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

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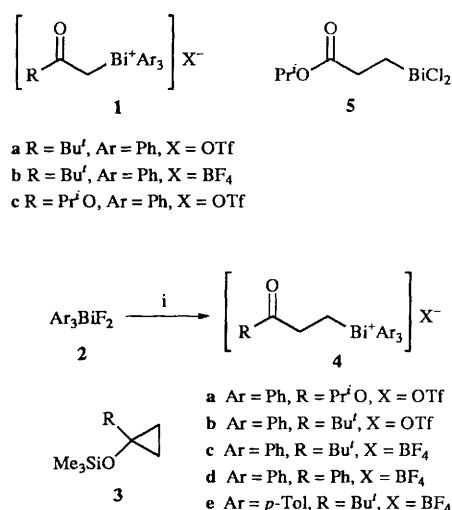
Treatment of triarylbismuth difluorides 2 with siloxycyclopropanes 3 in the presence of trimethylsilyl trifluoromethanesulfonate (triflate) or boron trifluoride–diethyl ether gave the corresponding triaryl(3-oxoalkyl)bismuthonium salts 4 as crystals. X-Ray crystallographic analysis of the triflate 4a 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, α,β-unsaturated carbonyl compounds 9a,b, diphenylbismuth triflate 10a or tetrafluoroborate 10b and alkoxysulfonium 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^t, the salt 4d underwent facile β-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 inaccessability. Published syntheses of alkylbismuthonium salts involve the alkylation of tertiary bismuthanes[1-4] and the metathetical reaction of triphenylbismuth dichloride in dry acetone;[5] 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$_{alkyl}$ bond.[6] Recently, we have reported an efficient method for the preparation of triaryl(2-oxoalkyl)bismuthonium salts 1 from triarylbismuth difluorides 2 and silyl enol ethers.[7,8] 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,[7-11] 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.[7,8] 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.[12,13] As shown in Scheme 1, treatment of triarylbismuth difluorides 2 with the cyclopropane 3 in the presence of trimethylsilyl triflate (Me$_3$SiOTf) or boron trifluoride–diethyl ether (BF$_3$·OEt$_2$) led to triaryl(3-oxoalkyl)-bismuthonium triflates 4a,b and tetrafluoroborates 4c–e in the

a R = Bu^t, Ar = Ph, X = OTf
b R = Bu^t, Ar = Ph, X = BF$_4$
c R = Pr^{i}O, Ar = Ph, X = OTf

a Ar = Ph, R = Pr^{i}O, X = OTf
b Ar = Ph, R = Bu^t, X = OTf
c Ar = Ph, R = Bu^t, X = BF$_4$
d Ar = Ph, R = Ph, X = BF$_4$
e Ar = p-Tol, R = Bu^t, X = BF$_4$

Scheme 1 *Reagents and conditions:* i, Lewis acid (Me$_3$SiOTf or BF$_3$·OEt$_2$) then 1-substituted 1-trimethylsiloxycyclopropane 3, CH$_2$Cl$_2$, 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$^+$ − OTf fragment from the triflate 4a,b or M$^+$ − BF$_4$ 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^{-1} (OTf$^-$) and 1150–950 cm^{-1} (BF$_4^-$),

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

Difluoride **2**	Lewis acid	Cyclopropane **3**	Salt **4**	Yield (%)[a]
2a (Ar = Ph)	Me₃SiOTf	**3a** (R = OPr^i)	**4a**	47
2a	Me₃SiOTf	**3b** (R = Bu^t)	**4b**	12
2a	BF₃·OEt₂	**3b**	**4c**	86
2a	BF₃·OEt₂	**3c** (R = Ph)	**4d**	80
2b (Ar = p-Tol)	BF₃·OEt₂	**3b**	**4e**	76

[a] 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. ¹³C NMR spectra showed a signal at δ_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 CHCl₃ solutions, the C=O stretching bands were shifted to lower frequencies ($\Delta \nu$ = 15–25 cm⁻¹) 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⁻¹).[12]

X-Ray structure analysis of compound 4a

In earlier papers,[7,8] 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 sp³ 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**.[8] 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),[14] 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
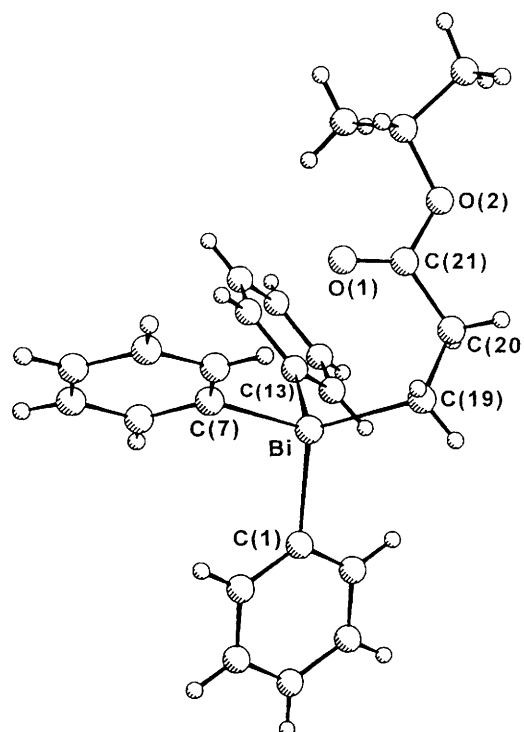
Fig. 1 A PLUTO drawing of compound **4a** with the atomic numbering scheme. Triflate anion is omitted for clarity.

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 CH₂Cl₂ or CHCl₃ 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 CDCl₃ to give the bismuthane **6** and the ester **7** with a rate constant k =

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

Salt **4**	Solvent	k/s^{-1}	Products[a]
4a	$CDCl_3$	8×10^{-6}	**6** (100), **7** (100)
4a	CD_3OD	2×10^{-4}	**6** (16), **8a** (81), **9a** (14), **10a** (84)
4a	$[^2H_6]$-DMSO	—[b]	**6** (84), **9a** (17), **10a** (16), **11a** (82)
4d	CD_3OD	5×10^{-4}	**6** (10), **8b** (66), **9b** (12), **10b** (90)
4d	$[^2H_6]$-DMSO	—[b]	**6** (87), **9b** (51), **10b** (13), **11b** (32)

[a] Numerals in parentheses refer to the yields based on the salt **4** at final stage of decomposition. [b] Not determined.
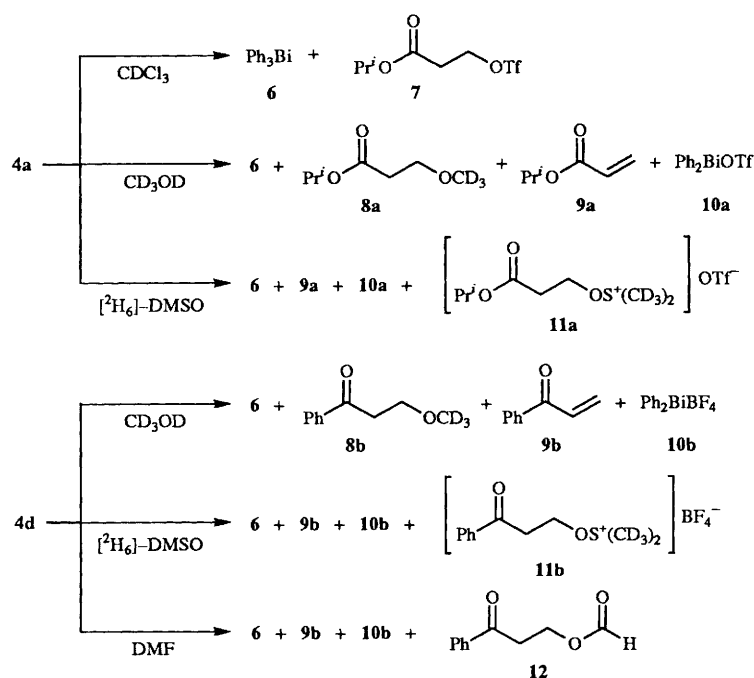
Scheme 2

8×10^{-6} s^{-1}. This implies that the triflate anion attacks the alkyl carbon atom adjacent to the bismuth *via* the reductive elimination pathway. In CD_3OD the triflate **4a** underwent decomposition at a faster rate ($k = 2 \times 10^{-4}$ 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 $[^2H_6]$-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$_{\text{alkyl}}$ bond, resulting in the formation of the coupling products with simultaneous elimination of the bismuthane **6**. The formation of the α,β-unsaturated ester **9a** in moderate amounts in DMSO suggests the weak base character of this solvent.† Although the tetrafluoroborate **4d** did not decompose in $CHCl_3$ and CH_2Cl_2, it decomposed in CD_3OD and $[^2H_6]$-DMSO in a manner similar to that of the triflate **4a** (Scheme 2). The salt **4d** underwent a coupling reaction in CD_3OD with the first-order kinetics ($k = 5 \times 10^{-4}$ 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 $[^2H_6]$-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 triarylbismuthane 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**.‡ The elongation of one methylene unit in the oxoalkyl chain

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† It has been reported that some β-stannyl and β-telluro ketones undergo β-elimination smoothly by treatment with DMSO in THF to give α,β-unsaturated ketones.[15]

‡ As an example, when a solution of the triflate **1c** in $CDCl_3$ (*ca.* 0.05 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 $k = 3 \times 10^{-7}$ s^{-1}.

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

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

[a] NMR yield based on unrecovered salt **4d**. [b] 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).
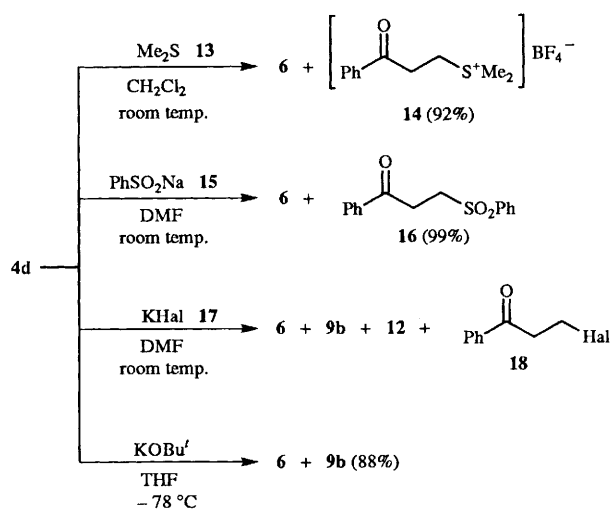
Scheme 3

Treatment of the salt **4d** with dimethyl sulfide **13** in CH$_2$Cl$_2$ readily gave dimethyl(3-oxo-3-phenylpropyl)sulfonium tetrafluoroborate **14** in 92% yield. When treated with sodium benzenesulfinate **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 I > Br > Cl, whereas those of the enone **9b** increased in the order I < Br < Cl. From a control experiment, the product **12** was found to be derived from salt **4d** and DMF. Treatment of the salt **4d** with KOBu^t in THF at −78 °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 α,β-epoxy ketone is formed.[9] 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

Synthesis of triaryl(3-oxoalkyl)bismuthonium salts 4

To a stirred solution of the triarylbismuth difluoride **2** (1 mmol) in CH$_2$Cl$_2$ (5 cm^3) at 0 °C was added trimethylsilyl triflate (0.19 cm^3, 1 mmol) or boron trifluoride–diethyl ether (0.12 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 CH$_2$Cl$_2$ as the eluent. The eluate was evaporated under reduced pressure to leave a crystalline solid, which was purified by recrystallization from Et$_2$O–CH$_2$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 °C; δ_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); δ_C 21.5, 31.1, 39.5, 70.5, 131.4, 131.5, 136.0, 140.3 (BiC$_{ipso}$) and 175.1; ν_{max}(KBr)/cm^{-1} 1719 (C=O), 1439, 1375, 1279, 1258, 1198, 1150, 1111, 1030, 727 and 637; $\nu_{C=O}$(CHCl$_3$)/cm^{-1} 1700; m/z (FAB) 555 (M$^+$ − OTf), 363, 286 and 209 (Found: C, 42.4; H, 3.6. C$_{25}$H$_{26}$BiF$_3$O$_5$S requires C, 42.6; H, 3.7%).

4,4-Dimethyl-3-oxopentyl(triphenyl)bismuthonium trifluoromethanesulfonate 4b. Mp 130–131 °C; δ_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); δ_C 26.2, 34.4, 37.4, 43.9, 131.4, 131.5, 136.0, 140.2 (BiC$_{ipso}$) and 218.5; ν_{max}(KBr)/cm^{-1} 1692 (C=O), 1478, 1437, 1275, 1256, 1157, 1144, 1028, 994, 741, 723 and 637; $\nu_{C=O}$(CHCl$_3$)/cm^{-1} 1686; m/z (FAB) 553 (M$^+$ − OTf), 399, 363, 286 and 209 (Found: C, 44.4; H, 4.0. C$_{26}$H$_{28}$BiF$_3$O$_4$S requires C, 44.45; H, 4.0%).

4,4-Dimethyl-3-oxopentyl(triphenyl)bismuthonium tetrafluoroborate 4c. Mp 144–146 °C; δ_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); δ_C 26.2, 34.2, 35.8, 43.9, 131.4, 131.5, 136.0, 139.4 (BiC$_{ipso}$) and 218.7; ν_{max}(KBr)/cm^{-1} 1684 (C=O), 1478, 1435, 1233, 1150–950, 727 and 687; $\nu_{C=O}$(CHCl$_3$)/cm^{-1} 1686; m/z (FAB) 553 (M$^+$ − BF$_4$), 399, 363, 286 and 209 (Found: C, 46.7; H, 4.3. C$_{25}$H$_{28}$BBiF$_4$O requires C, 46.9; H, 4.4%).

3-Oxo-3-phenylpropyl(triphenyl)bismuthonium tetrafluoroborate 4d. Mp 154–155 °C; δ_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); δ_C 35.4, 35.7, 128.6, 128.9, 131.4, 131.5, 132.5, 134.8, 135.9, 139.7 (BiC$_{ipso}$) and 201.7; ν_{max}(KBr)/cm^{-1} 1659 (C=O), 1474, 1435,

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

4,4-Dimethyl-3-oxopentyltris(4-methylphenyl)bismuthonium tetrafluoroborate 4e. Mp 138–139 °C; δ_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); δ_C 21.5, 26.2, 34.1, 34.6, 43.9, 132.1, 133.1, 135.7, 141.9 (BiC$_{ipso}$) and 218.6; ν_{max}(KBr)/cm^{-1} 1686 (C=O), 1489, 1395, 1235, 1190, 1150–950 and 797; m/z (FAB) 595 (M$^+$ − BF$_4$), 413, 391, 300 and 209 (Found: C, 49.0; H, 4.9. C$_{28}$H$_{34}$BBiF$_4$O requires C, 49.3; H, 5.0%).

Synthesis of isopropoxycarbonylmethyl(triphenyl)bismuthonium trifluoromethanesulfonate 1c

This compound was prepared according to the reported procedure,[8] using 1-isopropoxy-1-trimethylsiloxyethene as the alkylating reagent; mp 103–104 °C; δ_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); δ_C 21.4, 43.4, 71.5, 131.9, 132.1, 135.8, 139.4 (BiC$_{ipso}$) and 168.1; ν_{max}(KBr)/cm^{-1} 1725 (C=O), 1474, 1429, 1380–1200, 1190–1120, 1051, 1032, 729, 695, 662 and 637; m/z (FAB) 541 (M$^+$ − OTf), 363, 286 and 209 (Found: C, 41.7; H, 3.45. C$_{24}$H$_{24}$BiF$_3$O$_5$S requires C, 41.75; H, 3.5%).

^{1}H NMR monitoring of the decomposition of the triflate 4a

A CDCl$_3$ (0.5 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 AgOTf in CH$_2$Cl$_2$; δ_H 1.27 (6 H, d, J 6.2, CHMe_2), 2.80 (2 H, t, J 6.0, CH$_2$C=O), 4.78 (2 H, t, J 6.0, TfOCH$_2$) and 5.08 (1 H, sept, J 6.2, CHMe$_2$).

In CD$_3$OD (0.5 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 × 10^{-4} 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,[19] δ_H(CD$_3$OD) 1.23 (6 H, d, J 6.3, CHMe_2), 2.51 (2 H, t, J 6.2, CH$_2$C=O), 3.63 (2 H, t, J 6.2, CH$_2$OCD$_3$) and 4.99 (1 H, sept, J 6.3, CHMe$_2$). The methoxyl protons of the non-deuteriated compound appeared at δ_H(CD$_3$OD) 3.40 (3 H, s). Compound 9a,[19] δ_H(CD$_3$OD) 1.26 (6 H, d, J 6.3, CHMe_2), 5.03 (1 H, sept, J 6.3, 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$_2$) 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; δ_H(CD$_3$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 [^{2}H$_6$]-DMSO (0.5 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 AgOTf in CH$_2$Cl$_2$. Compound 9a, δ_H([^{2}H$_6$]-DMSO) 1.22 (6 H, d, J 6.2, CHMe_2), 4.96 (1 H, sept, J 6.2, 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$_2$) and 6.31 (1 H, dd, J 17.1 and 2.1, cis-CH=CHH). Compound 11a, δ_H([^{2}H$_6$]-DMSO) 1.21 (6 H, d, J 6.2, CHMe_2), 2.78 (2 H, t, J 5.7, CH$_2$C=O), 4.47

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

^{1}H NMR monitoring of the decomposition of the tetrafluoroborate 4d

The tetrafluoroborate 4d is comparatively stable in CH$_2$Cl$_2$ and CHCl$_3$, but it undergoes reductive coupling in MeOH, DMSO and DMF within a minute to a few hours. In CD$_3$OD (0.5 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 × 10^{-4} 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.[20,21] Because of its sensitivity to air, compound 10b was identified as a hexamethylphosphoric triamide (HMPA) complex 10b·(HMPA)$_2$.[22] Compound 8b,[20] δ_H(CD$_3$OD) 3.36 (2 H, t, J 6.2, CH$_2$C=O), 3.80 (2 H, t, J 6.2, CH$_2$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 δ_H 3.35 (3 H, s). Compound 9b,[21] δ_H(CD$_3$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$_2$), 7.46–7.68 (3 H, m, Ph) and 7.94–8.03 (2 H, m, Ph). Compound 10b, δ_H(CD$_3$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)$_2$,[22] δ_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 [^{2}H$_6$]-DMSO (0.5 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 AgBF$_4$ in CH$_2$Cl$_2$. Compound 9b, δ_H([^{2}H$_6$]-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$_2$), 7.50–7.72 (3 H, m, Ph) and 7.95–8.05 (2 H, m, Ph). Compound 11b, δ_H([^{2}H$_6$]-DMSO) 3.58 (2 H, t, J 5.6, CH$_2$C=O), 4.65 (2 H, t, J 5.6, CH$_2$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 δ_H([^{2}H$_6$]-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 cm^3) was stirred for 1 h at room temperature. The resulting mixture was diluted with water (10 cm^3) and extracted with Et$_2$O (5 cm^3 × 3). The combined extracts were washed with water (5 cm^3 × 2), dried (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); δ_H 3.36 (2 H, t, J 6.3, CH$_2$C=O), 4.63 (2 H, t, J 6.3, CH$_2$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); ν_{max}(neat)/cm^{-1} 1723, 1684, 1375, 1170 and 691; m/z (EI) 178 (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 CH$_2$Cl$_2$ (3 cm^3) was added dimethyl sulfide 13 (0.073 cm^3, 1.0 mmol) at room temperature. Colourless crystals which immediately separated were filtered off, washed with CH$_2$Cl$_2$ (3 cm^3 × 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; δ_H([^{2}H$_6$]-DMSO) 2.97 (6 H, s, Me), 3.55–3.76 (4 H, m, CH$_2$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); δ_C([^{2}H$_6$]-DMSO) 24.8, 32.6, 37.2, 128.1, 128.6, 133.7, 135.5 and 196.4; ν_{max}(KBr)/cm^{-1} 1682, 1431, 1362, 1210, 1150–950, 750, 691 and 629; *m/z* (FAB) 195 (M$^+$ − BF$_4$).

Reaction of the tetrafluoroborate 4d with sodium benzene-sulfinate 15

A mixture of tetrafluoroborate **4d** (66 mg, 0.10 mmol), sodium benzenesulfinate dihydrate **15** (200 mg, 1.0 mmol) and DMF (3 cm^3) was stirred at room temperature for 13 h and then diluted with water (5 cm^3). The organic layer was extracted with diethyl ether (3 cm^3 × 3) and the combined extracts were washed with brine (3 cm^3 × 3), dried (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.,[23] 97.8 °C); δ_H 3.42–3.65 (4 H, m, CH$_2$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); ν_{max}(KBr)/cm^{-1} 1688, 1308, 1260, 1142, 745 and 689; *m/z* (EI) 246 (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 cm^3) was stirred at room temperature for 8 h and then poured into water (5 cm^3). The organic layer was separated, extracted with Et$_2$O (3 cm^3 × 3) and the combined extracts were washed with water (3 cm^3 × 3), dried (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**. δ_H 3.44 (2 H, t, *J* 6.8, CH$_2$C=O), 3.91 (2 H, t, *J* 6.8, CH$_2$Cl), 7.40–7.65 (3 H, m, Ph) and 7.95 (2 H, m, Ph). Compound **18b**. δ_H 3.56 (2 H, m, CH$_2$C=O), 3.73 (2 H, m, CH$_2$Br), 7.40–7.65 (3 H, m, Ph) and 7.95 (2 H, m, Ph). Compound **18c**. δ_H 3.47 (2 H, m, CH$_2$C=O), 3.63 (2 H, m, CH$_2$I), 7.42–7.65 (3 H, m, Ph) and 7.94 (2 H, m, Ph).

Reaction of the tetrafluoroborate 4d with KOBu^t

To a suspension of the tetrafluoroborate **4d** (66 mg, 0.10 mmol) in THF (5 cm^3) was added 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 Et$_2$O (10 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**.[21] R_f 0.4 (hexane–ethyl acetate, 80:20); δ_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 × 0.130 × 0.050 mm, grown from Et$_2$O–CH$_2$Cl$_2$ (2:1), was coated with collodion.

Crystal data. C$_{25}$H$_{26}$BiF$_3$O$_5$S, *M* = 704.51. Triclinic, space group $P\bar{1}$, *a* = 11.192(4), *b* = 15.028(3), *c* = 8.657(3) Å, α = 97.26(2), β = 98.82(4), γ = 108.96(2)°, *V* = 1336.4(8) Å^3 (by

least-squares refinement on diffractometer angles for 22 automatically centred reflections in the range 20.02 < 2θ < 24.26°, 298 K, Mo-Kα radiation, λ = 0.710 69 Å), *Z* = 2, D_c = 1.751 g cm^{-3}. Prisms, μ(Mo-Kα, λ = 0.710 69 Å) = 67.02 cm^{-1}, *F*(000) = 684.

Data collection and processing. Intensity data were collected on a Rigaku AFC5R diffractometer using graphite-monochromated Mo-Kα radiation from a fine focus anode of 12 kW type rotating anode generator with the ω–2θ scan technique to a maximum 2θ value of 55.0°. Reflection intensities of standard reflections decayed gradually when the 2θ value was within 50° but decayed rapidly when it was beyond 50°. The intensity reduction was from 100 to 95% for a 2θ value within 50° and from 95% to 79% for a 2θ from 50 to 55°. Therefore, the reflection data beyond a 2θ value of 50° were disregarded. The azimuthal (ψ-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 ψ-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 θ) were made at a speed of 16.0° min^{-1} (in ω). Of the 6413 reflections which were collected, 4675 were unique (R_{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.[24] The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3401 observed reflections [*I* > 3.00σ(*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/σ^2(F_o), was employed. Neutral atom-scattering factors were taken from Cromer and Waber.[25] Anomalous dispersion effects were included in F_{calc};[26] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[27] All calculations were performed using the TEXSAN[28] crystallographic software package of Molecular Structure Corporation. The PLUTO[29] 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.§

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

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