

Unexpected formation of highly stabilized tetrakis-(2-alkoxyphenyl)bismuthonium salts in the oxidation of tris-(2-alkoxyphenyl)bismuthanes with iodosylbenzene

Hitomi Suzuki,^{*,a} Tohru Ikegami^a and Nagao Azuma^b

^a Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

^b Department of Chemistry, Faculty of Science, Ehime University, Bunkyo-cho, Matsuyama 790-77, Japan

Treatment of tris-(2-alkoxyphenyl)bismuthanes **1** with iodosylbenzene in methylene dichloride at 40 °C led to none of the expected bismuthane oxides **2** but, quite unexpectedly, gave tetrakis-(2-alkoxyphenyl)bismuthonium chlorides **3** in moderate to good yields. In some cases, bismuthonium formates **4** accompanied the main reaction products. Similar treatment in benzene in the presence of benzyl bromide, ethyl bromide, or 2,2,2-trifluoroethyl iodide led to the corresponding bismuthonium bromides **7** and iodides **8**. Through anion exchange, a variety of bismuthonium salts including formate **4**, tetrafluoroborate **11**, toluene-*p*-sulfonate **12**, bromide **7**, iodide **8** and perchlorate **13** were prepared from the salt **3** in good yields. In contrast to the known tetraphenylbismuthonium salts, all of these new bismuthonium salts exhibited high thermal stability. The molecular structure of compound **7a** was elucidated by X-ray analysis, where the four neighbouring oxygen atoms are found to surround the bismuth atom tetrahedrally *via* a weak through-space interaction with the metal, making the bismuth centre less susceptible to nucleophilic attack of the halide anion.

Introduction

In contrast to well documented triorganylnicogen oxides derived from lighter 15-group elements, R₃Pn=O (Pn = N, P, As and Sb), the oxides of triorganylbismuthanes as yet remain to be characterized.¹ These compounds are of interest because of their high potential as precursors to a variety of organobismuth(v) compounds. However, the literature to date contains only a few papers dealing with somewhat conflicting results. Many attempts by previous workers to obtain triarylbismuthane oxides by direct oxidation of triarylbismuthanes **1** have so far met with failure; attempted oxidation of triphenylbismuthane with hydrogen peroxide,² dinitrogen trioxide,³ potassium permanganate,⁴ selenium dioxide,⁵ and cyclic nitrones⁶ all led to none of the expected product.

Recently, we have found that iodosylbenzene was effective as an oxidant for this purpose; under ultrasonic irradiation or gentle heating in an appropriate organic solvent, some triarylbismuthanes were smoothly converted to the corresponding oxides in good yield.⁷ However, we could not isolate these oxides due to their high sensitivity towards moisture and carbon dioxide; during the course of evaporation under reduced pressure, the oxides were readily decomposed to intractable polymeric substances.

Results and discussion

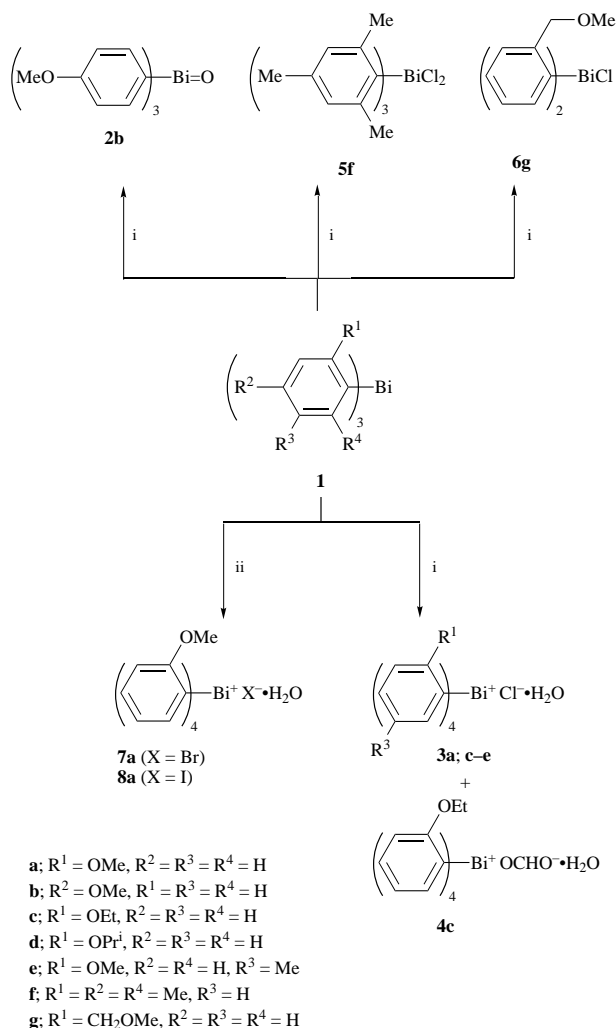
Since the 2-methoxy- and 2,6-dimethoxy-phenyl groups have been shown by PM3 calculations to stabilize the bismuthonium cation more effectively than the phenyl or 4-methoxyphenyl group,⁸ we came to the idea of obtaining tris-(2-methoxyphenyl)bismuthane oxide **2a** by the oxidation of tris-(2-methoxyphenyl)bismuthane **1a** with iodosylbenzene, expecting that the 2-alkoxyphenyl ligand might work effectively to stabilize the polar bismuth oxide function. Treatment of bismuthane **1a** with an excess of iodosylbenzene in boiling methylene dichloride led to rapid disappearance of the oxidizing agent to give an orange-coloured solution or suspension. Evaporation of the solution

under reduced pressure left a brown oily residue which could be crystallized out from CH₂Cl₂-Et₂O as a light brown solid. More conveniently, the reaction mixture was concentrated to a syrup, which was diluted with ethyl acetate to separate the same compound as a microcrystalline solid melting at 195–197 °C with decomposition. Elemental analysis of this compound showed a composition C₂₈H₃₀BiClO₅. Its ¹H NMR spectrum in CDCl₃ exhibited a broad 2 H absorption at δ 2.2, a singlet due to the methoxy group at δ 3.66, and two peak clusters at δ -7.22–7.32 and 7.55–7.75 due to aromatic protons. The broad resonance at high field suggests the presence of one water molecule, which was confirmed by an IR absorption at 3450 cm⁻¹. The ¹³C NMR spectrum exhibited absorptions at δ_C 56.46, 112.59, 124.50, 127.20 (Bi-C), 134.20, 134.79 and 159.74 (MeO-C), showing the presence of four intact 2-methoxyphenyl moieties. A peak at δ_C 127.20, assigned to the *ipso* carbon attached to the bismuth atom, was shifted 15.6 ppm upfield as compared with that of the parent bismuthane **1a**. Such a noticeable upfield shift of the signal due to the *ipso* carbon atom attached to a positively charged heteroatomic centre is generally observed for various heteroatom onium compounds.⁹ Thus the new compound may safely be formulated as a bismuthonium compound **3a** (2-MeOC₆H₄)₄BiCl·H₂O, which was further supported by a fast-atom-bombardment (FAB) mass spectrum showing diagnostic fragment peaks at *m/z* 637 (Ar₄Bi), 423 (Ar₂Bi), 316 (ArBi) and 209 (Bi). Formation of compound **3a** in a hydrated form may be attributed to adventitious water in the commercial solvent used for the work-up.

The present new oxidation reaction of triarylbismuthanes was highly dependent on the solvent system employed; in chloroform, only a trace amount of the onium salt **3a** was obtained and 50% of starting bismuthane **1a** was recovered intact, while in ethylene dichloride the salt **3a** was obtained in 43% yield. In benzene, the reaction did not proceed in the expected way; anisole and iodobenzene (phenyl iodide) were the major products with a recovery of 59% of initial bismuthane **1a**, no other organobismuth compounds being detected in the product mixture. Since iodosylbenzene is known to dis-

proportionate to iodylbenzene and iodobenzene on heating,¹⁰ low-boiling methylene dichloride was apparently the solvent of choice. Even in the presence of added water, the oxidation in methylene dichloride proceeded smoothly to give the onium salt **3a** in a similar or slightly reduced yield.

Tris-(2-ethoxyphenyl)bismuthane **1c**, tris-(2-isopropoxyphenyl)bismuthane **1d**, and tris-(2-methoxy-4-methylphenyl)bismuthane **1e** were all similarly oxidized by the present procedure to give the corresponding bismuthonium chlorides **3c–e** in moderate yield (Scheme 1). In the case of bismuthane **1c**, how-



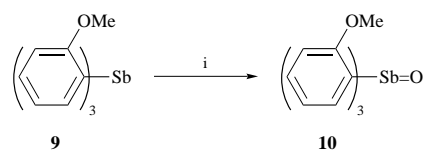
Scheme 1 Reagents and conditions: i, PhI=O, CH₂Cl₂, 40 °C; ii, PhI=O, RX (EtBr, PhCH₂Br, CF₃CH₂I), PhH, 40–50 °C

ever, bismuthonium formate **4c** was obtained as the major product. The **3c**:**4c** ratio was estimated as 1:3.3 by ¹H NMR analysis. Tris-(4-methoxyphenyl)bismuthane **1b** and tris-(2-methylphenyl)bismuthane behaved quite differently toward iodosylbenzene under similar reaction conditions; the former was converted to a presumed oxide **2b**, while the latter resisted oxidation. Interestingly, tris-(2,4,6-trimethylphenyl)bismuthane **1f** was converted to the corresponding dichloride **5f** in 80% yield, while tris-[2-(methoxymethyl)phenyl]bismuthane **1g** gave bis-[2-(methoxymethyl)phenyl]bismuth chloride **6g** in 22% yield. From these findings, it became clear that the alkoxy grouping attached to the position *ortho* to the bismuth atom is indispensable to stabilization of tetraarylbismuthonium salts **2** in the oxygen-transfer oxidation of bismuthanes **1** by iodosylbenzene.

The ozone oxidation of bismuthane **1a** was also examined; bismuthane **1a** was added to a solution of ozone in methylene dichloride at –40 °C, which was then gradually warmed to room temperature to afford a mixture of unchanged bismuth-

ane **1a** (44%) and tris-(2-methoxyphenyl)bismuth dichloride **5a** (23%). This result was similar to that observed in the ozone oxidation of triphenylbismuthane in methylene dichloride, in which triphenylbismuth dichloride was obtained in 42% yield. Supposedly, this oxidation reaction would proceed *via* the intermediacy of a bismuthane ozonide.¹¹

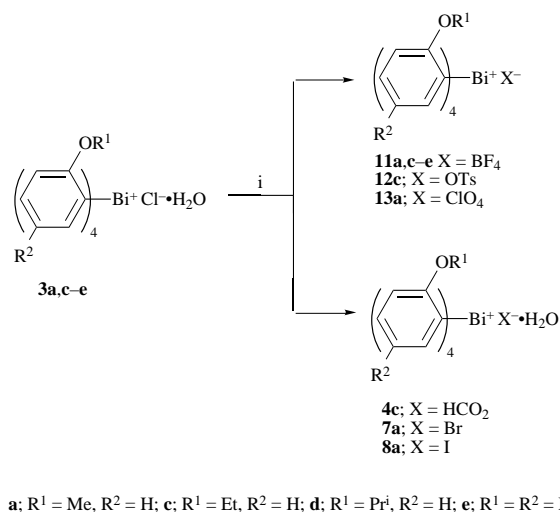
It would be pertinent to mention here that tris-(2-methoxyphenyl)stibane **9**^{12a} was smoothly oxidized with iodosylbenzene in benzene at reflux to give the expected oxide **10**^{12b} in almost quantitative yield (Scheme 2). Stibane oxides are more stable



Scheme 2 Reagents and conditions: i, PhI=O, PhH, 80 °C

against moisture as compared with the corresponding bismuthane oxides **2**.⁷

Onium salts **2** are readily soluble in methylene dichloride, chloroform, acetone, acetonitrile and ethanol, but almost insoluble in ethyl acetate, diethyl ether, hexane and benzene. When chlorides **3a,c–e** were treated with silver(i) tetrafluoroborate in acetonitrile, the corresponding tetrafluoroborates **11a,c–e** were obtained in good yield (Scheme 3). Similarly, the chlor-



Scheme 3 Reagents and conditions: i, MX (AgBF₄, HCO₂Na, NaOTs, NaBr, NaI or AgClO₄), water–CH₂Cl₂(CHCl₃), room temp.

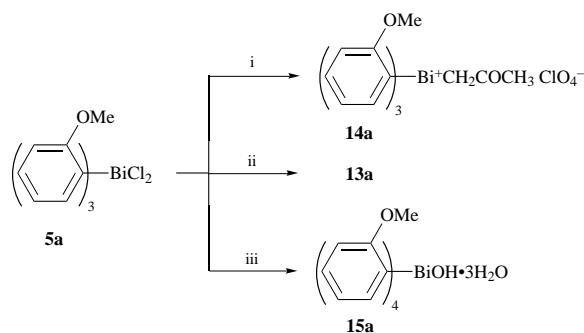
ide **3c** was converted to the formate **4c** and tosyl ester **12c** by treatment with an aqueous solution of sodium formate or toluene-*p*-sulfonate. All of these new bismuthonium compounds **3a,c–e**, **4c**, **11a,c–e** and **12c** were thermally stable; they did not show any significant sign of degradation after 3 months storage under ambient conditions.

The first preparation of tetraphenylbismuthonium chloride and bromide was reported by Wittig and Clauss, who obtained them by treating pentaphenylbismuth with hydrogen chloride or bromine.¹³ They described how these salts decomposed within several minutes at room temperature, producing the triphenylbismuthane and corresponding halogenobenzenes (phenyl halides). Hence, all stable bismuthonium salts so far known carry low-nucleophilic, bulky counter-anions such as perchlorate, tetrafluoroborate, trifluoromethanesulfonate and tetraphenylborate.^{14–18} Beaumont and Goel have prepared a variety of bismuth(v) compounds, Ph₄BiX, by anion-exchange reaction between tetraphenylbismuthonium chloride and appropriate metal salts.¹⁴ They observed that the nature of Ph₄BiX changes depending on the anions involved; when X was ClO₄, BF₄ or

PF₆, the compounds showed an ionic nature, while when X was NO₃, Cl₃CCO₂, NCO or NCS, they took a non-ionic pentacoordinate structure. An X-ray crystallographic study of tetraphenylbismuthonium perchlorate demonstrated that the bismuth centre possesses a tetrahedral onium structure.¹⁵ When X was N₃ or NCSe, the corresponding bismuth(v) compounds were thermolabile at room temperature and readily decomposed to triphenylbismuthane and other products.

We were also successful in obtaining the isolable bismuthonium bromide **7** and iodide **8** from the chloride **3** by anion exchange. Shaking of a chloroform solution of bismuthonium salt **3a** with aq. sodium bromide gave the corresponding bromide **7a** as crystals in 74% yield. Similar treatment with sodium iodide gave the iodide **8a** in 74% yield. Both salts **7a** and **8a** are remarkably stabilized and decompose only above 200 °C. Similarly for the chloride **3a** and tetrafluoroborate **11a**, they do not show any sign of degradation when stored at room temperature. Compounds **7a** and **8a** constitute the first example of tetraaryl-bismuthonium halides of indefinite shelf-life. These halides were also readily available by the oxidation of bismuthane **1a** with iodosylbenzene in benzene in the presence of the corresponding alkyl halides; bismuthane **1a** was oxidized in the presence of ethyl or benzyl bromide at 40–50 °C to give compound **7a** in 39 and 42% yield, respectively. In the latter case, the formation of benzaldehyde as by-product was observed. Similar oxidation of bismuthane **1a** in the presence of 2,2,2-trifluoroethyl iodide afforded compound **8a** in 13% yield (Scheme 1).

In connection with the anion exchange, the metathetical reaction of tris-(2-methoxyphenyl)bismuth dichloride **5a** with silver perchlorate was re-examined in both acetone¹⁸ and butan-2-one.¹⁴ In acetone, tris-(2-methoxyphenyl)(2-oxopropyl)bismuthonium perchlorate **14a** was obtained in 55% yield, while in butan-2-one the formation of a dark tarry substance was predominant, tetrakis-(2-methoxyphenyl)bismuthonium perchlorate **13a** being obtained in only a slight amount (~1%) (Scheme 4). Treatment of the salt **14a** with brine gave bismuthane **1a**



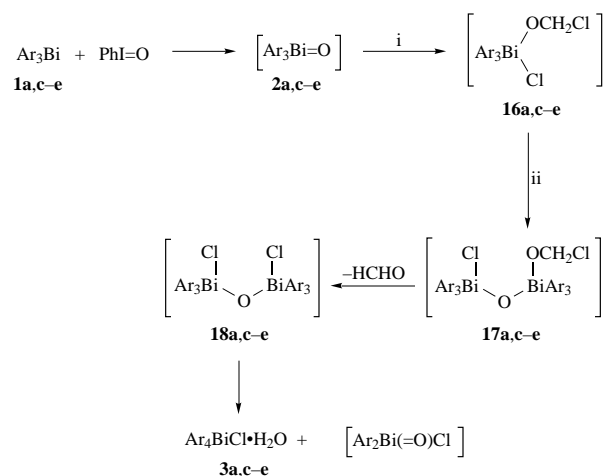
Scheme 4 Reagent and conditions: i, AgClO₄, Me₂CO, room temp.; ii, AgClO₄, MeCOEt, room temp.; iii, Ag₂O, CH₂Cl₂, 40 °C

(100%), probably *via* the intermediacy of a pentacoordinate bismuth compound. Metathesis of compound **5a** with silver(i) oxide in benzene–water gave bismuthane **1a** in a low yield, while the same reaction in methylene dichloride gave tetrakis-(2-methoxyphenyl)bismuthonium hydroxide **15a**, which probably arose from the metathesis of the initially formed chloride **3a** with silver(i) oxide. A trace amount of the formate **4a** was also detected by ¹H NMR monitoring. The likely source of the formate anion is formaldehyde, derived from methylene dichloride according to the sequence shown in Scheme 5. By treatment with tetrafluoroboric acid in acetonitrile–water, hydroxide **15a** was converted to tetrafluoroborate **11a** in good yield. A similar conversion of iodonium chloride to the tetrafluoroborate has previously been reported.¹⁹

Onium salts **3a**, **7a**, **8a**, **11a** and **13a** were all similar in their ¹H and ¹³C NMR and IR spectral patterns, although the salt

Table 1 Selected ¹H, ¹³C NMR (δ/ppm), and IR (ν_{max}/cm⁻¹) spectral data of tetraaryl-bismuthonium salts obtained

Compound	¹ H NMR (RO)	¹³ C NMR (RO, C-Bi)	IR (RO-Ar)
3a	3.67	56.46, 127.20	1244, 1044
11a	3.66	56.49, 127.40	1244
7a	3.67	56.66, 127.36	1244, 1044
8a	3.67	56.76, 127.33	1244, 1044
13a	3.66	56.39, 127.19	1244, 1044
3c	0.81, 3.98	13.72, 64.97, 127.19	1242, 1044
4c	0.81, 3.97	not determined	1242, 1044
11c	0.80, 3.98	13.73, 64.99, 127.28	1244, 1040
12c	0.79, 3.97	not determined	1240, 1042
3d	0.84, 4.60	20.96, 71.13, 128.31	1240
11d	0.83, 4.60	20.96, 71.10, 128.30	1242, 1038
3e	3.62	not determined	1250, 1042
11e	3.61	56.45, 127.15	1248



Scheme 5 Reagents: i, CH₂Cl₂; ii, Ar₃Bi=O

11a showed additional broad IR absorption due to the BF₄ anion (Table 1). The IR spectrum of salt **4c** contained a strong carbonyl absorption at 1632 cm⁻¹, which falls within the carboxylate anion region, endorsing the ionic structure for this salt. Spectral data showed that these bismuthonium salts have a similar ionic structure with a long separation between the bismuth atom and the corresponding anions, the decomposition of these salts *via* a ligand-coupling mode thereby being suppressed.

X-Ray structure analysis of compound **7a**

In order to get some insight into the extraordinarily enhanced thermal stability of tetrakis-(2-alkoxyphenyl)bismuthonium salts, an X-ray crystallographic analysis was performed for compound **7a**. As shown in Fig. 1 and Table 2, the bismuth centre has a tetrahedral geometry with the Bi–C bond lengths 2.194(8)–2.207(9) Å and C–Bi–C bond angles 105.9(3)–114.7(3)°. The values are in accordance with those of the previously reported tetraaryl-bismuthonium salts.^{15,20} Compound **7a** is subject to the interactions between Bi and four oxygen atoms and the intramolecular Bi–O distances are intermediate between the sum of their covalent radii (2.10 Å) and that of the estimated van der Waals radii (3.72 Å).²¹ All methoxy groups are found to lean slightly toward the bismuth atom with a deviation of about 5° from the standard sp² bond angle of 120°. A similar type of Bi–O interaction has been observed for tris-(2,6-dimethoxyphenyl)bismuthane.⁸ A large separation between the bismuth and bromine atoms [6.752(3) Å] is in accord with the ionic nature of compound **7a**. Since the previously reported bismuth–bromine covalent bond lengths are around 3 Å,²² we may safely conclude that there is little or no direct interaction between the bismuthonium moiety and the bromide anion.

Table 2 Selected bond lengths (Å) and angles (°) for compound **7a**, with estimated standard deviations in parentheses. Crystallographic numbering scheme (Fig. 1) is used

Bond length		Bond angle	
Bi–C(1)	2.201(9)	C(1)–Bi–C(8)	112.4(3)
Bi–C(8)	2.194(8)	C(1)–Bi–C(15)	105.9(3)
Bi–C(15)	2.203(9)	C(1)–Bi–C(22)	107.7(3)
Bi–C(22)	2.207(9)	C(8)–Bi–C(15)	114.7(3)
Bi···Br	6.752(3)	C(8)–Bi–C(22)	107.7(3)
Bi···O(1)	2.968(7)	C(15)–Bi–C(22)	108.2(3)
Bi···O(2)	3.099(2)	Bi–C(1)–C(2)	114.2(6)
Bi···O(3)	2.968(6)	Bi–C(1)–C(6)	124.0(7)
Bi···O(4)	3.091(6)	Bi–C(8)–C(9)	116.7(7)
		Bi–C(8)–C(13)	121.6(7)
		Bi–C(15)–C(16)	115.0(7)
		Bi–C(15)–C(20)	124.0(7)
		Bi–C(22)–C(23)	117.0(7)
		Bi–C(22)–C(27)	122.1(7)
		O(1)–C(2)–C(1)	114.2(8)
		O(1)–C(2)–C(3)	127.0(9)
		O(2)–C(9)–C(8)	116.8(8)
		O(2)–C(9)–C(10)	125.4(9)
		O(3)–C(16)–C(15)	114.0(9)
		O(3)–C(16)–C(17)	125.9(9)
		O(4)–C(23)–C(22)	116.1(8)
		O(4)–C(23)–C(24)	124.6(9)

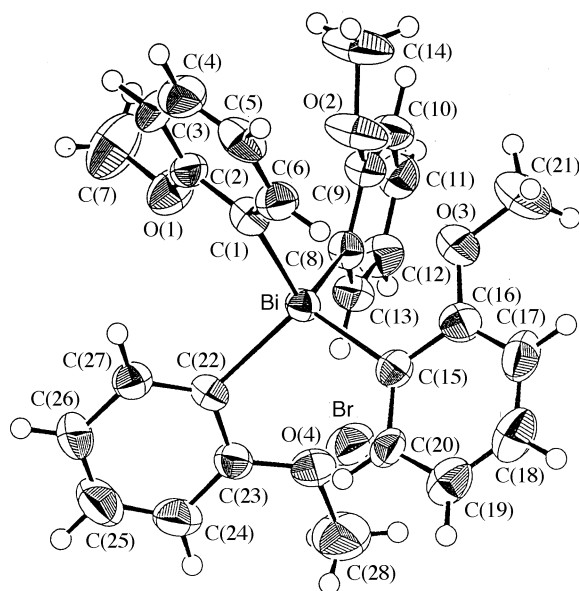


Fig. 1 ORTEP drawing of compound **7a**, with crystallographic numbering scheme. The percentage probability level of the ellipsoids in this drawing is 50%.

Possible mechanism for the formation of bismuthonium salts **3**

The mechanism of the formation of the salts **3** is not clear at present. However, one possible pathway leading to compounds **3** may be depicted as shown in Scheme 5. Of course, other possible mechanisms could not be ruled out.

Bismuthanes **1a,c–e** undergo oxygen-transfer reaction with iodosylbenzene to give the corresponding oxides **2a,c–e** as the initial product, which is assumed to react with methylene dichloride to form a pentacoordinate intermediate **16a,c–e**. Insertion of another molecule of oxide **2** into the bismuth–chlorine bond of this intermediate **16a,c–e** would result in the formation of a μ -oxo-type intermediate **17a,c–e**. Elimination of a formaldehyde molecule from products **17a,c–e** would give another μ -oxo-type intermediate **18a,c–e**, in which one of the aryl groups may migrate toward the neighbouring bismuth atom to form the corresponding bismuthonium chloride **3a,c–e**. The counterpart of the bismuth moieties is supposed to be transformed into the triarylbismuthane **1a,c–e** and other prod-

ucts by subsequent disproportionation reaction. Although compounds of type **18** have been reported previously,^{1a} their exact nature has not been established well to date. So we withhold detailed discussion on the mode of the formation of bismuthonium compounds **3a,c–e** at the present time.

To further the above mechanistic considerations, the following experiments were carried out. First, a possible involvement of aryl radical species is ruled out, since no aryl–aryl coupling products were detected from any of the present reactions; the oxidation proceeded smoothly even in the presence of a radical scavenger, 1,1-diphenylethylene. Oxidation of an equimolar mixture of bismuthanes **1a** and **1e** with an excess of iodosylbenzene gave a mixture of all four possible bismuthonium chlorides **3a, 3e**, $\text{Ar}^1_3\text{Ar}^2\text{BiCl}$, and $\text{Ar}^1\text{Ar}^2_3\text{BiCl}$ ($\text{Ar}^1 = 2$ -methoxy-4-methylphenyl, $\text{Ar}^2 = 2$ -methoxyphenyl), as was confirmed by FAB-mass spectroscopy. This observation is consistent with the formation and subsequent decomposition of the μ -oxo-type intermediates **17** and **18**. The main product from the oxidation of bismuthane **1c** was bismuthonium formate **4c** (*vide supra*). This result may be taken to support the elimination of a formyl moiety from the intermediate **17**. In accord with this observation, benzaldehyde was detected in the oxidation of bismuthane **1a** with iodosylbenzene in benzene in the presence of benzyl bromide.† In the present oxidation leading to bismuthonium compounds, alkyl halides including methylene dichloride should have worked not only as a halide anion source but also as an oxygen acceptor.

The formation of bismuthonium salt **15a** in the metathesis between dichloride **5a** and silver(i) oxide is also suggestive of the formation of the corresponding μ -oxo-type intermediate **18**. The conversion of triarylbismuth dichlorides **5** to the corresponding μ -oxo-type compounds have previously been reported by Goel and Prasad.¹⁷ However, Doak *et al.* had earlier reported that the reaction between triphenylbismuth dichloride and silver perchlorate in anhydrous ethanol gave a good yield of tetraphenylbismuthonium perchlorate.¹⁷ Additional conflicting results, also reported by Goel,¹⁴ suggest the possibility that the μ -oxo-type compound **18** may be converted to the bismuthonium salt **3** under certain conditions. With the intention of verifying the reaction pathway shown in Scheme 5, we attempted to prepare the μ -oxybis[tris-(2-methoxyphenyl)bismuth] dichloride **18a** by a few different approaches including the anion-exchange reaction of μ -oxybis[tris-(2-methoxyphenyl)bismuth]di(perchlorate) or di(trifluoromethanesulfonate) have been made. As has been mentioned above, the reaction of dichloride **5a** with silver perchlorate gave three different type of products, **13a, 14a** and **15a**, but any expected μ -oxybis[tris-(2-methoxyphenyl)bismuth] di(perchlorate) could not be obtained. The reaction was carried out in a benzene–water mixture, a typical reaction condition used to obtain a μ -oxo-type compound from the corresponding dichloride; however, the product was bismuthonium salt **13a** in 18% yield. A newly developed preparative method for μ -oxybis(triarylbismuth) di(trifluoromethanesulfonate)²³ was also applied to the present purpose; dichloride **5a** was treated successively with trimethylsilyl trifluoromethanesulfonate and hexamethyldisiloxane, but the reaction gave a mixture of at least four compounds including bismuthonium salt (checked by ¹H NMR analysis). By treatment of this mixture with brine, we could isolate the bismuthonium salt **3a** by chromatography over silica gel. These findings are highly suggestive of the ease of conversion of the μ -oxybis[tris-(2-methoxyphenyl)bismuth] derivative into tetrakis-(2-methoxyphenyl)bismuthonium salt. At present, the preparation of the μ -oxobis[tris-(2-methoxyphenyl)bismuth] compound is not successful and the development of more promising methodology for our purpose is under way.

† One referee suggested the possibility of direct formation of benzaldehyde from the adduct of type **16** formed from benzyl bromide and the corresponding bismuthane oxide.

Some of these stabilized bismuthonium salts have been found to exhibit prominent *in vitro* antimicrobial activity against *Helicobacter pylori*, and relevant biological data will be published elsewhere.

Experimental

All oxidation reactions were carried out under argon. All solvents were distilled from CaH₂ and were stored over molecular sieves 4 Å. Triarylbismuthanes were prepared from the corresponding arylmagnesium bromides or aryllithiums with bismuth(III) chloride and were recrystallized from benzene-methanol. Iodosylbenzene was prepared according to the reported procedure²⁴ and was stored at -20 °C. Other commercially available reagents were used without further purification. Column chromatography was performed on silica gel (Wakogel, 200 mesh). All mps were determined on a Yanagimoto hot-stage apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded on a Varian Gemini-200 (200 MHz) spectrometer for solutions in CDCl₃ with tetramethylsilane as internal standard. Coupling constants (*J* values) are given in Hz. IR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer. FAB-mass spectra were obtained on a JEOL JMS-HS 110 spectrometer with 3-nitrobenzyl alcohol as the matrix. Elemental analyses were performed at the Micro-analytical Laboratory, Institute of Chemical Research, Kyoto University.

Triarylbismuthanes

Compound 1a. Mp 159–161 °C (lit.,²⁵ 167–169 °C); δ_{H} 3.76 (9 H, s), 6.87 (3 H, dt, *J* 7.3 and 1.0), 6.99 (3 H, dd, *J* 8.1 and 1.0), 7.32 (3 H, ddd, *J* 8.1, 7.3 and 1.7) and 7.45 (3 H, dd, *J* 7.3 and 1.7); δ_{C} 55.49, 109.73, 123.99, 129.12, 139.05, 142.81 (BiC) and 162.14.

Compound 1c. Mp 123–124 °C (lit.,²⁶ 121–122 °C); δ_{H} 1.25 (9 H, t, *J* 7.0), 3.99 (6 H, q, *J* 7.0), 6.85 (3 H, dt, *J* 7.2 and 1.0), 6.96 (3 H, dd, *J* 8.1 and 1.0), 7.28 (3 H, ddd, *J* 8.1, 7.2 and 1.7) and 7.50 (3 H, dd, *J* 7.2 and 1.7); δ_{C} 14.74, 63.74, 110.72, 123.75, 128.86, 139.09, 143.55 (Bi-C) and 161.49.

Compound 1d. Mp 101–102 °C; δ_{H} 1.21 (18 H, d, *J* 6.0), 4.50 (3 H, hept, *J* 6.0), 6.82 (3 H, dt, *J* 7.2 and 1.0), 6.96 (3 H, d, *J* 8.1), 7.25 (3 H, ddd, *J* 8.1, 7.2 and 1.7) and 7.53 (3 H, dd, *J* 7.2 and 1.7); δ_{C} 22.13, 70.01, 111.88, 123.55, 128.66, 139.56, 145.04 (Bi-C) and 160.47 (Found: C, 52.65; H, 5.44. C₂₇H₃₃BiO₃ requires C, 52.77; H, 5.41%).

Compound 1e. Mp 151–153 °C; δ_{H} 2.13 (9 H, s), 3.72 (9 H, s), 6.89 (3 H, d, *J* 8.2), 7.10 (3 H, ddd, *J* 8.2, 2.2 and 0.7) and 7.29 (3 H, d, *J* 1.6); δ_{C} 20.59, 55.69, 109.63, 129.47, 132.84, 139.47, 142.5 (Bi-C) and 160.24 (Found: C, 50.42; H, 4.81. C₂₄H₂₇BiO₃ requires C, 50.35; H, 4.72%).

Preparation of tetrakis-(2-alkoxyphenyl)bismuthonium chloride monohydrates 3

In methylene dichloride. General procedure. Tris-(2-alkoxyphenyl)bismuthane **1** (1 mmol) and freshly prepared iodosylbenzene (330–440 mg, 1.5–2 mmol) were suspended in methylene dichloride (50 cm³) and heated to reflux until substrate **1** was consumed (usually 0.5–1.5 h). When a part of starting bismuthane **1** remained unchanged, an additional amount of iodosylbenzene was introduced to complete the reaction. The resulting solution or suspension was filtered through a Celite bed to remove any insoluble materials and the filtrate was concentrated under reduced pressure to give an oily residue. Ethyl acetate (20–30 cm³) was added to the residue and the separated microcrystalline salt **3** was collected, washed with a minimum amount of the same solvent, and dried *in vacuo*. Further crystallization from CH₂Cl₂-EtOAc (1 : 5) gave pure compound **3**, the yield of which was calculated on the basis of bismuth.

In chloroform. Typical procedure. Tris-(2-methoxyphenyl)bismuthane **1a** (530 mg, 1 mmol) and freshly prepared iodosylbenzene (330 mg, 1.5 mmol) were suspended in chloroform (30

cm³) and heated to reflux for 3 h. The resulting white suspension was filtered through a Celite bed to remove any insoluble materials and the filtrate was evaporated under reduced pressure to give a product (476 mg), the composition of which was estimated by ¹H NMR spectroscopy as follows; **3a** (0.01 mmol), anisole (0.48 mmol), 2-chloroanisole (0.1 mmol), iodobenzene (0.67 mmol) and substrate **1a** (0.57 mmol).

Tetrakis-(2-methoxyphenyl)bismuthonium chloride monohydrate 3a. Yield 68%; mp 195–197 °C (decomp.); δ_{H} 2.19 (2 H, br s), 3.67 (12 H, s), 7.22–7.32 (8 H, m) and 7.55–7.75 (8 H, m); δ_{C} 56.46, 112.59, 124.50, 127.20 (Bi-C), 134.20, 134.79 and 159.74; ν_{max} (KBr)/cm⁻¹ 3450 br, 1472, 1433, 1277, 1242, 1043, 785 and 760; *m/z* (FAB) 637 (Ar₄Bi), 423 (Ar₂Bi), 316 (ArBi) and 209 (Bi) (Found: C, 48.84; H, 4.28. C₂₈H₃₀BiClO₅ requires C, 48.66; H, 4.34%).

Tetrakis-(2-ethoxyphenyl)bismuthonium chloride monohydrate 3c. A product mixture from a similar oxidation of bismuthane **1c** was dissolved in chloroform (20 cm³) and the solution was stirred vigorously with brine (20 cm³) for 1 h. The organic layer was separated and the aqueous layer was extracted with chloroform (10 cm³ × 4). The combined extracts were dried (MgSO₄) and evaporated to give salt **3c** (28%), mp 212–214 °C (decomp.); δ_{H} 0.81 (12 H, t, *J* 7.0), 2.65 (2 H, br s), 3.98 (8 H, q, *J* 7.0), 7.18–7.30 (8 H, m) and 7.55–7.75 (8 H, m); δ_{C} 13.72, 64.97, 112.69, 124.20, 127.19 (Bi-C), 134.21, 134.86 and 159.15; ν_{max} (KBr)/cm⁻¹ 3450br, 1482, 1464, 1443, 1277, 1242, 1044, 1032 and 762; *m/z* (FAB) 693 (Ar₄Bi), 451 (Ar₂Bi), 330 (ArBi) and 209 (Bi) (Found: C, 51.43; H, 5.23. C₃₂H₃₈BiClO₅ requires C, 51.45; H, 5.13%).

Tetrakis-(2-isopropoxyphenyl)bismuthonium chloride monohydrate 3d. Yield 39%; mp 225–227 °C (decomp.); δ_{H} 0.84 (24 H, d, *J* 6.0), 2.17 (2 H, br s), 4.60 (4 H, hept, *J* 6.0), 7.15–7.25 (8 H, m) and 7.55–7.75 (8 H, m); δ_{C} 20.96, 71.13, 113.01, 123.72, 128.31 (Bi-C), 134.11, 135.58 and 157.96; ν_{max} (KBr)/cm⁻¹ 3450br, 1582, 1468, 1443, 1275, 1240, 1125, 1103, 947 and 758; *m/z* (FAB) 749 (Ar₄Bi), 479 (Ar₂Bi), 344 (ArBi) and 209 (Bi) (Found: C, 53.80; H, 5.68. C₃₆H₄₆BiClO₅ requires C, 53.83; H, 5.73%).

Tetrakis-(2-methoxy-4-methylphenyl)bismuthonium chloride dihydrate 3e. Yield 29%; mp 210–212 °C (decomp.); δ_{H} 2.19 (4 H, br s), 2.34 (12 H, s), 3.62 (12 H, s), 7.18 (4 H, br d, *J* 8), 7.30 (4 H, br s) and 7.43 (4 H, br d, *J* 8); ν_{max} (KBr)/cm⁻¹ 3450br, 1487, 1281, 1250, 1146, 1042, 1011, 806 and 729 (Found: C, 50.46; H, 5.10. C₃₂H₄₀BiClO₆ requires C, 50.26; H, 5.23%).

Oxidation of tris-[2-(methoxymethyl)phenyl]bismuthane 1g

A mixture of tris-[2-(methoxymethyl)phenyl]bismuthane **1g** (572 mg, 1 mmol), iodosylbenzene (330 mg, 1.5 mmol) and methylene dichloride (50 cm³) was heated to reflux for 1 h to obtain a bright yellow solution, which was filtered through a Celite bed and the filtrate was evaporated to leave a brown residue (910 mg), which was chromatographed on alumina, with CH₂Cl₂ as the eluent to give unchanged bismuthane **1g** (40% recovery) and *bis*-[2-(methoxymethyl)phenyl]bismuth chloride **6g** (22%), mp 140–142 °C; δ_{H} 3.45 (6 H, s), 4.60 (2 H, d, *J* 12), 4.78 (2 H, d, *J* 12), 7.33–7.55 (6 H, m) and 8.59 (2 H, d, *J* 7.6); ν_{max} (KBr)/cm⁻¹ 1453, 1208, 1088, 1046, 957, 760 and 737 (Found: C, 39.90; H, 3.87. C₁₆H₁₈BiClO₂ requires C, 39.47; H, 3.70%).

Ozone oxidation of bismuthane 1a in methylene dichloride

Ozonized oxygen (10 mmol h⁻¹) was passed into methylene dichloride (50 cm³) at -70 °C for 1 h to obtain a blue solution, to which was added a solution of the bismuthane **1a** (530 mg, 1 mmol) in the same solvent (15 cm³) in one portion. The resulting pale yellow suspension was allowed to warm to room temperature during the course of 30 min to give an orange suspension, which was filtered through a Celite bed. The filtrate was evaporated under reduced pressure to leave a brown residue, which was chromatographed on silica gel, with

CH₂Cl₂-EtOH (1:0-50:1) as the eluent, to give unchanged bismuthane **1a** (224 mg, 44% recovery) and tris-(2-methoxyphenyl)bismuth dichloride **5a** (137 mg, 23%). *Compound 5a* had mp 196-197 °C; δ_{H} 3.87 (9 H, s), 7.20-7.28 (6 H, m), 7.50 (3 H, dt, *J* 7.7 and 1.5) and 8.13 (3 H, dd, *J* 8.2, 1.6); δ_{C} 56.33, 113.36, 123.34, 132.53, 133.44, 151.65 and 157.65; ν_{max} (KBr)/cm⁻¹ 1588, 1472, 1431, 1273, 1248, 1046, 1019, 1001 and 750 (Found: C, 42.22; H, 3.51. C₂₁H₂₁BiCl₂O₃ requires C, 41.95; H, 3.52%). This compound was also prepared by treating bismuthane **1a** with sulfuryl dichloride in methylene dichloride at 0 °C.

Tris-(2-ethoxyphenyl)bismuth dichloride 5c was similarly obtained, mp 190 °C (decomp.); δ_{H} 1.10 (9 H, t, *J* 7.0), 4.14 (6 H, q, *J* 7.0), 7.15-7.30 (6 H, m), 7.46 (3 H, t, *J* 7.9) and 8.13 (3 H, d, *J* 8.4); ν_{max} (KBr)/cm⁻¹ 1584, 1480, 1466, 1441, 1397, 1279, 1248, 1163, 1125, 1044, 1003, 922 and 758 (Found: C, 44.73; H, 4.20. C₂₄H₂₇BiCl₂O₃ requires C, 44.81; H, 4.23%).

Oxidation of tris-(2-methoxyphenyl)stibane **9** with iodosylbenzene

A mixture of tris-(2-methoxyphenyl)stibane **9**^{2a} (443 mg, 1 mmol), iodosylbenzene (242 mg, 1.1 mmol) and benzene (50 cm³) was heated to reflux for 1 h to give a pale yellow suspension, which was filtered through a Celite bed while hot. The filtrate was concentrated under reduced pressure to give a mixture (556 mg) of phenyl iodide and tris-(2-methoxyphenyl)stibane oxide **10**. Trituration of this mixture with hexane gave pure oxide **10** (454 mg, 99%), mp 247-249 °C (lit.,^{12b} 247 °C); δ_{H} 3.78 (9 H, s), 7.00 (3 H, dd, *J* 8.3 and 1.0), 7.12 (3 H, dt, *J* 7.4 and 1.0), 7.44 (3 H, ddd, *J* 8.3, 7.4 and 1.7) and 7.88 (3 H, dd, *J* 7.4 and 1.7).

Preparation of bismuthonium tetrafluoroborates **11**

An acetonitrile solution (5 cm³) of silver(i) tetrafluoroborate (200 mg) was added to a solution of salt **3a** (517 mg, 0.75 mmol) in the same solvent (10 cm³) and the resulting mixture was stirred in the dark under ambient conditions. After 2 h silver(i) chloride was filtered off and the filtrate was evaporated to leave a brown solid, which was extracted with methylene dichloride (10 cm³ × 3). The combined extracts were evaporated and then treated with EtOAc (20 cm³) to give *tetrakis-(2-methoxyphenyl)bismuthonium tetrafluoroborate 11a* (468 mg, 86%) as fine crystals, mp 268-270 °C; δ_{H} 3.66 (12 H, s), 7.22-7.32 (8 H, m) and 7.55-7.75 (8 H, m); δ_{C} 56.49, 112.67, 124.60, 127.40 (Bi-C), 134.28, 134.94 and 159.92; ν_{max} (KBr)/cm⁻¹ 1472, 1433, 1279, 1244, 1097, 1061, 1009 and 762 (Found: C, 46.00; H, 3.84. C₂₈H₂₈BBiF₄O₄ requires C, 46.43; H, 3.90%).

Compound **3c** (0.154 mmol, 115 mg) was similarly converted to *compound 11c* (104 mg, 87%). Compounds **3d** (0.138 mmol, 111 mg) and **3e** (0.25 mmol, 186 mg) gave the corresponding *tetrafluoroborates 11d* (107 mg, 92%) and **11e** (156 mg, 80%), respectively, as fine crystals.

Tetrakis-(2-ethoxyphenyl)bismuthonium tetrafluoroborate 11c. Mp >300 °C; δ_{H} 0.80 (12 H, t, *J* 7.0), 3.98 (8 H, q, *J* 7.0), 7.15-7.30 (8 H, m) and 7.50-7.70 (8 H, m); δ_{C} 13.73, 64.99, 112.73, 124.20, 127.28 (Bi-C), 134.21, 134.90 and 159.25; ν_{max} (KBr)/cm⁻¹ 1584, 1466, 1445, 1244, 1279, 1063, 1040 and 772 (Found: C, 48.95; H, 4.62. C₃₂H₃₆BBiF₄O₄ requires C, 49.25; H, 4.65%).

Tetrakis-(2-isopropoxyphenyl)bismuthonium tetrafluoroborate 11d. Mp >300 °C; δ_{H} 0.83 (24 H, d, *J* 6.1), 4.60 (4 H, hept, *J* 6.1), 7.15-7.25 (8 H, m) and 7.55-7.75 (8 H, m); δ_{C} 20.96, 71.10, 113.00, 123.67, 128.30 (Bi-C), 134.08, 135.57 and 157.97; ν_{max} (KBr)/cm⁻¹ 1584, 1468, 1277, 1242, 1125, 1105, 1055, 1038, 947 and 754 (Found: C, 51.63; H, 5.28. C₃₆H₄₄BBiF₄O₄ requires C, 51.69; H, 5.30%).

Tetrakis-(2-methoxy-4-methylphenyl)bismuthonium tetrafluoroborate 11e. Mp 183-184 °C; δ_{H} 2.33 (12 H, s), 3.61 (12 H, s), 7.17 (4 H, d, *J* 8.4) 7.31 (4 H, br s) and 7.43 (4 H, ddd, *J* 8.4, 1.8 and 0.7); δ_{C} 20.70, 56.45, 112.32, 127.15 (Bi-C), 134.25, 134.59 134.74 and 157.82; ν_{max} (KBr)/cm⁻¹ 1601, 1487,

1441, 1279, 1248, 1150, 1097, 1061, 1011, 820 and 729 (Found: C, 49.06; H, 4.60. C₃₂H₃₆BBiF₄O₄ requires C, 49.25; H, 4.65%).

Preparations of bismuthonium formate **4c**, tosyl ester **12c**, bromide **7a** and iodide **8a**

Tetrakis-(2-ethoxyphenyl)bismuthonium formate monohydrate 4c. To a solution of compound **3c** (52 mg, 0.07 mmol) in chloroform (15 cm³) was added aq. sodium formate (1 g in 5 cm³) and the resulting mixture was stirred vigorously for 2 h at room temperature. The organic layer was separated and the aqueous layer was extracted with chloroform (5 cm³ × 4). The combined organic phase was dried (MgSO₄) and evaporated to give *formate 4c* (37 mg, 70%), mp 153-155 °C (decomp.); δ_{H} 0.81 (12 H, t, *J* 7.0), 3.84 (2 H, br s), 3.97 (8 H, q, *J* 7.0), 7.18-7.30 (8 H, m) 7.55-7.75 (8 H, m) and 8.80 (1 H, s); ν_{max} (KBr)/cm⁻¹ 1632, 1582, 1461, 1443, 1277, 1242, 1044 and 762 (Found: C, 52.92; H, 5.47. C₃₃H₃₉BiO₇ requires C, 52.38; H, 5.16%).

Tetrakis-(2-ethoxyphenyl)bismuthonium toluene-*p*-sulfonate 12c. Similarly obtained from compound **3c** (192 mg, 0.257 mmol) and sodium toluene-*p*-sulfonate (0.68 g per 15 cm³). The product was chromatographed on silica gel, with CH₂Cl₂-EtOH (1:0-10:1) as eluent, to give *tosyl ester 12c* (152 mg, 68%), mp 272-273 °C; δ_{H} 0.79 (12 H, t, *J* 7.0), 2.29 (3 H, s), 3.97 (8 H, q, *J* 7.0), 7.09 (2 H, d, *J*_{AB} 8.3), 7.15-7.28 (8 H, m), 7.55-7.75 (8 H, m) and 7.90 (2 H, d, *J*_{AB} 8.3); ν_{max} (KBr)/cm⁻¹ 1584, 1464, 1445, 1275, 1240, 1217, 1204, 1121, 1042, 1034, 1013, 762 and 681; *m/z* 693 (Ar₄Bi), 451 (Ar₂Bi), 330 (ArBi) and 209 (Bi) (Found: C, 54.07; H, 5.01. C₃₉H₄₃BiO₇S requires C, 54.17; H, 5.01%).

Tetrakis-(2-methoxyphenyl)bismuthonium bromide monohydrate 7a. To a solution of compound **3a** (235 mg, 0.34 mmol) in methylene dichloride (10 cm³) was added aq. sodium bromide (2 g in 10 cm³) and the resulting mixture was stirred vigorously for 30 min at room temperature. Usual work-up gave *compound 7a* (184 mg, 74%) as fine crystals, mp 220-223 °C (decomp.); δ_{H} 1.67 (2 H, br s), 3.67 (12 H, s), 7.22-7.32 (8 H, m) and 7.55-7.75 (8 H, m); δ_{C} 56.66, 112.75, 124.63, 127.36 (Bi-C), 134.31, 134.92 and 159.87; ν_{max} (KBr)/cm⁻¹ 3450br, 1470, 1435, 1277, 1244, 1044, 781 and 760 (Found: C, 46.00; H, 3.93. C₂₈H₃₀BiBrO₅ requires C, 45.71; H, 4.08%).

Tetrakis-(2-methoxyphenyl)bismuthonium iodide monohydrate 8a. Similarly obtained from compound **3a** (235 mg, 0.34 mmol) and sodium iodide (2 g) in 74% yield (198 mg), *compound 8a* had mp 202-204 °C (decomp.); δ_{H} 1.61 (2 H, br s), 3.67 (12 H, s), 7.22-7.32 (8 H, m) and 7.55-7.75 (8 H, m); δ_{C} 56.76, 112.76, 124.66, 127.33 (Bi-C), 134.30, 134.92 and 159.84; ν_{max} (KBr)/cm⁻¹ 3450br, 1470, 1435, 1277, 1244, 1044, 781 and 760 (Found: C, 42.73; H, 3.72. C₂₈H₃₀BiIO₅ requires C, 42.97; H, 3.84%).

Oxidation of bismuthane **1a** with iodosylbenzene

In benzene in the presence of alkyl halides: typical procedure. A mixture of bismuthane **1a** (530 mg, 1 mmol), iodosylbenzene (330 mg, 1.5 mmol), benzyl bromide (171 mg, 1 mmol) and benzene (50 cm³) was stirred at 40-50 °C for 5 h. The resulting suspension was filtered through a Celite bed and the filtrate was evaporated to give an oily residue (597 mg), which was passed through a short column of silica gel to give an oily mixture (278 mg), the composition of which was estimated by ¹H NMR analysis as follows; bismuthane **1a** (0.09 mmol), anisole (0.09 mmol), benzyl bromide (0.74 mmol), phenyl iodide (0.45 mmol) and benzaldehyde (0.02 mmol). The solid residue retained on the Celite bed was extracted with methylene dichloride (20 cm³ × 4) and the combined extracts were evaporated to give bismuthonium salt **7a** (309 mg, 42%). Similar oxidation of bismuthane **1a** in the presence of ethyl bromide and 2,2,2-trifluoroethyl iodide gave the bismuthonium bromide **7a** and the corresponding iodide **8a** in 39 and 13% yield, respectively.

Metathetical reaction of tris-(2-methoxyphenyl)bismuth dichloride **5a** with silver(i) perchlorate

In acetone. To a solution of compound **5a** in acetone (50 cm³) was added commercial silver(i) perchlorate (460 mg, 2 mmol; from Wako Pure Chemical Industries, Ltd.; content 90%) in the same solvent (10 cm³) and the resulting suspension was stirred at room temperature in the dark. After 1 h the precipitated silver chloride was filtered off and the filtrate was concentrated under reduced pressure to leave a dark brown oily residue, which was triturated with a mixture of acetone (2 cm³) and benzene (20 cm³) to give *tris*-(2-methoxyphenyl)(2-oxopropyl)-bismuthonium perchlorate **14a** as light brown crystals (375 mg, 55%), mp 149–150 °C (decomp.); δ_{H} 2.48 (3 H, s), 3.82 (9 H, s), 5.09 (2 H, s), 7.15–7.30 (6 H, m) and 7.50–7.65 (6 H, m); δ_{C} 30.28, 51.79, 56.54 (Bi–CH₂), 112.19, 124.34, 126.23 (Bi–C), 134.07, 135.14, 159.97 and 202.99 (C=O); ν_{max} (KBr)/cm⁻¹ 1458, 1429, 1233, 1092, 1049, 1021 and 758 (Found: C, 41.96; H, 3.77. C₂₄H₂₆BiClO₈ requires C, 41.97; H, 3.82%).

Treatment of salt **14a** with an excess of brine in chloroform at room temperature readily gave bismuthane **1a** quantitatively.

In butan-2-one. Dichloride **5a** in butan-2-one (50 cm³) was treated with silver(i) perchlorate (460 mg, 2 mmol; from Wako Pure Chemical Industries, Ltd.; content 90%). Usual work-up gave a dark brown oily residue, which was triturated with a mixture of MeOH (2 cm³) and EtOAc (20 cm³) to give *tetrakis*-(2-methoxyphenyl)bismuthonium perchlorate **13a** as light brown crystals (8 mg, 1%), mp 250–251 °C; δ_{H} 3.66 (12 H, s), 7.25–7.35 (8 H, m) and 7.55–7.75 (8 H, m); δ_{C} 56.39, 112.58, 124.51, 127.19 (Bi–C), 134.20, 134.86 and 159.79; ν_{max} (KBr)/cm⁻¹ 1472, 1435, 1279, 1244, 1098, 1044 and 762; m/z 637 (Ar₃Bi), 423 (Ar₂Bi), 316 (ArBi) and 209 (Bi) (Found: C, 45.67; H, 3.80. C₂₈H₂₈BiClO₈ requires C, 45.62; H, 3.80%).

Reaction of dichloride **5a** with silver(i) oxide in methylene dichloride

To a suspension of silver(i) oxide, freshly prepared from 4 mmol of silver(i) nitrate and sodium hydroxide in methylene dichloride (5 cm³), was added a solution of dichloride **5a** (601 mg, 1 mmol) in the same solvent (45 cm³) and the resulting suspension was heated at reflux in the dark. After 4 h, the mixture was filtered through a Celite bed and the filtrate was evaporated under reduced pressure to leave a light yellow solid, which contained *tetrakis*-(2-methoxyphenyl)bismuthonium hydroxide trihydrate **15a** and bismuthane **1a**. The presence of a formate in the product mixture was detected by ¹H NMR spectroscopy. The mixture was recrystallized from CH₂Cl₂–EtOAc (1:5) to deposit compound **15a** (271 mg, 38% based on Bi). *Compound 15a*, mp 155–160 °C (decomp.); δ_{H} 2.77 (6 H, br s), 3.67 (12 H, s), 7.22–7.32 (8 H, m) and 7.55–7.75 (8 H, m); OH group was not observed; ν_{max} (KBr)/cm⁻¹ 3450br, 1586, 1566, 1471, 1277, 1244, 1044, 1009, 783 and 760 (Found: C, 47.53; H, 4.60. C₂₈H₃₅BiO₈ requires C, 47.46; H, 4.94%).

Compound **15a** was also obtained by the reaction of salt **3a** and silver(i) oxide as follows: to a suspension of salt **3a** in tetrahydrofuran (THF) (30 cm³) [prepared from bismuthane **1a** (1 mmol, 530 mg) and iodosylbenzene (2 mmol, 440 mg)] was added a suspension of silver(i) oxide [prepared from silver nitrate (1.1 mmol) and sodium hydroxide] in water (5 cm³) and the resulting suspension was stirred for 40 min in the dark under ambient conditions. Organic solvent was removed under reduced pressure and the aqueous layer was extracted with methylene dichloride (20 cm³ × 4). The combined extracts were dried (MgSO₄) and evaporated under reduced pressure to leave compound **15a** (392 mg, 55%).

Treatment of compound **15a** with 42% tetrafluoroboric acid in acetonitrile at 0–5 °C gave the corresponding tetrafluoroborate **11a** (mp 268–270 °C) in 91% yield.

Oxidation of compound **1a** in the presence of a radical scavenger

A mixture of bismuthane **1a** (530 mg, 1 mmol), iodosylbenzene

(286 mg, 1.3 mmol), 1,1-diphenylethylene (2 mmol, 360 mg) and methylene dichloride (50 cm³) was heated to reflux, and after 1.5 h it was filtered through a Celite bed. Usual work-up gave the salt **3a** (299 mg, 43%). 1,1-Diphenylethylene was recovered unchanged from the mother liquor from which the salt **3a** had separated out.

Cross-over experiment between bismuthanes **1a** and **1e** during oxidation with iodosylbenzene

A mixture of bismuthanes **1a** (265 mg, 0.5 mmol) and **1e** (286 mg, 0.5 mmol), iodosylbenzene (330 mg, 1.5 mmol) and methylene dichloride (50 cm³) was heated to reflux for 1 h. Usual work-up gave a mixture of bismuthonium salts (284 mg), which was found by FAB-MS analysis to contain compounds **3a**, **3e**, tris-(2-methoxyphenyl)(2-methoxy-4-methylphenyl)bismuthonium and (2-methoxyphenyl)tris-(2-methoxy-4-methylphenyl)-bismuthonium chlorides; m/z 693 (Ar¹₄Bi), 679 (Ar¹₃Ar²Bi), 651 (Ar¹Ar²₃Bi), 637 (Ar²₄Bi), 451 (Ar¹₂Bi), 437 (Ar¹Ar²Bi), 423 (Ar²₂Bi), 330 (Ar¹Bi), 316 (Ar²Bi), and 209 (Bi) (¹Ar = 2-methoxy-4-methylphenyl, ²Ar = 2-methoxyphenyl).

Attempt to prepare μ -oxybis[tris-(2-methoxyphenyl)bismuth] di(trifluoromethanesulfonate)

To a suspension of dichloride **5a** (601 mg, 1 mmol) in dry methylene dichloride (8 cm³) was added trimethylsilyl trifluoromethanesulfonate (0.19 cm³, 1 mmol) at 0 °C, and the mixture was stirred at room temperature for 20 h. To the resulting yellow solution was added hexamethyldisiloxane (0.11 cm³, 0.5 mmol) and the whole was stirred for 48 h at room temperature to give a brown solution, which was evaporated under reduced pressure to obtain a grey solid (680 mg). The ¹H NMR spectrum of the mixture showed that the mixture contained at least four products, including bismuthonium salt. The starting material **5a** was found to have been consumed completely. The residue was dissolved in methylene dichloride (15 cm³) and shaken with brine vigorously for 3 h. After extractive work-up, a dark brown solid (245 mg) was obtained. The residue was chromatographed on silica gel with methylene dichloride–ethanol (1:0–10:1) as eluent to give dichloride **5a** (68 mg, 11%) and bismuthonium salt **3a** (113 mg, 16%).

X-Ray crystallography of compound **7a**

A crystal of dimensions 0.45 × 0.38 × 0.20 mm, grown from a mixture of EtOH–EtOAc (1:5) at room temperature, was sealed in a glass capillary and used for X-ray crystallography.

Crystal data. C₂₈H₂₈BiBrO₄, M = 717.41. Monoclinic. Space group *P*2₁/*c*, *a* = 11.466(4), *b* = 19.802(9), *c* = 12.369(5) Å, β = 103.30(3)°, *V* = 2733(2) Å³, *Z* = 4, *D*_c = 1.743 g cm⁻³. Prisms, μ (Mo–K α , λ = 0.710 69 Å) = 79.08 cm⁻¹.

Data collection and processing. Intensity data were collected on a Rigaku AFC5R diffractometer using graphite-monochromated Mo–K α radiation from a 12 kW rotating anode generator using the ω –2 θ scan technique to a maximum 2 θ -value of 55.0°. Scans of (0.79 + 0.30 tan θ)° were made at a speed of 16.0 deg min⁻¹ (in omega). Data were corrected for Lorentz and polarization effects. Of the 6754 reflections which were collected, 6446 were unique (*R*_{int} = 0.074). The intensities of three representative reflections which were measured after every 150 reflections declined by 5.7%. A linear correction factor was applied to the data to account for this phenomenon. An empirical absorption correction, based on azimuthal (ψ) scans of several reflections, was applied which resulted in correction factors ranging from 0.53 to 1.00.

Structure analysis and refinement. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated from those of the non-hydrogen atoms and were included in the *F*_c calculation. The final cycle of full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$, was based on

3547 observed reflections [$I > 2.50\sigma(I)$] and 308 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.042$ and $R_w = 0.036$. The weighting scheme $w = 1/\sigma^2(F_o)$ was employed. The standard deviation of an observation of unit weight was 1.17, ‡ and the maximum peak and minimum trough in the final ΔF syntheses surpluses which are 0.80 and -1.34 \AA^{-3} . All calculations were performed using the TEXSAN²⁷ crystallographic software package of the Molecular Structure Corporation. The ORTEP²⁸ program was used to obtain the drawing in Fig. 1. Selected bond lengths and bond angles are given in Table 2. §

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‡ Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/109.

§ Standard deviation of an observation of unit weight: $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$ where N_o = number of observations and N_v = number of variables.

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