

# Synthesis, X-ray structure, thermal stability and reactions of triaryl(3-oxoalkyl)bismuthonium salts

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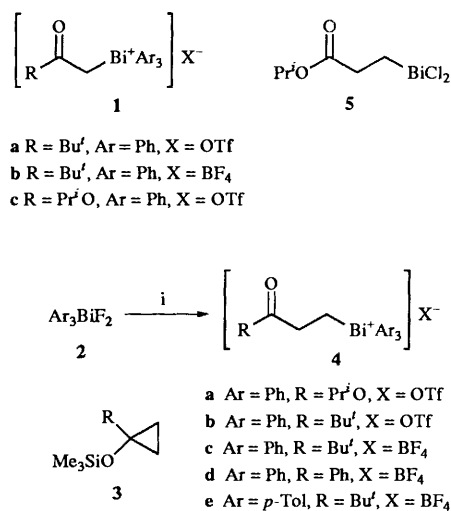
Treatment of triaryl(bismuth) difluorides **2** with siloxycyclopropanes **3** in the presence of trimethylsilyl trifluoromethanesulfonate (triflate) or boron trifluoride–diethyl ether gave the corresponding triaryl(3-oxoalkyl)bismuthonium salts **4** as crystals. X-Ray crystallographic analysis of the triflate **4a** showed that the central bismuth atom has a distorted tetrahedral geometry with weak intramolecular coordination by the oxygen atoms of the carbonyl group and triflate anion. Whilst all onium salts **4** are thermally stable in a solid state, the triflate **4a** slowly decomposed in chloroform to give triphenylbismuthane **6** and an ester **7** quantitatively. In nucleophilic solvents such as MeOH, DMSO and DMF, both triflate **4a** and tetrafluoroborate **4d** underwent decomposition in a complicated way to afford the bismuthane **6**, 3-methoxypropanoyl compounds **8a,b**,  $\alpha,\beta$ -unsaturated carbonyl compounds **9a,b**, diphenylbismuth triflate **10a** or tetrafluoroborate **10b** and alkoxy-sulfonium salts **11a,b**. The formate **12** was an additional product from **4d** in DMF. The bismuthonium salt **4d** reacted with dimethyl sulfide **13** and sodium benzenesulfinate **15** to afford the sulfonium salt **14** and the sulfonyl ketone **16**, respectively. Reaction of the salt **4d** with potassium halides **17** in DMF gave the enone **9b**, formate **12** and halogeno ketone **18** in varying yields depending on the nucleophilic nature of the halogen anions employed. When treated with KOBu<sup>t</sup>, the salt **4d** underwent facile  $\beta$ -elimination to yield the enone **9b**. In all of these reactions, the triphenylbismuthane moiety behaved as a good leaving group.

Although onium compounds with a functionalized alkyl group are of great importance in organic synthesis, the corresponding bismuthonium compounds have been little used in synthetic work because of their inaccessibility. Published syntheses of alkylbismuthonium salts involve the alkylation of tertiary bismuthanes<sup>1–4</sup> and the metathetical reaction of triphenylbismuth dichloride in dry acetone;<sup>5</sup> however, the variety of alkyl ligands so introduced is very limited owing to the low nucleophilicity of the bismuthane as well as the weakness of the resulting Bi–C<sub>alkyl</sub> bond.<sup>6</sup> Recently, we have reported an efficient method for the preparation of triaryl(2-oxoalkyl)bismuthonium salts **1** from triaryl(bismuth) difluorides **2** and silyl enol ethers.<sup>7,8</sup> In these bismuthonium salts, the 2-oxo function of the alkyl chain was found to play an important role in determining the relative stability, molecular geometry and reactivity of the compounds. As part of our systematic study on the chemistry of functionalized alkylbismuthonium compounds,<sup>7–11</sup> we report herein the synthesis of triaryl(3-oxoalkyl)bismuthonium triflates **4a,b** and tetrafluoroborates **4c–e** and discuss their structure, thermal stability, and reactions with some nucleophiles and a base in comparison with those of the salts **1**.

## Results and discussion

### Synthesis of triaryl(3-oxoalkyl)bismuthonium salts **4**

In order to obtain the bismuthonium salts **4**, we employed a methodology similar to that used for the preparation of the salts **1**.<sup>7,8</sup> Siloxycyclopropane **3** was chosen as a source of the 3-oxoalkyl group because the metal-induced ring-opening reaction of the cyclopropane **3** is known to provide ready access to the 3-oxoalkyl–metal bond.<sup>12,13</sup> As shown in Scheme 1, treatment of triaryl(bismuth) difluorides **2** with the cyclopropane **3** in the presence of trimethylsilyl triflate (Me<sub>3</sub>SiOTf) or boron trifluoride–diethyl ether (BF<sub>3</sub>·OEt<sub>2</sub>) led to triaryl(3-oxoalkyl)bismuthonium triflates **4a,b** and tetrafluoroborates **4c–e** in the



**Scheme 1** Reagents and conditions: i, Lewis acid (Me<sub>3</sub>SiOTf or BF<sub>3</sub>·OEt<sub>2</sub>) then 1-substituted 1-trimethylsilyloxy-cyclopropane **3**, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C–room temp.

yields listed in Table 1. The Lewis acids play a dual important role; they initially activate the difluoride **2** and then are transformed into the counter anions to stabilize the resulting bismuthonium salts **4**. In the absence of the Lewis acid, both difluoride and cyclopropane were recovered unchanged.

The triaryl(3-oxoalkyl)bismuthonium salts **4** were purified by recrystallization and characterized by microanalysis and FAB mass, IR and NMR spectroscopy. In the FAB mass spectra of the compounds, a strong peak due to the M<sup>+</sup> – OTf fragment from the triflate **4a,b** or M<sup>+</sup> – BF<sub>4</sub> fragment from the tetrafluoroborate **4c–e** was observed. In IR spectra, broad intense bands characteristic of their counter anions appeared at around 1320–1120 cm<sup>–1</sup> (OTf<sup>–</sup>) and 1150–950 cm<sup>–1</sup> (BF<sub>4</sub><sup>–</sup>),

**Table 1** Triaryl(3-oxoalkyl)bismuthonium salts **4** obtained

Difluoride <b>2</b>	Lewis acid	Cyclopropane <b>3</b>	Salt <b>4</b>	Yield (%) <sup>a</sup>
<b>2a</b> (Ar = Ph)	Me <sub>3</sub> SiOTf	<b>3a</b> (R = OPr <sup>i</sup> )	<b>4a</b>	47
<b>2a</b>	Me <sub>3</sub> SiOTf	<b>3b</b> (R = Bu <sup>i</sup> )	<b>4b</b>	12
<b>2a</b>	BF <sub>3</sub> ·OEt <sub>2</sub>	<b>3b</b>	<b>4c</b>	86
<b>2a</b>	BF <sub>3</sub> ·OEt <sub>2</sub>	<b>3c</b> (R = Ph)	<b>4d</b>	80
<b>2b</b> (Ar = <i>p</i> -Tol)	BF <sub>3</sub> ·OEt <sub>2</sub>	<b>3b</b>	<b>4e</b>	76

<sup>a</sup> Isolated yield.**Table 2** Selected bond lengths (Å) and angles (°) for compound **4a**, with estimated standard deviations in parentheses

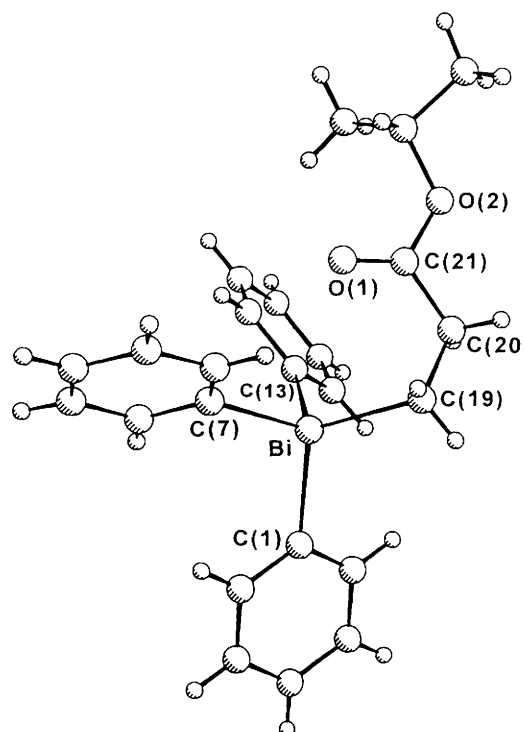
Bond length		Bond angle	
Bi–C(1)	2.213(8)	C(1)–Bi–C(7)	108.9(3)
Bi–C(7)	2.206(9)	C(1)–Bi–C(13)	101.0(3)
Bi–C(13)	2.229(9)	C(1)–Bi–C(19)	115.3(3)
Bi–C(19)	2.235(9)	C(7)–Bi–C(13)	105.5(3)
C(19)–C(20)	1.51(1)	C(7)–Bi–C(19)	115.5(3)
C(20)–C(21)	1.49(1)	C(13)–Bi–C(19)	109.1(3)
C(21)–O(1)	1.187(9)	Bi–C(19)–C(20)	110.7(6)
C(21)–O(2)	1.35(1)	C(19)–C(20)–C(21)	112.4(7)
Bi···O(1)	3.157(6)	C(20)–C(21)–O(1)	125.8(8)
Bi···O(5)	3.140(6)	O(1)–C(21)–O(2)	124.1(8)

respectively. <sup>13</sup>C NMR spectra showed a signal at  $\delta_c$  139.4–140.3 for the phenyl carbons adjacent to the bismuth atom. These spectral features are in accordance with the onium nature of the bismuth moiety in the salts **4**. IR absorption of the carbonyl function provided a further positive diagnosis. Both in KBr pellets and in CHCl<sub>3</sub> solutions, the C=O stretching bands were shifted to lower frequencies ( $\Delta\nu = 15$ –25 cm<sup>-1</sup>) compared to those of ordinary esters and ketones, indicating the operation of the intramolecular interaction between the carbonyl oxygen and bismuth atoms in the salts **4**. However, this type of interaction is much weaker for compound **4** as compared with the case reported for trivalent dichlorobismuthane **5** ( $\nu_{C=O} = 1650$  cm<sup>-1</sup>).<sup>12</sup>

#### X-Ray structure analysis of compound **4a**

In earlier papers,<sup>7,8</sup> we reported the crystal structures of two 2-oxoalkylbismuthonium salts **1a,b**, in which the central bismuth atom has a distorted tetrahedral geometry involving weak intramolecular coordination by the carbonyl oxygen atom. In order to compare the structure of the 3-oxoalkylbismuthonium salts **4** with those of the salts **1a,b** we have carried out an X-ray structure analysis of the triflate **4a**.

As shown in Fig. 1 and Table 2, the bismuth atom in the salt **4a** has a distorted tetrahedral geometry with the bond angles [C–Bi–C 101.0(3)–115.5(3)°] and the bond lengths [2.206(9)–2.235(9) Å]. The bond angle open to the carbonyl oxygen side [C(7)–Bi–C(19) 115.5(3)°] is considerably larger than the expected value for an sp<sup>3</sup> configuration (109° 28'), while the C–Bi–C angle remote from the carbonyl function [C(1)–Bi–C(13) 101.0(3)°] is appreciably reduced. The geometry around the bismuth centre is comparable with that of the 2-oxoalkylbismuthonium salt **1a**, and the whole structural feature clearly endorses the onium nature of the triflate **4a**. It is noteworthy, however, that the intramolecular distance between the bismuth and carbonyl oxygen atoms of **4a** [Bi–O(1) 3.157(6) Å] is much longer than that [2.93(1) Å] of the triflate **1a**.<sup>8</sup> Although the Bi–O(1) distance is intermediate between the sum of the covalent radii (2.10 Å) and that of the estimated van der Waals radii (3.72 Å),<sup>14</sup> this value is quite close to the distance between the bismuth and one of the nearest oxygen atoms of the triflate anion [Bi–O(5) 3.140(6) Å]. This finding suggests that the intramolecular coordinative interaction between the carbonyl

**Fig. 1** A PLUTO drawing of compound **4a** with the atomic numbering scheme. Triflate anion is omitted for clarity.

oxygen and bismuth atoms is rather weak in triflate **4a** as compared to triflate **1a**.

#### Thermal decomposition of triaryl(3-oxoalkyl)bismuthonium salts **4** in solutions

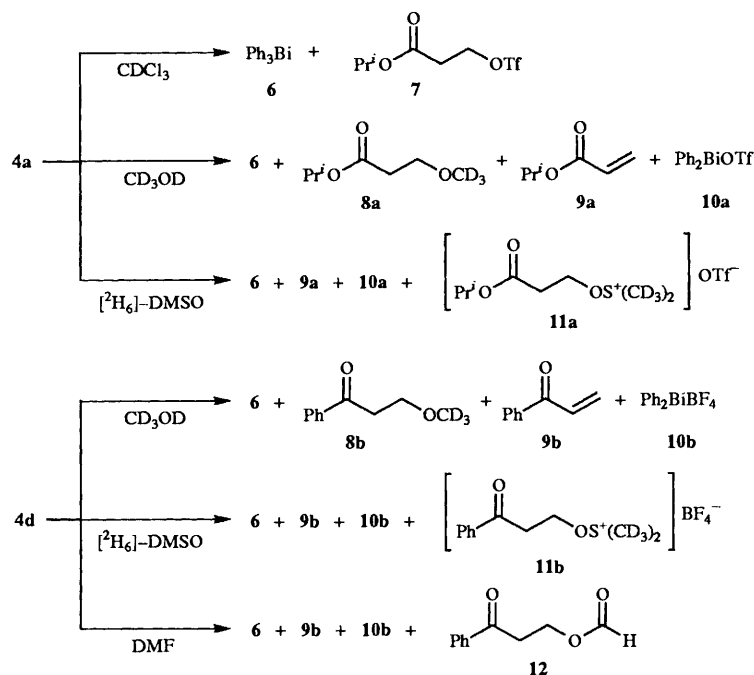
All bismuthonium salts **4a–e** are thermally stable in a solid state and show no signs of degradation on storage at room temperature. However, the triflate **4a** decomposed slowly in CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub> to give triphenylbismuthane **6** and 2-(isopropoxycarbonyl)ethyl triflate **7** quantitatively. The triflate **4b** underwent a similar mode of decomposition. Low isolated yields of the triflates **4a,b** may, in part, be attributed to their instability in solution (Table 1). On the other hand, in nucleophilic solvents such as methanol and dimethyl sulfoxide (DMSO), all the salts **4a–e** decomposed completely within a minute to a few hours, giving some reductive coupling products. In order to investigate the kinetics of this decomposition as well as the distribution of the resulting products, the NMR monitoring experiment was carried out for the thermal decomposition of compounds **4a** and **4d** in some deuteriated solvents.

Disappearance of the triflate **4a** obeyed first-order kinetics. The rate constants and products formed are summarized in Table 3 and Scheme 2. The triflate **4a** decomposed in CDCl<sub>3</sub> to give the bismuthane **6** and the ester **7** with a rate constant  $k =$

**Table 3**  $^1\text{H}$  NMR monitoring of the thermal decomposition of the salts **4a** and **4d** at 25 °C

Salt <b>4</b>	Solvent	$k/\text{s}^{-1}$	Products <sup>a</sup>
<b>4a</b>	$\text{CDCl}_3$	$8 \times 10^{-6}$	<b>6</b> (100), <b>7</b> (100)
<b>4a</b>	$\text{CD}_3\text{OD}$	$2 \times 10^{-4}$	<b>6</b> (16), <b>8a</b> (81), <b>9a</b> (14), <b>10a</b> (84)
<b>4a</b>	$[\text{}^2\text{H}_6]\text{-DMSO}$	— <sup>b</sup>	<b>6</b> (84), <b>9a</b> (17), <b>10a</b> (16), <b>11a</b> (82)
<b>4d</b>	$\text{CD}_3\text{OD}$	$5 \times 10^{-4}$	<b>6</b> (10), <b>8b</b> (66), <b>9b</b> (12), <b>10b</b> (90)
<b>4d</b>	$[\text{}^2\text{H}_6]\text{-DMSO}$	— <sup>b</sup>	<b>6</b> (87), <b>9b</b> (51), <b>10b</b> (13), <b>11b</b> (32)

<sup>a</sup> Numerals in parentheses refer to the yields based on the salt **4** at final stage of decomposition. <sup>b</sup> Not determined.

**Scheme 2**

$8 \times 10^{-6} \text{ s}^{-1}$ . This implies that the triflate anion attacks the alkyl carbon atom adjacent to the bismuth *via* the reductive elimination pathway. In  $\text{CD}_3\text{OD}$  the triflate **4a** underwent decomposition at a faster rate ( $k = 2 \times 10^{-4} \text{ s}^{-1}$ ) to afford the bismuthane **6**, isopropyl 3-methoxypropionate **8a**, isopropyl acrylate **9a** and diphenylbismuth triflate **10a**. In this reaction, the bismuthane **6**, the esters **8a** and **9a**, and triflic acid would be the initial products, and subsequently the bismuthane **6** would be cleaved by triflic acid to yield compound **10a** and benzene. In contrast, the triflate **4a** in  $[\text{}^2\text{H}_6]\text{-DMSO}$  was converted within a minute into the bismuthane **6**, the acrylate **9a**, the triflate **10a** and a sulfonium triflate **11a**. These results show that the triflate **4a** is susceptible to both the protic and aprotic nucleophilic solvents. The nucleophilic solvent molecule would attack the onium centre to cleave selectively the Bi-C<sub>alkyl</sub> bond, resulting in the formation of the coupling products with simultaneous elimination of the bismuthane **6**. The formation of the  $\alpha,\beta$ -unsaturated ester **9a** in moderate amounts in DMSO suggests the weak base character of this solvent.<sup>†</sup> Although the tetrafluoroborate **4d** did not decompose in  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$ , it decomposed in  $\text{CD}_3\text{OD}$  and  $[\text{}^2\text{H}_6]\text{-DMSO}$  in a manner similar to that of the triflate **4a** (Scheme 2). The salt **4d** underwent a coupling reaction in  $\text{CD}_3\text{OD}$  with the first-order kinetics ( $k = 5 \times 10^{-4} \text{ s}^{-1}$ ) to yield the bismuthane **6**, 3-

methoxy-1-phenylpropan-1-one **8b**, 1-phenylpropenone **9b** and diphenylbismuth tetrafluoroborate **10b**. As was the case with the triflate **4a**, the initially formed bismuthane **6** suffered cleavage by fluoroboric acid to yield compound **10b** and benzene. In  $[\text{}^2\text{H}_6]\text{-DMSO}$  compound **4d** was decomposed within a minute to the bismuthane **6**, the enone **9b**, the tetrafluoroborate **10b** and a sulfonium tetrafluoroborate **11b**. The mode of the reductive elimination which the fluoroborate **4d** suffered in DMF is of interest; the reaction was completed within 1 h to give the bismuthane **6**, the enone **9b** and 3-oxo-3-phenylpropyl formate **12** as the major products after aqueous work-up. Compound **12** was likely to be derived from the salt **4d** and DMF, but the mechanism of its formation is not clear at present.

The present results show that the triaryl(3-oxoalkyl)bismuthonium salts **4** can behave as a 3-oxoalkyl cation equivalent towards the counter anion and nucleophilic solvents. This characteristic behaviour may largely be attributed to the good leaving ability of the triaryl(bismuthane) moiety in the salts **4**. The 2-oxoalkylbismuthonium salts **1** undergo sluggish decomposition only by prolonged contact with the above solvents and the reaction rate was always much lower as compared to that of the 3-oxoalkyl counterpart **4**.<sup>‡</sup> The elongation of one methylene unit in the oxoalkyl chain

<sup>†</sup> It has been reported that some  $\beta$ -stannyl and  $\beta$ -telluro ketones undergo  $\beta$ -elimination smoothly by treatment with DMSO in THF to give  $\alpha,\beta$ -unsaturated ketones.<sup>15</sup>

<sup>‡</sup> As an example, when a solution of the triflate **1c** in  $\text{CDCl}_3$  (ca.  $0.05 \text{ mol dm}^{-3}$ ) was set aside for 3 days at 25 °C, only 8% of the salt decomposed and 92% was recovered unchanged. The estimated decay rate constant for salt **1c** was  $k = 3 \times 10^{-7} \text{ s}^{-1}$ .

**Table 4** Reactions of the salt **4d** with potassium halides **17**

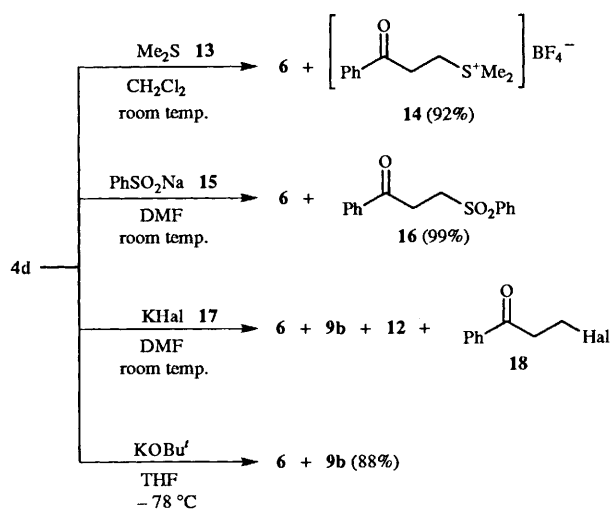
Halide <b>17</b>	Yield (%) <sup>a</sup>			
	<b>6</b>	<b>9b</b>	<b>12</b>	<b>18</b>
Hal = Cl	75	25	25	28 ( <b>a</b> ) <sup>b</sup>
Hal = Br	85	15	—	51 ( <b>b</b> ) <sup>b</sup>
Hal = I	81	10	—	65 ( <b>c</b> )

<sup>a</sup> NMR yield based on unrecovered salt **4d**. <sup>b</sup> Accompanied by small amounts of unidentified by-products.

appreciably decreases the steric congestion around the alkyl carbon atom adjacent to the bismuth atom. Thus, both the intra- and inter-molecular attack of a nucleophile would occur more easily at the alkyl carbon of the salt **4** as compared to the salt **1**. The difference in the coordination geometry of the carbonyl oxygen around the bismuth centre would be an additional factor which influences the relative stability of the salts **4** and **1**.

#### Reactions of 3-oxoalkylbismuthonium salt **4d** with some nucleophiles and a base

In order to compare the reactivity of 3-oxoalkylbismuthonium salts **4** with that of the 2-oxoalkylbismuthonium salts **1** and explore the synthetic potential of these onium compounds, the reactions of the salt **4d** with various nucleophiles and a base have been examined (Scheme 3).

**Scheme 3**

Treatment of the salt **4d** with dimethyl sulfide **13** in  $\text{CH}_2\text{Cl}_2$  readily gave dimethyl(3-oxo-3-phenylpropyl)sulfonium tetrafluoroborate **14** in 92% yield. When treated with sodium benzenesulfonate **15** in DMF, the salt **4d** underwent smooth C–S coupling to give 1-phenyl-3-phenylsulfonylpropan-1-one **16** in 99% yield.

The reaction of the salt **4d** with the potassium halides **17** proved to be a little complicated, the relative yields of the enone **9b**, the formate **12** and the 3-halogeno-1-phenylpropan-1-one **18** varying considerably according to the halogen ions involved (Table 4). The yields of the halogeno ketones **18** decreased in the order  $\text{I} > \text{Br} > \text{Cl}$ , whereas those of the enone **9b** increased in the order  $\text{I} < \text{Br} < \text{Cl}$ . From a control experiment, the product **12** was found to be derived from salt **4d** and DMF. Treatment of the salt **4d** with  $\text{KOBU}'$  in THF at  $-78^\circ\text{C}$  afforded the enone **9b** as the sole product, no transient colouration being shown during the reaction. When the reaction was carried out in the

presence of benzaldehyde, the enone **9b** was again the only product obtained while the aldehyde remained intact. This contrasts with the reaction between the 2-oxoalkylbismuthonium salt **1** and a base, where the yellow bismuthonium ylide is readily generated and, in the presence of aldehyde, the  $\alpha,\beta$ -epoxy ketone is formed.<sup>9</sup> In all of these reactions, the good leaving ability of triphenylbismuthane moiety is no doubt the key factor which determines the major reaction mode of 3-oxoalkylbismuthonium compounds toward nucleophile or base.

Further study on the chemistry of different types of functionalized alkylbismuthonium compounds is in progress.

### Experimental

For general experimental details see ref. 8. Triarylbi-muth difluorides **2**<sup>8,16</sup> and siloxycyclopropanes **3**<sup>17,18</sup> are all known and were prepared as previously reported. Other reagents were used as commercially received. <sup>1</sup>H (200 MHz) and <sup>13</sup>C (50 MHz) NMR spectra were recorded in  $\text{CDCl}_3$  unless otherwise stated with tetramethylsilane as an internal standard. Coupling constants *J* are given in Hz. FAB mass spectra were obtained using 3-nitrobenzyl alcohol as a matrix.

#### Synthesis of triaryl(3-oxoalkyl)bismuthonium salts **4**

To a stirred solution of the triarylbi-muth difluoride **2** (1 mmol) in  $\text{CH}_2\text{Cl}_2$  (5  $\text{cm}^3$ ) at  $0^\circ\text{C}$  was added trimethylsilyl triflate (0.19  $\text{cm}^3$ , 1 mmol) or boron trifluoride–diethyl ether (0.12  $\text{cm}^3$ , 1 mmol). This was followed after 30 min, by the siloxycyclopropane **3** (1 mmol) after which the resulting mixture was stirred for further 2–10 h at ambient temperature to complete the reaction. The solvent was removed under reduced pressure to leave an oily residue, which was chromatographed on a short silica gel column using  $\text{CH}_2\text{Cl}_2$  as the eluent. The eluate was evaporated under reduced pressure to leave a crystalline solid, which was purified by recrystallization from  $\text{Et}_2\text{O}-\text{CH}_2\text{Cl}_2$  (5:1) to afford the corresponding triaryl(3-oxoalkyl)-bismuthonium salt **4** in the yield listed in Table 1.

**2-(Isopropoxycarbonyl)ethyl(triphenyl)bismuthonium trifluoromethanesulfonate 4a.** Mp  $119-120^\circ\text{C}$ ;  $\delta_{\text{H}}$  1.08 (6 H, d, *J* 6.3), 3.76 (2 H, br s), 4.02 (2 H, t, *J* 6.2), 4.88 (1 H, sept, *J* 6.3), 7.48–7.62 (9 H, m) and 7.73–7.84 (6 H, m);  $\delta_{\text{C}}$  21.5, 31.1, 39.5, 70.5, 131.4, 131.5, 136.0, 140.3 ( $\text{BiC}_{\text{ipso}}$ ) and 175.1;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1719 (C=O), 1439, 1375, 1279, 1258, 1198, 1150, 1111, 1030, 727 and 637;  $\nu_{\text{C=O}}(\text{CHCl}_3)/\text{cm}^{-1}$  1700; *m/z* (FAB) 555 ( $\text{M}^+ - \text{OTf}$ ), 363, 286 and 209 (Found: C, 42.4; H, 3.6.  $\text{C}_{25}\text{H}_{26}\text{BiF}_3\text{O}_5\text{S}$  requires C, 42.6; H, 3.7%).

**4,4-Dimethyl-3-oxopentyl(triphenyl)bismuthonium trifluoromethanesulfonate 4b.** Mp  $130-131^\circ\text{C}$ ;  $\delta_{\text{H}}$  0.97 (9 H, s), 3.85 (2 H, t, *J* 5.9), 4.10 (2 H, br s), 7.48–7.63 (9 H, m) and 7.75–7.85 (6 H, m);  $\delta_{\text{C}}$  26.2, 34.4, 37.4, 43.9, 131.4, 131.5, 136.0, 140.2 ( $\text{BiC}_{\text{ipso}}$ ) and 218.5;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1692 (C=O), 1478, 1437, 1275, 1256, 1157, 1144, 1028, 994, 741, 723 and 637;  $\nu_{\text{C=O}}(\text{CHCl}_3)/\text{cm}^{-1}$  1686; *m/z* (FAB) 553 ( $\text{M}^+ - \text{OTf}$ ), 399, 363, 286 and 209 (Found: C, 44.4; H, 4.0.  $\text{C}_{26}\text{H}_{28}\text{BiF}_3\text{O}_4\text{S}$  requires C, 44.45; H, 4.0%).

**4,4-Dimethyl-3-oxopentyl(triphenyl)bismuthonium tetrafluoroborate 4c.** Mp  $144-146^\circ\text{C}$ ;  $\delta_{\text{H}}$  0.96 (9 H, s), 3.88 (2 H, t, *J* 5.5), 4.05 (2 H, br s), 7.47–7.63 (9 H, m) and 7.75–7.85 (6 H, m);  $\delta_{\text{C}}$  26.2, 34.2, 35.8, 43.9, 131.4, 131.5, 136.0, 139.4 ( $\text{BiC}_{\text{ipso}}$ ) and 218.7;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1684 (C=O), 1478, 1435, 1233, 1150–950, 727 and 687;  $\nu_{\text{C=O}}(\text{CHCl}_3)/\text{cm}^{-1}$  1686; *m/z* (FAB) 553 ( $\text{M}^+ - \text{BF}_4$ ), 399, 363, 286 and 209 (Found: C, 46.7; H, 4.3.  $\text{C}_{25}\text{H}_{28}\text{BBiF}_4\text{O}$  requires C, 46.9; H, 4.4%).

**3-Oxo-3-phenylpropyl(triphenyl)bismuthonium tetrafluoroborate 4d.** Mp  $154-155^\circ\text{C}$ ;  $\delta_{\text{H}}$  4.05 (2 H, t, *J* 6.0), 4.53 (2 H, br s), 7.35–7.70 (12 H, m), 7.75–7.85 (6 H, m) and 7.91 (2 H, m);  $\delta_{\text{C}}$  35.4, 35.7, 128.6, 128.9, 131.4, 131.5, 132.5, 134.8, 135.9, 139.7 ( $\text{BiC}_{\text{ipso}}$ ) and 201.7;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1659 (C=O), 1474, 1435,

1221, 1150–900, 727 and 685;  $\nu_{\text{C=O}}(\text{CHCl}_3)/\text{cm}^{-1}$  1667;  $m/z$  (FAB) 573 ( $\text{M}^+ - \text{BF}_4$ ), 363, 286 and 209 (Found: C, 48.8; H, 3.6.  $\text{C}_{27}\text{H}_{24}\text{BBiF}_4\text{O}$  requires C, 49.1; H, 3.7%).

**4,4-Dimethyl-3-oxopentyltris(4-methylphenyl)bismuthonium tetrafluoroborate 4e.** Mp 138–139 °C;  $\delta_{\text{H}}$  0.96 (9 H, s), 2.40 (9 H, s), 3.80 (2 H, t,  $J$  5.9), 4.03 (2 H, br s), 7.37 (6 H, d,  $J$  7.9) and 7.64 (6 H, d,  $J$  7.9);  $\delta_{\text{C}}$  21.5, 26.2, 34.1, 34.6, 43.9, 132.1, 133.1, 135.7, 141.9 ( $\text{BiC}_{\text{ipso}}$ ) and 218.6;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1686 (C=O), 1489, 1395, 1235, 1190, 1150–950 and 797;  $m/z$  (FAB) 595 ( $\text{M}^+ - \text{BF}_4$ ), 413, 391, 300 and 209 (Found: C, 49.0; H, 4.9.  $\text{C}_{28}\text{H}_{34}\text{BBiF}_4\text{O}$  requires C, 49.3; H, 5.0%).

#### Synthesis of isopropoxycarbonylmethyl(triphenyl)bismuthonium trifluoromethanesulfonate 1c

This compound was prepared according to the reported procedure,<sup>8</sup> using 1-isopropoxy-1-trimethylsilyloxyethene as the alkylating reagent; mp 103–104 °C;  $\delta_{\text{H}}$  1.05 (6 H, d,  $J$  6.2), 4.70 (2 H, s), 4.82 (1 H, sept,  $J$  6.2) and 7.50–7.85 (15 H, m);  $\delta_{\text{C}}$  21.4, 43.4, 71.5, 131.9, 132.1, 135.8, 139.4 ( $\text{BiC}_{\text{ipso}}$ ) and 168.1;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1725 (C=O), 1474, 1429, 1380–1200, 1190–1120, 1051, 1032, 729, 695, 662 and 637;  $m/z$  (FAB) 541 ( $\text{M}^+ - \text{OTf}$ ), 363, 286 and 209 (Found: C, 41.7; H, 3.45.  $\text{C}_{24}\text{H}_{24}\text{BiF}_3\text{O}_3\text{S}$  requires C, 41.75; H, 3.5%).

#### <sup>1</sup>H NMR monitoring of the decomposition of the triflate 4a

A  $\text{CDCl}_3$  (0.5  $\text{cm}^3$ ) solution of the triflate **4a** (35 mg, 0.050 mmol) in an NMR sample tube was kept at 25 °C and the progress of the thermal decomposition was monitored by NMR at intervals of *ca.* 1 h. The formation of triphenylbismuthane **6** and 2-(isopropoxycarbonyl)ethyl triflate **7** was quantitative. The decay rate constant of the salt **4a** was estimated from the integrated values of the methyl protons of compounds **4a** and **7**. Compound **7** was identified by direct comparison with an authentic specimen synthesized from isopropyl 3-iodopropionate and  $\text{AgOTf}$  in  $\text{CH}_2\text{Cl}_2$ ;  $\delta_{\text{H}}$  1.27 (6 H, d,  $J$  6.2,  $\text{CHMe}_2$ ), 2.80 (2 H, t,  $J$  6.0,  $\text{CH}_2\text{C=O}$ ), 4.78 (2 H, t,  $J$  6.0,  $\text{TFoCH}_2$ ) and 5.08 (1 H, sept,  $J$  6.2,  $\text{CHMe}_2$ ).

In  $\text{CD}_3\text{OD}$  (0.5  $\text{cm}^3$ ), the NMR monitoring was performed at *ca.* 5 min intervals and the decrease of the triflate **4a** (35 mg, 0.050 mmol) was found to obey first-order kinetics ( $k = 2 \times 10^{-4} \text{ s}^{-1}$ ). After 60 min, about 50% of the triflate **4a** was consumed and the products **6**, **8a**, **9a** and **10a** were formed in the respective (NMR) yields of 33, 42, 8 and 17%. The final product yields were 16, 81, 14 and 84%, respectively, with benzene also being produced. Compounds **8a**, **9a** and **10a** were identified by comparison with authentic specimens. Compound **8a**,<sup>19</sup>  $\delta_{\text{H}}(\text{CD}_3\text{OD})$  1.23 (6 H, d,  $J$  6.3,  $\text{CHMe}_2$ ), 2.51 (2 H, t,  $J$  6.2,  $\text{CH}_2\text{C=O}$ ), 3.63 (2 H, t,  $J$  6.2,  $\text{CH}_2\text{OCD}_3$ ) and 4.99 (1 H, sept,  $J$  6.3,  $\text{CHMe}_2$ ). The methoxyl protons of the non-deuteriated compound appeared at  $\delta_{\text{H}}(\text{CD}_3\text{OD})$  3.40 (3 H, s). Compound **9a**,<sup>19</sup>  $\delta_{\text{H}}(\text{CD}_3\text{OD})$  1.26 (6 H, d,  $J$  6.3,  $\text{CHMe}_2$ ), 5.03 (1 H, sept,  $J$  6.3,  $\text{CHMe}_2$ ), 5.84 (1 H, dd,  $J$  10.2 and 2.0, *trans*-CH=CHH), 6.11 (1 H, dd,  $J$  17.2 and 10.2, CH=CH<sub>2</sub>) and 6.35 (1 H, dd,  $J$  17.2 and 2.0, *cis*-CH=CHH). Compound **10a** was obtained from triphenylbismuthane **6** and triflic acid;  $\delta_{\text{H}}(\text{CD}_3\text{OD})$  7.51 (2 H, t,  $J$  7.5), 7.87 (4 H, t,  $J$  7.6) and 8.37 (4 H, m).

Since the triflate **4a** (35 mg, 0.050 mmol) completely decomposed in a  $[\text{H}_6]$ -DMSO (0.5  $\text{cm}^3$ ) within 1 min, the decay rate could not be determined. NMR yields of the products **6**, **9a**, **10a** and **11a** were 84, 17, 16 and 82%, respectively. Compound **11a** was identified by comparison with an authentic specimen synthesized from DMSO, isopropyl 3-iodopropionate and  $\text{AgOTf}$  in  $\text{CH}_2\text{Cl}_2$ . Compound **9a**,  $\delta_{\text{H}}([\text{H}_6]\text{-DMSO})$  1.22 (6 H, d,  $J$  6.2,  $\text{CHMe}_2$ ), 4.96 (1 H, sept,  $J$  6.2,  $\text{CHMe}_2$ ), 5.89 (1 H, dd,  $J$  9.9 and 2.1, *trans*-CH=CHH), 6.12 (1 H, dd,  $J$  17.1 and 9.9, CH=CH<sub>2</sub>) and 6.31 (1 H, dd,  $J$  17.1 and 2.1, *cis*-CH=CHH). Compound **11a**,  $\delta_{\text{H}}([\text{H}_6]\text{-DMSO})$  1.21 (6 H, d,  $J$  6.2,  $\text{CHMe}_2$ ), 2.78 (2 H, t,  $J$  5.7,  $\text{CH}_2\text{C=O}$ ), 4.47

(2 H, t,  $J$  5.7,  $\text{CH}_2\text{O}$ ) and 4.95 (1 H, sept,  $J$  6.2,  $\text{CHMe}_2$ ). The methyl protons of the non-deuteriated compound appeared at  $\delta_{\text{H}}([\text{H}_6]\text{-DMSO})$  3.29 (6 H, s).

#### <sup>1</sup>H NMR monitoring of the decomposition of the tetrafluoroborate 4d

The tetrafluoroborate **4d** is comparatively stable in  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ , but it undergoes reductive coupling in MeOH, DMSO and DMF within a minute to a few hours. In  $\text{CD}_3\text{OD}$  (0.5  $\text{cm}^3$ ), the NMR monitoring was performed at *ca.* 5 min intervals and the decrease of **4d** (33 mg, 0.050 mmol) obeyed first-order kinetics ( $k = 5 \times 10^{-4} \text{ s}^{-1}$ ). After 75 min, compound **4d** was completely consumed, and the products **6**, **8b**, **9b** and **10b** were formed in the respective (NMR) yields of 10, 66, 12 and 90%. Benzene was an additional product. Compounds **8b** and **9b** were identified by comparison with authentic specimens.<sup>20,21</sup> Because of its sensitivity to air, compound **10b** was identified as a hexamethylphosphoric triamide (HMPA) complex **10b**·(HMPA)<sub>2</sub>.<sup>22</sup> Compound **8b**,<sup>20</sup>  $\delta_{\text{H}}(\text{CD}_3\text{OD})$  3.36 (2 H, t,  $J$  6.2,  $\text{CH}_2\text{C=O}$ ), 3.80 (2 H, t,  $J$  6.2,  $\text{CH}_2\text{OCD}_3$ ), 7.45–7.63 (3 H, m, Ph) and 7.95–8.03 (2 H, m, Ph). The methoxyl protons of the non-deuteriated compound appeared at  $\delta_{\text{H}}$  3.35 (3 H, s). Compound **9b**,<sup>21</sup>  $\delta_{\text{H}}(\text{CD}_3\text{OD})$  5.97 (1 H, dd,  $J$  10.6 and 1.9, *trans*-CH=CHH), 6.40 (1 H, dd,  $J$  17.2 and 1.9, *cis*-CH=CHH), 7.31 (1 H, dd,  $J$  17.2 and 10.6, CH=CH<sub>2</sub>), 7.46–7.68 (3 H, m, Ph) and 7.94–8.03 (2 H, m, Ph). Compound **10b**,  $\delta_{\text{H}}(\text{CD}_3\text{OD})$  7.51 (2 H, t,  $J$  7.5), 7.87 (4 H, t,  $J$  7.6) and 8.37 (4 H, m). Complex **10b**·(HMPA)<sub>2</sub>,<sup>22</sup>  $\delta_{\text{H}}$  2.48 (36 H, d,  $J$  9.8, Me), 7.38 (2 H, t,  $J$  7.3, Ph), 7.74 (4 H, t,  $J$  7.3, Ph) and 8.28 (4 H, t,  $J$  7.3, Ph).

Since the tetrafluoroborate **4d** (33 mg, 0.050 mmol) in  $[\text{H}_6]$ -DMSO (0.5  $\text{cm}^3$ ) completely decomposed within 1 min, the decay rate could not be determined. Products **6**, **9b**, **10b** and **11b** were formed in 87, 51, 13 and 32% (NMR) yields, respectively. Compound **11b** was identified by comparison with an authentic specimen synthesized from DMSO, 3-iodo-1-phenylpropan-1-one and  $\text{AgBF}_4$  in  $\text{CH}_2\text{Cl}_2$ . Compound **9b**,  $\delta_{\text{H}}([\text{H}_6]\text{-DMSO})$  5.99 (1 H, dd,  $J$  10.5 and 2.0, *trans*-CH=CHH), 6.35 (1 H, dd,  $J$  17.1 and 2.0, *cis*-CH=CHH), 7.39 (1 H, dd,  $J$  17.1 and 10.5, CH=CH<sub>2</sub>), 7.50–7.72 (3 H, m, Ph) and 7.95–8.05 (2 H, m, Ph). Compound **11b**,  $\delta_{\text{H}}([\text{H}_6]\text{-DMSO})$  3.58 (2 H, t,  $J$  5.6,  $\text{CH}_2\text{C=O}$ ), 4.65 (2 H, t,  $J$  5.6,  $\text{CH}_2\text{O}$ ), 7.48–7.65 (3 H, m, Ph) and 7.95–8.04 (2 H, m, Ph). The methyl protons of the non-deuteriated compound appeared at  $\delta_{\text{H}}([\text{H}_6]\text{-DMSO})$  3.30 (6 H, s).

#### Decomposition of the tetrafluoroborate 4d in DMF

A solution of the tetrafluoroborate **4d** (132 mg, 0.20 mmol) in DMF (2  $\text{cm}^3$ ) was stirred for 1 h at room temperature. The resulting mixture was diluted with water (10  $\text{cm}^3$ ) and extracted with  $\text{Et}_2\text{O}$  (5  $\text{cm}^3 \times 3$ ). The combined extracts were washed with water (5  $\text{cm}^3 \times 2$ ), dried ( $\text{MgSO}_4$ ) and evaporated under reduced pressure to leave an oily residue, which was chromatographed on silica gel using hexane–ethyl acetate (100:0–80:20) as the eluent to give the bismuthane **6** (62 mg, 70%), the enone **9b** (12 mg, 45%) and the formate **12** (8 mg, 22%). Compound **12**,  $R_f$  0.2 (hexane–ethyl acetate, 80:20);  $\delta_{\text{H}}$  3.36 (2 H, t,  $J$  6.3,  $\text{CH}_2\text{C=O}$ ), 4.63 (2 H, t,  $J$  6.3,  $\text{CH}_2\text{O}$ ), 7.48 (2 H, t,  $J$  7.6, Ph), 7.60 (1 H, t,  $J$  7.0, Ph), 7.90–8.00 (2 H, m, Ph) and 8.05 (1 H, s, CHO);  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  1723, 1684, 1375, 1170 and 691;  $m/z$  (EI) 178 ( $\text{M}^+$ ), 132, 105 and 77.

#### Reaction of the tetrafluoroborate 4d with dimethyl sulfide 13

To a solution of tetrafluoroborate **4d** (66 mg, 0.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (3  $\text{cm}^3$ ) was added dimethyl sulfide **13** (0.073  $\text{cm}^3$ , 1.0 mmol) at room temperature. Colourless crystals which immediately separated were filtered off, washed with  $\text{CH}_2\text{Cl}_2$  (3  $\text{cm}^3 \times 3$ ), and dried *in vacuo* to give dimethyl(3-oxo-3-phenylpropyl)sulfonium tetrafluoroborate **14** (26 mg, 92%).

The filtrate was concentrated under reduced pressure to leave a residue, which was crystallized from MeOH to give the bismuthane **6** (42 mg, 98%). Compound **14**. Mp 122–123 °C;  $\delta_{\text{H}}([\text{}^2\text{H}_6\text{]}\text{-DMSO})$  2.97 (6 H, s, Me), 3.55–3.76 (4 H, m,  $\text{CH}_2\text{CH}_2$ ), 7.56 (2 H, t,  $J$  7.2, Ph), 7.69 (1 H, t,  $J$  7.0, Ph) and 8.02 (2 H, d,  $J$  7.1, Ph);  $\delta_{\text{C}}([\text{}^2\text{H}_6\text{]}\text{-DMSO})$  24.8, 32.6, 37.2, 128.1, 128.6, 133.7, 135.5 and 196.4;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1682, 1431, 1362, 1210, 1150–950, 750, 691 and 629;  $m/z$  (FAB) 195 ( $\text{M}^+ - \text{BF}_4$ ).

#### Reaction of the tetrafluoroborate **4d** with sodium benzenesulfinate **15**

A mixture of tetrafluoroborate **4d** (66 mg, 0.10 mmol), sodium benzenesulfinate dihydrate **15** (200 mg, 1.0 mmol) and DMF (3  $\text{cm}^3$ ) was stirred at room temperature for 13 h and then diluted with water (5  $\text{cm}^3$ ). The organic layer was extracted with diethyl ether (3  $\text{cm}^3 \times 3$ ) and the combined extracts were washed with brine (3  $\text{cm}^3 \times 3$ ), dried ( $\text{MgSO}_4$ ), and concentrated under reduced pressure to leave a crystalline residue, which was chromatographed on silica gel using hexane–ethyl acetate (100:0–80:20) as the eluent to give triphenylbismuthane **6** (41 mg, 93%) and 1-phenyl-3-phenylsulfonylpropan-1-one **16** (27 mg, 99%). Compound **16**.  $R_f$  0.2 (hexane–ethyl acetate, 80:20); mp 96–97 °C (lit.,<sup>23</sup> 97.8 °C);  $\delta_{\text{H}}$  3.42–3.65 (4 H, m,  $\text{CH}_2\text{CH}_2$ ), 7.47 (2 H, t,  $J$  7.7, Ph), 7.52–7.72 (4 H, m, Ph) and 7.88–8.02 (4 H, m, Ph);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1688, 1308, 1260, 1142, 745 and 689;  $m/z$  (EI) 246 ( $\text{M}^+ - 28$ ), 105 and 77.

#### Reaction of the tetrafluoroborate **4d** with potassium halides

A mixture of tetrafluoroborate **4d** (66 mg, 0.10 mmol), potassium halide **17** (1.0 mmol) and DMF (2  $\text{cm}^3$ ) was stirred at room temperature for 8 h and then poured into water (5  $\text{cm}^3$ ). The organic layer was separated, extracted with  $\text{Et}_2\text{O}$  (3  $\text{cm}^3 \times 3$ ) and the combined extracts were washed with water (3  $\text{cm}^3 \times 3$ ), dried ( $\text{MgSO}_4$ ), and concentrated under reduced pressure to leave a mixture of the bismuthane **6**, the enone **9b**, the formate **12** and the 3-halogeno-1-phenylpropan-1-one **18**. The yields of these products are summarized in Table 4. Compounds **18a–c** were identified by comparison with authentic specimens purchased commercially or synthesized from **18a** and the corresponding potassium halide in acetone.

Compound **18a**.  $\delta_{\text{H}}$  3.44 (2 H, t,  $J$  6.8,  $\text{CH}_2\text{C}=\text{O}$ ), 3.91 (2 H, t,  $J$  6.8,  $\text{CH}_2\text{Cl}$ ), 7.40–7.65 (3 H, m, Ph) and 7.95 (2 H, m, Ph). Compound **18b**.  $\delta_{\text{H}}$  3.56 (2 H, m,  $\text{CH}_2\text{C}=\text{O}$ ), 3.73 (2 H, m,  $\text{CH}_2\text{Br}$ ), 7.40–7.65 (3 H, m, Ph) and 7.95 (2 H, m, Ph). Compound **18c**.  $\delta_{\text{H}}$  3.47 (2 H, m,  $\text{CH}_2\text{C}=\text{O}$ ), 3.63 (2 H, m,  $\text{CH}_2\text{I}$ ), 7.42–7.65 (3 H, m, Ph) and 7.94 (2 H, m, Ph).

#### Reaction of the tetrafluoroborate **4d** with $\text{KOBU}^t$

To a suspension of the tetrafluoroborate **4d** (66 mg, 0.10 mmol) in THF (5  $\text{cm}^3$ ) was added  $\text{KOBU}^t$  (12 mg, 0.10 mmol) at  $-78$  °C and the resulting mixture was allowed to warm to room temperature. The solvent was removed under reduced pressure and the residue was extracted with  $\text{Et}_2\text{O}$  (10  $\text{cm}^3$ ). Evaporation of the extract afforded an oily residue, which was chromatographed on silica gel using hexane–ethyl acetate (100:0–80:20) as the eluent to give the bismuthane **6** (43 mg, 98%) and the enone **9b** (11 mg, 83%). Compound **9b**,<sup>21</sup>  $R_f$  0.4 (hexane–ethyl acetate, 80:20);  $\delta_{\text{H}}$  5.92 (1 H, dd,  $J$  10.6 and 1.8), 6.43 (1 H, dd,  $J$  17.2 and 1.8), 7.16 (1 H, dd,  $J$  17.2 and 10.6), 7.42–7.65 (3 H, m) and 7.90–7.98 (2 H, m).

#### X-Ray crystallography of compound **4a**

A crystal of dimensions 0.400  $\times$  0.130  $\times$  0.050 mm, grown from  $\text{Et}_2\text{O}-\text{CH}_2\text{Cl}_2$  (2:1), was coated with collodion.

**Crystal data.**  $\text{C}_{25}\text{H}_{28}\text{BiF}_3\text{O}_5\text{S}$ ,  $M = 704.51$ . Triclinic, space group  $P\bar{1}$ ,  $a = 11.192(4)$ ,  $b = 15.028(3)$ ,  $c = 8.657(3)$  Å,  $\alpha = 97.26(2)$ ,  $\beta = 98.82(4)$ ,  $\gamma = 108.96(2)$ °,  $V = 1336.4(8)$  Å<sup>3</sup> (by

least-squares refinement on diffractometer angles for 22 automatically centred reflections in the range  $20.02 < 2\theta < 24.26^\circ$ , 298 K, Mo-K $\alpha$  radiation,  $\lambda = 0.71069$  Å,  $Z = 2$ ,  $D_c = 1.751$  g  $\text{cm}^{-3}$ . Prisms,  $\mu(\text{Mo-K}\alpha, \lambda = 0.71069 \text{ \AA}) = 67.02$   $\text{cm}^{-1}$ ,  $F(000) = 684$ .

**Data collection and processing.** Intensity data were collected on a Rigaku AFC5R diffractometer using graphite-monochromated Mo-K $\alpha$  radiation from a fine focus anode of 12 kW type rotating anode generator with the  $\omega$ - $2\theta$  scan technique to a maximum  $2\theta$  value of  $55.0^\circ$ . Reflection intensities of standard reflections decayed gradually when the  $2\theta$  value was within  $50^\circ$  but decayed rapidly when it was beyond  $50^\circ$ . The intensity reduction was from 100 to 95% for a  $2\theta$  value within  $50^\circ$  and from 95% to 79% for a  $2\theta$  from 50 to  $55^\circ$ . Therefore, the reflection data beyond a  $2\theta$  value of  $50^\circ$  were disregarded. The azimuthal ( $\psi$ -scan) data at the end of intensity data collection were not so reliable because of the intensity decay mentioned above. Therefore, correction for the absorption was made by using the  $\psi$ -scan data of a single reflection observed at the beginning of the experiment; transmission factors were 0.623–1.000. Scans of  $(1.00 + 0.30 \tan \theta)$  were made at a speed of  $16.0^\circ \text{ min}^{-1}$  (in  $\omega$ ). Of the 6413 reflections which were collected, 4675 were unique ( $R_{\text{int}} = 0.033$ ). Data were corrected for Lorentz and polarization effects.

**Structure analysis and refinement.** The structure was solved by a combination of the Patterson method and direct methods.<sup>24</sup> The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3401 observed reflections [ $I > 3.00\sigma(I)$ ] and 317 variable parameters and converged with unweighted and weighted agreement factors of  $R = 0.037$  and  $R_w = 0.037$ . The weighting scheme,  $w = 1/\sigma^2(F_o)$ , was employed. Neutral atom-scattering factors were taken from Cromer and Waber.<sup>25</sup> Anomalous dispersion effects were included in  $F_{\text{calc}}$ .<sup>26</sup> The values for  $\Delta f'$  and  $\Delta f''$  were those of Cromer.<sup>27</sup> All calculations were performed using the TEXSAN<sup>28</sup> crystallographic software package of Molecular Structure Corporation. The PLUTO<sup>29</sup> program was used to obtain Fig 1. Selected bond lengths and bond angles are given in Table 2. All tables required have been deposited at the Cambridge Crystallographic Data Centre. §

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§ For details, see Instructions for Authors (1995), *J. Chem. Soc., Perkin Trans. 1*, 1995, Issue 1.

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