Synthesis, X-ray Structure and Reactions of (2-Oxoalkyl)triarylbismuthonium Salts

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Treatment of triarylbismuth difluorides 1 with silyl enol ethers 2 in the presence of boron trifluoride–diethyl ether or trimethylsilyl trifluoromethanesulfonate (triflate) gave (2-oxoalkyl)triarylbismuthonium tetrafluoroborates 3 and triflates 4 in good yields. A similar reaction of the difluorides 1 with hexamethyldisiloxane in the presence of the latter acid reagent led to the formation of oxybis-(triarylbismuth) ditriflates 5. X-Ray cyrstallographic analyses of compounds 3a, 4a and 5a showed that the first two onium salts have a distorted tetrahedral geometry and the last, a μ-oxo type compound, has a distorted trigonal bipyramidal geometry around the bismuth centre. The stability of these bismuthonium salts may reasonably be attributed to the intramolecular coordinative interaction between the bismuth and oxygen atoms and also low nucleophilicity of the counter ions employed. The bismuthonium salt 3f readily underwent onium exchange with the phosphine 6 and the sulfide 9 to afford the corresponding phosphonium and sulfonium salts 7 and 10. The salts 3 and 4 also underwent coupling with a variety of nucleophiles such as the enolate 11, piperidine 13, the phenoxides 15, the thiolates 17, the sulfinate 19 and the halides 21 to afford the corresponding α-substituted ketones 12, 14, 16, 18, 20 and 22 in moderate to good yields, together with a good recovery of triphenylbismuthine 8.

Of all the onium-type compounds derived from 15th and 16th elements, bismuthonium is the least well known. Except for sporadic reports,[1–6] the literature to date contains little information on the properties, structures and reactivities of bismuthonium salts probably because of the difficulty of access to this class of compounds. The first successful isolation of alkylbismuthonium compounds was reported by Goel and Prasad in 1971, who had carried out the metathetical reaction of triphenylbismuth dichloride with silver(I) salts in dry acetone to obtain acetonyltriphenylbismuthonium salts as a stable solid.[6] However, when a similar reaction was carried out in acetylacetone or ethyl methyl ketone, tetraphenyl-bismuthonium salts were the sole bismuth-containing products isolated.[7] Although the formation of alkylbismuthonium compounds has also been reported in the reactions of triphenyl-bismuthine with hexachloro-s-trithiane 1,1,3,3,5,5,-hexaoxide,[8] norbornadien-7-yl tetrafluoroborate[9] and a carbonyl-stabilized sulfonium ylide in the presence of sodium tetraphenylborate,[10] the products described therein were not well characterized. Although the above approaches are of interest from the mechanistic point of view, they lack generality as a preparative method for alkylbismuthonium salts since the alkyl ligands to be introduced are limited to specific cases. In a recent communication,[11] we have reported an efficient synthesis and X-ray structure analysis of a stable (2-oxoalkyl)triarylbis-muthonium tetrafluoroborate. In this article, we describe full details of the synthesis, properties, structures and reactions of such alkylbismuthonium salts and related compounds.
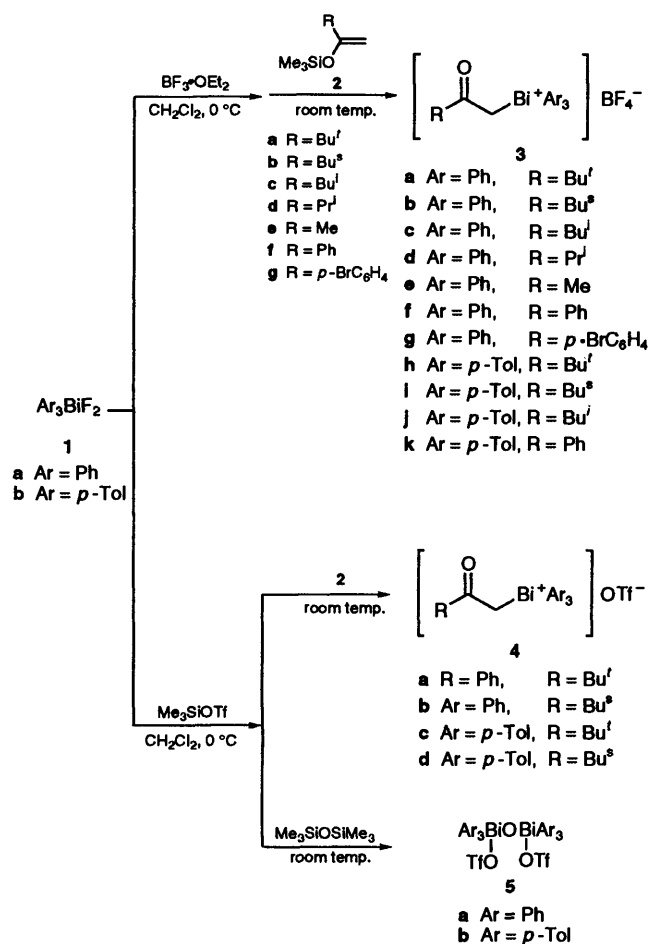
Results and Discussion

Synthesis of Stable (2-Oxoalkyl)triarylbismuthonium Salts.— In order to obtain alkylbismuthonium salts stable enough to be handled at room temperature, two key points must be taken into consideration. First is the combination of starting reagents. In contrast to the ease of access to the corresponding phosphonium and arsonium compounds, bismuthonium salts are not accessible by the direct interaction of triarylbismuthines with halogenoalkanes because of the low nucleophilicity of

tertiary bismuthines whose unshared electron pair is of a strong s character.† This implies that an alternative combination of an electrophilic hypervalent bismuth compound and a nucleo-philic alkyl-transfer reagent would be a more appropriate choice for preparing such onium-type compounds. Second is the choice of counter anions for bismuthonium salts. Tetra-phenylbismuthonium chloride decomposes within a few min-utes at room temperature to yield triphenylbismuthine and chlorobenzene through reductive elimination in accord with the high nucleophilicity of the chloride ion.[2] This instability of bismuthonium chlorides suggested to us the need to use less nucleophilic counter anions such as tetrafluoroborate and trifluoromethanesulfonate (triflate) for the successful isolation of the desired products. Based on these considerations, we chose a combination of triarylbismuth difluoride 1, silyl enol ether 2 and boron trifluoride–diethyl ether $(BF_3 \cdot OEt_2)$/trimethylsilyl triflate (Me_3SiOTf) as starting materials. As expected, the reaction of the difluorides 1 with $BF_3 \cdot OEt_2$ in dichloromethane, followed by treatment with the enolates 2 gave (2-oxoalkyl)triarylbismuthonium tetrafluoroborates 3 in high yields (Scheme 1). In this reaction, the Lewis acid $BF_3 \cdot OEt_2$ plays a dual important role, in that, initially it activates compound 1 and then in the second stage stabilizes the bismuthonium salt 3 as the counter anion BF_4^-. In the absence of $BF_3 \cdot OEt_2$, the starting materials 1 and 2 were recovered unchanged. This synthetic methodology proved to be quite efficient and generally applicable to the construction of homologous bismuthonium salts. When Me_3SiOTf was substi-tuted for $BF_3 \cdot OEt_2$, the corresponding bismuthonium triflates 4 were obtained (Scheme 1).

In order to gain insight into the reaction pathway, the process leading to the formation of the onium salt 3a was monitored by ^{1}H and ^{13}C NMR spectroscopy; mixing of the difluoride 1a and

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† For example, a mixture of triphenylbismuthine and phenacyl bromide were recovered unchanged after 48 h refluxing in benzene while triphenylphosphine and phenacyl bromide produced phenacyltriphenyl-phosphonium bromide in a quantitative yield within 5 min in dichloromethane at room temperature.

Scheme 1

for 30 min gave a dark purple mixture of degradation products composed of benzene, pinacolone and insoluble pale grey substances.

This type of compound exhibits highly characteristic spectral features; ^{1}H NMR spectra show a signal in the range δ_H 5.22–5.97 for the methylene group bound to the cationic bismuth atom. ^{13}C NMR signals due to the methylene and phenyl carbons adjacent to the bismuth atom are observed at δ_C 54.8–58.6 and 135.5–142.6, respectively. The appearance of these signals at lower field is in accord with the electron-withdrawing effect of the bismuthonium moiety. FAB mass spectra display a strong peak due to M^+-BF_4 fragment for the tetrafluoroborate 3 and M^+-OTf one for the triflate in accord with the cationic nature of the quaternary bismuth centre. The additional diagnostic feature is strong IR absorption characteristic of their counter anions. Broad intense bands appear around 1150–950 cm^{-1} (BF_4^-) for 3 and 1320–1120 cm^{-1} (OTf$^-$) for 4. Carbonyl stretching frequencies were observed as sharp absorption at 1674–1696 cm^{-1}. These spectral features clearly indicate the onium nature of compounds 3 and 4, accompanied by spatially separated counter anion. The salts 3 and 4 are soluble in dichloromethane, chloroform and acetonitrile, but very poorly soluble in benzene, hexane, ether and tetrahydrofuran (THF). All isolated bismuthonium salts are stable and can be handled without change exposed to the air.† In view of the instability of quaternary bismuth halides under ambient conditions,[2] the low nucleophilic nature of the counter anions BF_4^- and OTf$^-$ should be essential for the thermal stabilization of compounds 3 and 4. The twin advantages of our method for the preparation of alkylbismuthonium salts 3 and 4 over previous ones [5,6,8-10] is that it uses easily available reagents with simpler manipulation. As an extension, this methodology was applied to the synthesis of some μ-oxo type bismuth compounds. Treatment of the triarylbismuth difluorides 1 with hexamethyldisiloxane in the presence of Me_3SiOTf afforded oxybis(triarylbismuth) ditriflates 5 in good yields (Scheme 1). ^{13}C NMR spectra of this type of compounds show a characteristic peak for the *ipso* carbons of the aromatic rings at δ_C 150.1 and 150.9. The lowfield resonance is suggestive of the hypervalent nature of the bismuth centre in compound 5. IR absorption due to the asymmetric stretching of the Bi–O–Bi bond appears at 634 and 637 cm^{-1}, which is in accord with the reported values for the analogous system $(Ph_3BiOBiPh_3)X_2$.[13]

X-Ray Structure Analysis.—To date, X-ray structural data for bismuthonium salts has been reported for only three compounds: $[BiPh_4][ClO_4]$,[14] $[BiPh_4][OTs]$[15] and $[BiPh_4]$-$[Ph_2Bi(OCOCF_3)_2]$.[15] However, until now there has been no information for analogous alkyl substituted compounds. We disclose here the X-ray diffraction analysis results for two such alkylbismuthonium salts, namely compounds 3a and 4a (Table 1).‡

As shown in Figs. 1 and 2, the bismuth atom in each salt has a distorted tetrahedral geometry with the respective bond angles [C–Bi–C 102.1(7)–118.4(7)° for 3a and 102.6(6)–117.4(6)° for 4a], which clearly endorse the onium nature of the central bismuth atom (Tables 2 and 3).

The mean Bi–C bond lengths [2.20(2) Å for 3a and 2.19(2) Å

BF_3·OEt_2 in $CDCl_3$ at 0 °C gave a colourless solution, where the original sets of ^{1}H and ^{13}C NMR signals for the phenyl rings in the difluoride 1a changed into a new set of signals arising from a presumed association complex.* When the silyl enolate 2a was added to this solution, its spectral pattern immediately changed to that for the superimposed spectra of compound 3a and fluorotrimethylsilane (Me_3SiF).[12] It is likely that the coordination of BF_3 to difluoride 1a yields fluorotriphenylbismuthonium tetrafluoroborate $[BiFPh_3][BF_4]$ as an initial product, which suffers nucleophilic attack by the silyl enolate 2a on the bismuth centre with simultaneous elimination of Me_3SiF, ultimately leading to bismuthonium salt 3a as the final product. The high affinity of both boron and silicon atoms for fluorine is, no doubt, the key factor in driving the reaction.

The alkylbismuthonium salts 3 and 4 were purified by recrystallization or by column chromatography on silica gel and characterized on the basis of microanalysis and NMR, IR and FAB mass spectroscopy. All the crystalline alkylbismuthonium salts obtained showed sharp melting points and when the melt was rapidly cooled to ambient temperature, they were recovered unchanged. Prolonged heating of the melt at temperatures above the melting point, however, led to gradual decomposition to give a complex mixture of products. For example, compound 3a (m.p. 143–145 °C) heated at 155–160 °C

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* NMR (200 MHz; CDCl₃); 1a δ_H 7.49 (3 H, t, J 7.6), 7.66 (6 H, t, J 7.7) and 8.22 (6 H, d, J 7.8); δ_C 131.7, 131.9, 134.3 and 153.6; $Ph_3FBi^+BF_4^-$ δ_H 7.62 (3 H, t, J 7.8), 7.81 (6 H, t, J 7.9) and 8.07 (6 H, d, J 7.9); δ_C 133.0, 133.3, 134.0 and 154.1; Me_3SiF δ_H 0.22 (9 H, d, J_{HF} 7.3) [lit.,[12] δ_H 0.19 (9 H, d, J_{HF} 7.23)].

† Compounds 3 and 4 are not sensitive to atmospheric moisture, but prolonged contact of the latter with water led to gradual hydrolysis to form μ-oxo type of compound 5.

‡ The X-ray structure of 3a has been reported briefly in our recent letter,[11] and its PLUTO drawing and bond parameters are reproduced herein for comparison. The crystal structure of 4a consists of two isolated molecules which differ little from each other as to the configuration of central bismuth atom. The PLUTO structure shown in Fig. 3 and bond parameters listed in Table 4 are those of the selected molecule.

Table 1 Crystal data for compounds 3a, 4a and 5a

Compound	3a	4a	5a
Dimensions/mm	$0.180 \times 0.180 \times 0.300$	$0.180 \times 0.150 \times 0.200$	$0.130 \times 0.130 \times 0.480$
Formula	$C_{24}H_{26}BBiF_4O$	$C_{25}H_{26}BiF_3O_4S$	$C_{38}H_{30}Bi_2F_6O_7S_2$
Formula weight	626.25	688.51	1194.72
Crystal colour, Habit	Colourless, prism	Colourless, prism	Colourless, prism
Crystal structure	Rhombohedral (hexagonal axes)	Triclinic	Monoclinic
Space group	$R\bar{3}(h)$	$P\bar{1}$	$P2_1/a$
$a/\text{Å}$	30.606(7)	13.307(7)	19.730(4)
$b/\text{Å}$		19.974(3)	10.314(2)
$c/\text{Å}$	14.195(5)	10.480(3)	21.143(3)
$\alpha/°$		100.44(2)	
$\beta/°$		100.06(4)	109.26(1)
$\gamma/°$		82.03(3)	
$V/\text{Å}^3$	11 514(6)	2681(3)	4062(1)
z	18	2	4
$D_c/\text{g cm}^{-3}$	1.625	1.706	1.954
F_{000}	5436	1336	2264
μ/cm^{-1}	69.09	66.78	87.98
Radiation ($\lambda/\text{Å}$)	MoKα, 0.710 69	MoKα, 0.710 69	MoKα, 0.710 69
Temp. ($T/°C$)	27	27	25
$2\theta(\text{max})/°$	55.0	55.0	50.0
Scan rate (deg min^{-1})	8.0	16.0	16.0
Scan width (deg)	$[0.79 + 0.30 \tan\theta]$	$[0.94 + 0.30 \tan\theta]$	$[1.05 + 0.30 \tan\theta]$
Total data	6052	10 454	8537
Unique data	5684	9927	7557
$R(\text{int})$	0.091	0.052	0.051
No. observed	1899	3997	3348
	$[I > 3.00\sigma(I)]$	$[I > 3.00\sigma(I)]$	$[I > 3.00\sigma(I)]$
No. variables	280	613	497
R	0.049	0.045	0.039
R_w	0.045	0.045	0.034
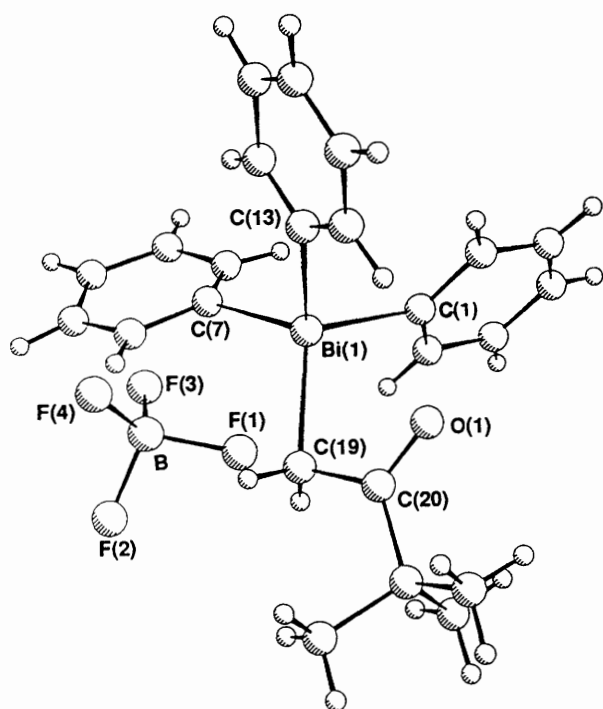
Fig. 1 A PLUTO drawing of compound 3a with the atomic numbering scheme

Fig. 2 A PLUTO drawing of compound 4a with the atomic numbering scheme. The triflate anion is omitted for clarity.

for 4a] are comparable with those of reported tetraaryl-bismuthonium compounds.[14,15] The bond angle open to the carbonyl oxygen side [C(13)–Bi(1)–C(19) 118.4(7)° for 3a and C(37)–Bi(2)–C(49) 117.4(6)° for 4a] is considerably larger than the expected value for an sp^3 configuration (109°28′), while the C–Bi–C angle remote from the carbonyl function [C(1)–Bi(1)–C(7) 102.1(7)° for 3a and C(31)–Bi(2)–C(43) 105.4(6)° for 4a]
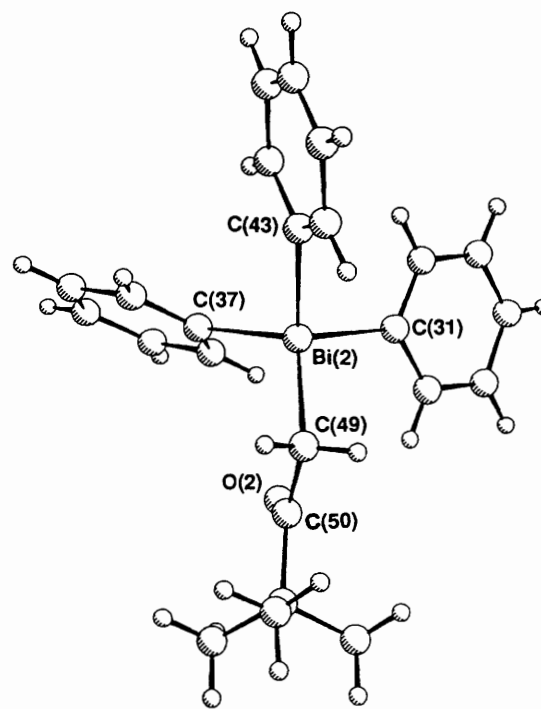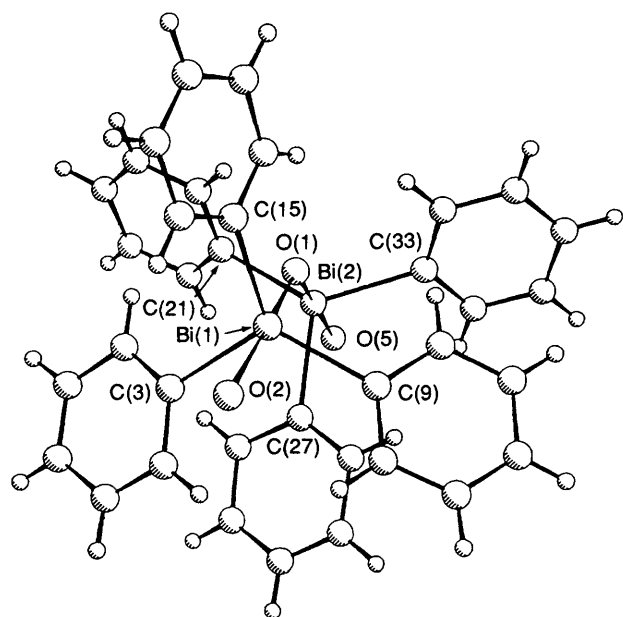
is appreciably reduced. Another noteworthy feature is the distance between the bismuth and carbonyl oxygen atoms [2.90(1) Å for 3a and 2.93(1) Å for 4a], which is longer than the sum of the covalent radii (2.10 Å) but shorter than that of the estimated van der Waals radii (3.72 Å).[16] These findings strongly suggest the existence of an intramolecular interaction between the carbonyl oxygen and electron-deficient bismuth

Table 2 Selected bond lengths (Å) and angles (°) for compound **3a**, with estimated standard deviations in parentheses

Bond length		Bond angle	
Bi(1)–C(1)	2.20(2)	C(1)–Bi(1)–C(7)	102.1(7)
Bi(1)–C(7)	2.21(2)	C(1)–Bi(1)–C(13)	107.0(7)
Bi(1)–C(13)	2.19(2)	C(1)–Bi(1)–C(19)	110.6(6)
Bi(1)–C(19)	2.20(2)	C(7)–Bi(1)–C(13)	105.6(8)
C(19)–C(20)	1.49(2)	C(7)–Bi(1)–C(19)	111.8(7)
C(20)–O(1)	1.22(2)	C(13)–Bi(1)–C(19)	118.4(7)
Bi(1)···O(1)	2.90(1)	C(19)–C(20)–O(1)	119(2)
		Bi(1)–C(19)–C(20)	106(1)

Table 3 Selected bond lengths (Å) and angles (°) for compound **4a**, with estimated standard deviations in parentheses

Bond length		Bond angle	
Bi(2)–C(31)	2.17(2)	C(31)–Bi(2)–C(37)	102.6(6)
Bi(2)–C(37)	2.24(2)	C(31)–Bi(2)–C(43)	105.4(6)
Bi(2)–C(43)	2.17(2)	C(31)–Bi(2)–C(49)	112.2(6)
Bi(2)–C(49)	2.17(2)	C(37)–Bi(2)–C(43)	105.5(6)
C(49)–C(50)	1.45(2)	C(37)–Bi(2)–C(49)	117.4(6)
C(50)–O(2)	1.22(2)	C(43)–Bi(2)–C(49)	112.5(6)
Bi(2)···O(2)	2.93(1)	C(49)–C(50)–O(2)	119(2)
		Bi(2)–C(49)–C(50)	109(1)

Table 4 Selected bond lengths (Å) and angles (°) for compound **5a**, with estimated standard deviations in parentheses

Bond length		Bond angle	
Bi(1)–C(3)	2.20(1)	C(3)–Bi(1)–C(9)	119.3(7)
Bi(1)–C(9)	2.20(2)	C(3)–Bi(1)–C(15)	112.7(6)
Bi(1)–C(15)	2.22(1)	C(9)–Bi(1)–C(15)	124.4(5)
Bi(2)–C(21)	2.19(1)	C(21)–Bi(2)–C(27)	113.9(6)
Bi(2)–C(27)	2.20(1)	C(21)–Bi(2)–C(33)	130.5(5)
Bi(2)–C(33)	2.21(1)	C(27)–Bi(2)–C(33)	113.3(5)
Bi(1)–O(1)	2.039(8)	O(1)–Bi(1)–O(2)	176.4(3)
Bi(1)–O(2)	2.58(1)	O(1)–Bi(1)–C(3)	98.9(5)
Bi(2)–O(1)	2.091(8)	O(1)–Bi(1)–C(9)	97.7(5)
Bi(2)–O(5)	2.527(9)	O(1)–Bi(1)–C(15)	92.4(5)
		O(1)–Bi(2)–O(5)	179.7(3)
		O(1)–Bi(2)–C(21)	93.2(5)
		O(1)–Bi(2)–C(27)	100.4(4)
		O(1)–Bi(2)–C(33)	92.6(4)
		Bi(1)–O(1)–Bi(2)	134.0(4)

Fig. 3 A PLUTO drawing of compound **5a** with the atomic numbering scheme. The triflate groups are omitted except for O(2) and O(5) atoms for clarity.

atoms. In both salts, the tetrafluoroborate and triflate anionic portions are spatially separated and seem to have only weak electrostatic interaction with the bismuth centre.* In order to determine what electronic influence the hetero atom attached to the bismuth has, an X-ray analysis of compound **5a** has also been carried out (Fig. 3 and Table 4). In this molecule, the geometry around each of the two bismuth centres linked by the oxygen bridge is somewhat distorted trigonal bipyramidal with

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* Although a possible interaction between the bismuth and the nearest sulfonyl oxygen atom in **4a** cannot be completely excluded, the observed distance [3.16(1) Å] is too long as compared with that (2.77 Å) of the distorted trigonal bipyramidal compound Ph₄-Bi⁺OTs⁻.[15]

three phenyl groups at equatorial sites. As expected, the electronegative oxygen atoms occupy axial positions with the bond angles O(1)–Bi(1)–O(2) 176.4(3)° and O(1)–Bi(2)–O(5) 179.7(3)°. The mean Bi–C(Ph) distance [2.20(1) Å] and the mean C(Ph)–Bi–C(Ph) angle (119.0°) are not significantly different from those [2.19(2) Å and 118.5°] reported for (Ph₃BiOBiPh₃)(ClO₄)₂.[17] The bismuth atoms are located above the plane formed by three *ipso* phenyl carbon atoms by 0.24 Å [for Bi(1)] and 0.20 Å [for Bi(2)] slightly bent towards the bridging oxygen atom with a mean O(bridge)–Bi–C(Ph) angle 95.9°. The Bi–O(bridge) distances 2.039(8) and 2.091(8) Å agree with the values expected for the covalent Bi–O single bond, while the Bi–O(triflate) distances 2.58(1) and 2.527(9) Å are too long to be covalent. These findings may be taken to suggest some contribution from the tetrahedral configuration to the bismuth centre in compound **5** and an intermediate character of the Bi–O(triflate) bonding between the formal covalent and ionic ones.

Thus, the bismuth atom in compound **4a** is of onium nature while those in **5a** are of hypervalent nature, as reflected by the tetrahedral configuration of **4a** and trigonal bipyramidal of **5a**, respectively. The origin of different geometry between compounds **4a** and **5a** may be attributed to the difference in ability for electron-withdrawal of the alkyl carbon atom in **4a** and the bridging oxygen atom in **5a**.

Reactions of Alkylbismuthonium Salts **3** *and* **4** *with some Nucleophiles.*—Although synthetic chemistry based on organobismuth(v) compounds was extensively developed by Barton's group in the 1980's,[1,18] the possible use of bismuthonium salts in such a way has not been explored. In order to estimate the synthetic potential of alkylbismuthonium salts, the reactions of compounds **3** and **4** with several nucleophiles have been examined (Schemes 2 and 3 and Table 5).

When treated with the triphenylphosphine **6** or the dimethyl sulfide **9**, compound **3f** readily underwent onium exchange to give phenacyltriphenylphosphonium tetrafluoroborate **7** and dimethylphenacylsulfonium tetrafluoroborate **10**, respectively. Triphenylbismuthine **8** was recovered quantitatively in accord with the high nucleophilic character of light pnictogen and chalcogen elements (Scheme 2).

Treatment of compound **3** with the sodium enolate **11** generated from dibenzoylmethane in THF at room temperature gave the corresponding tricarbonyl derivatives **12** and bismuthine **8**. Compound **3f** reacted with piperidine **13** to afford α-piperidinoacetophenone **14** in almost quantitative yield. Reaction of compounds **3** and **4** with sodium aryl oxides **15** in THF led to coupling between the alkyl carbon and oxygen atoms to give the α-aryloxy ketones **16** in moderate yields. With

Scheme 2

RT = room temp.

Scheme 3
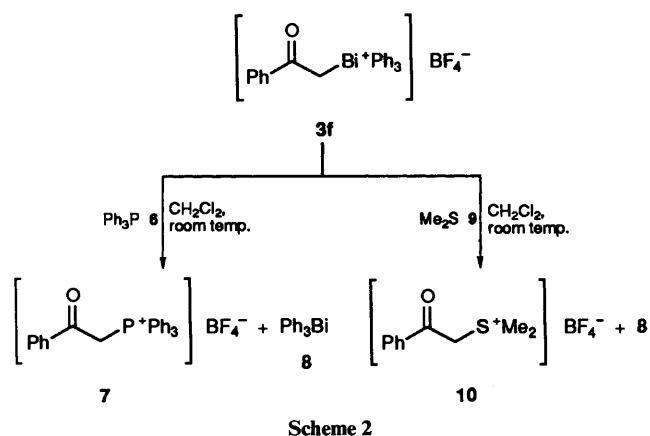
the sodium thiolate **17**, the salts **3** and **4** underwent a similar type of C(alkyl)–S coupling in THF, even at −20 °C, to afford α-arylthio ketones **18** in good yields, while the reaction with sodium toluene-p-sulfinate **19** led to α-sulfonyl ketones **20** in high yields. When treated with an excess of potassium bromide or iodide **21** in DMF at room temperature, the salt **3** underwent C(alkyl)–halogen coupling to give the corresponding α-halogeno ketones **22** together with bismuthine **8**.

Characteristic colouration was observed at the initial stage of the reaction with some nucleophiles. A clear yellow solution formed immediately after a nucleophile was mixed with compound **3** or **4** in THF at −50 °C; this colour was discharged, when the mixture was allowed to warm to room temperature (in the cases of **11** and **15**) or heated under gentle reflux (in the case of **17**). The resulting colourless solution was found to contain α-substituted ketones **12**, **16** or **18**, and triphenylbismuthine **8**. TLC monitoring of the reaction mixture showed that the discolouration is a sign that the coupling reaction is complete. Judging from these findings, it is reasonable to assume that an intermediary organobismuth(v) species generated from the salt **3** or **4** and a nucleophile is responsible for the yellow colouration, although there is as yet no direct evidence for the intermediacy of such a species.

In the reaction of compound **3a** or **4a** with p-tolylmagnesium bromide, phenyllithium or butyllithium at −78 °C, a characteristic colour initially developed (purple for the Grignard * and orange for the lithium reagents), which gradually turned colourless or pale yellow as the temperature was raised to ambient. In every case the products were triphenylbismuthine **8** and a complicated mixture of unidentified compounds.

It is interesting that the 2-oxoalkyl moiety, which is intrinsically preferred as an enolate anionic species, can be transferred as an acylmethyl cation equivalent from salt **3** or **4** to a nucleophile in these reactions, where the loss of triphenylbismuthine **8** as a neutral species from energy-rich bismuthonium salt should be a key factor for promoting the C–Nu bond formation whether an intermediary pentavalent species may be involved or not. The reactions described here are the first example of alkyl transfer from alkylbismuthonium salts, and its synthetic potential will be subject to our further study.

Experimental

General.—All reactions were carried out under an atmosphere of argon. Dichloromethane (CH_2Cl_2) and tetrahydro-

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* Pentaphenylbismuth has a deep-purple colour and decomposes in chloroform to give triphenylbismuthine, benzene, and tarry products presumably derived from an intermediary benzyne.[19] In the present case a similar type of quinquenary bismuth compound might be generated at the low temperatures.
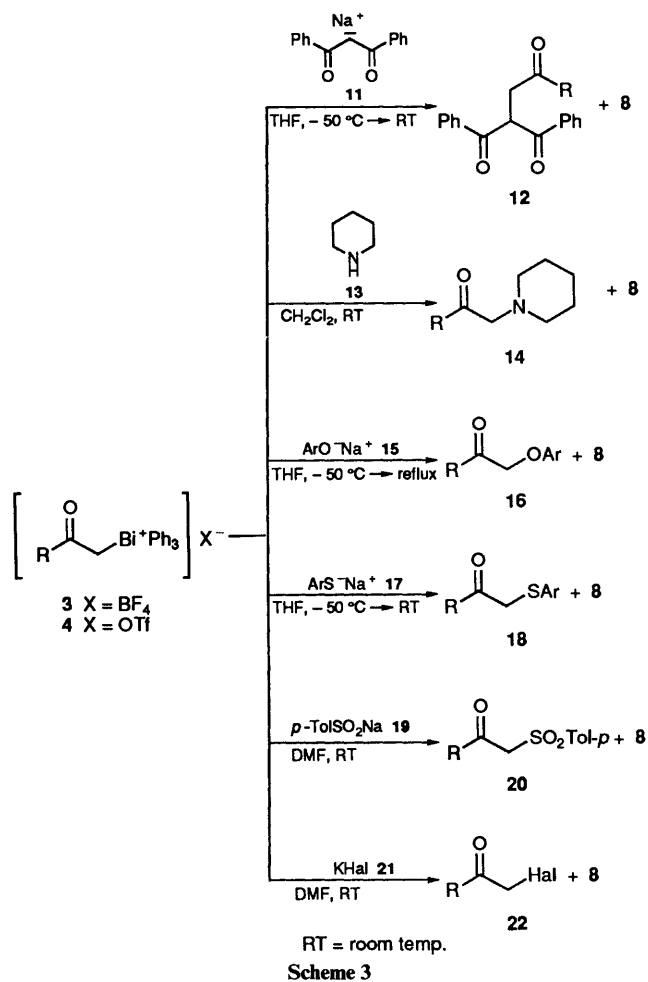
furan (THF) were distilled under argon from CaH_2 and sodium benzophenone ketyl, respectively, before use. N,N-Dimethylformamide (DMF) was distilled from CaH_2 and stored over molecular sieves 4 Å. Triarylbismuth difluorides **1** were prepared from the corresponding dichlorides according to the reported method[20] and recrystallized from hexane–CH_2Cl_2. Silyl enol ethers **2** were prepared by a standard procedure.[21] Other reagents were used as commercially received. Column chromatography was performed on silica gel (Wakogel, 200 mesh). All m.p.s 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 in $CDCl_3$ unless otherwise stated with tetramethylsilane as an internal standard. Coupling constants J are given in Hz. IR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer. EI mas spectra were obtained on a Shimadzu GCMS-QP2000A spectrometer and FAB mass spectra on a JEOL JMS-HS110 spectrometer using 3-nitrobenzyl alcohol as a matrix. Elemental analyses were performed at the Microanalytical Laboratories of Kyoto University.

Triarylbismuth difluorides. **1a**, m.p. 159–161 °C (lit.,[20] 158.5–159 °C); δ_H 7.49 (3 H, t, J 7.6), 7.66 (6 H, d, J 7.7) and 8.22 (6 H, d, J 7.8). **1b**, m.p. 123–125 °C; δ_H 2.39 (9 H, s), 7.45 (6 H, d, J 8.2) and 8.07 (6 H, d, J 8.2).

Silyl enol ethers. **2a**, b.p. 48–50 °C/18 mmHg (lit.,[21] 68 °C/80 mmHg); δ_H 0.20 (9H, s), 1.04 (9 H, s), 3.92 (1 H, d, J 1.6) and 4.08 (1 H, d, J 1.6). **2b**, b.p. 56–58 °C/18 mmHg; δ_H 0.20 (9 H, s), 0.85 (3 H, t, J 7.4), 0.99 (3 H, d, J 6.9), 1.18–1.55 (2 H, m), 1.95 (1 H, sext, J 6.9), 3.98 (1 H, s) and 4.00 (1 H, s). **2c**, b.p. 56–58 °C/18 mmHg; δ_H 0.20 (9 H, s), 0.89 (6 H, d, J 6.5), 1.82–1.90 (3 H, m), 4.01 (1 H, s) and 4.04 (1 H, s). **2d**, b.p. 74–76 °C/135 mmHg; δ_H

Table 5 Reactions of compounds **3** and **4** with some selected nucleophiles

Entry	Compd.	R	Nucleophile	Product	Yield (%)[a]
1	**3d**	Pr^i	**11**	**12a**	69
2	**3f**	Ph	**11**	**12b**	61
3	**3f**	Ph	**13**	**14**	95[b]
4	**3a**	Bu^t	**15a** (Ar = Ph)	**16a**	56
5	**3a**	Bu^t	**15b** (Ar = 1-Naphthyl)	**16b**	61
6	**3a**	Bu^t	**15c** (Ar = 4-ClC$_6$H$_4$)	**16c**	46
7	**4a**	Bu^t	**15b**	**16b**	55
8	**3a**	Bu^t	**17a** (Ar = Ph)	**18a**	77
9	**3a**	Bu^t	**17b** (Ar = 4-ClC$_6$H$_4$)	**18b**	72
10	**4a**	Bu^t	**17a**	**18a**	65
11	**4a**	Bu^t	**17b**	**18b**	73
12	**3a**	Bu^t	**19**	**20a**	87
13	**3f**	Ph	**19**	**20b**	82
14	**4a**	Bu^t	**19**	**20a**	79
15	**3a**	Bu^t	**21a** (Hal = Br)	**22a**	78[b]
16	**3a**	Bu^t	**21b** (Hal = I)	**22b**	65[b]
17	**3f**	Ph	**21a**	**22c**	64[b]
18	**3f**	Ph	**21b**	**22d**	76[b]

[a] Yield refers to isolated compound based on unrecovered salt **3** or **4**, unless otherwise indicated. Triphenylbismuthine was additional product isolated in 77–97% yields. [b] Determined by ^{1}H NMR.

0.21 (9 H, s), 1.02 (6 H, d, J 6.9), 2.20 (1 H, sept, J 6.9), 3.97 (1 H, s) and 4.04 (1 H, s). **2e**, b.p. 86–88 °C (lit.,[21] 100 °C); δ_H 0.21 (9 H, s), 1.78 (3 H, s) and 4.05 (2 H, s). **2f**, b.p. 117–119 °C/27–28 mmHg (lit.,[21] 82 °C/5 mmHg); δ_H 0.20 (9 H, s), 4.45 (1 H, d, J 1.7), 4.93 (1 H, d, J 1.7), 7.26–7.40 (3 H, m) and 7.59 (2 H, m). **2g**, b.p. 79–81 °C/0.4 mmHg; δ_H 0.26 (9 H, s), 4.44 (1 H, d, J 1.8), 4.90 (1 H, d, J 1.8) and 7.45 (4 H, s).

Synthesis of (2-*Oxoalkyl*)*triarylbismuthonium Tetrafluoroborates* **3**.—To a stirred solution of triarylbismuth trifluoride **1** (1 mmol) in CH$_2$Cl$_2$ (5 cm^3) at 0 °C was added boron trifluoride–diethyl ether (0.12 cm^3, 1 mmol). This was followed after 1 h, by the silyl enol ether **2** (1 mmol) and the resulting mixture was stirred for further 10 h at ambient temperature to complete the reaction. The solvent was removed under reduced pressure to leave an oily residue, which was purified by recrystallization from diethyl ether CH$_2$Cl$_2$ (5 : 1) or by column chromatography on silica gel using CH$_2$Cl$_2$ as the eluent to afford (2-oxoalkyl)triarylbismuthonium tetrafluoroborate **3** in the yield given in parentheses.

(3,3-*Dimethyl-2-oxobutyl*)*triphenylbismuthonium tetrafluoroborate* **3a**. M.p. 143–145 °C (96%); δ_H 1.26 [9 H, s, C(CH$_3$)$_3$], 5.60 (2 H, s, BiCH$_2$), 7.52–7.67 (9H, m, Ph) and 7.68–7.82 (6 H, m, Ph); δ_C 26.9, 45.9, 56.9 (BiCH$_2$), 131.8, 131.9, 135.8, 137.9 (BiC$_{ipso}$) and 212.2; ν_{max}(KBr)/cm^{-1} 3050–2950, 1674 (C=O), 1475, 1437, 1150–950 (BF$_4$), 727, 695 and 441; m/z (FAB) 539 (M$^+$ − BF$_4$), 363, 286 and 209 (Found: C, 45.8; H, 4.1. C$_{24}$H$_{26}$BBiF$_4$O requires C, 46.0; H, 4.2%).

(3-*Methyl-2-oxopentyl*)*triphenylbismuthonium tetrafluoroborate* **3b**. M.p. 94–96 °C (95%); δ_H 0.85 (3 H, t, J 7.5, CH$_2$CH_3), 1.18 (3 H, d, J 7.0, CHCH_3), 1.40–1.80 (2 H, m, CH_2CH$_3$), 2.90 (1 H, sext, J 6.7, CH), 5.37 (1 H, d, J 15.0, BiCH$_2$), 5.59 (1 H, d, J 15.0, BiCH$_2$), 7.25–7.66 (9 H, m, Ph) and 7.68–7.82 (6 H, m, Ph); δ_C 11.2, 15.6, 26.0, 47.8, 57.0 (BiCH$_2$), 131.8, 131.9, 135.8, 137.8 (BiC$_{ipso}$) and 210.2; ν_{max}(KBr)/cm^{-1} 3050–3000, 1688 (C=O), 1568, 1474, 1429, 1200–950 (BF$_4$), 727, 695, 523 and 446; m/z (FAB) 539 (M$^+$ − BF$_4$), 363, 286 and 209 (Found: C, 45.9; H, 4.2. C$_{24}$H$_{26}$BBiF$_4$O requires C, 46.0; H, 4.2%).

(4-*Methyl-2-oxopentyl*)*triphenylbismuthonium tetrafluoroborate* **3c**. Glass (95%); δ_H 0.87 [6 H, d, J 6.6, CH(CH_3)$_2$], 2.12 [1 H, sept, J 6.7, CH(CH$_3$)$_2$], 2.64 (2 H, d, J 6.8, CH_2CH), 5.32 (2 H, s, BiCH$_2$), 7.55–7.68 (9 H, m, Ph) and 7.70–7.82 (6 H, m, Ph); δ_C 22.3, 24.9, 50.8, 57.4 (BiCH$_2$), 131.8, 131.9, 135.8, 137.8 (BiC$_{ipso}$) and 206.4; ν_{max}(KBr)/cm^{-1} 3050–2900, 1684 (C=O),

1474, 1437, 1200–950 (BF$_4$), 731, 695 and 450; m/z (FAB) 539 (M$^+$ − BF$_4$), 363, 286 and 209 (Found: C, 45.8; H, 4.1. C$_{24}$H$_{26}$BBiF$_4$O requires C, 46.0; H, 4.2%).

(3-*Methyl-2-oxobutyl*)*triphenylbismuthonium tetrafluoroborate* **3d**. M.p. 156–157 °C (99%); δ_H 1.18 [6 H, d, J 6.9, CH(CH_3)$_2$], 3.01 [1 H, sept, J 6.9, CH(CH$_3$)$_2$], 5.44 (2 H, s, BiCH$_2$), 7.55–7.66 (9 H, m, Ph) and 7.68–7.82 (6 H, m, Ph); δ_C 18.4, 41.4, 56.7 (BiCH$_2$), 131.9, 132.0, 135.8, 137.8 (BiC$_{ipso}$) and 210.4; ν_{max}(KBr)/cm^{-1} 3050–3000, 1690 (C=O), 1474, 1429, 1200–950 (BF$_4$), 731, 695, 521 and 445; m/z (FAB) 525 (M$^+$ − BF$_4$), 363, 286 and 209 (Found: C, 44.9; H, 3.9. C$_{23}$H$_{24}$BBiF$_4$O requires C, 45.1; H, 3.95%).

Acetonyltriphenylbismuthonium tetrafluoroborate **3e**. M.p. 145–146 °C (lit.,[6] 128 °C; decomp.) (95%); δ_H 2.41 (3 H, s, CH$_3$), 5.35 (2 H, s, BiCH$_2$), 7.55–7.66 (9 H, m, Ph) and 7.68–7.82 (6 H, m, Ph); δ_C 29.7, 57.7 (BiCH$_2$), 131.9, 132.0, 135.8, 137.5 (BiC$_{ipso}$) and 204.5; ν_{max}(KBr)/cm^{-1} 3050–2950, 1696 (C=O), 1568, 1474, 1429, 1358, 1237, 1200–950 (BF$_4$), 729, 695, 521 and 440; m/z (FAB) 497 (M$^+$ − BF$_4$), 363, 286 and 209 (Found: C, 43.2; H, 3.3. C$_{21}$H$_{20}$BBiF$_4$O requires C, 43.2; H, 3.45%).

Phenacyltriphenylbismuthonium tetrafluoroborate **3f**. Pale yellow, m.p. 165–167 °C (97%); δ_H 5.97 (2 H, s, BiCH$_2$), 7.49 (2 H, t, J 7.1, Ph), 7.54–7.70 (10 H, m, Ph), 7.81 (6 H, m, Ph) and 8.10 (2 H, d, J 7.1, Ph); δ_C 56.4 (BiCH$_2$), 129.1, 130.1, 131.9, 132.0, 132.6, 135.1, 135.9, 137.7 (BiC$_{ipso}$) and 195.2; ν_{max}(KBr)/cm^{-1} 3050–2950, 1682 (C=O), 1568, 1474, 1428, 1279, 1200–950 (BF$_4$), 731, 693, 521 and 450; m/z (FAB) 559 (M$^+$ − BF$_4$), 363, 286 and 209 (Found: C, 48.1; H, 3.3. C$_{26}$H$_{22}$BBiF$_4$O requires C, 48.3; H, 3.4%).

(4-*Bromophenacyl*)*triphenylbismuthonium tetrafluoroborate* **3g**. Pale yellow, m.p. 65–67 °C (94%); δ_H 5.89 (2 H, s, BiCH$_2$), 7.56–7.87 (17 H, m, Ph and Ar) and 7.97 (2 H, d, J 8.5, Ar); δ_C 55.7 (BiCH$_2$), 131.6, 132.0, 132.1, 132.5, 132.5, 133.4, 135.9, 137.7 (BiC$_{ipso}$) and 194.5; ν_{max}(KBr)/cm^{-1} 3050–2950, 1696 (C=O), 1586, 1474, 1401, 1200–950 (BF$_4$), 781, 729, 685, 521 and 442; m/z (FAB) 639 (M$^+$ − BF$_4$, ^{81}Br), 637 (M$^+$ − BF$_4$, ^{79}Br), 363, 286 and 209 (Found: C, 43.15; H, 2.9. C$_{26}$H$_{21}$BBiBrF$_4$O requires C, 43.1; H, 2.9%).

(3,3-*Dimethyl-2-oxobutyl*)*tri*(p-*tolyl*)*bismuthonium tetrafluoroborate* **3h**. M.p. 97–98 °C (93%); δ_H 1.25 [9 H, s, C(CH$_3$)$_3$], 2.40 (9 H, s, ArCH_3), 5.50 (2 H, s, BiCH$_2$), 7.40 (6 H, d, J 8.1, ArH) and 7.61 (6 H, d, J 8.1, ArH); δ_C 21.5, 26.8, 45.8, 55.1 (BiCH$_2$), 132.5, 134.0, 135.5, 142.5 (BiC$_{ipso}$) and 212.2; ν_{max}(KBr)/cm^{-1} 3020–2850, 1682 (C=O), 1487, 1387, 1200–950

(BF₄), 793 and 480; *m/z* (FAB) 581 (M⁺ − BF₄), 391, 300 and 209 (Found: C, 48.2; H, 4.9. C₂₇H₃₂BBiF₄O requires C, 48.5; H, 4.8%).

(3-*Methyl*-2-*oxopentyl*)*tri*(p-*tolyl*)*bismuthonium tetrafluoroborate* **3i**. M.p. 142–144 °C (90%); δ_H 0.85 (3 H, t, *J* 7.4, CH₂C*H*₃), 1.16 (3 H, d, *J* 6.9, CHC*H*₃), 1.40–1.85 (2 H, m, C*H*₂CH₃), 2.41 (9 H, s, ArCH₃), 2.90 (1 H, sext, *J* 6.7, CH), 5.26 (1 H, d, *J* 15.0, BiCH₂), 5.39 (1 H, d, *J* 15.0, BiCH₂), 7.40 (6 H, d, *J* 8.0, ArH) and 7.61 (6 H, d, *J* 8.0, ArH); δ_C 11.3, 15.7, 21.5, 26.1, 48.0, 55.3 (BiCH₂), 132.5, 134.0, 135.6, 142.6 (BiC_ipso) and 210.3; ν_max(KBr)/cm⁻¹ 3050–2850, 1694 (C=O), 1487, 1387, 1200–950 (BF₄), 791, 521 and 480; *m/z* (FAB) 581 (M⁺ − BF₄), 391, 300 and 209 (Found: C, 48.8; H, 4.7. C₂₇H₃₂BBiF₄O requires C, 48.5; H, 4.8%).

(4-*Methyl*-2-*oxopentyl*)*tri*(p-*tolyl*)*bismuthonium tetrafluoroborate* **3j**. M.p. 58–60 °C (94%); δ_H 0.87 [6 H, d, *J* 6.6, CH(C*H*₃)₂], 2.12 [1 H, sept, *J* 6.7, C*H*(CH₃)₂], 2.40 (9 H, s, ArCH₃), 2.65 (2 H, d, *J* 6.9, C*H*₂CH), 5.22 (2 H, s, BiCH₂), 7.39 (6 H, d, *J* 8.1, ArH) and 7.61 (6 H, d, *J* 8.1, ArH); δ_C 21.5, 22.3, 24.9, 51.0, 55.8 (BiCH₂), 132.5, 133.8, 135.6, 142.5 (BiC_ipso) and 206.4; ν_max(KBr)/cm⁻¹ 3050–2850, 1688 (C=O), 1489, 1391, 1200–950 (BF₄), 793, 521 and 475; *m/z* (FAB) 581 (M⁺ − BF₄), 391, 300 and 209 (Found: C, 48.3; H, 4.7. C₂₇H₃₂BBiF₄O requires C, 48.5; H, 4.8%).

Phenacyltri(p-*tolyl*)*bismuthonium tetrafluoroborate* **3k**. M.p. 142–144 °C (87%); δ_H 2.41 (9 H, s, ArC*H*₃), 5.87 (2 H, s, BiCH₂), 7.41 (6 H, d, *J* 7.8, ArH), 7.43–7.75 (9 H, m, Ph and ArH) and 8.11 (2 H, d, *J* 7.3, Ph); δ_C 21.5, 54.8 (BiCH₂), 129.1, 130.1, 132.6, 133.9, 134.7, 135.1, 135.6, 142.6 (BiC_ipso) and 195.2; ν_max(KBr)/cm⁻¹ 3050–2800, 1685 (C=O), 1487, 1449, 1200–950 (BF₄), 793, 743, 689, 480 and 473; *m/z* (FAB) 601 (M⁺ − BF₄), 391, 300 and 209 (Found: C, 50.6; H, 4.0. C₂₉H₂₈BBiF₄O requires C, 50.6; H, 4.1%).

Synthesis of (2-*Oxoalkyl*)*triarylbismuthonium Trifluoromethanesulfonates* **4**.—These compounds were prepared according to the above procedure, using trimethylsilyl trifluoromethanesulfonate (0.19 cm³, 1 mmol) in place of boron trifluoridediethyl ether. Recrystallization of the crude product from Et₂O–CH₂Cl₂ (5:1) gave compound **4** as colourless crystals.

(3,3-*Dimethyl*-2-*oxobutyl*)*triphenylbismuthonium trifluoromethanesulfonate* **4a**. M.p. 152–154 °C (95%); δ_H 1.28 [9H, s, C(CH₃)₃], 5.64 (2 H, s, BiCH₂), 7.52–7.65 (9 H, m, Ph) and 7.70–7.80 (6 H, m, Ph); δ_C 26.9, 45.8, 58.6 (BiCH₂), 131.8, 131.9, 135.8, 139.0 (BiC_ipso) and 212.0; ν_max(KBr)/cm⁻¹ 3050–2900, 1674 (C=O), 1478, 1437, 1320–1220 (OTf), 1200–1120 (OTf), 1030, 994, 723 and 685; *m/z* (FAB) 539 (M⁺ − OTf), 363, 286 and 209 (Found: C, 43.45; H, 3.75. C₂₅H₂₆BiF₃O₄S requires C, 43.6; H, 3.8%).

(3-*Methyl*-2-*oxopentyl*)*triphenylbismuthonium trifluoromethanesulfonate* **4b**. M.p. 117–118 °C (93%); δ_H 0.85 (3 H, t, *J* 7.4, CH₂C*H*₃), 1.17 (3 H, d, *J* 6.9, CHC*H*₃), 1.40–1.80 (2 H, m, C*H*₂CH₃), 2.88 (1 H, sext, *J* 6.8, CH), 5.38 (1 H, d, *J* 15.8, BiCH₂), 5.50 (1 H, d, *J* 15.8, BiCH₂), 7.52–7.65 (9 H, m, Ph) and 7.70–7.80 (6 H, m, Ph); δ_C 11.3, 15.7, 26.1, 48.1, 58.3 (BiCH₂), 131.8, 131.9, 135.8, 137.5 (BiC_ipso) and 210.1; ν_max(KBr)/cm⁻¹ 3050–2900, 1688 (C=O), 1429, 1320–1220 (OTf), 1200–1130 (OTf), 1034, 729 and 695; *m/z* (FAB) 539 (M⁺ − OTf), 363, 286 and 209 (Found: C, 43.3; H, 3.6. C₂₅H₂₆BiF₃O₄S requires C, 43.6; H, 3.8%).

(3,3-*Dimethyl*-2-*oxobutyl*)*tri*(p-*tolyl*)*bismuthonium trifluoromethanesulfonate* **4c**. M.p. 55–57 °C (88%); δ_H 1.25 [9 H, s, C(CH₃)₃], 2.40 (9 H, s, ArC*H*₃), 5.55 (2 H, s, BiCH₂), 7.38 (6 H, d, *J* 7.9, ArH) and 7.62 (6 H, d, *J* 7.9, ArH); δ_C 21.5, 26.8, 45.8, 56.5 (BiCH₂), 132.4, 134.7, 135.5, 142.3 (BiC_ipso) and 212.0; ν_max(KBr)/cm⁻¹ 3050–2900, 1682 (C=O), 1487, 1389, 1320–1220 (OTf), 1200–1130 (OTf), 1032, 792 and 660; *m/z* (FAB) 581

(M⁺ − OTf), 391, 300 and 209 (Found: C, 45.8; H, 4.3. C₂₈H₃₂BiF₃O₄S requires C, 46.0; H, 4.4%).

(3-*Methyl*-2-*oxopentyl*)*tri*(p-*tolyl*)*bismuthonium trifloromethanesulfonate* **4d**. M.p. 127–128 °C (86%); δ_H 0.84 (3 H, t, *J* 7.4, CH₂C*H*₃), 1.16 (3 H, d, *J* 6.9, CHC*H*₃), 1.40–1.80 (2 H, m, C*H*₂CH₃), 2.41 (9 H, s, ArC*H*₃), 2.89 (1 H, sext, *J* 6.7, CH), 5.27 (1 H, d, *J* 15.0, BiCH₂), 5.39 (1 H, d, *J* 15.0, BiCH₂), 7.40 (6 H, d, *J* 8.1, ArH) and 7.61 (6 H, d, *J* 8.1, ArH); δ_C 11.3, 15.6, 21.5, 26.1, 48.2, 56.7 (BiCH₂), 132.4, 132.8, 135.6, 142.4 (BiC_ipso) and 210.2; ν_max(KBr)/cm⁻¹ 3100–2900, 1694 (C=O), 1489, 1320–1220 (OTf), 1200–1120 (OTf), 1030, 791 and 639; *m/z* (FAB) 581 (M⁺ − OTf), 391, 300 and 209 (Found: C, 46.1; H, 4.3. C₂₈H₃₂BiF₃O₄S requires C, 46.0; H, 4.4%).

NMR Monitoring of the Reaction of the Difluoride **1a** *with the Silyl Enol Ether* **2a** *in the Presence of* BF₃·OEt₂.—Into a CDCl₃ solution (0.5 cm³) of the difluoride **1a** (48 mg, 0.1 mmol) in an NMR sample tube was added BF₃·OEt₂ (0.012 cm³, 0.1 mmol) at 0 °C under argon and the solution was examined by ¹H and ¹³C NMR spectroscopy. The silyl enol ether **2a** (17 mg, 0.1 mmol) was then introduced into the tube and the resulting solution was examined similarly. The formation of product **3a** and fluorotrimethylsilane was quantitative, no other products being observed.

Synthesis of Oxybis(*triarylbismuth*) *Bis*(*trifluoromethanesulfonate*) **5**.—To a well stirred solution of the triarylbismuth difluoride **1** (1 mmol) in dichloromethane (5 cm³) at 0 °C was added trimethylsilyl trifluoromethanesulfonate (0.19 cm³, 1 mmol). After 1 h hexamethyldisiloxane (0.11 cm³, 0.5 mmol) was added to the mixture and stirring was continued for further 24 h at ambient temperature to complete the reaction. The solvent was removed under reduced pressure to leave an oily residue, which was purified by recrystallization from CH₂Cl₂ to give oxybis(triarylbismuth) bis(trifluoromethanesulfonate) as colourless crystals.

Oxybis(*triphenylbismuth*) *bis*(*trifluoromethanesulfonate*) **5a**. M.p. 205–206 °C (95%); δ_H(CDCl₃–CD₃OD, 10:1) 7.65 (6 H, t, *J* 7.3), 7.79 (12 H, t, *J* 7.5) and 7.99 (12 H, d, *J* 7.6); δ_C(CDCl₃–CD₃OD, 10:1) 132.7, 133.0, 134.4 and 150.1 (BiC_ipso) ν_max(KBr)/cm⁻¹ 3100–2900, 1561, 1470, 1330–1120, 1030, 986, 725 and 635 (Bi–O–Bi); *m/z* (FAB) 592, 363, 286 and 209 (Found: C, 37.8; H, 2.5. C₃₈H₃₀Bi₂F₆O₇S₂ requires C, 38.2, H, 2.5%).

Oxybis[*tri*(p-*tolyl*)*bismuth*] *bis*(*trifluoromethanesulfonate*) **5b**. M.p. 199–200 °C (96%); δ_H 2.43 (18 H, s), 7.33 (12 H, d, *J* 8.2) and 7.58 (12 H, d, *J* 8.2); δ_C 21.5, 132.5, 133.7, 143.0 and 150.9 (BiC_ipso); ν_max(KBr)/cm⁻¹ 1485, 1304, 1233, 1215, 1188, 1168, 1022, 790, 675, 637 (Bi–O–Bi) and 473; *m/z* (FAB) 634, 391, 300 and 209 (Found: C, 41.4; H, 3.3. C₄₄H₄₂Bi₂F₆O₇S₂ requires C, 41.3, H, 3.3%).

Reaction of Compound **3f** *with Triphenylphosphine* **6**.—A mixture of compound **3f** (162 mg, 0.25 mmol), triphenylphosphine **6** (65 mg, 0.25 mmol) and CH₂Cl₂ (5 cm³) was stirred at room temperature for 24 h, during which time colourless crystals were gradually precipitated. The crystals were filtered off, washed with CH₂Cl₂ (5 cm³ × 2), and dried *in vacuo* to give phenacyltriphenylphosphonium tetrafluoroborate **7** (111 mg, 95%). The filtrate was concentrated under reduced pressure to leave an oily residue, which was recrystallized from MeOH to give triphenylbismuthine **8** (107 mg, 97%). *Compound* **7**, m.p. 249–250 °C; δ_H(²[H]₆-dimethyl sulfoxide) 6.19 (2 H, d, *J*_P-H 13.1, CH₂), 7.61 (2 H, t, *J* 7.7, Ph), 7.70–7.92 (16 H, m, Ph) and 8.09 (2 H, d, *J* 7.7, Ph); δ_C(²[H]₆-dimethyl sulfoxide) 35.2 (d, *J*_P-C 61.7), 119.1 (d, *J*_P-C 88.8), 129.1, 129.2, 130.1 (d, *J*_P-C 12.9), 133.8 (d, *J*_P-C 10.8), 134.9, 135.1, 135.2 and 192.3 (d, *J*_P-C 6.2); ν_max(KBr)/cm⁻¹ 1669, 1593, 1439, 1327, 1302, 1204, 1150–

1000, 995, 747, 720, 689 and 515 (Found: C, 66.3; H, 4.7. $C_{26}H_{22}BF_4OP$ requires C, 66.7; H, 4.7%).

Reaction of Compound **3f** *with Dimethyl Sulfide* **9**.—To a solution of compound **3f** (162 mg, 0.25 mmol) in CH_2Cl_2 (5 cm^3) was added dimethyl sulfide **9** (0.18 cm^3, 2.5 mmol) at room temperature. Colourless crystals were immediately precipitated. Work-up as described above gave dimethylphenacylsulfonium tetrafluoroborate **10** (65 mg, 97%) and the bismuthine **8** (108 mg, 98%). *Compound* **10**, m.p. 169–170 °C (lit.,[22] 168.5–170 °C); δ_H(^{2}[H]$_6$-dimethyl sulfoxide) 2.95 (6 H, s, CH$_3$), 5.42 (2 H, s, CH$_2$), 7.64 (2 H, t, J 7.7, Ph), 7.79 (1 H, t, J 7.4, Ph) and 8.03 (2 H, d, J 7.7, Ph); δ_C(^{2}[H]$_6$-dimethyl sulfoxide) 23.4, 51.7, 127.3, 127.9, 132.5, 133.8 and 190.0; ν_{max}(KBr)/cm^{-1} 1682, 1599, 1456, 1431, 1341, 1331, 1318, 1217, 1150–950, 756, 689, 637 and 523.

Reaction of (2-*Oxoalkyl*)*triphenylbismuthonium Salts* **3** *with the Sodium Enolate* **11**.—To a suspension of the bismuthonium salt **3** (0.8 mmol) in THF (2 cm^3) cooled down to −50 °C was added a solution of the sodium enolate **11**, generated from well-washed sodium hydride (*ca.* 19 mg) and dibenzoylmethane (179 mg, 0.8 mmol) in the same solvent (3 cm^3). The resulting yellow solution was stirred for 10 h during which time the temperature was gradually raised to ambient. The colourless mixture was then concentrated under reduced pressure and extracted with diethyl ether (15 cm^3). Removal of the solvent afforded an oily residue, which was subjected to silica-gel column chromatography with hexane–ethyl acetate as the eluent to give the corresponding tricarbonyl compound **12** and triphenylbismuthine **8**.

2-*Benzoyl*-5-*methyl*-1-*phenylhexane*-1,4-*dione* **12a**. M.p. 92–93 °C; δ_H 1.16 [6 H, d, J 7.0, CH(CH$_3$)$_2$], 2.74 [1 H, hept, J 7.0, CH(CH$_3$)$_2$], 3.22 (2 H, d, J 6.5, CHCH$_2$), 5.91 (1 H, t, J 6.5, CHCH$_2$), 7.45 (4 H, t, J 7.3, Ph), 7.57 (2 H, t, J 7.3, Ph) and 7.97 (4 H, d, J 7.3, Ph); ν_{max}(KBr)/cm^{-1} 1696, 1671, 1595, 1449, 1273, 1238, 1000, 756 and 708; m/z (EI) 265 (M$^+$ − 43), 105 and 77 (Found: C, 78.3; H, 6.3. $C_{20}H_{20}O_3$ requires C, 77.9; H, 6.5%).

2-*Benzoyl*-1,4-*diphenylbutane*-1,4-*dione* **12b**. M.p. 148–149 °C (lit.,[23] 99–100 °C); δ_H 3.78 (2 H, d, J 6.4, CHCH$_2$), 6.13 (1 H, t, J 6.4, CHCH$_2$), 7.44 (6 H, t, J 7.3, Ph), 7.57 (3 H, t, J 7.2, Ph) and 7.98–8.05 (6 H, m, Ph); ν_{max}(KBr)/cm^{-1} 1686, 1669, 1595, 1449, 1277, 1221, 1000 and 685; m/z (EI) 237 (M$^+$ − 105), 220, 105 and 77 (Found: C, 80.5; H, 5.25. $C_{23}H_{18}O_3$ requires C, 80.7; H, 5.3%).

Reaction of Compound **3f** *with Piperidine* **13**.—To a solution of compound **3f** (162 mg, 0.25 mmol) in CH_2Cl_2 (5 cm^3) was added piperidine (85 mg, 1.0 mmol) and the resulting mixture was stirred for 6 h at room temperature. The reaction mixture was filtered over a Celite and the filtrate was concentrated under reduced pressure to leave a mixture of unchanged amine **13**, α-piperidino ketone **14** and triphenylbismuthine **8** as an oily residue. Products were identified by comparison with the authentic specimens.[24]

Reactions of (2-*Oxoalkyl*)*triphenylbismuthonium Salts* **3** *and* **4** *with Sodium Aryl Oxides* **15** *or Arenethiolates* **17**.—To a well stirred suspension of the bismuthonium salt **3** or **4** (0.8 mmol) in THF (2 cm^3) at −50 °C was added a solution of the sodium aryl oxide **15** or arenethiolate **17** in the same solvent (3 cm^3) generated from well-washed sodium hydride (*ca.* 19 mg) and hydroxyarene or arenethiol (0.8 mmol). The resulting yellow solution turned colourless after 1 h under gentle reflux in the former case, and upon warming to room temperature in the latter. The mixture was concentrated under reduced pressure and extracted with diethyl ether (15 cm^3). Removal of the solvent from the extract afforded an oily residue, which was

purified by column chromatography on silica gel using hexane–ethyl acetate as the eluent to give the corresponding α-aryloxy- or α-arylthio-ketone **16** or **18** and triphenylbismuthine **8**.

3,3-*Dimethyl*-1-*phenoxybutan*-2-*one* **16a**. M.p. 44–45 °C (lit.,[25] 46 °C); δ_H 1.24 [9 H, s, C(CH$_3$)$_3$], 4.86 (2 H, s, OCH$_2$), 6.87 (2 H, d, J 7.6, Ph), 6.97 (1 H, t, J 7.3, Ph) and 7.27 (2 H, t, J 7.5, Ph); ν_{max}(KBr)/cm^{-1} 1725, 1601, 1497, 1370, 1310, 1229, 1175, 1049, 990, 754 and 691; m/z (EI) 192 (M$^+$), 149, 107, 85 and 77 (Found: C, 74.9; H, 8.4. $C_{12}H_{16}O_2$ requires C, 75.0; H, 8.4%).

3,3-*Dimethyl*-1-*naphthyloxybutan*-2-*one* **16b**. M.p. 56–57 °C (lit.,[25] 80–81 °C); δ_H 1.27 [9 H, s, C(CH$_3$)$_3$], 5.01 (2 H, s, OCH$_2$), 6.63 (1 H, d, J 7.6, Ar), 7.31 (1 H, t, J 7.9, Ar), 7.42–7.45 (3 H, m, Ar), 7.78 (1 H, m, Ar) and 8.38 (1 H, m, Ar); ν_{max}(KBr)/cm^{-1} 1728, 1582, 1509, 1460, 1393, 1271, 1242, 1090, 1061, 1019, 789 and 766; m/z (EI) 242 (M$^+$), 158, 157, 127, 115 and 57 (Found: C, 79.3; H, 7.3. $C_{16}H_{18}O_2$ requires C, 79.3; H, 7.5%).

1-(4-*Chlorophenoxy*)-3,3-*dimethylbutan*-2-*one* **16c**. M.p. 61–62 °C (lit.,[25] 62 °C); δ_H 1.23 [9 H, s, C(CH$_3$)$_3$], 4.84 (2 H, s, OCH$_2$), 6.79 (2 H, d, J 9.0, Ar) and 7.21 (2 H, d, J 9.0, Ar); ν_{max}(KBr)/cm^{-1} 1719, 1595, 1579, 1491, 1435, 1285, 1246, 1051, 994, 824, 801 and 654; m/z (EI) 228 (M$^+$, ^{37}Cl), 226 (M$^+$, ^{35}Cl), 141, 139, 113, 111, 85 and 57 (Found: C, 63.3; H, 6.8. $C_{12}H_{15}ClO_2$ requires C, 63.6; H, 6.7%).

3.3-*Dimethyl*-1-*phenylthiobutan*-2-*one* **18a**. Oil (lit.,[26] b.p. 112–114 °C/0.1 mmHg); δ_H 1.19 [9 H, s, C(CH$_3$)$_3$], 3.95 (2 H, s, SCH$_2$) and 7.15–7.45 (5 H, m, Ph); ν_{max}(neat)/cm^{-1} 1707, 1582, 1478, 1439, 1059, 1024, 999 and 739; m/z (EI) 208 (M$^+$), 125, 123, 109, 85 and 77 (Found: C, 68.9; H, 7.6. $C_{12}H_{16}OS$ requires C, 69.2; H, 7.7%).

1-(4-*Chlorophenylthio*)-3,3-*dimethylbutan*-2-*one* **18b**. M.p. 42–43 °C (lit.,[25] 42 °C); δ_H 1.18 [9 H, s, C(CH$_3$)$_3$], 3.92 (2 H, s, SCH$_2$), 7.24 (2 H, d, J 8.9, Ar) and 7.32 (2 H, d, J 8.9, Ar); ν_{max}(KBr)/cm^{-1} 1707, 1477, 1391, 1366, 1096, 1059, 1013 and 822; m/z (EI) 244 (M$^+$, ^{37}Cl), 242 (M$^+$, ^{35}Cl), 159, 157, 85 and 57 (Found: C, 59.4; H, 6.3. $C_{12}H_{15}ClOS$ requires C, 59.4; H, 6.2%).

Reaction of (2-*Oxoalkyl*)*triphenylbismuthonium Salts* **3** *or* **4** *with Sodium Toluene*-p-*sulfinate* **19**.—A mixture of compound **3** or **4** (0.3 mmol), hydrated sodium toluene-*p*-sulfinate **19** (750 mg, 3 mmol) and DMF (5 cm^3) was stirred at room temperature for 24 h and then poured into water (10 cm^3). The organic layer was extracted with diethyl ether (10 cm^3 × 3) and the combined extracts were washed with brine (10 cm^3 × 3), dried (MgSO$_4$) and concentrated under reduced pressure to leave a crystalline residue, which was purified by column chromatography on silica gel using hexane–ethyl acetate as the eluent to give the α-sulfonyl ketone **20** and triphenylbismuthine **8**.

3,3-*Dimethyl*-1-(p-*tolylsulfonyl*)*butan*-2-*one* **20a**. M.p. 113–114 °C; δ_H 1.11 [9 H, s, C(CH$_3$)$_3$], 2.44 (3 H, s, ArCH$_3$), 4.33 (2 H, s, SO$_2$CH$_2$), 7.36 (2 H, d, J 8.4, Ar) and 7.82 (2 H, d, J 8.4, Ar); ν_{max}(KBr)/cm^{-1} 1717, 1595, 1370, 1320, 1291, 1167, 1140, 1055, 884, 756, 556 and 515; m/z (EI) 170, 155, 105, 91, 65 and 57 (Found: C, 61.2; H, 7.1. $C_{13}H_{18}O_3S$ requires C, 61.4; H, 7.1%).

1-*Phenyl*-2-(p-*tolylsulfonyl*)*ethanone* **20b**. M.p. 106–107 °C (lit.,[27] 105.5–106.5 °C); δ_H 2.43 (3 H, s, ArCH$_3$), 4.72 (2 H, s, SO$_2$CH$_2$), 7.32 (2 H, d, J 8.3, Ar), 7.46 (2 H, t, J 7.7, Ph), 7.61 (1 H, t, J 7.6, Ph), 7.76 (2 H, d, J 8.3, Ar) and 7.94 (2 H, d, J 7.8, Ph); ν_{max}(KBr)/cm^{-1} 1680, 1597, 1449, 1320, 1271, 1150, 1086, 994, 824, 739, 693, 590, 534 and 502; m/z (EI) 210, 155, 149, 105, 91, 77 and 65.

Reaction of (2-*Oxoalkyl*)*triphenylbismuthonium Salts* **3** *with Potassium Halides* **21**.—A mixture of compound **3** (1 mmol), potassium halide **21** (10 mmol) and DMF (5 cm^3) was stirred at room temperature for 24 h and then poured into water (10 cm^3). The organic layer was extracted with diethyl ether (10 cm^3 × 3)

and the combined extracts were washed with brine (10 cm³ × 3), dried (MgSO₄) and concentrated under reduced pressure to leave a mixture of the α-halogeno ketone **22** and triphenylbismuthine **8** as an oily residue. Products were identified by comparison with the authentic specimens.

X-*Ray Crystallography of Compounds* **3a**, **4a** *and* **5a**.—Intensity data were recorded on a Rigaku AFC5R diffractometer with graphite-monochromated MoKα radiation and a 12 kW rotating anode generator using the ω-2θ scan technique to a maximum 2θ-value listed in Table 1. Data were corrected for Lorentz and polarization effects. The structure was solved by a combination of the Patterson method and direct methods.[28] The non-hydrogen atoms were refined anisotropically. The weighting scheme, $w = 1/\sigma^2(F_0)$, was employed. Neutral atom-scattering factors were taken from Cromer and Waber.[29] Anomalous dispersion effects were included in F_c;[30] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[31] All calculations were performed using the TEXSAN[32] crystallographic software package of Molecular Structure Corporation. The PLUTO[33] program was used to obtain Figs. 1–3. Crystal data, selected bond lengths and bond angles are given in Tables 1–4. Full details of crystal data, fractional atomic coordinates, bond lengths, bond angles, hydrogen coordinates and thermal parameters of compounds **3a**, **4a** and **5a** have been deposited at the Cambridge Crystallographic Data Centre.*

Acknowledgements

* For details see 'Instructions for Authors (1994)', *J. Chem. Soc., Perkin Trans 1*, 1994, Issue 1.

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