



# The Formation of 1,2-Propadiene-1,3-dithione (Carbon Subulfide) from Flash Vacuum Pyrolysis of 1,2-Dithiole-3-thiones.

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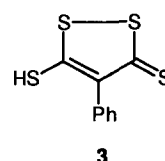
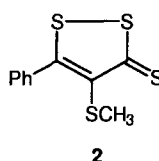
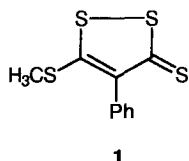
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**Abstract:** 1,2-Propadiene-1,3-dithione (carbon subulfide) has been obtained by flash vacuum pyrolysis of alkylthio substituted 1,2-dithiole-3-thiones in the temperature range 800-1000°C. The dithione was isolated and characterized in an argon matrix at 10K. Copyright © 1996 Elsevier Science Ltd

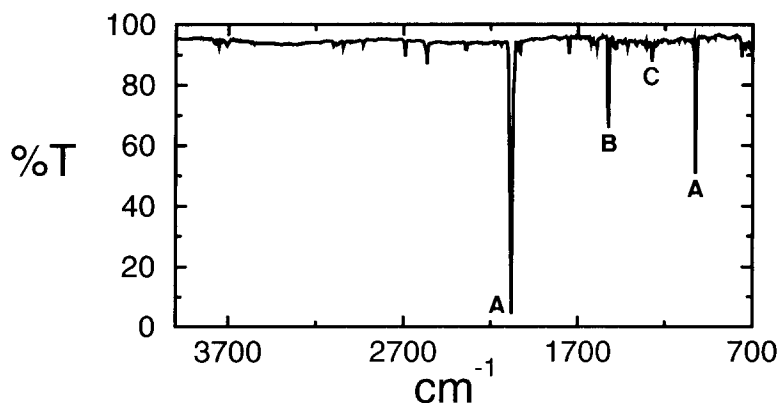
Carbon subulfide  $C_3S_2$  is the only member of the class of sulfur containing heterocumulenes  $C_nS_2$  ( $n > 1$ ) which is stable enough to allow isolation for a shorter time at room temperature.<sup>1</sup> Whereas carbon suboxide  $C_3O_2$  has been used in a variety of chemical reactions,<sup>2</sup> the thio-analogue, due to the difficulties to find an appropriate synthetic method,<sup>1</sup> has only found little use in synthetic organic chemistry.<sup>3,4</sup>

During a study of the formation of thioacyl thioketenes by flash vacuum pyrolysis (FVP) of 1,2-dithiole-3-thiones we observed that  $C_3S_2$  was in some cases formed in substantial amounts.<sup>5,6</sup> This was particularly the case in the FVP of the parent 1,2-dithiole-3-thione. This encouraged us to study various 1,2-dithiole-3-thiones as potential precursors for  $C_3S_2$ .

We have found that 1,2-dithiole-3-thiones with an alkylthio substituent in the 5-position *e.g.* 5-methylthio-4-phenyl-1,2-dithiole-3-thione (**1**)<sup>7</sup> gave high amounts of carbon subulfide and minor amounts of carbon disulfide as the main products upon pyrolysis at 800 - 1000°C, at lower temperature the compounds were thermostable. The IR spectrum of the pyrolysis products in an Ar matrix at 10K shows the characteristic absorptions of  $\nu$  ( $cm^{-1}$ )  $CS_2$ : 2177 and 1526,  $C_3S_2$ : 2079 and 1024, CS: 1275. Fig 1 assigned according to ref. 8.

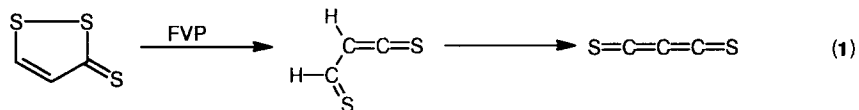


Dissociative ionization of 1,2-dithiole-3-thiones has recently been used to study a series of carbon disulfide radical cations  $\text{SC}_n\text{S}^{*+}$  in the gas phase of a mass spectrometer.<sup>9</sup>

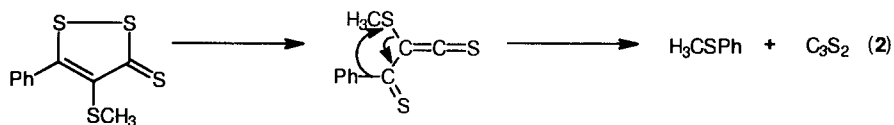


**Fig 1.** IR spectrum of the pyrolysis products of compound **2** (Ar-matrix 10K) produced by FVP (900°C,  $10^{-5}$  mbar). Bands A are due to  $\text{C}_3\text{S}_2$ , band B is due to  $\text{CS}_2$  and band C to CS.

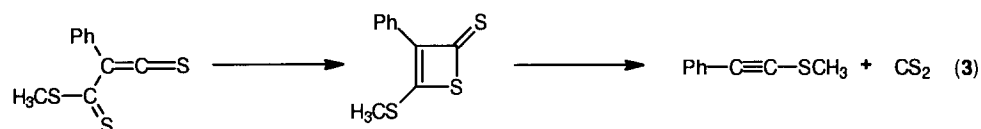
In the case of 1,2-dithiole-3-thione the primary product is thioformyl thioketene<sup>5</sup> and the carbon subsulfide may be formed from this Eq. 1.



When an alkylthio substituent is located in the 5-position an obvious pathway is present for the formation of  $\text{C}_3\text{S}_2$  primarily by a loss of the two disulfide sulfurs and a subsequent loss of the *S*-alkyl group and the phenyl group. However, this pathway is not possible in the case where the alkylthio group is in the 4 position *e.g.* 4-methylthio-5-phenyl-1,2-dithiole-3-thione (**2**). It is therefore in all cases more reasonable to assume that the primary product for the formation of  $\text{C}_3\text{S}_2$  is a thioacyl thioketene.<sup>5</sup> Eq. 2.



In both cases the formation of  $C_3S_2$  from the thioacyl thioketene can be explained by a 1,3-shift of the phenyl group on to the alkythio group with a subsequent loss of an *S*-alkyl thiophenol. We have, however, not been able to locate the peaks with certainty due to the phenyl alkylsulfide in the IR spectra. Apart from the  $C_3S_2$  and  $CS_2$  peaks only very small peaks are observed. Furthermore, the strong absorptions of the phenyl alkylsulfides are mainly due to the aromatic part, which is also found in the normal fragmentation product an alkythio phenyl alkyne from the decomposition of the thioacyl thioketenes<sup>5,10</sup> Eq. 3.



When 5-mercapto-4-phenyl-1,2-dithiole-3-thione<sup>11</sup> (3) is pyrolysed the formation of  $C_3S_2$  is less pronounced. The reason may be that the thioketene initially formed, *i.e.* dithiocarboxy phenyl thioketene, fragments *via* another reaction pathway.

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## REFERENCES AND NOTES

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7. The FVP apparatus employed a 10 cm length (0.8 cm i.d.) quartz tube in housings flanged to a Leybold-Heraeus closed-cycle liquid He-cryostat for Ar-matrix isolation (10-15K). Pressures were  $10^{-5}$  -  $10^{-6}$  mbar. For matrix isolation samples were codeposited with *ca.* 200 mbar Ar in 20 min. on a BaF<sub>2</sub> disk. IR spectra were recorded on a Perkin-Elmer FTIR-PARAGON 1000 spectrometer at a resolution of 2 cm<sup>-1</sup>. As it is not possible to obtain a quantitative value for the amount of C<sub>3</sub>S<sub>2</sub>, the amount was estimated by comparison of the C<sub>3</sub>S<sub>2</sub> peaks versus the CS<sub>2</sub> peaks. The ratios  $A_{2079}/A_{1527}$  for pyrolysis at 900°C are for the three compounds (1) : 4.0; (2) : 2.5; (3) : 0.40 giving a reasonable estimate of the relative amounts of C<sub>3</sub>S<sub>2</sub> formed in the pyrolysis.
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