Unexpected Formation of Triarylbismuth Diformates in the Oxidation of Triarylbismuthines with Ozone at Low Temperatures

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Oxidation of triphenylbismuthine 1 with ozone in toluene at −78 °C gave, unexpectedly, a high yield of triphenylbismuth diformate 3, which was also obtainable as a minor product by a similar oxidation in ethyl acetate and acetone. An X-ray crystallographic study revealed that compound 3 has C_2 symmetry, the geometry around the bismuth atom being best described as a distorted trigonal bipyramid as a result of strong intramolecular interaction between the bismuth and carbonyl oxygen atoms. Treatment of compound 3 with aqueous sodium acetate or halides readily converted it into the corresponding triphenylbismuth diacetate 5 or dihalides 7–9.

Oxides of organic bismuthines are a class of compounds which have potential as a versatile precursor for a variety of organobismuth(v) compounds.[1] To date, however, their chemistry has been little studied. The first synthesis of this class of compounds was reported by Goel and Prasad in 1972,[2] who carried out the metathetical reaction of triphenylbismuth dichloride and silver(I) oxide in a benzene–water system to obtain triphenylbismuth oxide as a white powder in 10–40% isolated yields. The same oxide was also obtained by a similar type of reaction between triphenylbismuth dicyanide and mercuric oxide.[3] Rather surprisingly, very few attempts appear to have hitherto been made to oxidize triarylbismuthines directly with oxygen-transfer reagents.[4] Herein we report our unexpected results for the oxidation of triarylbismuthines 1 and 2 with ozone at low temperatures, which we obtained during our systematic study to oxidize compounds 1 and 2 with several oxygen-transfer reagents.

Results and Discussion

Direct oxidation of triphenylbismuthine 1 was first examined using hydrogen peroxide or *tert*-butyl hydroperoxide as an oxygen-transfer reagent. In every case, however, a complex mixture of decomposition products resulted. We then tried the oxidation of compound 1 with ozone. Horner and co-workers previously reported that the oxidations of tertiary amines, phosphines and arsines with ozone in ethyl chloride[5] gave the corresponding oxides in good yields. Disappointingly, however, our attempts to oxidize compound 1 with ozone in dichloromethane at −78 °C led to a complex mixture, from which triphenylbismuth dichloride 8 was isolated in 42% yield.

We then examined the oxidation of compound 1 in toluene. Bubbling of ozonized oxygen (10 mmol h^{-1}) into a toluene solution (80 cm^3) of compound 1 (1 mmol) for 100 min at −78 °C afforded a yellowish green suspension which, after being filtered through Celite, was concentrated under reduced pressure. To our surprise, the light brown residue obtained was found to be triphenylbismuth diformate 3 (33%), accompanied by small amounts of triphenylbismuth diacetate 5.

Compound 3, as far as we know previously unknown, was identified as such on the basis of elemental analysis, ^1H and ^{13}C NMR, IR and FAB-MS spectroscopy and X-ray analysis. A ^1H NMR spectrum of compound 3 in CDCl$_3$ exhibited two characteristic peaks; a doublet at δ 8.16 for protons adjacent to the bismuth atom and a singlet at δ 8.51 for the formyloxy
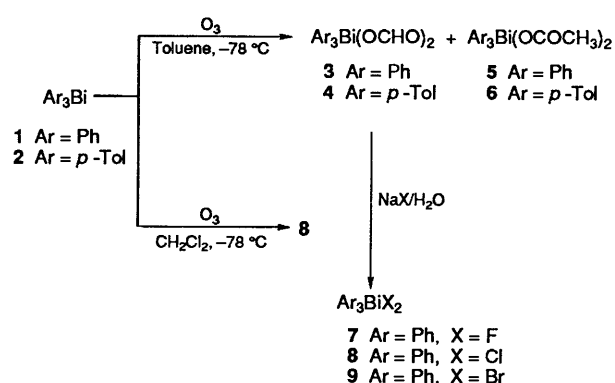

Scheme 1

groups. A ^{13}C NMR spectrum of compound 3 in CDCl$_3$ exhibited two characteristic peaks at δ 158.6 for the *ipso* ring carbons and δ 167.5 for the formyloxy groups. A fast atom bombardment (FAB) mass spectrum showed diagnostic peaks due to Ar$_3$BiOCHO, Ar$_2$Bi, ArBi and Bi fragments. IR absorption for the carbonyl groups of compound 3 were observed at 1605 and 1352 cm^{-1}, which are close to those of triphenylbismuth diacetate.[6] Definitive evidence for the structure was furnished by an X-ray crystallographic study on compound 3, good crystals of which had been grown from an acetone solution at ambient temperature. Appreciable decay of the crystal was observed during X-ray irradiation and some correction had to be made for the decline.

The crystal structure of compound 3 consists of isolated molecules which have C_2 molecular symmetry, the Bi–C(1)–C(4) atoms forming the C_2 axis (Fig. 1). The coordination geometry around the bismuth centre is best described as a distorted trigonal bipyramid (TBP), in which three phenyl groups occupy the equatorial sites, while two formyloxy groups occupy the apical sites. In the equatorial plane of the molecule of compound 3, the C(5)–Bi–C(5) angle is 145.2(6)°, appreciably larger than the normal 120°, while the C(1)–Bi–C(5) angle 107.4(3)° is considerably smaller than the expected one (Table 1). Although the bond lengths of compound 3 are similar to those of triphenylbismuth bis(trifluoroacetate) 12,[6,7] the deviations from the normal angle are slightly larger in diformate 3 than in the bis(trifluoroacetate) 12. The variations may be attributed to the difference in electron-delocalizing ability

Table 1 Selected bond lengths (Å) and angles (°) for compound 3, with estimated standard deviations in parentheses

Intramolecular distances	
Bi–O(1)	2.270(8)
Bi–C(1)	2.23(1)
Bi–C(5)	2.19(1)
Bi–O(2)	2.91(1)
O(1)–C(11)	1.28(2)
O(2)–(C11)	1.22(2)
Bond angles	
O(1)–Bi–O(1)	171.6(4)
O(1)–Bi–C(1)	85.8(2)
O(1)–Bi–C(5)	90.9(4)
O(1)–Bi–O(5)	91.6(4)
C(1)–Bi–C(5)	107.4(3)
C(5)–Bi–C(5)	145.2(6)
Bi–O(1)–C(11)	108.7(9)
Bi–C(1)–C(2)	119.1(7)
Bi–C(5)–C(6)	121.2(9)
Bi–C(5)–C(10)	117.9(9)
O(1)–C(11)–O(2)	123(1)
O(2)–Bi–O'(2)	91(5)
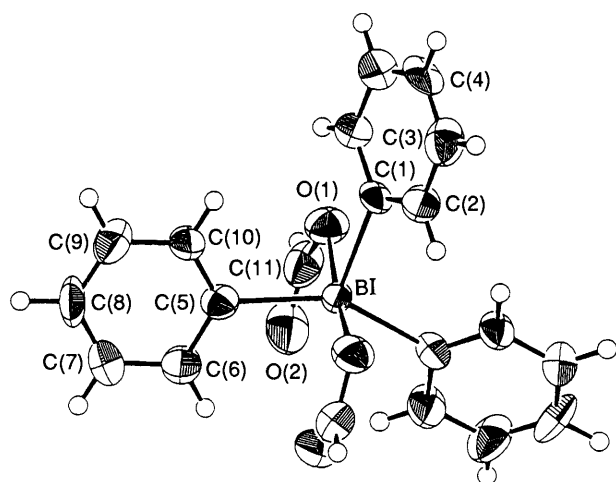
Fig. 1 An ORTEP[17] drawing of compound 3 with the atomic numbering

between the formyloxy and trifluoroacetoxy groups. The Bi–C bond distances, 2.19(1) and 2.23(1) Å, are comparable with those in compound 12, whereas the Bi–O bond length 2.27(0) Å is slightly shorter than the corresponding one in compound 12. The non-bonding Bi–O distance, 2.91(1) Å, is only 28% longer than the covalent Bi–O bond and shorter than the corresponding one in compound 12. Judging from these findings, the formyloxy groups in compound 3 seem to be bound to the bismuth atom more tightly than the trifluoroacetoxy groups in 12.

In order to optimize the reaction conditions for the preparation of compound 3, the effect of concentration was examined for substrate 1. The more dilute the concentration of substrate 1, the better the yield of compound 3; the yield of compound 3 increased from 30% ([1] = 0.0375 mol dm⁻³) to 33% (0.0250 mol dm⁻³), to 57% (0.0125 mol dm⁻³), as the concentration of substrate 1 decreased. Even under highly dilute conditions, however, the formation of some insoluble bismuth-containing polymeric powder was unavoidable. The most satisfactory result was obtained by the following procedure: a solution of substrate 1 (1 mmol) in toluene (2 cm³) was added to a dark green, saturated solution of ozone in toluene (60 cm³) at −78 °C, to give, immediately, a pale yellow suspension. This was allowed to warm to room temperature when it was

evaporated under reduced pressure to give compound 3 in 96% yield. By using this procedure, the formation of by-product 5 was reduced to a trace amount, no insoluble polymeric materials being observed. Judging from a rapid disappearance of the dark green colour, the ozone oxidation of compound 1 appears to have been complete almost immediately. Similarly, tri(p-tolyl)bismuthine 2 was converted into tri(p-tolyl)bismuth diformate 4 nearly quantitatively. However, tri(o-tolyl)bismuthine and trimesitylbismuthine could not be converted into the corresponding diformates; instead, they turned into a complex mixture largely composed of insoluble polymeric materials. Alkyl substituents *ortho* to the bismuth atom should have disturbed the formation of triarylbismuth diformates, simply leading to oxidative degradation. When toluene as a reaction medium was replaced by [²H₈]toluene, the formyloxy groups of the diformate obtained were deuteriated. This observation led us at first to the astonishing idea that the bismuth atom might have fixed carbon dioxide from the atmosphere! In order to discover the carbon source of the formyloxy groups in compounds 3 and 4, the effects of solvents and additives on the product distribution of the ozone oxidation were examined for compound 1 under the above optimized conditions. The oxidation of 1 with ozone in the presence of carbon dioxide gave a mixture of 1 (35%), 3 (25%) and triphenylbismuth carbonate 10 (40%) (Scheme 2). The formation of the last compound is suggestive that triphenylbismuth oxide was generated *in situ* and trapped by carbon dioxide.
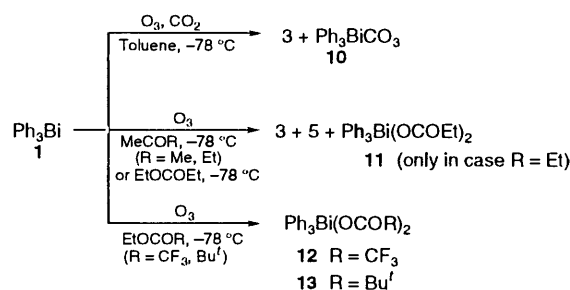
Scheme 2

Oxidation of 1 with ozone when conducted in toluene at −78 °C in the presence of ¹³C-enriched carbon dioxide, gave a diformate showing only the natural abundance of ¹³C in the formyloxy group as judged from the peak strength of its ¹³C NMR spectrum; this ruled out our possible serendipity. Since it is well established that ozone breaks down the aromatic ring[8] we reasoned that this could be the key process in the present reaction. Following this line of reasoning, some highly reactive intermediates, generated during the ozonization of toluene, would be the probable source of the formyloxy group. This working hypothesis was tested by the following control experiment: ozonized oxygen was passed into toluene (60 cm³) at −78 °C for 1 h after which the solution was warmed to ambient temperature while being flushed with argon. Compound 1 (1 mmol) was added to the resulting *ozonized toluene* and the mixture was stirred for an additional 1 h. Removal of solvent under reduced pressure left a mixture of compounds 1 and 3 in the ratio of 3:1. Loss of the substrate as a bismuth-containing polymeric powder was negligible. A similar oxidation of 1 in ethylbenzene gave 3 in a good yield, accompanied by small amounts of triphenylbismuth dipropionate 11. Additional by-products identified were acetophenone and 1-phenylethanol.

We then examined the ozone oxidation of 1 in ethyl acetate at −78 °C. Ethyl acetate is generally taken to be inert toward ozone and this was confirmed by the following experiment; ethyl acetate (30 cm³) was saturated with ozone at −78 °C and then allowed to warm to ambient temperature at which point

compound 1 (0.5 mmol) was added to it. Evaporation of the solution gave quantitative recovery of unchanged 1. Interestingly enough, the ozone oxidation of 1 in ethyl acetate at $-78\ °C$ gave a mixture of 1 (6%), 3 (13%) and 5 (39%). A similar oxidation in ethyl propionate gave a mixture of 1 (6%), 3 (15%). 5 (14%) and 11 (17%) as estimated by ^1H NMR spectroscopy.

We suspected that the α carbon atom of the esters used as solvent might also be a possible source of the formyloxy group under the above conditions. Thus, the oxidation of substrate 1 with ozone was carried out in ethyl pivalate and ethyl trifluoroacetate at $-78\ °C$. In the former solvent, a mixture of 1, triphenylbismuth dipivalate 13 and several other unidentified products was obtained, but the formation of compound 3 was not observed. In the latter solvent, the main product was compound 12. These two esters should have resisted the attack of ozone and, therefore, the carbon atom next to the ester function is also the likely carbon source of the formyloxy groups in 3. This finding rules out a possibility of the ring carbon atoms of bismuthine 1 as the major source for the formyloxy groups. Quite unexpectedly, compound 3 was also formed by the ozone oxidation of compound 1 in acetone at $-78\ °C$. A solution of compound 1 (1 mmol) in acetone was added to ozone-saturated acetone (60 cm³) to afford a yellow suspension, from which a mixture of 1 (28%), 3 (21%) and 5 (34%) was obtained. A similar oxidation of 1 in ethyl methyl ketone gave a mixture of 1 (14%), 3 (14%), 5 (61%) and 11 (6%), the yields being estimated by ^1H NMR spectroscopy. Interestingly, the oxidation of compound 1 in acetone with dimethyldioxirane at ambient temperature gave a mixture of 1 (68%), 5 (8%) and 10 (10%), which clearly indicates that compound 3 is a product characteristic of the ozone oxidation. In a ketone solution containing bismuthine 1, some Baeyer–Villigar type reaction might have occurred to generate an ester, which might then have trapped triphenylbismuth oxide formed *in situ* to produce the corresponding triphenylbismuth dicarboxylate.

A reaction mixture from the ozone oxidation of 1 when quenched with aqueous sodium chloride gave triphenylbismuth dichloride 8 as the sole product (90%); indeed, the same compound was formed simply by shaking a benzene solution of 3 with brine. Similarly, treatment of 3 with aqueous sodium fluoride, bromide or acetate gave triphenylbismuth difluoride 7 (90%), dibromide 9 (91%) and diacetate 5 (74%) (Scheme 1).

Ligand exchange between triphenylbismuth dibenzenesulfonate 14 and brine was previously reported by Rüther and co-workers.[9] Their X-ray crystallographic study established that the bismuth atom in compound 14 has a distorted TBP structure, the non-bonding Bi–O distance being 37% longer than the covalent Bi–O bond length. Enhanced reactivity of 3 and 14 toward common nucleophiles seems to be closely connected with their unique structures, in which the bismuth atom has a quite distorted TBP geometry and the prominent intramolecular interaction between the bismuth and oxygen atoms forces the formyloxy and phenylsulfonyloxy groups to coordinate to the bismuth atom nearly in a bidentate fashion.

Experimental

General Experimental Details.—Dichloromethane, toluene, ethylbenzene, ethyl acetate, and ethyl propionate were all distilled from calcium hydride under argon before use. Acetone and ethyl methyl ketone were distilled from calcium sulfate under argon before use. Triarylbismuthines 1 and 2 were prepared by the reaction between bismuth(III) chloride and the corresponding arylmagnesium bromides. All m.p.s were determined on a Yanagimoto hot-stage apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 (200 MHz) spectrometer for solutions in $CDCl_3$

with tetramethylsilane as an internal standard. *J* Values are recorded in Hz. IR spectra were obtained on a Shimadzu FTIR-8100 spectrophotometer. FAB-MS spectra were determined on a JEOL JMS HS 110 mass spectrometer. Elemental analyses were performed at Microanalytical Laboratory, Institute for Chemical Research, Kyoto University. X-Ray analysis was performed on a Rigaku AFC5R X-ray diffractometer.

Oxidation of Compounds 1 and 2 with Ozone.—In toluene. (a) In a two-necked flask equipped with an inlet tube and an outlet tube a solution of compound 1 (440 mg, 1 mmol) in toluene (80 cm³) was cooled to $-78\ °C$. Ozonized oxygen was then passed into this solution at a rate of 10 mmol h^{-1} until its colour turned yellowish green (100 min). The resulting suspension was allowed to warm to room temperature while being flushed with argon after which it was filtered through Celite. The pale yellow filtrate was evaporated under reduced pressure to leave a pale brown powder, which was washed with cold hexane (10 cm³ × 3) and recrystallized from benzene–hexane (1:3) to give *product* 3 (300 mg, 57%) as pale yellow fine crystals, m.p. 140–150 °C (decomp.); $δ_H$ 7.51–7.55 (3 H, m), 7.64 (6 H, t, *J* 7.8), 8.16 (6 H, d, *J* 8.2) and 8.51 (2 H, s); $δ_C$ 131.19, 131.46, 134.11, 158.56 and 167.46; $ν_{max}$(KBr)/cm^{-1} 1610, 1576, 1558, 1469, 1437, 1352, 1271, 1010, 985, 779, 733, 681 and 447; *m/z* 485 (M − OCHO), 363 (Ph$_2$Bi), 286 (PhBi) and 209 (Bi) (Found: C, 44.9; H, 3.2. $C_{20}H_{17}BiO_4$ requires C, 45.2; H, 3.2%).

(b) Ozonized oxygen (10 mmol h^{-1}) was passed into toluene (60 cm³) for 1 h at $-78\ °C$ to give a dark green solution, to which was added compound 1 (440 mg, 1 mmol) in toluene (2 cm³) in one portion. The resulting pale yellow suspension was allowed to warm to ambient temperature while being flushed with argon to give a pale yellow solution; this was evaporated under reduced pressure to leave a light brown residue, recrystallization of which from benzene–hexane (1:3) gave product 3 (510 mg, 96%) as crystals.

Compound 2 (482 mg, 1 mmol) was similarly treated to give the diformate 4 (560 mg, 98%) as crystals, m.p. 126–128 °C; $δ_H$ 2.40 (9 H, s), 7.42 (6 H, d, J_{AB} 8.0), 8.02 (6 H, d, J_{AB} 8.0) and 8.45 (2 H, s); $δ_C$ 21.41, 131.98, 133.91, 141.57, 155.20 and 167.31; $ν_{max}$(KBr)/cm^{-1} 1632, 1605, 1483, 1388, 1348, 1282, 1205, 1184, 997, 798 and 476; *m/z* 527 (M − OCHO), 391 (*p*-Tol$_2$Bi), 300 (*p*-TolBi) and 209 (Bi) (Found: C, 47.9; H, 4.3. $C_{23}H_{23}BiO_4$ requires C, 48.2; H, 4.0%). ^1H NMR inspection of the reaction mixture confirmed the presence of a minor product *tri*-p-*tolylbismuth diacetate* 6 by direct comparison with an authentic specimen. Compound 6; m.p. 196–198 °C (decomp.); $δ_H$ 1.82 (6 H, s), 2.39 (9 H, s), 7.38 (6 H, d, J_{AB} 8.0) and 8.02 (6 H, d, J_{AB} 8.0); $δ_C$ 21.34, 22.05, 131.60, 133.73, 140.79, 157.60 and 177.73; $ν_{max}$(KBr)/cm^{-1} 1601, 1587, 1487, 1381, 1327, 1309, 1205, 1186, 999, 993, 795, 665, 621 and 476; *m/z* 541 (M − OCOCH$_3$), 391 (*p*-Tol$_2$Bi), (*p*-TolBi) and 209 (Bi) (Found: C, 49.8; H, 4.5. $C_{25}H_{27}BiO_4$ requires C, 50.0; H, 4.5%).

In dichloromethane. Ozonized oxygen (10 mmol h^{-1}) was passed into a solution of compound 1 (440 mg, 1 mmol) in dichloromethane (60 cm³) at $-78\ °C$ for 1 h after which the resulting yellowish green suspension was allowed to warm to ambient temperature when it was filtered through Celite. The filtrate was evaporated under reduced pressure to leave a residue, which was chromatographed on silica gel using dichloromethane as eluent to give triphenylbismuth dichloride 8 (215 mg, 42%) as crystals, m.p. 156–158 °C (lit.,[6] 159–160 °C); $δ_H$ 7.51–7.57 (3 H, m), 7.66 (6 H, t, *J* 8.0) and 8.52 (6 H, d, *J* 8.0).

Oxidation of Compound 1 with Ozone in the Presence of CO_2.—Compound 1 (880 mg, 2 mmol) and solid CO_2 (*ca.* 1.5 g) were mixed in toluene (80 cm³), through which was passed ozonized oxygen (10 mmol h^{-1}) for 1 h at $-78\ °C$. The resulting suspension was filtered to remove compound 10 (400 mg, 40%)

and the filtrate was evaporated under reduced pressure. The light brown residue was carefully washed with cold hexane (10 cm^3 × 3) to give *product* 3 (265 mg, 25%). The hexane washings were combined and evaporated to give recovery of starting material 1 (300 mg, 34%). Compound 10; m.p. 150–155 °C (decomp.) [lit.,[10] 164–165 °C, (decomp.)]; ν_{max}(KBr)/cm^{-1} 1576, 1556, 1469, 1307, 1032, 985, 744, 735, 715, 700, 681, 646 and 451.

Oxidation of Compound 1 with Ozone in the Presence of $^{13}CO_2$.

—To ozone-saturated toluene (30 cm^3) was added at −78 °C a solution of 1 (132 mg, 0.3 mmol) and ^{13}C-enriched carbon dioxide in the same solvent (30 cm^3), the latter being generated from barium [^{13}C]carbonate (400 mg, 2 mmol) and 60% perchloric acid (2 cm^3). After work-up, the residue was washed with cold hexane (2 cm^2 × 3) and *product* 3 (152 mg, 96%) was subjected to ^{13}C NMR and FAB-MS inspection for ^{13}C-enrichment.

Oxidation of Compound 1 with Ozone in Ethylbenzene.

—Compound 1 (440 mg, 1 mmol) was oxidized in ethylbenzene (60 cm^3) as solvent. Work-up gave a mixture (560 mg) of 3 (94%), 11 (4%), acetophenone (<1%) and 1-phenylethanol (<1%) as estimated by ^{1}H NMR spectroscopy. Compound 11; needles, m.p. 157–159 °C; δ_H 0.91 (6 H, t, J 7.6), 2.08 (4 H, q, J 8.0), 7.44–7.48 (3 H, m), 7.58 (6 H, t, J 7.6) and 8.16 (6 H, d, J 8.6); δ_C 10.14, 28.78, 130.54, 131.02, 133.94, 161.05 and 180.97 (Found: C, 48.8; H, 4.3. $C_{24}H_{25}BiO_4$ requires C, 49.15; H, 4.3%).

Oxidation of Compound 1 with Ozone in Esters and Ketones.

—*In ethyl acetate.* Compound 1 (440 mg, 1 mmol) was oxidized in ethyl acetate (60 cm^3) as solvent. The suspension was filtered through Celite and the filtrate was evaporated to give a mixture (157 mg) of 1 (6%), 3 (13%) and 5 (39%) as estimated by ^{1}H NMR.

In ethyl pivalate. To ozone-saturated ethyl pivalate (5 cm^3) was added at −78 °C a solution of compound 1 (44 mg, 0.1 mmol) in the same ester (1 cm^3) to give, immediately, a pale yellow suspension which was slowly warmed to ambient temperature and then filtered through Celite. The filtrate was evaporated under reduced pressure to give a solid residue (30 mg of products), ^{1}H NMR inspection of which confirmed that it was triphenylbismuth dipivalate 13 by direct comparison with an authentic specimen. Compound 13; crystals, m.p. 146–148 °C; δ_H 0.96 (18 H, s), 7.39–7.46 (3 H, m), 7.56 (6 H, t, J 7.0) and 8.14 (6 H, d, J 7.4); δ_C 25.57, 38.89, 130.77, 133.87, 161.24 and 184.64; ν_{max}(KBr)/cm^{-1} 2953, 2864, 1599, 1568, 1475, 1441, 1396, 1340, 1215, 985, 893, 804, 727, 681, 603 and 451; m/z 565 (M − Ph), 541 (M − OCOC$_4$H$_9$), 363 (Ph$_2$Bi), 286 (PhBi) and 209 (Bi) (Found: C, 52.3; H, 5.4. $C_{28}H_{33}BiO_4$ requires C, 52.3; H, 5.2%).

In ethyl trifluoroacetate. Ozonized oxygen (10 mmol h^{-1}) was passed into a solution of compound 1 (30 mg, 0.07 mmol) in ethyl trifluoroacetate (3 cm^3) for 6 min at −78 °C to give a white suspension which was filtered through Celite. The filtrate was evaporated to leave a white solid, ^{1}H NMR inspection of which confirmed that it was the product 12[6,7] by direct comparison with an authentic specimen; m.p. 147–149 °C (lit.,[6] 133 °C); δ_H 7.48–7.56 (3 H, m), 7.65 (6 H, t, J 7.6) and 8.12 (6 H, d, J 7.4) (Found: C, 39.6; H, 2.3. $C_{22}H_{15}BiF_6O_4$ requires C, 39.6; H, 2.3%).

In acetone. A solution of compound 1 (440 mg, 1 mmol) in acetone (2 cm^3) was added to ozone-saturated acetone (60 cm^3) at −78 °C to give a bright yellow suspension, which was warmed to ambient temperature and filtered through Celite. The filtrate was evaporated under reduced pressure to give a mixture (527 mg) of 1 (28%), 3 (21%) and 5 (34%) as estimated by ^{1}H NMR.

Oxidation of Compound 1 with Dimethyldioxirane.

—Compound 1 (220 mg, 0.5 mmol) was added to a 0.25 mol dm^{-3} solution of dimethyldioxirane[11] in acetone (22 cm^3) and the mixture was stirred for a day at ambient temperature exposed to the air. The suspension was filtered to remove 10 (25 mg, 10%) and the filtrate was evaporated under reduced pressure. The residue was washed with cold hexane (2 cm^3 × 3) to give 5 (22 mg, 8%). The hexane washings were combined and evaporated to give recovery of 1 (150 mg, 68%).

Ligand Exchange Reaction of Compound 3: General Procedure.

— An excess of the appropriate aqueous sodium salt was added to a solution of compound 3 (530 mg, 1 mmol) in benzene (30 cm^3) and the mixture was stirred vigorously for 10 min. The organic layer was separated, dried (MgSO$_4$) and evaporated under reduced pressure to give the corresponding product 5 or 7–9.

Triphenylbismuth diacetate 5. Use of sodium acetate gave the product 5 as fine crystals (413 mg, 74%); m.p. 160–164 °C (lit.,[6] 173 °C); δ_H 1.84 (6 H, s), 7.44–7.51 (3 H, m), 7.60 (6 H, t, J 8.0) and 8.16 (6 H, d, J 8.0).

Triphenylbismuth difluoride 7. Use of sodium fluoride gave the product 7 as crystals (430 mg, 90%); m.p. 158–161 °C (lit.,[6] 127 °C; lit.,[12] 159 °C); δ_H 7.45–7.52 (3 H, m), 7.65 (6 H, t, J 8.0) and 8.21 (6 H, d, J 8.0) (Found: C, 44.95; H, 3.1. $C_{18}H_{15}BiF_2$ requires C, 45.2; H, 3.2%).

Triphenylbismuth dichloride 8. Use of sodium chloride gave the product 8 as needles (459 mg, 90%); m.p. 156–158 °C (lit.,[6] 159–160 °C).

Triphenylbismuth dibromide 9. Use of sodium bromide gave the product 9 as pale yellow crystals (546 mg, 91%); m.p. 139–141 °C (lit.,[6] 139 °C); δ_H 7.49–7.56 (3 H, m), 7.65 (6 H, t, J 8.0) and 8.50 (6 H, d, J 8.0).

X-Ray Crystallography of Compound 3.

—A crystal of dimensions 0.350 × 0.100 × 0.130 mm was used for X-ray crystallography.

Crystal data $C_{20}H_{17}BiO_4$, M = 530.33. Monoclinic, space group $C2/c$, a = 7.770(6) Å, b = 19.73(2) Å, c = 12.240(4) Å, β = 103.18(4)°, V = 1827(2) Å^3, Z = 4, D_c = 1.928 g cm^{-3}. Colourless rhomboid. μ(Mo-Kα,λ = 0.71069 Å) = 96.41 cm^{-1}. Intensity data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo-Kα radiation and a 12 KW rotating anode generator using the ω–2θ scan technique to a maximum 2θ value of 55.2°. Scans of (1.47 + 0.30 tan θ)° were made at a speed of 8.0 deg min^{-1} (in omega). Of the 2323 reflections which were collected, 2166 were unique (R_{int} = 0.047). Three standard reflections monitored at every 150 reflections showed intensity deterioration down to 66% of initial ones due to X-ray radiolysis. The falling-off of intensities with the elapse of time was corrected based on the non-linear decay (polynomials up to order 5) in the standard reflections. An empirical absorption correction, based on azimuthal (Ψ) scans of several reflections, was applied which resulted in transmission factors in the range 0.62–1.00. Data were corrected for Lorentz and polarization effects. The structure was solved by a combination of the Patterson method and direct methods.* The non-hydrogen atoms were refined anisotropically. The

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* Structure solution methods: PHASE J. C. Calbrese; PHASE—Patterson Heavy Atom Solution Extractor. Univ. of Wisconsin-Madison, Ph.D. Thesis (1972). DIRDIF P. T. Beurskens; DIRDIF: Direct Method for Difference Structures—an automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984/1 Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands.

† Least-squares: Function minimized: $\Sigma w(|F_o| - |F_c|)^2$ where: $w = 1/\sigma^2(F_o)$.

positions of hydrogen atoms were calculated from those of the non-hydrogen atoms and were included in F_c calculation.[13] The final cycle of full-matrix least-squares refinement† was based on 1111 observed reflections $[I > 3.00\sigma(I)]$ and 116 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.044$ and $R_w = 0.038$. The weighting scheme, $w = 1/\sigma^2 (F_o)$, was employed. The goodness of fit was $S = 1.26$.‡ Neutral atomic scattering factors were taken from Cromer and Waber.[14] Anomalous dispersion effects were included in F_c; the values for Δf and $\Delta f''$ were those of Cromer.[15] All calculations were performed using the TEXAN[16] crystallographic software package of the Molecular Structure Corporation. The ORTEP[17] program was used to obtain the drawing in Fig. 1. Selected bond lengths and bond angles, and fractional atomic coordinate are given in Table 1.

Full details of crystal data, fractional atomic co-ordinates, structure factors and thermal parameters of compound **3** have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

‡ $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where: N_o = number of observations and N_v = number of variables.

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