Pentavalent Organobismuth Reagents. Part 2.† The Phenylation of Phenols

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The phenylation of a variety of phenols by pentavalent bismuth reagents under neutral, acid and basic conditions has been investigated. Under basic conditions well defined pentavalent intermediates have been isolated and fully characterised. Their decomposition gives only *ortho*-*C*-phenylation (except in the case of a *p*-nitrophenol derivative). *O*-Phenylation is seen under neutral or acidic conditions. Another mechanism is proposed to explain this reaction with no pentavalent bismuth intermediate.

In a series of preliminary Communications[1-3] we have established the general usefulness of pentavalent organobismuth reagents for the regiospecific phenylation of phenols or phenolate anions at either *ortho*-carbon or oxygen. The regiochemistry associated with the transformation of phenols or phenolate anions into phenylated products is determined by the nature of the organobismuth reagent.

In this paper we summarise and supplement our investigations of the regiochemistry of phenylation of phenols by organobismuth(v) reagents.‡ These serve for the synthesis of (*a*) *ortho*-mono- and di-phenylated phenols, (*b*) for the preparation of 6-phenylated cyclohexa-2,4-dienones and (*c*) for the synthesis of *O*-phenyl ethers.

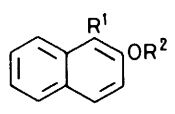
Mechanistic Considerations.—We have previously suggested that reaction of 2-naphthol (**1**) with pentavalent organobismuth reagents (Ph_4BiX or Ph_5Bi) under neutral conditions involves the formation of an intermediate (**4**)[3] possessing a covalent bismuth–oxygen bond, and that the breakdown of this intermediate to give 1-phenyl-2-naphthol (**2**) or 2-naphthyl phenyl ether (**3**) is determined by the nature of the ancillary group X (X = electron-withdrawing group or phenyl) in the intermediate (**4**). Our reason for postulating the existence of the intermediate (**4**) was provided by the observation that in addition to the product (**3**), benzene was also formed when 2-naphthol (**1**) was treated with tetraphenylbismuth trifluoroacetate under neutral conditions.[3] We postulated that the breakdown of the intermediate (**4**) occurred to give either 2-naphthyl phenyl ether (**3**) when the group X was strongly electron-withdrawing, or 1-phenyl-2-naphthol (**2**) when the group X was phenyl. In accord with this postulate, 2-naphthol (**1**) and tetraphenylbismuth trifluoroacetate afforded, under neutral conditions with elimination of benzene only, the *O*-phenylated product (**3**),[3] whereas 2-naphthol (**1**) and pentaphenylbismuth afforded only the *C*-phenylated product (**2**).[1] Some results obtained under neutral, acidic and basic conditions for the phenylation of 2-naphthol are given in Table 1. Under basic conditions good yields (90 ± 5%) of 1-phenyl-2-naphthol are obtained with all the reagents examined. The reagent tetraphenylbismuth trifluoromethanesulphonate has its phenyl groups stabilised by the electron-withdrawing trifluoromethanesulphonate group and under neutral and acidic conditions it is very stable and is recovered unchanged. The same is partially true for its toluene-*p*-sulphonyl analogue. The trifluoroacetate is less stabilised and is a good *O*-phenylating reagent under acidic conditions. In general, in the chemistry of Bi^V compounds, electron-withdrawing groups stabilise aryl–bismuth bonds. Thus $BiPh_5$ (**5**) is unstable even at room temperature, Ph_3BiCl_2 (**6**) is stable up to the melting point and our $Ph_4BiOSO_2CF_3$ is very stable.

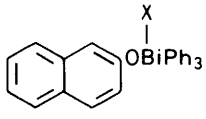
We had noted earlier[1] that *p*-nitrophenol reacted with $BiPh_5$ to give an intermediate (see later) that decomposed exclusively to *p*-nitrophenyl phenyl ether. Mechanistically this was a misleading observation, because it led us to postulate that an electron-withdrawing group on the intermediate would give *O*-phenylation and not *C*-phenylation. We reasoned that reaction of the 2-naphtholate anion with tetraphenylbismuth trifluoroacetate should preclude the formation of benzene and

Table 1. The reaction of 2-naphthol (**1**) with esters of tetraphenylbismuth Ph_4BiX

X	pH[a]	(1) (%)	(2) (%)	(3) (%)
OCOMe	A	19	25	25
	C		95	
$OCOCF_3$	A	20	9	67
	B			91
	C		94	
$OSO_2C_6H_4Me$-*p*	A	58		42
	B	45		43
	C		90	
OSO_2CF_3	A	95		
	B	96		
	C		86	

[a] A Neutral conditions, B addition of trichloroacetic acid (0.6 mol equiv.), C preformed anion using tetramethyl-2-t-butylguanidine.





	R^1	R^2
(**1**)	H	H
(**2**)	Ph	H
(**3**)	H	Ph

(**4**)

Ph_5Bi (**5**)

Ph_3BiCl_2 (**6**)

† For Part 1, see D. H. R. Barton, J. P. Kitchin, D. J. Lester, W. B. Motherwell, and M. T. Barros Papoula, *Tetrahedron*, 1981, **37**, Supplement 1, 73.

‡ In this paper we have formulated tetraphenyl- and triphenyl-bismuth reagents as Ph_4BiX and Ph_3BiX_2. Unless otherwise stated, the group X is electron-withdrawing.

Table 2. The reaction of 2-naphthol (**1**) with organobismuth reagents (Ph_3BiX_2) under basic conditions

Bismuth reagent	Reaction conditions[a] Base[b]	Solvent	Time (h)	Yield of product (**2**) (%)
(*a*) $Ph_3Bi(OCOCF_3)_2$	BTMG	THF	3	70
(*b*) $Ph_3Bi(OCOCF_3)_2$	NaH	THF	3	77
(*c*) Ph_3BiCl_2	BTMG	Benzene	4.5	90
(*d*) Ph_3BiCl_2	NaH	THF	3	86
(*e*) $Ph_3Bi(ONO_2)_2$	TMG	CH_2Cl_2	6.5	60
(*f*) $Ph_3Bi(OTs)_2$	TMG	CH_2Cl_2	7.5	59
(*g*) Ph_3BiCO_3	TMG	CH_2Cl_2	12	76

[a] All reactions at room temperature. [b] BTMG: tetramethyl-2-t-butylguanidine; TMG = tetramethylguanidine.

preferential nucleophilic displacement of the trifluoroacetate anion from the bismuth reagent should occur to give the intermediate (**4**; X = Ph).[3] This intermediate (**4**; X = Ph), being identical with that postulated in the reaction between 2-naphthol (**1**) and pentaphenylbismuth under neutral conditions would be expected to yield the *C*-phenylated product (**2**) exclusively. Indeed, under basic conditions, 2-naphthol (**1**) and tetraphenylbismuth trifluoroacetate afforded only the *C*-phenylated product (**2**). We then examined the reaction of the 2-naphtholate anion with triphenylbismuth bistrifluoroacetate. Nucleophilic displacement of a trifluoroacetate anion from triphenylbismuth bistrifluoroacetate by the 2-naphtholate anion would be expected to yield the intermediate (**4**; X = $OCOCF_3$). This intermediate, being identical with that postulated for the reaction under neutral conditions of 2-naphthol (**1**) with tetraphenylbismuth trifluoroacetate would be expected to yield the *O*-phenylated product (**3**).

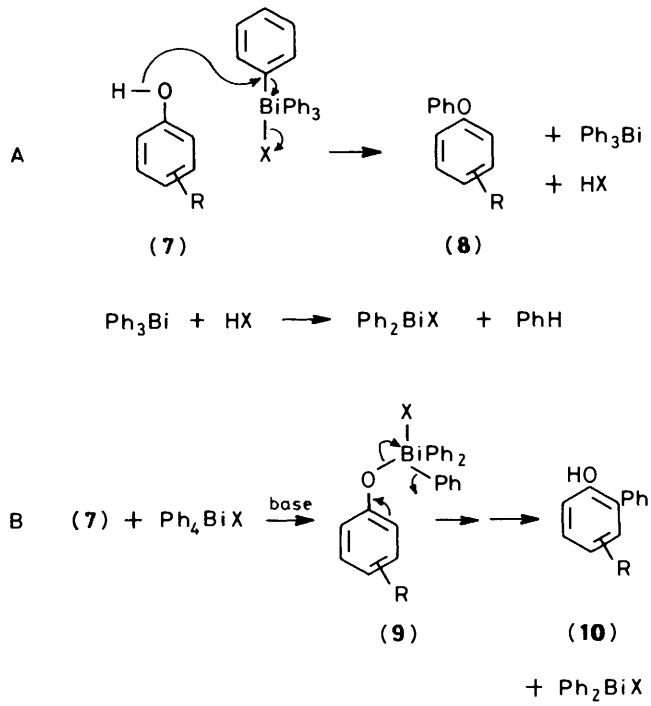
When the bistrifluoroacetate was treated with the 2-naphtholate anion generated by treatment of 2-naphthol (**1**) with (preferably) tetramethyl-2-t-butylguanidine, or sodium hydride, only the *C*-phenylated product (**2**) was isolated in excellent yield (Table 2). None of the *O*-phenylated product (**3**) could be detected. We then studied the reaction under basic conditions of 2-naphthol (**1**) with other organobismuth reagents of the type Ph_3BiX_2. Our results are recorded in Table 2. In all cases the *C*-phenylated product (**2**) was obtained in good yield. None of the *O*-phenylated product (**3**) was formed in these reactions. In many of these reactions triphenylbismuth was also isolated as a by-product. Triphenylbismuth is presumably formed by the disproportionation of the diphenylbismuth compound, Ph_2BiX, which was formed first.

We can now state that under basic conditions phenols *without* electron-withdrawing groups afford with Bi^V reagents intermediates of type (**4**) which rearrange *exclusively* to *ortho*-phenylated phenols for both X = Ph and X = electron-withdrawing group. In the case of *p*-nitrophenol and pentaphenylbismuth the intermediate has been isolated and fully characterised (see later). Its decomposition is an exception and gives only *O*-phenylation. Other examples of phenols with electron-withdrawing groups are now known and will be published later.

It is now clear that the *O*-phenylation of phenols under neutral and slightly acidic conditions does not involve the intermediates of type (**4**) observed in *C*-phenylation.

We have already made reference to the formation of benzene in the reactions of *O*-phenylation under neutral or acidic conditions. This, however, is also misleading because the acid produced in the reaction reacts immediately with the other product Ph_3Bi to give benzene and Ph_2BiX.

The totality of our results in this and subsequent papers (Part 3, following paper) are best explained by two mechanisms. The first is a direct displacement mechanism (Scheme 1, A) [(**7**) ⟶ (**8**)] where the positive charge on carbon of the phenyl attached to Bi is sufficient to induce an S_N2 type displacement of the nucleophile onto phenyl with departure of the bismuth fragment concerted with loss of the anion attached to bismuth. This may seem to be a remarkable proposal, but it will find support in the sequel.



Scheme 1.

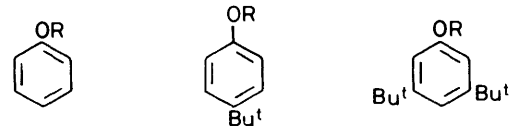
In the second mechanism (Scheme 1, B) under basic conditions, an intermediate (**9**) is postulated which decomposes on heating to give only *ortho*-phenylation (**10**). The exceptions to this rule are the derivatives of phenols with electron-withdrawing groups which give *O*-phenylation on decomposition of (**9**). We cannot explain the reason for these exceptions: it remains an interesting challenge for a theoretical chemist.

When the base used is not strong enough to form the anion of the phenol an intermediate is not formed. Reaction of 2-naphthol (**1**) with tetraphenylbismuth trifluoroacetate using pyridine as the base slowly gave only *O*-phenylation (Scheme 1, A). Intermediates are easily recognised by their colour and by their n.m.r. spectra (see later).

We now report our observations on the phenylation of phenols without electron-withdrawing groups by organobismuth reagents. Results which support the mechanistic proposals described above will be elucidated where relevant.

Reaction of Phenols with Organobismuth Reagents under Neutral Conditions (*Table* 3)*: Phenylation at either Carbon or Oxygen.*—The reaction of phenols with tetraphenylbismuth trifluoroacetate under neutral conditions in boiling benzene solution afforded the corresponding *O*-phenylethers (Table 3). Products were obtained in moderate to good yields.

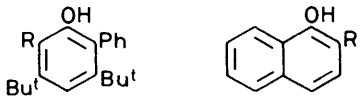
Pentaphenylbismuth (**5**) reacts rapidly with any acid, even phenols, to give Bi^V intermediates and benzene. The intermediates decompose to give *ortho*-phenylation in the case of 1-naphthol (**19**) giving (**20**). With (**5**) and estradiol (**21**), oxidation of the alcohol function also occurred. As reported earlier (**5**) can act as an oxidant for the hydroxy group.[1,2,4]



(11) R = H
(12) R = Ph

(13) R = H
(14) R = Ph

(15) R = H
(16) R = Ph



(17) R = H
(18) R = Ph

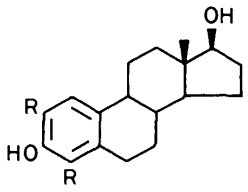
(19) R = H
(20) R = Ph

We envisaged that reaction of (**5**) with phenols possessing *ortho*-substituents would provide an interesting route to phenylated cyclohexa-2,4-dienone derivatives. Such compounds are not easily accessible by other routes. Our results (Table 3) illustrate the general applicability of this postulate. Thus, the phenols (**27**) and (**30**) reacted with pentaphenylbismuth in either benzene or methylene dichloride solution at room temperature giving moderate to good yields of the corresponding cyclohexa-2,4-dienone derivatives. 2,4-Dimethylphenol (**33**) afforded with pentaphenylbismuth a mixture of the phenol (**34**) (26% yield) and the cyclohexa-2,4-dienone derivative (**35**) (21% yield) after a reaction time of 1 h at room temperature.

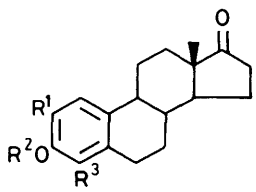
Table 3. Reaction of phenols with organobismuth reagents under neutral conditions

Substrate	Bismuth reagent	Reaction conditions[a] Solvent	Temp. (°C)	Time (h)	Products yield (%)
(**1**)	$Ph_4BiOCOCF_3$	Benzene	80	140	(**3**) 77, (**2**) 4
(**11**)	$Ph_4BiOCOCF_3$	Benzene	80	12	(**12**) 100
(**13**)	$Ph_4BiOCOCF_3$	Benzene	80	4	(**14**) 53
(**15**)	$Ph_4BiOCOCF_3$	Benzene	80	4	(**16**) 68
(**19**)	Ph_5Bi	Benzene	R.t.	0.5	(**20**) 48
(**21**)	Ph_5Bi	Benzene	R.t.	72	(**21**) 20, (**22**) 12, (**25**) 13, (**26**) 14
(**23**)	$Ph_4BiOCOCF_3$	Benzene	80	18	(**23**) 20, (**24**) 75
(**23**)	Ph_5Bi	Benzene	R.t.	48	(**23**) 25, (**25**) 14, (**26**) 41
(**27**)	$Ph_4BiOCOCF_3$	Benzene	80	72	(**27**) 32, (**28**) 58
(**27**)	Ph_5Bi	Benzene	R.t.	3	(**29**) 75
(**30**)	$Ph_4BiOCOCF_3$	Benzene	80	24	(**31**) 57
(**30**)	Ph_5Bi	Benzene	R.t.	4	(**32**) 83
(**33**)	Ph_5Bi	CH_2Cl_2	R.t.	1	(**34**) 26, (**35**) 21

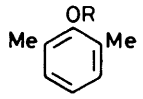
[a] R.t. = Room temperature



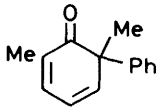
(21) R = H
(22) R = Ph



	R^1	R^2	R^3
(**23**)	H	H	H
(**24**)	H	Ph	H
(**25**)	H	H	Ph
(**26**)	Ph	H	Ph



(27) R = H
(28) R = Ph



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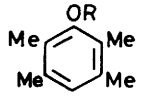
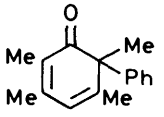


(30) R = H
(31) R = Ph



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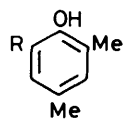
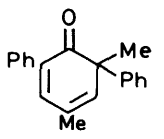


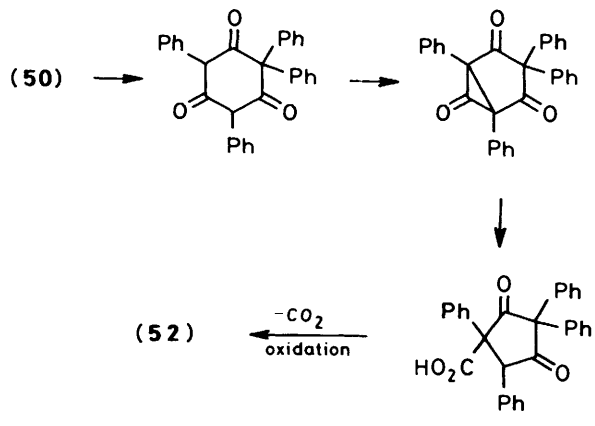
(33) R = H
(34) R = Ph



(35)

Reaction of Phenols with Organobismuth Reagents Under Basic Conditions: Phenylation at Carbon.—We have previously reported[3] that the reaction of 2-naphthol (**1**) with organobismuth reagents of the type Ph_4BiX (X = OAc, $OCOCF_3$, $OSO_2C_6H_4Me$-*p*, and OSO_2CF_3) under basic conditions afforded exclusively the *C*-phenylated product (**2**) (Table 1).

We have noted (Table 2) that reaction of 2-naphthol (**1**) with organobismuth reagents of the type Ph_3BiX_2 under basic conditions also gave only the *C*-phenylated product (**2**). We have found that these reagents can also be used to synthesize highly hindered perphenylated phenols. Reaction of phloroglucinol with triphenylbismuth carbonate (2.5 mol equiv.) gave the perphenylated phloroglucinol (**50**) (24%) characterised as its acetate (**51**), along with the product of over-oxidation and phenylation (**52**) (40%). When the reaction was performed with 5 mol equiv. of triphenylbismuth carbonate, only (**52**) was produced (60%). This is an interesting reaction, possibly explained as in Scheme 2.



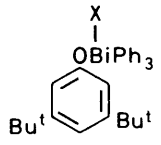
Scheme 2.

Table 4. ^{1}H N.m.r. spectrum of the intermediates[a]

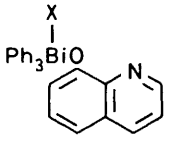
	$\delta_{H\text{-}ortho}$[b]	$\delta_{H\text{-}para}$[c]
(15) + TMG	6.67	6.82
(15) + TMG + Ph_3BiCl_2	6.10	6.50
(15) + TMG + $Ph_3Bi(OCOCF_3)_2$	6.13	6.46
(15)	6.66	6.97
(15) + Ph_5Bi	6.15	6.47

[a] All experiments were run in deuteriochloroform at 60 MHz. [b] H *ortho* signals appeared as doublets (*J* 2 Hz). [c] H *para* signals appeared as broad triplets (*J* 2 Hz).

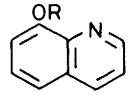
When 3,5-di-t-butylphenol (**15**) was treated with over 2 equivalents of triphenylbismuth dichloride or triphenylbismuth bistrifluoroacetate under basic conditions, 2,6-diphenyl-3,5-di-t-butylphenol (**18**) (77% and 54% yield respectively) were isolated. The compounds (**36**) and (**37**) were postulated as intermediates in the transformation with these reagents. Spectroscopic evidence for their existence was obtained by ^{1}H n.m.r. monitoring of the reactions (Table 4). When a solution of phenol (**15**) and 1,1,3,3-tetramethylguanidine in deuteriochloroform was treated with triphenylbismuth dichloride or triphenylbismuth bistrifluoroacetate, an immediate orange colouration was observed and the ^{1}H n.m.r. spectrum of the solution indicated an upfield shift for the *ortho* (δ 6.10—6.15 instead of δ 6.67) and *para* (δ 6.46—6.50 instead of δ 6.82) protons of the phenolic moiety of the intermediates (**36**) and (**37**). Similarly,



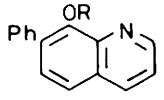
(**36**) X = Cl
(**37**) X = $OCOCF_3$
(**38**) X = Ph



(**40**) X = Cl
(**41**) X = $OCOCF_3$



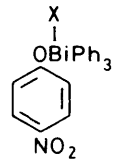
(**39**) R = H
(**42**) R = $COCH_3$



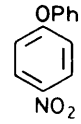
(**43**) R = H
(**44**) R = $COCH_3$

when the phenol (**15**) was treated with pentaphenylbismuth in deuteriochloroform, the solution turned orange instantly and the ^{1}H n.m.r. spectrum indicated the similar upfield shift in the protons of the phenolic moiety of (**38**), together with a signal for the benzene which was formed. Eventually, the intermediates (**38**) and (**36**) were isolated from the reaction of the phenol (**15**) with pentaphenylbismuth or its performed anion (with tetramethylguanidine) and triphenylbismuth dichloride respectively, and their assigned structures were fully supported by spectral and analytical data. Carefully controlled thermal decomposition of these compounds produced the *C*-phenylated phenol (**17**) as the major product [82% from (**36**), 58% from (**38**)].

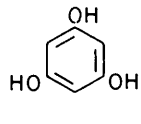
The phenolate anion of 8-hydroxyquinoline (**39**) has been reported to react with triphenylbismuth dichloride to give the adduct (**40**),[5] and we have reported an *X*-ray crystallographic investigation which supports its assigned structure.[6] We have now prepared the adduct (**41**) by a similar method. Thermal decomposition of these adducts gave only the *C*-phenylated compound (**43**) [40% from (**40**), 11% from (**41**), isolated as the acetate (**44**)]. 8-Hydroxyquinoline, characterised as its acetate (**42**) was also formed.



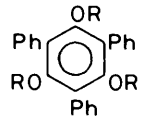
(**45**) X = Cl
(**46**) X = $OCOCF_3$
(**47**) X = Ph



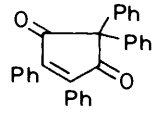
(**48**)



(**49**)



(**50**) R = H
(**51**) R = $COCH_3$



(**52**)

The phenolate anion of *p*-nitrophenol with organobismuth reagents of the type Ph_3BiX_2 also yielded crystalline adducts possessing a covalent Bi–O bond. Adducts (**45**) and (**46**) were prepared from the phenolate anion of *p*-nitrophenol and triphenylbismuth dichloride and triphenylbismuth bistrifluoroacetate respectively. Thermal decomposition of the adduct (**47**) gave only the *O*-phenyl ether (**48**) as already reported above.

Phenylation at Carbon: Concerted or Radical Mechanism?— We have considered two possible mechanisms, concerted and radical, for the transformation of intermediates possessing a covalent Bi–O bond into *ortho*-phenylated products.

The *exclusive* formation of *ortho*-phenylated products is better explained by a concerted mechanism, as is the fact that reactions can be carried out in benzene, tetrahydrofuran *etc.*, solvents normally capable of trapping radicals. Further definite disproof of a radical mechanism will be reported in due course.

Conclusion

For phenols not containing an electron-withdrawing group the formation of a defined intermediate with a bismuth–oxygen bond leads on pyrolysis to *ortho*-*C*-phenylation often in high yield. Phenols such as *p*-nitrophenol are an exception and give only *O*-phenylation.

For phenols without an electron-withdrawing group *O*-phenylation is observed under neutral or acidic conditions where a Bi^V intermediate is not formed. For this reaction a different mechanism is postulated which accounts for the *O*-phenylation.

We have already referred to the *O*-phenylation of 2-naphthol by tetraphenylbismuth trifluoroacetate when pyridine is present (no intermediate). Another example of this phenomenon was the *O*-phenylation of (**15**) to give (**16**) under the same conditions. In these reactions benzene is not formed and the other product of the reaction is triphenylbismuth. It is difficult to explain these results by other than the direct phenylation mechanism (Scheme 1, A).

Experimental

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. N.m.r. spectra were determined for solutions in deuteriochloroform or carbon tetrachloride with $SiMe_4$ as an

internal standard on Varian T-60, Varian E-M 360 or Bruker WP-80 instruments. I.r. spectra were recorded on Perkin-Elmer 257 or 297 instruments. U.v. spectra were recorded on a Jobin-Yvon DUOSPAC 203 spectrometer. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. Mass spectra were recorded with an AEI MS-9 or MS-50 instrument. Electron capture negative ion desorption chemical ionization mass spectra were recorded on a RIBER R-1010 quadrupole mass spectrometer (Nermag, France) by Dr. Jankowski at C.E.N. Saclay. All solvents and reagents were purified and dried by standard techniques. Chromatographic separations were performed using Merck Kieselgel 60 GF 254 (Preparative t.l.c.) and Merck Kieselgel 60H (column chromatography). Ether refers to diethyl ether.

Preparation of Organobismuth Reagents.—Pentaphenylbismuth,[7] tetraphenylbismuth trifluoroacetate,[6] tetraphenylbismuth toluene-*p*-sulphonate,[6] triphenylbismuth bistrifluoroacetate,[8] triphenylbismuth dichloride,[7] and triphenylbismuth dinitrate[9] were prepared by literature methods.

Tetraphenylbismuth Trifluoromethanesulphonate.—To a solution of pentaphenylbismuth (3 g, 5 mmol) in dry benzene (8 ml) under an argon atmosphere was added, dropwise, with stirring, a solution of trifluoromethanesulphonic acid (0.750 g, 5 mmol) in ether (10 ml) with cooling in a water bath at 15 °C. Addition was continued until complete decolourisation occurred. After the addition of ether, the white solid thus formed was filtered off, washed with cold ether and dried *in vacuo* to give the title compound (2.9 g, 4.5 mmol) (90%), m.p. 205—215 °C (hexane–methylene dichloride); $\nu_{max.}(CHCl_3)$ 3 050, 2 950, 1 560, 1 420, and 1 160; $\delta_H(CDCl_3)$ 8—7.25 (m, ArH); $\delta_C(CDCl_3)$ 138.15 (C-1), 135.66 (C-2), 132.41 (C-3), 132.25 (C-4), and 120.3 (CF_3); *m/z* 597 (Ph_4BiSO_3), 517 (Ph_4Bi), 440 (Ph_3Bi), 383 (Ph_2BiF), 363 (Ph_2Bi), 286 (PhBi), 209 (Bi), 154 (Ph–Ph), and 77 (Ph) (Found: C, 45.0; H, 2.9. $C_{25}H_{20}BiF_3O_3S$ requires C, 44.99; H, 3.02%).

Improved Preparation of Triphenylbismuth Carbonate.—To a well stirred solution of triphenylbismuth dichloride (13 g) in acetone (100 ml) was added a solution of K_2CO_3 (3.6 g) in water (100 ml). After 5 min, the precipitated triphenylbismuth carbonate was filtered off, washed with acetone, and dried; yield 12.7 g, (100%), m.p. 155 °C (decomp.) lit.,[10] 164 °C (Found: C, 45.3; H, 3.2. $C_{19}H_{15}BiO_3$ requires C, 45.6; H, 2.9%).

*Triphenylbismuth Ditoluene-*p*-sulphonate.*—A solution of triphenylbismuth carbonate (2.5 g) and toluene-*p*-sulphonic acid monohydrate (2.0 g) in acetone (25 ml) was heated (3.5 h) under reflux, cooled, filtered, and evaporated to give *triphenylbismuth ditoluene-*p*-sulphonate* (3.0 g, 77%) as white plates, m.p. 190—194 °C (methylene dichloride–hexane); $\nu_{max.}(CHCl_3)$ 1 140 and 1 130 cm^{-1}; $\delta(CDCl_3)$ 8.13—7.83 (8 H, m), 7.70—7.33 (9 H, m), 6.95 (8 H, AB system, δ_A 6.85 and δ_B 7.05, *J* 9 Hz), and 2.27 (6 H, s, Me) (Found: C, 49.0; H, 3.8; S, 8.2. $C_{32}H_{29}BiO_6S_2$ requires C, 49.0; H, 3.7; S, 8.2%).

Phenylation of 2-Naphthol with Tetraphenylbismuth Monoester under Neutral Conditions (Table 1): General Method.—A stirred solution of 2-naphthol (**1**) and tetraphenylbismuth monoester in anhydrous benzene (*ca.* 5 ml $mmol^{-1}$ substrate) was heated under reflux under an atmosphere of argon for 24 h. The mixture was evaporated and the residue fractionated by preparative thick layer chromatography using pentane–methylene dichloride (4:1) as the eluant.

(*a*) 2-Naphthol (**1**) (0.10 g), and tetraphenylbismuth acetate [from pentaphenylbismuth (0.830 g) and acetic acid (0.084 g)] gave 2-naphthyl phenyl ether (**3**) (0.040 g, 25%), m.p. 45 °C (ethanol) [lit.,[11] 42—46 °C (ethanol)], 1-phenyl-2-naphthol[12] (0.040 g, 25%) and 2-naphthol (0.019 g, 19%).

(*b*) 2-Naphthol (0.072 g) and tetraphenylbismuth trifluoroacetate (0.470 g) gave 2-naphthyl phenyl ether (**3**) (0.074 g, 67%), 1-phenyl-2-naphthol (0.010 g, 9%) and 2-naphthol (0.015 g, 20%).

(*c*) 2-Naphthol (0.080 g) and tetraphenylbismuth toluene-*p*-sulphonate (0.516 g) gave 2-naphthyl phenyl ether (**3**) (0.053 g, 42%) and 2-naphthol (0.047 g, 58%).

(*d*) 2-Naphthol (0.072 g) and tetraphenylbismuth trifluoromethanesulphonate (1.33 g) gave 2-naphthol (0.067 g, 95%).

Phenylation of 2-Naphthol with Tetraphenylbismuth Monoester under Acidic Catalysis (Table 1): General Method.—A stirred solution of 2-naphthol (**1**), tetraphenylbismuth monoester (1.5 mol equiv.), and trichloroacetic acid (0.6 mol equiv.) in anhydrous benzene (*ca.* 5 ml $mmol^{-1}$ substrate) was heated at 60 °C for 24 h under an atmosphere of argon. The mixture was evaporated and the residue fractionated by preparative thick layer chromatography to afford 2-naphthyl phenyl ether (**3**) and 2-naphthol (**1**).

(*a*) 2-Naphthol (0.036 g), tetraphenylbismuth trifluoroacetate (0.240 g), and trichloroacetic acid (0.025 g) gave 2-naphthyl phenyl ether (0.050 g, 91%).

(*b*) 2-Naphthol (0.036 g), tetraphenylbismuth toluene-*p*-sulphonate (0.260 g), and trichloroacetic acid (0.025 g) gave 2-naphthyl phenyl ether (0.024 g, 43%) and 2-naphthol (0.016 g, 45%).

(*c*) 2-Naphthol (0.036 g), tetraphenylbismuth trifluoromethanesulphonate (0.495 g), and trichloroacetic acid (0.025 g) gave 2-naphthol (0.034 g, 96%).

Phenylation of β-Naphthol under Basic Conditions (Tables 1 and 2): General Method.—To a stirred solution of 2-naphthol (**1**) in either benzene or tetrahydrofuran solution at room temperature under an atmosphere of nitrogen or argon, was added the base indicated in Tables 1 and 2. The bismuth reagent was added, and the mixture was stirred for the period indicated in Table 1 and then evaporated. The residue was fractionated by preparative thick layer chromatography using ether–hexane (1:4) as the eluant to give 1-phenyl-2-naphthol (**2**), identical with an authentic sample. In some cases triphenylbismuth identical with an authentic sample was also isolated.

(*a*) 2-Naphthol (**1**) (0.144 g), tetramethyl-2-t-butylguanidine (0.205 g) and triphenylbismuth bistrifluoroacetate (0.8 g) gave 1-phenyl-2-naphthol (**2**) (0.154 g, 70%).

(*b*) 2-Naphthol (**1**) (0.144 g), sodium hydride [55% dispersion in oil (0.053 g)], and triphenylbismuth bistrifluoroacetate (0.8 g) gave 1-phenyl-2-naphthol (**2**) (0.169 g, 77%).

(*c*) 2-Naphthol (**1**) (0.14 g), tetramethyl-2-t-butylguanidine (0.5 g), and triphenylbismuth dichloride (0.55 g) gave 1-phenyl-2-naphthol (**2**) (0.193 g, 90%) and triphenylbismuth (0.102 g, 21%).

(*d*) 2-Naphthol (**1**) (0.144 g), sodium hydride [55% dispersion in oil (0.053 g)] and triphenylbismuth dichloride (0.565 g) gave 1-phenyl-2-naphthol (**2**) (0.190 g, 86%).

(*e*) 2-Naphthol (**1**) (0.140 g), 1,1,3,3-tetramethylguanidine (0.140 g) and triphenylbismuth dinitrate (0.53 g) gave 1-phenyl-2-naphthol (**2**) (0.127 g, 60%) and triphenylbismuth (0.148 g, 35%).

(*f*) 2-Naphthol (**1**) (0.070 g), tetramethylguanidine (0.14 g), and triphenylbismuth ditoluene-*p*-sulphonate (0.4 g) gave 1-phenyl-2-naphthol (**1**) (0.051 g, 59%) and triphenylbismuth (0.031 g, 15%).

(*g*) *Phenylation with triphenylbismuth carbonate.* 2-Naphthol (**1**) (0.072 g), 1,1,3,3-tetramethylguanidine (0.115 g) and triphenylbismuth carbonate (0.250 g) gave 1-phenyl-2-naphthol (**2**) (0.084 g, 76%).

(*h*) *Phenylation with tetraphenylbismuth monoester.* 2-Naphthol (**1**) (0.100 g), tetramethyl-2-t-butyl-guanidine (0.140 g) and tetraphenylbismuth acetate [from pentaphenylbismuth (0.700 g) and acetic acid (0.071 g)] gave 1-phenyl-2-naphthol (**2**) (0.145 g, 95%). 2-Naphthol (**1**) (0.050 g), tetramethyl-2-t-butylguanidine (0.075 g) and tetraphenylbismuth trifluoroacetate (0.220 g) gave 1-phenyl-2-naphthol (**2**) (0.073 g, 94%). 2-Naphthol (**1**) (0.036 g), tetramethyl-2-t-butylguanidine (0.051 g) and tetraphenylbismuth toluene-*p*-sulphonate (0.350 g) gave 1-phenyl-2-naphthol (**2**) (0.050 g, 90%). 2-Naphthol (**1**) (0.072 g), tetramethyl-2-t-butylguanidine (0.105 g) and tetraphenylbismuth trifluoromethanesulphonate (0.670 g) gave 1-phenyl-2-naphthol (**2**) (0.095 g, 86%).

Phenylation with Pentaphenylbismuth (*Table* 3)*: General Method.*—To a stirred solution of the substrate in either benzene or methylene dichloride (*ca.* 5 ml mmol^{-1} substrate) at room temperature under an atmosphere of argon was added pentaphenylbismuth. The mixture was stirred for the period indicated in Table 3 and then evaporated. The residue was fractionated by preparative thick layer chromatography.

(*a*) 1-Naphthol (**19**) (0.144 g) and pentaphenylbismuth (0.9 g) [eluant CH_2Cl_2–hexane (1:1)] gave 2-phenyl-1-naphthol (**20**) (0.105 g, 48%), isolated as the p-*nitrobenzoate*,[13] m.p. 148—149 °C (benzene–hexane); $\nu_{max.}$($CHCl_3$), 1 740, 1 600, 1 510, 1 340, 1 240, 1 070, 1 010, and 905 cm^{-1}; δ($CDCl_3$) 8.63 (4 H, s, $NO_2C_6H_4$), and 8.33—7.5 (13 H, m, ArH); *m/z* 369 (M^+), 219 ($M^+ - COC_6H_4NO_2$), 150 ($COC_6H_4NO_2$), and 78 (C_6H_6) (Found: C, 74.95; H, 4.35; N, 3.65. $C_{23}H_{15}NO_4$ requires C, 74.80; H, 4.07; N, 3.79%).

(*b*) Estradiol (**21**) (0.272 g) and pentaphenylbismuth (1.19 g) [eluant hexane–ether (4:1)] gave estradiol (**21**) (0.054 g, 20%), 2,4-*diphenylestradiol* (**22**) (0.054 g, 12%), 4-*phenylestrone* (**25**) (0.045 g, 13%), and 2,4-*diphenylestrone* (**26**) (0.060 g, 14%). Compound (**22**) was isolated as a white foam, m.p. 109 °C; $\lambda_{max.}$(EtOH) 302 nm (ε 6 110); $\nu_{max.}$($CHCl_3$) 3 600 and 3 550 cm^{-1}; δ($CDCl_3$) 7.6—7.2 (11 H, m), 4.5 (1 H, s, 3-OH), 3.4 (1 H, m, 17-H), 2.7—1.0 (15 H, m, aliphatic H), and 0.72 (3 H, s, Me); $[\alpha]_D^{20}$ +39° (*c* 0.9 $CHCl_3$); *m/z* 424 (M^+). Compound (**25**) was isolated as a white foam; $\lambda_{max.}$(EtOH) 288 nm (ε 2 990); $\nu_{max.}$($CHCl_3$) 3 525 and 1 730 cm^{-1}; δ($CDCl_3$) 7.8—6.8 (7 H, m), 4.80 (1 H, s, 3-OH), 2.8—1.1 (15 H, m, aliphatic H), and 0.93 (3 H, s, Me); $[\alpha]_D^{20}$ +83.1° (*c* 1.77, EtOH); *m/z* 346 (M^+). 4-Phenylestrone acetate was prepared (Found: C, 80.3; H, 7.3. $C_{26}H_{25}O_3$ requires C, 80.4; H, 7.3%). Compound (**26**) was obtained as a white foam, m.p. 118 °C; $\nu_{max.}$($CHCl_3$) 3 525 and 1 730 cm^{-1}; δ($CDCl_3$) 7.6—7.0 (11 H, m), 4.57 (1 H, s, 3-OH), 3.0—1.2 (13 H, m, aliphatic H), and 0.88 (3 H, s, Me); *m/z* 422 (M^+). 2,4-Diphenylestrone acetate, m.p. 20 °C, was prepared; $\lambda_{max.}$($CHCl_3$) 255 nm (ε 16 150); $\nu_{max.}$(CCl_4) 1 760 and 1 735 cm^{-1}; δ($CDCl_3$) 7.7—7.0 (11 H, m), 1.60 (3 H, s, OCOMe), 2.7—1.2 (15 H, m, aliphatic H), and 0.94 (3 H, s, Me); *m/z* 464 (M^+) (Found: C, 82.4; H, 6.9. $C_{32}H_{32}O_3$ requires C, 82.8; H, 6.9%).

(*c*) Estrone (**23**) (0.27 g) and pentaphenylbismuth (0.9 g) [eluant hexane–ether (6:4)] gave estrone (**23**) (0.067 g, 25%), identical with an authentic sample, 4-phenylestrone (**25**) (0.064 g, 14%), identical with an authentic sample, and 2,4-diphenylestrone (**26**) (0.175 g, 41%), identical with an authetic sample.

(*d*) 2,6-Dimethylphenol (**27**) (0.122 g) and pentaphenylbismuth (0.713 g) [eluant hexane–ether (95:5)] gave 2,6-dimethyl-6-phenylcyclohexa-2,4-dienone (**29**) (0.148 g, 75%) as a yellow oil, $\lambda_{max.}$(CCl_4) 314 nm (ε 4 230); $\nu_{max.}$(CCl_4) 1 660—1 640sh cm^{-1}; δ(CCl_4) 7.1 (5 H, narrow m, ArH), 6.67 (1 H, m, 5-H), 6.40—5.87 (2 H, m, 3-H and 4-H), 1.80 (3 H, d, *J* 1 Hz, 2-Me), and 1.53 (3 H, s, 6-Me); *m/z* 198 (M^+) (Found: C, 84.7; H, 7.2 $C_{14}H_{14}O$ requires C, 84.8; H, 7.1%).

(*e*) 2,3,5,6-Tetramethylphenol (**30**) (0.150 g) and pentaphenylbismuth (0.890 g) [eluant hexane–methylene dichloride (3:1)] gave 2,3,5,6-tetramethyl-6-phenylcyclohexa-2,4-dienone (**32**) (0.186 g, 83%) as a yellow oil, $\lambda_{max.}$(CCl_4) 330 nm (ε 6 210); $\nu_{max.}$(CCl_4) 1 658 and 1 640 cm^{-1}; δ(CCl_4) 7.0 (5 H, narrow m, ArH), 5.87 (1 H, m, 4-H), 2.0 (3 H, s, 2-Me), 1.74 (3 H, s, Me), 1.67 (3 H, s, Me), and 1.54 (3 H, s, 6-Me); *m/z* 226 (M^+) (Found: C, 84.7; H, 8.2. $C_{16}H_{18}O$ requires C, 84.9; H, 8.0%).

(*f*) 2,4-Dimethylphenol (**33**) (0.061 g) and pentaphenylbismuth (0.300 g) gave (after 0.25 h) 2,4-dimethylphenol (**33**) (0.061 g, 77%) and 2,4-dimethyl-6-phenylphenol (**34**) (0.021 g, 21%).

(*g*) 2,4-Dimethylphenol (**33**) (0.061 g) and pentaphenylbismuth (0.300 g) gave (after 1 h) 2,4-dimethyl-6-phenylphenol (**34**) (0.025 g, 26%), isolated as the naphthoylurethane, m.p. 118—121 °C, (lit.,[14] 126—127.5 °C), and 2,4-dimethyl-2,6-diphenylcyclohexa-3,5-dienone (**35**) (0.029 g, 21%) as an unstable oil, $\nu_{max.}$(CCl_4) 1 665, 1 645, 780, and 695 cm^{-1}; δ(CCl_4) 7.1 (10 H, m, ArH), 6.7 (1 H, m, 5-H), 6.1 (1 H, m, 3-H), 2.0 (3 H, d, *J* 1 Hz, 4-Me), and 1.6 (3 H, s, 2-Me).

Phenylation with Tetraphenylbismuth Trifluoroacetate (*Table* 3) *under Neutral Conditions: General Method.*—A stirred solution of the substrate and tetraphenylbismuth trifluoroacetate in boiling benzene was treated for the time indicated in Table 3 under an atmosphere of nitrogen or argon. The cooled mixture was evaporated and the residue was fractionated by preparative thick layer chromatography.

(*a*) Phenol (**11**) (0.047 g) and tetraphenylbismuth trifluoroacetate (0.475 g) (eluant hexane) gave diphenyl ether (**12**) (0.084 g, 100%), identical with an authentic sample.

(*b*) 4-t-Butylphenol (**13**) (0.078 g) and tetraphenylbismuth trifluoroacetate (0.4 g) (eluant hexane) gave phenyl 4-t-butylphenyl ether (**14**) (0.062 g, 53%), m.p. 54—55 °C, (lit.,[15] 54 °C).

(*c*) 3,5-Di-t-butylphenol (**15**) (0.1 g) and tetraphenylbismuth trifluoroacetate (0.4 g) (eluant hexane) gave *phenyl 3,5-di-t-butylphenyl ether* (**16**) (0.093 g, 68%) as white needles, m.p. 72—73 °C (methanol); $\nu_{max.}$($CHCl_3$) 1 580, 1 290, and 960 cm^{-1}; δ($CDCl_3$) 7.50—6.88 (8 H, m, ArH) and 1.30 (18 H, s, 2 × CMe_3); *m/z* 282 (M^+) (Found: C, 84.8; H, 9.3. $C_{20}H_{26}O$ requires C, 85.0; H, 9.3%).

(*d*) Estrone (**23**) (0.135 g) and tetraphenylbismuth trifluoroacetate (0.480 g) [eluant hexane–ether (9:1)] gave estrone (**23**) (0.027 g, 20%) and *estrone phenyl ether* (**24**) (0.091 g, 75%) m.p. 124—125 °C and 141—142 °C, (hexane–methylene dichloride); $\nu_{max.}$(CCl_4) 3 005, 2 900, 1 730, 1 280, 1 260, 1 230, and 1 200 cm^{-1}; δ(CCl_4) 7.3—6.5 (8 H, m, ArH), and 0.87 (3 H, s, 18-Me); $[\alpha]_D^{20}$ +136.8° (*c* 0.94, ethanol); *m/z* 346 (M^+) (Found: C, 83.4; H, 7.6. $C_{24}H_{26}O_2$ requires C, 83.2; H, 7.6%).

(*e*) 2,6-Dimethylphenol (**27**) (0.122 g) and tetraphenylbismuth trifluoroacetate (0.950 g) (eluant hexane–ether 95:5) gave 2,6-dimethylphenol (**27**) (0.040 g, 32%) and 2,6-dimethylphenyl phenyl ether (**28**) (0.115 g, 58%), m.p. 54—55 °C (hexane–ether), [lit.,[16] 55—56 °C (hexane)]

(*f*) 2,3,5,6-Tetramethylphenol (**30**) (0.075 g) and tetraphenylbismuth trifluoroacetate (0.630 g) (eluant hexane–ether 95:5) gave 2,3,5,6-*tetramethylphenyl phenyl ether* (**31**) (0.065 g, 57%), m.p. 105—106 °C (pentane–methylene dichloride); $\lambda_{max.}$(EtOH) 278, 271, 265, and 258 nm (ε 1 790, 2 030, 1 580, and 1 105); $\nu_{max.}$(CCl_4) 1 580, 1 300, 1 220, and 1 160 cm^{-1}; δ(CCl_4) 7.4—6.4 (6 H, m, ArH), 2.20 (6 H, s, Me), and 1.97 (6 H, s, Me); *m/z* 226 (M^+) (Found: C, 84.9; H, 8.0. $C_{16}H_{18}O$ requires C, 84.9; H, 8.0%).

3,5-*Di-t-butyl*-2,6-*diphenylphenol* (**18**).—*Method* (*a*). A stirred solution of 3,5-di-t-butylphenol (**15**) (0.2 g) 1,1,3,3-tetramethylguanidine (0.4 ml) and triphenylbismuth dichloride (1.1 g) in boiling benzene (10 ml) under a nitrogen atmosphere was heated (17 h), cooled, and evaporated. The residue was fractionated by column chromatography (eluant ether–hexane,

1:7) giving triphenylbismuth (0.414 g, 44%) identical with an authentic sample and 3,5-*di-t-butyl*-2,6-*diphenylphenol* (**18**) (0.268 g, 77%) as white needles, m.p. 212—213 °C (hexane); $\nu_{max.}$($CHCl_3$) 3 500, 2 900br, 1 600, 1 370, and 960 cm^{-1}; δ($CDCl_3$) 7.30 (11 H, br s, 2 × Ph and ArH), 4.25 (1 H, s, OH), and 1.20 (18 H, s, 2 × CMe_3); *m/z* 358 (M^+) (Found: C, 87.1; H, 8.5. $C_{26}H_{30}O$ requires C, 87.1; H, 8.5%).

Method (*b*). As for method (*a*) except triphenylbismuth bistrifluoroacetate replaced triphenylbismuth dichloride. In this experiment triphenylbismuth (35%) and phenol (**18**) (54%) were isolated.

2-*Phenyl*-3,5-*di-t-butyl-phenol* (**17**).—To a stirred solution of 3,5-di-t-butylphenol (**15**) (0.4 g) in benzene (15 ml) at room temperature under an atmosphere of nitrogen was added sodium hydride (80% dispersion in oil; 120 mg). The mixture was boiled (0.5 h) under reflux, cooled to room temperature, and triphenylbismuth dichloride (1.0 g) was added. After being stirred for 0.5 h the mixture was boiled under reflux for 3 h, cooled, and excess methanol was added (to destroy residual NaH). The mixture was evaporated and the residue was fractionated by column chromatography (using ether–hexane (1:9) as the eluant to give a mixture (0.151 g) of phenol (**18**) (1—2%) and 2-phenyl-3,5-di-t-butylphenol (**17**) (26%) by n.m.r. spectroscopy. The *phenol* (**17**) (0.053 g), m.p. 99—101 °C was obtained pure by fractional recrystallisation from methanol, $\nu_{max.}$($CHCl_3$) 3 500, 1 610, 1 300, and 960 cm^{-1}; δ($CDCl_3$) 7.35—7.18 (5 H, m, Ph), 7.00 (1 H, d, *J* 2 Hz, ArH), 6.75 (1 H, d, *J* 2 Hz, ArH), 4.27 (1 H, s, OH), 1.33 (9 H, s, CMe_3), and 1.13 (9 H, s, CMe_3); *m/z* 282 (M^+) (Found: C, 85.3; H, 9.2. $C_{20}H_{26}O$ requires C, 85.0; H, 9.3%).

Isolation of (3,5-*Di-t-butylphenoxy*)*triphenylbismuth Chloride* (**36**).—A solution of 3,5-di-t-butylphenol (**15**) (0.2575 g) and 1,1,3,3-tetramethylguanidine (0.156 g) in degassed THF (10 ml) was stirred under argon at room temperature for 20 min. A solution of triphenylbismuth dichloride (0.664 g) in degassed THF (10 ml) was then added dropwise over a period of 15 min. The solution quickly became yellow-orange and was stirred for a further 45 min. The THF was then distilled off under reduced pressure at room temperature and the residue extracted with degassed hexane (10 ml). The hexane solution was evaporated to dryness under reduced pressure at room temperature and the residue crystallised from pentane (2 ml) at −20 °C to give *compound* (**36**). The crystals were washed several times with pentane (precooled to −20 °C), and dried *in vacuo* at room temperature (0.383 g, 45%), m.p. 98—101 °C; *m/z* (Electron capture negative ion desorption chemical ionisation) 681 and 679 (M^+ − 1); δ($CDCl_3$) 8.57—7.20 (15 H, m, Ph), 6.50 (1 H, t, *J* 2 Hz, 4-H), 6.10 (2 H, d, *J* 2 Hz, 2-H and 6-H), and 1.02 (18 H, s, CMe_3) (Found: C, 56.8; H, 5.4; Cl, 5.1. $C_{32}H_{36}BiClO$ requires C, 56.4; H, 5.3; Cl, 5.2%).

Thermal Decomposition of (3,5-*Di-t-butylphenoxy*)*triphenylbismuth Chloride* (**36**).—A cooled (−20 °C) solution of the intermediate (**36**) (0.160 g) in degassed toluene (1 ml) was added dropwise to degassed refluxing toluene (2 ml) under argon. The mixture was refluxed for a further 45 min and then filtered and the filtrate evaporated. The residue was fractionated by preparative thick layer chromatography using hexane–ethyl acetate (9:1) as the eluant, to afford triphenylbismuth (0.047 g, 45%); 3,5-di-t-butyl-2,6-diphenylphenol (**18**) (trace amount), 2-phenyl-3,5-di-t-butylphenol (**17**) (0.054 g, 82%) and 3,5-di-t-butylphenol (**15**) (0.007 g, 14%). All these compounds were identical with authentic samples.

Synthesis of (3,5-*Di-t-butylphenoxy*)*tetraphenylbismuth* (**38**).—A solution of 3,5-di-t-butylphenol (**15**) (0.103 g) in degassed THF (5 ml) was added dropwise at 0 °C to a stirred solution of pentaphenylbismuth (0.312 g) in degassed THF (10 ml) and the reaction mixture was stirred for 30 min. The THF was distilled off under reduced pressure at 0 °C and the residue was extracted with cold degassed hexane (5 ml) and the extract evaporated to dryness at 0 °C. The oily residue of *compound* (**38**) resisted crystallisation and was not very stable at room temperature; δ($CDCl_3$) 8.16—7.50 (20 H, m, Ph), 6.67 (1 H, t *J* 2 Hz, 4-H), 6.35 (2 H, d, *J* 2 Hz, 2-H and 6-H), and 1.08 (18 H, s, CMe_3) (Found: C, 62.9; H, 5.9. $C_{38}H_{41}BiO$ requires C, 63.2; H, 5.7%).

Thermal Decomposition of (3,5-*Di-t-butylphenoxy*)*tetraphenylbismuth* (**38**).—A solution of the intermediate (**38**) (0.2 g) in degassed toluene (1 ml) cooled to −20 °C was added dropwise to refluxing degassed toluene (2 ml). The solution was refluxed for 45 min, and then evaporated. The residue was fractionated by preparative thick layer chromatography to afford triphenylbismuth (0.037 g, 30%), 2,6-diphenyl-3,5-di-t-butylphenol (**18**) (0.002 g, 2%), 3,5-di-t-butyl-2-phenylphenol (**17**) (0.452 g, 58%) and 3,5-di-t-butylphenol (0.018 g, 32%); all the compounds were identical with authentic samples.

Compound (**41**).—A mixture of 8-hydroxyquinoline (**39**) (0.285 g) and sodium hydride (80% dispersion in oil; 0.070 g) was stirred at room temperature in dry tetrahydrofuran (10 ml) under an argon atmosphere until the evolution of hydrogen gas had ceased. A solution of triphenylbismuth bistrifluoroacetate (1.34 g) in dry tetrahydrofuran (15 ml) was then added dropwise over 15 min. The solution was stirred (0.5 h) and evaporated. The residue was dissolved in dry methylene dichloride and the solution filtered and evaporated to give an orange foam (1.45 g). Addition of hexane gave compound (**41**) (1.2 g, 86%) as an orange solid, m.p. 129—130 °C (decomp.). Dissolution of this in methylene dichloride and filtration and dilution with methanol (*ca.* 5 volumes) of the solution afforded, after cooling, *compound* (**41**) as orange rods, m.p. 134—137 °C (decomp.); $\nu_{max.}$($CHCl_3$) 1 660, 1 560, 1 450, 1 310, and 980 cm^{-1}; δ($CDCl_3$) 9.00 (1 H, d, *J* 5 Hz, 2-H) and 8.14—6.80 (20 H, m); *m/z* 585 (M^+ − $OCOCF_3$) (Found: C, 50.1; H, 3.3; N, 1.7. $C_{29}H_{21}BiF_3NO_3$ requires C, 49.9; H, 3.0; N, 2.0%).

Thermal Decomposition of 8-*Quinolyloxytriphenylbismuth Chloride* (**40**).—A solution of compound (**40**) (0.3 g) in dry toluene (5 ml) was heated under reflux (14 h) under an argon atmosphere, cooled, and evaporated. The residue was heated under reflux (3 h) with a mixture of acetic anhydride (2 ml) and acetic acid (2 ml) and then cooled and evaporated. Potassium carbonate solution was added to the residue. The mixture was extracted with ether and the combined ethereal extracts were washed with aqueous potassium carbonate and water, dried (Na_2SO_4), and evaporated. The residue was fractionated by column chromatography using ether–hexane (1:1) as the eluant to give a mixture of compounds (**42**) and (**44**) (0.100 g) which had almost identical R_F values. Examination of this mixture by ^1H n.m.r. spectroscopy established the yields of compound (**42**) (51%) and (**44**) (42%). 7-*Phenyl*-8-*quinolyl acetate* (**44**) was obtained pure by fractional crystallisation from hexane as cream plates, m.p. 121—123 °C; $\nu_{max.}$($CHCl_3$) 1 730 cm^{-1}; δ($CDCl_3$) 8.80 (1 H, dd, *J* 5 and 2 Hz, 2-H), 8.06 (1 H, dd, *J* 8 and 2 Hz, ArH), 7.87—7.10 (8 H, m, ArH), and 2.37 (3 H, s, COMe); *m/z* 263 (M^+) and 220 (M^+ − COMe) (Found: C, 77.5; H, 5.2; N, 5.6. $C_{17}H_{13}NO_2$ requires C, 77.5; H, 5.0; N, 5.3%).

Preparation of 7-*Phenylquinolin*-8-*ol* (**43**).—Treatment of 7-phenyl-8-quinolyl acetate (**44**) with methanolic potassium hydroxide solution under reflux afforded 7-phenylquinolin-8-ol (**43**) (77%) as colourless plates, m.p. 146—149 °C (hexane), (lit.,[17] 142—146 °C).

Thermal Decomposition of 8-Quinolyloxytriphenylbismuth Trifluoroacetate (**41**).—A stirred solution of compound (**41**) (0.1 g) in dry toluene (5 ml) was heated (14 h) under reflux under an argon atmosphere. Work-up as above afforded a pale yellow oil (0.045 g) which was fractionated by preparative thick layer chromatography using ether–hexane (1:1) as the eluant to afford a mixture of compound (**42**) and (**44**) (0.014 g). The yields of these two compounds (37 and 11% respectively) were determined by ^{1}H n.m.r. spectroscopy as above.

Compound (**45**).—A mixture of *p*-nitrophenol (0.139 g) and sodium hydride (80% dispersion in oil; 0.30 g) was stirred at room temperature in dry tetrahydrofuran (5 ml) under a nitrogen atmosphere until the evolution of hydrogen gas had ceased. A solution of triphenylbismuth dichloride (0.51 g) in dry tetrahydrofuran (10 ml) was then added dropwise over 10 min. The solution was stirred (0.5 h) and evaporated. The residue was dissolved in methylene dichloride and the solution filtered and evaporated to give *compound* (**45**) (0.529 g, 86%) as yellow plates, m.p. 157 °C (decomp.) (methylene dichloride–hexane); $\nu_{max.}(CHCl_3)$ 1 580, 1 470, and 980 cm^{-1}; $\delta(CDCl_3)$ 8.50—7.00 (17 H, m) and 5.90 (2 H, dd, *J* 9 and 2 Hz); *m/z* 578 (M^+ − Cl) (Found: C, 46.8; H, 3.3; N, 2.4. $C_{24}H_{19}BiClNO_3$ requires C, 47.0; H, 3.1; N, 2.3%).

Compound (**46**).—By a similar method to that described for the preparation of compound (**45**), *p*-nitrophenol (0.139 g), sodium hydride (80% dispersion in oil; 0.030 g) and triphenylbismuth bistrifluoroacetate (0.666 g) afforded *compound* (**46**) (0.628 g, 91%) as pale yellow plates, m.p. 139—145 °C (decomp.) (methylene dichloride–hexane); $\nu_{max.}(CHCl_3)$ 1 670 cm^{-1}; $\delta(CDCl_3)$ 8.42—7.25 (17 H, m) and 6.12 (2 H, d, *J* 8 Hz) (Found: C, 45.7; H, 3.1; N, 2.1. $C_{26}H_{19}BiF_3NO_5$ requires C, 45.2; H, 2.8; N, 2.0%).

Compound (**47**).—From pentaphenylbismuth and *p*-nitrophenol. A solution of pentaphenylbismuth (0.594 g) in anhydrous benzene (2 ml) was added to a solution of *p*-nitrophenol (0.139 g) in anhydrous benzene (3 ml) under an atmosphere of argon. The mixture became orange instantly. Addition of ether to the cooled solution gave *compound* (**47**) (0.58 g, 88%) as an amorphous yellow solid, m.p. 118—122 °C (methylene dichloride–ether); $\nu_{max.}(CHCl_3)$ 1 580, 1 510small, and 1 330small; $\delta(CDCl_3)$ 8.12—7.12 (22 H, m, ArH) and 5.75 (2 H, d, J_{AX} 9 Hz, 2-H); *m/z* 517 (Ph_4Bi), 440 (Ph_3Bi), 418 (BiBi), 363 ($BiPh_2$), 347 ($BiO\text{-}C_6H_4\text{-}NO_2$), 286 (BiPh), 215 ($PhOC_6H_4\text{-}NO_2$), 209 (Bi), 154 (Ph-Ph), and 77 (Ph) (Found: C, 54.9; H, 3.8. $C_{30}H_{24}BiNO_3$ requires C, 55.0; H, 3.7%).

From tetraphenylbismuth toluene-p-sulphonate and sodium p-nitrophenolate. A solution of *p* nitrophenol (0.278 g) in anhydrous ether (3 ml) was added to a suspension of sodium hydride (50% suspension in oil, washed with pentane; 0.1 g), under an atmosphere of argon. The solution was evaporated under reduced pressure at 0 °C, and methanol (4 ml) was added. Tetraphenylbismuth toluene-*p*-sulphonate (1.38 g) was added to the cooled (0 °C) solution. Addition of ether gave a yellow precipitate, which was dissolved in methylene dichloride, washed with water, dried (Na_2SO_4), and evaporated to afford (**47**) (0.85 g, 65%) identical with the previous sample.

Thermal Decomposition of p-*Nitrophenoxytetraphenylbismuth* (**47**).—A solution of (**47**) (0.132 g) in anhydrous toluene (2 ml) was heated under reflux for 4 h under an atmosphere of argon. The mixture was evaporated and the residue fractionated by preparative thick layer chromatography using hexane–ethyl acetate (95:5) as the eluant to afford (**48**) (0.043 g, 98%), m.p. 55—56 °C (methanol) [lit.,[18] m.p. 56 °C (ethanol)].

Phenylation of Phloroglucinol with Triphenylbismuth Carbonate.—A mixture of phloroglucinol (**49**) (0.3 g) and triphenylbismuth carbonate (3 g) in dioxane (10 ml) was heated under reflux for 11 h under an atmosphere of argon. The mixture was filtered, the filtrate evaporated, and the residue fractionated by column chromatography using hexane–ethyl acetate (7:3) as the eluant to give 1,3,5-trihydroxy-2,4,6-triphenylbenzene (**50**) (0.195 g, 24%) and 2,2,4,5-tetraphenylcyclopent-4-ene-1,3-dione (**52**) (0.368 g, 40%). Compound (**50**) was isolated as an amorphous solid, m.p. 110—111 °C (hexane); $\nu_{max.}(CH_2Cl_2)$ 3 530, 1 700, 1 620, 1 170, and 1 050 cm^{-1}; $\lambda_{max.}(CH_2Cl_2)$ 258 nm (ε 15 500); $\delta(CDCl_3)$ 7.29 (15 H, s, 3 × Ph) and 4.89 (3 H, s, 3 × OH); *m/z* 354 (M^+). Compound (**50**) gave a *triacetate* (acetic anhydride–pyridine) (**51**), m.p. 240 °C (methanol); $\nu_{max.}(CH_2Cl_2)$ 1 770, 1 600, 1 500, 1 360, 1 200, and 1 040; $\delta(CDCl_3)$ 7.10 (15 H, s, 3 × Ph) and 1.54 (9 H, s, 3 × Me); *m/z* 480 (M^+) (Found: C, 74.9; H, 5.1. $C_{30}H_{24}O_6$ requires C, 75.0; H, 5.0%). Compound (**52**) was isolated as yellow crystals, m.p. 190—193 °C (hexane) [lit.,[19] 196.5—197.5 °C (ethanol)].

A mixture of phloroglucinol (**49**) (0.1 g) and triphenylbismuth carbonate (2 g) in dioxane (5 ml) was stirred at 80 °C for 24 h under an atmosphere of argon. Further triphenylbismuth carbonate (1 g) was added and the mixture stirred at 80 °C for a further 24 h. The mixture was filtered, the solution evaporated, and the residue fractionated by column chromatography to afford (**52**) (0.192 g, 60%) identical with the previous sample.

O-*Phenylation of 2-Naphthol with Tetraphenylbismuth Trifluoroacetate in the Presence of Pyridine.*—A solution of 2-naphthol (**1**) (0.074 g, 0.51 mmol), tetraphenylbismuth trifluoroacetate (0.470 g, 0.76 mmol) and pyridine (0.049 g, 0.62 mmol) in dry benzene (3 ml) was stirred under reflux for 48 h under an atmosphere of argon. Evaporation of the solvent and preparative t.l.c. using hexane as the eluant afforded a mixture of triphenylbismuth and 2-naphthyl phenyl ether (**3**) (0.152 g) and unchanged 2-naphthol (0.043 g, 58%) The solution of the mixture of (**3**) and triphenylbismuth in ether was stirred with concentrated aqueous HCl at room temperature for 10 min. After work-up, the ethereal phase gave 2-naphthyl phenyl ether (**3**) (0.045 g, 40%). By substraction, the yield of triphenylbismuth was 0.107 g (47%).

O-*Phenylation of* 3,5-*Di-t-butylphenol with Tetraphenylbismuth Trifluoroacetate in the Presence of Pyridine.*—A solution of 3,5-di-t-butylphenol (**15**) (0.1 g, 0.485 mmol), tetraphenylbismuth trifluoroacetate (0.4 g, 0.65 mmol) and pyridine (0.049 g, 0.62 mmol) in benzene (3 ml) was stirred under reflux for 30 h under an atmosphere of argon. The mixture was evaporated and the residue fractionated by preparative t.l.c. using hexane as the eluant to afford 3,5-di-t-butylphenyl phenyl ether (**16**) (0.058 g, 43%), triphenylbismuth (0.130 g, 61%) and unchanged (**15**) (0.055 g, 55%).

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