

# Formation of thioketenes by thermal fragmentation of 1,2-dithiol-3-ones

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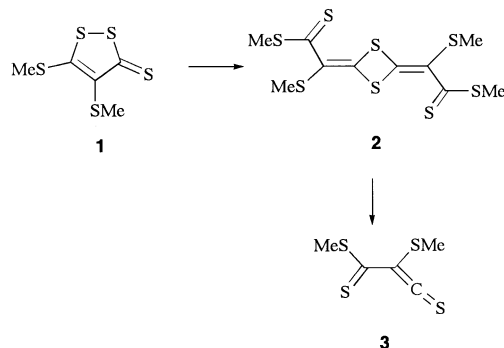
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Thioketenes **6** are formed in a Wolff-type rearrangement together with OCS by flash vacuum thermolysis (FVT) of 1,2-dithiol-3-ones **4** and identified by a combination of Ar matrix isolation FTIR spectroscopy and collisional activation mass spectrometry (CAMS). The thioketenes all have strong IR absorptions in the 1750 cm<sup>-1</sup> region ascribed to the C=C=S stretching vibration. The matrix IR and the CAMS of thioketenes **6a**, **6d** and **6e** are identical with those of authentic samples generated by FVT of 1,2,3-thiadiazoles **7a**, **7d** and 2,3-dihydrobenzothiophene-2,3-dione **9**, respectively. A competing fragmentation of the dithiolones leads to the corresponding acetylenes. CO and S<sub>2</sub> were also identified.

## Introduction

The generation of thioketenes from precursors such as 1,2,3-thiadiazoles and dithietanes has been described in the literature.<sup>1,2</sup> In previous work from these laboratories<sup>3,4</sup> we reported the first evidence for thioacylthioketenes **3**, obtained by flash vacuum thermolysis (FVT) of certain methylthio-substituted 1,3-dithietanes **2**. The 1,3-dithietanes can be considered as dimers of the thioacylthioketenes and are themselves formed by desulfuration of 1,2-dithiole-3-thiones **1**. The fate of the dithiol-



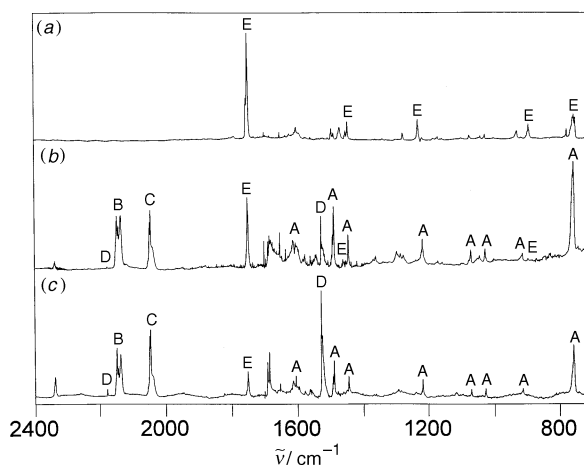
ethiones on thermolysis is more tenuous, largely because these compounds are very stable thermodynamically and therefore require extremely high temperatures for decomposition under FVT conditions.<sup>3</sup> An important side-reaction of several dithiolethiones is the formation of C<sub>3</sub>S<sub>2</sub>.<sup>3,4</sup> A further complication is the occurrence of a sulfur scrambling process in labelled 1,2-dithiole-3-thione in the condensed phase at 80–100 °C.<sup>5</sup>

In order to gain more insight into these thermal reactions, we have investigated a series of 1,2-dithiol-3-ones **4** and found that these undergo a major fragmentation to OCS and thioketenes **6**, assumed to take place *via* a Wolff-type rearrangement of carbene or diradical intermediates **5**. The results are reported herein.

## Results and discussion

### Thermolysis of the 1,2-dithiol-3-ones **4a–c** and 4-phenyl-1,2,3-thiadiazole **7a**

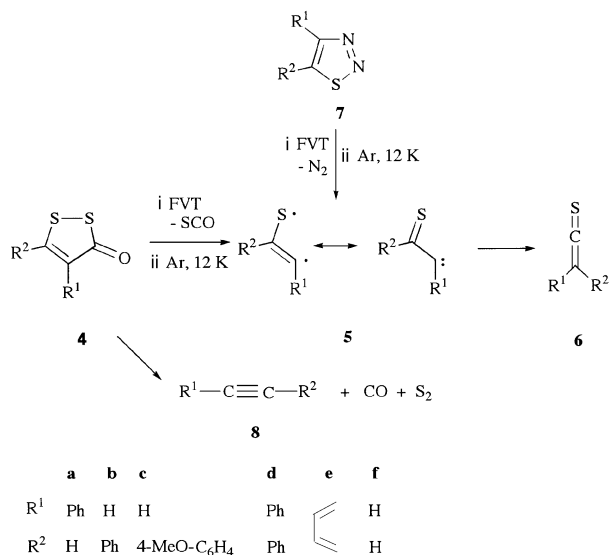
Compounds **4a** and **4b** give rise to practically identical IR



**Fig. 1** IR spectra (Ar matrix, 12 K; abscissa in wavenumbers) of the products of FVT of (a) **7a**, (b) **4a** and (c) **4b** at 980 °C. Bands due to (A) phenylacetylene **8a** (also absorbing at 3339 cm<sup>-1</sup>), (B) CO, (C) SCO (D) SCS and (E) phenylthioketene **6a** are labelled.

absorptions upon FVT at 980 °C, although **4a** decomposes more readily than **4b** and hence produces a stronger spectrum [Fig. 1(b) and 1(c)]. These IR spectra show bands at (ν̄/cm<sup>-1</sup>): 3339, 1606, 1490, 1445, 1218, 1071, 1028, 914 and 758 (phenylacetylene),<sup>6</sup> 2149 and 2138 (CO),<sup>7</sup> 2047 (SCO), 2178 and 1528 (CS<sub>2</sub>),<sup>6</sup> and 1751 (thioketene **6a**).

In order to identify the thioketene formed, it was desirable to generate an authentic sample from another precursor. Seybold and Heibl obtained phenylthioketene **6a** by FVT of 4-phenylthiadiazole **7a** and recorded a thioketene absorption at 1745 cm<sup>-1</sup> in trichlorofluoromethane solution.<sup>1</sup> Because the matrix effect on IR absorption maxima can be very significant, we submitted **7a** to FVT at 480 °C with Ar matrix isolation of the product at 12 K. The resulting IR spectrum [Fig. 1(a)] shows a very intense absorption at 1751 cm<sup>-1</sup>, identical with those obtained from the dithiolones **4a** and **4b**; other bands ascribable to thioketene **6a** are at 1451, 1232, 896 and 761 cm<sup>-1</sup>. Some of these minor peaks are also identifiable in the FVT spectrum from **4a** [Fig. 1(b)]. When **7a** is used as the precursor, there is practically no decomposition to phenylacetylene **8a**. As can be seen in [Fig. 1(b) and (c)], however, phenylacetylene is a very significant product from dithiolones **4a** and **4b**, and its



Scheme 1

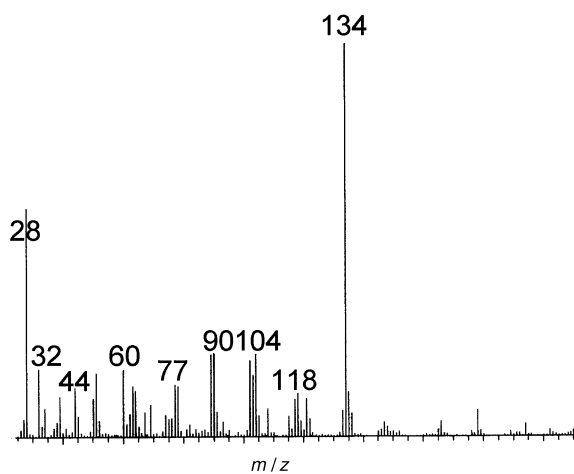


Fig. 2 FVT-EI-MS of **4a** at 760 °C ( $m/z$  134 = phenylthioketene **6a**)

formation commences before that of the thioketene **6a**. One of several possible routes to phenylacetylene would be a competing electrocyclic fragmentation of **4** to CO, S<sub>2</sub> and the alkyne (Scheme 1). S<sub>2</sub> is a short-lived intermediate,<sup>8</sup> not easily detectable by IR spectroscopy. We therefore investigated these reactions by online mass spectrometry in order to (i) confirm the formation of thioketenes, and (ii) detect possible disulfur production. A possible alternative source of the acetylene would be loss of sulfur atom, formation of a thioacylketene (not observed in any of the IR spectra in this work), ring closure to a thiet-2-one (also not observed) and elimination of OCS.<sup>9</sup>

FVT-MS of **4a** and **4b** was investigated between 500 and ca. 800 °C. No reaction took place below 500 °C. Again, **4a** decomposed more readily, giving a strong  $m/z$  134 ion at an FVT temperature of 760 °C, corresponding to thioketene **6a** (Fig. 2). In order to achieve a similar degree of decomposition of **4b**, it was necessary to pack the quartz FVT tube with a loose plug of quartz wool (see below).

In the normal EI-MS of **4a**,  $m/z$  134 is only a minor peak (12% of the base peak,  $m/z$  194), thus clearly demonstrating that the thioketene is a thermal product. However, the mass spectrometrically and thermally produced thioketene molecular ions give rise to identical CAMS. Furthermore, the CAMS of  $m/z$  134 from **4a** and **4b** are identical (Fig. 3), and an identical spectrum is also obtained on FVT-MS-CAMS of thiadiazole **7a** at 680 °C. The CAMS of  $m/z$  134 is dominated by losses of CS and CS plus H ( $m/z$  90 and 89).

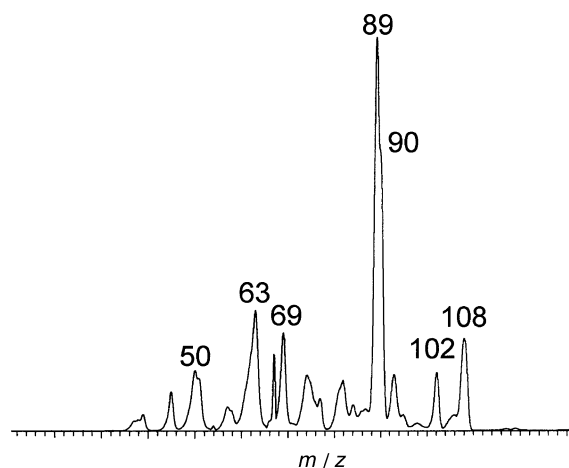


Fig. 3 CA(O<sub>2</sub>) mass spectrum of the  $m/z$  134 ion (phenylthioketene) from **4a** (obtained by FVT over quartz wool at 700 °C). Identical CAMS were obtained of the products of FVT of **4b** and **7a**.

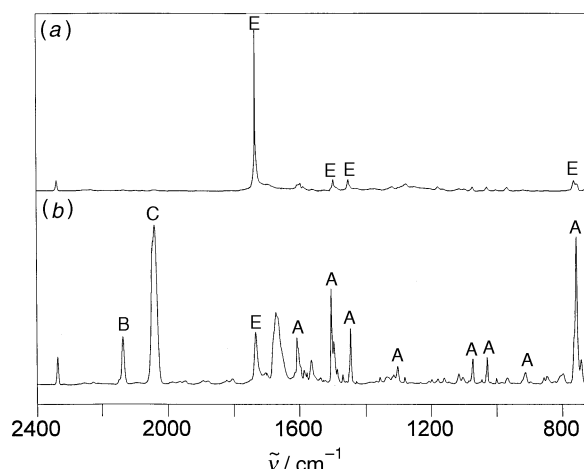


Fig. 4 IR spectra (Ar matrix, 12 K; abscissa in wavenumbers) of the products of FVT of (a) **7d** and (b) **4d**. Bands due to (A) diphenylacetylene **8d**, (B) CO, (C) SCO and (E) diphenylthioketene **6d** are labelled.

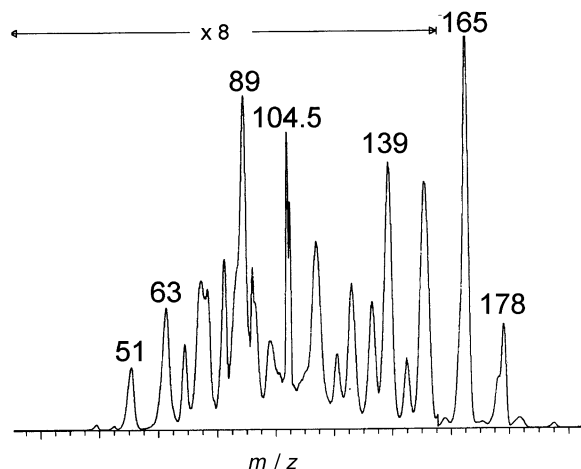
The mass spectra of **4a** and **4b** also permitted the detection of thermally produced S<sub>2</sub>: the peak at  $m/z$  64 (S<sub>2</sub>) increased markedly in intensity with the temperature. This effect was more clearly observed with the unsubstituted compound **4e** (see below). The fragmentation to phenylacetylene was negligible in the normal FVT of **4a**, but became the dominant process on FVT over quartz wool for both **4a** and **4b**. The identity of phenylacetylene was ascertained by comparison of its CAMS with that of an authentic sample.

The *p*-methoxy analogue **4c** was examined cursorily. FVT under the same conditions as used for **4b** gave rise to an absorption at 1751 cm<sup>-1</sup> in the IR spectrum (Ar, 12 K), ascribed to **6c** in analogy with **6a** and **b**.

#### Thermolysis of 4,5-diphenyl-1,2-dithiol-3-one **4d** and 4,5-diphenyl-1,2,3-thiadiazole **7d**

Compound **4d** is very stable thermally and was therefore subjected to FVT over quartz wool at 800 °C. The resulting IR spectrum [Fig. 4(b)] shows formation of diphenylthioketene **6d** (1734 cm<sup>-1</sup>) together with diphenylacetylene<sup>6</sup> **8d** (1607, 1504, 1446, 1073, 1030, 914 and 757 cm<sup>-1</sup>), CO (2139 cm<sup>-1</sup>) and SCO (2047 cm<sup>-1</sup>). The identity of thioketene **6d** was established by FVT of **7d** at 550 °C [Fig. 4(a)]. The thioketene absorbs at 1734 (vs), 1495, 1450 and 764 cm<sup>-1</sup>.

FVT-MS confirmed the identity of thioketene **6d** from the two sources. The intensity of the peak at  $m/z$  210 (**6d**) in the EI-MS of **4d** increased from 5% at 200 °C to 42% at 760 °C. Moreover, the CAMS of this  $m/z$  210 derived from FVT-MS-

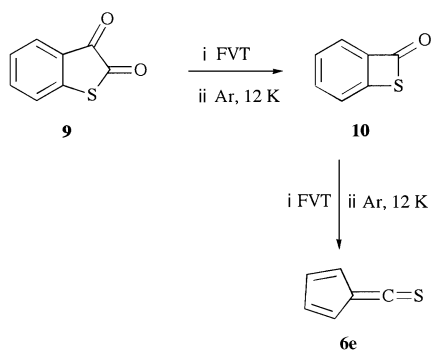


**Fig. 5** CA(O<sub>2</sub>) mass spectrum of *m/z* 210 (diphenylthioetene **6d**), produced by FVT of **4d** over quartz wool at 600 °C. An identical spectrum was obtained from **7d** at 600 °C.

MS of **4d** and **7d** (600 °C) were identical (Fig. 5). The major peak in the CAMS at *m/z* 165 is undoubtedly due to the fluorenyl cation C<sub>13</sub>H<sub>9</sub><sup>+</sup> (*cf.* ref. 10).

#### Thermolysis of benzo-1,2-dithiol-3-one **4e** and benzothiophene 2,3-dione **9**

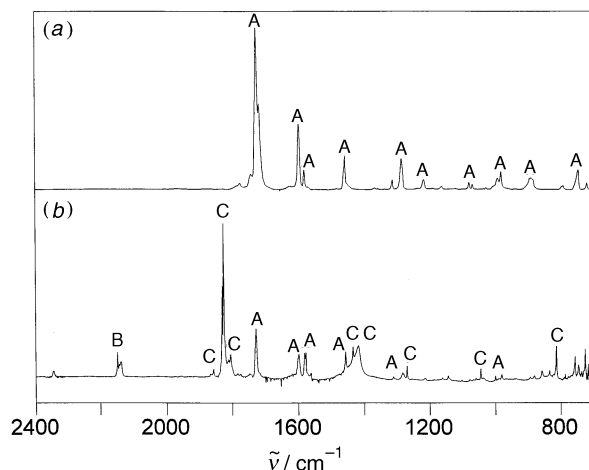
Compound **4e** was again very stable thermally and when subjected to FVT at 1030 °C produced a thioetene absorbing at 1757, 1447, 1368 and 870 cm<sup>-1</sup> which we ascribe to the cyclopentadienoid thioetene **6e**. The matrix isolation of this compound has been mentioned in the literature before,<sup>11</sup> but no spectroscopic data was given. Seybold and Heibl were unable to detect this thioetene spectroscopically because it decomposed above -120 °C.<sup>1</sup> We have generated the same compound previously by FVT of 2,3-dihydrobenzothiophene-2,3-dione **9** which reacts *via* benzothietan-2-one **10**.<sup>9</sup> However, this earlier work used neat isolation of the materials at liquid nitrogen temperature, and the IR data are not compatible with Ar matrix values. We therefore repeated the FVT of **5** with Ar matrix isolation of **10** and **6e** (Scheme 2 and Figs. 6 and 7). The start-



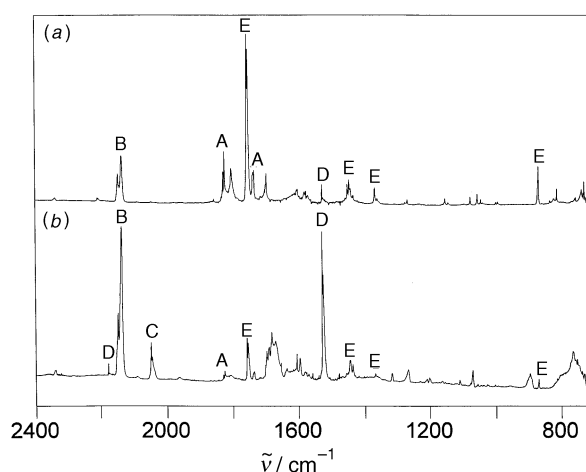
**Scheme 2**

ing material **9** has IR absorptions at 1727, 1596, 1580, 1456, 1313, 1283, 1218, 1079, 1069, 980, 889 and 746 cm<sup>-1</sup> in the matrix. Benzothietan-2-one **10**, obtained at 625 °C, shows bands at 1857, 1826, 1806, 1436, 1418, 1269, 1045 and 813 cm<sup>-1</sup>. Further FVT of **9** above 800 °C produces the thioetene **6e** with the same four major IR absorptions [Fig. 7(a)] as obtained from **4e** [Fig. 7(b)].

For further proof, identical CAMS of **6e** (*m/z* 108) were obtained on FVT-MS-MS of **4e** and **9** (Fig. 8). The results clearly establish the identity of thioetene **6e** and demonstrate the stepwise thermal elimination of CO from **9**. The relative



**Fig. 6** IR spectra (Ar matrix, 12 K; abscissa in wavenumbers) of (a) benzothiophene-2,3-dione **9** and (b) the product of FVT at 625 °C (benzothietan-2-one **10**). Bands due to (A) **9**, (B) CO and (C) **10** are labelled.



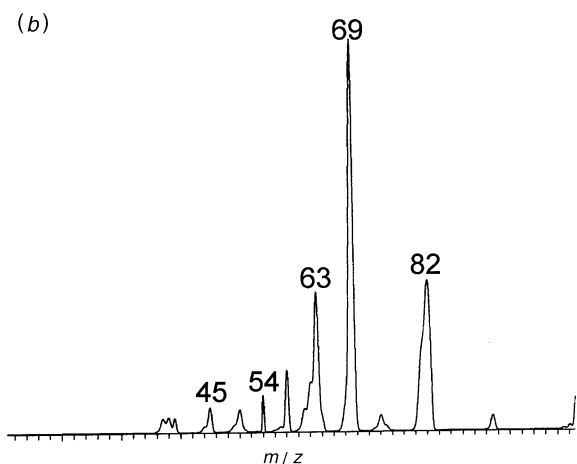
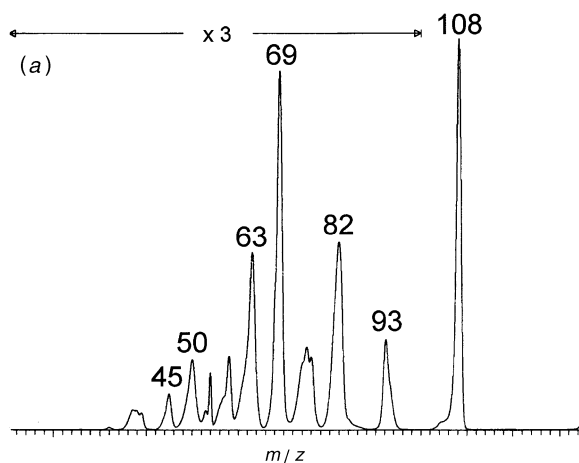
**Fig. 7** IR spectra (Ar matrix, 12 K; abscissa in wavenumbers) of the FVT products of (a) **9** at 980 °C and (b) **4e** at 1030 °C. Bands due to (A) SCO, (B) CO, (C) benzothietan-2-one **10**, (D) SCS and (E) thioetene **6e** are labelled.

intensities of ions at *m/z* 164 (**9**), 136 (**10**) and 108 (**6e**) changed as follows as a function of FVT temperature: at 200 °C: 7, 100 and 55%; at 750 °C: 0, 100 and 87%; at 750 °C over quartz wool: 0, 36 and 100%, respectively.

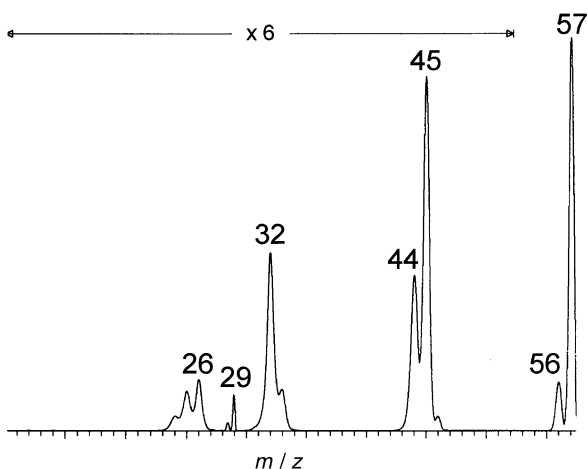
The CAMS of *m/z* 136 and 108 remained unchanged during the thermolysis, indicating that the same ions are produced on dissociative ionisation of **9** and by FVT followed by ionisation. In the FVT-MS of **4e**, the intensity of the *m/z* 108 species rose from 4% at 200 °C to 20% at 750 °C over quartz. Here, a competing elimination of CO was observed, giving rise to a strong signal at *m/z* 140, presumably corresponding to dithiobenzo-1,2-quinone. The main fragmentation of this latter species on CAMS is loss of CS (44 Da) to give *m/z* 96. As expected, there is little evidence for fragmentation of **4e** to benzyne **8e** (isobaric with CS<sub>2</sub>, which is always present) and S<sub>2</sub> in this case. The CAMS of **10** and **6e** are illustrated in Fig. 8.

#### Thermolysis of 1,2-dithiol-3-one **4f**

The parent compound **4f** was submitted to FVT at 800 °C with Ar matrix isolation at 12 K. The following IR absorptions can be ascribed to thioetene **6f** by comparison with the spectrum reported by Krantz and Laurenzi:<sup>12</sup> (ν/cm<sup>-1</sup>) 3012 (m), 1838 (m), 1754 (vs) and 1323 (m). Moreover, the FVT-MS-MS again verified the formation of the thioetene (*m/z* 58) concerted with formation of OCS (*m/z* 60). Another pathway giving ethyne **8f** (and S<sub>2</sub>) was also evident, and significant amounts of CS<sub>2</sub> were



**Fig. 8** CA(O<sub>2</sub>) mass spectra of (a) benzothietan-2-one **10** (*m/z* 136) obtained by FVT of **9**; (b) thioketene **6e** (*m/z* 108), obtained by FVT of **9** over quartz wool at 700 °C



**Fig. 9** CA(O<sub>2</sub>) mass spectrum of unsubstituted thioketene **6f** (*m/z* 58), produced by FVT of **4f** over quartz wool at 700 °C

formed as well. The relative intensities of the peaks at *m/z* 118, 64 and 60 (**4f**, S<sub>2</sub> and OCS) changed from 100:40:3 at 200 °C to 100:62:24 at 700 °C (FVT over quartz wool). The CAMS of **6f** is shown in Fig. 9.

### Conclusions

It has been established that 1,2-dithiol-3-ones **4** give simple thioketenes **6** upon FVT. The dithiolones are very stable thermally and therefore require very high FVT temperatures. The thioketenes were rigorously identified by comparison of Ar matrix IR as well as collision-activation mass spectra with those

of authentic compounds prepared from precursors **7** or **9**. Thioketene formation from **4** is accompanied by fragmentation to OCS. In all cases, there is a significant second, thermal pathway leading to the corresponding alkyne **8**. It appears that alkyne formation starts at lower temperatures than thioketene formation. Since CO and S<sub>2</sub> are also detected, it seems likely that an electrocyclic fragmentation of **4** to alkyne, CO and S<sub>2</sub> competes with fragmentation to OCS and thioacylcarbenes **5**, the latter being the precursors of thioketenes **6**.

### Experimental

#### General details

The FVT-IR and Ar matrix isolation apparatus employing a quartz thermolysis tube (10 cm length, 8 mm internal diameter) has been described earlier.<sup>13</sup> KBr or BaF<sub>2</sub> optics were used. The FVT-MS equipment, based on a six-sector Micromass (VG) AutoSpec 6F tandem mass spectrometer fitted with a quartz thermolysis tube (5 cm length, 3 mm diameter) directly in the source housing was as previously described.<sup>4a,14</sup> Owing to differences in design, the temperatures used in IR and MS experiments should not be directly compared. In FVT experiments over quartz wool, a loose plug of quartz wool was inserted in the centre of the quartz thermolysis tube in order to increase contact times and hence the efficiency of decomposition. Collisional activation (CA) was carried out with oxygen (80% transmittance). The resulting spectra are referred to as CA(O<sub>2</sub>) spectra.

#### Materials

4-Phenyl-1,2-dithiol-3-one **4a**,<sup>15</sup> 5-phenyl-1,2-dithiol-3-one **4b** and the *p*-methoxy analogue **4c**,<sup>15</sup> 4,5-diphenyl-1,2-dithiol-3-one **4d**,<sup>15</sup> benzo-1,2-dithiol-3-one **4e**,<sup>15</sup> 1,2-dithiol-3-one **4f**,<sup>16</sup> 4-phenyl-1,2,3-thiadiazole **7a**,<sup>17</sup> 4,5-diphenyl-1,2,3-thiadiazole **7d**<sup>18</sup> and 2,3-dihydrobenzothiophene-2,3-dione **9**<sup>9</sup> were prepared according to literature procedures.

**FVT-matrix isolation of 4-phenyl-1,2-dithiol-3-one 4a.** Approximately 50 mg of **4a** were placed in the sublimation zone of the quartz thermolysis tube. After evacuating the oven to  $3 \times 10^{-4}$  mbar, the cryostat was turned on and the pressure brought to  $2 \times 10^{-5}$  mbar while the KBr window reached a temperature of 12 K. **4a** was sublimed at 55 °C through the FVT tube at 970 °C and the products co-deposited with Ar on the KBr window at a rate of 10 mbar min<sup>-1</sup>.

**FVT-matrix isolation of 5-phenyl-1,2-dithiol-3-one 4b** and the *p*-methoxy analogue **4c** was carried out in a manner analogous to that described for **4a** using a sublimation temperature of 52 °C and an FVT temperature of 990 °C.

**FVT-matrix isolation of 4-phenyl-1,2,3-thiadiazole 7a.** This was carried out in a manner analogous to that described for **4a** at a sublimation temperature of 22 °C and an FVT temperature of 480 °C.

**FVT-matrix isolation of 4,5-diphenyl-1,2-dithiol-3-one 4d.** FVT-matrix isolation was carried out in a manner analogous to that described for **4a**, but with a plug of quartz wool in the thermolysis tube. It was sublimed at 85 °C and a pyrolysed at 800 °C.

**FVT-matrix isolation of 4,5-diphenyl-1,2,3-thiadiazole 7d.** This was carried out in a manner analogous to that described for **4a** at a sublimation temperature of 80 °C and an FVT temperature of 550 °C.

**FVT-matrix isolation of benzo-1,2-dithiol-3-one 4e.** FVT-matrix isolation was carried out in a manner analogous to that described for **4a** at a sublimation temperature of 22 °C and an FVT temperature of 1030 °C.

**FVT-matrix isolation of 2,3-dihydrobenzothiophene-2,3-dione 9.** This compound was deposited with Ar using a sublimation temperature at 30 °C; the remainder of the deposition system was kept at 320 °C in order to prevent condensation of **9**. An Ar matrix of benzothietan-2-one **10** was obtained by FVT of **9** at

625 °C. An Ar matrix of **6e** was obtained by FVT of **9** at 980 °C.

**FVT-matrix isolation of 1,2-dithiol-3-one 4f.** This compound is a liquid; it was vapourised at 36 °C and subjected to FVT at 980 °C.

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