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### The Formation of Thioacylthioketenes by Flash Vacuum Pyrolysis of 1,2-Dithiole Derivatives

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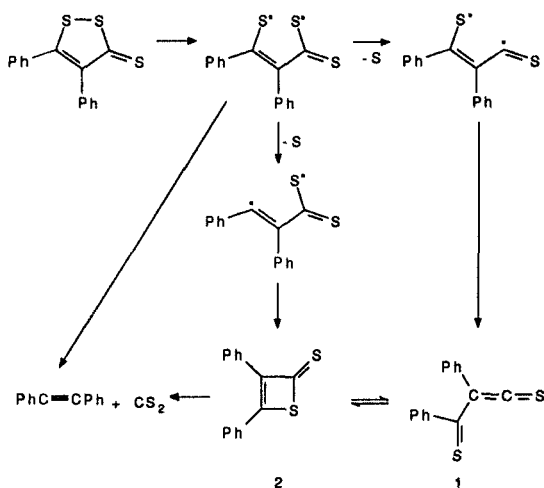
## THE FORMATION OF THIOACYLTHIOKETENES BY FLASH VACUUM PYROLYSIS OF 1,2-DITHIOLE DERIVATIVES.

Carl Th. Pedersen<sup>a</sup> and C. Oliver Kappe<sup>b</sup>

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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-dithiolylum salts, 3-methylthio-1,2-dithiolylum 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.<sup>1</sup>

As many methods which have been used successfully to prepare 1,3-TTF's (2,2'-bis(1,3-dithiolylylidenes)) 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-dithiolylylidenes)) 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.<sup>2</sup>

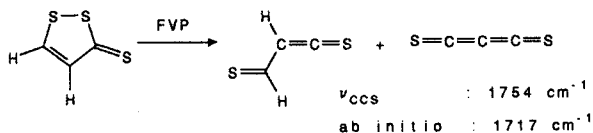
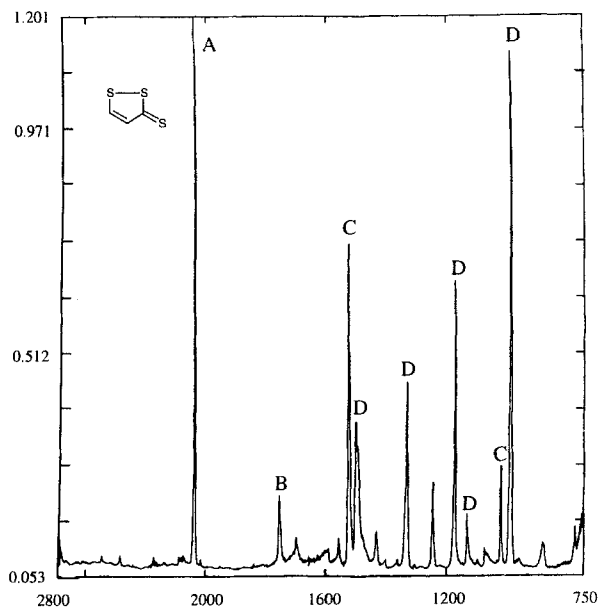


Fig. 1 shows the IR-spectrum of an argon matrix obtained from the FVP-products formed from 1,2-dithiole-3-thione at 1000°.



**Fig.1** IR spectrum of the pyrolysis products of 1,2-dithiole-3-thione (Ar-matrix, 17 K) produced by FVP (1000°, 10<sup>-5</sup>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.

<sup>1</sup> C.Th. Pedersen, J. Oddershede and J. Sabin, *J.Chem.Soc., Perkin Trans. 1*, 1981, 1062.

<sup>2</sup> C. Oliver Kappe, C.Th. Pedersen, J.-M. Catel and Y. Mollier, *J.Chem.Soc., Perkin. Trans.2*, 1994, 351.