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## HETEROCUMULENES AND THIOKETENES FROM 1,2-DITHIOLE DERIVATIVES BY FLASH VACUUM PYROLYSIS

**Abstract:** In the paper the formation of heterocumulenes and thioketenes in the flash vacuum pyrolysis (FVP) process of 1,2-dithiole derivatives is presented. The pyrolysis was investigated using 1,2-dithiole-3-thiones, *N*-substituted 3,6-dihydrodithiolimines and 1,6-dioxathiapentalenes.

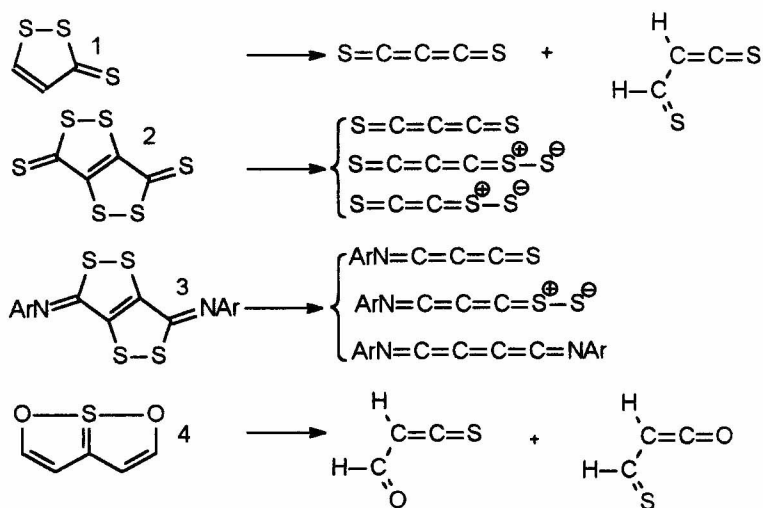
### Introduction

Heterocumulenes of the types  $X=C(C)_nY$  where *X* and *Y* can be O, S or NR or even a lone pair have for a long period attracted much interest from a theoretical point of view but also because they are observed by astrophysicists in the interstellar space. We have studied the pyrolysis of different 1,2-dithiole derivatives by means of FVP combined with matrix isolation spectroscopy and online MS experiments and observed the formation of such heterocumulenes and thioketenes.

We have shown that 1,2-dithiole-3-thiones (1), in particular such which are substituted with alkylthiosubstituents give rise to  $S=C=C=C=S$  when pyrolysed in the temperature range 500-1000 °C. The "double" 1,2-dithiole-3-thione (2) affords  $C_3S_2$  and also compounds with an extra sulfur atom formulated as *S*-sulfides.

The bis-aryliminocompounds (3) lead to monoiminoheterocumulenes and to bis-aryliminoheterocumulenes with four carbon atoms.

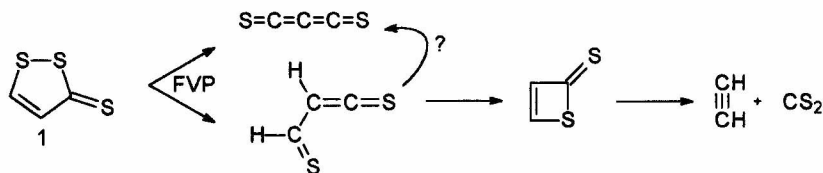
1,6-Dioxa-6aλ<sup>4</sup>-thiapentalene (4) gives upon pyrolysis initially acylthioketenes which isomerise to thioacylketenes (Scheme 1).



Scheme 1

## 1,2-Dithiole-3-thiones and -3-ones

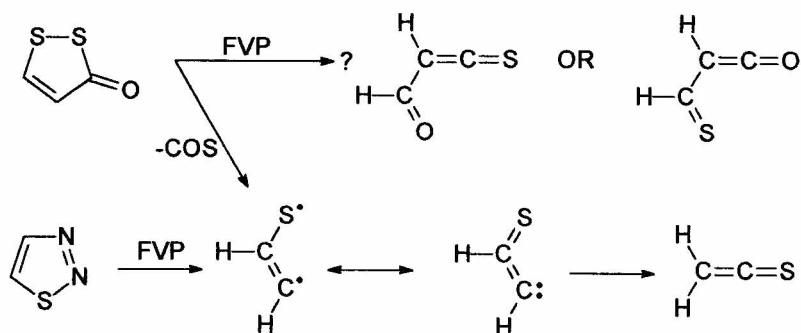
FVP of 1,2-dithiole-3-thiones (**1**) in the range 500-1000 °C gave rise to thioacylthioketenes, alkynes, carbon disulfide and carbon subsulfide<sup>1</sup> (Scheme 2). This was observed by IR-matrix isolation spectroscopy and online MS.



Scheme 2

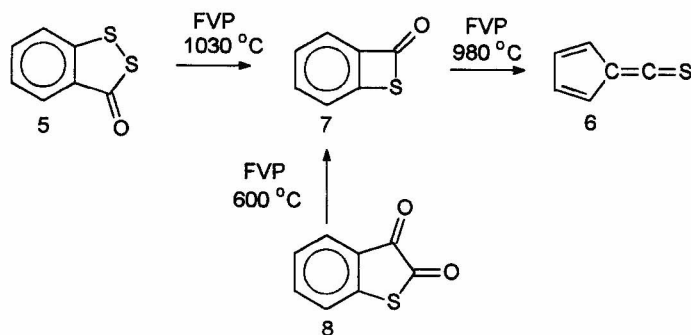
There is no evidence whether carbon subsulfide is formed from the thioformylthioketene or directly from compound **1**. As no satisfactory synthetic methods for synthesis of carbon subsulfide are known<sup>2</sup> it was of interest to study the pyrolysis of **1** as a preparative method. It was shown that the introduction of methylthio groups in the 1,2-dithiole nucleus augmented the yield of  $\text{C}_3\text{S}_2$ <sup>3</sup>. However, even with methylthio substituted compounds the yield of  $\text{C}_3\text{S}_2$  was rather low<sup>4</sup>.

The pyrolysis of the analogous 1,2-dithiol-3-ones could be expected to result in the formation of either acylthioketenes or thioacylketenes. However, FVP of such compounds gave simple thioketenes instead<sup>5</sup>. These could also be formed by pyrolysis of 1,2,3-thiadiazoles (Scheme 3).



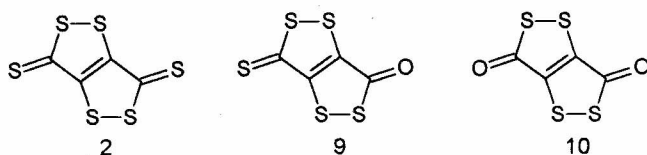
Scheme 3

The benzocondensed 1,2-dithiole-3-thione (5) was thermally very stable but pyrolysed at 1030 °C gave the ring contracted thioketene (6). This could proceed *via* the thietanone (7). Due to the high pyrolysis temperature we were, however, not able to observe the thietanone. If another precursor (8) which pyrolysed at a lower temperature (600 °C) was used, the benzocondensed thietanone could be observed at 600 °C. By loss of CO (8) gives the same thioketene (6) as the 1,2-benzodithiol-3-one (5) (Scheme 4).



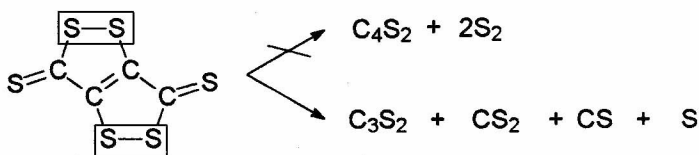
Scheme 4

3,6-Dihydro[1,2]dithiolo[4,3-*c*][1,2]dithiole-3,6-dithione and oxygen analogues (Scheme 5).



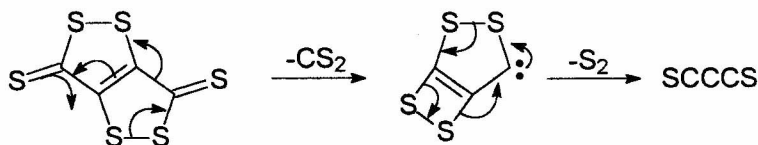
Scheme 5

Compound 2 has the perfect backbone to give  $C_4S_2$  after loss of  $2S_2$  (Scheme 6).



Scheme 6

However, in this case it was also observed that the predominant fragmentation products from (2) were  $C_3S_2$  and  $CS_2$ <sup>6</sup>. This may be due to the general instability of heterocumulenes with an even number of carbon atoms<sup>7</sup>. The formation of carbon subsulfide can be explained in the following way (Scheme 7).



Scheme 7

The Ar-matrix IR spectrum of the pyrolysis products from (2) is shown in Fig. 1.

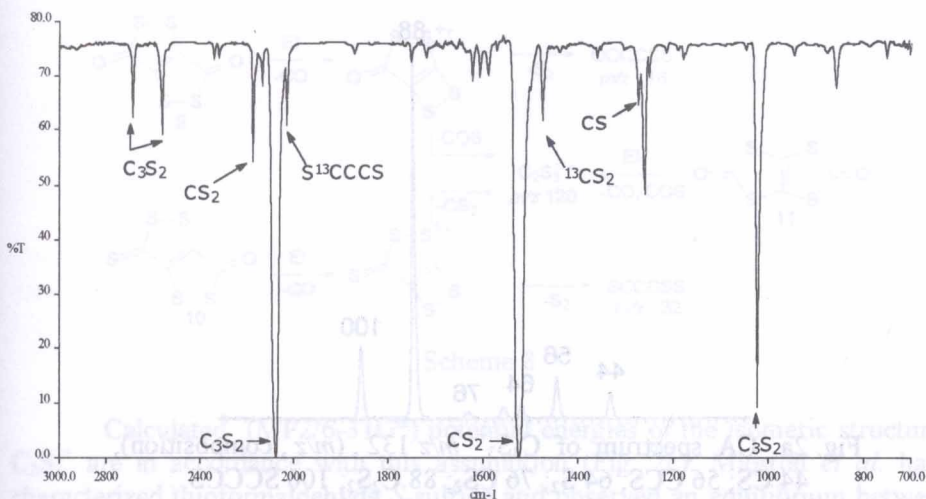


Fig. 1 IR spectrum of pyrolysate (10K, argon matrix) of compound 2 at 1000 °C.

Dissociative ionization of (2) and (9) generated radical cations  $C_3S_3^+$  and  $C_3S_2O^+$ . The Collision Activation (CA) spectra of these ions are shown in Figs 2a, b.

The CA spectrum of  $C_3S_3^+$  (Fig. 2a) is in accordance with a SCCCCS connectivity and not the isomeric C-sulfide structure SCCCS<sub>2</sub>. This was further confirmed by ion molecule reactions with NO giving rise to ONS<sup>+</sup> ions.<sup>6</sup> Analogous oxygen ions  $C_3S_2O^+$  (Fig. 2b) formed from the mixed oxygen-sulfur compound (10). Attempts to observe compounds of this type by FVP were without success, this is also in accordance with the negative results from Neutralisation-Reionisation Mass Spectrometry (NRMS) which did not show a recovery signal of the  $m/z$  132 ions. This demonstrates the instability of the neutral molecule.

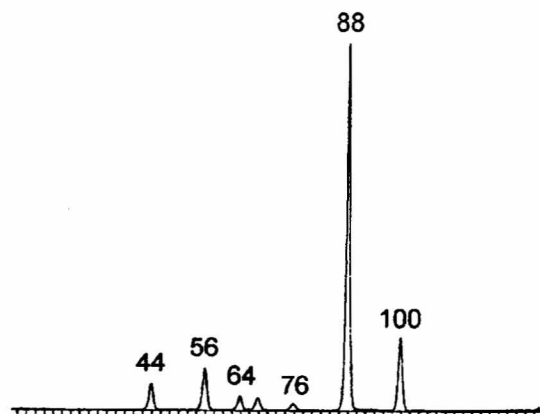


Fig. 2a. CA spectrum of  $C_3S_3^{+}$   $m/z$  132, ( $m/z$ , composition), 44 CS; 56 CCS; 64  $S_2$ ; 76  $CS_2$ ; 88  $C_2S_2$ ; 100 SCCCS.

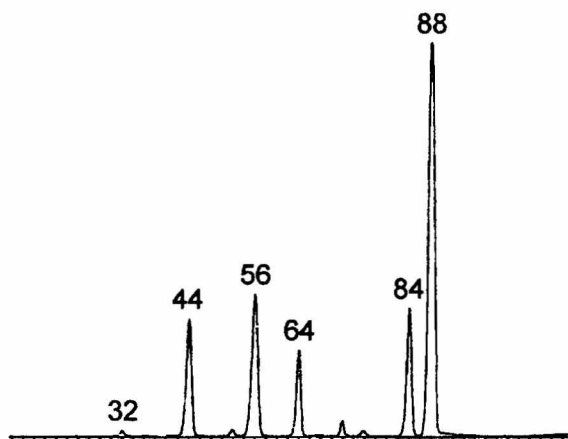
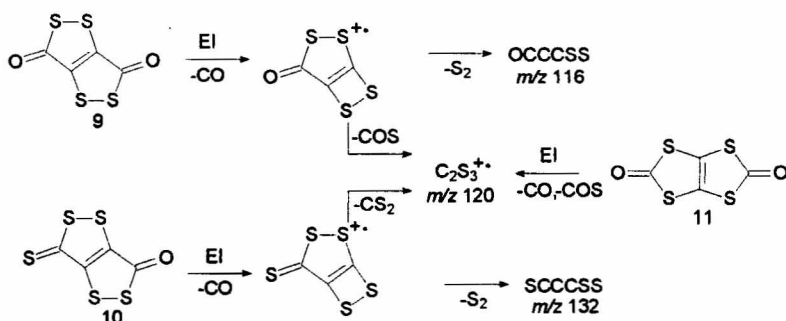


Fig. 2b. CA spectrum of  $C_3S_2O^{+}$   $m/z$  116, ( $m/z$ , composition), 32 S; 44 CS; 56 CCS; 64  $S_2$ ; 84 OCCCS; 88  $C_2S_2$ .

Dissociative ionization of 3,6-dihydro[1,2]dithiolo[4,3-*c*][1,2]dithiole-3,6-dithione also gave rise to ions  $C_2S_3^{+}$ <sup>8</sup>. The structure of these ions could, however, not effectively be characterized by CA and NRMS-spectroscopy.

If the CA spectra of the  $m/z$  120 ions derived from the three precursors (9), (10) and (11) were recorded it was observed that the three CA spectra were different. Due to the geometry of the precursors the ions derived from (9) most probably have the connectivity SCCSS, those derived from (11) the connectivity SCCS<sub>2</sub>, and those from (10) are a mixture of the two (Scheme 8). Ion-molecule reactions (in particular with nitric oxide) could readily differentiate between the *C*-sulfide ethenedithione ion SCCS<sub>2</sub><sup>+</sup> and the *S*-sulfide ethenedithione ion SCCSS<sup>+</sup>.



Calculated (MP2/6-31G\*) potential energies of the isomeric structures  $C_2S_3^+$  are in accordance with this assumption (Fig. 2c). Młostoń *et al.* have characterized thioformaldehyde *S*-sulfide and observed an equilibrium between the open form and a dithiirane<sup>9</sup>. In our case such dithiiranes seem not to be present.

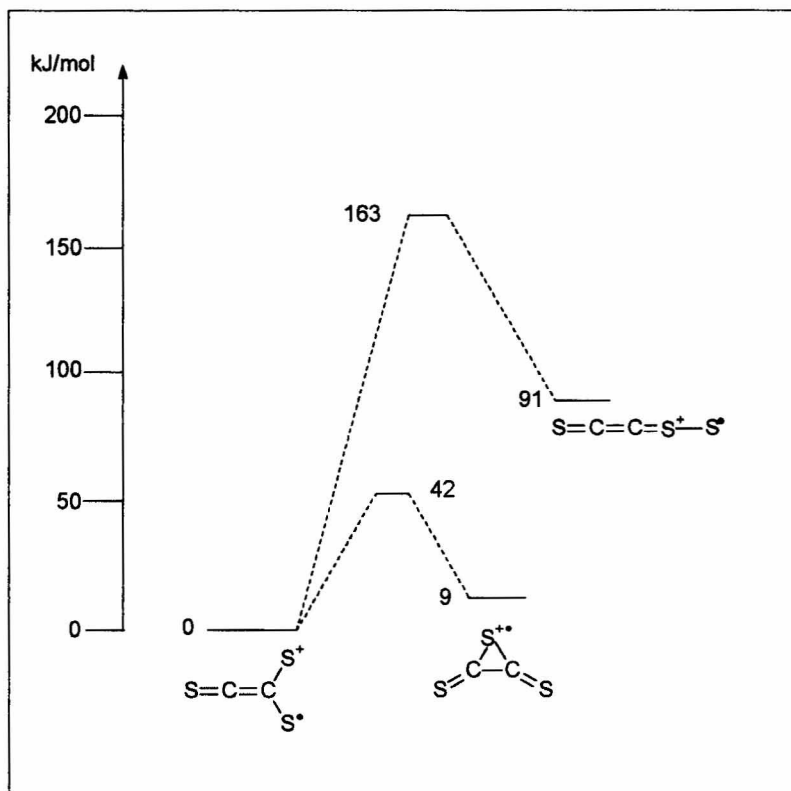
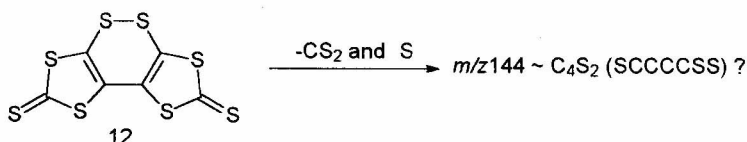


Fig. 2c. Selected points on the potential energy surface of  $C_2S_3^+$  species<sup>8,10</sup>.

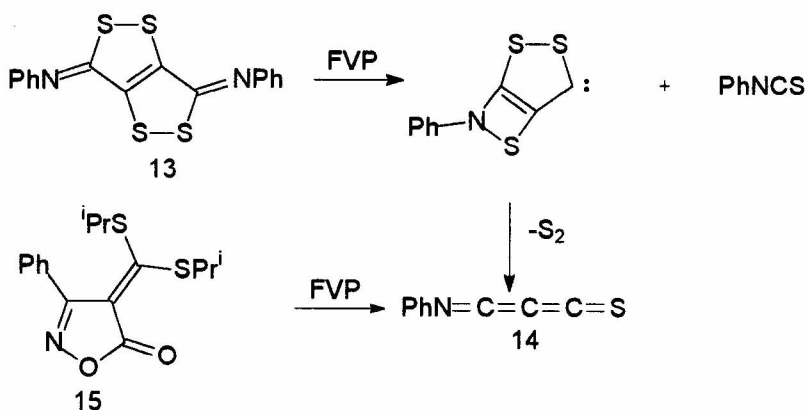
We have also studied more complex systems such as (12).



In this case we have observed ions corresponding to the composition  $C_4S_3$ . Ion-molecule reactions with nitric oxide suggest these ions to be a mixture of the isomeric species<sup>10</sup>.

### *N*-Substituted 3,6-dihydro[1,2]dithiolo[4,3-*c*][1,2]dithiolimines

In the same way as 3,6-dihydro[1,2]dithiolo[4,3-*c*][1,2]dithiole-3,6-dithione (2) has a perfect backbone to give  $C_4S_4$ , the *N*-substituted 3,6-dihydro[1,2]dithiolo[4,3-*c*][1,2]dithiolimines (13) should by loss of  $2S_2$  give rise to  $RN=C=C=C=NR$ . However, as seen below, the pyrolysis resulted in a three carbon compound (14)<sup>11</sup> (Scheme 9).



Scheme 9

The IR spectrum of the pyrolysis products from 13 is shown in Fig. 3.



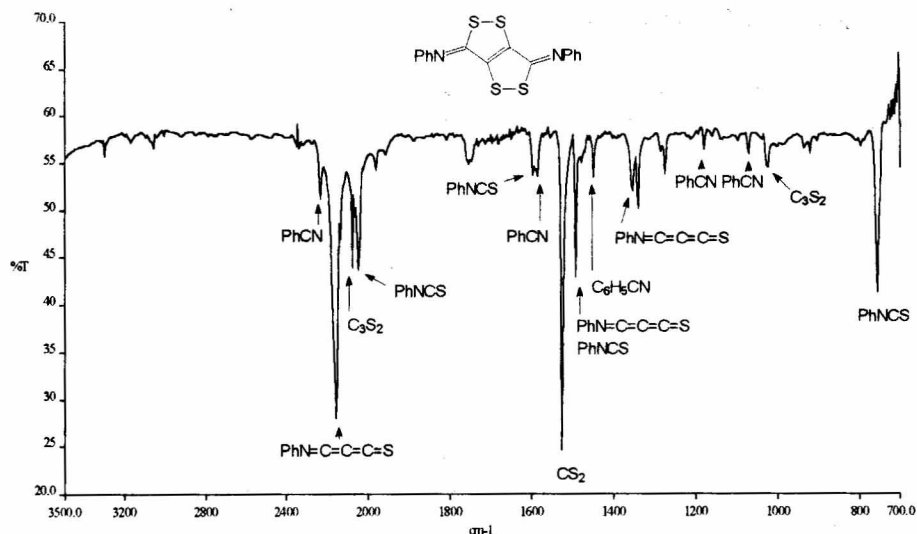
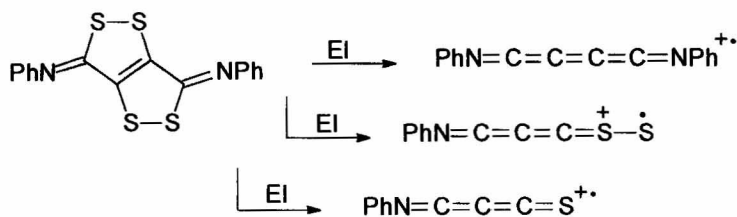


Fig.3. IR spectrum of the pyrolysate(10K, argon matrix) of compound 13 at 1000 °C.

$\text{PhN}=\text{C}=\text{C}=\text{C}=\text{S}$  can be formed from another precursor (15)<sup>12</sup> and is known to have its strongest absorption band at  $2159\text{ cm}^{-1}$ .

Dissociative electron ionization of (13) resulted in formation of the cations shown below<sup>11</sup> (Scheme 10).



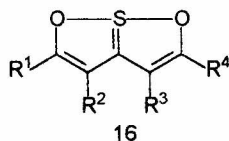
Scheme 10

The  $m/z$  230 ion could be neutralized and reionized even though the recovery signal due to  $\text{PhN}=\text{C}=\text{C}=\text{C}=\text{C}=\text{NPh}$  has a low intensity showing the low stability of the neutral molecule; this is in accordance with the observation that it is not present under FVP conditions.

Similar results were obtained from the monoimino compound. In an attempt to synthesize an aliphatic compound of the same type as (13) the *N*-*tert*-butyl compound was pyrolysed. This process resulted, however, in loss of the *tert*-butyl group as isobutene and formation of  $\text{C}_3\text{S}_2$ .

## 1,6-Dioxo-6aλ<sup>4</sup>-thiapentalenes

Acylthioketenes could not be isolated from the pyrolysis of 1,2-dithiol-3-ones<sup>5</sup>, however, they resulted from the FVP of 1,6-dioxo-6aλ<sup>4</sup>-thiapentalenes 16<sup>13</sup>.



As shown in Scheme 11 these compounds can fragment in several ways giving rise to a complex mixture of compounds. It was, however, possible by combination of matrix IR spectroscopy and mass spectrometry to solve this problem (Fig 4).

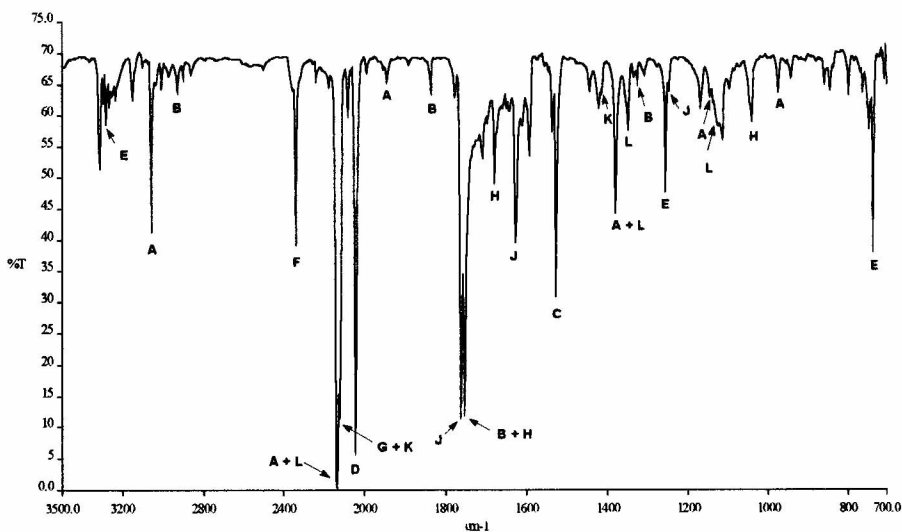
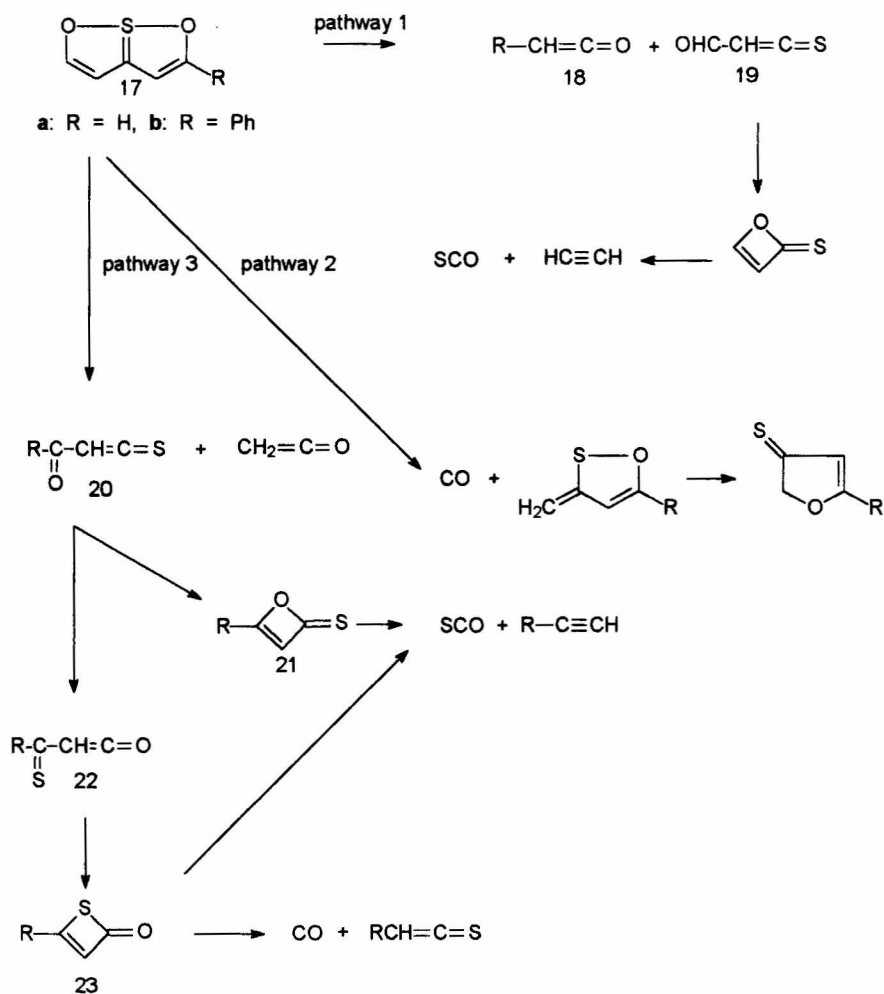
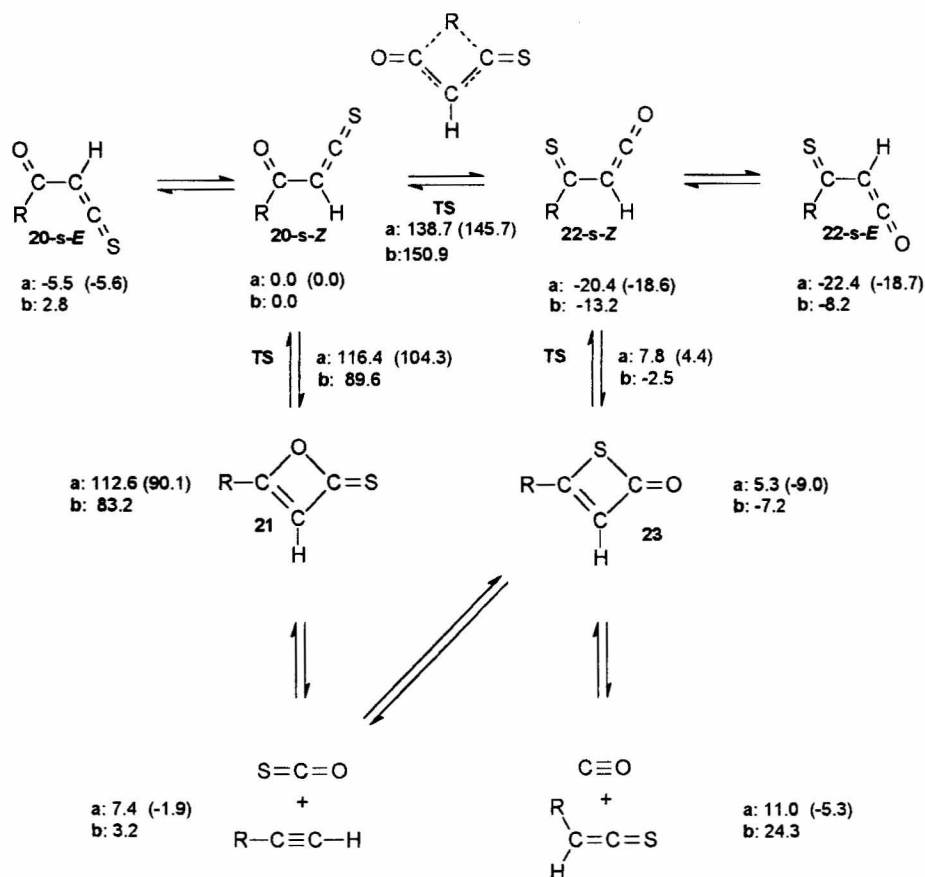


Fig.4. IR spectrum of pyrolysate (10K, argon matrix) of compound 4 at 1000 °C. A: CH<sub>2</sub>=C=O, B: CH<sub>2</sub>=C=S, C: CS<sub>2</sub>, D: COS, E: acetylene, F: CO<sub>2</sub>, G: CO, H: CHO-CH=C=S (*s-E*), J: CHS-CH=C=O (*s-Z*), K: CHS-CH=C=O (*s-E*), L: CHS-CH=C=O (*s-Z*).



Scheme 11

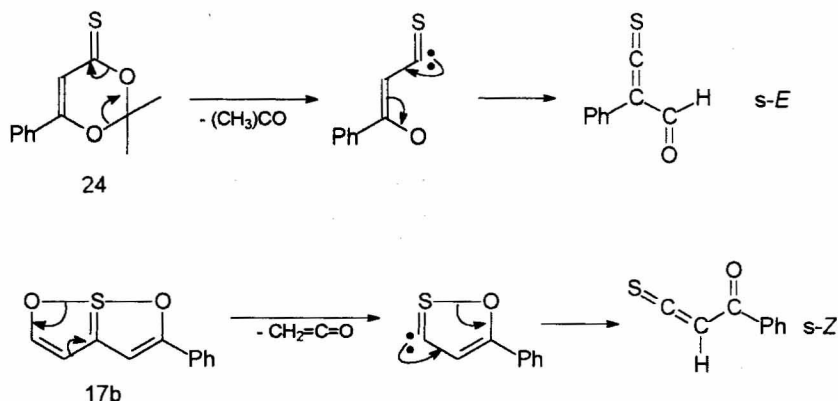
The identification of the pyrolysis products was further complicated by the fact that the different rotamers were observed in the argon matrix. The calculated energy of the different rotamers and the transition energies for the different equilibria are shown in Scheme 12.



Scheme 12

The IR bands observed for benzoylthioketene (**20b**) are slightly different from those observed by Wentrup<sup>13</sup>. The bands we have observed are in accordance with the *s-Z*-form of benzoylthioketene whereas the bands observed by Wentrup from another precursor (**24**) are in accordance with the *s-E*-form. This is in agreement with the geometrical structure of the two precursors.

Loss of ketene from 2-phenyl-1,6-dioxo-6aλ<sup>4</sup>-thiapentalene (**17b**) via a concerted process should, due to the cyclic structure of this precursor, lead preferentially to the *s-Z* conformation. This conformer is then frozen in the argon matrix before it can equilibrate to the more stable *s-E* conformer formed from Wentrup's precursor (Scheme 13).



Scheme 13

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**Powstawanie heterokumulenów i tioketenów  
w procesie próżniowej pirolizy błyskowej  
pochodnych 1,2-ditiolowych**

**Streszczenie:** W artykule przedstawiono powstawanie heterokumulenów i tioketenów w procesie pirolizy 1,2-ditiolowych pochodnych. Pirolizę prowadzono stosując 1,2-ditiolo-3-tiony, *N*-podstawione 3,6-dihydroditiol-iminy i 1,6-dioksatipentaleny.

