



for the trithiapentalenes.<sup>7</sup> We have earlier studied the fragmentation upon electron impact of 1,2-dithiol-3-ones (IV), 1,2-dithiole-3-thiones (V),<sup>8</sup> 1,6,6a<sup>1</sup>S-trithiapentalenes (VI)<sup>9</sup> and 1,2-dithiol-3-ylidene ketones (VII).<sup>10</sup> In the light of the above mentioned relationship between I – III and IV – VII

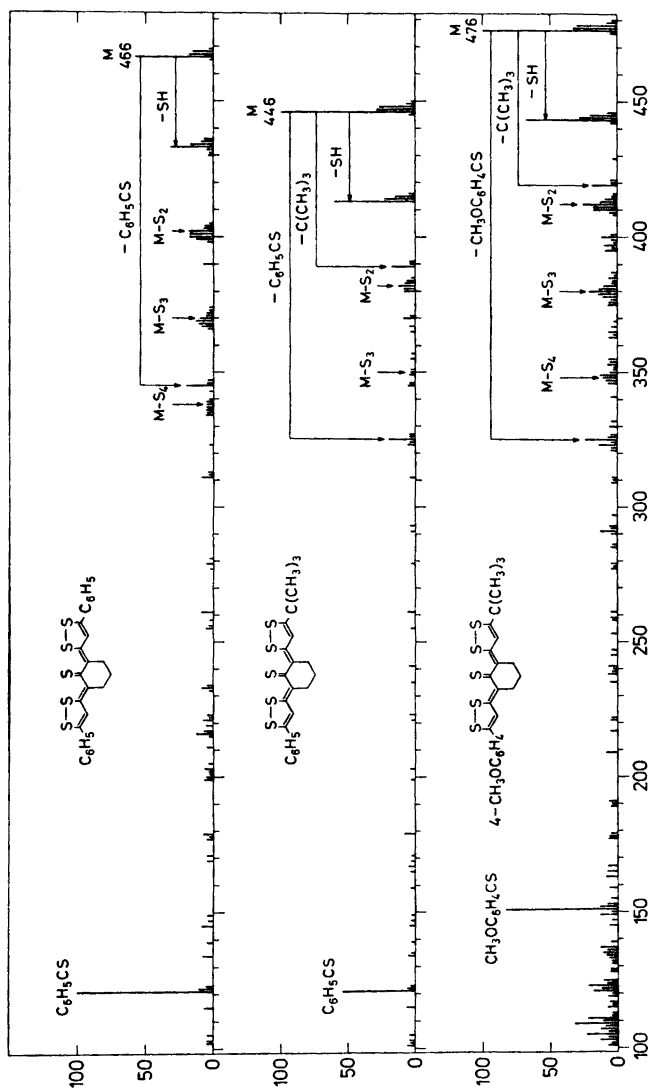


Fig. 1. Mass spectra of 2,6-bis(1,2-dithiol-3-ylidene)cyclohexanethiones (III).

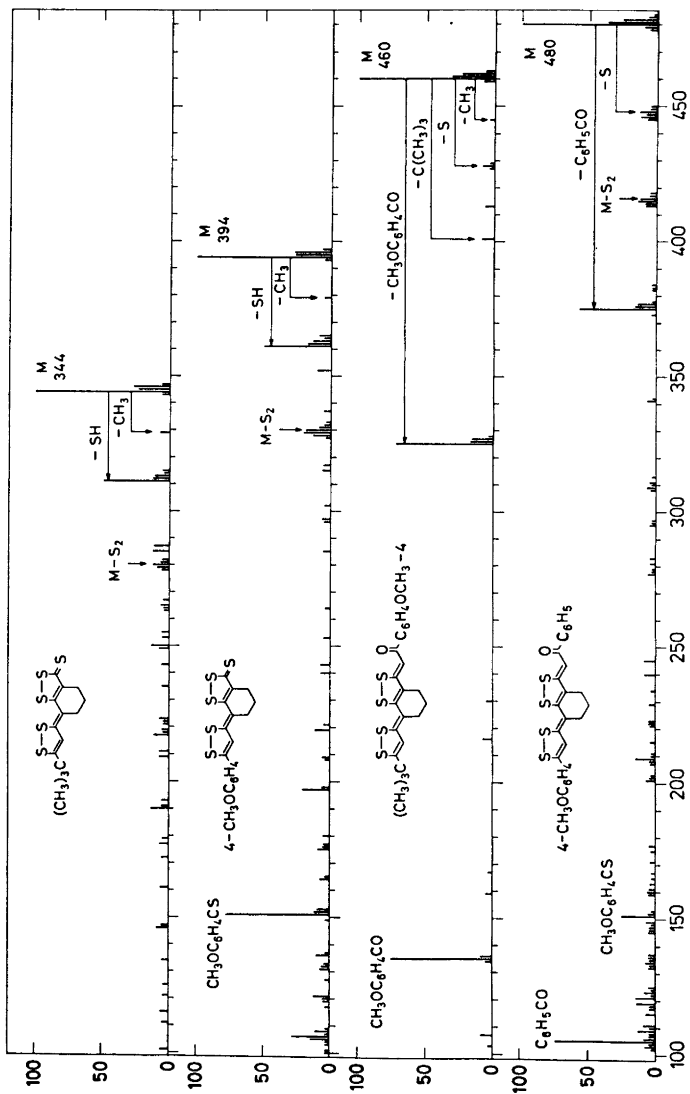
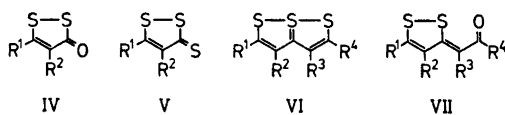


Fig. 2. Mass spectra of 7-(1,2-dithiol-3-ylidene)4,5,6,7-tetrahydro-1,2-benzodithiole-3-thiones (I) and  $\alpha$ -[7-(1,2-dithiol-3-ylidene)4,5,6,7-tetrahydro-1,2-benzodithiol-3-ylidene]-acetophenones (III).

it was of interest to study the fragmentation upon electron impact of compounds of groups I–III.



It has not been possible to make a systematic study of the influence of the substitution pattern of the fragmentation mode in the series I–III because the presence of the cyclohexane unit is an absolute prerequisite for the synthesis of these compounds.<sup>11,12</sup>

Although high temperatures of 250–300°C are necessary to introduce the compounds into the ion source, it was possible to obtain mass spectra, shown in Figs. 1 and 2, in which the base peaks are due to the molecular ions. This may be due to the stability of the aromatic multisulfur systems (for III, *cf.* Fig. 3). In multisulfur systems such as VIII<sup>13</sup> where there is no possibility of

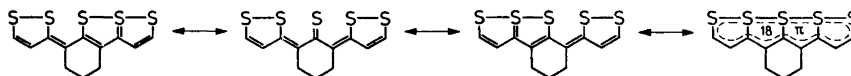
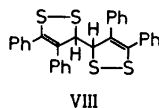


Fig. 3. The 2,6-bis(1,2-dithiol-3-ylidene)cyclohexanethione system.

stabilization *via* an aromatic sulfur system the abundance of the molecular ions is lower than 1 % and the base peak is due to  $M - H_2S_2$ .



#### A. 2,6-BIS(1,2-DITHIOL-3-YLIDENE)CYCLOHEXANETHIONES (III)

The most characteristic feature of the mass spectra of this type of compound is the loss of  $HS \cdot$  directly from the molecular ion, which gives rise to ions with abundances of 55–70 %. The loss of  $HS \cdot$  from the molecular ions was found to be a characteristic fragmentation also for the 1,6,6a<sup>IV</sup>S-trithiapentalenes.<sup>9</sup>

The spectra further exhibit peaks formally corresponding to losses of  $S$ ,  $S_2$ ,  $S_3$ , and  $S_4$  from the molecular ions, and are followed by peaks generated by accompanying hydrogen rearrangements. In the spectra of trithiapentalenes peaks corresponding to  $M - S$  and  $M - S_2$  are also present.

If  $R = (CH_3)_3C$  a peak corresponding to the direct loss of the tertiary butyl group from the molecular ion is present. If  $R$  is aromatic no peaks correspond-

ing to the M-R ions are found, but prominent peaks corresponding to thiobenzoyl or substituted thiobenzoyl ( $\text{RCS}^+$ ) ions are observed. A peak corresponding to M-76 is found in all spectra of compounds of type III and is most probably due to loss of  $\text{CS}_2$  or  $\text{S} + \text{CS}^\cdot$  from the molecular ions.

B.  $\alpha$ -[7-(1,2-DITHIOL-3-YLIDENE)-4,5,6,7-TETRAHYDRO-1,2-BENZODITHIOL-3-YLIDENE]ACETOPHENONES (II)

The loss of  $\text{HS}^\cdot$  from the molecular ions is only minor in spectra of these compounds and is surpassed by the loss of S. Prominent peaks corresponding to  $\text{R}^2\text{CO}^+$ , benzoyl or substituted benzoyl ions, as well as M- $\text{R}^2\text{CO}$  are present.  $\text{R}^1$  is expelled in the form of thiobenzoyl or substituted thiobenzoyl ions but gives rise to ions of lower abundances than the analogous oxygen-containing ions. No peaks corresponding to M- $\text{R}^1\text{CS}$  are observed.

These compounds are analogous to the dithiolylidene ketones (VII). It was found to be a characteristic feature in the spectra of VII<sup>10</sup> that they exhibited prominent peaks corresponding to M-OH. Such peaks were not found in spectra of II.

C. 7-(1,2-DITHIOL-3-YLIDENE)4,5,6,7-TETRAHYDRO-1,2-BENZODITHIOLE-3-THIONES (I)

Expulsion of  $\text{HS}^\cdot$  from the molecular ions in these compounds gives rise to ions with abundances of *ca.* 50 %. If R is aromatic intense peaks corresponding to  $\text{RCS}^+$  are observed, whereas such peaks are not present if R is *tert.*-butyl. In spectra of simple disubstituted 1,2-dithiole-3-thiones (V) intense peaks corresponding to M- $\text{HS}_2$ <sup>8</sup> were found. Such peaks are not present in the spectra of I.

### CONCLUSIONS

A general feature of the mass spectra of the compounds I-III is that although reproducible the spectra are rather uncharacteristic; *e.g.*, there are only small differences between the spectra of group I and group III compounds. The similarities between spectra of the two groups I-III and IV-VII are mostly due to the presence of intense molecular ions, indicating the stability of the sulfur-containing aromatic system in contrast to systems like VIII.

### EXPERIMENTAL

Mass spectra were obtained on an MS 902 mass spectrometer operating at 70eV using the direct sample insertion system and the lowest feasible ion source temperature. Peaks corresponding to doubly charged ions appearing at half mass numbers and peaks of abundance lower than 3 % were omitted.

For the preparation of the compounds I-III, *cf.* Refs. 1, 2, 3, and 4.

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