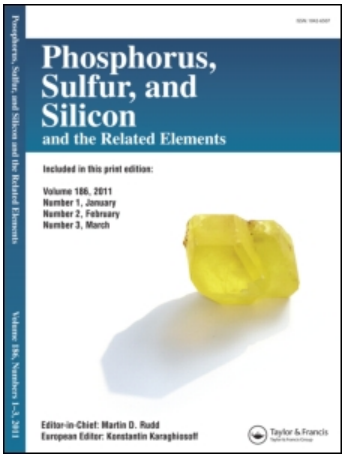

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THE FORMATION OF THIOACYLTHIOKETENES BY FLASH VACUUM PYROLYSIS OF 1,2-DITHIOLE DERIVATIVES.

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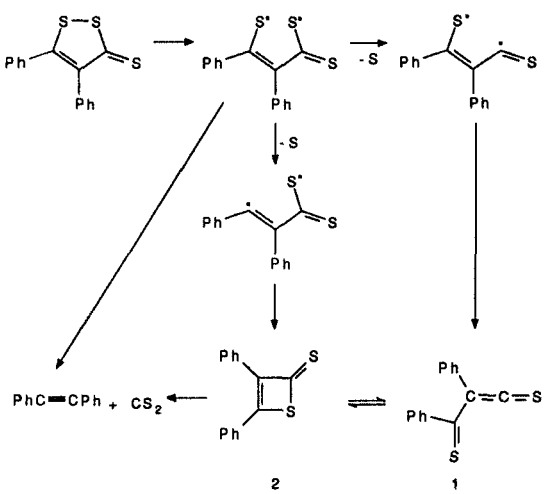
Abstract The formation of thioacylthioketenes has been observed in Flash Vacuum Pyrolysis of various 1,2-dithiole derivatives. In some cases C_3S_2 , 1,2-propadiene-1,3-dithione is formed too.

Thioacylthioketenes **1** has hitherto been an unknown class of compounds. We have shown the existence of such compounds by flash vacuum pyrolysis of various 1,2-dithiole derivatives, such as 1,2-dithiole-3-thiones, 3-iodo-1,2-dithiolylium salts, 3-methylthio-1,2-dithiolylium salts and 1,2-dithiole-3-one-tosylhydrazone sodium salts. Possible reaction pathways for the pyrolysis of 1,2-dithiole-3-thiones are depicted below.



It has further been shown that the thioacylthioketenes rearrange to give thiete-2-thiones **2**, which fragment into CS_2 and alkynes.
As the primary products from the iodo salt and the tosylhydrazone salt probably are the 1,2-dithiole-3-ylidenes (1,2-dithiole carbenes) the rapid rearrangement of the

carbenes to thioacylthioketenes has been experimentally shown. This rearrangement has earlier been suggested based on CNDO calculations.[1]

As many methods which have been used succesfully to prepare 1,3-TTF's (2,2'-bis(1,3-dithiolylidenes)) proceed via carbenes, this easy rearrangement explains why methods giving excellent yields of 1,3-TTF fail to give 1,2-TTF's (3,3'-bis(1,2-dithiolylidenes)) as the carbenes rearrange before they can react further to give the 1,2-TTF's.

In the pyrolysis of the unsubstituted 1,2-dithiole-3-thione both the formation of the expected thioformyl thioketene and substantial amounts of C_3S_2 (1,2-propandiene-1,3-dithione) are observed.[2]

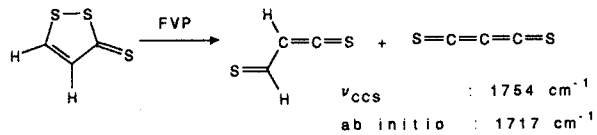


Fig. 1 shows the IR-spectrum of an argon matrix obtained from the FVP-products formed from 1,2-dithiole-3-thione at 1000°.

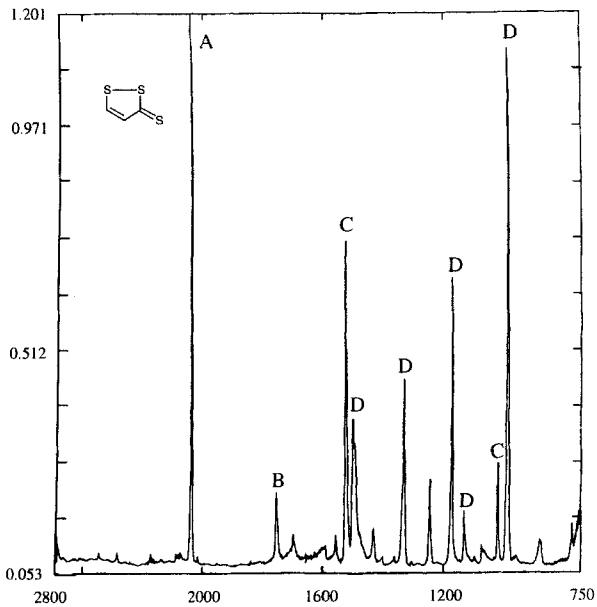


Fig.1 IR spectrum of the pyrolysis products of 1,2-dithiole-3-thione (Ar-matrix, 17 K) produced by FVP (1000°, 10^{-5}mbar). A band due to C_3S_2 , B band due to thioformyl thioketene, C band due to CS_2 and D bands due to unpyrolysed starting material, 1,2-dithiole-3-thione.

[1] C.Th. Pedersen, J. Oddershede and J. Sabin, *J.Chem.Soc., Perkin Trans. 1*,1981, 1062.

[2] C. Oliver Kappe, C.Th. Pedersen, J.-M. Catel and Y. Mollier, *J.Chem.Soc., Perkin. Trans.2*,1994, 351.