

# Reactions of triphenylbismuthonium 2-oxoalkylides † with 1,2-dicarbonyl compounds

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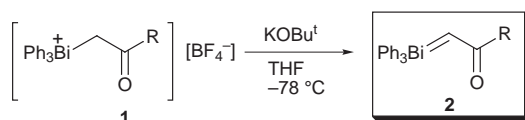
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Triphenylbismuthonium 2-oxoalkylides **2**, generated *in situ* from bismuthonium salts **1** and a base in THF at low temperature, react with  $\alpha$ -keto esters **3** and  $\alpha$ -diketones **6** to give oxiranes **4** or **7** and/or *O*-aroyl enolates of unsymmetrical  $\beta$ -diketones **8**, depending on the structures of substrates. Similar treatment of **2** with *o*-quinones **10** results in the ring expansion to 2-acyl-3-hydroxytropones **11**. The enolates **8** and tropones **11** are most likely to be formed *via* the 1,2-carbon-to-oxygen and carbon-to-carbon migrations of the acyl group, respectively, both under simultaneous elimination of the triphenylbismuthonio group as bismuthine **5**. Tropone **11c** readily condenses with hydrazine hydrate to give a functionalized pyrazole **18**.

## Introduction

In these past two decades, both organic and inorganic bismuth compounds have been receiving increasing attention as a new class of reagents and catalysts in organic synthesis.<sup>1,2</sup> However, little information is available at present on the reactivity of bismuthonium ylides,<sup>3</sup> in contrast to extensive studies on phosphonium, arsonium and stibonium ylides.<sup>4</sup> Recently, we have disclosed that bismuthonium 2-oxoalkylides **2**, generated *in situ* from the corresponding 2-oxoalkylbismuthonium tetrafluoroborates **1** and a base, readily couple with a variety of aldehydes<sup>5</sup> and *N*-sulfonylaldimines<sup>6</sup> to give  $\alpha,\beta$ -epoxy and  $\alpha,\beta$ -aziridino ketones, respectively (Scheme 1).



Scheme 1

These reaction modes are only characteristic of bismuth among the 15th group elements; phosphonium, arsonium and stibonium 2-oxoalkylides all undergo Wittig-type olefination with those substrates to form  $\alpha,\beta$ -unsaturated ketones and the corresponding pnictogen oxides or imides.<sup>4</sup> In order to get further information on the reactivity of **2**, other types of carbonyl compounds have been examined as substrates. Although ylides **2** were unreactive towards simple ketones such as acetophenone and benzophenone or an ester such as ethyl acetate, they were found to readily couple with various  $\alpha$ -dicarbonyl compounds in unique reaction modes.<sup>7-9</sup> In this paper, we report full aspects of the reaction modes of ylides **2** toward  $\alpha$ -keto esters,  $\alpha$ -diketones and *ortho*-quinones.

## Results and discussion

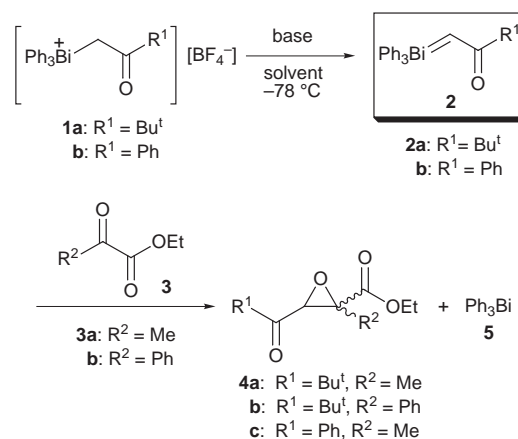
Triphenylbismuthonium 2-oxoalkylide **2a**, generated *in situ*

**Table 1** Reaction of (2-oxoalkyl)triphenylbismuthonium salts **1** with  $\alpha$ -keto esters **3** in the presence of a base

| Entry | Salt      | Ester     | Base                                 | Product <sup>a</sup> | Yield (%)<br>( <i>cis</i> : <i>trans</i> ) |
|-------|-----------|-----------|--------------------------------------|----------------------|--|
| 1     | <b>1a</b> | <b>3a</b> | KOBu <sup>t</sup>                    | <b>4a</b>            | 70 (12:88)                                 |
| 2     | <b>1a</b> | <b>3a</b> | KN(SiMe <sub>3</sub> ) <sub>2</sub>  | <b>4a</b>            | 79 (10:90)                                 |
| 3     | <b>1a</b> | <b>3a</b> | NaN(SiMe <sub>3</sub> ) <sub>2</sub> | <b>4a</b>            | 82 (34:66)                                 |
| 4     | <b>1a</b> | <b>3b</b> | KOBu <sup>t</sup>                    | <b>4b</b>            | 80 <sup>b</sup>                            |
| 5     | <b>1b</b> | <b>3a</b> | KN(SiMe <sub>3</sub> ) <sub>2</sub>  | <b>4c</b>            | 62 (13:87)                                 |
| 6     | <b>1b</b> | <b>3a</b> | NaN(SiMe <sub>3</sub> ) <sub>2</sub> | <b>4c</b>            | 62 (9:91)                                  |

<sup>a</sup> In all reactions triphenylbismuthine **5** was recovered in good yield (>80%). <sup>b</sup> A single stereoisomer was formed.

from the corresponding bismuthonium salt **1a** and a base in THF at  $-78^\circ\text{C}$ , reacted with ethyl pyruvate **3a** to give a *cis/trans* mixture of oxiranes **4a** and triphenylbismuthine **5** in good yield (Scheme 2). Similar reaction of ylide **2a** with ethyl



Scheme 2

benzoylformate **3b** afforded oxiranes **4b**. The reaction between **3a** and ylide **2b** also gave oxiranes **4c**. The bases used include potassium *tert*-butoxide (KOBu<sup>t</sup>), potassium bis(trimethylsilyl)amide [KN(SiMe<sub>3</sub>)<sub>2</sub>], and sodium bis(trimethylsilyl)amide [NaN(SiMe<sub>3</sub>)<sub>2</sub>] (Table 1). Oxiranes **4a–c** were characterized by spectroscopic methods. An analogous sulfur ylide, Me<sub>2</sub>S=CHCO<sub>2</sub>Et, has been known to undergo the Corey–Chaykovsky

† IUPAC name: 2-oxo-1-(triphenylbismuthonio)alkan-1-ides.

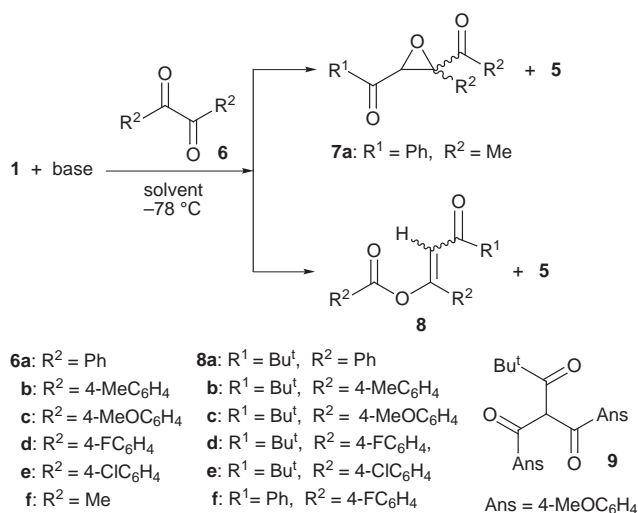
**Table 2** reaction of bismuthonium salts **1** with benzils **6** in the presence of a base<sup>a</sup>

| Entry | Salt      | Benzil    | Base                                 | Solvent                             | Product   | Yield (%) <sup>b</sup> | <i>E/Z</i> ratio |
|-------|-----------|-----------|--------------------------------------|-------------------------------------|-----------|------------------------|------------------|
| 1     | <b>2a</b> | <b>6a</b> | KOBu <sup>t</sup>                    | THF                                 | <b>8a</b> | 58 (88)                | 39/61            |
| 2     | <b>2a</b> | <b>6b</b> | KOBu <sup>t</sup>                    | THF                                 | <b>8b</b> | 53 (86)                | 42/58            |
| 3     | <b>2a</b> | <b>6b</b> | KOBu <sup>t</sup> <sup>c</sup>       | THF                                 | <b>8b</b> | 55 (85)                | 42/58            |
| 4     | <b>2a</b> | <b>6b</b> | NaN(SiMe <sub>3</sub> ) <sub>2</sub> | THF                                 | <b>8b</b> | 43 (67)                | 41/59            |
| 5     | <b>2a</b> | <b>6b</b> | KN(SiMe <sub>3</sub> ) <sub>2</sub>  | THF                                 | <b>8b</b> | 44 (69)                | 40/60            |
| 6     | <b>2a</b> | <b>6b</b> | KOBu <sup>t</sup>                    | THF-CH <sub>2</sub> Cl <sub>2</sub> | <b>8b</b> | 65 (90)                | 42/58            |
| 7     | <b>2a</b> | <b>6b</b> | NaN(SiMe <sub>3</sub> ) <sub>2</sub> | THF-CH <sub>2</sub> Cl <sub>2</sub> | <b>8b</b> | 47 (72)                | 41/59            |
| 8     | <b>2a</b> | <b>6c</b> | KOBu <sup>t</sup>                    | THF                                 | <b>8c</b> | 34 (54) <sup>d</sup>   | 60/40            |
| 9     | <b>2a</b> | <b>6d</b> | KOBu <sup>t</sup>                    | THF                                 | <b>8d</b> | 55 (78)                | 50/50            |
| 10    | <b>2a</b> | <b>6d</b> | KOBu <sup>t</sup>                    | THF-CH <sub>2</sub> Cl <sub>2</sub> | <b>8d</b> | 67 (91)                | 51/49            |
| 11    | <b>2a</b> | <b>6e</b> | KOBu <sup>t</sup>                    | THF                                 | <b>8e</b> | 63 (88)                | 45/55            |
| 12    | <b>2b</b> | <b>6d</b> | KOBu <sup>t</sup>                    | THF                                 | <b>8f</b> | 20 (80)                | — <sup>e</sup>   |

<sup>a</sup> All reactions were carried out using an equimolar amount of substrate and reagents. A 1 : 1 mixture of THF-CH<sub>2</sub>Cl<sub>2</sub> was used as the solvent in entries 6, 7 and 10. In every case, bismuthine **5** was recovered in good yield. <sup>b</sup> Yields refer to the isolated compounds. Numerals in parentheses refer to the conversion yields based on unrecovered benzil. <sup>c</sup> KOBu<sup>t</sup> was added to a solution of **2a** and **6b** in THF at -78 °C. <sup>d</sup> Triketone **9** was obtained in 10% isolated yield. <sup>e</sup> A single stereoisomer was formed.

reaction with **3a** under more harsh conditions (55 °C, 30 min) to give 2-methyl-2,3-epoxysuccinate,<sup>10</sup> indicating the enhanced reactivity of bismuthonium ylides **2** over the sulfonium ylides.

Reaction of triphenylbismuthonium 2-oxoalkylides **2a,b** with benzils **6** gave an unexpected result. Treatment of benzil **6a** with **2a**, generated *in situ* from **1a** and a base, yielded an intimate *E/Z* mixture of *O*-aroyl enolates **8a** and triphenylbismuthine **5** (Scheme 3). To optimize the reaction, ylide **1a** and 4,4'-

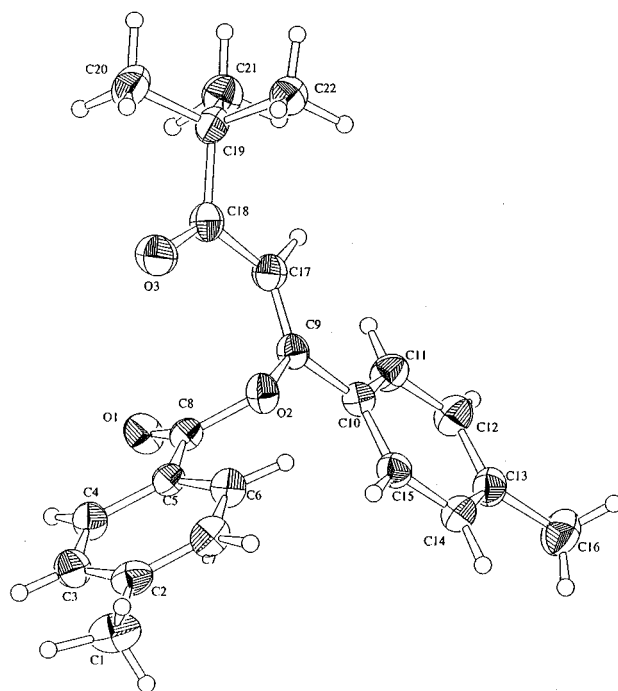
**Scheme 3**

dimethylbenzil **6b** were reacted together under a variety of conditions and the results are summarized in Table 2. Regardless of the order of addition of the base and a substrate, enolate **8b** was obtained in very similar yields (entries 2 and 3). Among the bases used, KOBu<sup>t</sup> gave the better results as compared to NaN(SiMe<sub>3</sub>)<sub>2</sub> and KN(SiMe<sub>3</sub>)<sub>2</sub> (entries 2–7). 4,4'-Dimethoxybenzil **6c** reacted with **2a** in the presence of KOBu<sup>t</sup> to give enolate **8c** and triketone **9** in 12 and 10% yields, respectively (entry 8). 4,4'-Difluorobenzil **6d** and 4,4'-dichlorobenzil **6e** underwent similar coupling reactions to yield enolates **8d–e**. The reaction between benzil **6d** and ylide **2b**, generated *in situ* from **1b** and KOBu<sup>t</sup>, afforded the corresponding enolate **8f** (entry 12). In marked contrast, however, the reaction of ylide **2b** with biacetyl **6f** gave 2,3-diacyloxirane **7a**. The sulfur ylide, Me<sub>2</sub>S=CHCO<sub>2</sub>Et, reacts with both **6a** and **6f** at 25–45 °C to afford similar epoxy esters *via* the Corey–Chaykovsky reaction.<sup>10</sup>

*O*-Aroyl enolates **8** obtained were characterized by spectral and analytical data. In the <sup>1</sup>H NMR spectra of **8a–e** in CDCl<sub>3</sub>, the olefinic protons of the *E*- and *Z*-isomers were observed at

**Table 3** Selected bond lengths and bond angles for compound **8b**, with estimated standard deviation in parentheses

| Bond length/Å |          | Bond angle (°)    |          |
|---------------|----------|-------------------|----------|
| O(1)–C(8)     | 1.190(6) | C(8)–O(2)–C(9)    | 118.8(3) |
| O(2)–C(9)     | 1.385(3) | C(1)–C(2)–C(7)    | 120.3(4) |
| O(2)–C(8)     | 1.371(3) | C(3)–C(4)–C(5)    | 120.3(3) |
| C(9)–C(10)    | 1.471(4) | C(9)–C(10)–C(11)  | 121.5(3) |
| C(9)–C(17)    | 1.335(6) | C(18)–C(19)–C(20) | 108.6(3) |
| C(5)–C(8)     | 1.469(4) | C(4)–C(5)–C(8)    | 118.6(3) |
| C(18)–C(19)   | 1.528(4) | H(19)–C(21)–H(20) | 116(2)   |

**Fig. 1** ORTEP drawing of compound **8b** with atomic numbering scheme.

around  $\delta$  6.7–6.9, each as a singlet peak. The IR spectra of **8a–e** showed two strong carbonyl absorptions at 1746–1760 and 1672–1684 cm<sup>-1</sup>; the former was assigned to an ester carbonyl and the latter to a keto carbonyl stretching band, respectively. The structural assignment was further confirmed by an X-ray diffraction analysis for the *Z* isomer of **8b**. Fig. 1 shows an ORTEP drawing of **8b**, and selected bond distances and bond angles are listed in Table 3. The dihedral angles among the planes are 114.31° between planes 1 [C(2)–C(7)] and 2 [C(10)–

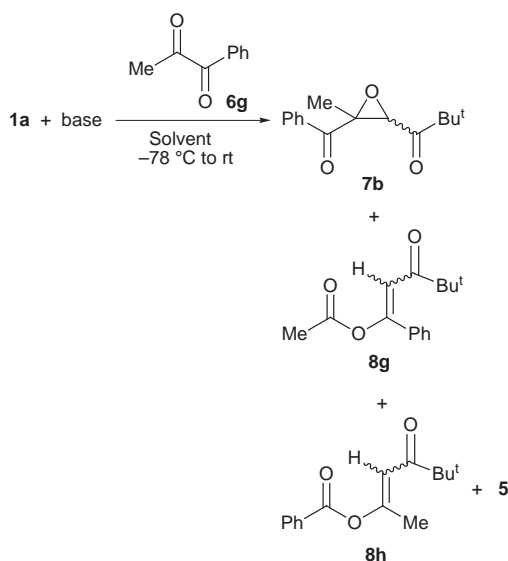
**Table 4** Reaction of triphenylbismuthonium 2-oxoalkylide **2a** with 1-phenylpropane-1,2-dione **6g**

| Entry | Base                                | Solvent                                   | Additive           | Yield (%) <sup>a</sup> |           |           |
|-------|-------------------------------------|---|--------------------|------------------------|-----------|-----------|
|       |                                     |   |                    | <b>7b</b>              | <b>8g</b> | <b>8h</b> |
| 1     | KOBu <sup>t</sup>                   | THF                                       | —                  | 20                     | 4         | 39        |
| 2     | KOBu <sup>t</sup>                   | THF-CH <sub>2</sub> Cl <sub>2</sub> (3:1) | —                  | 40                     | trace     | 33        |
| 3     | KOBu <sup>t</sup>                   | THF-CH <sub>2</sub> Cl <sub>2</sub> (1:1) | —                  | 62                     | trace     | 10        |
| 4     | KOBu <sup>t</sup>                   | THF-CH <sub>2</sub> Cl <sub>2</sub> (1:3) | —                  | 71                     | trace     | 6         |
| 5     | KOBu <sup>t</sup>                   | CH <sub>2</sub> Cl <sub>2</sub>           | —                  | 82                     | trace     | trace     |
| 6     | KN(SiMe <sub>3</sub> ) <sub>2</sub> | THF                                       | —                  | 78                     | —         | —         |
| 7     | KN(SiMe <sub>3</sub> ) <sub>2</sub> | THF                                       | —                  | 80                     | —         | —         |
| 8     | KOBu <sup>t</sup>                   | THF                                       | HMPA               | 22                     | trace     | 44        |
| 9     | KOBu <sup>t</sup>                   | THF                                       | dibenzo-18-crown-6 | 25                     | trace     | 39        |

<sup>a</sup> All reactions were carried out using an equimolar amount of substrate and reagents. In all reactions triphenylbismuthine **5** was recovered in good yield.

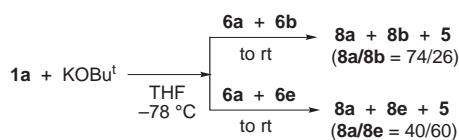
C(15)], 106.05° between planes 1 and plane 3 [C(9), C(17), C(18)], and 15.48° between planes 2 and 3. Eight carbon atoms C(9), C(10) to C(15) and C(17) are all in the same plane.

We also investigated the reaction of ylide **2** with an unsymmetrical diketone, 1-phenylpropane-1,2-dione **6g**. Treatment of ylide **2a** with **6g** in the presence of KOBu<sup>t</sup> in THF gave epoxide **7b** together with an intimate *E/Z*-mixture of *O*-aroyl enolates **8g** and **8h** in 63% yield (Scheme 4). Product distribution was



considerably dependent on the solvents and bases employed (Table 4). A mixture of *E/Z*-*O*-aroyl enolates **8h** was the major product from the reaction of ylide **2a** with **6g** in the presence of KOBu<sup>t</sup> in THF (entry 1). The use of dichloromethane as the solvent worked favorably for the formation of epoxide **7b** (entries 2–5). When KN(SiMe<sub>3</sub>)<sub>2</sub> or NaN(SiMe<sub>3</sub>)<sub>2</sub> was used as a base, **7b** was formed exclusively (entries 6 and 7). Additives such as HMPA and dibenzo-18-crown-6 did not affect the product distribution (entries 8 and 9).

In order to gain an insight into the mechanistic pathways, competitive reactions have been examined for pairs of diketones **6a/6b** and **6a/6e**. Scheme 5 shows the reactivity of *para*-substituted benzils **6b,e** relative to unsubstituted benzil **6a**, where the electron-withdrawing substituent was found to facili-



tate the reaction. These data suggest that nucleophilic attack of the ylide carbanion on the carbonyl carbon would be involved in a rate-determining step. Under similar conditions, *N*-phenylated benzil monoimine was totally unreactive toward **2a**.

The unique reactivity of **2** was also manifested in the reaction with *ortho*-quinones. Bismuthonium ylides **2**, generated *in situ* from **1** and a base, smoothly underwent ring expansion with *o*-quinones **10** to give 2-acyl-3-hydroxytropones **11** in good yield (Scheme 6). Thus, treatment of onium salts **1a,b** with 3,5-di-*tert*-butyl-*o*-benzoquinone **10a** in the presence of KOBu<sup>t</sup> afforded 2-acyl-3-hydroxytropones **11a,b** in good yield (Table 5, entries 1–9). Irrespective of whether the salt **1a** was treated with KOBu<sup>t</sup> before (Method A) or after (Method B) the addition of quinone **10a**, tropone **11a** was obtained in almost identical yield. To optimize the reaction, the base-promoted condensation of **1a** with **10a** was carried out under several different conditions, and the results are summarized in Table 5. A mixed solvent system THF-CH<sub>2</sub>Cl<sub>2</sub> (1:1) gave better yields than THF alone, probably because of improved solubility of **1a** in the former solvent (entries 1, 5 vs. 4, 7). Among four bases examined, KOBu<sup>t</sup> gave the best results as to the conversion yield (entries 4, 6, 7, 8).

We examined the reaction of ylide **2a,b** with variously substituted *o*-quinones. Reaction of **2a,b** with 4,5-dimethyl-*o*-benzoquinone **10b** afforded tropones **11c,d** in moderate yields (entries 10, 11). Treatment of bismuthonium salt **1a** with 3,4,5-trimethyl-*o*-benzoquinone **10c** in the presence of KOBu<sup>t</sup> gave tropone **11e** in 22% isolated yield, together with 9% of compound **12a** (entry 12). The reaction with 4,5-dimethoxy-*o*-benzoquinone **10d** afforded tropone **11f** in 12% yield, together with 25% of **12b** (entry 13). Under similar conditions, the reaction between **1b** and **10d** gave compound **11g** in 14% yield (entry 14). Similarly, ylide **2a** and *o*-chloranil **10e** gave a tropone **11h** in 33% yield (entry 15). When onium salts **1a,b** were treated with 1,2-naphthoquinone **10f** in the presence of a base, tropones **11i,j** were obtained in moderate yield (entries 16, 17). When 9,10-phenanthrenequinone **10g** was used as a substrate, a similar type of ring enlargement led to products **11k,l** (entries 18, 19).

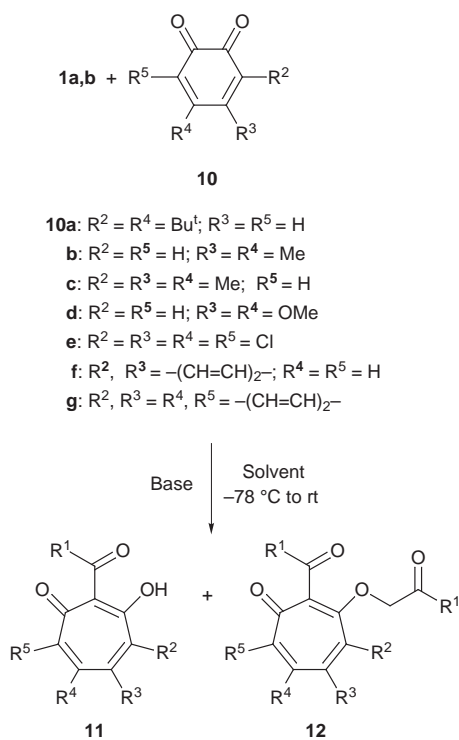
All products **11a–l** and **12a,b** were characterized by spectral and analytical data. In the <sup>1</sup>H NMR spectra of tropones **11a–l** in CDCl<sub>3</sub>, the hydroxy proton was observed as a sharp singlet peak at δ 10.41–18.16 due to intramolecular hydrogen bonding. In this solvent, the aromatic protons in **11k,l** were observed as unsymmetrical multiplets. In such a polar solvent as DMSO-*d*<sub>6</sub>, however, the intramolecular hydrogen bonding became weaker, making resonances of these aromatic protons appear as symmetrical multiplets.

The reaction modes of bismuthonium ylide **2** leading to *O*-aroyl enolates **8** of 1,3-diketones and hydroxytropones **11** are in marked contrast to those of phosphonium ylides, which undergo Wittig reaction with benzil<sup>11</sup> and *o*-quinones<sup>4,12</sup> to give the expected α,β-unsaturated carbonyl compounds.

**Table 5** Reaction of bismuthonium salts **1** with *o*-quinones **10** in the presence of a base<sup>a</sup>

| Entry | Salt      | Quinone    | Base                                 | Solvent                             | Product    | Yield (%) <sup>b</sup> |
|-------|-----------|------------|--------------------------------------|-------------------------------------|------------|------------------------|
| 1     | <b>1a</b> | <b>10a</b> | KOBu <sup>t</sup>                    | THF                                 | <b>11a</b> | 46 (95)                |
| 2     | <b>1a</b> | <b>10a</b> | KOBu <sup>t</sup> <sup>c</sup>       | THF                                 | <b>11a</b> | 48 (93)                |
| 3     | <b>1a</b> | <b>10a</b> | KOBu <sup>t</sup>                    | CH <sub>2</sub> Cl <sub>2</sub>     | <b>11a</b> | 50 (90)                |
| 4     | <b>1a</b> | <b>10a</b> | KOBu <sup>t</sup>                    | THF-CH <sub>2</sub> Cl <sub>2</sub> | <b>11a</b> | 57 (90)                |
| 5     | <b>1a</b> | <b>10a</b> | NaN(SiMe <sub>3</sub> ) <sub>2</sub> | THF                                 | <b>11a</b> | 47 (68)                |
| 6     | <b>1a</b> | <b>10a</b> | KN(SiMe <sub>3</sub> ) <sub>2</sub>  | THF-CH <sub>2</sub> Cl <sub>2</sub> | <b>11a</b> | 52 (70)                |
| 7     | <b>1a</b> | <b>10a</b> | NaN(SiMe <sub>3</sub> ) <sub>2</sub> | THF-CH <sub>2</sub> Cl <sub>2</sub> | <b>11a</b> | 55 (75)                |
| 8     | <b>1a</b> | <b>10a</b> | LiN(SiMe <sub>3</sub> ) <sub>2</sub> | THF-CH <sub>2</sub> Cl <sub>2</sub> | <b>11a</b> | 54 (60)                |
| 9     | <b>1b</b> | <b>10a</b> | KOBu <sup>t</sup>                    | THF                                 | <b>11b</b> | 42 (80)                |
| 10    | <b>1a</b> | <b>10b</b> | KOBu <sup>t</sup>                    | THF-CH <sub>2</sub> Cl <sub>2</sub> | <b>11c</b> | 44 (70)                |
| 11    | <b>1b</b> | <b>10b</b> | KOBu <sup>t</sup>                    | THF                                 | <b>11d</b> | 40 (72)                |
| 12    | <b>1a</b> | <b>10c</b> | KOBu <sup>t</sup>                    | THF                                 | <b>11e</b> | 22 (65)                |
| 13    | <b>1a</b> | <b>10d</b> | KOBu <sup>t</sup>                    | THF-CH <sub>2</sub> Cl <sub>2</sub> | <b>11f</b> | 12 (43) <sup>d</sup>   |
| 14    | <b>1b</b> | <b>10d</b> | KOBu <sup>t</sup>                    | THF                                 | <b>11g</b> | 14 (75)                |
| 15    | <b>1b</b> | <b>10e</b> | KOBu <sup>t</sup>                    | THF                                 | <b>11h</b> | 33 (85)                |
| 16    | <b>1a</b> | <b>10f</b> | KOBu <sup>t</sup>                    | THF                                 | <b>11i</b> | 35 (72)                |
| 17    | <b>1b</b> | <b>10f</b> | KOBu <sup>t</sup>                    | THF                                 | <b>11j</b> | 20 (70)                |
| 18    | <b>1a</b> | <b>10g</b> | KOBu <sup>t</sup>                    | THF                                 | <b>11k</b> | 71 (90)                |
| 19    | <b>1b</b> | <b>10g</b> | KOBu <sup>t</sup>                    | THF                                 | <b>11l</b> | 66 (89)                |

<sup>a</sup> All reactions were carried out using an equimolar amount of substrates and reagents. A 1 : 1 mixture of THF-CH<sub>2</sub>Cl<sub>2</sub> was used as the solvent in entries 4, 6, 8, 10 and 13. In every case, bismuthine **5** was recovered in good yield. <sup>b</sup> Yields refer to the isolated compounds. Numerals in parentheses refer to the conversion yields based on unrecovered quinone. <sup>c</sup> KOBu<sup>t</sup> was added to a solution of **1a** and **10a** in THF at -78 °C. <sup>d</sup> Compound **12b** was obtained in 25% yield.

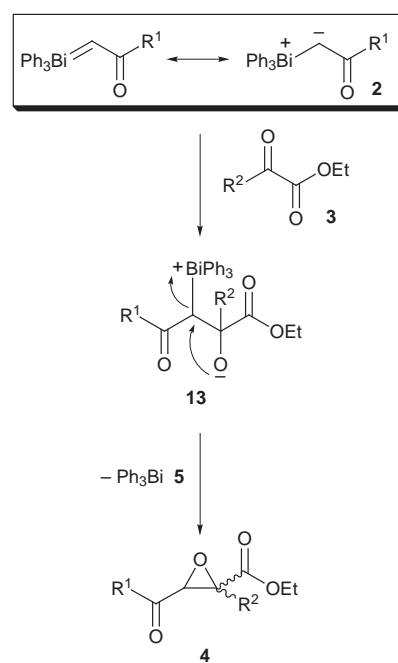


- 11a:** R<sup>1</sup> = R<sup>2</sup> = R<sup>4</sup> = Bu<sup>t</sup>; R<sup>3</sup> = R<sup>5</sup> = H  
**b:** R<sup>1</sup> = Ph; R<sup>2</sup> = R<sup>4</sup> = Bu<sup>t</sup>; R<sup>3</sup> = R<sup>5</sup> = H  
**c:** R<sup>1</sup> = Bu<sup>t</sup>; R<sup>2</sup> = R<sup>5</sup> = H; R<sup>3</sup> = R<sup>4</sup> = Me  
**d:** R<sup>1</sup> = Ph; R<sup>2</sup> = R<sup>5</sup> = H; R<sup>3</sup> = R<sup>4</sup> = Me  
**e:** R<sup>1</sup> = Bu<sup>t</sup>; R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = Me; R<sup>5</sup> = H  
**f:** R<sup>1</sup> = Bu<sup>t</sup>; R<sup>2</sup> = R<sup>5</sup> = H; R<sup>3</sup> = R<sup>4</sup> = OMe  
**g:** R<sup>1</sup> = Ph; R<sup>2</sup> = R<sup>5</sup> = H; R<sup>3</sup> = R<sup>4</sup> = OMe  
**h:** R<sup>1</sup> = Ph; R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = R<sup>5</sup> = Cl  
**i:** R<sup>1</sup> = Bu<sup>t</sup>; R<sup>2</sup>, R<sup>3</sup> = -(CH=CH)<sub>2</sub>-; R<sup>4</sup> = R<sup>5</sup> = H  
**j:** R<sup>1</sup> = Ph; R<sup>2</sup>, R<sup>3</sup> = -(CH=CH)<sub>2</sub>-; R<sup>4</sup> = R<sup>5</sup> = H  
**k:** R<sup>1</sup> = Bu<sup>t</sup>; R<sup>2</sup>, R<sup>3</sup> = R<sup>4</sup>, R<sup>5</sup> = -(CH=CH)<sub>2</sub>-  
**l:** R<sup>1</sup> = Ph; R<sup>2</sup>, R<sup>3</sup> = R<sup>4</sup>, R<sup>5</sup> = -(CH=CH)<sub>2</sub>-

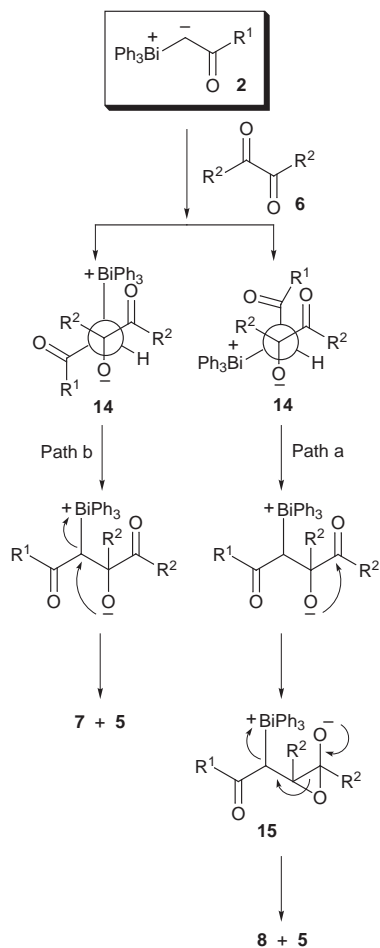
- 12a:** R<sup>1</sup> = Bu<sup>t</sup>; R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = Me; R<sup>5</sup> = H  
**b:** R<sup>1</sup> = Bu<sup>t</sup>; R<sup>2</sup> = R<sup>3</sup> = OMe; R<sup>4</sup>, R<sup>5</sup> = H

**Scheme 6**

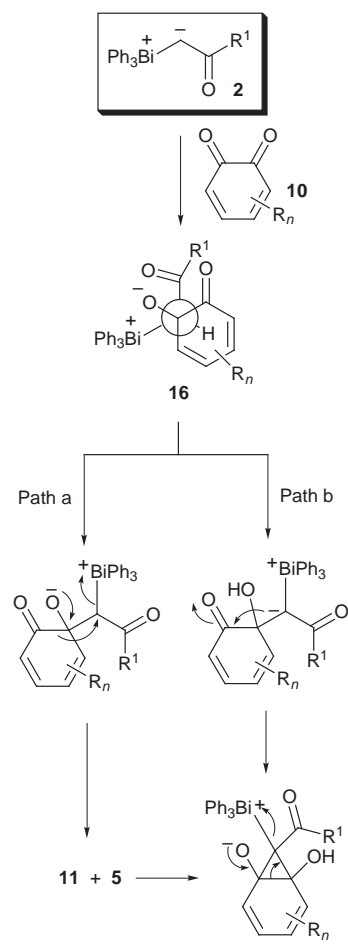
Plausible reaction mechanisms for the present novel types of C-C and C-O bond formation are depicted in Schemes 7-9. It



seems that all reactions involve the rate-determining nucleophilic attack of the ylidic carbon on the carbonyl carbon in the initial stages. The subsequent pathways are strongly dependent on the structure of the  $\alpha$ -dicarbonyl compounds. In the reaction with  $\alpha$ -keto esters **3** (Scheme 7), the negatively charged carbonyl oxygen in **13** would attack the ylidic carbon attached to the bismuth, resulting in the formation of oxiranes **4** under simultaneous elimination of bismuthine **5**. In the reaction with benzils **6** (Scheme 8), the anionic oxygen in **14** would attack the neighboring carbonyl carbon to form an intermediate **15**, in which the aryl group formally migrates from the carbon to oxygen through the elimination of the nucleofugal bismuthonium group as bismuthine. This interpretation may be supported by a finding that oxirane **17**, formed from the Darzens reaction of  $\alpha$ -bromopicolone and **6b**, did not isomerize to enolate **8b**



Scheme 8

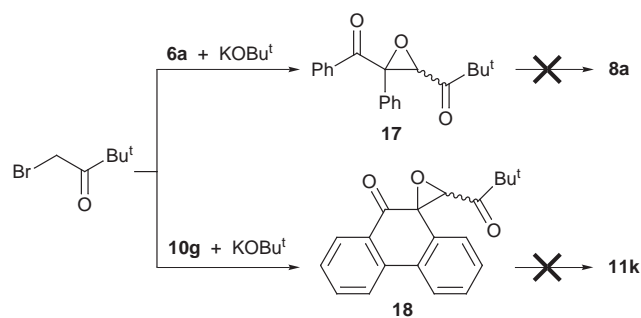


Scheme 9

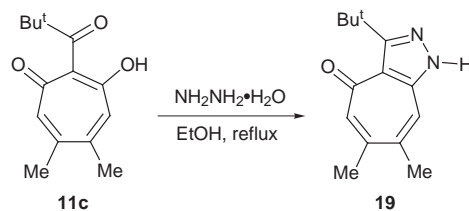
under the present reaction conditions (Scheme 10). The reaction mode leading to enolates **8** is unprecedented in ylide chemistry and only characteristic of bismuth in the group 15 family. We assume that the bulky triphenylbismuthonium group would avoid the antiperiplanar geometry in the transition state **14** due to steric crowding. It is noteworthy that in the reaction of ylide **2a** and unsymmetrical  $\alpha$ -diketone **6g**, the distribution of enolates **8g,h** and oxirane **7b** was found to depend considerably on the bases, solvents, and additives employed (Table 4). Although no direct evidence is in our hands, coordination by the counter cation is also likely to play an important role in determining the transition state geometry.

In the reaction with *o*-quinones **10** (Scheme 9), the tropone skeleton may be constructed by a direct 1,2-acyl migration (path a) or by a stepwise process (path b) from the initial common intermediate **16**. An oxirane **18**, obtained by the Darzens reaction of 9,10-phenanthrenequinone **10g** and  $\alpha$ -bromopinacolone, failed to form **11k**, ruling out the possibility of **18** as a precursor to tropone **11k** (Scheme 10). We can also rule out a possible intermediacy of acylcarbene, since the carbenes generated *in situ* from the decomposition of diazoalkanes are known to add to *o*-quinones to form the expected cycloadducts.<sup>13</sup> Although there are a few methods available for the synthesis of tropones starting from *o*-quinones,<sup>14</sup> the present transformation constitutes the first example based on ylide chemistry. On mild heating with hydrazine hydrate in ethanol, 2-acyl-3-hydroxytropone **11c** was readily converted to multifunctionalized pyrazol **19** (Scheme 11), showing the potent ability of this class of tropones as useful building blocks.

In conclusion, we have discovered novel types of the C–C and C–O bond forming reactions of moderately stabilized bismuth ylides, triphenylbismuthonium 2-oxoalkylides **2**, with some  $\alpha$ -dicarbonyl compounds. The reaction provides a new and efficient method for converting  $\alpha$ -dicarbonyl compounds to multi-



Scheme 10



Scheme 11

functionalized carbonyl compounds, which may be potential building blocks in organic synthesis. The ylide precursors **1** are readily available from silyl enol ethers, triphenylbismuth difluoride and boron trifluoride–diethyl ether in good yield. The one-pot transformation from benzils to *O*-aroyl enolates of 1,3-diketones and from *o*-quinones to 3-hydroxytropones, which are laborious to carry out *via* existing methodologies, feature in particular the heaviest pnictogen element among the 15th family, *bismuth*.

## Experimental

All reactions were performed under an atmosphere of argon. THF and dichloromethane were distilled from sodium benzo-phenone ketyl and CaH<sub>2</sub>, respectively, before use. Bismuthonium salts **1a**, **b** were prepared as reported previously.<sup>15</sup> Column chromatography was performed on silica gel (Wako-gel, C200). 4,5-Dimethyl-*o*-benzoquinone,<sup>16</sup> 3,4,5-trimethyl-*o*-benzoquinone<sup>17</sup> and 4,5-dimethoxy-*o*-benzoquinone<sup>18</sup> were prepared according to the reported procedures. Other substrates were commercially received. All melting points were measured on a Yanagimoto hot-stage apparatus and are uncorrected. <sup>1</sup>H NMR spectra were recorded on a Varian Gemini-200 spectrometer at 200 MHz using tetramethylsilane as an internal standard. Coupling constants *J* are given in Hz. Infrared spectra were observed on a Shimadzu FTIR-8100 spectrophotometer. Chemical ionization (CI) mass spectra were obtained on a Shimadzu GCMS QP-5000 instrument using isobutane as an ionizing gas. EI mass spectra were obtained on a Shimadzu GCMS-QP-2000A spectrometer. Elemental analyses were performed at Microanalytical Laboratory of Kyoto University.

### Reaction of bismuthonium ylides **2** with ethyl pyruvate **3**

**Typical procedure.** To a stirred suspension of salt **1a** (125 mg, 0.20 mmol) in THF (5 cm<sup>3</sup>) was added NaN(SiMe<sub>3</sub>)<sub>2</sub> (1.0 mol dm<sup>-3</sup> THF solution; 0.2 cm<sup>3</sup>, 0.2 mmol) at -78 °C. After 10 min, ethyl pyruvate **3a** (23 mg, 0.20 mmol) was added and the resulting mixture was gradually allowed to warm to room temperature. Evaporation of the solvent under reduced pressure gave an oily residue, which was diluted with benzene (15 cm<sup>3</sup>) and the insoluble material was filtered off through Celite. The filtrate was concentrated under reduced pressure to leave an oily residue, the composition of which was estimated by <sup>1</sup>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 triphenylbismuthine **5** (85 mg, 97%), *cis*-**4a** (12 mg, 28%) and *trans*-**4a** (23 mg, 54%) in this order.

**Ethyl *cis*-2,3-epoxy-2,5,5-trimethyl-4-oxohexanoate **4a**.** Oil;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.22 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.32 (3H, t, *J* 7.2, CH<sub>2</sub>CH<sub>3</sub>), 1.44 (3H, s, CH<sub>3</sub>), 4.17 (1H, s, CH) and 4.27 (2H, q, *J* 7.2, CH<sub>2</sub>CH<sub>3</sub>);  $\nu_{\text{max}}$  (neat)/cm<sup>-1</sup> 1744 (C=O), 1717 (C=O); *m/z* (EI) 141 (M<sup>+</sup> - 73) (Found: C, 61.51; H, 8.42. C<sub>11</sub>H<sub>18</sub>O<sub>4</sub> requires C, 61.66; H, 8.47%).

**Ethyl *trans*-2,3-epoxy-2,5,5-trimethyl-4-oxohexanoate **4a**.** Oil;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.23 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.27 (3H, t, *J* 7.2, CH<sub>2</sub>CH<sub>3</sub>), 1.67 (3H, s, CH<sub>3</sub>), 3.79 (1H, s, CH) and 4.19 (2H, q, *J* 7.2, CH<sub>2</sub>CH<sub>3</sub>);  $\nu_{\text{max}}$  (neat)/cm<sup>-1</sup> 1740 (C=O), 1719 (C=O); *m/z* (EI) 141 (M<sup>+</sup> - 73) (Found: C, 61.65; H, 8.42. C<sub>11</sub>H<sub>18</sub>O<sub>4</sub> requires C, 61.66; H, 8.47%).

**Ethyl 2,3-epoxy-5,5-dimethyl-4-oxo-2-phenylhexanoate **4b**.** Mp 47–48 °C;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.25–1.33 (12H, m, C(CH<sub>3</sub>)<sub>3</sub> and CH<sub>2</sub>CH<sub>3</sub>), 3.94 (1H, s, CH), 4.24 (2H, q, *J* 7, CH<sub>2</sub>CH<sub>3</sub>), 7.38–7.41 (3H, m, Ph) and 7.52–7.60 (2H, m, Ph);  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 1755 (C=O), 1719 (C=O); *m/z* (EI) 203 (78%, M<sup>+</sup> - 73), 146 (67), 105 (100) (Found: C, 69.42; H, 7.42. C<sub>16</sub>H<sub>20</sub>O<sub>4</sub> requires C, 69.55; H, 7.29%). Stereochemical assignment was not made.

**Ethyl 2,3-epoxy-2-methyl-4-oxo-4-phenylbutanoate **4c**.** Oil;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.03 (3H, t, *J* 7.1, CH<sub>2</sub>CH<sub>3</sub>), 1.78 (3H, s, CH<sub>3</sub>), 4.02 (1H, s, CH), 4.04 (2H, q, *J* 7.1, CH<sub>2</sub>CH<sub>3</sub>), 7.44–7.68 (3H, m, Ph) and 7.97–8.05 (2H, m, Ph);  $\nu_{\text{max}}$  (neat)/cm<sup>-1</sup> 1740 (C=O), 1692 (C=O); *m/z* (EI) 189 (M<sup>+</sup> - 45), 161, 105, 77 (Found: C, 66.40; H, 6.05. C<sub>13</sub>H<sub>14</sub>O<sub>4</sub> requires C, 66.66; H, 6.02%).

### Reaction of bismuthonium ylides **2** with benzils **6**

**Typical procedure. Method A:** To a stirred suspension of **1a** (313 mg, 0.50 mmol) in a given solvent (8 cm<sup>3</sup>) was added KOBu<sup>t</sup> (56 mg, 0.50 mmol) at -78 °C. After 10 min, 4,4'-dimethylbenzil **6b** (119 mg, 0.50 mmol) was added and the resulting solution was allowed gradually to warm to room temperature. Evaporation of the solvent under reduced pressure gave an oily residue, which was chromatographed on silica gel using hexane-EtOAc as the solvent to elute triphenylbismuthine **5** (185 mg, 84%), recovered **6b** (47 mg, 40%) and an intimate mixture of isomeric enolates **8b** (90 mg, 53%; *E/Z* = 42/58), in this order.

**Method B:** To a stirred mixture of **1a** (313 mg, 0.50 mmol), **6b** (119 mg, 0.50 mmol) and THF (8 cm<sup>3</sup>) was added KOBu<sup>t</sup> (56 mg, 0.50 mmol) at -78 °C. After stirring for 1 h at this temperature, the reaction mixture was allowed to warm to room temperature. Work up as described above gave **5**, **6b** and **8b**. The *E/Z* isomer ratio was estimated by <sup>1</sup>H NMR integration of olefinic protons. The equation proposed by Pascual *et al.*<sup>19</sup> was used for stereochemical assignment of compounds **8**, where the olefinic proton peak appearing at higher field was assigned to the *E* isomer.

**4,4-Dimethyl-1-phenyl-3-oxopent-1-en-1-yl benzoate **8a**.** Mp 110–111 °C (*E/Z* = 4:6);  $\delta_{\text{H}}$  (*E*-isomer/CDCl<sub>3</sub>) 1.30 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 6.77 (1H, s, olefinic-CH), 7.36–7.62 (6H, m, Ph), 7.88 (2H, d, *J* 7, Ph) and 8.11 (2H, d, *J* 7, Ph);  $\delta_{\text{H}}$  (*Z*-isomer/CDCl<sub>3</sub>) 1.21 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 6.95 (1H, s, olefinic-CH), 7.36–7.62 (6H, m, Ph), 7.64 (2H, d, *J* 8, Ph) and 8.11 (2H, d, *J* 7, Ph);  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 1748 (C=O), 1684 (C=O); *m/z* (EI) 251 (13%, M<sup>+</sup> - 57), 105 (100) (Found: C, 77.50; H, 6.35. C<sub>20</sub>H<sub>20</sub>O<sub>3</sub> requires C, 77.89; H, 6.54%).

**4,4-Dimethyl-1-(4-methylphenyl)-3-oxopent-1-en-1-yl 4-methylbenzoate **8b**.** Mp 89–90 °C (*E/Z* = 4:6);  $\delta_{\text{H}}$  (*E*-isomer/CDCl<sub>3</sub>) 1.29 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 2.36 (3H, s, CH<sub>3</sub>), 2.42 (3H, s, CH<sub>3</sub>), 6.74 (1H, s, olefinic-CH), 7.19 (2H, d, *J* 8, Ar), 7.29 (2H, d, *J* 7, Ar), 7.78 (2H, d, *J* 8, Ar) and 8.00 (2H, d, *J* 8, Ar);  $\delta_{\text{H}}$  (*Z*-isomer/CDCl<sub>3</sub>) 1.20 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 2.36 (3H, s, CH<sub>3</sub>), 2.42 (3H, s, CH<sub>3</sub>), 6.90 (1H, s, olefinic-CH), 7.19 (2H, d, *J* 8, Ar), 7.29 (2H, d, *J* 7, Ar), 7.55 (2H, d, *J* 8, Ar) and 8.09 (2H, d, *J* 8, Ar);  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 1746 (C=O), 1684 (C=O); *m/z* (EI) 279 (11%, M<sup>+</sup> - 57), 119 (100) (Found: C, 78.43; H, 7.31. C<sub>22</sub>H<sub>24</sub>O<sub>3</sub> requires C, 78.54; H, 7.19%).

**4,4-Dimethyl-1-(4-methoxyphenyl)-3-oxopent-1-en-1-yl 4-methoxybenzoate **8c**.**  $\delta_{\text{H}}$  (*E*-isomer/CDCl<sub>3</sub>) 1.29 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 3.82 (3H, s, OCH<sub>3</sub>), 3.86 (3H, s, OCH<sub>3</sub>), 6.71 (1H, s), 6.86–6.97 (4H, m, Ar), 7.87 (2H, d, *J* 9, Ar) and 8.06 (2H, d, *J* 9, Ar);  $\delta_{\text{H}}$  (*Z*-isomer/CDCl<sub>3</sub>) 1.20 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 3.82 (3H, s, OCH<sub>3</sub>), 3.86 (3H, s, OCH<sub>3</sub>), 6.85 (1H, s), 6.88–7.0 (4H, m, Ar), 7.61 (2H, d, *J* 9, Ar) and 8.16 (2H, d, *J* 9, Ar);  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 1738 (C=O), 1667 (C=O); *m/z* (CI) 369 (25%, M<sup>+</sup> + 1), 311, 135.

**1-(4-Fluorophenyl)-4,4-dimethyl-3-oxopent-1-en-1-yl 4-fluorobenzoate **8d**.** Mp 90–91 °C (*E/Z* = 4:6);  $\delta_{\text{H}}$  (*E*-isomer/CDCl<sub>3</sub>) 1.30 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 6.73 (1H, s, olefinic-CH), 7.04–7.19 (4H, m, Ar), 7.87–7.91 (2H, m, Ar) and 8.0–8.2 (2H, m, Ar);  $\delta_{\text{H}}$  (*Z*-isomer/CDCl<sub>3</sub>) 1.21 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 6.89 (1H, s, olefinic-CH), 7.04–7.19 (4H, m, Ar), 7.63–7.69 (2H, m, Ar) and 8.0–8.2 (2H, m, Ar);  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 1746 (C=O), 1672 (C=O); *m/z* (EI) 287 (25%, M<sup>+</sup> - 57), 123 (100) (Found: C, 70.04; H, 5.34. C<sub>20</sub>H<sub>18</sub>F<sub>2</sub>O<sub>3</sub> requires C, 69.76; H, 5.27%).

**1-(4-Chlorophenyl)-4,4-dimethyl-3-oxopent-1-en-1-yl 4-chlorobenzoate **8e**.** Mp 105–106 °C (*E/Z* = 5:5);  $\delta_{\text{H}}$  (*E*-isomer/CDCl<sub>3</sub>) 1.30 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 6.73 (1H, s, olefinic-CH), 7.34–7.40 (2H, m, Ar), 7.43–7.50 (2H, m, Ar), 7.81 (2H, d, *J* 8, Ar)

and 8.08 (2H, d,  $J$  8, Ar);  $\delta_{\text{H}}$  (*Z*-isomer/ $\text{CDCl}_3$ ) 1.20 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 6.92 (1H, s, olefinic-CH), 7.34–7.40 (2H, m, Ar), 7.43–7.50 (2H, m, Ar), 7.60 (2H, d,  $J$  8, Ar) and 8.12 (2H, d,  $J$  8, Ar);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  1760 (C=O), 1672 (C=O);  $m/z$  (EI) 320 (2%,  $\text{M}^+ - 57$ ), 139 (100) (Found: C, 63.47; H, 4.68.  $\text{C}_{20}\text{H}_{18}\text{Cl}_2\text{O}_3$  requires C, 63.67; H, 4.81%).

**2-Benzoyl-1-(4-fluorophenyl)ethenyl 4-fluorobenzoate 8f.** Mp 124–125 °C (single isomer);  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 7.07–7.25 (4H, m, Ar), 7.30 (1H, s, olefinic-CH), 7.40–7.47 (3H, m, Ph), 7.77–7.73 (2H, m, Ar), 7.94–7.99 (2H, m, Ph) and 8.17–8.24 (2H, m, Ar);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  1744 (C=O), 1668 (C=O);  $m/z$  (EI) 364 (2%,  $\text{M}^+$ ), 259 (5,  $\text{M}^+ - 105$ ), 241 (9), 123 (100) (Found: C, 72.28; H, 3.68.  $\text{C}_{22}\text{H}_{14}\text{F}_2\text{O}_3$  requires C, 72.52; H, 3.87%). Stereochemical assignment was not made.

**2-(4-Methoxybenzoyl)-1-(4-methoxyphenyl)-4,4-dimethylpentane-1,3-dione 9.** Mp 150–153 °C;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.24 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 3.85 (6H, s,  $\text{OCH}_3$ ), 6.60 (1H, s, olefinic-CH), 6.91 (4H, d,  $J$  9, Ar) and 7.91 (4H, d,  $J$  9, Ar);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  1707 (C=O), 1670 (C=O);  $m/z$  (EI) 311 (10%,  $\text{M}^+ - 57$ ), 135 (100) (Found: C, 71.40; H, 6.42.  $\text{C}_{22}\text{H}_{24}\text{O}_5$  requires C, 71.72; H, 6.57%).

**2,3-Epoxy-3-methyl-1-phenylpentane-1,4-dione 7a.** Mp 85–87 °C;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.71 (3H, s,  $\text{CH}_3$ ), 2.20 (3H, s,  $\text{COCH}_3$ ), 4.21 (1H, s, CH), 7.45–7.70 (3H, m, Ph) and 7.90–7.97 (2H, m, Ph);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  1715 (C=O), 1688 (C=O);  $m/z$  (EI) 161 ( $\text{M}^+ - 43$ ), 148, 105, 77 (Found: C, 70.41; H, 5.83.  $\text{C}_{12}\text{H}_{12}\text{O}_3$  requires C, 70.58; H, 5.92%).

#### Reaction of bismuthonium ylide 2a with 1-phenylpropane-1,2-dione 6g

To a suspension of **1a** (626 mg, 1.0 mmol) in THF (15  $\text{cm}^3$ ) was added  $\text{KOBU}^t$  (112 mg, 1.0 mmol) at  $-78$  °C. After stirring for 10 min, 1-phenylpropane-1,2-dione **6g** (148 mg, 1.0 mmol) was added and the resulting mixture was allowed gradually to warm to room temperature. The solvent was evaporated under reduced pressure and the residue was extracted with benzene. Removal of solvent from the extract gave an oily residue, which was chromatographed on silica gel using hexane–ethyl acetate as the solvent to elute successively triphenylbismuthine **5** (380 mg, 86%), **8g** (7.6 mg, 3%), **8h** (96 mg, 39%) and epoxide **7b** (49 mg, 20%).

**4,4-Dimethyl-3-oxo-1-phenylpent-1-en-1-yl acetate 8g.**  $\delta_{\text{H}}$  (*Z*-isomer/ $\text{CDCl}_3$ ) 1.22 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 2.35 (3H, s,  $\text{COCH}_3$ ), 6.78 (1H, s, olefinic-CH), 7.40–7.45 (3H, m) and 7.66–7.70 (2H, m);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  1748 (C=O), 1684 (C=O);  $m/z$  (EI) 189 (21%,  $\text{M}^+ - 57$ ), 147 (100), 105 (25) (Found: C, 72.77; H, 7.16.  $\text{C}_{15}\text{H}_{18}\text{O}_3$  requires C, 73.15; H, 7.37%).

**5,5-Dimethyl-4-oxohex-2-en-2-yl benzoate 8h.**  $\delta_{\text{H}}$  (*E*-isomer/ $\text{CDCl}_3$ ) 1.22 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 2.16 (3H, s,  $\text{CH}_3$ ), 6.10 (1H, s, olefinic-CH), 7.44–7.60 (3H, m, Ph) and 8.11 (2H, d,  $J$  8, Ph);  $\delta_{\text{H}}$  (*Z*-isomer/ $\text{CDCl}_3$ ) 1.13 (9H, s), 2.16 (3H, s), 6.27 (1H, s), 7.44–7.60 (3H, m) and 8.11 (2H, d,  $J$  8);  $\nu_{\text{max}}$  (neat)/ $\text{cm}^{-1}$  1746 (C=O), 1698 (C=O);  $m/z$  (EI) 189 (9%,  $\text{M}^+ - 57$ ), 105 (100%) (Found: C, 72.84; H, 7.44.  $\text{C}_{15}\text{H}_{18}\text{O}_3$  requires C, 73.15; H, 7.37%).

**2,3-Epoxy-2,5,5-trimethyl-1-phenylhexane-1,4-dione 7b.** Mp 72–74 °C;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.24 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 1.77 (3H, s,  $\text{CH}_3$ ), 3.95 (1H, s, CH), 7.44–7.63 (3H, m, Ph) and 8.10 (2H, d,  $J$  7, Ph);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  1717 (C=O), 1684 (C=O);  $m/z$  (EI) (5%,  $\text{M}^+ - 57$ ), 105 (100) (Found: C, 72.86; H, 7.36.  $\text{C}_{15}\text{H}_{18}\text{O}_3$  requires C, 73.15; H, 7.37%).

#### Competitive reaction of bismuthonium ylide 2a with *para*-substituted benzils 6b,e

To a stirred mixture of the salt **1a** (626 mg, 1.0 mmol), benzil **6a**

(210 mg, 1.0 mmol) and a given *p*-substituted benzil (1.0 mmol) in THF (15  $\text{cm}^3$ ) was added  $\text{KOBU}^t$  (112 mg, 1.0 mmol) at  $-78$  °C. The resulting mixture was allowed to warm to room temperature and worked up as usual to give bismuthine **5**, unchanged benzils and *O*-aroyl enolates **8**. The isomer ratios of *O*-aroyl enolates given in Scheme 4 were determined by  $^1\text{H}$  NMR integration of the product mixture.

#### Reaction of bismuthonium ylide 2a with *ortho*-quinones 10

**Typical procedure.** To a stirred suspension of **1a** (313 mg, 0.50 mmol) in a given solvent (7  $\text{cm}^3$ ) was added  $\text{KOBU}^t$  (56 mg, 0.50 mmol) at  $-78$  °C. Within a few minutes, the reaction mixture turned clear and yellow. After 15 min the *o*-quinone **10a** (110 mg, 0.50 mmol) was added and the resulting mixture was allowed to warm to room temperature. Evaporation of the solvent under reduced pressure gave an oily residue, which was diluted with benzene (30  $\text{cm}^3$ ) and the insoluble matter was filtered off through Celite. The filtrate was concentrated under reduced pressure to leave an oily residue, which was chromatographed on silica gel with hexane–ethyl acetate as the eluent to yield triphenylbismuthine **5** (200 mg, 91%), unchanged quinone **10a** (57 mg, 52%), and tropone **11a** (73 mg, 46%). Compounds **11c,d,f,g,h** showed a symmetrical NMR peak pattern in both  $\text{CDCl}_3$  and  $\text{DMSO}-d_6$ , indicating the rapid tautomerism of these tropones on the NMR time scale.

**4,6-Di-*tert*-butyl-3-hydroxy-2-(2,2-dimethylpropanoyl)-tropone 11a.** Mp 205–207 °C;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.28 (18H, s,  $\text{C}(\text{CH}_3)_3$ ), 1.40 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 6.71 (1H, s, Ar), 7.27 (1H, s, Ar) and 10.41 (1H, s, OH);  $\delta_{\text{H}}$  ( $\text{DMSO}-d_6$ ) 1.11 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 1.25 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 1.31 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 6.92 (1H, s, Ar) and 7.24 (1H, s, Ar), the hydroxy proton could not be located;  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 28.3, 29.7, 30.6, 38.3, 39.1, 45.1, 124.0, 126.0, 129.5, 155.8, 158.8, 163.0, 187.0 and 217.4;  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3437 (OH), 1703 (C=O), 1630 (C=O);  $m/z$  (CI) 319 (100%,  $\text{M} + 1$ ), 261 (18,  $\text{M}^+ - 57$ ) (Found: C, 75.19; H, 9.52.  $\text{C}_{20}\text{H}_{30}\text{O}_3$  requires C, 75.43; H, 9.50%).

**2-Benzoyl-4,6-di-*tert*-butyl-3-hydroxytropone 11b.** Mp 125–127 °C;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.21 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 1.29 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 6.72 (1H, s, Ar), 7.11 (1H, s, Ar), 7.35–7.44 (3H, m, Ph), 7.54 (2H, d,  $J$  7, Ph) and 14.90 (1H, s, OH);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3450 (OH), 1630 (C=O), 1582 (C=O);  $m/z$  (CI) 339 (100%,  $\text{M} + 1$ ) (Found: C, 77.78; H, 7.54.  $\text{C}_{22}\text{H}_{26}\text{O}_3$  requires C, 78.07; H, 7.74%).

**3-Hydroxy-5,6-dimethyl-2-(2,2-dimethylpropanoyl)tropone 11c.** Mp 195–200 °C;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.29 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 2.22 (6H, s,  $\text{CH}_3$ ), 6.84 (2H, s, Ar) and 12.7 (1H, s);  $\delta_{\text{H}}$  ( $\text{DMSO}-d_6$ ) 1.13 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 2.20 (6H, s,  $\text{CH}_3$ ), 6.86 (2H, s, Ar) and 10.8 (1H, s, OH);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 25.1, 28.2, 45.0, 122.0, 134.7, 145.8, 173.6 and 216.1;  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3437 (OH), 1705 (C=O), 1626 (C=O);  $m/z$  (CI) 235 (100%,  $\text{M} + 1$ ) (Found: C, 71.51; H, 7.45.  $\text{C}_{14}\text{H}_{18}\text{O}_3$  requires C, 71.77; H, 7.74%).

**2-Benzoyl-3-hydroxy-5,6-dimethyltropone 11d.** Mp 217–219 °C;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.26 (6H, s,  $\text{CH}_3$ ), 6.83 (2H, s, Ar), 7.39–7.49 (3H, m, Ph), 7.59–7.64 (2H, m, Ph) and 14.29 (1H, s, OH);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3438 (OH), 1688 (C=O), 1625 (C=O);  $m/z$  (CI) 255 (100%,  $\text{M} + 1$ ) (Found: C, 75.29; H, 5.36.  $\text{C}_{16}\text{H}_{14}\text{O}_3$  requires C, 75.57; H, 5.55%).

**3-Hydroxy-2-(2,2-dimethylpropanoyl)-4,5,6-trimethyltropone 11e.** Mp 131–133 °C;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.30 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 2.06 (3H, s,  $\text{CH}_3$ ), 2.20 (3H, s,  $\text{CH}_3$ ), 2.29 (3H, s,  $\text{CH}_3$ ), 6.50 (1H, s, Ar) and 14.80 (1H, s, OH);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 18.6, 19.4, 25.8, 28.8, 44.8, 116.5, 125.5, 136.1, 144.1, 149.5, 169.8, 193.9 and 214.7;  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3437 (OH), 1690 (C=O), 1650 (C=O);  $m/z$  (CI) 249 (100,  $\text{M} + 1$ ) (Found: C, 72.23; H, 7.93.  $\text{C}_{15}\text{H}_{20}\text{O}_3$  requires C, 72.55; H, 8.12%).

**3-Hydroxy-5,6-dimethoxy-2-(2,2-dimethylpropanoyl)tropone 11f.** Mp 217–220 °C;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.31 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 3.86 (6H, s, OCH<sub>3</sub>) and 9.40 (2H, s, Ar), hydroxy proton could not be located clearly;  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 3400 (OH), 1700 (C=O), 1632 (C=O);  $m/z$  (CI) 267 (100%, M + 1) (Found: C, 62.85; H, 6.55. C<sub>14</sub>H<sub>18</sub>O<sub>5</sub> requires C, 63.15; H, 6.81%).

**2-Benzoyl-3-hydroxy-5,6-dimethoxytropone 11g.** Mp 200–205 °C;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 3.89 (6H, s, OCH<sub>3</sub>), 6.13 (1H, s, Ar), 6.36 (1H, s, Ar), 7.26–7.44 (3H, m, Ph), 7.59–7.63 (2H, m, Ph) and 14.75 (1H, s, OH);  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 3450 (OH), 1673 (C=O), 1634 (C=O);  $m/z$  (CI) 287 (100%, M + 1) (Found: C, 66.92; H, 4.90. C<sub>16</sub>H<sub>14</sub>O<sub>5</sub> requires C, 67.13; H, 4.93%).

**2-Benzoyl-4,5,6,7-tetrachloro-3-hydroxytropone 11h.** Mp 138–139 °C;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 7.46 (2H, t, *J* 7.7, Ph), 7.52–7.60 (3H, m, Ph) and 16.78 (1H, s, OH);  $m/z$  (EI) 364 (M<sup>+</sup>) (Found: C, 46.26; H, 1.63. C<sub>14</sub>H<sub>6</sub>Cl<sub>4</sub>O<sub>3</sub> requires C, 46.19; H, 1.66%).

**1-Hydroxy-2-(2,2-dimethylpropanoyl)-3H-benzocycloheptatrien-3-one 11i.** Mp 179–181 °C;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.33 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 6.62 (1H, d, *J* 14, Ar), 7.33 (1H, d, *J* 12.5, Ar), 7.52–7.67 (3H, m, Ar), 8.0–8.04 (1H, m, Ar) and 14.59 (1H, s, OH);  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 3262 (OH), 1684 (C=O), 1645 (C=O);  $m/z$  (CI) 257 (100%, M + 1), 199 (35, M<sup>+</sup> - 57) (Found: C, 74.67; H, 6.04. C<sub>16</sub>H<sub>16</sub>O<sub>3</sub> requires C, 74.98; H, 6.29%).

**2-Benzoyl-1-hydroxy-3H-benzocycloheptatrien-3-one 11j.** Mp 222–225 °C;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 6.70 (1H, d, *J* 12.5, Ar), 7.36–7.51 (4H, m, Ar and Ph), 7.54–7.61 (3H, m, Ar), 7.62–7.70 (2H, m, Ph), 7.88–7.90 (1H, m, Ar) and 15.23 (1H, s, OH);  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 3410 (OH), 1674 (C=O), 1638 (C=O);  $m/z$  (CI) 277 (100%, M + 1) (Found: C, 77.93; H, 4.25. C<sub>18</sub>H<sub>12</sub>O<sub>3</sub> requires C, 78.25; H, 4.38%).

**7-Hydroxy-6-(2,2-dimethylpropanoyl)-5H-dibenzo[*a,c*]cycloheptatrien-5-one 11k.** Mp 154–155 °C;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.40 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 7.43–7.65 (6H, m, Ar), 7.67–7.75 (1H, m, Ar), 8.15 (1H, d, *J* 7.5, Ar) and 18.16 (1H, s, OH);  $\delta_{\text{H}}$  (DMSO-*d*<sub>6</sub>) 1.20 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 7.62 (2H, t, *J* 7.6, Ar), 7.71 (2H, t, *J* 7.4, Ar), 7.75–7.90 (2H, br s, Ar), 7.88 (2H, d, *J* 7.8, Ar) and 13.2 (1H, br s, OH);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 28.2, 44.1, 118.8, 126.2, 128.1, 128.3, 128.4, 130.2, 130.3, 131.9, 132.5, 134.0, 137.5, 144.8, 179.9, 197.0 and 209.2 (two aromatic peaks overlapped);  $\delta_{\text{C}}$  (DMSO-*d*<sub>6</sub>) 27.0, 44.2, 124.6, 127.6, 128.3, 130.0, 131.0, 134.9 and 208.7 (two sets of aromatic peaks overlapped);  $m/z$  (EI) 306 (100%, M<sup>+</sup>) (Found: C, 78.61; H, 5.94. C<sub>20</sub>H<sub>18</sub>O<sub>3</sub> requires C, 78.41; H, 5.92%).

**6-Benzoyl-7-hydroxy-5H-dibenzo[*a,c*]cycloheptatrien-5-one 11l.** Mp 118–119 °C (lit.<sup>20</sup> 117.5 °C);  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 7.40–7.82 (12H, m, Ar and Ph), 8.27–8.35 (1H, m, Ar) and 17.17 (1H, s, OH);  $\delta_{\text{H}}$  (DMSO-*d*<sub>6</sub>) 7.42–7.62 (5H, m, Ar and Ph), 7.66 (2H, t, *J* 7.3, Ar), 7.76 (2H, t, *J* 7.3, Ar), 7.85 (2H, br d, Ar), 7.88 (2H, d, *J* 7.9, Ph) and 15.9 (1H, br s, OH);  $\delta_{\text{C}}$  (DMSO-*d*<sub>6</sub>) 120.5, 127.5, 128.1, 128.5, 129.0, 130.5, 132.2, 135.7, 137.7 and 197.1 (three sets of aromatic peaks overlapped);  $m/z$  (EI) 326 (100%, M<sup>+</sup>) (Found: C, 80.61; H, 4.24. C<sub>22</sub>H<sub>14</sub>O<sub>3</sub> requires C, 80.97; H, 4.32%).

**4,5,6-Trimethyl-3-(3,3-dimethyl-2-oxobutoxy)-2-(2,2-dimethylpropanoyl)cycloheptatrien-1-one 12a.** Mp 153–155 °C;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.21 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.23 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 2.21 (3H, s, CH<sub>3</sub>), 2.27 (6H, s, CH<sub>3</sub>), 4.83 (2H, s, CH<sub>2</sub>) and 6.50 (1H, s, Ar);  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 1719 (C=O), 1696 (C=O), 1618 (C=O);  $m/z$  (CI) 347 (100%, M + 1) (Found: C, 72.52; H, 8.68. C<sub>21</sub>H<sub>30</sub>O<sub>4</sub> requires C, 72.80; H, 8.73%).

**4,5-Dimethoxy-3-(3,3-dimethyl-2-oxobutoxy)-2-(2,2-dimethylpropanoyl)cycloheptatrien-1-one 12b.** Mp 154–156 °C;

$\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.20 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.23 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 3.84 (6H, s, OCH<sub>3</sub>), 4.80 (2H, s, CH<sub>2</sub>), 6.17 (1H, s, Ar) and 6.52 (1H, s, Ar);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 26.1, 27.1, 43.0, 44.3, 56.0, 56.2, 72.8, 103.9, 104.1, 118.4, 157.2, 157.4, 157.8, 181.5, 209.5 and 212.3;  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 1725 (C=O), 1696 (C=O), 1626 (C=O);  $m/z$  (CI) 364 (100%, M + 1) (Found: C, 65.63; H, 7.55. C<sub>20</sub>H<sub>28</sub>O<sub>6</sub> requires C, 65.92; H, 7.74%).

#### Darzens reactions of $\alpha$ -bromopinacolone with benzil **6a** and **9,10-phenanthrenequinone 10g**

To a mixture of  $\alpha$ -bromopinacolone (0.135 cm<sup>3</sup>, 1.0 mmol), benzil **6a** (210 mg, 1.0 mmol) and THF (10 cm<sup>3</sup>) was added KOBu<sup>t</sup> (112 mg, 1.0 mmol) at -78 °C. The resulting yellow solution was allowed gradually warm to room temperature. The mixture was evaporated under reduced pressure to leave an oily residue. Benzene (10 cm<sup>3</sup>) was added and an insoluble substance was filtered off through Celite. The filtrate was concentrated under reduced pressure to leave a crystalline residue, which was recrystallized from dichloromethane–hexane to afford **17** (280 mg, 91%) as a single isomer. Similarly, compound **18** was obtained in 90% yield by the reaction with **9,10-phenanthrenequinone 10g**.

**2,3-Epoxy-5,5-dimethyl-1,2-diphenylhexane-1,4-dione 17.** Mp 123–124 °C (single isomer);  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.27 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 4.00 (1H, s, CH), 7.35–7.60 (8H, m, Ph) and 7.98–8.06 (2H, m, Ph);  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 1717 (C=O), 1674 (C=O);  $m/z$  (CI) 251 (M<sup>+</sup> - 57), 223, 203, 165, 105, 77, 57 (Found: C, 77.74; H, 6.59. C<sub>20</sub>H<sub>20</sub>O<sub>3</sub> requires C, 77.90; H, 6.54%).

**9',10'-Dihydro-3-(2,2-dimethylpropanoyl)spiro[oxirane-2,9'-phenanthren]-10'-one 18.** Mp 139–140 °C (single isomer);  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.07 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 3.93 (1H, s, CH), 7.38–7.55 (4H, m, Ar), 7.72 (1H, dt, *J* 1.5, 7.6, Ar) and 7.96–8.08 (3H, m, Ar);  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 1721 (C=O), 1690 (C=O);  $m/z$  (CI) 306 (M<sup>+</sup>) (Found: C, 78.42; H, 5.85. C<sub>20</sub>H<sub>18</sub>O<sub>3</sub> requires C, 78.41; H, 5.92%).

Stereochemical assignments were not made for **17** and **18**. These compounds failed to form the corresponding enolate **8a** and tropone **11b** in the presence of KOBu<sup>t</sup>, triphenylbismuthine and/or Bu<sup>t</sup>OH in THF (Scheme 10).

#### Cyclocondensation of tropone **11c** with hydrazine hydrate

To a solution of ketone **11c** (23 mg, 0.10 mmol) in ethanol (10 cm<sup>3</sup>) was added an excess of hydrazine hydrate (50 mg, 1.0 mmol) in one portion and the resulting mixture was heated under gentle reflux. After 5 h, the reaction mixture was cooled, diluted with water until the solution became cloudy, and allowed to stand at room temperature. The crystalline deposit was collected by filtration and recrystallized from ethanol to obtain pure *3-tert-butyl-6,7-dimethyl-1H-cyclohepta[*c*]pyrazol-4-one 19* (13 mg, 56%); mp 269–271 °C;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.61 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 2.27 (6H, s, CH<sub>3</sub>), 6.92 (1H, s, CH), 7.19 (1H, s, Ar) and 7.26 (1H, s, Ar);  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 3200 (NH), 1635 (C=O);  $m/z$  (EI) 230 (30%, M<sup>+</sup>), 215 (100), 187 (28) (Found: C, 72.74; H, 7.90; N, 12.15. C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O requires C, 73.01; H, 7.88; N, 12.16%).

#### X-Ray crystallographic analysis of **8b**

A colourless prismatic crystal of **8b**, obtained by slow evaporation of a dichloromethane–hexane (1:4) solution of **8b** at room temperature, was used for the X-ray diffraction analysis. The data were collected on a Rigaku AFC7S diffractometer with graphite monochromated Cu-K $\alpha$  radiation using the  $\omega$ - $2\theta$  scan technique to a maximum  $2\theta$  value of 120.8°. Scans of (1.47 + 0.30 tan $\theta$ )° were made at a speed of 8.0° min<sup>-1</sup> (in  $\omega$ ). Final unit cell parameters were obtained by least-square analysis of setting angles for 25 reflections; 56.37 <  $2\theta$  < 78.75°. The



**Table 6** Crystal data for compound **8b**

|                          |  |
|--------------------------|--|
| Chemical formula         | C <sub>22</sub> H <sub>24</sub> O <sub>3</sub> |
| Formula weight           | 336.43   |
| Crystal system           | Monoclinic                                     |
| $\mu(\text{Cu-K}\alpha)$ | 6.22 cm <sup>-1</sup>                          |
| Unit cell dimensions     | 0.19 × 0.06 × 0.44 mm                          |
| Space group              | <i>P</i> 2 <sub>1</sub> / <i>n</i>             |
| <i>Z</i>                 | 4  |
| <i>F</i> <sub>000</sub>  | 720.00   |
| <i>a</i>                 | 5.83(4) Å                                      |
| <i>b</i>                 | 17.42(3) Å                                     |
| <i>c</i>                 | 18.44(3) Å                                     |
| $\beta$                  | 91.6(3)°                                       |
| <i>V</i>                 | 1872(12) Å <sup>3</sup>                        |
| <i>D</i> <sub>c</sub>    | 1.194 g cm <sup>-3</sup>                       |
| Radiation                | Cu-K $\alpha$ ( $\lambda$ = 1.54178 Å)         |
| <i>T</i>                 | 24 °C  |
| <i>R</i>                 | 0.046  |
| <i>R</i> <sub>w</sub>    | 0.076  |
| Observed reflections     | 3233   |
| Unique reflections       | 2914   |
| <i>R</i> <sub>int</sub>  | 0.013  |

intensities of three representative reflections were measured after every 250 reflections. No decay correction was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods<sup>21</sup> and expanded using Fourier techniques.<sup>22</sup> The non-hydrogen atoms were refined anisotropically. All calculations were performed using the teXsan<sup>23</sup> crystallographic software package of Molecular Structure Corporation. Other parameters are summarized in Table 6. CCDC reference number 207/323. See <http://www.rsc.org/suppdata/p1/1999/1533> for crystallographic files in .cif format.

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