# Formation of thiophenethiols by flash vacuum pyrolysis of 1,6,6a$\lambda^4$-trithiapentalenes

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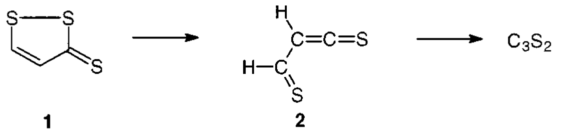
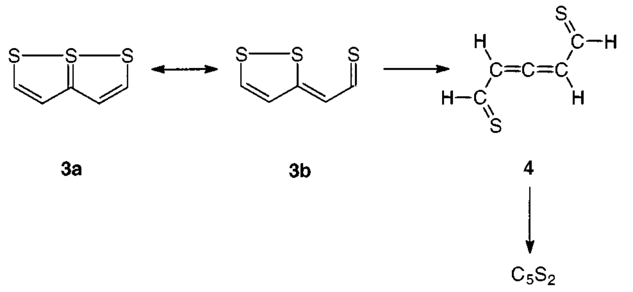
**The thermal behaviour of 1,6,6a$\lambda^4$-trithiapentalene 3 and some methyl-substituted derivatives 5–7 has been investigated using a combination of flash vacuum pyrolysis (FVP), tandem mass spectrometry (MS–MS) and matrix isolation IR spectroscopy. The main products of the fragmentation (losses of CS and/or $CH_2$=C=S) are shown to be thiophene-3-thiones (or the thiol tautomers) which are also shown to be readily available by direct sulfuration of thiophenes in chemical ionization ($CS_2$ reagent gas) conditions.**

## Introduction

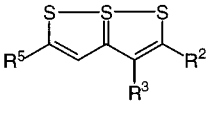
Sulfur containing heterocumulenes of the type X=$C_n$=Y ($n > 1$) such as $C_nS_2$ and :$C_nS$ have recently attracted extraordinary interest from a theoretical point of view, but also from their presence in the interstellar space.[1] Carbon subsulfide, $C_3S_2$, is the only member of this class of compounds which is stable enough to allow isolation for a short time at room temperature.[2,3]

The formation of carbon subsulfide from 3*H*-1,2-dithiole-3-thione **1**[4,5] and substituted 1,2-dithiole-3-thiones[6–8] has previously been reported. It was assumed that $C_3S_2$ was formed *via* a thioformyl thioketene intermediate **2**.[4,5]





1,6,6a$\lambda^4$-Trithiapentalene **3** which can be considered as a vinylogue of 1,2-dithiole-3-thione is normally considered as a bicyclic 10π-electron system.[8,9] However, reversible, photochemical isomerization of such compounds indicates that they may exist in the excited state as the monocyclic dithiolylidene valence-tautomeric form **3b**.[10] It was therefore assumed that $C_5S_2$ could be formed from the trithiapentalene **3** *via* **4** in the same way as $C_3S_2$ was formed from the dithiole thiones. In that context, we therefore decided to investigate the behaviour of the parent trithiapentalene **3** and some methyl substituted derivatives **5**–**7** upon FVP.



$R^2 = R^3 = R^5 = H$ **3**
$R^2 = CH_3$ $R^3 = R^5 = H$ **5**
$R^3 = CH_3$ $R^2 = R^5 = H$ **6**
$R^2 = R^5 = CH_3$ $R^3 = H$ **7**

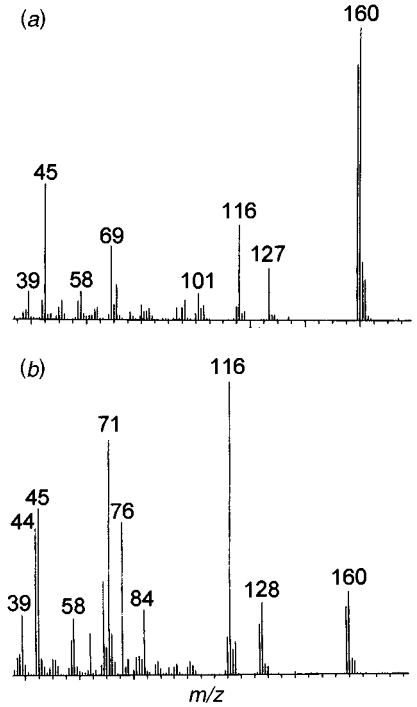


**Fig. 1** Electron impact (70 eV) mass spectra of the parent trithiapentalene **3** at (*a*) 200 °C and (*b*) 680 °C oven temperatures

## Results and discussion

### 1,6,6a$\lambda^4$-Trithiapentalene 3

The mass spectrum (EI, 200 °C) of the parent trithiapentalene **3** is depicted in Fig. 1(*a*). This spectrum is very similar to a previously published spectrum[11] except for the complete absence of a peak at *m/z* 128 ascribed to a thermally induced sulfur loss. The main fragmentations of the molecular ions are the losses of H˙ (*m/z* 159), HS˙ (*m/z* 127) and CS (*m/z* 116). Important changes in the mass spectra are seen when the temperature of the oven is increased [Fig. 1(*b*)]; appearance of peaks at *m/z* 128, 76 and 44 and also intensification of the peaks at *m/z* 116 and 71. FVP–MS–MS identifies readily carbon disulfide and carbon monosulfide which are also clearly seen in the IR spectrum (10 K argon matrix) (Fig. 2). Weak absorptions are also seen at 2078 and 1754 cm$^{-1}$ and attributed to the formation of small amounts of carbon subsulfide and thioketene, respectively. These compounds are not observed in the MS experiments probably because the temperature regime and thus the contact times were different.

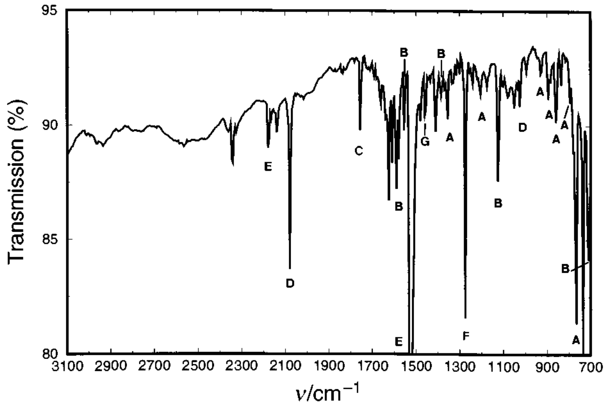


**Fig. 2** IR spectrum (10 K argon matrix) of the pyrolysis products of **3** (1000 °C, $10^{-5}$ mbar). Bands due to thiophene-3-thiol (A) appear at 1499, 1356, 1206, 925, 892, 856, 794 and 765 cm$^{-1}$. Bands due to thiapyran-4-thione (B) appear at 1582, 1554, 1386, 1126 and 712 cm$^{-1}$. Band due to thioketene (C) appears at 1754 cm$^{-1}$. Bands due to $C_3S_2$ (D) appear at 2078 and 1025 cm$^{-1}$. Bands due to $CS_2$ (E) appear at 2172 and 1527 cm$^{-1}$. Band due to CS (F) appears at 1275 cm$^{-1}$. Band due to starting material (G) appears at 1458 cm$^{-1}$. The strongest peaks are out of scale.

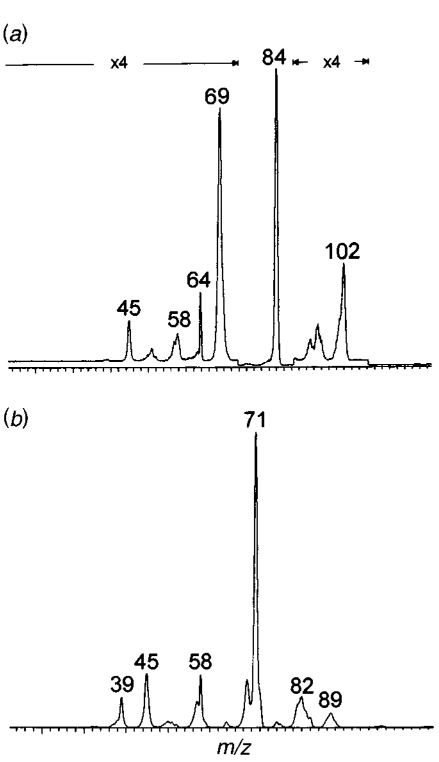
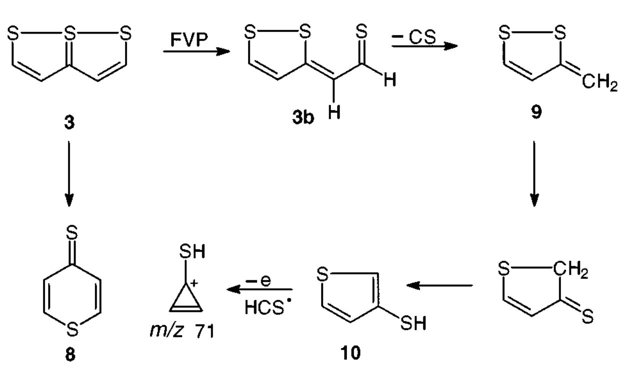


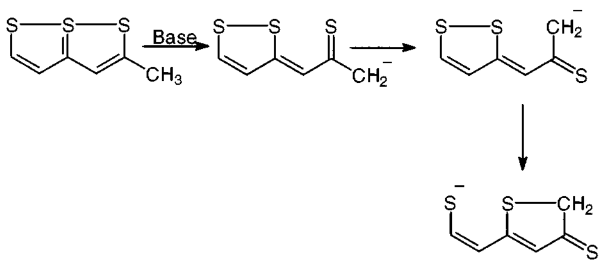
**Fig. 3** CA ($O_2$) mass spectra of the main pyrolysis products of **3**, (*a*) [**3**-S] *m/z* 128 and (*b*) [**3**-CS] *m/z* 116

The CA mass spectra of the two other pyrolysis products, [**3**-S] and [**3**-CS], are shown in Fig. 3. The spectrum of the *m/z* 128 ions is dominated by a very intense peak at *m/z* 84 (loss of CS) due to the formation of thiophene radical cations as evidenced by an MS–MS–MS experiment. It is moreover identical to the CA spectrum of the molecular ions of authentic 4*H*-thiapyran-4-thione **8**. The mechanism of the thermal fragmentation of **3** into **8** is not yet elucidated.

The loss of CS is the prominent fragmentation pathway at elevated temperatures. Based on the initial neutral structure **3**, the 3-methylene-1,2-dithiole structure **9** was the first product taken into account. However, on-line FVP and methanol chemical ionization produce *m/z* 117 ions whose CA spectrum is dominated by the loss of a sulfhydryl radical. This loss of $HS^{\bullet}$ is unexpected[12] for a dithiole structure **9**H$^+$, especially because it contradicts the even electron rule.[13,6] Such a fragmentation is more readily explained if the product is in fact thiophene-3-thiol **10** resulting from a ring-opening of **9**, recyclization of the diradical intermediate and tautomerization *via* collisions with the walls of the pyrolyser. This reaction sequence is depicted in Scheme 1. This rearrangement is analogous to the rearrangement observed when trithiapentalene, with a $CH_3$ or $RCH_2$ group in the C-2 position, is treated with strong base (Scheme 2).[14]



**Scheme 1**



**Scheme 2**

Confirmation of the actual structure **10** for the pyrolysis product is found in the CA spectrum [Fig. 3(*b*)] identical to the corresponding spectrum of the molecular ions of an authentic sample of thiophene-3-thiol [Fig. 4(*a*)]. Note however that the CA spectrum of the isomeric thiophene-2-thiol radical cations $\mathbf{11}^{\bullet+}$ is also surprisingly similar. Only minor differences are noticed [Fig. 4(*b*)]; an inversion of the intensities of the peaks at *m/z* 89 and 76 and a more intense charge stripping peak at *m/z* 58 in the thiophene-3-thiol case.

We have recently shown that ionization of carbon disulfide in a chemical ionization source produces with a reasonable yield, the radical cations $CS_3^{\bullet+}$.[15] Using the tandem mass spectrometer in the hybrid configuration (see Experimental section),[16] these distonic ions were shown to be efficient sulfur transfer reagent to various molecules, like nitriles[17] and nitrogen-containing heterocycles.[18] In the context of the present work, we have tried to sulfurate thiophene under CI ($CS_2$) conditions. The ions formed (*m/z* 116) are produced readily and the CA spectrum of these ions is superimposable on the spectrum shown in Fig. 3(*b*). $CS_3^{\bullet+}$ radical cations realize therefore a regiospecific insertion of $S^{\bullet+}$ into the C-3–H bond of thiophene.

The presence of $C_5S_2$ (*m/z* 124) could not be observed in the mass spectrum of the pyrolysis products of **3**. $C_5S_2$ has been reported to have a strong absorption band at 2105 cm$^{-1}$[19] however, we have not observed an absorption at this position in the IR spectrum of the pyrolysis products of **3**. From this we have to conclude that $C_5S_2$ is not formed, or it does not survive the pyrolysis conditions used.

### 2-Methyl-1,6,6a$\lambda^4$-trithiapentalene 5

A methyl group in position C-2 of the trithiapentalene (**5**) introduces a new, competitive, thermal fragmentation; the loss of thioketene indicated by prominent peaks at *m/z* 116 and 58 in the EIMS. Collisional activation indicates that these ions correspond, respectively, to thiophene-3-thiol ions and thioketene ions. The loss of CS still occurs and yields *m/z* 130 ions which,

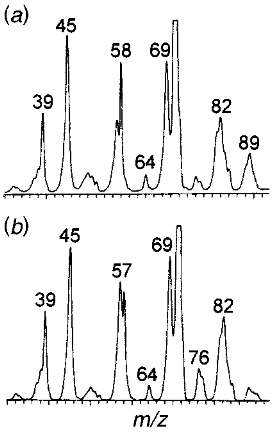
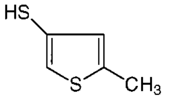
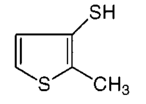


**Fig. 4** Part of the CA ($O_2$) mass spectra of the molecular ions (*m/z* 116) of (*a*) thiophene-3-thiol **10** and (*b*) thiophene-2-thiol **11**; the base peaks at *m/z* 71 are out of scale

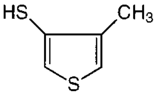
following the mechanism depicted in Scheme 1, should correspond to 5-methylthiophene-3-thiol **12**.



**12**



**13**



**14**

### 3-Methyl-1,6,6aλ$^4$-trithiapentalene 6

If the methyl group is situated at position C-3, the loss of thioketene is, as expected, not observed. As carbon monosulfide can be expelled from either dithiole rings, it is expected that a mixture of isomeric thiophenes could be produced; 2-methylthiophene-3-thiol **13** and/or 4-methylthiophene-3-thiol **14**. We have used the sulfuration procedure of 2- and 3-methylthiophenes under chemical ionization ($CS_2$ conditions) for the preparation of the reference compounds. All the CA spectra of the *m/z* 130 ions are collected in Fig. 5. Fragmentations are again found to be very similar whatever the origin of the ions (FVP or CI). A small intensity increase of the peak at *m/z* 59 ascribed to methyl thioacylium ions seems to be indicative of a methyl group in position C-2 of the thiophene ring. The other differences (*m/z* 71 and 89 more intense in the CI and FVP experiments, respectively) seem to be dependent on the mode of production of the ions or/and on the possible occurrence of mixture of isomers.

### 2,5-Dimethyl-1,6,6aλ$^4$-trithiapentalene 7

As expected, FVP of the symmetrical 2,5-dimethyl-1,6,6aλ$^4$-trithiapentalene **7** induces a unique (no loss of CS) and very intense loss of thioketene yielding 5-methylthiophene-3-thiol **12** identified again by the CA spectrum identical to the spectrum depicted in Fig. 5(*a*). These results are again confirmed by IR (10 K argon matrix) (Fig. 6) showing a very strong absorption at 1753 cm$^{-1}$. Due to the more drastic temperature conditions used, $CS_2$ and $C_3S_2$ are also formed and identified owing to the absorptions at 2078 and 1526 cm$^{-1}$, respectively.

## Conclusions

It has been shown that 1,6,6aλ$^4$-trithiapentalene and methyl-substituted trithiapentalenes give rise to CS and/or $CH_2{=}C{=}S$ when pyrolysed in the temperature range 300–1000 °C under FVP conditions. The pyrolysis further results in formation of thiophenethiols which were identified by comparison of their CA spectra with independent formed thiophenethiols. These thiols were prepared by conventional synthetic methods or in the mass spectrometer by using carbon disulfide *S*-sulfide ions, $CS_3^{\cdot+}$ as sulfur transfer reagents for sulfurating thiophene, 2-methylthiophene and 3-methylthiophene.

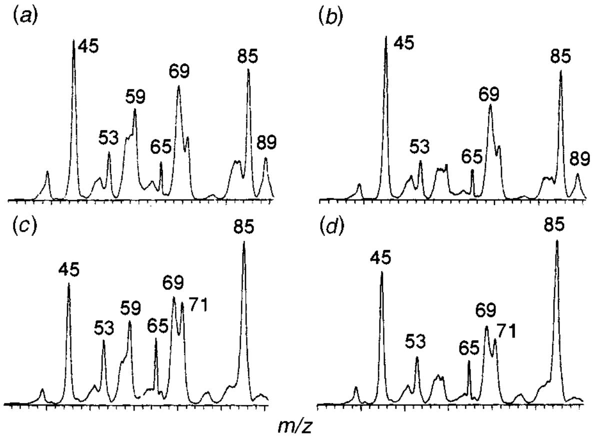


**Fig. 5** Part of the CA ($O_2$) mass spectra of the *m/z* 130 ions formed by FVP–EI of the trithiapentalene (*a*) **5** and (*b*) **6** or $CS_2$ chemical ionization of (*c*) 2-methylthiophene and (*d*) 3-methylthiophene; the base peak at *m/z* 97 is not shown

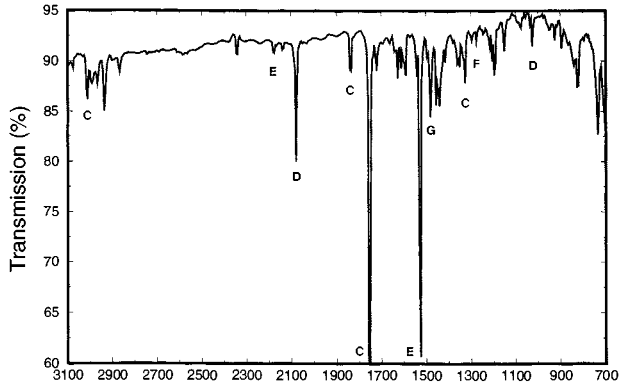


**Fig. 6** IR spectrum (10 K argon matrix) of the pyrolysate of the trithiapentalene **7** (900 °C, $10^{-5}$ mbar). Bands due to thioketene (C) appear at 3012, 1838, 1754 and 1324 cm$^{-1}$. Bands due to $C_3S_2$ (D) appear at 2078 and 1025 cm$^{-1}$. Bands due to $CS_2$ (E) appear at 2172 and 1527 cm$^{-1}$. Band due to CS (F) appears at 1275 cm$^{-1}$. Band due to starting material (G) appears at 1480 cm$^{-1}$. The strongest peaks are out of scale.

It was not found possible to observe $C_5S_2$ as a pyrolysis product of 1,6,6aλ$^4$-trithiapentalene either by MS–FVP or IR–FVP. This may be due to the fact that $C_5S_2$ is unstable under the pyrolysis conditions used.

## Experimental

### General

The mass spectra have been recorded on a large scale tandem mass spectrometer already described elsewhere.[20] Briefly, it consists of a combination of six sectors EBEEBE (E stands for electric sector and B for magnetic sector). Typical conditions were 8000 V accelerating voltage, 70 eV energy of the ionizing electrons and 200 μA trap current (electron impact mode) or 1 mA emission current (chemical ionization mode). This tandem mass spectrometer can also be fitted with an RF-only quadrupole collision cell in order to investigate ion–molecule reactions.[16]

The ion source of the spectrometer was also fitted with a flash-vacuum pyrolysis device consisting of an electrically heated quartz tube (50 mm length, 3 mm inner diameter).[21] In some experiments, a small quantity of quartz wool was introduced in the tube in order to increase the contact time.

In the collisional activation experiments, a beam of mass-selected ions, from a combination of the first three sectors, was focused in a collision cell pressurized with oxygen (*ca.* 30% transmittance). The fragments produced were recorded by scanning the field of the third electric sector and collecting the ions in the fifth field-free region with an off-axis photomultiplier detector.

Chemical ionization was performed using carbon disulfide (3–4 μl injected in a heated septum inlet) as the reagent gas at an indicated source housing pressure of *ca.* $5 \times 10^{-5}$ mbar.

The IR–FVP apparatus employed a 10 cm length (0.8 cm id) quartz tube in housings flanged to a Leybold–Heraeus closed-cycle liquid He-cryostat for Ar-matrix isolation (10–15 K). Pressures were $10^{-5}$–$10^{-6}$ mbar. For matrix isolation, samples were codeposited with *ca.* 200 mbar Ar for 20 min on a $BaF_2$ disk. IR spectra were recorded on a Perkin-Elmer FTIR-PARAGON 1000 spectrometer at a resolution of 2 $cm^{-1}$.

### Samples

1,6,6a$\lambda^4$-Trithiapentalene **3**,[22] 2-methyl-1,6,6a$\lambda^4$-trithiapentalene **5**,[23] 3-methyl-1,6,6a$\lambda^4$-trithiapentalene **6**,[24] 2,5-dimethyl-1,6,6a$\lambda^4$-trithiapentalene **7**,[25] thiapyrane-4-thione **8**,[26] thiophene-3-thiol **10**[27] and thiophene-2-thiol **11**[28] were prepared according to literature procedures.

## Acknowledgements

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