The Chemistry of Pentavalent Organobismuth Reagents. Part 8.* Phenylation and Oxidation of Alcohols by Tetraphenylbismuth Esters

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Tetraphenylbismuth trifluoroacetate under neutral or slightly acidic conditions *O*-phenylates primary alcohols in reasonable (65—75%) yield, but gives only moderate yields with secondary alcohols and no *O*-phenylation with tertiary alcohols. An S_N2 type mechanism is proposed with attack of oxygen on aryl carbon. In contrast, the reaction of Bi^V reagents with alcohols under basic conditions gives, exclusively, oxidation, often with benzene as a leaving group. The presence of a Bi^V intermediate with a bismuth–oxygen bond has been proved in several different ways using n.m.r. spectroscopy. Thus the reactions of alcohols with Bi^V reagents parallel the corresponding reactions with phenols.

Tetraphenylbismuth esters are regiospecific *O*- or *C*-phenylating reagents for phenolic and enolic compounds and for other anions.[1,2] Under acidic or neutral conditions, tetraphenylbismuth trifluoroacetate (**1**) gives *O*-phenylation, while tetraphenylbismuthtoluene-*p*-sulphonate (**2**) and acetate (**3**) give mixtures of *O*- and *C*-phenylated products and tetraphenylbismuth trifluoromethanesulphonate (**4**) does not react at all.

Ph_4BiX

(**1**) X = $OCOCF_3$
(**2**) X = OTos
(**3**) X = $OCOCH_3$
(**4**) X = OSO_2CF_3
(**5**) X = $2,4,6\text{-}(NO_2)_3C_6H_2O$
(**6**) X = $OCOCCl_3$
(**7**) X = $OCOCH_2Cl$
(**8**) X = $OCOCHPh_2$

$CH_3(CH_2)_{16}CH_2OR$

(**9**) R = H
(**10**) R = Ph

$PhCH_2OR$

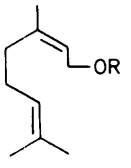
(**11**) R = H
(**12**) R = Ph

$PhCH_2CH_2OR$

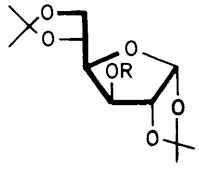
(**13**) R = H
(**14**) R = Ph

Bu^tCH_2OR

(**15**) R = H
(**16**) R = Ph
(**17**) R = $COCF_3$



(**18**) R = H
(**19**) R = Ph



(**20**) R = H
(**21**) R = Ph

Under basic conditions, *C*-phenylated products are formed exclusively and in good yields, except in the case of phenols bearing electronegative groups which give *O*-phenylation. We now report our investigations of the reactivity of tetraphenylbismuth esters towards alcohols, amides, and imides.

Reactivity of Tetraphenylbismuth Trifluoroacetate (**1**).—Under neutral conditions, (**1**) (1.2—1.5 equiv.) reacts with alcohols in benzene or toluene at 80 °C or above to give the corresponding phenyl ethers (Table 1). Reasonable yields were obtained with primary alcohols (65—75%), moderate yields with allylic alcohols and diols (45—60%), and low yields with secondary alcohols (15—30%). Tertiary alcohols gave only intractable mixtures. The proximity of a second OH group greatly accelerates the reaction. In benzene under reflux,

Table 1. Reaction of tetraphenylbismuth trifluoroacetate (**1**) with alcohols[a]

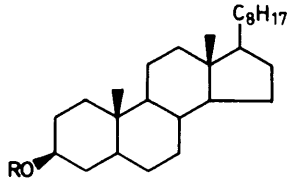
Substrate	Solvent[b]	Reaction time (h)	Yield of phenyl ether (%)
(**9**)	T	8	(**10**) 76
(**11**)	T	3	(**12**) 65
(**13**)	T	3	(**14**) 69
(**15**)	B	17	(**16**) 61
(**18**)	B	12	(**19**) 57
(**20**)	T	26	(**21**) 30
(**22**)	B	36	(**23**) 29
(**25**)	B	36	(**26**) 13
(**27**)	B	19	(**28**) 22
(**29**)	B	12	(**30**) 48[c]
(**29**)	B	19	(**30**) 52,[d] (**31**) 13
(**32**)	B	24	(**33**) 60[e]
(**34**)	B	24	(**35**) 58, (**36**) 13

[a] All reactions performed with (**1**) [1.3 equiv., except for (**29**)] in the indicated solvent under reflux. [b] B = benzene, T = toluene. [c] (**1**): 1 equiv. [d] (**1**): 1.5 equiv. [e] Phenylated on the secondary oxygen.

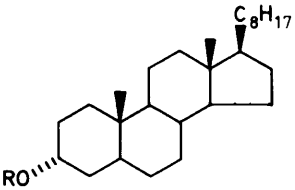
cyclohexanol gave the phenyl ether (22%) in 18 h, while *cis*-cyclohexane-1,2-diol gave the mono-phenyl ether (52%) and the diphenyl ether (13%) during the same time.

The decrease in the yields from primary to tertiary alcohols results (i) from steric hindrance in secondary or the bulkier tertiary alcohols, and (ii) from a competing trifluoroacetylation of the alcohol by phenyl trifluoroacetate produced by thermal reductive elimination from the bismuth reagent (**1**). These two reactions are simultaneous as evidenced by ^1H n.m.r. monitoring of the reaction of (**1**) with methanol, 2,2-dimethylpropan-1-ol (**15**), propan-2-ol and 3β-cholestanol (**22**). In each case, the two derivatives appeared simultaneously: methanol gave anisole (67%) and methyl trifluoroacetate (33%) after 2.25 h, propan-2-ol gave the phenyl ether (45%) and the trifluoroacetate (55%) after 4 h, and 2,2-dimethylpropan-1-ol (**15**) gave the phenyl ether (**16**) (62%) and the trifluoroacetate (**17**) (38%) after 25 h. 3β-Cholestanol (**22**) behaved similarly to give after 8 h at 80 °C, the phenyl ether (**23**) (26%) and the trifluoroacetate (**24**) (65%), with some unchanged substrate. Spectroscopic studies performed on the chromatography fraction containing 3β-phenoxycholestane (**23**) showed C=O absorption ($\nu_{max.}$ 1 785 cm^{-1}) and a peak of m/z 484 [M^+, corresponding to the trifluoroacetate (**24**)]. The close R_F values of the crude reaction mixtures components (phenyl ether, trifluoroacetate, and triphenylbismuth) made their resolution impossible. After acid treatment with Cl_3CCO_2H and basic treatment with

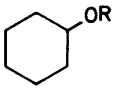
* Part 7., preceding paper.



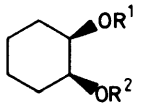
(22) R = H
(23) R = Ph
(24) R = $COCF_3$



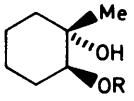
(25) R = H
(26) R = Ph



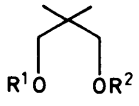
(27) R = H
(28) R = Ph



(29) $R^1 = R^2 = H$
(30) R^1 = Ph, R^2 = H
(31) $R^1 = R^2$ = Ph



(32) R = H
(33) R = Ph



(34) $R^1 = R^2 = H$
(35) R^1 = Ph, R^2 = H
(36) $R^1 = R^2$ = Ph

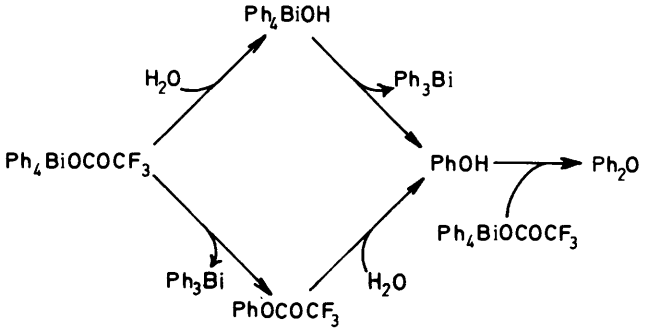
(37) Ph_2O
(38) Ph_5Bi
(39) Ph_3BiCO_3
(40) $Ph_3Bi(OTos)_2$
(41) $Ph_3Bi(OCOCF_3)_2$
(42) Ph_3BiCl_2
(43) Bu^tCHO

aqueous NaOH, the mixtures of phenyl ethers and alcohols were easily resolved.

Acid catalysis of the reaction (Cl_3CCO_2H, 0.6 equiv.) did not improve the yields of the reaction, but accelerated the rates.

In the crude reaction mixture, diphenyl ether was also present as the main by-product. A study of the pyrolysis of (1) showed the formation of diphenyl ether and phenyl trifluoroacetate. When a solution of (1) in benzene was kept under reflux for 24 h, varying amounts of diphenyl ether were produced, depending on the reaction conditions. When the reaction was performed without special care, 38% of diphenyl ether was obtained. Under an atmosphere of argon, the yield dropped to 20%. When the reagent (1) was dried azeotropically for 1 h, followed by 24 h under reflux, the yield of Ph_2O was only 6%, and if water (2%) was added, the yield increased to 34%. When the azeotropic drying of (1) was performed in toluene, only traces of Ph_2O were obtained after 24 h. Phenol reacted with (1) to give Ph_2O quantitatively.[1] Thermal decomposition of (1) in the presence of a trace of water can proceed either through hydrolysis followed by reductive elimination or through reductive elimination followed by hydrolysis (Scheme 1). When (1) was heated at 145 °C for 30 min, phenyl trifluoroacetate was detected by i.r. spectroscopy ($\nu_{max.}$ 1 790 cm^{-1}).

Trifluoroacetic acid does not react with (1) in benzene solution at room temperature. However when a solution of (1) and trifluoroacetic acid in deuteriated benzene was kept under reflux for 10 h, the OH signal (δ 15.7) disappeared and a new signal (δ 7.2) for benzene appeared with a white precipitate of triphenylbismuth bistrifluoroacetate. Trifluoroacetic acid reacts quickly with triphenylbismuth at room temperature in benzene or methylene dichloride.[3] The reaction rate is slower in the presence of pyridine, the reaction being complete only after 12 h.



Scheme 1.

Table 2. Reaction of 3β-cholestanol (22) with pentavalent bismuth derivatives

Bismuth compd.	Solvent	Temp. (°C)	Reaction time (h)	Conditions	Yields (%) (22)	(23)	(44)
(3)	Benzene	80	24	*a*	47		
(1)	Toluene	110	8	*a*	65[e]	26	
(2)	Toluene	110	72	*a*	44	10	32
(2)	Toluene	110	100	*b*	54	15	
(2)	Benzene	20	12	*c*			92
(5)	Benzene	80	100	*a*	80	14	
(6)	Benzene	80	100	*a*	41		30
(7)	Benzene	80	48	*a*	14	20	
(8)	Benzene	80	48	*a*	55	14	9
(39)	CH_2Cl_2	20	30	*d*			75
(38)	Benzene	20	48	*a*			70
(40)	THF	20	48	*c*	46		43
(41)	Benzene	20	48	*c*	20		80
(42)	Benzene	20	48	*c*	4		88

[a] Neutral conditions. [b] Addition of toluene-*p*-sulphonic acid (0.6 equiv.). [c] Addition of BTMG (1.2 equiv.). [d] Addition of 1,1,3,3-tetramethylguanidine (1.2 equiv.). [e] Yield after hydrolysis of the trifluoroacetic ester.

Reactivity of Tetraphenylbismuth Sulphonates.—Tetraphenylbismuth toluene-*p*-sulphonate (2) reacted slowly with 3β-cholestanol (22) in toluene to give the phenyl ether (23) in poor yield (15%). Acid conditions did not improve the yield. Tetraphenylbismuth trifluoromethanesulphonate (4) did not react on prolonged heating in either neutral or acid conditions.

Reactivity of various Tetraphenylbismuth Esters.—To improve the yield of the phenyl ethers, the competitive esterification reaction had to be avoided. Thus, since sulphonic acid esters were not reactive enough to afford high yields of phenyl ethers, we next investigated the reactivity of some tetraphenylbismuth esters and related derivatives.

Tetraphenylbismuth picrate (5) and esters (6)—(8) were prepared by addition of the acid (1 equiv.) to a benzene solution of pentaphenylbismuth (1 equiv.) at 5 °C.

The reactivity of the esters (3) and (5)—(8) was tested against 3β-cholestanol under neutral conditions in benzene solution under reflux for 1 to 4 days. None of these reagents proved better than (1) as a phenylating agent (Table 2). The acetate (3) and the trichloroacetate (6) failed to give any phenyl ether.

Reactivity of Pentavalent Organobismuth Derivatives under Basic Conditions.—The oxidising properties of μ-oxo-bis-(chlorotriphenylbismuth) and triphenylbismuth carbonate

towards alcohols have already been described, particularly for the selective oxidation of allylic alcohols.[5] Triphenylbismuth diesters[6] and pentaphenylbismuth are also efficient oxidants of alcohols.

We tested the reactivity of the tetraphenylbismuth esters towards alcohols under basic conditions and compared them with the previously described organobismuth reagents (Table 2). In the presence of *N*-t-butyl-*N'*,*N'*,*N''*,*N''*-tetramethylguanidine (BTMG), tetraphenylbismuth esters are efficient oxidants of alcohols. 3β-Cholestanol was oxidised in 92% yield, in 12 h at room temperature. All the other bismuth reagents gave good yields (better than 75%). Only triphenylbismuth ditoluene-*p*-sulphonate (**40**) was less efficient (only 43% oxidation after 2 days). If weaker bases were used, significant oxidation did not occur. Similarly neopentyl alcohol (**15**) was oxidised to the aldehyde (**43**) in good yields (65—78%).

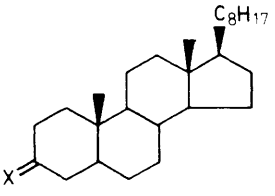
Reactivity of (**1**) *and* (**2**) *towards Nitrogen Derivatives.*—The reactivity of tetraphenylbismuth trifluoroacetate (**1**) and toluene-*p*-sulphonate (**2**) towards oximes, imides, and amides was also tested. Under neutral or acidic conditions, cholestanone oxime (**45**) gave complex mixtures and under basic conditions, only cholestanone (**44**) was obtained (39%). Imides gave the *N*-phenyl derivatives in moderate yields (35—60%) but amides gave poor yields (<21%), when the reaction was performed in benzene under neutral conditions.

Mechanism of the Reactions with Alcohols.—Tetraphenylbismuth esters react with alcohols to give phenyl ethers under neutral or acidic conditions, and oxidation products under basic conditions.

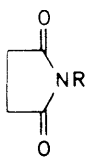
Under Basic Conditions.—Under basic conditions, the ester function behaves as a good leaving group, and a covalent intermediate is formed and decomposes in a second step to the carbonyl derivative, triphenylbismuth, and benzene.

A solution of 3β-cholestanol (**22**), tetraphenylbismuth-toluene-*p*-sulphonate (**2**), and BTMG was prepared in 1,2-dimethoxyethane. Distillation before any reaction had occurred showed no benzene in the distillate. If the reaction was performed for 2 days at room temperature followed by distillation of the solvent, benzene was detected (90%, by comparison with trichlorethylene as internal standard). Chromatography of the residue afforded cholestanone (88%) and triphenylbismuth (74%). Blank experiments indicated the stability of the reagents under these conditions (Ph_4BiX and Ph_3Bi).

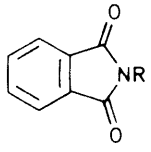
In the reactions of phenols with pentavalent organobismuth reagents under basic conditions covalently bonded Bi–O–Ar intermediates have been detected and even in some cases isolated.[1] In order to detect an intermediate by ^1H n.m.r. spectroscopy 2,2-dimethylpropan-1-ol (**15**) was chosen as substrate: δ CH_2 3.15 (s) and δ CH_3 0.90 (s). Reaction of (**15**) with (**1**) or (**2**) in the presence of TMG or BTMG was followed by ^1H n.m.r. spectrometry. Minor modifications appeared, but only one signal was noticed for CH_2 (δ 3.45) and for CH_3 (δ 1.0) after 5 min. The signals progressively disappeared and two new signals apppared: δ 9.55 or 9.25 p.p.m. for CHO and δ 0.75 for CH_3 of the aldehyde (**43**). Similar results were obtained in the reaction of the alcohol (**15**) with pentaphenylbismuth under neutral conditions. The fact that two different signals were not observed for the CH_2 can be explained, either by the absence of a covalent intermediate, or rather by its rapid decomposition as it is formed to the carbonyl derivative. Since in the phenol series,[1] the chlorotriphenylbismuth intermediate was more stable than the tetraphenylbismuth derivative, we then studied the reaction of (**15**) with Ph_3BiCl_2 and BTMG. Two singlets were noticed (δ 3.25 and 3.45) for CH_2, and two singlets (δ 1.0 and 0.9) for CH_3. After 30 min these signals began to disappear and two new singlets appeared (δ 9.45 and 0.75) for the aldehyde



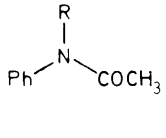
(**44**) X = O
(**45**) X = NOH



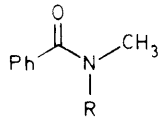
(**46**) R = H
(**47**) R = Ph



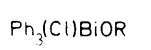
(**48**) R = H
(**49**) R = Ph



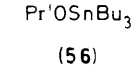
(**50**) R = H
(**51**) R = Ph



(**52**) R = H
(**53**) R = Ph

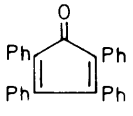


(**54**)
(**55**) R = Bu^tCH_2

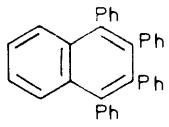


(**56**)

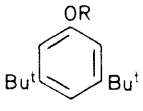
(**57**)



(**58**)



(**59**)



(**60**) R = H
(**61**) R = Ph

(**43**). In this reaction, decomposition of the intermediate (**55**) (signals at δ 3.25 and 0.9) is the slow step. After 30 h, 63% of the aldehyde was detected.

A different approach in the synthesis of intermediates of type (**54**) could be the reaction of a hypobromite with triphenylbismuth. Such hypobromites derived from primary and secondary alcohols are unstable. However, they can be prepared from the corresponding tributylstannyl ether and bromine.[8] Thus, reaction of (**56**) with bromine at room temperature gave only acetone, the oxidation product, but no hypobromite (**57**). However, when triphenylbismuth dichloride was added to a solution of (**56**), ligand exchange occurred. In the ^1H n.m.r. spectrum, two types of CH_3 were detected, as two doublets: δ 1.1 (stannyl ether) and δ 1.15 (bismuth–oxygen compound). After 90 min, two singlets at δ 2.15 and 7.27 (benzene) slowly began to appear.

Eventually, when bromine was added to a cooled (−42 °C) $CDCl_3$ solution of (**56**), quickly followed by addition of triphenylbismuth, the intermediate (**54**) was detected before any decomposition of the hypobromite (**57**) to acetone had occurred. Warming up to room temperature then allowed the decomposition to proceed.

There is, therefore, convincing evidence for the formation and subsequent decomposition of an intermediate in the oxidation process.

Under Neutral and Acidic Conditions.—The formation of a covalently bonded intermediate such as (**54**) cannot be involved in the *O*-phenylation reaction, as synthesis of such an intermediate by reaction of an alcoholate with triphenylbismuth diacylate, followed by its decomposition, always results in oxidation products.

A second mechanism could be, in principle, the reaction of the alcohol with benzyne. Razuvaev *et al.* recently studied the decomposition of pentaphenylbismuth in pyridine or carbon tetrachloride at room temperature. Addition of furan gave the

benzyne adduct, and decomposition in the presence of t-butyl alcohol afforded t-butyl phenyl ether.[9] In our hands reaction of pentaphenylbismuth with 2,3,4,5-tetraphenylcyclopentadienone (**58**)[10] in carbon tetrachloride under reflux gave the adduct 1,2,3,4-tetraphenylnaphthalene (**59**) (50%), and triphenylbismuth (76%). However reaction of tetraphenylbismuth trifluoroacetate with (**58**) in benzene under reflux for 20 h gave triphenylbismuth (41%) but no benzyne adduct (**59**). Moreover, t-butyl alcohol did not react with (**1**) under these conditions. Therefore, a benzyne mechanism can also be excluded.

In the phenylation of alcohols by triarylsulphonium salts[11] and diaryliodonium salts,[12] under basic conditions, two competing pathways are involved. Oxidation derivatives, aromatic hydrocarbons and biphenyl result from a radical pathway, while alkyl aryl ethers are formed by aromatic S_N2 displacement. However, with (**1**), no biphenyls nor oxidation products were detected under the *O*-phenylation reaction conditions. A radical pathway can therefore be excluded.

These reactions are better explained as a direct aromatic S_N2 displacement, facilitated by the partial positive charge on the aromatic carbon bonded to Bi. This mechanism closely parallels the one proposed for the *O*-phenylation of phenols and enols by (**1**).[1,2]

Thus, tetraphenylbismuth esters react with alcohols to give phenyl ethers, or their oxidation products, depending on the reaction conditions. Under neutral or acidic conditions, direct nucleophilic substitution gives the phenyl ether (Scheme 2, pathway A) while under basic conditions, a covalently bonded intermediate is formed which decomposes to the oxidation product (Scheme 2, pathway B).

When an oxidation is carried out as in (Scheme 2, pathway B) benzene becomes an obligatory leaving group. In our previous work[5] on oxidations with triphenylbismuth carbonate benzene was also seen as a leaving group in competition with the expected mechanism involving the elimination of triphenylbismuth. The formation of benzene could be a concerted four-centre process but, as several of our organometallic colleagues have pointed out, a β-hydrogen elimination to carbonyl + tetraphenylbismuth hydride would also explain the experimental facts. The latter should undergo reductive elimination to triphenylbismuth and benzene. In experiments carried out in collaboration with Dr. Charles Giannotti and Mr. Halley we have shown that the reduction of a tetraphenyl derivative of bismuth with sodium borohydride gives, quantitatively, triphenylbismuth and benzene. This reaction must surely involve the postulated tetraphenylbismuth hydride.

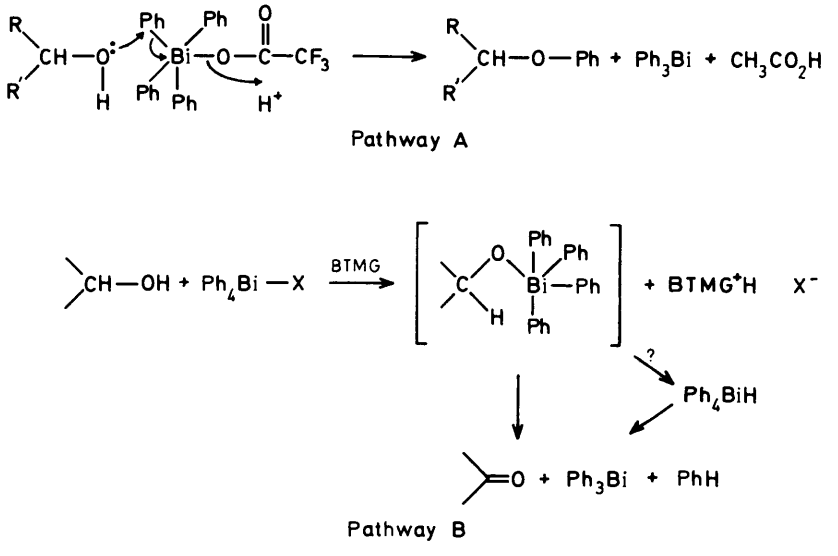
Other methods for the *O*-phenylation of alcohols using Bi^V reagents have recently been reported. Triphenylbismuth diacetate has been shown by David and Thieffry to react with diols to give good to excellent yields of monophenylated diols.[13,14] We have recently shown[15] that this reaction is not restricted to diols, and that a number of bifunctional compounds can be phenylated in this way. Dodonov *et al.*[16] made the important observation that simple aliphatic alcohols are phenylated (without solvent) by triphenylbismuth diacetate in presence of copper salts [$CuCl_2$, Cu_2Cl_2, and $Cu(OAc)_2$]. We showed[14] that copper salts had a dramatic effect in speeding up the phenylation of diols and related bifunctional molecules. S_N2 Type phenylation of a hydroxy group with diphenylbromonium[17] or diphenyliodonium[18] ions is also known, but these reactions are not now of synthetic value.

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 with $SiMe_4$ as internal standard on Varian T-60, Varian EM-360 or Bruker WP-80 instruments. I.r. spectra were recorded on a Perkin-Elmer 257 apparatus. Mass spectra were recorded with an AEI MS-9 or MS-50 instrument. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. 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 60 H (column chromatography). Ether refers to diethyl ether.

Preparation of Organobismuth Reagents.—Tetraphenylbismuth trifluoroacetate, tetraphenylbismuthtoluene-*p*-sulphonate, tetraphenylbismuth trifluoromethanesulphonate, tetraphenylbismuth acetate, pentaphenylbismuth, triphenylbismuth dichloride, triphenylbismuth carbonate, triphenylbismuth di-toluene-*p*-sulphonate, and triphenylbismuth bistrifluoroacetate were prepared by literature methods as previously reported.[1]

Tetraphenylbismuth Esters: General Method.—A solution of the acid (7 mmol) in benzene (2 ml) was added dropwise to a suspension of pentaphenylbismuth (**35**) (4.16 g, 7 mmol) in



Scheme 2.

benzene (5 ml) under argon, with cooling in an ice–water bath. At the end of the addition, the mixture became homogeneous and after addition of ether the ester precipitated and was filtered off and recrystallised.

(a) *Tetraphenylbismuth Picrate* (**5**). Picric acid (1.6 g) and (**35**) gave (**5**) as orange crystals (4.16 g, 78%), m.p. 158—165 °C (methylene dichloride–hexane); $\nu_{max.}$(Nujol) 1 620, 1 600, 1 550, 1 430, 1 330, 1 300, and 990 cm^{-1}; δ($CDCl_3$) 8.55 (2 H, s, picric acid 3-H and 5-H) and 7.9—7.2 (20 H, m, ArH); *m/z* 668 (M^+ − Ph), 517 (Ph_4Bi), 440 (Ph_3Bi), 363 (Ph_2Bi), 305 [$PhOC_6H_2(NO_2)_3$], 286 (PhBi), 229 [$HOC_6H_2(NO_2)_3$], 209 (Bi), 154 (Ph–Ph), and 77 (Ph) (Found: C, 48.2; H, 2.95. $C_{30}H_{22}BiN_3O_7$ requires C, 48.34; H, 2.95%).

(b) *Tetraphenylbismuth Trichloroacetate* (**6**). Trichloroacetic acid (1.15 g) and (**35**) gave (**6**) as white crystals (2.33 g, 50%), m.p. 87—90 °C (methylene dichloride–hexane); $\nu_{max.}$(Nujol) 1 670, 1 430, 1 300, and 990 cm^{-1}; δ($CDCl_3$) 8.1—7.8 (8 Hz, m, *o*-ArH) and 7.65—7.4 (12 H, m, *m*- and *p*-ArH); *m/z* 517 (Ph_4Bi), 440 (Ph_3Bi), 418 (BiBi), 363 (Ph_2Bi), 286 (PhBi), 209 (Bi), 154 (Ph–Ph), and 77 (Ph) (Found: C, 45.9; H, 3.1. $C_{26}H_{20}BiCl_3O_2$ requires C, 45.94; H, 2.94%).

(c) *Tetraphenylbismuth monochloroacetate* (**7**). Monochloroacetic acid (0.660 g) and (**35**) gave (**7**) as white crystals (3.06 g, 71%), m.p. 125—132 °C (methylene dichloride–hexane); $\nu_{max.}$(Nujol) 3 050, 1 640, 1 560, 1 430, 1 340, 1 230, 990, and 730 cm^{-1}; δ($CDCl_3$) 8.0—7.55 (8 H, m, *o*-ArH), 7.5—7.1 (12 H, m, *m*- and *p*-ArH), and 3.55 (2 H, s, CH_2); *m/z* 517 (Ph_4Bi), 476, 474, 472 [$PhBi(OCOCH_2Cl)_2$], 458, 456 ($Ph_2BiOCOCH_2Cl$), 440 (Ph_3Bi), 418 (Bi–Bi), 381, 379 ($PhBiOCOCH_2Cl$), 363 (Ph_2Bi), 323, 321 (PhBiCl), 304, 302 ($BiOCOCH_2Cl$), 286 (PhBi), 209 (Bi), 172, 170 ($PhOCOCH_2Cl$), 154 (Ph–Ph), 94 ($ClCH_2CO_2H$), and 77 (Ph) (Found: C, 51.0; H, 3.75. $C_{26}H_{22}BiClO_2$ requires C, 51.10; H, 3.60%).

(d) *Tetraphenylbismuth* 2,2-*diphenylacetate* (**8**). 2,2-Diphenylacetic acid (1.48 g) and (**35**) gave (**8**) as white crystals (3.45 g, 67%), m.p. 150—158 °C (benzene–ether); $\nu_{max.}$(Nujol) 3 000sh, 1 600, 1 560, 1 330, 990, and 700 cm^{-1}; δ($CDCl_3$) 7.7—7.4 (8 H, m, *o*-ArH), 7.4—7.07 (12 H, m, *m*- and *p*-ArH), 6.9 (10 H, s, ArH), and 4.6 (1 H, s, CH); *m/z* 728 (M^+), 651, (M^+ − Ph), 574 (M^+ − 2 Ph), 517 (Ph_4Bi), 497 (M^+ − 3 Ph), 440 (Ph_3Bi), 363 (Ph_2Bi), 286 (PhBi) 209 (Bi), 194 (Ph_2CCO), 167 (Ph_2CH), 154 (Ph–Ph), and 77 (Ph) (Found: C, 62.8; H, 4.45. $C_{38}H_{31}BiO_2$ requires C, 62.63; H, 4.25%).

Reaction of Tetraphenylbismuth Trifluoroacetate (**1**) *with Alcohols under Neutral Conditions: General Method.*—A solution of the substrate and tetraphenylbismuth trifluoroacetate (**1**) (1.2—1.5 equiv.) was stirred under argon under reflux for the time indicated. The reaction was monitored by t.l.c. and stopped when no evolution was noticed or when the substrate had disappeared. The mixture was filtered and the solution distilled under reduced pressure. The residue was dissolved in methylene dichloride and the solution stirred under reflux in the presence of trichloroacetic acid (2—3 equiv.) for 2 h. The cooled mixture was washed with 5% aqueous sodium hydrogen carbonate, and the solvent distilled off under reduced pressure. The residue was stirred in a mixture water–ether (1:1) containing sodium hydroxide (2 equiv.) for 4 h at 40 °C. The cooled mixture was washed with water, dried ($MgSO_4$) and the solvent distilled off under reduced pressure. The reaction products were isolated after preparative t.l.c. of the residue.

(a) 1-*Phenoxyoctadecane* (**10**). Compound (**9**) (0.135 g) and (**1**) (0.570 g) in toluene (5 ml) gave after 8 h (**10**) (0.135 g) [eluant: hexane–ether (1:1)], m.p. 46—48 °C (hexane–methanol) (lit.,[19] m.p. 53.5 °C).

(b) *Benzyl phenyl ether* (**12**). Benzyl alcohol (0.054 g) and (**1**) (0.525 g) in toluene (4 ml) gave after 3 h (**13**) (0.063 g, 69%) [eluant: hexane–ether (3:2)], as an oil, $\nu_{max.}$($CHCl_3$) 1 580 and 1 470 cm^{-1}; δ($CDCl_3$) 7.2—6.5 (10 H, m, ArH) and 4.85 (2 H, s, CH_2); *m/z* 184 (M^+), 91 (M^+ − Ph), and 77 (Ph), and (**9**) (0.004 g, 8%).

(c) 2-*Phenoxyphenylethane* (**14**). Compound (**13**) (0.061 g) and (**1**) (0.525 g) in toluene (4 ml) gave after 3 h (**14**) (0.066 g, 66%) [eluant: hexane–ether (3:2)] as an oil, $\nu_{max.}$($CHCl_3$) 2 900, 1 580, 1 470, 1 030, and 860 cm^{-1}; δ($CDCl_3$) 7.25—6.55 (10 H, m, ArH), 4.05 (2 H, t, *J* 7 Hz, CH_2), and 3.0 (2 H, t, *J* 7 Hz, CH_2); *m/z* 198 (M^+), 105 (M^+ − PhO), 91 (Ph–CH_2^+), and 77 (Ph), and (**13**) (0.014 g, 23%).

(d) 1-*Phenoxy*-2,2-*dimethylpropane* (**16**). Compound (**15**) (0.088 g) and (**1**) (0.945 g) in benzene (5 ml) gave after 17 h (**16**) (0.102 g, 61%) [eluant: hexane–ether (3:2)] as an oil, $\nu_{max.}$($CHCl_3$) 2 975, 1 580, 1 470, 1 280, 1 160, 1 010, and 860 cm^{-1}; δ($CDCl_3$) 7.7—6.9 (5 H, m, ArH), 3.6 (2 H, s, CH_2), and 1.05 (9 H, s, 3 × CH_3); *m/z* 164 (M^+), 94 (PhOH), and 77 (Ph).

(e) *Geranyl phenyl ether* (**19**). Compound (**18**) (0.077 g) and (**1**) (0.475 g) in benzene (5 ml) gave after 12 h (**19**) (0.066 g, 57%) (eluant: hexane), as an oil,[20] $\nu_{max.}$($CHCl_3$) 2 950, 2 905, 2 840, 1 600, 1 580, 1 485, 1 375, and 790 cm^{-1}; δ($CDCl_3$) 7.5—6.8 (5 H, m, ArH), 5.55 (1 H, t, *J* 6 Hz, 2-H), 5.15 (1 H, m, 6-H), 4.55 (2 H, d, *J* 6 Hz, 1-H), 2.1 (4 H, m, 4-H and 5-H), and 0.75, 0.70, and 0.65 (9 H, 3 s, 3 × CH_3); *m/z* 230 (M^+), 136 (M^+ − PhOH), and 94 (PhOH), and (**18**), (0.027 g, 20%).

(f) 1,2;5,6-*Di-isopropylidene*-D-*glucofuranose* 3-O-*phenyl ether* (**21**). Compound (**20**) (0.130 g) and (**1**) (0.475 g) in toluene (5 ml) gave after 48 h (**21**) (0.049 g, 30%) [eluant: hexane–ether (3:1)], m.p. 95—97 °C (ether–methanol); $\nu_{max.}$($CHCl_3$) 2 925, 2 875, 1 600, 1 590, 1 480, 1 370, 1 200, 1 160, 1 080, 1 020, and 840 cm^{-1}; δ($CDCl_3$) 7.5—6.8 (5 H, m, ArH), 5.95 (1 H, d, *J* 4 Hz, 1-H), 4.8—4.05 (6 H, m, 2-, 3-, 4-, 5-, and 6-H), and 1.6—1.4 (12 H, m, 4 × CH_3); $[\alpha]_D$ −45.8° (*c* 1.7, $CHCl_3$); *m/z* 336 (M^+), 321 (M^+ − CH_3), 101 ($C_5H_9O_2$), 94 (PhOH), and 77 (Ph) (Found: C, 64.4; H, 7.2; O, 28.35. $C_{22}H_{24}O_6$ requires C, 64.28; H, 7.14; O, 28.57%).

(g) 3β-*Phenoxycholestane* (**23**). Compound (**22**) (0.194 g) and (**1**) (0.475 g) in benzene (5 ml) gave after 36 h (**23**) (0.067 g, 29%) [eluant: hexane–ether (7:3)], m.p. 112—115 °C (ether–methanol); $\nu_{max.}$($CHCl_3$) 2 800, 1 600, and 1 450 cm^{-1}; δ($CDCl_3$) 7.15—6.6 (5 H, m, ArH) and 4.1 (1 H, m, $W_{\frac{1}{2}}$ 16 Hz, 3α-H); $[\alpha]_D$ +13.5° (*c* 2.32, $CHCl_3$); *m/z* 464 (M^+), 370 (M^+ − OPh), and 355 [M^+ − (OPh + CH_3)] (Found: C, 85.3; H, 11.45; O, 3.22. $C_{33}H_{52}O$ requires C, 85.34; H, 11.21; O, 3.45%), and (**34**) (0.031 g, 25%) followed by (**22**) (0.113 g, 58%).

(h) 3α-*Phenoxycholestane* (**26**). Compound (**25**) (0.194 g) and (**1**) (0.475 g) in benzene (5 ml) gave after 36 h (**26**) (0.027 g, 12%) [eluant: hexane–ether (7:3)], m.p. 79—81 °C (methanol–ether) (lit.,[21] m.p. 76—78 °C; $[\alpha]_D$ +19.5° (*c* 1.18, $CHCl_3$); *m/z* 464 (M^+).

(i) *Phenoxycyclohexane* (**28**). Compound (**27**) (0.050 g) and (**1**) (0.475 g) in benzene (5 ml) gave after 19 h (**28**) (0.019 g, 22%) as an oil, [22] *m/z* 176 (M^+) and 94 (PhOH).

(j) cis-2-*Phenoxycyclohexanol* (**30**). Compound (**29**) (0.058 g) and (**1**) (0.309 g, 1 equiv.) in benzene (3 ml) gave after 12 h (**30**) (0.046 g, 48%) as an oil [eluant: hexane–ethyl acetate (7:3)]; *m/z* 192 (M^+), identical with an authentic sample.[13]

(k) cis-1,2-*Diphenoxycyclohexane* (**31**). Compound (**29**) (0.058 g) and (**1**) (0.475 g, 1.5 equiv.) in benzene (5 ml) gave after 19 h (**31**) (0.018 g, 13%) as an oil, $\nu^{max.}$($CHCl_3$) 2 925, 2 850, 1 600, 1 400, 1 040, and 980 cm^{-1}; δ($CDCl_3$) 7.5—6.4 (10 H, m, ArH), 4.45 (2 H, m, C*H*–OPh), and 2.3—0.8 (10 H, m, cyclic CH_2); *m/z* 268 (M^+), 94 (PhOH), and 77 (Ph), and (**30**) (0.050 g, 52%).

(l) 1-*Methyl*-2-*phenoxy*-trans-*cyclohexanol* (**33**). Compound (**32**) (0.065 g) and (**1**) (0.370 g) in benzene (5 ml) gave after 24 h (**33**) (0.059 g, 60%) as an oil [eluant: hexane–ethyl acetate (7:3)]; *m/z* 206 (M^+), identical with an authentic sample.[13]

(m) 2,2-*Dimethyl*-3-*phenoxypropanol* (**35**) *and* 2,2-*dimethyl*-

1,3-*diphenoxypropane* (**36**). Compound (**34**) (0.104 g) and (**1**) (0.820 g, 1.3 equiv.) in benzene (5 ml) gave after 2 days [eluant: hexane–ether (1:1)], (**36**) (0.032 g, 13%), as an oil $\nu_{max.}$(CHCl$_3$) 2 900, 2 850, 1 590, 1 580, 1 460, 1 280, 1 200, and 1 020 cm^{-1}; δ(CDCl$_3$) 7.7—7.0 (10 H, m, ArH), 3.95 (4 H, s, 2 × CH$_2$), and 1.2 (6 H, s, 2 × CH$_3$); *m/z* 256 (M^+), 163 (M^+ − OPh), 148 [PhOCH$_2$C(CH$_3$)CH$_2$], 133 (PhOCH$_2$CCH$_2$), 107 (PhOCH$_2$), 94 (PhOH), and 77 (Ph) (Found: C, 79.55; H, 7.75; O, 12.1. $C_{17}H_{20}O_2$ requires C, 79.69; H, 7.81; O, 12.50%), and (**35**) (0.104 g, 58%) as an oil, $\nu_{max.}$(CHCl$_3$) 3 550, 2 900, 2 860, 1 600, 1 590, 1 470, 1 290, 1 170, and 1 120 cm^{-1}; δ(CDCl$_3$) 8.6—6.73 (5 H, m, Ph), 3.83 (2 H, s, C*H*$_2$OPh), 3.60 (2 H, d, *J* 4 Hz, C*H*$_2$OH), 2.40 (1 H, m, OH), and 1.03 (6 H, s, 2 × CH$_3$); *m/z* 180 (M^+), 149 (M^+ − CH$_2$OH), 107 (PhOCH$_2$), 94 (PhOH), 86 (M^+ − PhO), and 77 (Ph) (Found: C, 73.2; H, 8.7; O, 17.9. $C_{11}H_{16}O_2$ requires C, 73.33; H, 8.89; O, 17.78%); compound (**35**) gave, after treatment with *p*-nitrobenzoyl chloride and pyridine, a crystalline *derivative*, m.p. 60—62 °C (ether–hexane); $\nu_{max.}$(CHCl$_3$) 3 050, 2 900, 1 700, 1 600, 1 590, 1 520, 1 490, 1 460, 1 350, 1 200, 1 110, and 1 100 cm^{-1}; δ(CDCl$_3$) 8.27 (4 H, s, NO$_2$C$_6$*H*$_4$), 7.5—6.8 (5 H, m, Ph), 4.35 (2 H, s, PNB-OC*H*$_2$), 3.83 (2 H, s, Ph-OC*H*$_2$), and 1.2 (6 H, s, 2 × CH$_3$); *m/z* 329 (M^+), 236 (M^+ − OPh), 150 (NO$_2$C$_6$H$_4$CO), 94 (PhOH), and 77 (Ph) (Found: C, 65.4; H, 5.9; N, 4.35; O, 24.6. $C_{18}H_{19}NO_5$ requires C, 65.65; H, 5.78; N, 4.26; O, 24.32%). When the reaction was performed with (**34**) (0.043 g) and (**1**) (0.650 g, 2.5 equiv.) in benzene (3 ml), (**35**) (0.018 g, 24%) and (**36**) (0.070 g, 66%) were recovered after 36 h.

Reaction of Tetraphenylbismuth Trifluoroacetate (**1**) *with Alcohols under Acid Catalysis: General Method.*—A solution of the alcohol, compound (**1**) (1.5—2 equiv.), and trichloroacetic acid (0.6 equiv.) in benzene or toluene was stirred under argon under reflux for the time indicated. Work-up as in the neutral conditions afforded the products.

(a) *Compound* (**10**). Compound (**9**) (0.135 g), (**1**) (0.570 g), and trichloroacetic acid (0.049 g) in toluene (5 ml) gave after 2 h (**10**) (0.133 g, 76%).

(b) *Compound* (**21**). Compound (**20**) (0.130 g), (**1**) (0.470 g), and trichloroacetic acid (0.049 g) in toluene (4 ml) gave after 12 h (**21**) (0.031 g, 18%).

(c) *Compound* (**23**). Compound (**22**) (0.194 g), (**1**) (0.475 g), and trichloroacetic acid (0.049 g) in toluene (5 ml) gave after 7 h (**23**) (0.046 g, 20%) and (**22**) (0.139 g, 71%).

(d) *Compound* (**26**). Compound (**25**) (0.194 g), (**1**) (0.475 g), and trichloroacetic acid (0.049 g) in benzene (5 ml) gave after 12 h (**26**) (0.037 g, 16%), (**37**) (0.016 g, 12%), and (**25**) (0.070 g, 36%).

Thermal Stability of (**1**) *in Solution General Method.*—A solution of (**1**) (0.315 g) in benzene or toluene (3 ml) was stirred at 80 °C for 24 h. The mixture was filtered, the filtrate evaporated under reduced pressure and trichloroacetic acid in methylene dichloride (0.245 g in 3 ml) was added to the residue. The mixture was stirred under reflux for 2 h, cooled, washed with 5% aqueous sodium carbonate, dried (Na$_2$SO$_4$), and the residue purified by preparative t.l.c. [eluant: hexane–ether (7:3)].

(a) *In benzene.* Diphenyl ether (**37**) was isolated as an oil (0.032 g, 38%), identical with an authentic sample.

(b) *In benzene under argon.* Compound (**37**) (0.017 g, 20%) was isolated.

(c) *After azeotropic distillation, under argon.* Compound (**1**) was dried by azeotropic distillation for 1 h, and (**37**) (0.005 g, 6%) was isolated.

(d) *Addition of water.* Water (0.1 ml) was added to the anhydrous solution of (**1**) in benzene, and (**37**) was isolated (0.029 g, 34%).

(e) *After azeotropic distillation in toluene.* A solution of (**1**) in toluene was dried by azeotropic distillation for 1 h, and (**37**) was detected only as traces (0.001 g).

Reaction of (**1**) *with phenol.* A solution of phenol (0.047 g) and (**1**) (0.475 g) in benzene (3 ml) was stirred under argon overnight under reflux. Preparative t.l.c. [eluant: hexane–ether (1:1)] of the residue afforded (**37**) (0.086 g, 100%).

Thermal decomposition of (**1**). Compound (**1**) (0.315 g) was heated up to its melting point (145 °C) and the decomposition was monitored by i.r. spectroscopy of a Nujol mull. After 30 min, an absoption at $\nu_{max.}$ 1 790 cm^{-1} appeared. Then the melt turned to a tar.

Reaction of (**1**) *with trifluoroacetic acid.* A solution of (**1**) (0.063 g) and trifluoroacetic acid (8 μl) in [$^2H_6$]benzene (1 ml) [δ 15.7 (1 H, s, OH), 7.85—7.6 (6 H, m, *o*-ArH), and 7.1—6.8 (9 H, m, *m*- and *p*-ArH)] was stirred overnight at room temperature. No evolution was noticed in the ^{1}H n.m.r. spectrum. However, if the reaction was stirred under reflux for 10 h, the signal at δ 15.7 disappeared, while a signal at δ 7.2 (Ph*H*) appeared.

Reaction of Tetraphenylbismuth Toluene-p-*sulphonate* (**2**) *with Alcohols under Neutral and Acidic Conditions: General Method.*—A solution of the alcohol (0.5 mmol) and (**2**) (1.5—2 equiv.) in the indicated solvent, was stirred under argon under reflux. When the substrate had disappeared, or when no evolution was noticed, the mixture was filtered, the solvent distilled off under reduced pressure and the residue purified by preparative t.l.c.

(a) Compound (**20**) (0.130 g) and (**2**) (0.690 g) in toluene (5 ml) gave after 4 days (**21**) (0.021 g, 12%).

(b) Compound (**22**) (0.194 g) and (**2**) (0.690 g) in toluene (5 ml) gave after 3 days (**23**) (0.023 g, 10%), (**44**) (0.062 g, 32%), and (**22**) (0.086 g, 44%).

(c) Compound (**22**) (0.194 g), (**2**) (0.520 g), and trichloroacetic acid (0.049 g) in toluene (5 ml) gave after 14 h 3β-cholestanyl trichloroacetate (0.166 g, 60%), m.p. 142—144 °C (acetone) (lit.,[23] m.p. 145—146 °C, $\nu_{max.}$(CHCl$_3$) 2 925, 2 875, 1 750, 1 400, 1 280, 1 200, 990, 970, 910, 890, 860, and 660 cm^{-1}; δ(CDCl$_3$) 4.75 (1 H, m, 3α-H); *m/z* 534, 532 (M^+) 529, 527 (M^+ − CH$_3$), 500, 498 (M^+ − Cl), 370 (M^+ − Cl$_3$CCO$_2$), and 355 (M^+ − Me and CCl$_3$CO$_2$).

(d) Compound (**22**) (0.194 g), (**2**) (0.520 g), and toluene-*p*-sulphonic acid (0.052 g) in toluene (5 ml) gave after 4 days (**23**) (0.035 g, 15%) and (**22**) (0.108 g, 54%).

Reaction of 3β-*Cholestanol* (**22**) *with Pentavalent Organobismuth Derivatives:* (A) *Under Neutral Conditions: General Method.*—A solution of (**22**) (0.194 g, 0.5 mmol) and the bismuth derivative (1.5—2 equiv.) in benzene (5 ml) was stirred under argon under reflux for the time indicated. Filtration, distillation under reduced pressure and preparative t.l.c. of the residue afforded the products.

(*a*) Compounds (**22**) and (**3**) [from (**38**) (0.549 g) and acetic acid (0.06 ml)] gave after 24 h (**22**) (0.092 g, 47%).

(*b*) Compounds (**22**) and (**4**) (0.500 g) gave after 24 h (**22**) as the sole product.

(*c*) Compounds (**22**) and (**5**) (0.745 g) gave after 4 days (**23**) (0.031 g, 14%) and (**22**) (0.157 g, 80%).

(*d*) Compounds (**22**) and (**6**) (0.680 g) gave after 4 days 3β-cholestanyl trichloroacetate[23] (0.008 g, 4%), (**37**) (0.034 g, 20%), triphenylbismuth (0.267 g, 60%), (**44**) (0.070 g, 30%), and (**22**) (0.081 g, 41%).

(*e*) Compounds (**22**) and (**7**) (0.610 g) gave after 2 days (**23**) (0.046 g, 20%), triphenylbismuth (0.216 g, 49%), (**37**) (0.021 g, 12%), and (**22**) (0.026 g, 14%).

(*f*) Compounds (**22**) and (**8**) (0.728 g) gave after 2 days (**23**) (0.032 g, 14%), triphenylbismuth (0.180 g, 41%), (**37**) (0.038 g, 22%), and 3β-*cholestanyl diphenylacetate* (0.032 g, 11%), m.p.

148—151 °C (methanol–ether); $\nu_{max.}$($CHCl_3$) 2 925, 2 850, 1 730, 1 140, and 850 cm^{-1}; δ($CDCl_3$) 7.35 (10 H, s, ArH), 5.0 (1 H, s, Ph_2CHCO), and 4.75 (1 H, m, 3α-H); *m/z* 582 (M^+), 538 ($M^+ - CO_2$), 370 ($M^+ - Ph_2CHCO_2$), and 167 (Ph_2CH) (Found: C, 84.5; H, 9.9; O, 5.5. $C_{41}H_{58}O_2$ requires C, 84.54; H, 9.97; O, 5.50%), phenyl diphenylacetate (0.089 g, 31%), $\nu_{max.}$($CHCl_3$) 1 710 and 1 590 cm^{-1}; δ($CDCl_3$) 8.1—7.0 (15 H, m, ArH) and 5.35 (1 H, s, Ph_2CH–CO), (**44**) (0.018 g, 9%) and (**22**) (0.107 g, 55%).

(*g*) Compounds (**22**) and (**38**) (0.594 g) gave after 2 days at room temperature (**44**) (0.135 g, 70%).

(B) *Under Basic Conditions.* (*a*) Compound (**22**) (0.116 g), (**1**) (0.285 g), and pyridine (37 μl) in benzene (3 ml) gave after 2 days under reflux under argon, (**23**) (0.018 g, 13%), (**37**) (0.011 g, 14%), triphenylbismuth (0.128 g, 64%), and (**22**) (0.091 g, 78%).

(*b*) Compounds (**22**) (0.116 g), (**1**) (0.285 g), and triethylamine (65 μl) in benzene (3 ml) gave after 2 days under reflux under argon, triphenylbismuth (0.198 g, 100%), (**44**) (0.004 g, 3%) and (**22**) (0.096 g, 86%).

(*c*) Compounds (**22**) (0.194 g), (**2**) (0.520 g), and BTMG (0.090 g) in benzene (7 ml) gave after 12 h at room temperature (**44**) (0.177 g, 92%).

(*d*) Compounds (**22**) (0.116 g), (**39**) (0.3 g), and TMG (0.115 g) in methylene dichloride (5 ml) gave after 30 h at room temperature (**44**) (0.087 g, 75%).

(*e*) Compounds (**22**) (0.194 g), (**40**), (0.590 g), and BTMG (0.086 g) in THF (7 ml) gave after 2 days at room temperature under argon (**44**) (0.083 g 43%) and (**22**) (0.090 g, 46%).

(*f*) Compounds (**22**) (0.194 g), (**41**) (0.5 g), and BTMG (0.086 g) in benzene (7 ml) gave after 2 days at room temperature under argon (**44**) (0.153 g, 80%) and (**22**) (0.039 g, 20%).

(*g*) Compounds (**22**) (0.194 g), (**42**) (0.390 g), and BTMG (0.130 g) in benzene (5 ml) gave after 2 days at room temperature under argon (**44**) (0.170 g, 88%) and (**22**) (0.008 g, 4%).

Oxidation of 2,2-*Dimethylpropanol* (**15**).—(a) A solution of (**15**) (0.088 g), (**1**) (0.820 g) and BTMG (0.122 g) in benzene (5 ml) was stirred under argon at room temperature for 7.5 h. A solution of 2,4-dinitrophenylhydrazine in methanol was added to the reaction mixture, and the solvents then distilled off under reduced pressure. Column chromatography of the residue [eluant: hexane–methylene dichloride (1:1)] afforded the 2,4-DNP derivative of (**43**) as orange crystals (0.207 g, 78%), m.p. 209—210 °C (ethanol) (lit.,[24] m.p. 210 °C), $\nu_{max.}$($CHCl_3$) 3 300, 2 950, 1 620, 1 590, and 1 330 cm^{-1}; δ($CDCl_3$) 9.43—9.40 (1 H, 2 s, CH), 8.8—8.2 (2 H, m, 3- and 5-ArH), 7.65 (1 H, s, 6-ArH), 1.55 (1 H, s, NH), and 1.25 (9 H, s, 3 × CH_3); *m/z* 266 (M^+) and 251 ($M^+ - CH_3$).

(b) A mixture of (**15**) (0.088 g) and (**38**) (0.890 g) in benzene (5 ml) was stirred for 24 h at room temperature. Treatment as in (a) gave the 2,4-DNP derivatives of (**43**) (0.174 g, 65%).

(c) A solution of (**15**) (0.088 g), (**42**) (0.770 g), and BTMG (0.260 g) in benzene (7 ml) was stirred under argon for 24 h at room temperature. Treatment as in (a) afforded the 2,4-DNP of (**43**) (0.182 g, 69%).

Reactivity of Tetraphenylbismuth Trifluoroacetate (**1**) *and Toluene*-p-*sulphonate* (**2**) *towards Nitrogen Derivatives.*—(A) *Oximes.* A solution of (**45**) (0.200 g), sodium hydride (50% suspension in oil; 0.050 g) and (**1**) (0.600 g) was stirred under argon at room temperature for 4 days. After filtration, the solvent was distilled off under reduced pressure, and the residue dissolved in a solution of trichloroacetic acid (0.325 g) in methylene dichloride (5 ml). The solution was stirred under reflux for 2 h after which the organic phase was washed with 5% aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and distilled under reduced pressure. Preparative t.l.c. of the residue [eluant: hexane–ether (4:1)] afforded (**44**) (0.075 g, 39%).

(B) *Imides.* (*a*) *N*-Phenylsuccinimide (**47**). Compound (**46**) (0.050 g) and (**1**) (0.480 g) in benzene (5 ml) gave after 2 days under reflux, followed by the work-up and preparative t.l.c. [eluant: hexane–ethyl acetate (1:1)] (**47**) (0.031 g, 34%), m.p. 153—154 °C (ether–methanol) [lit.,[25] m.p. 156 °C; *m/z* 175 (M^+)].

(*b*) *N*-Phenylphthalimide (**49**). A solution of (**48**) (0.074 g) and (**1**) (6 × 0.080 g, added every hour) in benzene (5 ml) was stirred under reflux for 3 days. Work-up and preparative t.l.c. [eluant: hexane–ethyl acetate (1:1)] afforded (**49**) (0.063 g, 57%), m.p. 203—207 °C (ether–methanol) [lit.,[25] m.p. 210 °C; *m/z* 233 (M^+)].

(C) *Amides.* (*a*) *N*,*N*-Diphenylacetamide (**51**). A solution of (**50**) (0.063 g) and (**1**) (0.750 g) in benzene (3 ml) was stirred under reflux for 3 days. Preparative t.l.c. [eluant: hexane–ethyl acetate (1:1)] gave (**51**) (0.021 g, 21%), m.p. 99—100 °C (hexane–ether) (lit.,[26] m.p. 99.5 °C); *m/z* 211 (M^+), and (**50**) (0.037 g, 59%).

(*b*) Reaction with (**52**). Compound (**52**) (0.068 g), lithium hydride (0.016 g), and (**2**) (0.516 g) in benzene (7 ml) gave after 4 days under reflux (**52**) (0.066 g, 96%) and only traces of (**53**) (0.003 g, 2%).

Formation of Benzene and Triphenylbismuth in the Oxidation of (**22**) *with* (**2**) *and BTMG.*—Compound (**2**) (0.520 g) was added to a solution of (**22**) (0.194 g) and BTMG (0.094 g) in anhydrous 1,2-dimethoxyethane (2 ml). The solvent was distilled off and recovered in a cooled (−75 °C) flask. Cyclohexane (0.046 g) was added to the distillate, and an ^1H n.m.r. spectrum of this solution showed the absence of benzene. 1,2-Dimethoxyethane (2 ml) was added to the distillation residue and the mixture stirred at 60 °C for 24 h. The solvent was distilled, and an ^1H n.m.r. study of the distillate indicated the presence of benzene (90%). The residue was extracted with ether. Preparative t.l.c. [eluant: hexane–ether (7:3)] afforded triphenylbismuth (0.163 g, 74%) and (**44**) (0.170 g, 88%).

^1H *N.m.r. Studies of the Phenylation Reaction.*—(A) *With* (**1**) *under neutral conditions.* (*a*) 3β-Cholestanol (**22**). A solution of (**22**) (0.097 g) and (**1**) (0.190 g) in deuteriobenzene (2 ml) was stirred under argon at room temperature. The evolution was monitored by ^1H n.m.r. spectrometry. Nothing was noticeable after 20 h. The solution was then stirred under reflux for 8 h. A signal (δ 7.15) slowly appeared (C_6H_6), and 3-H signal, δ 3.6 slowly disappeared, and was replaced by two other signals: δ 4.1 [for (**23**)] and 4.8 [for (**24**)].

(*b*) Methanol. A solution of methanol (0.008 g) and (1) in deuteriobenzene (0.5 ml) in a sealed n.m.r. tube was heated at 80 °C, and the reaction followed by ^1H n.m.r. spectrometry: (i) *t* = 0, δ 7.95—7.6 (8 H, m, *o*-ArH), 7.3—7.0 (12 H, m, *m*- and *p*-ArH), 3.75 (1 H, s, OH), and 3.3 (3 H, s, CH_3); (ii) *t* = 1 h, δ 8.5—6.75 (m, ArH), 7.25 (s, C_6H_6), 3.3 (1.8 H, s, 0.6 × CH_3), and 2.95 (1.2 H, s, 0.4 × CH_3); (iii) *t* = 2.25 h, δ 8.0—6.65 (m, ArH), 7.25 (s, C_6H_6), 3.3 (2 H, s, 0.67 × CH_3, $PhOCH_3$), and 2.95 (1 H, s, 0.33 × CH_3, CF_3COOCH_3).

(*c*) Isopropyl alcohol. A solution of isopropyl alcohol (0.015 g) and (**1**) (0.170 g) in deuteriobenzene (0.5 ml) in a sealed n.m.r. tube was heated at 80 °C, and the reaction followed by ^1H n.m.r. spectrometry: (i) *t* = 0, δ 7.85—7.5 (8 H, m, *o*-ArH), 7.2—6.85 (12 H, m, *m*- and *p*-ArH), 3.85 (1 H, sept., *J* 6 Hz, 2-H), 2.95 (1 H, s, OH), and 1.1 (6 H, d, *J* 6 Hz, 2 × CH_3); (ii) *t* = 1 h, δ 7.85—6.85 (m, ArH), 7.25 (s, C_6H_6), 4.75 (sept., $Me_2CHOCOCF_3$), 4.25 (sept., Me_2CHOPh), 3.85 (sept., Me_2CHOH), and 1.15—0.75 (Me); (iii) *t* = 4 h, δ 7.9—7.7 (m, ArH), 7.30 (s, C_6H_6), 7.35—6.95 (m, ArH), 4.75 (sept., $Me_2CHOCOCF_3$), 4.25 (sept., Me_2CHOPh), 1.15 (d, Me_2CHOPh, 45%), and 0.8 (d, $Me_2CHOCOCF_3$, 55%).

(*d*) 2,2-Dimethylpropan-1-ol (**15**). A solution of (**15**) (0.026 g)

and (1) (0.283 g) in deuteriobenzene (1 ml) was heated at 80 °C, and the reaction followed by ^{1}H n.m.r. spectrometry. Three products were detected: (**15**), δ 3.15 (s, CH_2) and 0.9 (s, CH_3); (**16**), δ 3.43 (s, CH_2) and 0.97 (s, CH_3); and (**17**), δ 3.65 (s, CH_2) and 0.65 (s, CH_3). The evolution of the reaction was monitored by integration of the CH_2 peaks.

t (h)	(**15**) (%)	(**16**) (%)	(**17**) (%)
0.5	86	11	3
1	73	22	5
2	64	29	7
3	58	34	8
6	48	43	9
8	42	48	10
12	31	53	16
16	23	58	19
25	0	62	38

(B) 2,2-*Dimethylpropan*-1-*ol* (**15**) *with* (**1**) *and* (**42**) *under basic conditions, and* (**38**) *under neutral conditions.* (*a*) With (**1**) and BTMG. A solution of (**15**) (0.018 g), (**1**) (0.160 g), and BTMG (0.043 g) in deuteriobenzene (1 ml) was maintained at room temperature under argon and the evolution monitored by ^{1}H n.m.r. spectrometry. The signals of two products were detected: (**15**), δ 3.45 (CH_2) and 1.0 (CH_3) and (**43**), δ 9.55 (CHO) and 0.75 (CH_2). Relative percentage were given by CH_2 integration. At *t* = 10 min, (**15**) 89%, (**43**) 11%. At *t* = 30 min, (**15**) 24%, (**43**) 76%. At *t* = 100 min, (**15**) 17%, (**43**) 83%. In blank experiments, addition of BTMG to a solution of (**15**) in deuteriobenzene did not change the signals of (**15**). But upon addition of trichloroacetic acid to the solution of (**15**) and BTMG, a downfield shift was observed, δ 3.45 instead of 3.15 for CH_2.

(*b*) With (**42**) and BTMG. A solution of (**15**) (0.009 g), (**42**) (0.051 g), and BTMG (0.035 g) in deuteriobenzene (1 ml) was stirred under argon at room temperature. The evolution of the reaction was followed by ^{1}H n.m.r. spectrometry. At *t* = 0, (**15**): δ 3.15 (2 H, s, CH_2), 1.9 (1 H, m, OH), and 0.9 (9 H, s, 3 × CH_3). At *t* = 0.5 h, two singlets for CH_2: δ 3.45 and 3.25 and 3 singlets for CH_3 δ 1.0, 0.95, and 0.75 appeared. At *t* = 30 h, three products were detected: (**15**), δ 3.15 and 0.85; (**43**), δ 9.45 (CHO) and 0.75 (CH_3), and (**55**), δ 3.25 (s, CH_2) and 1.0 (s, CH_3). The ratio (**43**):(**15**) was 63:37.

(*c*) With (**38**) under neutral condition. A solution of (**15**) (0.009 g) and (**38**) (0.060 g) in deuteriobenzene (1 ml) was maintained at room temperature under argon and the evolution of the reaction monitored by ^{1}H n.m.r. spectrometry. The signals at δ 3.05 (CH_2) and 0.8 (CH_3) progressively disappeared, and three new signals appeared: δ 9.35 (CHO), 0.75 (CH_3), and 7.25 (benzene). After 2.5 h, no further change was noticed. The ratio (**43**):(**15**) was 63:37.

Reaction of (**56**) *with* Br_2 *and* Bi *Derivatives.*—(a) *With bromine.* Bromine (2.6 μl) was added to a solution of (**56**)[27] in $CDCl_3$ [δ: 3.87 (1 H, sept., CH), 2.2—0.7 (33 H, m, CH_2 and CH_3), and 1.1 (6 H, d, $Me_2CHOSnBu_3$)]. Instantly, the signal δ 1.1 disappeared while a new singlet appeared, δ 2.17 (CH_3COCH_3).

(b) *With* (**42**). A solution of (**56**) (0.035 g) and (**42**) (0.051 g) in $CDCl_3$ was kept at room temperature and the evolution of the reaction followed by ^{1}H n.m.r. spectrometry. At *t* = 5 min, δ 9.0—6.9 (15 H, m, ArH), 3.87 (1 H, sept., C*H*), 2.1—0.3 (33 H, m, CH_2 and CH_3), 1.15 (d, Me_2CH–$OBiPh_3Cl$), and 1.1 (d, $Me_2CHOSnBu_3$). At *t* = 90 min, two signals appeared: δ 2.15 (acetone) and 7.27 (benzene). During the reaction, the signal at δ 1.1 p.p.m. slowly disappeared, the signal at δ 1.15 first grew, and then began to disappear, while the two signals δ 7.27 and 2.15 slowly appeared. After 24 h, the yield of acetone was 44%, and 64% after 48 h.

(c) *With bromine and triphenylbismuth.* Bromine (5.2 μl) was added to a cooled (−42 °C) solution of (**56**) (0.035 g) in $CDCl_3$ (0.3 ml), followed by triphenylbismuth (0.044 g). The reaction was followed by ^{1}H n.m.r. spectrometry. At *t* = 1 min, δ 9.0—6.9 (15 H, m, ArH), 3.83 (1 H, m, CH), 2.0—0.3 (33 H, m, CH_2 and CH_3), and 1.15 (d, $Me_2CHOBiPh_3Cl$). At room temperature, the signals δ 3.83 and 1.15 disappeared, while two signals appeared δ 7.27 and 2.15 and the reaction was complete in 24 h.

Reaction of (**58**) *with Bismuth Derivatives.* (a) *With* (**38**). A solution of (**38**) (0.297 g) and (**58**) (0.192 g) in carbon tetrachloride (10 ml) was stirred under argon under reflux for 20 h. The solvent was distilled off under reduced pressure. Column chromatography of the residue (eluant: hexane) afforded triphenylbismuth (0.166 g, 76%), (**59**) (0.108 g, 50%), m.p. 198—203 °C (hexane–ether) (lit.,[28] m.p 204—205 °C) *m*/*z* 432 (M^+), and (**58**) (0.096 g, 50%).

(b) *With* (**1**). A solution of (**1**) (0.480 g) and (**58**) (0.290 g) in benzene (7 ml) was stirred under argon under reflux for 20 h. Column chromatography afforded triphenylbismuth (0.135 g, 41%) and (**58**) (0.285 g, 99%).

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