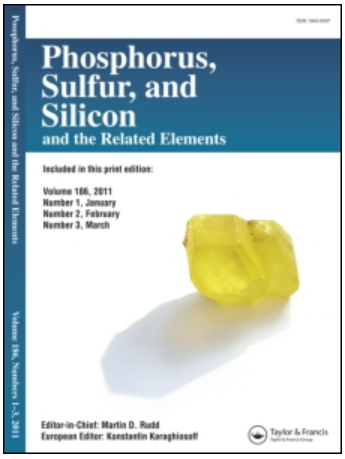

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Pedersen, Carl Th.(1997) 'The Formation of Heterocumulenes from 1,2-Dithiole Derivatives upon Flash Vacuum Pyrolysis', Phosphorus, Sulfur, and Silicon and the Related Elements, 120: 1, 399 — 400
To link to this Article: DOI: 10.1080/10426509708545567
URL: http://dx.doi.org/10.1080/10426509708545567

Phosphorus, Sulfur, and Silicon, 1997, Vol. 120 & 121, pp. 399–400
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THE FORMATION OF HETEROCUMULENES FROM 1,2-DITHIOLE DERIVATIVES UPON FLASH VACUUM PYROLYSIS.

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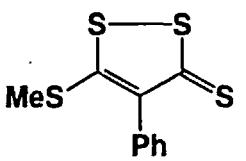
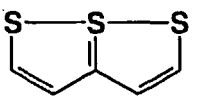
Abstract 1,2-Dithiole derivatives such as alkylthio substituted 1,2-dithiole-3-thiones, 1,6,6aλ^4-tritiapentalenes and 1,2-dithiolo[4,3-*c*]-[1,2]dithiole-3,6-dithione gives rise to C_3S_2, $:C_4S$ and thioketenes upon flash vacuum pyrolysis in the temperature range 800-1000 °C.

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.

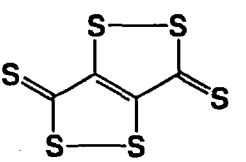
During more general studies of 1,2-dithiole derivatives we have studied the flash vacuum pyrolysis (FVP) of 1,2-dithiole derivatives such as **1**, **2** and **3**.



(1)



(2)



(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[1]. 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[2] the preparative aspects of this pyrolysis i studied further.

1,6,6aλ⁴-Tritiapentalene **2** could be a potential precusor for the formation of C_5S_2 upon FVP. However, no evidence for the presence of this heterocumulene, which has a strong absorption at 2100 cm^{-1}, [3] was found in the IR spectrum of the pyrolysis products. The main products observed were C_3S_2, CS_2 and CS. A small absorption at 1754 cm^{-1} was observed; this is in the thioketene region.[4] When 2,5-dimethyl-1,6,6aλ⁴-tritiapentalene was pyrolysed under the same conditions this peak was the strongest peak followed by the CS_2 absorption at 1526 cm^{-1}.

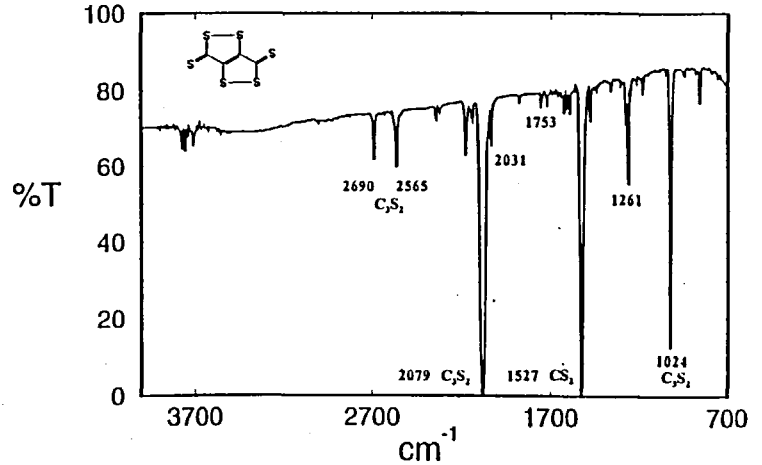


Fig 1. IR spectrum (Ar matrix, 10K) of FVP-products from 1,2-dithiolo[4,3-*c*][1,2]dithiole-3,6-dithione, **3**.

The absorption at 1754 cm^{-1} 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^{-1} which is characteristic for ethynyl thiol which is isobar to thioketene.

Compound **3** could be a possible candidate for the formation of C_4S_2 as the presence of this species has been observed by neutralisation-reionization mass spectrometry (NRMS) of **3**.[5] However, we were not able to locate absorptions for C_4S_2 in the IR spectrum of the pyrolysis products.

We ascribe two absorptions at 2031 and 1753 cm^{-1} to $:C_4S$, which has hitherto not been identified by matrix isolation with certainty[6] but observed by NRMS.[7] Ab initio calculations at the level MP2/6-31G* give the theoretical values of 2102 and 1818 cm^{-1} for the two observable absorptions, if these values are reduced by 3% they correspond to 2038 and 1763 cm^{-1}. We have not been able to confirm the presence of $:C_4S$ by FVP-MS due to the high pyrolysis temperature of **3**.

Acknowledgment. This work has been supported by The Carlsberg Foundation and The Danish Natural Science Research Council.

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