

## Reaction of Thioketones with Carbonyl Oxides and 3,3-Dimethyl-1,2-dioxirane. [3 + 2] Cycloaddition vs. Oxygen Atom Transfer

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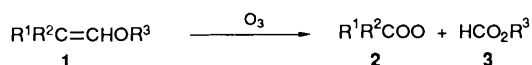
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The ozonolysis of vinyl ethers **1a, b** in the presence of adamantane-2-thione **4a** and bicyclo[3.3.1]nonan-9-thione **4b** gave in each case the corresponding thioozonides **5a–c** in moderate yields, whilst ozonolysis of a mixture of vinyl ethers **1a–d** and thiobenzophenone derivatives **4f–h** gave the corresponding thione *S*-oxides **8f–h** in isolated yields of 10–40%, together with the benzophenones **7f–h**. 3,3-Dimethyl-1,2-dioxirane, generated *in situ* from the reaction of acetone and 'oxone' (2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>), transferred an oxygen atom to compounds **4a, f, g, i** providing the thione *S*-oxides **8a, f, g, i** in 29–97% yield.

The chemistry of carbonyl oxide and the isomeric 1,2-dioxirane has attracted much attention. Cycloaddition<sup>1</sup> and oxygen atom transfer<sup>2</sup> are the main pathways involved in the reactions of carbonyl oxides, whilst the latter occurs predominantly in the case of 1,2-dioxiranes.<sup>3</sup> Consistent with this, we report here that in the reaction of thioketones with carbonyl oxides both of these mechanistic alternatives participate and, moreover, the structure of the thioketones plays an important role in determining the course of the reaction.<sup>4</sup> In contrast, in the reaction with 3,3-dimethyl-1,2-dioxirane only the oxygen atom transfer, yielding the thione *S*-oxide, could be observed.

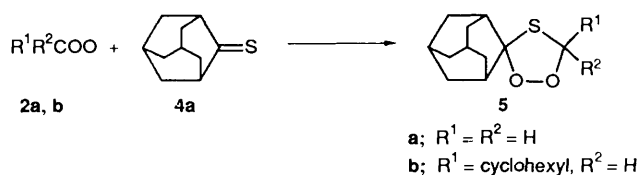
### Results and Discussion

A solution of vinyl ether **1a** (8 mol) and adamantane-2-thione **4a** (4 mmol) in ether or methylene dichloride (20 cm<sup>3</sup>) was treated with ozone (4 mmol) at –70 °C. The <sup>1</sup>H NMR spectra of the crude products showed the formation of the thioozonide **5a** in around 70% yield, suggesting that [3 + 2] cycloaddition of formaldehyde *O*-oxide **2a** with **4a** is a facile process (Schemes 1 and 2).<sup>5</sup> Compound **5a** was, however, labile on silica gel and



- a;** R<sup>1</sup> = R<sup>2</sup> = H, R<sup>3</sup> = CH<sub>2</sub>CHMe<sub>2</sub>  
**b;** R<sup>1</sup> = cyclohexyl, R<sup>2</sup> = H, R<sup>3</sup> = Me  
**c;** R<sup>1</sup> = Ph, R<sup>2</sup> = H, R<sup>3</sup> = Me  
**d;** R<sup>1</sup>, R<sup>2</sup> = –[CH<sub>2</sub>]<sub>5</sub>–, R<sup>3</sup> = Me

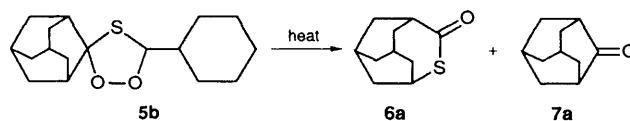
Scheme 1



Scheme 2

hence isolated in low yield (10–40%) by silica gel column chromatography, together with thioester **6a** (20–40%) and adamantanone **7a** (20–40%) (Table 1). It should be noted that, as judged from the <sup>1</sup>H and <sup>13</sup>C NMR spectra, the products **5a** and **6a** were isolated in fairly pure states; however, the analytical figures and/or the melting points clearly suggest that they contained small amounts of unidentified impurities. Also, the labile compounds **5b–c**, **6b–c** and **9**, mentioned later, could not be isolated in rigorously pure states (see Experimental section).

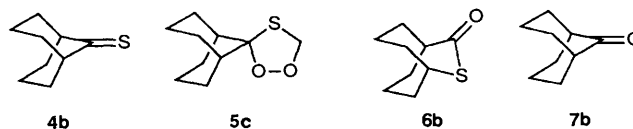
From the ozonolysis of a mixture of vinyl ethers **1b** and **4a**, the corresponding thioozonide **5b** was isolated in *ca.* 70% yield without significant decomposition during column chromatography. However, neat **5b** decomposed gradually even at 0 °C, giving unidentified high-melting-point materials; consequently, the correct melting point of **5b** was not determined (see Experimental Section). Consistent with the structure, the thermolysis of **5b** in refluxing *tert*-butylbenzene led to the formation of a mixture of **6a** (29%) and **7a** (69%), as expected (Scheme 3).



Scheme 3

Benzaldehyde *O*-oxide **2c**, derived by reaction of vinyl ether **1c** and ozone, however, did not provide the expected cycloadduct; the product consisted of a mixture of **7a** (85%) and benzaldehyde (60%). The ozonolysis of a mixture of vinyl ether **1d** and **4a** also resulted in the formation of a complex mixture of unidentified products. These results imply that the structure of carbonyl oxide is important for efficient cycloaddition to **4a**.

Bicyclo[3.3.1]nonan-9-thione **4b** could also be efficiently captured by formaldehyde *O*-oxide **2a**; the corresponding thioozonide **5c** was isolated in 30% yield. Thermolysis of **5c** in refluxing *tert*-butylbenzene gave a mixture of the thioester **6b** (31%) and the ketone **7b** (65%). In the case of cyclohexanecar-



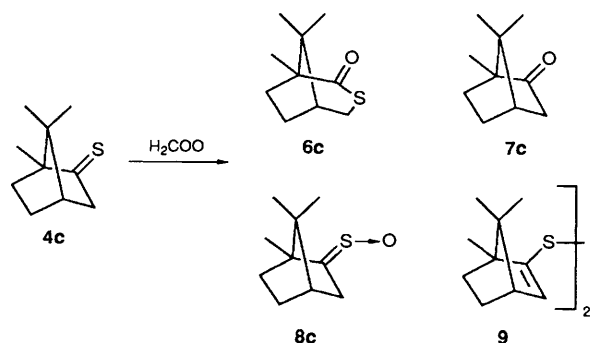
baldehyde *O*-oxide **2b**, the <sup>1</sup>H NMR spectra of the crude products showed that the expected thioozonide might be formed in around 50% yield [ $\delta$  5.22 (d, *J* 7 Hz)]. During column chromatography on silica gel, the compound having this signal decomposed and the ketone **7b** was isolated in 65%.

The ozonolysis of a mixture of **1a** and thiocamphor **4c** was more complex; the product consisted of a mixture of the thioester **6c** (26%), the ketone **7c** (10%), the sulfine **8c** (6%), and the disulfide **9** (24%) (Scheme 4 and Table 1). When the same reaction was repeated in methanol–ether, the starting material **4c** was recovered in 80% yield, together with the *S*-oxide **8c** (6%). As Zwanenburg and Janssen have already found,<sup>6</sup> the direct reaction of **4c** with ozone gives **8c** in excellent yield, while

**Table 1** Ozonolysis of a vinyl ether in the presence of a thioketone<sup>a</sup>

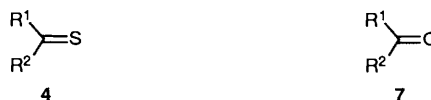
Thio-ketone	Vinyl ether	Solvent	Products (% yields) <sup>b</sup>	Recovered <b>4</b> (%)
<b>4a</b>	<b>1a</b>	CH <sub>2</sub> Cl <sub>2</sub>	<b>5a</b> 10, <b>6a</b> 40, <b>7a</b> 40 <sup>c</sup>	
<b>4a</b>	<b>1a</b>	ether	<b>5a</b> 40, <b>6a</b> 25, <b>7a</b> 25 <sup>c</sup>	
<b>4a</b>	<b>1b</b>	ether	<b>5b</b> 70	
<b>4a</b>	<b>1c</b>	ether	<b>7a</b> 85	
<b>4a<sup>d</sup></b>		ether	<b>7a</b> 90	
<b>4b</b>	<b>1a</b>	ether	<b>5c</b> 30, <b>7b</b> 40 <sup>c</sup>	23
<b>4b</b>	<b>1b</b>	ether	<b>7b</b> 65 <sup>c</sup>	21
<b>4c</b>	<b>1a</b>	ether	<b>6c</b> 26, <b>7c</b> 10, <b>8c</b> 6, <b>9</b> 24	29
<b>4c</b>	<b>1a</b>	ether-MeOH <sup>f</sup>	<b>8c</b> 6	80
<b>4c<sup>d</sup></b>		ether	<b>7c</b> 8, <b>8c</b> 76	
<b>4d</b>	<b>1a</b>	ether	<b>7d</b> 95	
<b>4d</b>	<b>1a</b>	ether-MeOH <sup>f</sup>		90
<b>4d<sup>d</sup></b>		ether	<b>7d</b> 100	
<b>4e</b>	<b>1a</b>	ether	<b>7e</b> 90	
<b>4e<sup>d</sup></b>		ether	<b>7e</b> 95	
<b>4f</b>	<b>1a</b>	CH <sub>2</sub> Cl <sub>2</sub>	<b>7f</b> 50, <b>8f</b> 15	
<b>4f</b>	<b>1b</b>	CH <sub>2</sub> Cl <sub>2</sub>	<b>7f</b> 77, <b>8f</b> 18	5
<b>4f</b>	<b>1c</b>	CH <sub>2</sub> Cl <sub>2</sub>	<b>7f</b> 75, <b>8f</b> 9	9
<b>4f</b>	<b>1d</b>	CH <sub>2</sub> Cl <sub>2</sub>	<b>7f</b> 37, <b>8f</b> 33	30
<b>4f</b>	<b>1d</b>	CH <sub>2</sub> Cl <sub>2</sub> -MeOH <sup>f</sup>	<b>7f</b> 80	
<b>4f<sup>d</sup></b>		CH <sub>2</sub> Cl <sub>2</sub>	<b>7f</b> 74	
<b>4g</b>	<b>1a</b>	CH <sub>2</sub> Cl <sub>2</sub>	<b>7g</b> 29	9
<b>4g</b>	<b>1d</b>	CH <sub>2</sub> Cl <sub>2</sub>	<b>7g</b> 46, <b>8g</b> 41	
<b>4g</b>	<b>1d</b>	CH <sub>2</sub> Cl <sub>2</sub> -MeOH <sup>f</sup>	<b>7g</b> 48, <b>8g</b> 19	33
<b>4g<sup>d</sup></b>		CH <sub>2</sub> Cl <sub>2</sub>	<b>7g</b> 71, <b>8g</b> 26	3
<b>4h</b>	<b>1a</b>	CH <sub>2</sub> Cl <sub>2</sub>	<b>7h</b> 50, <b>8h</b> 16	34
<b>4h</b>	<b>1c</b>	CH <sub>2</sub> Cl <sub>2</sub>	<b>7h</b> 50, <b>8h</b> 19	31
<b>4h</b>	<b>1d</b>	CH <sub>2</sub> Cl <sub>2</sub>	<b>7h</b> 36, <b>8h</b> 36	28
<b>4h</b>	<b>1d</b>	CH <sub>2</sub> Cl <sub>2</sub> -MeOH <sup>f</sup>	<b>7h</b> 69, <b>8h</b> 7	24
<b>4h<sup>d</sup></b>		CH <sub>2</sub> Cl <sub>2</sub>	<b>7h</b> 56, <b>8h</b> 24	19
<b>4i</b>	<b>1a</b>	CH <sub>2</sub> Cl <sub>2</sub>	<b>8i</b> 5	68
<b>4i</b>	<b>1b</b>	CH <sub>2</sub> Cl <sub>2</sub>		95
<b>4i</b>	<b>1c</b>	CH <sub>2</sub> Cl <sub>2</sub>	<b>8i</b> 12	74
<b>4i</b>	<b>1d</b>	CH <sub>2</sub> Cl <sub>2</sub>	<b>8i</b> 7	84
<b>4i</b>	<b>1c</b>	CH <sub>2</sub> Cl <sub>2</sub> -MeOH <sup>f</sup>	<b>8i</b> 6	74
<b>4i<sup>d</sup></b>		CH <sub>2</sub> Cl <sub>2</sub>	<b>8i</b> 71	14

<sup>a</sup> The reaction of a mixture of a vinyl ether (8 mmol) and a thioketone (4 mmol) with 4 mmol of ozone in an appropriate solvent (20 cm<sup>3</sup>) at -70 °C. <sup>b</sup> The isolated yield. <sup>c</sup> The <sup>1</sup>H NMR spectra of the crude products showed the formation of the corresponding thioozonide in ca. 70% yield. <sup>d</sup> The reaction of a thioketone with ozone at -70 °C. <sup>e</sup> The <sup>1</sup>H NMR spectra of the crude products suggested the formation of the expected thioozonide in around 50% yield; column chromatography on silica gel, however, resulted in the elution of a complex mixture of products containing **7b**. <sup>f</sup> The reaction in a mixed solvent system (20 cm<sup>3</sup>: 1:1 v/v).

**Scheme 4**

in the case of less bulky **4a**, the ketone **7a** was the sole product (Table 1). Although no direct evidence was obtained, the formation of **6c** would imply the production of the labile [3 + 2] cycloadduct between **2a** and **4c**.

The ozonolysis of a 2:1 mixture of **1a** and dicyclopropyl thioketone **4d** in ether yielded exclusively dicyclopropyl ketone **7d**. When the same reaction was undertaken in methanol-ether, however, thioketone **4d** was recovered almost quantitatively. This fact suggests that in the reaction in ether the carbonyl oxide



**d**; R<sup>1</sup> = R<sup>2</sup> = cyclopropyl

**e**; R<sup>1</sup> = cyclopropyl, R<sup>2</sup> = Ph

**f**; R<sup>1</sup> = R<sup>2</sup> = *p*-C<sub>6</sub>H<sub>4</sub>OMe

**g**; R<sup>1</sup> = R<sup>2</sup> = *p*-C<sub>6</sub>H<sub>4</sub>Me

**h**; R<sup>1</sup> = R<sup>2</sup> = Ph

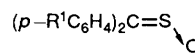
**d**; R<sup>1</sup> = R<sup>2</sup> = cyclopropyl

**e**; R<sup>1</sup> = cyclopropyl, R<sup>2</sup> = Ph

**f**; R<sup>1</sup> = R<sup>2</sup> = *p*-C<sub>6</sub>H<sub>4</sub>OMe

**g**; R<sup>1</sup> = R<sup>2</sup> = *p*-C<sub>6</sub>H<sub>4</sub>Me

**h**; R<sup>1</sup> = R<sup>2</sup> = Ph



**8**

**f**; R<sup>1</sup> = OMe

**g**; R<sup>1</sup> = Me

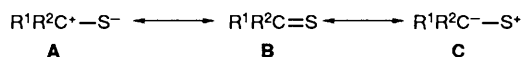
**h**; R<sup>1</sup> = H

**2a** certainly participates in the formation of the ketone **7d**; the [3 + 2] cycloadduct between **2a** and **4d** would be a probable precursor of **7d**. A similar trend was observed for phenyl cyclopropyl thioketone **4e**; the ketone **7e** was isolated quantitatively.

A remarkably different trend was observed for the reaction with thiobenzophenone derivatives **4f-h**. The reaction of a mixture of a vinyl ether **1a** (4 mmol) and 4,4'-dimethoxythiobenzophenone **4f** (2 mmol) with ozone (2 mmol) in methylene dichloride at -70 °C gave the corresponding *S*-oxide **8f** (33%), together with 4,4'-dimethoxybenzophenone **7f** (31%) and the unreacted thioketone (30%). Also, in the ozonolysis of a mixture of **1a-c** and **4f**, the thione *S*-oxide **8f** was obtained, albeit in a lower yield (ca. 15%), together with the ketone **7f** (ca. 60%) (Table 1). Thus, the most bulky cyclohexanone *O*-oxide **2d** was the most efficient oxygen-transfer agent. The same trends were observed for the ozonolysis of a mixture of vinyl ethers **1a, c, d** and thioketones **4g, h**.

When the reaction of a mixture of **1d** and **4f** with ozone was conducted in the 'participating' solvent system, methanol-methylene dichloride (1:1 v/v), the production of **8f** was completely suppressed. The crude products showed the characteristic purple colour of **4f**, but the sole isolated product by silica gel column chromatography was ketone **7f**. Probably, some unidentified impurities induced the decomposition of **4f** during the column chromatography.

The remarkable difference in behaviour between dialkyl-substituted thioketones **4a-c** and diaryl-substituted thioketones **4f-h** would be due to the substituent electronic effects on the structure of the resonance hybrid of these thioketones. Of the



three possible structures A-C, the contribution of structure A is important for **4a-c**, while in the case of **4f-h** structure C has the major contribution.<sup>7</sup> Thus, in the case of **4a-c**, which has a high dipolarophilicity, cycloaddition with the 1,3-dipole **2** is predominant, while in the case of **4f-h** the nucleophilic oxygen-transfer agent **2** attacks preferentially at the terminal sulphur atom.

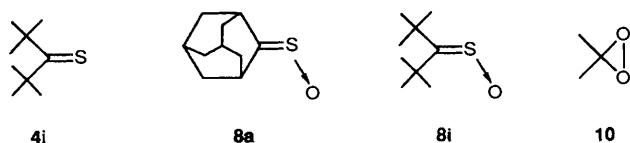
It is noteworthy that the reaction of bulky di-*tert*-butyl thioketone **4i** with ozone in methylene dichloride gave the thione *S*-oxide **8i** in 71% yield.<sup>8</sup> When this reaction was conducted in the presence of the vinyl ether **1a-d**, however, the formation of **8i** was significantly suppressed; **8i** was obtained in

**Table 2** Reaction of a thioketone with 3,3-dimethyl-1,2-dioxirane **10**<sup>a</sup> or oxone<sup>b</sup>

Reagent	Thio-ketone	Reaction time/h	Products (% yield)	Recovered <b>4</b> (%)
<b>10</b>	<b>4a</b>	4	<b>7a</b> 20, <b>8a</b> 29	33
<b>10</b>	<b>4f</b>	6	<b>8f</b> 97	
<b>10</b>	<b>4g</b>	2	<b>7g</b> 19, <b>8g</b> 79	
<b>10</b>	<b>4i</b>	72	<b>8i</b> 33	24
'oxone'	<b>4a</b>	24	<b>7a</b> 3	97
'oxone'	<b>4f</b>	4	<b>7f</b> 18, <b>8f</b> 10	69
'oxone'	<b>4g</b>	4	<b>7g</b> 17, <b>8g</b> 11	70
'oxone'	<b>4i</b>	48		100

<sup>a</sup> The reaction of a 1:2 mixture of a thioketone and the 1,2-dioxirane **10** in benzene-water in the presence of 18-crown-6 at room temperature.

<sup>b</sup> The reaction of a 1:2 mixture of a thioketone and 'oxone' (2KHSO<sub>5</sub>-KHSO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>) in benzene-water in the presence of 18-crown-6.



*ca.* 7% yield, together with the unchanged **4i** (*ca.* 80%). In the ozonolysis of a mixture of **1c** and **4i** in methanol-methylene dichloride, **8i** was isolated in 6% yield, suggesting that: (i), the reaction of ozone with the vinyl ether **1a-d** is significantly faster than that with **4i**; and (ii), the formation of small amounts of **8i** is probably the result of the direct attack of ozone on the thioketone **4i**.

3,3-Dimethyl-1,2-dioxirane **10**, generated *in situ* from the reaction of acetone and 'oxone' (2KHSO<sub>5</sub>-KHSO<sub>4</sub>-K<sub>2</sub>SO<sub>4</sub>), could transfer an oxygen atom to **4a**, **f**, **g**, **i** yielding the thione S-oxide **8a**, **f**, **g**, **i** (Table 2). The yields of **8f**, **g** were excellent, suggesting that this method would be useful for the preparation of thiobenzophenone derivatives. In contrast, in the case of bulky **4i** the reaction was very slow and, moreover, the yield of **8i** was poor. The oxygen-atom transfer from 'oxone' to thioketones **8a**, **f**, **g**, **i** did not occur efficiently (Table 2).

## Experimental

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained in CDCl<sub>3</sub> (unless otherwise noted) with JNM-PS-100 and JEOL-GSX-400 spectrometers, respectively. *J*-Values are given in Hz. Infrared spectra were obtained with a Hitachi 215 spectrometer. Thioketones **4a**, **b**,<sup>9</sup> **4c**, **d**,<sup>10</sup> **4f-h**,<sup>11</sup> and **4i**<sup>12</sup> were prepared by the reported methods.

**Ozonolysis of a Mixture of a Vinyl Ether and a Thioketone 4a, b.**—The ozonolysis of a mixture of a vinyl ether **1a** and adamantanethione **4a** is representative. To a solution of adamantanethione (4 mmol) and isobutyl vinyl ether (8 mmol) in methylene dichloride (20 cm<sup>3</sup>), was passed a slow stream of ozone (4 mmol) at -70 °C. After evaporation of the solvent under reduced pressure, the crude products were column chromatographed on silica gel. The first fraction (elution with benzene-hexane, 1:4) gave the thioozonide **5a**. From the second fraction (elution with benzene-ether 20:1), was obtained the thioester **6a**. The final fraction contained adamantanone **7a**. Compound **5a** had m.p. 48-52 °C (Found: C, 61.9; H, 7.55; S, 15.15. C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>S requires C, 62.27; H, 7.55; S, 15.09%); δ<sub>H</sub> 1.6-2.2 (14 H, m), 5.25 (2 H, s); δ<sub>C</sub> 26.03 (CH), 26.79 (CH), 34.33 (2 C, CH<sub>2</sub>), 37.12 (CH<sub>2</sub>), 37.37 (2 C, CH<sub>2</sub>), 38.85 (2 C, CH), 76.01 (CH<sub>2</sub>), 105.02.

Compound **5b** had m.p. 45-70 °C (Found: C, 69.65; H, 8.8; S, 11.45. C<sub>17</sub>H<sub>26</sub>O<sub>2</sub>S requires C, 69.40; H, 8.84; S, 10.88%); δ<sub>H</sub> 0.9-

2.3 (25 H, m), 5.29 (1 H, d, *J* 7.7); δ<sub>C</sub> 25.53, 25.80, 26.08, 26.20, 26.88, 29.83, 29.91, 34.07, 34.12, 36.64, 39.19, 95.35, 105.18.

Compound **5c** had m.p. 35-43 °C (Found: C, 59.65; H, 7.95; S, 16.3. C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>S requires C, 60.00; H, 8.00; S, 16.00%); δ<sub>H</sub> 1.3-2.7 (14 H, m), 5.18 (2 H, s); δ<sub>C</sub> 19.89, 20.73, 28.34 (2 C), 32.09 (2 C), 38.64 (2 C), 75.66, 104.80.

Compound **6a** had m.p. 170-180 °C (sublime) (Found: C, 65.75; H, 7.7; S, 17.45. C<sub>10</sub>H<sub>14</sub>OS requires C, 65.94; H, 7.69; S, 17.58%); δ<sub>H</sub> 1.7-2.4 (13 H, m), 2.9-3.2 (1 H, m); δ<sub>C</sub> 26.64 (2 C), 29.80 (2 C), 33.72, 37.02, 39.14 (2 C), 51.27, 211.29.

Compound **6b** had m.p. 90-100 °C (decomp.) (Found: C, 63.4; H, 8.3; S, 19.2. C<sub>9</sub>H<sub>14</sub>OS requires C, 63.53; H, 8.24; S, 18.82%); ν<sub>max</sub>/cm<sup>-1</sup> 2930, 2850, 1655, 1445, 1135, 1050, 885, 770 and 560.

**Ozonolysis of a Mixture of 1a and (1R)-(-)-Thiocamphor 4c.**—The ozonolysis of a 2:1 mixture of **1a** and **4c** was undertaken as described above. After evaporation of the solvent, the products were separated by column chromatography on silica gel. Elution with 1:50 ether-hexane gave **9**; m.p. 56-66 °C (Found: C, 71.95; H, 9.0; S, 19.7. C<sub>20</sub>H<sub>30</sub>S<sub>2</sub> requires C, 71.86; H, 8.98; S, 19.16%); δ<sub>H</sub> 0.6-2.9 (8 H, m), 0.77 (6 H, s), 0.81 (6 H, s), 1.08 (6 H, s), 2.42 (2 H, t, *J* 4.5), 6.00 (2 H, d, *J* 4.5); δ<sub>C</sub> 11.41, 19.43, 19.68, 25.88, 31.58, 52.25, 56.78, 57.22, 132.61, 141.63; *m/z* (CI; isobutane) 335 (M<sup>+</sup> + 1).

Elution with 3:97 ether-hexane gave **4c**. Elution with 1:20 ether-hexane gave camphor **7c**. Elution with 1:10 ether-hexane gave **6c**; m.p. 175-180 °C (Found: C, 65.7; H, 8.65; S, 16.95. C<sub>10</sub>H<sub>16</sub>OS requires C, 65.21; H, 8.70; S, 17.39%); δ<sub>H</sub> 0.7-3.2 (7 H, m), 1.05 (3 H, s), 1.26 (6 H, s); δ<sub>C</sub> 19.61, 20.41, 23.85, 27.33, 42.59, 44.02, 44.57, 48.81, 61.86, 203.38; ν<sub>max</sub>/cm<sup>-1</sup> 2950, 1665, 1450, 1100, 1015 and 605.

Elution with 1:1 ether-hexane gave **8c** as an oil; δ<sub>H</sub> 0.89 (3 H, s), 0.99 (3 H, s), 1.16 (3 H, s), 0.9-3.2 (7 H, m); ν<sub>max</sub>/cm<sup>-1</sup> 1055.<sup>13</sup>

4,4'-Dimethoxythiobenzophenone S-oxide **8f** had m.p. 84-85 °C; ν<sub>max</sub>/cm<sup>-1</sup> 1095 and 1010; δ<sub>H</sub> 3.87 (6 H, s), 6.8-8.0 (8 H, m).<sup>14</sup> 4,4'-Dimethylthiobenzophenone S-oxide **8g** had m.p. 89-91 °C; ν<sub>max</sub>/cm<sup>-1</sup> 1100 and 1010; δ<sub>H</sub> 2.39 (3 H, s), 2.42 (3 H, s), 7.2-7.9 (8 H, m).<sup>15</sup> Thiobenzophenone S-oxide **8h** had m.p. 30-32 °C; ν<sub>max</sub>/cm<sup>-1</sup> 1105 and 1005.<sup>14</sup> 2,2,4,4-Tetramethyl-3-pentanethione S-oxide **8i** was an oil; ν<sub>max</sub>/cm<sup>-1</sup> 1180 and 1080; δ<sub>H</sub>(CCl<sub>4</sub>) 1.37 (9 H, s), 1.54 (9 H, s).<sup>16</sup>

**Reaction of 3,3-Dimethyl-1,2-dioxirane and Adamantanethione.**—In a 200 cm<sup>3</sup> flask, equipped with a magnetic stirrer and maintained under nitrogen, was added a solution of adamantanethione (260 mg, 1.56 mmol) in benzene (10 cm<sup>3</sup>), acetone (1.5 cm<sup>3</sup>), and then a solution of KHCO<sub>3</sub> (1.32 g, 13.1 mmol) in water. Subsequently, 'oxone' (Aldrich, 1.56 mmol) dissolved in water (10 cm<sup>3</sup>) was added during 30 min and the reaction was continued at room temperature for a further 4 h. The products were extracted with ether, and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the crude products were column chromatographed on silica gel. First fraction (elution with benzene-hexane, 1:1) contained adamantanethione. From the second fraction (elution with ether-benzene, 1:20), was obtained adamantanone. From the final fraction (elution with ether-benzene 1:1), was obtained the S-oxide **8a**. Compound **8a** had m.p. 130 °C; δ<sub>H</sub>(CCl<sub>4</sub>) 2.00 (12 H, br s), 2.87 (1 H, br s), 4.02 (1 H, br s).<sup>17</sup>

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