# Triphenylbismuthonium 2-Oxoalkylide, A Moderately Stabilized Bismuthonium Ylide: Generation and Reactions with Some Electrophiles

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Treatment of (2-oxoalkyl)triphenylbismuthonium tetrafluoroborates 3 with potassium tert-butoxide in tetrahydrofuran at −78 °C produced triphenylbismuthonium 2-oxoalkylides 4, which readily underwent epoxidation with the aldehydes 5 to give the α,β-epoxy ketones 7 with high trans selectivity. The ylide 4a reacted with dimedone 11, the sulfonic acid 13, the thiol 15 and the isocyanate 17 to afford the corresponding ketones 12, 14, 16 and 19 in moderate to good yields. Reaction of the ylide 4c with the α,β-unsaturated ketones 10 and 21 afforded the 1,2-dibenzoyl- and the 1,2,3-tribenzoyl- cyclopropanes 20 and 22, respectively, although the yields were low. In the presence of a catalytic amount of nitrosobenzene 23, the ylide 4a suffered a unique decomposition to give the 2,2,7,7-tetramethyloct-4-ene-3,6-dione 24 in quantitative yield, while the reaction with the nitrile oxide 25 yielded the isoxazoline 26. In all of these reactions, triphenylbismuthane 6 was the additional major product.

Of the ylides which may be derived from the pnicogen and chalcogen elements, the bismuthonium ylides are the ones which have attracted the least attention as possible synthetic tools.[1] This may, in part, be due to the lack of a facile synthesis for these ylides. The first synthesis of a bismuthonium ylide was claimed by Lloyd et al. in 1967, who obtained a deep blue substance by heating a mixture of triphenylbismuthane and diazotetraphenylcyclopentadiene at 140 °C and assigned it a structure triphenylbismuthonium tetraphenylcyclopentadienylide 1 simply on the basis of its electronic spectrum.[2] Later in 1985, Barton et al. allowed 5,5-dimethylcyclohexan-1,3-dione (dimedone) to react with triphenylbismuth carbonate to obtain triphenylbismuthonio-4,4-dimethyl-2,6-dioxocyclohexan-1-ide 2 as a gummy substance.[3] Suzuki et al. have isolated this ylide 2 in a crystalline form and elucidated its structure by X-ray diffraction measurements.[4] The high stability of the ylide 2 was attributed to the interaction between the carbonyl oxygen atom and the cationic bismuth centre. Additional examples of this type of stabilized bismuthonium ylides have been presented.[5,6] but their synthetic potentials have not been explored extensively.
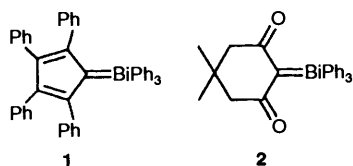
The literature contains very few examples of moderately stabilized bismuthonium ylides. The most common approach to this type of ylide is the proton abstraction from the onium salts by a base. Accordingly, this methodology was adopted to generate the bismuthonium ylides and here the generation and reactions of a moderately stabilized ylide, triphenylbismuthonium 2-oxoalkylide 4 are reported and discussed.

Results and Discussion

Recently, the efficient synthesis of (2-oxoalkyl)triphenylbismuthonium tetrafluoroborates 3 was reported.[7] Removal of a proton from the methylene carbon adjacent to the bismuth cation of the salts 3 should yield the bismuthonium ylides 4, as
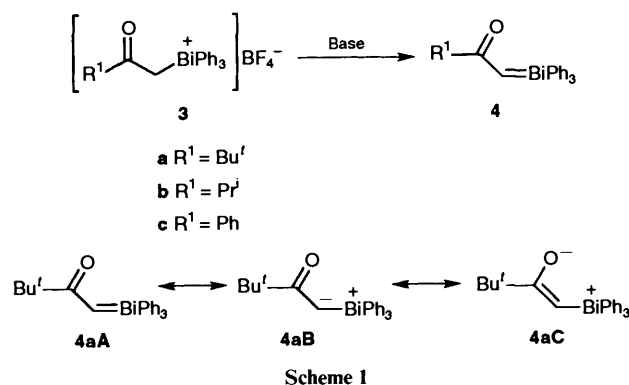
Scheme 1

shown in Scheme 1. Thus, treatment of a suspension of the salts 3a–c in tetrahydrofuran (THF) with a base at low temperatures gave the expected ylides 4a–c as a yellow solution. However, many attempts to isolate these ylides under ambient conditions were unsuccessful, probably owing to their thermal instability and moisture sensitivity.
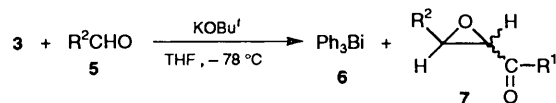
In order to confirm the in situ generation of the ylides 4, NMR monitoring was performed for the reaction of (3,3-dimethyl-2-oxobutyl)triphenylbismuthonium tetrafluoroborate 3a and potassium tert-butoxide (KOBu^t) in [^{2}H$_8$]THF. Addition of an equimolar amount of KOBu^t to a suspension of the salt 3a in [^{2}H$_8$]THF at −78 °C gave a yellow solution, where new sets of ^{1}H and ^{13}C NMR peaks replaced those due to the salt 3a.† The new species generated was assigned to (3,3-dimethyl-2-oxobutylidene)triphenyl-λ^5-bismuthane 4a on the basis of the NMR spectra, where the signals due to the α-proton, ylidic and carbonyl carbons were observed at δ_H 5.84, δ_C 86.4 and 187.9, respectively, the last two ^{13}C signals being especially diagnostic. The peak of the ylidic carbon of compound 4a (δ_C 86.4) appeared at lower field than that of the corresponding α-carbon of the parent salt 3a (δ_C 59.6) in accord

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† Compound 4a in [^{2}H$_8$]THF; δ_H 1.22 (9 H, s), 5.84 (1 H, s), 7.45–7.55 (9 H, m) and 7.88 (6 H, m); δ_C 29.9 (q, J 127), 40.8 (s), 86.4 (d, J 186), 131.0 (d, J 157), 131.3 (d, J 160), 136.7 (d, J 163), 143.3 (s) and 187.9 (s). Salt 3a in [^{2}H$_8$]THF; δ_H 1.27 (9 H, s), 5.94 (2 H, s), 7.50–7.63 (9 H, m) and 7.85 (6 H, m); δ_C 27.15 (q), 46.4 (s), 59.6 (t, J 147), 132.2 (d, J 160), 132.2 (d, J 160), 137.0 (d, J 166), 140.6 (s) and 213.2 (s).

with the change in hybridization mode of the carbon atom from sp^3 to sp^2. A large value for the C–H coupling constant of the ylide **4a** (J 186) as compared with the salt **3a** (J 147) is also a reflection of the increase of s character in the C–H bond. Furthermore, the resonance of the carbonyl carbon of compound **4a** (δ_C 187.9) was observed at higher field than that of compound **3a** (δ_C 213.2). This is indicative of a relatively high electron density localized on the relevant carbon atom. Judging from these spectral features, the ylide **4a** may well be represented as a hybrid of the canonical forms **4aA**, **4aB** and **4aC**, in which the role of the last two would be more important (Scheme 1).

Ylide **4a** was sufficiently stable in THF at −78 °C, but it completely decomposed at room temperature. When the solution was allowed to warm to ambient temperature, the NMR peaks of the ylide **4a** were gradually replaced by those of decomposition products, the major component of which being triphenylbismuthane **6**. By monitoring the decaying of the peak at δ_H 5.84, the half-life of the ylide **4a** was estimated to be ca. 30 min at −30 °C. Reaction of the other onium salts **4b–c** with KOBu^t also led to similar results. Bismuthonium ylides **4** bearing one electron-withdrawing substituent on the ylidic carbon may be classified as moderately stabilized ylides. This is in contrast to the phosphonium[8] and arsonium isologues,[9] which are stable enough to be isolated without significant decomposition. Because of the lower electronegativity as well as large difference in p-orbital size, the role of the bismuth cation would be less important than that of phosphorus and arsenic cations in delocalizing the negative charge on the adjacent carbanion centre. Indeed, the stability of bismuthonium 2-oxoalkylide **4** is much lower than the ylide **2**, which enjoys the double stabilizing effect of the β,β′-dicarbonyl function attached to the bismuth atom.

*Reaction of the Bismuthonium Ylides **4** with Various Electrophiles.*—Since bismuthonium 2-oxoalkylides **4** undergo facile thermal decomposition, all of their reactions with electrophiles were examined at low temperatures. Treatment of the salt **3a** with KOBu^t at −78 °C in THF afforded a yellow solution, to which was added benzaldehyde **5a** at the same temperature. As the temperature was allowed to rise to ambient, the colour of the solution was gradually lost and the *trans*- and *cis*-1,2-epoxy-4,4-dimethyl-1-phenylpentan-3-ones **7a** were obtained as the sole coupling products, along with bismuthane **6** (Scheme 2). Irrespective of whether the salt **3a** was treated with
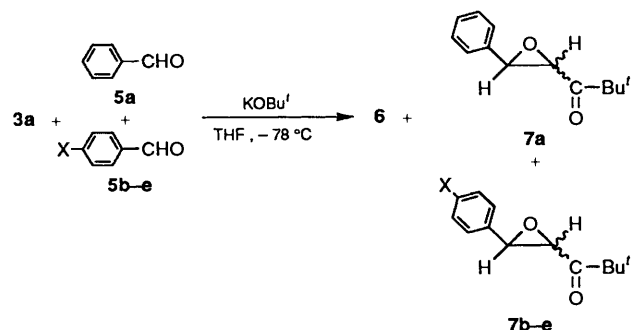
Table 1 The effect of bases on the yields and isomeric ratios of the epoxy ketones **7a** in the reaction of bismuthonium salt **3a** with benzaldehyde **5a**

Entry	Base	Solvent	Method[a]	Yield/%[b]	
				6	7a (trans:cis)
1	KOBu^t	THF	A	89	90 (94:6)
2	KOBu^t	THF	B	84	85 (88:12)
3	KN(SiMe₃)₂	THF	A	97	69 (95:5)
4	NaH	THF	A	93	59 (85:15)
5	NaNH₂	THF	A	90	74 (91:9)
6	NaN(SiMe₃)₂	THF	A	97	74 (97:3)
7	LDA	THF	A	91	85 (83:17)
8	LiBu	THF	A	39	66 (86:14)[c]
9	DBU	THF	A	93	83 (76:24)
10	KOBu^t	Toluene	A	94	47 (92:8)[c]
11	DBU	Toluene	A	92	74 (84:16)[c]

[a] For the detail of each method, see Experimental section. [b] Yield refers to isolated compound and is based on unrecovered salt **3a**. The *trans:cis* isomer ratio was determined on the basis of the integration area of each epoxy ring proton (J_{trans} ca. 2 Hz; J_{cis} ca. 5 Hz). [c] Some unidentified products were formed.

a variety of aldehydes **5** to give the corresponding α,β-epoxy ketones **7**, along with triphenylbismuthane **6** (Table 2). In all cases examined, no Wittig-type products could be detected. While the *trans* selectivity was always dominant, it was sensitive to the steric influences of substituent groups. Thus, the higher *trans:cis* ratio was observed in the reactions with *ortho*-substituted aromatic aldehydes as compared with *para*-substituted ones (entries 2 vs. 8 and 5 vs. 9). The polar effect of substituent groups on the isomer ratio was not so significant. Nitro and cyano functions remained intact (entries 5, 6, 9 and 14). The reaction could also be applied to aliphatic and α,β-unsaturated aldehydes (entries 15, 16, 18 and 19), but 2,2-dimethylpropanal **5l** could not be converted into an epoxy ketone, probably for steric reasons (entry 17).

Table 3 shows the reactivities of the *para*-substituted benzaldehydes **5b–e** relative to benzaldehyde **5a**, determined by the competition method (Scheme 3). Electron-withdrawing

Scheme 2

KOBu^t before (Method A) or after (Method B) the addition of the aldehyde **6a**, a mixture of *trans* and *cis* epoxy ketones **7a** was obtained almost in similar yield, the former isomer being always predominant. This is the first example of the epoxy-ring formation from the pnicogen ylides having the β-oxoalkylidene group. Bases such as potassium bis(trimethylsilyl)amide [KN(SiMe₃)₂], sodium hydride (NaH), sodium amide (NaNH₂), sodium bis(trimethylsilyl)amide [NaN(SiMe₃)₂], lithium diisopropylamide (LDA), butyllithium (LiBu) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were all effective in producing the epoxides **7** (Table 1). No reaction took place without a base. The effect of solvents is not so marked, thus ruling out the contribution of a highly polar transition state. Because of the good solubility of the reagents, as well as simplicity of the procedure, all ylide reactions were performed using KOBu^t as the base and THF as the solvent, unless otherwise noted.

Bismuthonium ylides **4** underwent the epoxidation with

Scheme 3

substitutents on the aromatic ring were found to facilitate the reaction, suggesting that the nucleophilic attack of the ylide carbanion on the carbonyl group is the rate-determining stage.

Phosphonium and arsonium ylides with an acyl group at the α-position are generally classified as stabilized ylides, since the negative charge on the ylidic carbon is delocalized by resonance with the carbonyl moiety.[8,9] This class of stabilized ylides usually undergo the Wittig-type reaction with aldehydes to give α,β-unsaturated carbonyl compounds, along with the corresponding organoheteroatom oxides. For example, triphenylphosphonium and triphenylarsonium phenacylides **8** react with benzaldehyde **5a** to afford the chalcone **10** as the sole coupling product.[10,11] The same Wittig-type product **10** was formed in

**Table 2** Reaction of the bismuthonium salts **3a–c** with aldehydes **5a–n** in the presence of KOBu^t

Entry	Salt 3	Aldehyde 5	Method[a]	Ketone 7	Yield (%)[b]	Ratio trans:cis
1	**a** (R^1 = Bu^t)	**a** (R^2 = Ph)	B	**a**	85	88:12
2	**a**	**b** (R^2 = 4-MeC$_6$H$_4$)	B	**b**	75	91:9
3	**a**	**c** (R^2 = 4-ClC$_6$H$_4$)	B	**c**	70	91:9
4	**a**	**d** (R^2 = 4-MeOC$_6$H$_4$)	B	**d**	70	100:0
5	**a**	**e** (R^2 = 4-NO$_2$C$_6$H$_4$)	A	**e**	83	84:16
6	**a**	**f** (R^2 = 4-CNC$_6$H$_4$)	B	**f**	72	96:4
7	**a**	**g** (R^2 = 1-naphthyl)	B	**g**	66	100:0
8	**a**	**h** (R^2 = 2-MeC$_6$H$_4$)	B	**h**	66	100:0
9	**a**	**i** (R^2 = 2-NO$_2$C$_6$H$_4$)	A	**i**	94	93:7
10	**b** (R^1 = Pr^i)	**b** (R^2 = 4-MeC$_6$H$_4$)	B	**j**	85	100:0
11	**b**	**c** (R^2 = 4-ClC$_6$H$_4$)	B	**k**	77	93:7
12	**c** (R^1 = Ph)	**a** (R^2 = Ph)	B	**l**	71	88:12
13	**c**	**c** (R^2 = 4-ClC$_6$H$_4$)	B	**m**	67	97:3
14	**c**	**e** (R^2 = 4-NO$_2$C$_6$H$_4$)	B	**n**	75	91:9
15	**c**	**j** (R^2 = Bu)	A	**o**	53	66:34
16	**c**	**k** (R^2 = Bu^i)	A	**p**	54	71:29
17	**c**	**l** (R^2 = Bu^t)	A	N.R.[c]	—	—
18	**a**	**m** [R^2 = (E)-CH=CHPh]	A	**q**	60	78:22
19	**c**	**n** [R^2 = (E)-CH=CHPr]	A	**r**	41	83:17

[a] For the detail of each method, see experimental section. [b] Yield refers to isolated compound and is based on unrecovered salt **3**. Triphenylbismuthane **6** was another major product isolated in 79–97% yields. [c] No reaction took place and the aldehyde was recovered.

Table 3 Relative reactivities of the *p*-substituted benzaldehydes **5b–e** *vs.* benzaldehyde **5a**

Entry	Aldehyde 5	Product ratio 7b–e:7a
1	**d** (X = MeO)	16:84
2	**b** (X = Me)	38:62
3	**c** (X = Cl)	71:29
4	**e** (X = NO$_2$)	77:23

the reaction of phenacylstibonium salt **9** with the aldehyde **5a** in the presence of KOBu^t (Scheme 4).

Scheme 4
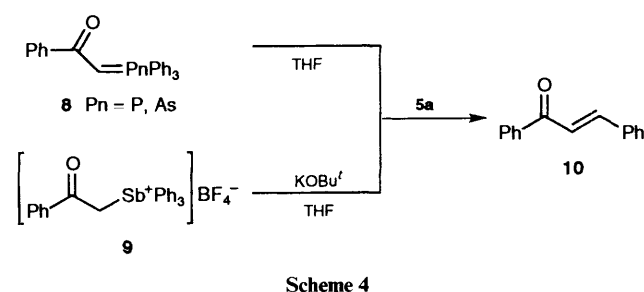
However, this general trend does not hold with the bismuthonium ylides **4**, which form exclusively the epoxides **7**, as has been demonstrated. The difference in reaction mode may be attributed to the weaker interaction to form a bismuth–oxygen bond, as compared with those to form a phosphorus–, arsenic– or antimony–oxygen bond. The diastereoisomer of epoxide **7** that is formed should be determined by interaction between the ylide **4** and the aldehyde **5** during the carbon–carbon bond-forming process. Although further studies need to be performed for a better understanding of this process, the preference seems to line up the ylide and aldehyde functions in such a way as to give the *trans* isomer ultimately, avoiding the steric congestion between the substituents in the transition state.

Ketones such as acetophenone and benzophenone did not react with the bismuthonium ylide **4**. *N*-Ethylimines also failed to react. The chemoselectivity between aldehydes and ketones was clearly demonstrated by a competitive reaction of benzaldehyde and acetophenone with the ylide **4a**, where the

aldehyde was completely converted into the α,β-epoxy ketone **7a** while the ketone remained unchanged. On the other hand, the ylide **4a** readily reacted with dimedone **11**, the sulfonic acid **13** and benzenethiol **15** to give the corresponding α-alkoxy ketone **12**, the α-sulfoxy ketone **14** and the α-phenylsulfanyl ketone **16**, respectively, together with triphenylbismuthane **6** as the common additional product (Scheme 5). When treated with phenyl isocyanate **17**, the ylide **4a** transferred both 2-oxoalkylidene and phenyl groups to the substrate to afford the β-keto amide **19** along with a moderate recovery of bismuthane **6**. In the last reaction, the intermediate carbamoyl bismuthonium ylide **18**, generated during the initial stage,

Scheme 5
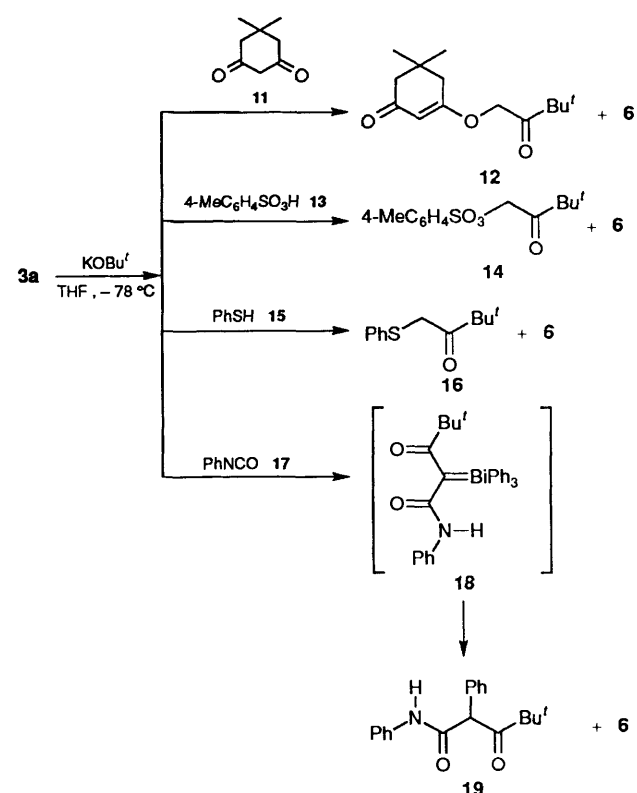
decomposed *via* the intramolecular migration of a phenyl group from the bismuth to the ylidic carbon atom.

The ylide **4c**, generated from the salt **3c** and LDA, underwent the cyclopropanation reaction with chalcone **10** to form 1,2-dibenzoyl-3-phenylcyclopropane **20**, although the yield was not high. A similar reaction with (*E*)-1,4-diphenylbut-2-ene-1,4-dione **21** led to 1,2,3-tribenzoylcyclopropanes **22** (Scheme 6).
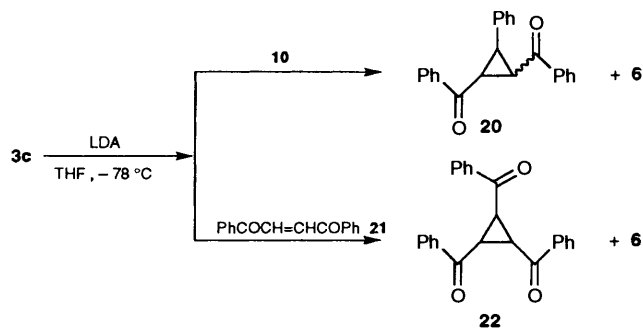
Scheme 6

Decomposition of the Bismuthonium Ylide **4**.—Thermal decomposition of the bismuthonium ylides **4** has been found to be fairly complex. For example, when a THF solution of the ylide **4a** (generated at −78 °C using KOBu^t as the base) was allowed to warm to ambient temperature, bismuthane **6** was obtained in *ca.* 80% yield, together with small to trace amounts of pinacolone, α-phenylpinacolone and other unidentified products.* The use of NaH or LDA as the base also led to similar results. These products may be accounted for by assuming the fragmentation of the ylide **4** leading to carbene formation, phenylation and hydrolysis. Rather surprisingly, some additives were found to have a dramatic effect on the decomposition mode of the ylide **4**. Thus, when a catalytic amount of nitrosobenzene **23** was added to a THF solution of the ylide **4a** at −78 °C, triphenylbismuthane **6** and (*E*)-2,2,7,7-tetramethyloct-4-ene-3,6-dione **24** were formed in good yields (Scheme 7). It has previously been reported that β-carotene
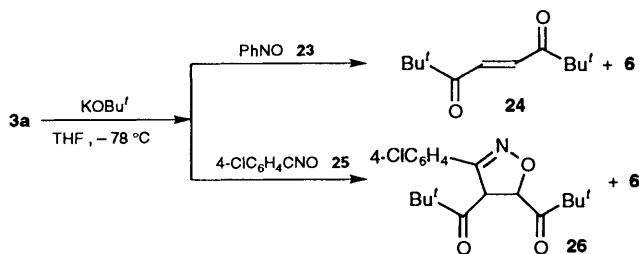
Scheme 7

could be obtained by the dimerization of phosphonium ylides induced by *p*-(dimethylamino)nitrosobenzene.[12] The present reaction is unique in that catalytic amounts of nitrosobenzene can induce the dimeric decomposition of the ylide **4a** leading to the olefin **24**. It is not possible to comment on the mechanism of this interesting coupling reaction at present. The reaction of the ylide **4a** with the nitrile oxide **25** afforded the isoxazoline **26**, which probably arose from the 1,3-dipolar cycloaddition of the substrate **25** with the initially formed olefin **24** (Scheme 7). In this reaction, the nitrile oxide **25** apparently catalysed the decomposition of the ylide **4a**.

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* A similar decomposition of the ylide **4c** gave the bismuthane **6**, acetophenone, 1,4-diphenylbut-2-ene-1,4-dione, 1,2,3-tribenzoylcyclo-propane, α-phenylacetophenone, α,α-diphenylacetophenone, and several unidentified products.

Further studies on the synthetic applications of function-alized bismuthonium compounds are in progress.

Experimental

General.—All reactions were performed under an atmos-phere of argon. THF was distilled from sodium benzophenone ketyl before use. Toluene was distilled from sodium wire and stored over molecular sieves 4 Å. Bismuthonium salts **3a–c** were prepared as reported previously.[7] 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 or a JEOL JNM-α-500 (500 MHz) spectrometer in CDCl₃ unless otherwise noted, using tetramethylsilane as an internal standard. Coupling constants *J* are given in Hz. IR spectra were observed on a SHIMADZU FTIR-8100 spectrophotometer. EI mass spectra were obtained on a SHIMADZU GCMS-QP2000A spectrometer and FAB mass spectra on a JEOL JMS-HS 110 spectrometer with 3-nitrobenzyl alcohol as the matrix. Elemental analyses were performed at the Microanalytical Laboratories of Kyoto University.

NMR Monitoring of the Generation and Decomposition of the Bismuthonium Ylide **4a**.—To a suspension of (3,3-dimethyl-2-oxobutyl)triphenylbismuthonium tetrafluoroborate **3a** (63 mg, 0.1 mmol) in [²H₈]THF (0.5 cm³) in an NMR tube was added KOBu^t (12 mg, 0.1 mmol) at −78 °C under argon. NMR monitoring was performed over the temp. range −78 °C to ambient (at 10 °C intervals) using variable temperature equipment. At −78 °C the ylide **4a** did not show any sign of decomposition, whilst at room temp. it had completely decomposed to give a complex mixture.

Reaction of the Bismuthonium Ylides **4** *with the Aldehydes* **5**; *Method A*.—To a stirred suspension of the (2-oxoalkyl)-triphenylbismuthonium salt **3** (0.2 mmol) in a given solvent (5 cm³) was added a base (0.2 mmol) at −78 °C. Within a few minutes the reaction mixture turned clear and yellow. After 30 min the aldehyde **5** (0.2 mmol) was added and the resulting mixture was allowed to warm to ambient temp., concentrated under reduced pressure and then extracted with benzene (10 cm³ × 2). Removal of the solvent gave an oily residue, which was chromatographed on a silica-gel column with hexane–ethyl acetate as the eluent to yield the bismuthane **6** and α,β-epoxy ketone **7**.

Method B.—To a stirred mixture of the salt **3** (0.2 mmol), the aldehyde **5** (0.2 mmol) and the solvent (5 cm³) was added a base (0.2 mmol) at −78 °C. Then the temp. was allowed to rise to ambient. Work-up as described above gave compounds **6** and **7**. The results are summarized in Tables 1 and 2. All the bases used were of reagent grade and NaH was thoroughly washed with dry pentane before use.

1,2-*Epoxy*-4,4-*dimethyl*-1-*phenylpentan*-3-*one* **7a**. *trans* Iso-mer; m.p. 40–41 °C; δ$_H$ 1.24 (9 H, s), 3.86 (2 H, s) and 7.27–7.40 (5 H, m); ν$_{max}$(KBr)/cm⁻¹ 1713, 1480, 1458, 1368, 1071, 1000, 885, 756 and 698; *m/z* 204 (M⁺), 189, 120, 105, 91 and 77 (Found: C, 76.2; H, 7.9. C₁₃H₁₆O₂ requires C, 76.4; H, 7.9%). *cis* Isomer; m.p. 40–41 °C; δ$_H$ 0.98 (9 H, s), 4.22 (1 H, d, *J* 4.9), 4.34 (1 H, d, *J* 4.9) and 7.27–7.45 (5 H, m); ν$_{max}$(KBr)/cm⁻¹ 1717, 1478, 1452, 1368, 1075, 994, 754 and 700; *m/z* 204 (M⁺), 189, 120, 105, 91 and 77 (Found: C, 76.1; H, 7.9. C₁₃H₁₆O₂ requires C, 76.4; H, 7.9%).

1,2-*Epoxy*-4,4-*dimethyl*-1-(4-*methylphenyl*)*pentan*-3-*one* **7b**. *trans* Isomer; m.p. 60–61 °C; δ$_H$ 1.23 (9 H, s), 2.36 (3 H, s), 3.81 (1 H, d, *J* 1.9), 3.85 (1 H, d, *J* 1.9) and 7.19 (4 H, s);

ν_{max}(KBr)/cm^{-1} 1707, 1520, 1478, 1429, 1397, 1075, 1007, 893, 831, 804 and 777; m/z 218 (M$^+$), 145, 134, 119, 105, 91, 85, 77 and 57 (Found: C, 76.9; H, 8.4. $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.3%). cis Isomer; m.p. 50–51 °C; δ_H 0.99 (9 H, s), 2.31 (3 H, s), 4.20 (1 H, d, J 4.8), 4.30 (1 H, d, J 4.8), 7.10 (2 H, d, J 8.1) and 7.22 (2 H, d, J 8.1); ν_{max}(KBr)/cm^{-1} 1707, 1520, 1478, 1429, 1397, 1075, 1007, 893, 831, 804 and 777; m/z 218 (M$^+$), 145, 134, 119, 105, 91, 85, 77 and 57 (Found: C, 76.9; H, 8.4. $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.3%).

1-(4-*Chlorophenyl*)-1,2-*epoxy-4,4-dimethylpentan-3-one* **7c**. trans Isomer; m.p. 66–67 °C; δ_H 1.24 (9 H, s), 3.82 (1 H, d, J 1.9), 3.84 (1 H, d, J 1.9), 7.25 (2 H, d, J 8.6) and 7.36 (2 H, d, J 8.6); ν_{max}(KBr)/cm^{-1} 1709, 1495, 1429, 1397, 1366, 1076, 1015, 891, 830 and 740; m/z 240 (M$^+$; ^{37}Cl), 238 (M$^+$; ^{35}Cl), 156, 154, 127, 125 and 89 (Found: C, 65.55; H, 6.4. $C_{13}H_{15}ClO_2$ requires C, 65.4; H, 6.3%). cis Isomer; m.p. 80–81 °C; δ_H 1.00 (9 H, s), 4.23 (1 H, d, J 4.8), 4.31 (1 H, d, J 4.8) and 7.30 (4 H, s); ν_{max}(KBr)/cm^{-1} 1709, 1493, 1476, 1370, 1090, 1073, 1015, 994, 912, 874, 824, 804, 766 and 727; m/z 240 (M$^+$; ^{37}Cl), 238 (M$^+$; ^{35}Cl), 156, 154, 127, 125 and 89 (Found: C, 65.0; H, 6.3. $C_{13}H_{15}ClO_2$ requires C, 65.4; H, 6.3%).

1,2-*Epoxy*-1-(4-*methoxyphenyl*)-4,4-*dimethylpentan-3-one***7d**. trans Isomer; oil; δ_H 1.23 (9 H, s), 3.81 (4 H, m), 3.86 (1 H, d, J 1.9), 6.90 (2 H, d, J 8.8) and 7.23 (2 H, d, J 8.8); ν_{max}(neat)/cm^{-1} 1703, 1605, 1578, 1512, 1460, 1260, 1165, 1100, 1030, 833 and 770; m/z 234 (M$^+$), 165, 150, 137, 135, 121, 77 and 57.

1,2-*Epoxy*-4,4-*dimethyl*-1-(4-*nitrophenyl*)*pentan-3-one* **7e**. trans Isomer; m.p. 134–135 °C; δ_H 1.25 (9 H, s), 3.85 (1 H, d, J 1.8), 4.00 (1 H, d, J 1.8), 7.50 (2 H, d, J 8.8) and 8.24 (2 H, d, J 8.8); ν_{max}(KBr)/cm^{-1} 1713, 1600, 1526, 1478, 1401, 1341, 1105, 1078, 1011, 857, 843, 793, 729 and 693; m/z 249 (M$^+$), 85 and 57 (Found: C, 62.5; H, 6.1; N, 5.6. $C_{13}H_{15}NO_4$ requires C, 62.6; H, 6.1; N, 5.6%). cis Isomer; m.p. 108–109 °C; δ_H 1.01 (9 H, s), 4.32 (1 H, d, J 4.9), 4.42 (1 H, d, J 4.9), 7.56 (2 H, d, J 8.8) and 8.18 (2 H, d, J 8.8); ν_{max}(KBr)/cm^{-1} 1711, 1605, 1514, 1345, 1078, 995, 918, 884, 853, 749 and 696; m/z 249 (M$^+$), 234, 136, 89 and 57 (Found: C, 62.4; H, 6.1; N, 5.7. $C_{13}H_{15}NO_4$ requires C, 62.6; H, 6.1; N, 5.6%).

1-(4-*Cyanophenyl*)-1,2-*epoxy-4,4-dimethylpentan-3-one* **7f**. trans Isomer; m.p. 104–105 °C; δ_H 1.25 (9 H, s), 3.86 (1 H, d, J 1.9), 3.95 (1 H, d, J 1.9), 7.46 (2 H, d, J 8.4) and 7.69 (2 H, d, J 8.4); ν_{max}(KBr)/cm^{-1} 2230, 1711, 1609, 1485, 1397, 1076, 1009, 891, 878, 831 and 793; m/z 229 (M$^+$), 145, 116 and 57 (Found: C, 73.55; H, 6.6; N, 6.0. $C_{14}H_{15}NO_2$ requires C, 73.3; H, 6.6; N, 6.1%). cis Isomer; m.p. 107–108 °C; δ_H 1.01 (9 H, s), 4.31 (1 H, d, J 4.8), 4.39 (1 H, d, J 4.8), 7.50 (2 H, d, J 8.3) and 7.62 (2 H, d, J 8.3); ν_{max}(KBr)/cm^{-1} 2228, 1711, 1611, 1478, 1420, 1372, 1075, 1040, 994, 912, 874, 831 and 731; m/z 229 (M$^+$), 214, 156, 144, 116 and 57 (Found: C, 73.3; H, 6.6; N, 5.95. $C_{14}H_{15}NO_2$ requires C, 73.3; H, 6.6; N, 6.1%).

1,2-*Epoxy-4,4-dimethyl*-1-(1-*naphthyl*)*pentan-3-one* **7g**. trans Isomer; oil; δ_H 1.28 (9 H, s), 3.86 (1 H, d, J 1.9), 4.54 (1 H, d, J 1.9), 7.42–7.60 (4 H, m) and 7.80–8.02 (3 H, m); ν_{max}(neat)/cm^{-1} 1713, 1597, 1510, 1478, 1389, 1368, 1078, 999, 890, 803, 793 and 776; m/z 254 (M$^+$), 197, 181, 169, 141, 139, 115 and 57 (Found: C, 80.2; H, 7.1. $C_{17}H_{18}O_2$ requires C, 80.3; H, 7.1%).

1,2-*Epoxy-4,4-dimethyl*-1-(2-*methylphenyl*)*pentan-3-one* **7h**. trans Isomer; oil; δ_H 1.26 (9 H, s), 2.37 (3 H, s), 3.76 (1 H, d, J 1.9), 4.02 (1 H, d, J 1.9) and 7.12–7.27 (4 H, m); ν_{max}(neat)/cm^{-1} 1713, 1478, 1465, 1404, 1368, 1071, 1003, 893, 756 and 725; m/z 218 (M$^+$), 134, 119, 105, 91 and 57 (Found: C, 76.9; H, 8.3. $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.3%).

1,2-*Epoxy-4,4-dimethyl*-1-(2-*nitrophenyl*)*pentan-3-one* **7i**. trans Isomer; oil; δ_H 1.27 (9 H, s), 3.78 (1 H, d, J 2.0), 4.48 (1 H, d, J 2.0), 7.50–7.80 (3 H, m) and 8.20 (1 H, d, J 8.8); ν_{max}(KBr)/cm^{-1} 1715, 1615, 1578, 1528, 1478, 1347, 1069, 1003, 905, 847, 793, 745, 730, 698 and 673; m/z 164 (M$^+$ − 85), 135, 85, 65 and 57 (Found: C, 62.5; H, 6.1; N, 5.6. $C_{13}H_{15}NO_4$ requires C, 62.6;

H, 6.1; N, 5.6%). cis Isomer; m.p. 95–96 °C; δ_H 1.05 (9 H, s), 4.45 (1 H, d, J 5.0), 4.87 (1 H, d, J 5.0), 7.49 (1 H, t, J 7.7), 7.70 (1 H, t, J 7.4), 7.88 (1 H, d, J 7.7) and 8.15 (1 H, d, J 8.0); ν_{max}(KBr)/cm^{-1} 1711, 1615, 1522, 1339, 1076, 995, 916, 849, 797, 720 and 673; m/z 249 (M$^+$), 135, 85, 65 and 57 (Found: C, 62.4; H, 5.9; N, 5.55. $C_{13}H_{15}NO_4$ requires C, 62.6; H, 6.1; N, 5.6%).

1,2-*Epoxy-4-methyl*-1-(4-*methylphenyl*)*pentan-3-one* **7j**. trans Isomer; oil; δ_H 1.15 (3 H, d, J 6.8), 1.16 (3 H, d, J 7.0), 2.35 (3 H, s), 2.81 (1 H, sept, J 6.9), 3.60 (1 H, d, J 1.9), 3.89 (1 H, d, J 1.9) and 7.17 (4 H, s); ν_{max}(neat)/cm^{-1} 1709, 1607, 1470, 1400, 1385, 1100, 1045, 812 and 757; m/z 204 (M$^+$), 133, 119, 105, 91 and 71 (Found: C, 76.2; H, 7.9. $C_{13}H_{16}O_2$ requires C, 76.4; H, 7.9%).

1-(4-*Chlorophenyl*)-1,2-*epoxy-4-methylpentan-3-one* **7k**. trans Isomer; oil; δ_H 1.16 (3 H, d, J 6.7), 1.17 (3 H, d, J 7.0), 2.81 (1 H, sept, J 6.9), 3.56 (1 H, d, J 1.8), 3.91 (1 H, d, J 1.8), 7.22 (2 H, d, J 8.5) and 7.35 (2 H, d, J 8.5); ν_{max}(neat)/cm^{-1} 1719, 1601, 1495, 1468, 1429, 1395, 1150, 1092, 1044, 1015, 874 and 824; m/z 226 (M$^+$; ^{37}Cl), 224 (M$^+$; ^{35}Cl), 127, 125, 91, 89 and 71 (Found: C, 64.3; H, 5.8. $C_{12}H_{13}ClO_2$ requires C, 64.15; H, 5.8%).

1-*Benzoyl*-2-*phenyloxirane* **7l**. trans Isomer; m.p. 89–90 °C (lit.,[13] 90 °C); δ_H 4.09 (1 H, d, J 1.9), 4.31 (1 H, d, J 1.9), 7.37–7.42 (5 H, m), 7.49 (2 H, t, J 7.7), 7.63 (1 H, t, J 7.7) and 8.02 (2 H, d, J 7.7); ν_{max}(KBr)/cm^{-1} 1688, 1595, 1451, 1412, 1354, 1238, 1009, 893, 777, 752, 700 and 668; m/z 224 (M$^+$), 105, 91, 89 and 77.

1-*Benzoyl*-2-(4-*chlorophenyl*)*oxirane* **7m**. trans Isomer; m.p. 73–74 °C (lit.,[13] 80–81 °C); δ_H 4.06 (1 H, d, J 1.9), 4.26 (1 H, d, J 1.9), 7.30 (2 H, d, J 8.7), 7.39 (2 H, d, J 8.7), 7.50 (2 H, t, J 7.3), 7.64 (1 H, t, J 7.3) and 8.01 (2 H, d, J 7.3); ν_{max}(KBr)/cm^{-1} 1661, 1597, 1493, 1449, 1322, 1092, 1015, 887, 860, 808 and 704; m/z 260 (M$^+$; ^{37}Cl), 258 (M$^+$; ^{35}Cl), 141, 139, 113, 111, 105, 85 and 77.

1-*Benzoyl*-2-(4-*nitrophenyl*)*oxirane* **7n**. trans Isomer; m.p. 151–152 °C (lit.,[13] 150 °C); δ_H 4.21 (1 H, d, J 1.8), 4.29 (1 H, d, J 1.8), 7.51 (2 H, t, J 7.6), 7.56 (2 H, d, J 8.9), 7.66 (1 H, t, J 7.4), 8.02 (2 H, d, J 7.3) and 8.27 (2 H, d, J 8.9); ν_{max}(KBr)/cm^{-1} 1680, 1599, 1518, 1449, 1397, 1343, 1233, 1107, 1007, 882, 860, 745, 704 and 666; m/z 269 (M$^+$), 105, 89 and 77.

2,3-*Epoxy*-1-*phenylheptan*-1-*one* **7o**. trans Isomer; oil; δ_H 1.01 (3 H, t, J 7.0), 1.40–1.80 (6 H, m), 3.17 (1 H, dt, J 2.0 and 6.1), 4.02 (1 H, d, J 2.0), 7.50 (2 H, t, J 7.4), 7.63 (1 H, t, J 7.4) and 7.98–8.05 (2 H, m); ν_{max}(neat)/cm^{-1} 1693, 1599, 1451, 1231, 980, 907, 780, 698 and 666; m/z 204 (M$^+$), 147, 122, 105 and 77 (Found: C, 76.3; H, 8.0. $C_{13}H_{16}O_2$ requires C, 76.4; H, 7.9%).

2,3-*Epoxy*-5-*methyl*-1-*phenylhexan*-1-*one* **7p**. trans Isomer; oil; δ_H 1.01 (3 H, d, J 6.6), 1.02 (3 H, d, J 6.6), 1.50–1.75 (2 H, m), 1.91 (1 H, sept, J 6.7), 3.17 (1 H, ddd, J 2.0, 5.0 and 6.7), 4.00 (1 H, d, J 2.0), 7.50 (2 H, t, J 7.3), 7.62 (1 H, t, J 7.2) and 8.02 (2 H, m); ν_{max}(neat)/cm^{-1} 1690, 1599, 1451, 1428, 1370, 1287, 1231, 1181, 1003, 909, 845, 779 and 700; m/z 147 (M$^+$ − 57), 120, 105 and 77 (Found: C, 76.45; H, 7.9. $C_{13}H_{16}O_2$ requires C, 76.4; H, 7.9%). cis Isomer; δ_H 0.87 (3 H, d, J 6.6), 0.95 (3 H, d, J 6.6), 1.37 (2 H, t, J 6.9), 1.80 (1 H, sept, J 6.9), 3.47 (1 H, dt, J 4.8 and 6.9), 4.27 (1 H, d, J 4.8), 7.50 (2 H, t, J 7.3), 7.63 (1 H, t, J 7.3) and 8.02 (2 H, m); ν_{max}(neat)/cm^{-1} 1693, 1597, 1451, 1420, 1385, 1227, 972 and 700; m/z 147 (M$^+$ − 57), 120, 105 and 77 (Found: C, 76.5; H, 7.8. $C_{13}H_{16}O_2$ requires C, 76.4; H, 7.9%).

(E)-3,4-*Epoxy-2,2-dimethyl-7-phenylhept-6-en-5-one* **7q**. trans Isomer; oil; δ_H 1.24 (9 H, s), 3.52 (1 H, dd, J 2.0 and 8.0), 3.89 (1 H, d, J 2.0), 5.94 (1 H, dd, J 8.0 and 16.0), 6.84 (1 H, d, J 16.0) and 7.30–7.50 (5 H, m); ν_{max}(neat)/cm^{-1} 1713, 1478, 1399, 1368, 1071, 970, 895, 750 and 693; m/z 230 (M$^+$), 173, 145, 131, 117, 115, 86, 84 and 57. cis Isomer; m.p. 80–81 °C; δ_H 1.21 (9 H, s), 3.83 (1 H, dd, J 4.8 and 8.7), 4.22 (1 H, d, J 4.8), 5.87 (1 H, dd, J 8.7 and 16.1), 6.88 (1 H, d, J 16.1) and 7.25–7.40 (5 H, m); ν_{max}(KBr)/cm^{-1} 1711, 1480, 1372, 1109, 1069, 967, 916, 758 and 693; m/z 230 (M$^+$), 173, 145, 131, 117, 115, 91 and 57.

(E)-2,3-*Epoxy*-1-*phenyloct*-4-*en*-1-*one* **7r**. *trans* Isomer; oil; δ_H 0.93 (3 H, t, J 7.3), 1.44 (2 H, sext, J 7.3), 2.10 (2 H, ddt, J 1.4, 6.8 and 7.3), 3.53 (1 H, dd, J 2.0 and 8.2), 4.17 (1 H, d, J 2.0), 5.32 (1 H, ddt, J 8.2, 15.5 and 1.4), 6.06 (1 H, dt, J 15.5 and 6.8), 7.49 (2 H, t, J 7.2), 7.62 (1 H, t, J 7.3) and 8.00 (2 H, m); ν_{max}(neat)/cm^{-1} 1690, 1599, 1451, 1414, 1231, 1005, 967, 887 and 700; m/z 187 (M$^+$ − 29), 145, 105 and 77 (Found: C, 77.5; H, 7.6. $C_{14}H_{16}O_2$ requires C, 77.75; H, 7.5%).

Competitive Reaction of the Bismuthonium Ylide **4a** *for para-Substituted Benzaldehydes* **5b–e**.—To a stirred mixture of the salt **3a** (125 mg, 0.2 mmol), benzaldehyde **5a** (21 mg, 0.2 mmol) and a given *p*-substituted aldehyde (0.2 mmol) in THF (5 cm^3) was added KOBu^t (23 mg, 0.2 mmol) at −78 °C. The resulting mixture was allowed to warm to ambient temp. and worked up as usual to give the bismuthane **6**, the unchanged aldehydes **5** and the α,β-epoxy ketones **7**. Ratios of each epoxy ketones listed in Table 3 were determined by ^{1}H NMR integration of the product mixture.

Synthesis of Phenacyltriphenylstibonium Tetrafluoroborate **9**.—A mixture of phenacyltriphenylbismuthonium tetrafluoroborate **3c** (646 mg, 1.0 mmol), triphenylstibane (353 mg, 1.0 mmol) and CH_2Cl_2 (10 cm^3) was stirred for 24 h at room temp. The solvent was removed under reduced pressure to leave an oily residue, which was crystallized from Et_2O–CH_2Cl_2 (2:1) to give phenacyltriphenylstibonium tetrafluoroborate **9** (475 mg, 85%) as pale yellow crystals; m.p. 161–162 °C; δ_H 5.56 (2 H, s), 7.44–7.80 (18 H, m) and 8.16 (2 H, m); ν_{max}(KBr)/cm^{-1} 1649, 1597, 1578, 1482, 1451, 1437, 1383, 1284, 1200–950, 743, 691, 521 and 448; m/z (FAB) 473 (M$^+$ − BF$_4$, ^{123}Sb), 471 (M$^+$ − BF$_4$, ^{121}Sb), 373, 371, 277, 275, 200 and 198.

Reaction of the Stibonium Salt **9** *with the Aldehyde* **5a** *in the Presence of Potassium* tert-*Butoxide*.—To a stirred suspension of the stibonium salt **9** (112 mg, 0.2 mmol) in THF (5 cm^3) was added KOBu^t (23 mg, 0.2 mmol) at −78 °C. After 30 min, benzaldehyde **5a** (21 mg, 0.2 mmol) was added and the resulting mixture was stirred for 36 h at ambient temp. Usual work-up gave an oily residue, which was chromatographed on a silica gel column with hexane–ethyl acetate as the eluent to yield chalcone **10** (25 mg, 60%).

Competitive Reaction of the Bismuthonium Ylide **4a** *for Acetophenone–Benzaldehyde*.—To a stirred suspension of the salt **3a** (125 mg, 0.2 mmol) in THF (5 cm^3) was added KOBu^t (23 mg, 0.2 mmol) at −78 °C. After 30 min, a solution of acetophenone (24 mg) and benzaldehyde **5a** (21 mg, 0.2 mmol) in the same solvent (5 cm^3) was added and the resulting mixture was allowed to warm gradually to ambient temp. Usual work-up gave the bismuthane **6** (79 mg, 90%), unchanged acetophenone (17 mg, 71%) and the α,β-epoxy ketone **7a** (38 mg, 93%).

Reaction of the Bismuthonium Ylide **4a** *with 5,5-Dimethyl-cyclohexane*-1,3-*dione* (*Dimedone*) **11**.—To a stirred suspension of the salt **3a** (125 mg, 0.2 mmol) in THF (5 cm^3) was added KOBu^t (23 mg, 0.2 mmol) at −78 °C. After 30 min, dimedone **11** (28 mg, 0.2 mmol) was added and the temp. was allowed to rise to ambient. The resulting pale yellow solution was concentrated under reduced pressure and then taken up with benzene (10 cm^3 × 2). Removal of the solvent gave an oily residue, which was chromatographed on a silica gel column with hexane–ethyl acetate (100:0–70:30) as the eluent to yield the bismuthane **6** (73 mg, 83%) and 5,5-dimethyl-3-(3,3-dimethyl-2-oxobutyl-oxy)cyclohex-2-enone **12** (29 mg, 65%); R_f 0.1 (hexane–ethyl acetate, 70:30); m.p. 65–66 °C; δ_H 1.09 (6 H, s), 1.22 (9 H, s), 2.22 (2 H, s), 2.40 (2 H, s), 4.78 (2 H, s) and 5.15 (1 H, s); ν_{max}(KBr)/cm^{-1} 1728, 1653, 1609, 1391, 1370, 1231, 1163,

1150, 1092, 1046, 990, 876, 783 and 613; m/z 238 (M$^+$), 223, 154, 139, 125, 109, 85, 69, 67 and 57 (Found: C, 70.1; H, 9.3. $C_{14}H_{22}O_3$ requires C, 70.6; H, 9.3%).

Reaction of the Bismuthonium Ylide **4a** *with 4-Methyl-benzenesulfonic Acid* **13**.—To a stirred suspension of the salt **3a** (188 mg, 0.3 mmol) in THF (5 cm^3) was added KOBu^t (35 mg, 0.3 mmol) at −78 °C. After 30 min 4-methylbenzenesulfonic acid monohydrate **13** (57 mg, 0.3 mmol) was added and the mixture was allowed to warm to ambient temp. The resulting colourless solution was concentrated under reduced pressure and then extracted with benzene (10 cm^3 × 2). Removal of the solvent gave an oily residue, which was chromatographed on a silica gel column with hexane–ethyl acetate (100:0–70:30) as the eluent to yield the bismuthane **6** (106 mg, 80%) and 3,3-dimethyl-1-(tosyloxy)butan-2-one **14** (52 mg, 64%); R_f 0.15 (hexane–ethyl acetate, 70:30); oil; δ_H 1.14 (9 H, s), 2.45 (3 H, s), 4.89 (2 H, s), 7.36 (2 H, d, J 8.0) and 7.84 (2 H, d, J 8.0); ν_{max}(KBr)/cm^{-1} 1732, 1599, 1364, 1190, 1177, 1096, 1034, 980, 816, 750 and 666; m/z 155 (M$^+$ − 115), 91, 85, 65 and 57 (Found: C, 57.9; H, 6.8. $C_{13}H_{18}O_4S$ requires C, 57.8; H, 6.7%).

Reaction of the Bismuthonium Ylide **4a** *with Benzenethiol* **15**.— To a stirred suspension of the salt **3a** (125 mg, 0.2 mmol) in THF (5 cm^3) was added KOBu^t (23 mg, 0.2 mmol) at −78 °C. After 30 min, benzenethiol **15** (22 mg, 0.2 mmol) was added and the mixture was allowed to warm to ambient temp. The resulting colourless solution was concentrated under reduced pressure and then extracted with benzene (10 cm^3 × 2). Removal of the solvent gave an oily residue, which was chromatographed on a silica gel column with hexane–ethyl acetate (100:0–80:20) as the eluent to yield the bismuthane **6** (84 mg, 95%) and 3,3-dimethyl-1-phenylsulfanylbutan-2-one **16** (36 mg, 87%), which was identified by comparison with the authentic specimen.[7]

Reaction of the Bismuthonium Ylide **4a** *with Phenyl Isocyanate* **17**.—To a stirred suspension of the salt **3a** (125 mg, 0.2 mmol) in THF (5 cm^3) was added KOBu^t (24 mg, 0.2 mmol) at −78 °C. After 30 min, phenyl isocyanate **17** (24 mg, 0.2 mmol) was added and the mixture was allowed to warm to ambient temp. The resulting pale yellow suspension was concentrated under reduced pressure and then extracted with benzene (10 cm^3 × 2). Removal of the solvent gave an oily residue, which was chromatographed on a silica gel column with hexane–ethyl acetate (100:0–80:20) as the eluent to yield the bismuthane **5** (56 mg, 64%) and 4,4-dimethyl-3-oxo-N,2-diphenylpentan-amide **19** (50 mg, 85%); R_f 0.2 (hexane–ethyl acetate, 80:20); m.p. 184–185 °C; δ_H 1.18 (9 H, s), 5.26 (1 H, s), 7.11 (1 H, t, J 7.3), 7.22–7.47 (9 H, m) and 8.89 (1 H, s); ν_{max}(KBr)/cm^{-1} 1705, 1671, 1603, 1541, 1495, 1441, 1327, 1057, 764, 731 and 698; m/z 295 (M$^+$), 211, 193, 177, 118, 93, 91, 85, 77 and 57 (Found: C, 76.9; H, 7.0; N, 4.8. $C_{19}H_{21}NO_2$ requires C, 77.3; H, 7.2; N, 4.7%).

Reaction of the Bismuthonium Ylide **4c** *with the* α,β-*Unsaturated Ketones* **10** *and* **21**.—To a stirred suspension of the salt **3c** (129 mg, 0.2 mmol) in THF (5 cm^3) was added LDA prepared from diisopropylamine (20 mg, 0.2 mmol) and LiBu (hexane solution; 1.5 mol dm^{-3} × 0.13 cm^3, 0.2 mmol) in the same solvent (5 cm^3) at −78 °C. After 30 min, the α,β-unsaturated ketone **10** (or **21**) (0.2 mmol) was added and the mixture was allowed to warm to ambient temp. The resulting pale yellow solution was concentrated under reduced pressure and then extracted with benzene (10 cm^3 × 2). Removal of the solvent gave an oily residue, which was chromatographed on a silica gel column with hexane–ethyl acetate (100:0–80:20) as the eluent to yield the bismuthane **6** (85–97%) and the benzoylcyclopropane **20** (or **22**).

1,2-*Dibenzoyl-3-phenylcyclopropane* **20** (16%). *r*-1,*t*-2,*c*-3-

Isomer (8%); m.p. 113–114 °C (lit.,[14] 116 °C); δ_H 3.56 (1 H, dd, J 6.0 and 10.0), 3.79 (1 H, dd, J 5.0 and 10.0), 4.26 (1 H, dd, J 5.0 and 6.0), 7.20–7.70 (11 H, m), 8.00 (2 H, d, J 7.0) and 8.16 (2 H, d, r 6.6). r-1,c-2,t-3-isomer (8%); m.p. 150–151 °C (lit.,[14] 151 °C); δ_H 3.39 (2 H, d, J 6.2), 3.55 (1 H, t, J 6.2), 7.28–7.60 (11 H, m) and 8.00 (4 H, m).

r-1,t-2,c-3-1,2,3-*Tribenzoylcyclopropane* **22** (28%). M.p. 217–218 °C (lit.,[15] 217.5–218 °C); δ_H 3.77 (2 H, d, J 5.6), 4.24 (1 H, t, J 5.6), 7.38–7.65 (9 H, m), 8.01 (4 H, m) and 8.20 (2 H, m).

Decomposition of the Bismuthonium Ylide **4a** *in the Presence of Nitrosobenzene* **23**.—To a stirred suspension of the salt **3a** (125 mg, 0.2 mmol) in THF (5 cm³) was added KOBu^t (23 mg, 0.2 mmol) at −78 °C. After 30 min, nitrosobenzene **23** (4 mg, 0.04 mmol) was added and the mixture was allowed to warm to ambient temp. The resulting colourless solution was concentrated under reduced pressure and then extracted with benzene (10 cm³ × 2). Removal of the solvent gave an oily residue, which was chromatographed on a silica gel column with hexane–ethyl acetate (100:0–80:20) as the eluent to yield the bismuthane **6** (87 mg, 99%) and 2,2,7,7-tetramethyloct-4-ene-3,6-dione **24** (17 mg, 87%); R_f 0.75 (hexane–ethyl acetate, 80:20); m.p. 109–110 °C (lit.,[15] 110–111 °C); δ_H 1.20 (18 H, s) and 7.45 (2 H, s); ν_{max}(KBr)/cm^{-1} 1676, 1464, 1393, 1368, 1304, 1238, 1084. 1001, 843 and 731; m/z 140 (M$^+$ − 56), 125, 111, 97 and 57.

Reaction of Bismuthonium Ylide **4a** *with* p-*Chlorobenzonitrile Oxide* **25**.—To a stirred suspension of the salt **3a** (250 mg, 0.4 mmol) in THF (5 cm³) was added KOBu^t (45 mg, 0.4 mmol) at −78 °C. After 30 min, a solution of p-chlorobenzonitrile oxide **25** in the same solvent (5 cm³), *in situ* generated from 4-chlorobenzenecarbohydroximoyl chloride (62 mg, 0.4 mmol) and triethylamine (40 mg, 0.4 mmol), was added and the mixture was allowed to warm to ambient temp. The resulting pale yellow solution was concentrated under reduced pressure and then extracted with benzene (10 cm³ × 2). Removal of the solvent gave an oily residue, which was chromatographed on a silica gel column with hexane–ethyl acetate (100:0–80:20) as the eluent to yield the bismuthane **6** (150 mg, 85%) and 3-(4-chlorophenyl)-4,5-bis(2,2-dimethyl-1-oxopropyl)-4,5-dihydro-isoxazole **26** (39 mg, 56%); R_f 0.45 (hexane–ethyl acetate, 80:20); m.p. 158–159 °C; δ_H 1.21 (9 H, s), 1.29 (9 H, s), 5.23 (1 H, d, J 4.0), 5.55 (1 H, H, d, J 4.0), 7.35 (2 H, d, J 8.5) and 7.50 (2 H, d, J 8.5); ν_{max}(KBr)/cm^{-1} 1700, 1495, 1487, 1341, 1090, 1067, 897, 888 and 835; m/z 264 (M$^+$ − 85, ^{35}Cl), 182, 180, 85 and 57 (Found: C, 65.0; H, 7.0; N, 4.0. $C_{19}H_{24}ClNO_3$ requires C, 65.2; H, 6.9; N. 4.0%).

References

1 For a general survey of organic bismuth compounds see: L. D. Freedman and G. O. Doak, *Chem. Rev.*, 1982, **82**, 15; P. G. Harrison, *Organomet. Chem. Rev.*, 1970, **5**, 183; J.-P. Finet, *Chem. Rev.*, 1989, **89**, 1487.

2 D. Lloyd and M. I. C. Singer, *J. Chem. Soc., Chem. Commun.*, 1967, 1042.

3 D. H. R. Barton, J.-C. Blazejewski, B. Charpiot, J.-P. Finet, W. B. Motherwell, M. T. B. Papoula and S. P. Stanforth, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2667.

4 H. Suzuki, T. Murafuji and T. Ogawa, *Chem. Lett.*, 1988, 847; T. Ogawa, T. Murafuji, K. Iwata and H. Suzuki, *Chem. Lett.*, 1989, 325; M. Yasui, T. Kikuchi, F. Iwasaki, H. Suzuki, T. Murafuji and T. Ogawa, *J. Chem. Soc., Perkin Trans. 1*, 1990, 3367; T. Ogawa, T. Murafuji and H. Suzuki, *Chem. Lett.*, 1988, 849.

5 C. Glidewell, D. Lloyd and S. Metcalfe, *Synthesis*, 1988, 319; G. Ferguson, C. Glidewell, I. Gosney, D. Lloyd, S. Metcalfe and H. Lumbroso, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1829.

6 T. Ogawa, T. Murafuji and H. Suzuki, *J. Chem. Soc., Chem. Commun.*, 1989, 1749; H. Suzuki and T. Murafuji, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 950.

7 Y. Matano, N. Azuma and H. Suzuki, *Tetrahedron Lett.*, 1993, **34**, 8457; Y. Matano, N. Azuma and H. Suzuki, *J. Chem. Soc., Perkin Trans. 1*, 1994, 1739.

8 For recent reviews, see: S. M. Bachrach and C. I. Nitsche, in *The Chemistry of Organophosphorus Compounds*, ed. F. R. Hartley, Wiley, Chichester, 1994, vol. 3, p. 273; A. W. Johnson, *Ylide and Imines of Phosphorus*, Wiley, Chichester, 1993; B. E. Maryanoff and A. B. Reitz, *Chem. Rev.*, 1989, **89**, 863 and references cited therein.

9 For a recent review, see: D. Lloyd, I. Gosney and R. A. Ormiston, *Chem. Soc. Rev.*, 1987, **16**, 45 and references cited therein.

10 F. Ramirez and S. Dershowitz, *J. Org. Chem.*, 1957. **22**, 41.

11 N. A. Nesmeyanov, E. V. Binshtok and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, 1971, **198**, 1102.

12 A. Nurrenbach and H. Pommer, *Liebigs Ann. Chem.*, 1969, **721**, 34.

13 E. Weitz and A. Scheffer, *Chem. Ber*, 1921, **54**, 2327.

14 E. P. Kohler and W. N. Jones, *J. Am. Chem. Soc.*, 1919, **41**, 1249.

15 J. Quintana, M. Torres and F. Serratosa, *Tetrahedron*, 1973, **29**, 2065.