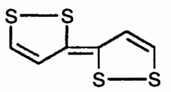
Thioacylthioketenes by Pyrolysis of 1,3-Dithiethanes and 1,2-Dithiole Derivatives

C. Oliver Kappe,[a] Carl Th. Pedersen,[*,†,a] Jean-Marie Catel[b] and Yves Mollier[b]
[a] *Department of Chemistry, The University of Queensland, Brisbane, QLD 4072, Australia*
[b] *ISMRA, Laboratoire de Chimie des Composés Thio-organiques, 14050 Caen Cedex, France*

Thioacylthioketenes are formed by flash vacuum pyrolysis (FVP) of 1,3-dithiethanes **6**, 1,2-dithiole-3-thiones **11**, **14**, **15**, 3-iodo-1,2-dithiolylium iodide **9**, 3-methylthio-1,2-dithiolylium iodides **16**, **17** and 1,2-dithiol-3-one tosylhydrazone sodium salt **10**. They show IR absorption in the region 1754–1700 cm^{-1} due to the C=C=S grouping. It is proposed based on the results obtained that 1,2-dithiol-3-ylidenes (1,2-dithiole carbenes) rearrange to give thioacylthioketenes which further rearrange forming thiete-2-thiones. The latter finally fragment into carbon disulfide and alkynes. Formation of C_3S_2 has been observed in the pyrolysis of the dithiethanes and 1,2-dithiole-3-thione.

Only a few examples of the 3,3′-bis(1,2-dithiolylidenes) **1** are known, whereas the isomeric 2,2′-bis(1,3-dithiolylidenes), TTFs, **2** are a class of compounds well known for their behaviour as the donor part of organic conductors.[1]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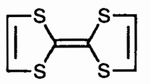
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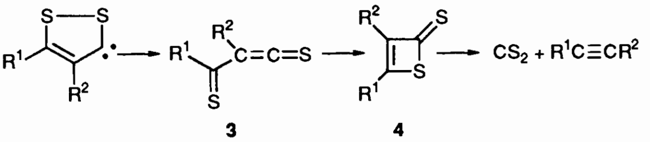
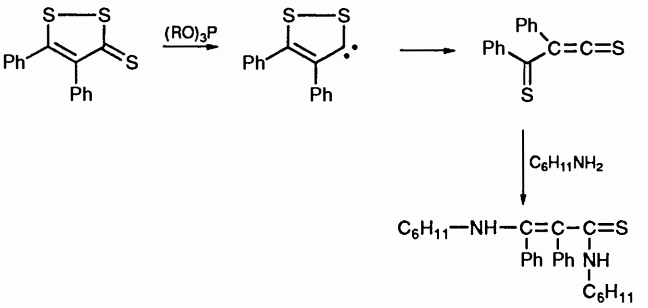
It has in many cases been observed that methods giving excellent yields for the synthesis of **2** were not suitable, or only gave low yields, when used for the synthesis of **1**.[2,3] As many of the methods used in the 1,3-dithiole series are assumed to proceed *via* carbenes or carbenoid species it has been proposed, based on theoretical calculations, that the difference between the two series is due to the different stabilities of the carbenes 1,3-dithiol-2-ylidene *versus* 1,2-dithiol-3-ylidene.[4] CNDO calculations suggested that the S–S bond is easily broken in the 1,2-dithiole carbene to give thioacylthioketenes **3** which undergo rearrangement to give thiete-2-thiones **4** which further fragment into CS_2 and alkynes,[4] as shown in Scheme 1.



3	a	b	c	d	e	f
R^1	SMe	SMe	Ph	H	Ph	H
R^2	SMe	4-MePh	Ph	Ph	H	H

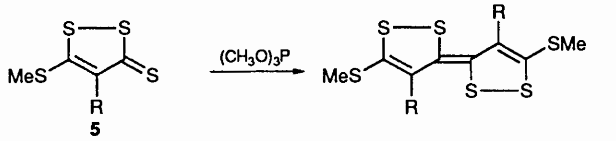
Scheme 1

One of the successful synthetic methods in the 1,3-dithiole series is desulfurization of thiones using trivalent phosphorus compounds. However, it has been shown that 1,2-dithiole-3-thiones in most cases do not react with trivalent phosphorus compounds or give complex reaction mixtures. In a few cases in the presence of cyclohexylamine, compounds corresponding to the reaction of two moles of amine with one mole of a thioacylthioketene have been isolated (Scheme 2).[3] The thioacylthioketene itself, however, has never been identified.



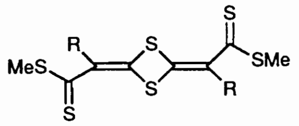
Scheme 2

It has recently been claimed that 1,2-dithiole-3-thiones with a methylthio substituent in the 5-position **5** give reasonable yields (50%) of methylthio substituted 1,2-TTFs by reaction with phosphites (Scheme 3).[5]



Scheme 3

However, it has been shown that the compounds formed are not 1,2-TTF's but the isomeric 1,3-dithiethanes **6**.[6]


6a R = SMe
b R = *p*-MePh

Results and Discussion

Pyrolysis of 1,3-*Dithiethanes* **6a**, **b**.—The dithiethanes **6a**, **b** are the dimers of thioacylthioketenes **3a**, **b**. Seybold *et al.*[7] have shown that dithiethanes bearing only simple alkyl or aryl substituents under flash vacuum pyrolysis (FVP) conditions fragment to alkyl or aryl substituted thioketenes. However, they were not able to prepare acylthioketenes by this method. In this paper we show that dithiethanes **6a**, **b** upon FVP give rise to the monomeric thioacylthioketenes **3a**, **b**. These display an IR absorption in the region 1790–1700 cm^{-1} *i.e.* the region for simple thioketenes.[8] The thioacylthioketenes could not be isolated because they fragment to give CS_2 and alkynes.

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† *Permanent address*, Department of Chemistry, Odense University, DK-5230 Odense M, Denmark.

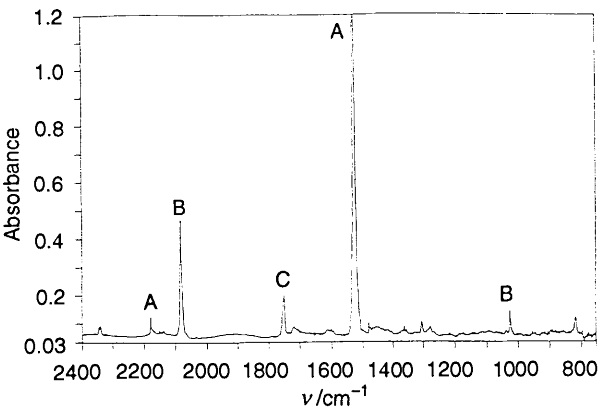
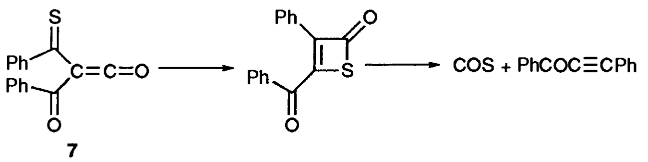


Fig. 1 IR spectrum of the pyrolysis products of **6b** (Ar-matrix, 17 K) produced by FVP (900 °C, 10^{-5} mbar). No significant peaks are present higher than 2400 cm^{-1}. Bands due to CS_2 (A) appear at 2173 and 1528 cm^{-1}. Bands due to C_3S_2 (B) appear at 2073 and 1025 cm^{-1}. Band due to thioketene (C) appears at 1746 cm^{-1}.

Analogous reactions have been described for the thioacylketene **7**[9] (Scheme 4) and for acylthioketenes.[7]

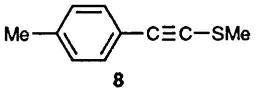


Scheme 4

It has further been shown that imidoylketenes undergo a similar rearrangement. In this case, however, the presence of the corresponding azetin-2-one could be directly observed.[10]

The IR spectra (Fig. 1) recorded of the pyrolysis products of **6a** and **6b** in an Ar-matrix at 17 K show the following bands (ν/cm^{-1}): 2177 and 1528 (CS_2), 2073 and 1025 (C_3S_2, propadiene-1,3-dithione) assigned according to ref. 11. The two spectra further show bands at 1700 and 1746 cm^{-1} respectively, ascribed to C=C=S groups.[8] The value 1700 cm^{-1} is unusually low for the thioketene absorption. A value of 1698 cm^{-1} has, however, been reported for phenyl (methylthio)thioketene.[12] A value near 1700 cm^{-1} is also in agreement with *ab initio* calculations.[13]

The acetylene **8** formed by decomposition of the corresponding thiete-2-thione from the preparative pyrolysis of **6b** was isolated and identified by GC–MS and comparison with an authentic mass spectrum.[14]



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The pyrolysis of **6b** was further monitored by direct on-line mass spectrometry (Fig. 2).

The mass spectral analysis demonstrates the formation of a species *m/z* 238 which corresponds to the monomeric thioacylthioketene **3b** or the corresponding thiete-2-thione. At approximately 470 °C the amount of thioketene begins to decrease at the same time as the amount of CS_2 (*m/z* 76) and the acetylene **8** (*m/z* 162) increase. As the thioacylthioketene and the thiete-2-thione are isomeric, nothing can be said about the relative amounts of the two species. The observation is in accordance with Scheme 1, although the dramatic increase of *m/z* 76 and 162 at higher temperatures (compared with the only moderate decrease of *m/z* 238) suggest that other pathways for the formation of CS_2 and acetylene **8** might be involved.

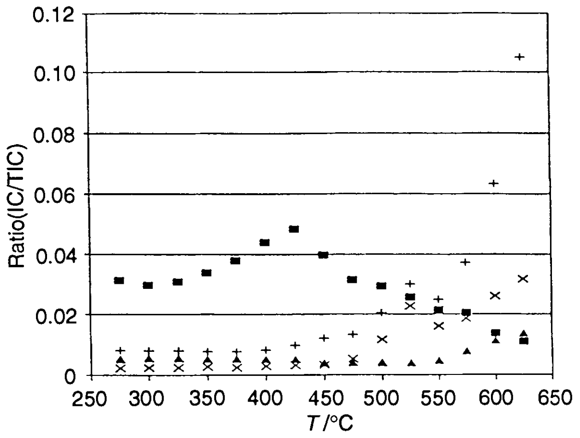


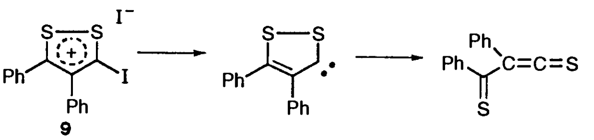
Fig. 2 FVP–MS monitoring of the pyrolysis of **6b**. Ion current *vs.* total iron current (TIC) as a function of temperature (°C). ■: *m/z* 238; ×: *m/z* 162; +: *m/z* 76; ▲: *m/z* 100 (C_3S_2). Due to the high mass of M^+, *m/z* 476, it could not be monitored.

The thioketene **3a** was only observable up to 750 °C whereas the other thioketenes showed a remarkable thermal stability, being observable under FVP conditions at nominal temperatures above 1000 °C.

In the IR spectra from the pyrolysis of **6a** and **6b**, abundant peaks corresponding to C_3S_2 are observed. It is known that C_3S_2 can be formed by pyrolysis of CS_2.[15] However, if CS_2 is subjected to FVP under the same conditions as used here for the pyrolysis of the dithietanes, no bands corresponding to C_3S_2 could be observed. This means that C_3S_2 is formed directly, either from the dithietanes or the thioacylthioketenes.*

Abundant peaks corresponding to C_3S_2 are also observed in the IR spectra from pyrolysis products of 1,2-dithiole-3-thione **18** (*vide infra*).

Pyrolysis of 3-*Iodo*-4,5-*diphenyl*-1,2-*dithiolylium Iodide* **9**.—Behringer *et al.*[2b] have pyrolysed 1,2-dithiolylium iodide **9** in solution in an attempt to obtain the 1,2-dithiole-3-carbene but did not find evidence for its formation (Scheme 5).



Scheme 5

If the iodide **9** is subjected to FVP, a signal at 1734 cm^{-1} is observed, ascribable to C=C=S. In addition, bands corresponding to the principal bands of diphenylacetylene in an Ar-matrix are found (see Experimental). A strong CS_2 band is also present. This indicates the formation of the thioacylthioketene **3c** which decays *via* the thiete-2-thione to diphenylacetylene and CS_2 according to Scheme 1.

Pyrolysis of the 4,5-*Diphenyl*-1,2-*dithiol*-3-*one Tosylhydrazone Sodium Salt* **10**.—Pyrolysis of tosylhydrazone salt **10** gave rise to an IR spectrum very close to that obtained from the

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* As the ratios between the two C_3S_2 bands and the CS_2 band are the same in the case of the *E*-isomer **6a** and the *Z*-isomer, C_3S_2 is probably not formed from the dithietane but from the thioacylthioketene by a 1,3 shift of *e.g.* the 4-methylphenyl group of **3b** onto the methylthio sulfur atom with subsequent loss of (4-methylphenyl)methyl sulfide. This is in accordance with the observation that the signals corresponding to C_3S_2 are less pronounced in the case of **6b** than **6a**, MeS being a better leaving group than an aryl group.

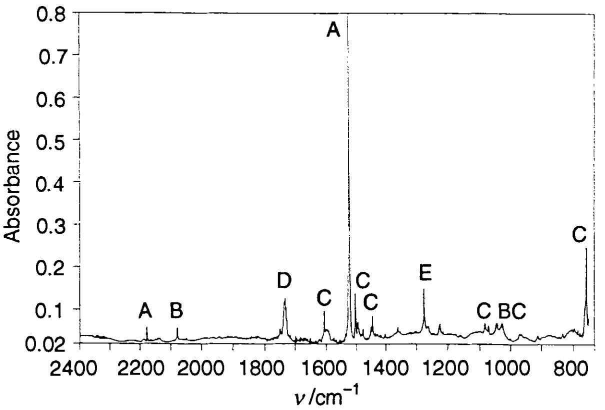
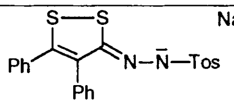


Fig. 3 IR spectrum of the pyrolysis products of **11** (Ar-matrix, 17 K) produced by FVP (930 °C, 10^{-5} mbar). No significant peaks are present above 2400 cm^{-1}. Bands due to CS_2 (A), bands due to C_3S_2 (B), bands due to diphenylacetylene (C), see Experimental, band due to thioketene (D) at 1734 cm^{-1}, and a band possibly due to CS (E) at 1275 cm^{-1}.

iodide **9**. As the tosylhydrazone will undergo a Steven–Bamford reaction leading to a carbene, under the pyrolysis conditions used, the formation of a thioketene is again a strong evidence for the rearrangement of the 1,2-dithiole-3-carbene to a thioacylthioketene.



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Pyrolysis of 1,2-*Dithiole*-3-*thiones* **11**, **14** *and* **15** *and* 3-*Methylthio*-1,2-*dithiolylium Iodides* **16**, **17**.—Pyrolysis of 4,5-diphenyl-1,2-dithiol-3-thione **11** at 950 °C with IR monitoring (Fig. 3) of the products in an Ar-matrix gave rise to a strong CS_2 band, bands corresponding to diphenylacetylene, and a band at 1734 cm^{-1}. A band at 1275 cm^{-1} was also present. It has been proposed[16] that a band at this position in a coordination compound with 3-methylthiete-2-thione as a ligand is due to the thiete–thione system. In the pyrolysis of **11** (Scheme 6) it is, however, more likely that this band is due to CS which absorbs at 1275 cm^{-1} ref. 11.[*]

The pyrolysis of **11** can proceed by various pathways.

The primary reaction is probably in all cases an opening of the weak S–S bond and subsequent loss of sulfur to give **12** or **13**. This is supported by the easy scrambling among all 3 sulfur atoms at temperatures above 125 °C if the thione sulfur in 1,2-dithiole-3-thione is marked with ^{34}S.[17]

However, it cannot be excluded that species in which a C–S bond is broken primarily is present, as this has been observed in mass spectrometric fragmentation of 1,2-dithiole-3-thiones.[18]

Monitoring of the pyrolysis of thione **11** by direct on-line mass spectrometry (Fig. 4) demonstrates that the ion *m*/*z* 286 corresponding to **11** begins to decrease at the same temperature at which the ion *m*/*z* 254 corresponding to the thioketene **3c** increases. When *m*/*z* 254 reaches its maximum, *m*/*z*s 76 and 178 corresponding to CS_2 and diphenylacetylene, respectively, increase.

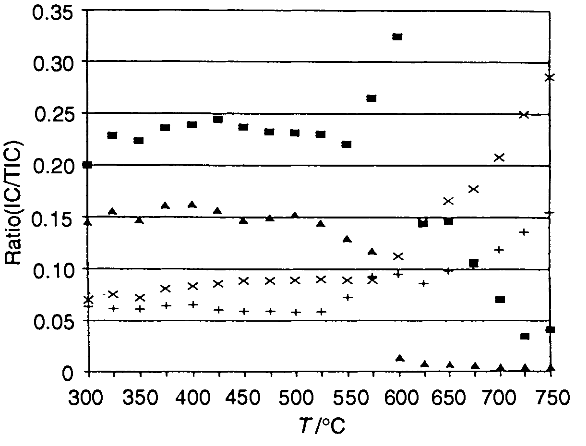
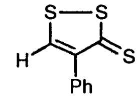


Fig. 4 FVP–MS monitoring of the pyrolysis products of **11**. Ion currents *vs*. total ion current (TIC) as a function of temperature (°C) ■: *m*/*z* 254; ▲: *m*/*z* 286; ×: *m*/*z* 178; +: *m*/*z* 76.



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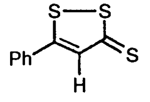

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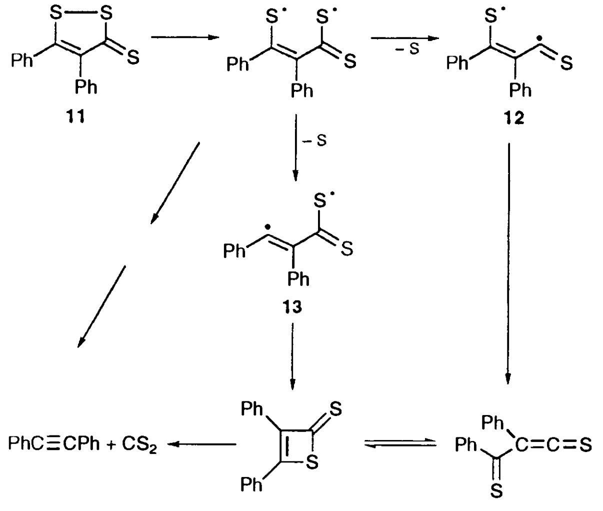
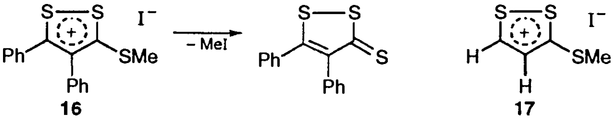


Scheme 6

The 4- and 5-phenyl-1,2-dithiol-3-thiones **14** and **15** behave in the same manner as **11** and give rise to the thioacylthioketenes **3d** and **3e**, respectively, together with phenylacetylene and CS_2 (see Experimental).

If 3-methylthio-4,5-diphenyl-1,2-dithiolylium iodide **16** or 3-methylthio-1,2-dithiolylium iodide **17** is pyrolysed, the result is the same as that obtained by pyrolysis of **11** and **18**, respectively (Scheme 7).



Scheme 7

This indicates that the primary step is a demethylation of the methylthio salts with formation of the thione. Indeed, peaks corresponding to MeI can be observed in the matrix IR spectra.

The parent 1,2-dithiole-3-thione **18** gives rise to thioformylthioketene **3f** with a strong IR absorption at 1754 cm^{-1}. The

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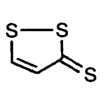
[*] However, the same band is also found in the spectra of the pyrolysis products from the iodide **9** and the tosylhydrazone sodium salt **10**. In these cases it is less likely that CS should be formed. It can therefore not be excluded that this band is due to the presence of 3,4-diphenylthiet-2-thione stabilized by the phenyl substituents. This is further substantiated by *ab initio* molecular orbital calculations at the HF/6-31G* level which gives a value at 1307 cm^{-1} for the most intense band in the parent thiete-2-thione.[13]

Table 1 IR absorption of thioketenes **3g–f** (Ar-matrix, 17 K)

	3a	**3b**	**3c**	**3d**	**3e**	**3f**
$\nu_{C=C=S}$/cm^{-1}	1700	1748	1734	1749	1751	1754

absorption at this value is in accordance with *ab initio* molecular orbital calculations at the MP2/6-31G* level which gives a value at 1717 cm^{-1} for the S-*E* form **19** of the thioketene.[13]



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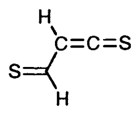

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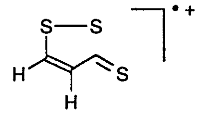
In contrast to other 1,2-dithiole-3-thiones, a strong absorption due to C_3S_2 is present when the unsubstituted thione **18** is pyrolysed. By comparison of the intensity of the C_3S_2 band with those of the thioketene and CS_2 at various temperatures, it is seen that the formation of C_3S_2 is more pronounced at lower temperatures. C_3S_2 could be formed by loss of hydrogen directly from the thioketene **3f**. However, it has been shown by Sülzle *et al.*[18] that ions corresponding to **20** are formed in the mass spectrum of thione **18**. Such species will by elimination of H_2S give C_3S_2.



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Conclusions

The existence of thioacylthioketenes **3a–f** has been demonstrated. They are formed by FVP of 1,3-dithietane diylidene bis(methyldithioacetates) **6a, b** and 4,5-substituted 1,2-dithiole-3-thiones **11**, **14**, **15** and **18** as well as 3-iodo-1,2-dithiolylium iodides **16**, **17** and the sodium salt of 4,5-diphenyl-1,2-dithiol-3-one tosylhydrazone **10**. As 1,2-dithiole-3-ylidenes are probably the primary reaction products from the last two groups of compounds, this is an indication of the easy rearrangement of these carbenes into thioacylthioketenes. The C=C=S group gives rise to an IR absorption in the region 1700–1754 cm^{-1} (Table 1) in accordance with *ab initio* calculations.[13] Thiete-2-thiones have not been directly observed with certainty because of their rapid fragmentation to CS_2 and acetylenes at the high temperatures required, but their existence has been proven indirectly by the formation of CS_2 and acetylenes by the decay of the thioacylthioketenes. Although the present study focused mainly on arylsubstituted thioacylthioketenes and their precursors, it may be assumed that other derivatives will behave in the same way.

Formation of C_3S_2 has also been observed in the pyrolysis of 1,3-dithiethanes and 1,2-dithiole-3-thione.

Experimental

General.—The FVP apparatus employed a 10 cm length (0.8 cm i.d.) quartz tube in housings flanged to a Leybold–Hereaeus closed-cycle liquid He cryostat for Ar-matrix isolation (14–18 K). Pressures were 10^{-3}–10^{-5} mbar.† For matrix isolation, samples were codeposited with *ca.* 200 mbar of Ar in 20 min on BaF_2 disks. IR spectra were recorded on a Perkin–Elmer 1700X FT-IR spectrometer at a resolution of 1 cm^{-1}. Further details and apparatus for preparative FVP were as previously described.[19] FVP–MS was carried out in an apparatus similar to the one used for matrix isolation, employing a quartz tube directly connected to the ion source of a Kratos MS25RFA mass spectrometer. There was a *ca.* 3 cm unheated length of quartz tube between the pyrolysis zone (200–1000 °C) and the ion source (200 °C). FVP temperatures used for mass spectrometry and IR spectroscopy should not be directly compared. Due to different apparatus design, temperatures are usually lower in the MS investigations. FVP–MS plots were obtained from full scan spectra with specific ions being monitored.

GC–MS was carried out on a Hewlett Packard 7970 MSD/5890 GC apparatus on a fused silica column with 5% polydiphenylsiloxane and 95% polydimethylsiloxane as stationary phase. Helium was used as carrier gas.

Preparations.—1,3-Dithietane diylidene bis(methyldithioacetates) **6a, b**,[6] 3-iodo-4,5-diphenyl-1,2-dithiolylium iodide **9**,[2b] 4,5-diphenyl-1,2-dithiol-3-one tosylhydrazone sodium salt **10**,[2b] 4,5-diphenyl-1,2-dithiol-3-thione **11**,[20] 4-phenyl-1,2-dithiol-3-thione **14**,[20] 5-phenyl-1,2-dithiol-3-thione **15**,[20] 3-methylthio-4,5-diphenyl-1,2-dithiolylium iodide **16**,[20] 3-methylthio-1,2-dithiolylium iodide **17**,[20] and 1,2-dithiole-3-thione **18**[20] were prepared according to literature procedures.

FVP of 1,3-*Dithiethanes.*—Samples of dithiethanes **6a** and **6b** were sublimed through a hot quartz tube at temperatures 650–1050 °C. For discussion of spectra see text.

Preparative FVP of Dithiethane **6b**.—Dithiethane **6b** (30 mg) was sublimed at 200 °C through a hot quartz tube (30 cm) at 750 °C over 3 h. The pyrolysis products were collected on a liquid nitrogen cooled cold finger. The compounds were washed off the finger with chloroform. By GC–MS the presence of 4-methylphenyl(methylthio)ethyne was established;[14] *m/z* 163 (10%), 162 (M$^+$, 100), 147 (92), 145 (9), 115 (7), 103 (34), 93 (8), 77 (10), 69 (13) and 45 (8).

FVP of Aryl Substituted 1,2-*Dithiole*-3-*thiones* **11**, **14** *and* **15**.—Samples of the thiones were sublimed through a hot quartz tube at 900–1050 °C. For comparison the matrix spectra of 1,2-diphenylacetylene (Ar-matrix, 17 K: ν/cm^{-1} 1608, 1505, 1446, 1071, 1028, 913 and 757) and phenylacetylene (Ar-matrix, 17 K: ν/cm^{-1} 1608, 1495, 1446, 1265, 1218, 1071, 1028, 914 and 558) were recorded.

FVP of 1,2-*Dithiole*-3-*thione* **18**.—Due to the high vapour pressure of this compound, it was necessary to place it in a side arm which could be closed off outside the Ar stream. Even with this arrangement it was not possible to avoid the starting material reaching the cold target unpyrolysed. The compound was sublimed through the quartz tube at 900–1080 °C. For comparison, a matrix spectrum of the thione **18** was recorded (Ar-matrix 17 K: ν/cm^{-1} 1557, 1502, 1332, 1133, 1173 and 991).

Pyrolysis of 1,2-*Dithiolylium Salts and Tosylhydrazone Sodium Salt.*—Samples of the salts **9**, **16** and **17** and the tosylhydrazone sodium salt **10** were pyrolysed in the sublimation oven at temperatures 100–200 °C. The pyrolysis products were conducted through the pyrolysis oven at temperatures 900–1080 °C to avoid recombination of monomers formed before they reached the cold window.

Acknowledgements

This research was carried out in the laboratory of Professor C.

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† 1 bar = 10^5 Pa.

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References

1 G. Schukat, A. M. Richter and E. Fanghänel, *Sulfur. Rep.*, 1987, **7**, 155.
2 (*a*) H. Behringer and E. Meinetsberger, *Tetrahedron Lett.*, 1973, 1915; (*b*) H. Behringer and E. Meinetsberger, *Liebigs Ann. Chem.*, 1981, 1729; (*c*) H. Behringer and E. Meinetsberger, *Liebigs Ann. Chem.*, 1981, 1928.
3 J. Goerdeler, J. Haag, C. Lindner and R. Losch, *Chem. Ber.*, 1974, **107**, 502.
4 C. Th. Pedersen, J. Oddershede and J. Sabin, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1062.
5 G. C. Papavassiliou, *Chem. Scr.*, 1985, **25**, 167.
6 J. Amzil, J.-M. Catel, G. LeCoustumer, Y. Mollier and J.-P. Sauvé, *Bull. Soc. Chim. Fr.*, 1988, 101.
7 G. Seybold and C. Heibl, *Chem. Ber.*, 1977, **110**, 1225.
8 E. Schaumann, *Tetrahedron*, 1988, **44**, 1827.
9 C. Wentrup, H.-W. Winter, G. Gross, K.-P. Netsch, G. Kollenz, W. Ott and A. G. Biedermann, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 800.
10 C. O. Kappe, G. Kollenz, K.-P. Netsch, R. Leung-Toung and C. Wentrup, *J. Chem. Soc., Chem. Commun.*, 1992, 488.
11 N. Takeuchi and M. Tasumi, *J. Mol. Spectrosc.*, 1981, **90**, 116.
12 N. Nørkjær and A. Senning, *Chem. Ber.*, 1993, **126**, 63.
13 M. W. Wong and C. Wentrup, to be published.
14 V. F. Plotnikov, M. L. Petrov, G. M. Bogolyubov and P. A. Petrov, *Zh. Org. Khim.*, 1972, **8**, 967.
15 W. Stadlbauer and T. Kappe, *Chem. -Ztg.*, 1977, **101**, 137.
16 J. P. Selegue, *J. Am. Chem. Soc.*, 1982, **104**, 119.
17 H. Egsgaard and L. Carlsen, *J. Chem. Res. (S)*, 1991, 226.
18 D. Sülzle, H. Egsgaard, L. Carlsen and H. Schwarz, *J. Am. Chem. Soc.*, 1990, **112**, 3750.
19 C. Wentrup, R. Blanch, H. Briehl and G. Gross, *J. Am. Chem. Soc.*, 1988, **110**, 1874.
20 C. Th. Pedersen, *Adv. Heterocycl. Chem.*, 1982, **31**, 63.

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