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## THE FORMATION OF HETEROCUMULENES FROM 1,2-DITHIOLE DERIVATIVES UPON FLASH VACUUM PYROLYSIS.

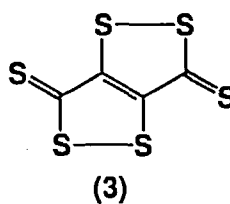
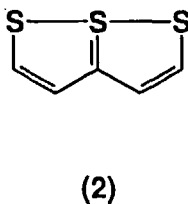
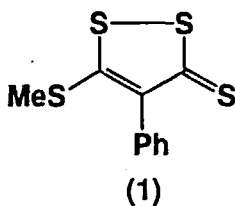
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**Abstract** 1,2-Dithiole derivatives such as alkylthio substituted 1,2-dithiole-3-thiones, 1,6,6a $\lambda^4$ -tritiapentalenes and 1,2-dithiolo[4,3-c]-[1,2]dithiole-3,6-dithione gives rise to  $C_3S_2$ ,  $:C_4S$  and thioketenes upon flash vacuum pyrolysis in the temperature range 800-1000 °C.

Sulfur containing heterocumulenes of the types  $X=C_n=Y$ , 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.

During more general studies of 1,2-dithiole derivatives we have studied the flash vacuum pyrolysis (FVP) of 1,2-dithiole derivatives such as 1, 2 and 3.



It has been observed that alkylthio substituted 1,2-dithiole-3-thiones such as 1 give rise to the formation of substantial amounts of  $C_3S_2$  (carbon subsulfide) upon FVP in the temperature range 800-1000 °C<sup>1</sup>.  $C_3S_2$  was isolated and characterized in an argon matrix at 10K by its strong IR absorptions at 2078 and 1025  $cm^{-1}$ . Surprisingly, it was found that even the isomeric 5-phenyl-4-methylthio-1,2-dithiole-3-thione gave rise to  $C_3S_2$  upon FVP.

As carbon subsulfide, which is an interesting synthon, is preparatively very difficultly accessible<sup>2</sup> the preparative aspects of this pyrolysis is studied further.

1,6,6a $\lambda^4$ -Tritiapentalene **2** could be a potential precursor for the formation of C<sub>5</sub>S<sub>2</sub> upon FVP. However, no evidence for the presence of this heterocumulene, which has a strong absorption at 2100 cm<sup>-1</sup>,<sup>3</sup> was found in the IR spectrum of the pyrolysis products. The main products observed were C<sub>3</sub>S<sub>2</sub>, CS<sub>2</sub> and CS. A small absorption at 1754 cm<sup>-1</sup> was observed; this is in the thioketene region.<sup>4</sup> When 2,5-dimethyl-1,6,6a $\lambda^4$ -tritiapentalene was pyrolysed under the same conditions this peak was the strongest peak followed by the CS<sub>2</sub> absorption at 1526 cm<sup>-1</sup>.

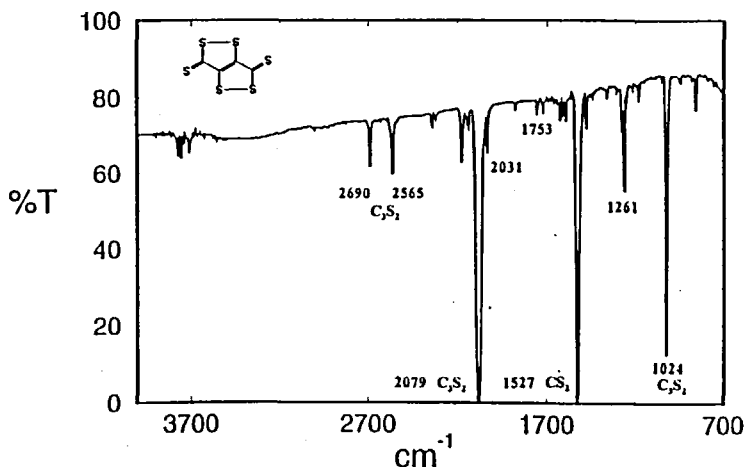


Fig 1. IR spectrum (Ar matrix, 10K) of FVP-products from 1,2-dithiolo[4,3-c][1,2]dithiole-3,6-dithione, **3**.

The absorption at 1754 cm<sup>-1</sup> corresponds to thioketene. The presence of thioketene was further substantiated by combined FVP-MS studies. However, it was observed that the *m/z* 58 peak corresponding to thioketene was a mixture. Closer examination of the IR spectrum showed two peaks at 3322 and 3012 cm<sup>-1</sup> which is characteristic for ethynyl thiol which is isobar to thioketene.

Compound **3** could be a possible candidate for the formation of C<sub>4</sub>S<sub>2</sub> as the presence of this species has been observed by neutralisation-reionization mass spectrometry (NRMS) of **3**.<sup>5</sup> However, we were not able to locate absorptions for C<sub>4</sub>S<sub>2</sub> in the IR spectrum of the pyrolysis products.

We ascribe two absorptions at 2031 and 1753 cm<sup>-1</sup> to :C<sub>4</sub>S, which has hitherto not been identified by matrix isolation with certainty<sup>6</sup> but observed by NRMS.<sup>7</sup> Ab initio calculations at the level MP2/6-31G\* give the theoretical values of 2102 and 1818 cm<sup>-1</sup> for the two observable absorptions, if these values are reduced by 3% they correspond to 2038 and 1763 cm<sup>-1</sup>. We have not been able to confirm the presence of :C<sub>4</sub>S by FVP-MS due to the high pyrolysis temperature of **3**.

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