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

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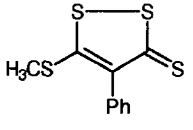
Abstract: 1,2-Propadiene-1,3-dithione (carbon subsulfide) has been obtained by flash vacuum pyrolysis of alkylthio substituted 1,2-dithiole-3-thiones in the temperature range 800-1000°C. The dithione was isolated and characterized in an argon matrix at 10K. Copyright © 1996 Elsevier Science Ltd

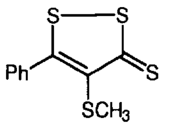
Carbon subsulfide C_3S_2 is the only member of the class of sulfur containing heterocumulenes C_nS_2 (n>1) which is stable enough to allow isolation for a shorter time at room temperature.[1] Whereas carbon suboxide C_3O_2 has been used in a variety of chemical reactions,[2] the thio-analogue, due to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

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.[5,6] 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**)[7] gave high amounts of carbon subsulfide 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 ν (cm^{-1}) CS_2: 2177 and 1526, C_3S_2: 2079 and 1024, CS: 1275. Fig 1 assigned according to ref. 8.



1



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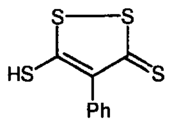


3

Dissociative ionization of 1,2-dithiole-3-thiones has recently been used to study a series of carbon disulfide radical cations $SC_nS^{•+}$ in the gas phase of a mass spectrometer.[9]

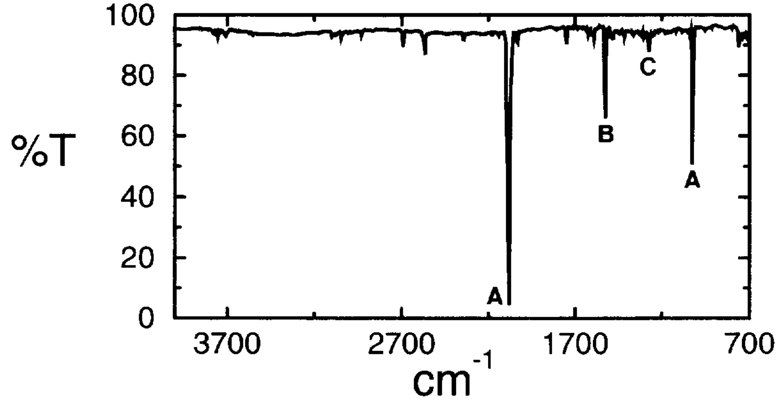
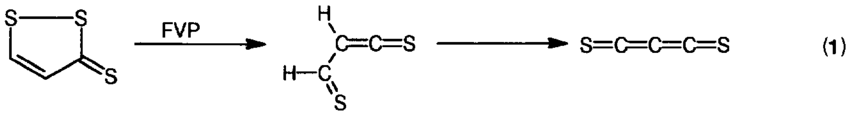
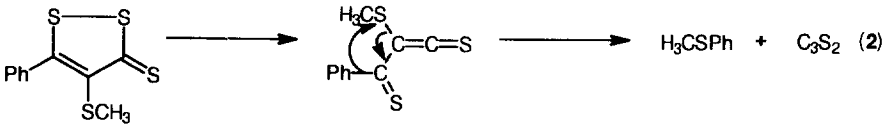


Fig 1. IR spectrum of the pyrolysis products of compound **2** (Ar-matrix 10K) produced by FVP (900°C, 10^{-5} mbar). Bands A are due to C_3S_2, band B is due to CS_2 and band C to CS.

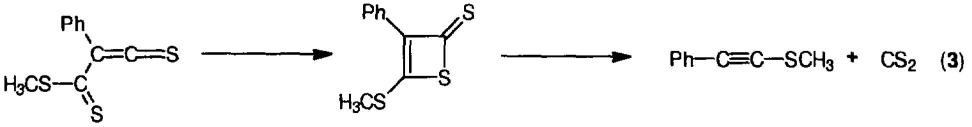
In the case of 1,2-dithiole-3-thione the primary product is thioformyl thioketene[5] and the carbon subsulfide may be formed from this Eq. 1.



When an alkylthio substituent is located in the 5-position an obvious pathway is present for the formation of C_3S_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 C_3S_2 is a thioacyl thioketene.[5] 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[5,10] Eq. 3.



When 5-mercapto-4-phenyl-1,2-dithiole-3-thione[11] (**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

1. (a) Stadlbauer, W and Kappe, Th. *Chem.-Ztg.* **1977**, 101, 137-141.
   (b) Mihály, T. B. and Kauffman, G. B. *Polyhedron*, **1985**, 4, 775-781.
   (c) Schaumann, E. In *Methoden Org. Chem. (Houben-Weyl)* **1985**, Vol. E11, Thieme Verlag, Stuttgart 1985, 232-233.
2. (a) Kappe, Th. and Ziegler, E. *Angew. Chem.*, **1974**, 86, 529-42.
   (b) Kappe, Th. In *Methoden Org. Chem. (Houben-Weyl)* **1993**, Vol. E15, Thieme Verlag, Stuttgart 1993, 3119-3145.
3. Stadlbauer, W.; Kappe, Th. and Ziegler, E. *Z. Naturforsch., B,* **1977**, 32B, 893-897.

4. Stadlbauer, W.; Kappe, Th. and Ziegler, E. *Z. Naturforsch., B,* **1978**, 33B, 89-93.

5. Kappe, C. O.; Pedersen, C. Th.; Catel, J. -M. and Mollier, Y. *J. Chem. Soc., Perkin Trans.* 2, **1994**, 351-355.

6. Pedersen, C. Th. and Kappe, C. O. *Phosphorus Sulfur,* **1994**, 95-96, 485-486.

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_2 disk. IR spectra were recorded on a Perkin-Elmer FTIR-PARAGON 1000 spectrometer at a resolution of 2 cm^{-1}. As it is not possible to obtain a quantitative value for the amount of C_3S_2, the amount was estimated by comparison of the C_3S_2 peaks versus the CS_2 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_3S_2 formed in the pyrolysis.

8. Takeuchi, N. and Tasumi M. *J. Mol. Spectrosc.*, **1981**, 90, 116.

9. Wong, M. W.; Wentrup, C. and Flammang, R. *J. Phys. Chem.*, **1995**, 99, 16849-16856.

10. Pedersen. C. Th.; Oddershede, J. and Sabin, J. R. *J. Chem. Soc., Perkin Trans. 2,* **1981**,1062-1065.

11. The dithiole-3-thiones pyrolysed were prepared by conventional methods *cf.* ref. 12 and 13.

12. Pedersen, C. Th. *Adv. Heterocycl. Chem.*, **1982**, 31, 63-113.

13. Pedersen, C. Th. *Sulfur Reports*, **1995**, 16, 173-221.

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