The thermal fragmentation of 1,6-dioxa-6aλ^4-thiapentalenes: formation of acylthioketenes and thioacylketenes †

PERKIN 2

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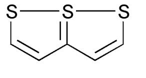
Received (in Cambridge, UK) 14th May 2001, Accepted 16th August 2001
First published as an Advance Article on the web 4th October 2001

Formylthioketene (**4a**) was observed in the flash vacuum pyrolysis of 1,6-dioxa-6aλ^4-thiapentalene (**2a**) ‡ and identified by a combination of Ar matrix isolation IR spectroscopy and on-line collisional activation mass spectrometry. Bands due to both the s-*Z* and s-*E* conformers could be observed in the IR spectra. Rearrangement of **4a** to thioformylketene (**8a**) was observed at 900 °C. s-*Z*-Benzoylthioketene (**4b**) as well as thiobenzoylketene (**8b**) could be observed in the pyrolysis of 2-phenyl-1,6-dioxa-6aλ^4-thiapentalene (**2b**); in this case only the s-*Z* thioketene could be observed directly in the IR of the pyrolysis products. The final pyrolysis products SCO and phenylacetylene could also be observed. In the MS experiment, both benzoylthioketene and its rearrangement product thiobenzoylketene could be unambiguously identified. In both cases, a competing fragmentation leading to furan and thiophene derivatives was observed, and in the case of **2b**, 5-phenylfuran-3-thione was identified. The observed interconversion of acylthioketenes and thioacylketenes and the identification of the IR spectra of **4a** and **8a** were supported by *ab initio* calculations.

Introduction

We have recently studied the thermal fragmentation upon flash vacuum pyrolysis FVP of 1,6,6aλ^4-trithiapentalenes **1**[1] and observed that the principal fragmentation was the loss of CS followed by a rearrangement of the 3-methylene-1,2-dithiole to form a thiophene derivative. We have now studied the thermal fragmentation of 1,6-dioxa-6aλ^4-thiapentalenes **2**, which are the dioxa-analogues of 1,6,6aλ^4-trithiapentalenes[2] in order to determine whether the fragmentation patterns observed for the trithiapentalenes were of a more general nature for other trichalcogenapentalenes which have been a group of compounds of great interest for a long time.[2–4] The fragmentation should then result in the formation of analogues of thiophene with other chalcogens as the heteroatom. Both **1** and **2** are considered to be aromatic 10π-electron systems.[3,4] We have therefore studied the fragmentation of the parent compound **2a** and the 2-monophenyl substituted compound **2b** using a combination of FVP matrix isolation FTIR spectroscopy and FVP combined with tandem mass spectrometry.



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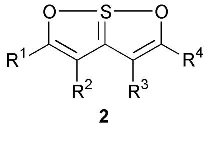

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2a $R^1 = R^2 = R^3 = R^4 = H$

2b $R^1 = R^2 = R^3 = H$, $R^4 = Ph$

Results and discussion

Molecular orbital calculations

Geometry optimization of acylthioketenes **4**, thioacylketenes **8** (Scheme 1), and related isomers and transition states (**a** = H, and **b** = C_6H_5) were calculated using density functional theory at the B3LYP/6-31G* level,[5] using the Gaussian98 suite of programs.[6] To assist the experimental characterization of acylthioketenes and thioacylketenes, harmonic vibrational frequencies and infrared intensities were calculated at the same level of theory. The directly calculated frequencies were scaled by a factor of 0.9613[7] to account for the overestimation of vibrational frequencies at the B3LYP/6-31G* level. Improved relative energies were obtained through B3LYP/6-311+G** calculations, including B3LYP/6-31G* zero-point energy corrections (scaled by 0.9804).[7] For the parent system, the reaction profile was also examined at high-level G3(MP2) theory.[8] Unless otherwise noted, the relative energies in the text correspond to the B3LYP/6-311+G**//B3LYP/6-31G*+ZPVE level.

First, we examine the structures and energies of the parent compounds, formylthioketene (**4a**) and thioformylketene (**8a**). There are two possible conformations of **4a** and **8a**: s-*E* and s-*Z*. The descriptors s-*E* and s-*Z* are used to describe the conformers as the use of s-*cis* and s-*trans* would not be unambiguous in this case. In both cases, the s-*E* conformation is the preferred structure (Scheme 1). Thioformylketene is predicted to be more stable than formylthioketene by 22 kJ mol^{-1} (19 kJ mol^{-1} at the G3(MP2) level). As with α-oxoketenes,[9] imidoylketenes,[10] and vinylketenes,[11] acylthioketenes are expected to undergo 1,3-migration, which should be particularly facile for migrating groups with an unshared pair of electrons (*e.g.* NH_2, OH, SH, OCH_3 and $N(CH_3)_2$). The 1,3-H shift in formylthioketene, *via* a four-centre transition state **11**, is predicted to have a moderate barrier of 137 kJ mol^{-1} (146 kJ mol^{-1} at the G3(MP2) level), comparable to that in α-oxoketene (142 kJ mol^{-1}).[9b] Thus, one would expect to see the interconversion of **4a** to **8a** at high-temperature in the FVP experiment. Indeed, thioformylketene was observed at 900 °C (Fig. 1), with characteristic IR absorptions in good agreement with theory. The calculated infrared spectra of **4a** and **8a** are given in Table 1. For formylthioketene **4a**, the calculated key IR absorptions of both conformers (Table 1) were readily observed in the experimental spectra at 600 and 900 °C (Fig. 1). It is important to note that the calculated C=C=S stretching frequencies in

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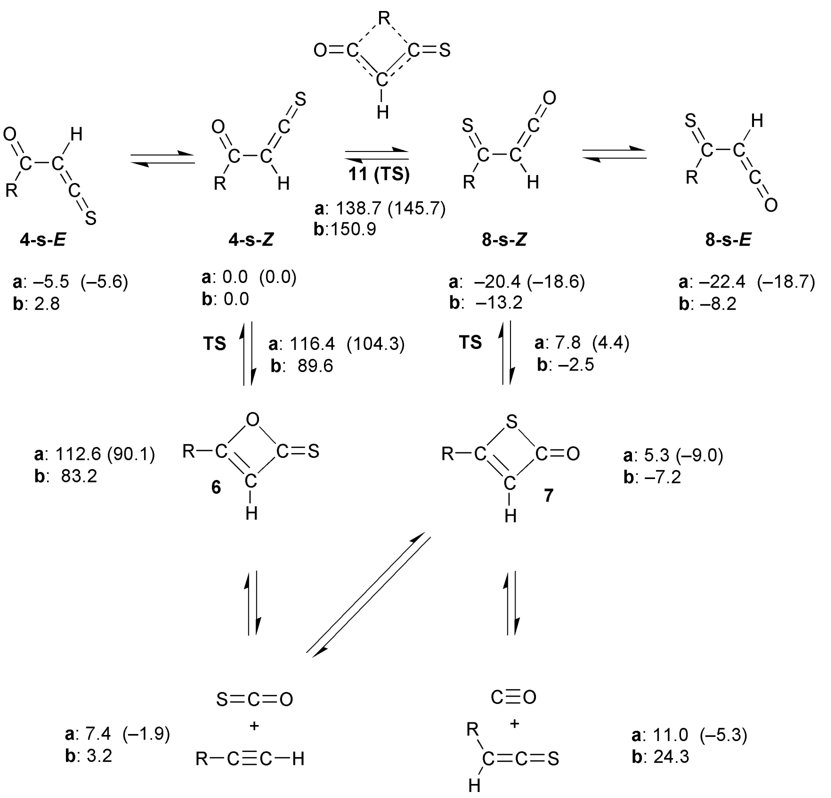
† Electronic supplementary information (ESI) available: calculated B3LYP/6-31G* IR spectra of **4b**, **7b**, **8b** and **10**. See http://www.rsc.org/suppdata/p2/b1/b104186j/

‡ The IUPAC name for this compound is 7λ^4-[1,2]oxathiolo[2,3-*b*]-oxathiole.

DOI: 10.1039/b104186j



Scheme 1 Calculated relative energies (kJ mol^{-1}) at the B3LYP/6-311+G**//B3LYP/6-31G* + ZPE level (**a**: R = H and **b**: R = C_6H_5). Numbers in parentheses correspond to the G3(MP2) values.

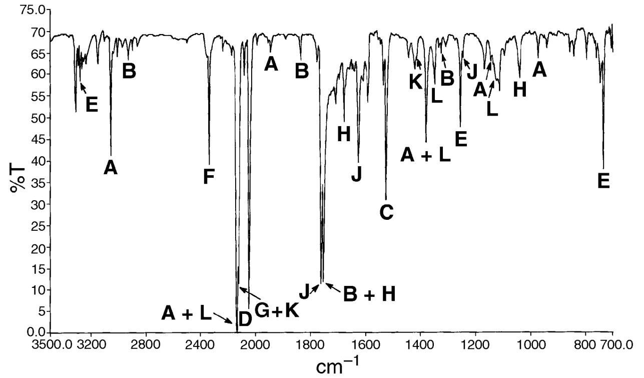


Fig. 1 IR spectrum (10 K, Ar matrix, cm^{-1}) of the pyrolysis products of compound **2a** (900 °C, 10^{-5} mbar). No significant peaks are present above 3500. Bands due to CH_2=C=O (A) at 3061, 2141, 1944, 1379, 1114, and 973; CH_2=C=S (B) at 2933, 1837, 1753 and 1335; CS_2 (C) at 1527, SCO (D) at 2048; C_2H_2 (E) at 3286 and 736; CO_2 (F) at 2344; HC(=O)–CH=C=S (s-*E*) (H) at 1753, 1679 and 1041, HC(=O)–CH=C=S (s-*Z*) (J) at 1762, 1627 and 1256; CO (G) at 2138; HC(=S)–CH=C=O (s-*E*) (K) at 2127, 1413 and 1145, HC(=S)–CH=C=O (s-*Z*) (L) at 2141, 1380, 1349 and 1127.

thioketene and formylthioketene are very close. Thus, the observed band at 1753 cm^{-1} corresponds to both compounds. We have also examined the stability of the related cyclic isomers. Oxete-2-thione (**6a**) is a high energy isomer, 113 kJ mol^{-1} above s-*Z*-**4a**. On the other hand, thiet-2-one **7a** lies close in energy, 8 kJ mol^{-1}, above **4a**. Ring opening of **7a**, to form s-*Z*-thioformylketene (s-*Z*-**8a**), requires a small activation barrier of just 3 kJ mol^{-1}. Hence, it is unlikely that this four-membered ring compound would be observable, in distinct contrast to the stable 3-arylthiet-2-ones.[15]

In contrast to the parent analogues, the phenyl substituted acylthioketene and thioacylketene, namely **4b** and **8b**, favour the s-*Z* conformation because of steric repulsion between the phenyl group and the ketene moiety. Structure **8b** is more stable than **4b** by 13 kJ mol^{-1}. A 1,3-phenyl shift in **4b** is predicted to have a moderate energy barrier of 151 kJ mol^{-1}, similar to that of a 1,3-H shift. Thus, one would also expect the rearrangement of **4b** to **8b** at high-temperature in the FVP experiment. This calculated result is in excellent accord with observation for both **4b** and **8b** in the MS experiment at 900 °C. The calculated vibrational frequencies of the s-*Z* conformation of **4b** agree well with the observed wavenumbers (see Fig. 3). A recent theoretical study has shown that the four-membered ring thiet-2-one (**7b**) is slightly more stable than the open form thioacylketene (s-*Z*-**8b**) by 1 kJ mol^{-1} at QCISD(T)/6-311+G-(3df,2p) level and the polar cyclic species is strongly stabilized in the presence of a dielectric medium.[15] Structure **7b** was observed in an Ar matrix by Wentrup *et al.* at 1827, 1528 and 741 cm^{-1}.[15] Our Ar matrix experiment above 750 °C also shows an absorption peak at 1833 cm^{-1} (see Fig. 3c), which corresponds to **7b**. Since ring opening of **7b** requires a small barrier of just 5 kJ mol^{-1}, it is unlikely that s-*Z*-**8b** and **7b** could coexist. Thus, the interconversion of **4b** and **8b** is also established in the matrix isolation experiment.

For a migrating group with a lone pair of electrons, the four-center transition structure is stabilized by the donor–acceptor interaction between the ion pair of electrons of the migrating donor substituent and the vacant central carbon p orbital of the ketene LUMO.[9b,10b,11a] For instance, 1,3-migration of an amino group (R = NH_2) in acylthioketene is predicted to have an energy barrier of 89 kJ mol^{-1}, significantly smaller than those of 1,3-H and 1,3-phenyl shifts. In sharp contrast, a 1,3-methyl shift is calculated to have a substantial activation barrier of 215 kJ mol^{-1}. This high barrier may be attributed to the fact that a pentacoordinated carbon is required in the four-center transition structure.

Experimental results

Flash-vacuum pyrolysis of 1,6-dioxa-6aλ⁴-thiapentalene (2a). The matrix IR spectrum of the pyrolysis products obtained from **2a** is shown in Fig. 1. A dominant absorption is at 2141 cm^{-1} both at 700 and 900 °C, corresponding to the strongest absorption band of the ketene. A series of weaker bands of ketene are also observed.[12]

Table 1 Calculated (B3LYP/6-31G*) frequencies and infrared intensities for **4a** and **8a**[a,b]

s-*E*-**4a**		s-*Z*-**4a**		s-*E*-**8a**		s-*Z*-**8a**	
Calc	Expt	Calc	Expt	Calc	Expt	Calc	Expt
3071 (11)		3068 (4)		3090 (13)		3076 (6)	
2841 (85)		2827 (160)		2983 (16)		2994 (25)	
1753 (100)	1753	1770 (260)	1762	2134 (1173)	2127	2142 (790)	2141
1692 (1029)	1679	1664 (802)	1627	1412 (244)	1413	1375 (80)	1380
1386 (5)		1381 (20)		1254 (31)		1350 (158)	1349
1184 (2)		1248 (82)	1256	1135 (126)	1145	1133 (65)	1127
1059 (176)	1041	990 (41)		1077 (46)		1043 (33)	
962 (2)		964 (3)		973 (28)		871 (6)	
878 (47)		824 (12)		860 (16)		835 (3)	
662 (40)		682 (78)		671 (40)		676 (10)	
507 (28)		603 (30)		573 (5)		591 (76)	
452 (16)		447 (1)		511 (15)		530 (0)	
436 (2)		393 (1)		347 (3)		342 (7)	
133 (7)		187 (9)		147 (7)		212 (0)	
133 (3)		107 (2)		125 (3)		119 (1)	

[a] Frequency in cm^{-1} and intensity (given in parentheses) in km mol^{-1}. [b] Calculated frequencies were scaled by 0.9613 (Ref. 13).

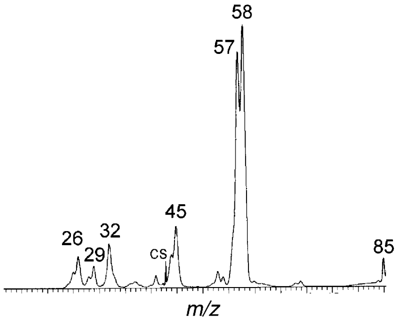


Fig. 2 CA (He) spectrum of the *m*/*z* 86 ions produced by ionization of the pyrolysate of **2a** after flash-vacuum pyrolysis at 750 °C. CS refers to charge stripping.

The formation of ketene may be rationalized as shown in Scheme 2 (pathway 3). By ring-opening of the remaining 1,2-oxathiole part following pathway 3, formylthioketene (**4a**) should be formed. Indeed, both the s-*E* (at 1753, 1679 and 1041 cm^{-1}) and the s-*Z* (at 1762, 1627 and 1256 cm^{-1}) conformations are observed. The observed wavenumbers are in excellent agreement with the calculated values (see Molecular orbital calculations section). Thioketene **12a** also shows its strongest absorption at 1753 cm^{-1}, but **12a** can be identified unambiguously by its weaker signals at 3011 cm^{-1} and 1837 cm^{-1} in the IR spectrum at 900 °C. At 600 °C, the 1753 cm^{-1} peak is absent.

At 600 °C, the intensity ratio $A_{1762} : A_{1679}$ is 5.1, and at 900 °C, the ratio is decreased to 3.0 which is in accordance with the fact that the s-*E* conformer should be slightly more stable than the s-*Z* form.

In close analogy with the fragmentation of acyl- and thioacylketenes[13] and thioacylthioketenes,[14] formylthioketene (**4a**) gives rise to acetylene and SCO *via* oxete-2-thione (**6a**); peaks associated with SCO and acetylene are observed in the IR spectrum at 2048 cm^{-1} and at 736 cm^{-1} and 3286 cm^{-1}, respectively, in accordance with pathway 3 suggested in Scheme 2.

It has been shown[15] that acylthioketenes **4** at higher temperatures rearrange to thioacylketenes **8**. For **4a**, rearrangement to **8a**, *via* a 1,3-H shift, is observed at 900 °C. Both the s-*E* and s-*Z* forms of **8a** are readily seen in the IR spectrum (Fig. 1). Compounds **4a** and **8a** could dissociate either to SCO and acetylene or to thioketene **12a** and CO (Scheme 2). All four fragments are observed in the IR-matrix spectrum of the pyrolysis products. In both cases, thiet-2-one (**7a**) is proposed as the intermediate. It is observed that the thioketene formation is more pronounced at higher temperatures in agreement with the suggested pathway.

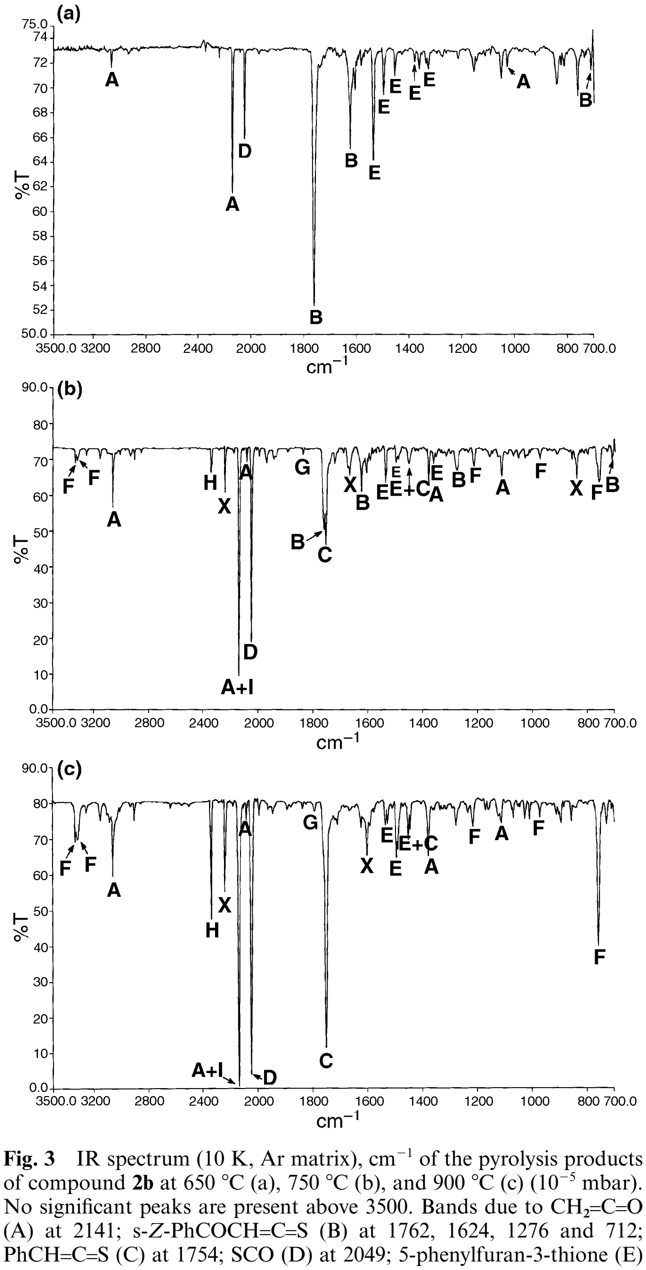
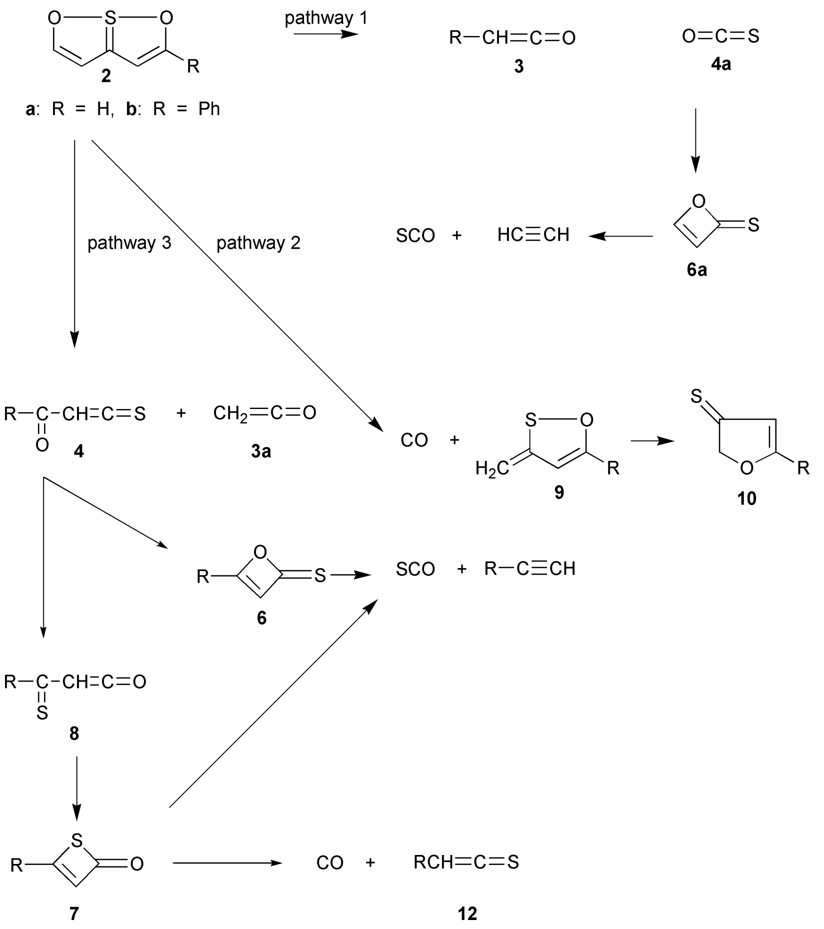


Fig. 3 IR spectrum (10 K, Ar matrix), cm^{-1} of the pyrolysis products of compound **2b** at 650 °C (a), 750 °C (b), and 900 °C (c) (10^{-5} mbar). No significant peaks are present above 3500. Bands due to CH_2=C=O (A) at 2141; s-*Z*-PhCOCH=C=S (B) at 1762, 1624, 1276 and 712; PhCH=C=S (C) at 1754; SCO (D) at 2049; 5-phenylfuran-3-thione (E) at 1536, 1498, 1276 and 1361; phenylacetylene (F) at 3338, 3320, 1216 and 758; 4-phenylthiet-2-one (G) at 1833; CO_2 (H) at 2344. (X) unidentified.

Table 2 Relative intensities (%) of the most significant peaks observed in the electron ionization mass spectra of dioxathiapentalene **2a** after flash-vacuum pyrolysis at 200 °C, 750 °C, and 750 °C with quartz wool inside the pyrolyzer (*)

	m/*z*											
T/°C	128	100	86	71	60	58	45	42	40	39	28	26
200	100	37	—	37	—	—	23	—	—	19	21	—
750	100	71	37	65	13	46	48	33	15	83	38	—
*	**2**	**6**	**5**	**12**	**86**	**94**	–	**56**	**65**	**71**	**100**	**19**



Scheme 2

A closer inspection of the ketene band at 2141 cm^{-1} shows it to be a badly resolved doublet at 2141 cm^{-1} and 2138 cm^{-1}, the latter corresponding to CO. We assume that this doubling is not due to site effects from heating up the matrix. A weak band is observed at 2085 cm^{-1}; however, this can be due both to ^{13}CO and a band from the ketene.[12] Nevertheless, the formation of CO is unambiguously shown by FVP–MS (*vide infra*). No reliable evidence could be found for pathway 1 in the FVP–IR experiment.

The matrix observations are confirmed by on-line FVP–MS experiments (Table 2). At 200 °C, the molecular ion *m*/*z* 128 is the base peak of the electron ionization mass spectrum (EIMS) and the most intense fragmentation corresponds to the loss of CO. At 750 °C, the loss of CO is somewhat enhanced and intense peaks appear at *m*/*z* 86 corresponding to formylthioketene (**4a**), at *m*/*z* 58 corresponding to thioketene, and at *m*/*z* 42 corresponding to ketene. Furthermore, a peak is also observed at *m*/*z* 60 corresponding to SCO. This peak becomes prominent (Table 2) if the contact time is increased by inserting a small amount of quartz wool in the pyrolysis tube. Under these conditions, acetylene is also detected by the appearance of a peak at *m*/*z* 26.

The collisional activation (CA) spectrum of the *m*/*z* 86 ions is shown in Fig. 2. The intense peaks at *m*/*z* 58 and 57 (loss of CO and CHO) are in accordance with the formylthioketene connectivity. The same is true for *m*/*z* 29 (formyl cations). Nevertheless, the peak at *m*/*z* 45 (HCS$^+$) may indicate the presence of the isomeric thioformylketene (**8a**) in the pyrolysate.

The formation of CO is also observed in the FVP–MS as an intense peak at *m*/*z* 28 which is the base peak of MS in the pyrolysis experiment at 750 °C (longer contact times). The thermal CO loss may originate from pathway 3 (Scheme 2). However, a primary fragmentation mode analogous to the one observed for the thermal fragmentation of 1,6,6aλ^4-trithiapentalene with loss of CS will also give rise to the formation of CO (pathway 2). In the case of 1,6,6aλ^4-trithiapentalene, it was shown that the CS loss gave rise after a rearrangement to the formation of thiophene-3-thiole.[1]

The remaining part of **2a** gives rise after loss of CO in the mass spectrum to *m*/*z* 100 ions. This corresponds formally to 3-methylene-1,2-oxathiole (**9**) (Scheme 2). However, in accordance with the observations for the 1,6,6aλ^4-trithiapentalene,[1] this may rearrange to give a furan-3-thiol or the isomeric thiophen-3-ol. The CA spectrum of the *m*/*z* 100 ions closely resembles the CA spectrum of the molecular ions of furan-3-thiol, but has also some resemblance to that of the isomeric thiophen-3-ol. It is therefore not possible to distinguish between these two possibilities and the formation of a mixture of products appears more likely.

Two intense peaks are observed at *m*/*z* 40 and 39 in the EIMS

Table 3 Relative intensities (%) of the most significant peaks observed in the electron ionization mass spectra of dioxathiapentalene 2b after flash-vacuum pyrolysis at 400 °C, 700 °C and 900 °C

	m/*z*										
T / °C	204	176	162	147	134	115	105	102	77	60	51
400	100	98	—	32	—	32	66	—	68	—	22
700	26	51	13	21	100	32	89	30	87	—	36
900	–	**4**	**4**	–	**62**	**43**	**13**	**100**	**15**	**28**	**17**

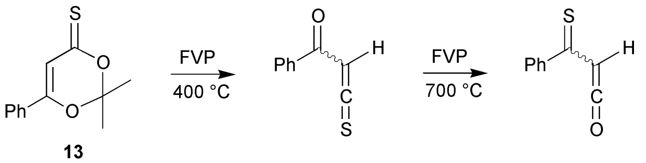
(Table 2). The CA spectrum of the *m*/*z* 40 ions indicates the presence of four hydrogens which means that the *m*/*z* 40 ions probably correspond to propyne formed by further thermolysis of either of the two isomers.

Flash-vacuum pyrolysis of 2-phenyl-1,6-dioxa-6aλ^4-thiapentalene (2b). The matrix-IR spectrum of the pyrolysis products obtained from **2b** is shown in Fig. 3. In contrast to **2a**, compound **2b** may give a different product. In accordance with the observations for the parent compound, the IR spectrum of the pyrolysis products from **2b** shows an intense peak at 2141 cm^{-1} corresponding to ketene (Scheme 2, pathway 2).

A closer inspection of this spectrum shows, as in the case of the parent compound **2a**, that the 2141 cm^{-1} peak has a shoulder of nearly the same intensity at 2138 cm^{-1} corresponding to CO; also in this case, the "mixed" ^{13}CO, ketene band at 2085 cm^{-1} is observed. The formation of both ketene and CO is readily confirmed by the mass spectrometry experiment.

If the other S–O bond in the substituted ring (*cf.* Scheme 2, pathway 1) were broken, it should result in the formation of phenylketene, PhCH=C=O (**3b**). However, no evidence is found for the presence of PhCH=C=O either in the IR spectra, where it is reported to absorb around 2170 cm^{-1},[16] nor in the mass spectrometry experiment. Accordingly, no band due to formylthioketene (**4a**) was observed (*vide supra*).

The loss of ketene from the unsubstituted ring should, *via* pathway 3, give rise to benzoylthioketene (**4b**) which, *via* 4-phenyloxete-2-thione (**6b**), decays into SCO, observed at 2049 cm^{-1} (S^{13}CO is observed at 1996 cm^{-1}), and phenylacetylene, of which all the eight strongest bands are observed.[17] Wentrup *et al.*[15] have recently reported the IR spectrum of benzoylthioketene; they also reported that the corresponding bands disappeared at 750 °C due to rearrangement to thiobenzoylketene (**8b**). In the present study, however, we did not observe the bands reported by Wentrup *et al.* Instead, we observed a new set of bands at 1762, 1624, 1276 and 712 cm^{-1} which were present from 600–750 °C (Fig. 4a, b). These bands are ascribed to the s-*Z* conformation of benzoylthioketene (s-*Z*-**4b**), in good agreement with the theoretical calculated wavenumbers (*cf.* the molecular orbital calculations section). The bands observed by Wentrup are likely to correspond to the s-*E* conformation (s-*E*-**4b**). Loss of ketene from **2b** *via* a concerted process should, due to the cyclic structure, lead preferentially to the s-*Z* conformation which is the lower energy conformation. This conformer is frozen in the Ar-matrix before it can equilibrate to form the s-*E* conformer. Wentrup's precursor **13** has not the predetermined structure for the exclusive formation of the s-*Z* conformer. The spectra (Fig. 4a, b) also show weak bands due to the s-*E* isomer but this is less clear. Pyrolysis of Wentrup's precursor (**12**, Scheme 3) clearly shows a band at 1768 cm^{-1}, which is most probably due to the strongest band in the s-*Z* conformer. At 900 °C (Fig. 3c), the four bands from **4b** have disappeared and only SCO and phenylacetylene could be observed from the decay of **6b**. We were not able to observe the isomeric thiobenzoylketene (**8b**) in the IR–FVP experiment; only the final products CO and phenylthioketene **12b** from the decay of **7b**. Ketene **8b** could be identified unambiguously in the MS–FVP experiment, *vide infra*.



Scheme 3

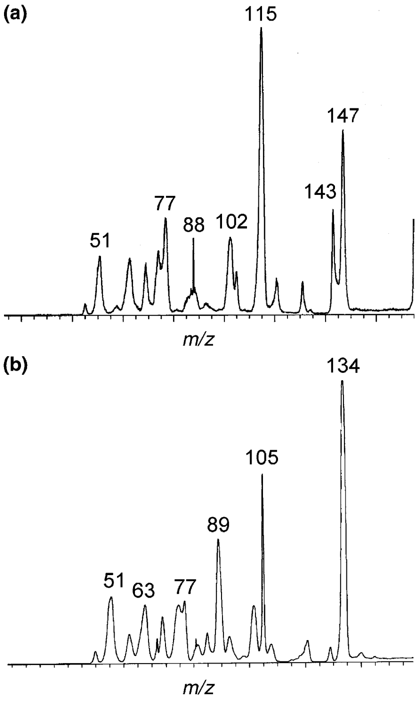


Fig. 4 CA (He) mass spectrum of the *m*/*z* 176 ions (a) and *m*/*z* 162 ions (b) produced by ionization of the pyrolysate of **2b** after flash vacuum pyrolysis at 700 °C.

The most significant peaks in the EIMS spectra of the pyrolysis products of **2b** as a function of pyrolysis temperature are shown in Table 3. The starting material **2b** (*m*/*z* 204) has almost disappeared at 700 °C. No peaks corresponding to phenylketene (**3b**) (*m*/*z* 118) and formylthioketene (**4a**) (*m*/*z* 86) could be observed, which excludes pathway 1 in accordance with the matrix isolation experiment.

The ions at *m*/*z* 176, formed by loss of CO, formally correspond to the molecular ions of 5-phenyl-3-methylene-1,2-oxathiole (**9b**); however, by analogy with the formation of the analogous ions from 1,6,6aλ^4-trithiapentalene,[1] it is assumed that neutral **9b** rearranges to the isomeric furan-3-thiol. The IR spectrum of the pyrolysis product in the temperature range 600–900 °C shows four bands at 1536, 1498, 1276 and 1361 cm^{-1}, which is in agreement with the calculated spectrum of 5-phenylfuran-3-thione **10**. This is further supported by the CA spectrum of the *m*/*z* 176 ions (Fig. 4a), where the intense peak at *m*/*z* 115 may correspond to the phenylcyclopropenium cation.

At 500 °C a relatively intense peak (15% of the base peak) is present at *m*/*z* 162, this peak is ascribed to the formation of benzoylthioketene **4b** generated along pathway 3. This is confirmed by the CA spectrum of the *m*/*z* 162 ions shown in Fig. 4b. This spectrum features an intense signal at *m*/*z* 105 corresponding to the benzoyl cation. Nevertheless, the base peak of the spectrum is associated with a loss of CO (broader peak) and the occurrence of this decarbonylation is readily ascribed to the thermal isomerization of **4b** into thiobenzoylketene (**8b**). The most significant peaks depicted in Table 3 are in fact very similar to the spectrum recorded previously[8] after FVP of the precursor **13** at 700–800 °C (Scheme 3).

At the highest temperatures (Table 3), the final products are clearly identified as phenylthioketene **12b** (*m*/*z* 134) plus CO (*m*/*z* 28) and phenylacetylene (*m*/*z* 102) plus SCO (*m*/*z* 60) which most probably arise from intermediate thiet-2-one **7b** and oxete-2-thione **6b**, respectively.

Conclusions

The thermal formation of acylthioketenes and their thermal rearrangement to thioacylketenes followed by electrocyclization to thiet-2-ones which decay to acetylenes, SCO and CO, have been demonstrated. Formylthioketene has been observed both in the s-*Z* and the s-*E* conformations, whereas benzoylthioketene was only observed in the s-*Z* conformation. The rearrangements and the IR spectra observed were in good accord with theoretical calculations.

Experimental

General details

The FTIR and argon matrix isolation apparatus employing a quartz thermolysis tube (150 mm length and 8 mm internal diameter) has been described earlier.[18] BaF_2 optics were used. The FVP–MS–MS equipment based on a six-sector tandem mass spectrometer (Micromass AutoSpec 6F)[19] fitted with a quartz thermolysis tube (50 mm length, 3 mm inner diameter) directly connected to the outer ion source was as previously described.[20] Unless otherwise stated, the CA spectra were recorded by scanning the field of the second electric sector and collecting the ions with the first off-axis photomultiplier detector, the collision gas being helium.

Materials

1,6-Dioxa-6aλ^4-thiapentalene (**2a**)[21] and 2-phenyl-1,6-dioxa-6aλ^4-thiapentalene (**2b**),[21] were prepared according to literature procedures.

Matrix spectra of authentic samples

Ar-matrix 10 K: ν/cm^{-1} (intensity). *1,6-Dioxa-6aλ^4-thiapentalene* 1624(w), 1545(w), 1531(m), 1515(m), 1450(s), 1436(s), 1400(w), 1242(s), 1211(m), 1204(m), 1159(w), 1075(w), 933(w), 853(m), 794(m), 769(w). *2,5-Dimethyl-1,6-dioxa-6aλ^4-thiapentalene* 1530(vs), 1486(s), 1460(w), 1435(w), 1422(m), 1410(s), 1369(m), 1308(w), 1294(s), 1174(w), 1139(m), 1035(w), 992(w), 983(m), 955(m), 794(m). *Thiophene* 3106(m), 3079(m), 1800(w), 1767(w), 1600(m), 1557(w), 1409(s), 1252(vs), 1082(s) 1035(s), 871(w), 836(vs), 726(vs).

The complete spectra corresponding to Tables 2 and 3 and calculated B3LYP/6-31G* IR spectra of compounds **4b**, **7b**, **8b** and **10** are deposited as electronic supplementary information.

Acknowledgements

The Mons laboratory thanks the Fonds National de la Recherche Scientifique (FNRS) for its contribution towards the purchase of the Micromass AutoSpec 6F mass spectrometer. CThP thanks the Danish National Science Council and The Carlsberg Foundation for financial support.

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