Reaction of a moderately stabilized bismuthonium ylide with 1,2-dicarbonyl compounds. A novel ring enlargement of *ortho*-quinones to 3-hydroxytropones

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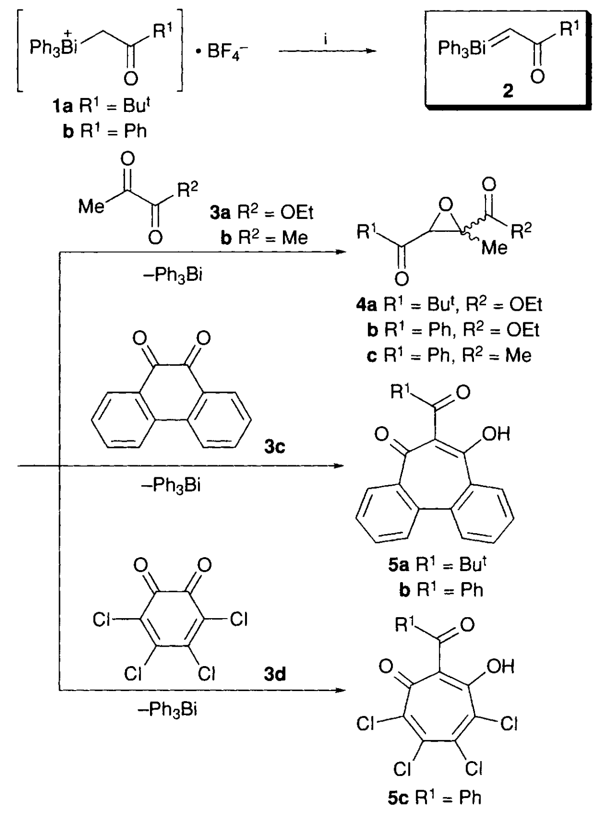
Triphenylbismuthonium 2-oxoalkylide 2, generated *in situ* from salt 1 in THF at low temperature, readily reacts with 1,2-dicarbonyl compounds 3 to give 2,3-diacyloxiranes 4 or 2-acyl-3-hydroxytropones 5 depending on the structure of the electrophiles involved.

Organic transformations based on bismuth reagents have proved to be of synthetic utility.[1] However, in spite of the well-established uses of phosphonium, arsonium and stibonium ylides as reagents for carbon–carbon bond formation,[2–4] the bismuthonium ylide has received attention only recently.[5–7] Moderately stabilized bismuthonium 2-oxoalkylides **2**, generated from the corresponding 2-oxoalkyl(triphenyl)bismuthonium salts **1**, readily react with aldehydes[6] and activated imines[7] to give the respective α,β-epoxy and α,β-aziridino ketones in good yields. This mode of reaction leading to oxirane and aziridine is characteristic of the bismuth, since the analogous ylides of phosphorus, arsenic and antimony all undergo Wittig-type olefination with the same substrates to give α,β-unsaturated ketones. Here we report that triphenylbismuthonium 2-oxoalkylides **2** can easily convert 1,2-dicarbonyl compounds to 2,3-diacyloxiranes **4** or 2-acyl-3-hydroxytropones **5**, depending on the structure of the substrates employed.



Scheme 1 *Reagents and conditions*: i, base, THF, −78 °C to room temp.

Triphenylbismuthonium 2-oxoalkylides **2a,b**, generated *in situ* from the corresponding bismuthonium salts **1a,b** and a base in THF at −78 °C, did not react with simple ketones such as acetophenone and benzophenone or with an ester such as ethyl acetate. However, they readily underwent a carbon–carbon bond forming reaction with an α-keto ester, ethyl pyruvate **3a**, at low temperature to give the 2,3-difunctionalized oxiranes **4a,b** and triphenylbismuthane in good yields,† probably owing to the enhanced electrophilicity of the α-carbonyl carbon atom in **3a** through the adjacent electron withdrawing ethoxycarbonyl moiety. Potassium *tert*-butoxide (KOBu^t), potassium bis(trimethylsilyl)amide [KN(SiMe$_3$)$_2$] and sodium bis(trimethylsilyl)amide [NaN(SiMe$_3$)$_2$] were the bases used, and *trans* selectivity was always prominent in the oxiranes (Table 1, runs 1–5).‡ When diacetyl **3b** was used as a 1,2-dicarbonyl counterpart, 2,3-diacyloxirane **4c** was obtained as the single stereoisomer (run 6). To our knowledge, there have been very few reported synthesis of 2,3-diacyloxiranes from 1,2-dicarbonyl compounds and an ylide bearing the 2-oxoalkylidene group.[9,10] Therefore, the present epoxidation of 1,2-dicarbonyl compounds with bismuthonium 2-oxoalkylides **2** should provide a new addition to the existing synthesis of 2,3-difunctionalized oxiranes.

The reaction of bismuthonium 2-oxoalkylides **2a,b** with *ortho*-quinones **3c,d** led to a quite unexpected result. Treatment of the salts **1** with KOBu^t in the presence of 9,10-phenanthrenequinone **3c** afforded 2-acyl-3-hydroxytropones **5a,b** in good yield (runs 7–9).§ A similar reaction of the salt **1b** with *ortho*-chloranil **3d** gave rise to a tropone **5c** in 33% yield (run 10). In the ^{1}H NMR spectra of tropones **5** in CDCl$_3$, the hydroxy group was observed as a sharp singlet at δ_H 16.78–18.16, suggesting the operation of strong intramolecular hydrogen bonding in these molecules. The hydrogen bonding became weaker in a polar solvent such as (CD$_3$)$_2$SO; resonances of the hydroxy and dibenzo ring protons of **5a,b** turned into a broad singlet and a symmetrical multiplet pattern, respectively. Direct ring expansion of *ortho*-quinones to functionalized tropones based on the use of the bismuthonium ylides **2** may provide a new attractive route to some types of substituted tropones.[12]

Table 1 Reaction of 2-oxoalkyl(triphenyl)bismuthonium salts **1** with 1,2-dicarbonyl compounds **3** in the presence of a base

Entry	Salt	Base	Substrate	Product[a]	Yield (%) (*cis* : *trans*)
1	**1a**	KOBu^t	**3a**	**4a**	70 (12:88)
2	**1a**	KN(SiMe$_3$)$_2$	**3a**	**4a**	79 (10:90)
3	**1a**	NaN(SiMe$_3$)$_2$	**3a**	**4a**	82 (34:66)
4	**1b**	KN(SiMe$_3$)$_2$	**3a**	**4b**	62 (13:87)
5	**1b**	NaN(SiMe$_3$)$_2$	**3a**	**4b**	62 (9:91)
6	**1b**	NaN(SiMe$_3$)$_2$	**3b**	**4c**	26 (0:100)
7	**1a**	KOBu^t	**3c**	**5a**	71
8	**1a**	KN(SiMe$_3$)$_2$	**3c**	**5a**	75
9	**1b**	KOBu^t	**3c**	**5b**	66
10	**1b**	KOBu^t	**3d**	**5c**	33

[a] All products gave satisfactory spectral and analytical data. In all reactions triphenylbismuthane was recovered in good yield.

Although we are not in a position to explain the mechanism of the novel ring enlargement, this coupling mode of the bismuthonium ylide **2** leading to compound **4** or **5** is in marked contrast with the well established behaviour of phosphonium ylides, which undergo the Wittig reaction with 1,2-diketones and *ortho*-quinones to yield α,β-unsaturated carbonyl compounds.[2,13] It is noteworthy that two different types of carbonyl compounds **4** and **5** are accessible from the same bismuthonium ylides **2** *via* an appropriate modification of the structure of the 1,2-dicarbonyl compounds. Compounds like **4** and **5** have great synthetic potential, since their highly functionalized structures are readily subject to either ring opening or ring enlargement or new ring framework construction.

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Footnotes

† Typical procedure: to a stirred suspension of the salt **1a** (125 mg, 0.2 mmol) in THF (5 cm^3) was added NaN(SiMe$_3$)$_2$ (1.0 mol dm^{-3} THF solution; 0.2 cm^3, 0.2 mmol) at −78 °C. After 10 min, ethyl pyruvate **3a** (23 mg, 0.2 mmol) was added and the resulting mixture was gradually allowed to warm to room temp. Evaporation of the solvent under reduced pressure gave an oily residue, which was diluted with benzene (15 cm^3) and the insoluble matter was filtered off through a Celite bed. The filtrate was concentrated under reduced pressure to leave an oily residue, the composition of which was estimated by ^{1}H NMR integration. The product was subjected to chromatographic separation on silica gel using hexane–ethyl acetate (100 : 0 to 80 : 20) as the solvent to elute triphenylbismuthane (85 mg, 97%), *cis*-**4a** (12 mg, 54%) and *trans*-**4a** (23 mg, 28%) in this order. *Selected data* for *cis*-**4a**: δ_H(CDCl$_3$) 1.22 (9 H, s), 1.32 (3 H, t, J = 7.2 Hz), 1.44 (3 H, s), 4.17 (1 H, s) and 4.27 (2 H, q, J = 7.2 Hz); *m/z* (EI) 141 (M$^+$ −73); ν_{max}(neat) 1744 (C=O) and 1717 (C=O) cm^{-1}. Found: C, 61.51; H, 8.42. $C_{11}H_{18}O_4$ requires C, 61.66; H, 8.47%. For *trans*-**4a**: δ_H(CDCl$_3$) 1.23 (9 H, s), 1.27 (3 H, t, J = 7.2 Hz), 1.67 (3 H, s), 3.79 (1 H, s) and 4.19 (2 H, q, J = 7.2 Hz); *m/z* (EI) 141 (M$^+$ −73); ν_{max}(neat) 1740 (C=O) and 1719 (C=O) cm^{-1}. Found: C, 61.65; H, 8.42. $C_{11}H_{18}O_4$ requires C, 61.66; H, 8.47%.

‡ The major product was assigned as the *trans* isomer by ^{1}H NMR spectral comparison with analogous compounds.[8,9]

§ *Selected data* for **5a**: mp 154–155 °C; δ_H(CDCl$_3$) 1.40 (9 H,s), 7.43–7.65 (6 H, m), 7.67–7.75 (1 H, m), 8.15 (1 H, d, J = 7.5 Hz) and 18.16 (1 H, s); δ_H[(CD$_3$)$_2$SO] 1.20 (9 H, s), 7.62 (2 H, t, J = 7.6 Hz), 7.71 (2 H, t, J = 7.4 Hz), 7.75–7.90 (2 H, br s), 7.88 (2 H, d, J = 7.8 Hz) and 13.2 (1 H, br s); *m/z* (EI) 306 (M$^+$). Found: C, 78.61; H, 5.94. $C_{20}H_{18}O_3$ requires C, 78.41; H, 5.92%. For **5b**: mp 118–119 °C (lit.,[11] 117.5 °C); δ_H(CDCl$_3$) 7.40–7.82 (12 H, m), 8.27–8.35 (1 H, m) and 17.17 (1 H, s); δ_H[(CD$_3$)$_2$SO] 7.42–7.62 (5 H, m), 7.66 (2 H, t, J = 7.3 Hz), 7.76 (2 H, t, J = 7.3 Hz), 7.85 (2 H, br d), 7.88 (2 H, d, J = 7.9 Hz) and 15.9 (1 H, br s); *m/z* (EI) 326 (M$^+$). For **5c**: mp 138–139 °C; δ_H(CDCl$_3$) 7.46 (2 H, t, J = 7.7 Hz), 7.52–7.60 (3 H, m) and 16.78 (1 H, s); *m/z* (EI) 364 (M$^+$). Found: C, 46.26; H, 1.63. $C_{14}H_6Cl_4O_3$ requires C, 46.19; H, 1.66%.

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