. $C_{15}H_{13}NO_4$ requires: C, 66.41; H, 4.83; N, 5.16%). Unreacted **(12)** was also isolated (0.025 g, 18%).

Reaction of (2) with copper diacetate : A mixture of copper diacetate (0.020 g) and **(2)** (0.200 g) in dichloromethane (10 mL) was stirred under reflux for 48 h. The solvent was distilled and the residue purified by flash column chromatography on silicagel (eluant: pentane-ethyl acetate 24:1) to afford 1-acetoxy-2-allyloxybenzene **(15)** as a colorless oil (0.030 g, 57%); δ_H 2.29 (3H, s, Me), 4.54 (2H, d, J 5.0, CH_2O), 5.24 (1H, d, J 10.5, 9A-H), 5.36 (1H, d, J 17.4, 9B-H), 5.99 (1H, ddt, J_{H7-H8} 5.0, J_{H8-H9A} 10.5 and J_{H8-H9B} 17.4, 8-H) and 6.89-7.20 (4H, m, ArH) (Found: C, 68.70; H, 6.33. $C_{11}H_{12}O_3$ requires: C, 68.74; H, 6.29%). Tris(2-allyloxyphenyl)bismuthane **(1)** (0.012 g, 7%) and allyloxybenzene **(9)** (0.068 g, 62%) were also isolated.

Reaction of (2) with 3,4-dimethylaniline (16) : Copper diacetate (0.018 g) and **(2)** (0.725 g) were added to a solution of 3,4-dimethylaniline **(16)** (0.115 g) in dichloromethane (10 mL) and the resulting mixture was stirred for 2 h at room temperature. The solvent was distilled and the residue was purified by flash column chromatography on silicagel (eluant: pentane-ethyl acetate) and by preparative layer chromatography (eluant: pentane-ethyl acetate 19:1). The diarylamine, (2-allyloxyphenyl)(3,4-dimethylphenyl)amine **(17)**, was obtained as a brown oil, (0.217 g, 91%); δ_H 2.21 (3H, s, CH_3), 2.22 (3H, s, CH_3), 4.59 (2H, d, J 5.3, 7'-H), 5.28 (1H, dd, $J_{H8'-H9'A}$ 10.5 and $J_{H9'A-H9'B}$ 1.2, 9'A-H), 5.54 (1H, dd, $J_{H8'-H9'B}$ 17.2 and $J_{H9'A-H9'B}$ 1.2, 9'B-H), 5.99-6.18 (1H, m, 8'-H), 6.07 (1H, s, NH), 6.72-6.95 (5H, m, 2-H, 6-H, 3'-H, 4'-H and 5'-H), 7.04 (1H, d, J 7.8, 5-H) and 7.19 (1H, dd, J 7.9 and J 2.1, 6'-H); δ_C 8.9 (Me), 19.8 (Me), 69.3 (C-7'), 111.8 (C-3'), 113.8 (C-6'), 116.9 (C-2 or C-6), 117.6 (C-9'), 118.8 (C-5'), 121.0 (C-6 or C-2), 121.1 (C-4'), 129.7 (C-4), 130.1 (C-5), 133.3 (C-8'), 134.1 (C-1'), 137.3 (C-3), 140.1 (C-2') and 146.6 (C-1) (Found: C, 80.64; H, 7.46; N, 5.47. $C_{17}H_{19}NO$ requires: C, 80.60; H, 7.56; N, 5.53%).

Reaction of (1) with 3,4-dimethylaniline (16) and stoichiometric copper diacetate : 3,4-Dimethylaniline **(16)** (0.121 g) was added to a stirred mixture of **(1)** (0.728 g) and copper diacetate (0.362 g) in dichloromethane (10 mL). The mixture was stirred under reflux for 1.5 h. The solvent was distilled off under reduced pressure and the residue purified by column chromatography (eluant: pentane-ethyl acetate) followed by preparative layer chromatography (eluant: pentane-ethyl acetate 19:1) to afford (2-allyloxyphenyl)(3,4-dimethylphenyl)amine **(17)** (0.161 g, 64%), allyloxybenzene **(9)** (0.351 g, 73%) and 3,4-dimethylaniline **(16)** (0.040 g, 33%).

Reaction of (2) with 2,2-dimethyl-1,3-propanediol (18) : A mixture of copper diacetate (0.018 g), 2,2-dimethyl-1,3-propanediol **(18)** (0.104 g) and **(2)** (0.870 g) in dichloromethane (10 mL) was stirred for 2 h under reflux. The solvent was distilled and the residue was purified by column chromatography on silicagel (eluant: pentane-ether 7:3) to afford 3-(2'-allyloxyphenoxy)-2,2-dimethylpropan-1-ol **(19) (0.160 g, 68%)** as a colorless oil; δ_H 1.06 (6H, s, Me), 3.24 (1H, t, *J* 6.3, OH), 3.55 (2H, d, *J* 6.3, 1-H), 3.81 (2H, s, 3-H), 4.53 (2H, d, *J* 5.3, 7'-H), 5.27 (1H, dd, $J_{\mathrm{H8'-H9'A}}$ 10.5 and $J_{\mathrm{H9'A-H9'B}}$ 1.4, 9'A-H), 5.41 (1H, dd, $J_{\mathrm{H8'-H9'B}}$ 17.2 and $J_{\mathrm{H9'A-H9'B}}$ 1.4, 9'B-H), 6.06 (1H, ddt, $J_{\mathrm{H7'-H8'}}$ 5.3, $J_{\mathrm{H8'-H9'A}}$ 10.5 and $J_{\mathrm{H8'-H9'B}}$ 17.2, 8'-H) and 6.83-6.93 (4H, m, Ar-H); δ_C 21.9 (Me), 36.3 (C-2), 69.6 (CH_2O), 71.5 (C-1), 78.5 (C-3), 113.4 (C-3' or C-6'), 113.7 (C-6' or C-3'), 117.7 (C-9'), 121.2 (C-4' or C-5'), 121.5 (C-5' or C-4'), 133.0 (C-8'), 148.5 (C-1' or C-2') and 148.7 (C-2' or C-1') (Found: C, 71.06; H, 8.49. $C_{14}H_{20}O_3$ requires: C, 71.16; H, 8.53%). (2-Allyloxyphenyl) acetate **(15)** (0.028 g, 12%), tris(2-allyloxyphenyl)bismuth **(1)** (0.036 g, 5%), allyloxybenzene **(9)** (0.230 g, 48%) and unreacted 2,2-dimethyl-1,3-propanediol **(18)** (0.030 g, 29%) were also recovered.

Reaction of (2) with 3,5-di-*tert*-butylphenol (20) at room temperature : A mixture of copper diacetate (0.018 g), 3,5-di-*tert*-butylphenol **(20)** (0.196 g) and **(2)** (0.725 g) in dichloromethane (10 mL) was stirred for 20 h at room temperature. The solvent was distilled and the residue was purified by flash column chromatography on silicagel (eluant: pentane-ethyl acetate) and by preparative layer chromatography (pentane-ethyl acetate 24:1) to afford unreacted 3,5-di-*tert*-butylphenol **(20)** (0.189 g, 97%) and tris(2-allyloxyphenyl)bismuthane **(1)** (0.200 g, 33%).

Reaction of bis(acetato)tris(2-methylphenyl)bismuth (4) with 3,5-di-*tert*-butylphenol (20) at room temperature : A mixture of copper diacetate (0.018 g), 3,5-di-*tert*-butylphenol **(20)** (0.196 g) and bis(acetato) tris(2-methylphenyl)bismuth **(4)** (0.6 g) in dichloromethane (10 mL) was stirred for 3 days at room temperature. The solvent was distilled and the residue was purified by flash column chromatography on silicagel (eluant: pentane-ethyl acetate 49:1) to afford 3,5-di-*tert*-butylphenyl-(2-methylphenyl) ether **(21)** (0.045 g, 16%) as a colorless oil; δ_H 1.27 (18H, s, CMe_3), 2.27 (3H, s, CH_3), 6.78 (2H, d, *J* 1.6, 2-H and 6-H), 7.12 (1H, t, *J* 1.6, 4-H), and 6.80-7.21 (4H, m, Ar-H); δ_C 16.4 (Me), 31.5 ($C\underline{Me}_3$), 35 ($\underline{C}Me_3$), 112.6 (C-2 and C-6), 116.9 (C-4), 118.3 (C-6'), 123.1 (C-4'), 127 (C-3'), 129.3 (C-2'), 131.3 (C-5'), 152.6 (C-3 and C-5), 155.4 (C-1 or C-1') and 156.9 (C-1' or C-1) (Found: C, 85.03; H, 9.53. $C_{21}H_{28}O$ requires: C, 85.08; H, 9.52%). Unreacted phenol **(20)** was also recovered (0.152 g, 78%).

Reaction of (2) with 3,5-di-*tert*-butylphenol (20) under reflux : A mixture of copper diacetate (0.018 g), 3,5-di-*tert*-butylphenol **(20)** (0.196 g) and **(2)** (0.870 g) in dichloromethane (10 mL) was stirred for 18 h under reflux. The solvent was distilled and the residue was purified by column chromatography on silicagel (eluant: pentane-ethyl acetate 24:1) to afford tris(2-allyloxyphenyl)bismuthane **(1)** (0.277 g, 38%), allyloxybenzene **(9)** (0.131 g, 27%) and a mixture of two products. This mixture was resolved by bulb-to-bulb distillation to give unreacted phenol **(20)** (0.044 g, 23%) and (2-allyloxyphenyl)acetate **(15)** (0.078 g, 33%).

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