Mass Spectrometric Fragmentation of 2,6-Bis(1,2-dithiol-3-ylidene) cyclohexanethiones and Other Multisulfur Heterocycles Related to the 1,2-Dithiole Series

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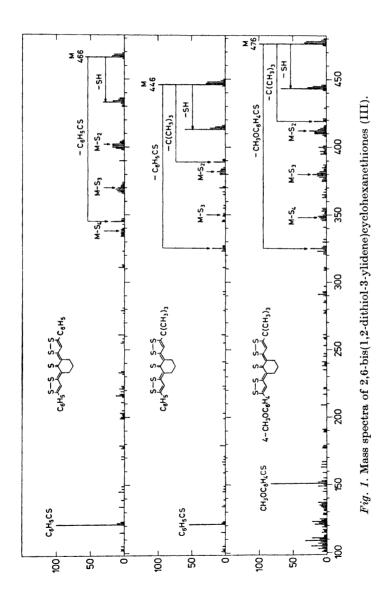
The mass spectra of cyclic sulfur compounds containing four or five sulfur atoms have been recorded. The molecular ion peaks are normally found to be the base peaks in the spectra. In the spectra of dithiolylidene cyclohexanethiones peaks corresponding to the loss of one, two, three, and four sulfur atoms can be discerned, followed by peaks resulting from accompanying hydrogen rearrangements. Prominent peaks corresponding to loss of HS- from the molecular ions are a general feature in the spectra of dithiolylidene cyclohexanethiones and dithiolylidene tetrahydrobenzodithiole thiones. The aromatic substituents present could be recognized by the formation of benzoyl or thiobenzoyl ions which give rise to prominent peaks in all spectra.

Theoretically the $1,6,6a^{\text{IV}}$ S-trithiapentalene system may be extended to include compounds with four, five, or even an infinite row of sulfur atoms. Compounds with four and five sulfur atoms of the types $I-III^{**}$ have been synthesized $^{1-4}$ and many similarities to the trithiapentalenes have been found. It has been shown by X-ray crystallography that the four sulfur atoms in I^{5} and the five sulfur atoms in II^{6} are in a straight line as is the case

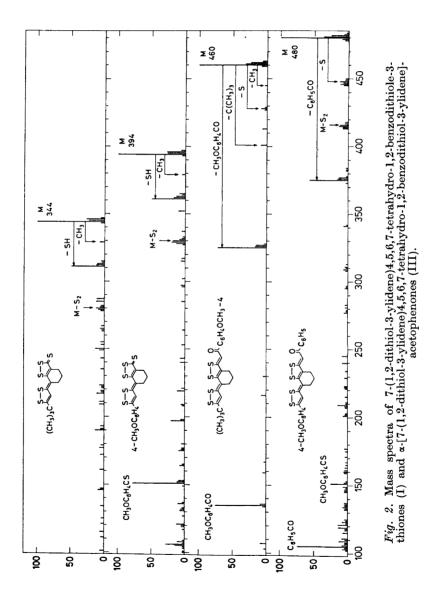
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** The choice of the formulas I—III and the corresponding names is without prejudice toward the contribution of other resonance forms and should therefore not be taken as a statement of the electron distribution in these compounds.

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



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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.^{11,12}

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 ¹³ 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 · directly from the molecular ion, which gives rise to ions with abundances of 55-70 %. The loss of HS · from the molecular ions was found to be a characteristic fragmentation also for the 1,6,6a^{IV}S-trithiapentalenes.9

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 $R = (C\bar{H}_3)_3C$ 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-

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ing to the M-R ions are found, but prominent peaks corresponding to thiobenzoyl or substituted thiobenzoyl (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 CS₂ or S+CS from the molecular ions.

B. α-[7-(1,2-DITHIOL-3-YLIDENE)-4,5,6,7-TETRAHYDRO-1,2-BENZODITHIOL-3-YLIDENEIACETOPHENONES (II)

The loss of HS: from the molecular ions is only minor in spectra of these compounds and is surpassed by the loss of S. Prominent peaks corresponding to R²CO⁺, benzoyl or substituted benzoyl ions, as well as M-R²CO are present. R¹ is expelled in the form of thiobenzoyl or substituted thiobenzoyl ions but gives rise to ions of lower abundances than the analogous oxygencontaining ions. No peaks corresponding to $M-R^{1}CS$ are observed.

These compounds are analogous to the dithiolylidene ketones (VII). It was found to be a characteristic feature in the spectra of VII 10 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 HS from the molecular ions in these compounds gives rise to ions with abundances of ca. 50 %. If R is aromatic intense peaks corresponding to 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 $M-HS_2$ 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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