

Mass Spectrometric Studies of Methyl- and Phenyl-substituted 1,2-Dithiole-3-thiones and 1,2-Dithiole-3-ones

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The mass spectra of 14 methyl- and phenyl-substituted 1,2-dithiole-3-thiones and 1,2-dithiole-3-ones have been recorded. All show intense molecular ion peaks, which often are the base peaks. The compounds monosubstituted at the 5-position all exhibit prominent peaks corresponding to the direct loss of $\cdot\text{HS}_2$ from the molecular ion. The compounds with a phenyl group at the 4-position have the $\text{M}-\text{H}$ peak as base peak, whereas compounds with a 4-methyl group do not exhibit $\text{M}-\text{H}$ peaks. The mass spectra of methyl-substituted 1,2-dithiole-3-ones all show a peak interpreted as the 1,2-dithiolylium ion, the formation of which is initiated by loss of HCO from the molecular ion.

In order to elucidate the modes of fragmentation of substituted 1,2-dithiole-3-thiones and 1,2-dithiole-3-ones upon electron impact, we have recorded the mass spectra of monomethyl and monophenyl as well as dimethyl and diphenyl compounds. The substances investigated are shown in Table 1, and the mass spectra are given in Figs. 1 and 2.

Table 1.



	IA	IA'	IIA	IIIA	IVA	VA	VIA	IB	IIB	IIB'	IIIB	IVB	VB	VIB
R ¹	C ₆ H ₅	C ₆ D ₅	H	C ₆ H ₅	CH ₃	H	CH ₃	C ₆ H ₅	H	H	C ₆ H ₅	CH ₃	H	CH ₃
R ²	H	H	C ₆ H ₅	C ₆ H ₅	H	CH ₃	CH ₃	H	C ₆ H ₅	C ₆ D ₅	C ₆ H ₅	H	CH ₃	CH ₃
X	S	S	S	S	S	S	S	O	O	O	O	O	O	O

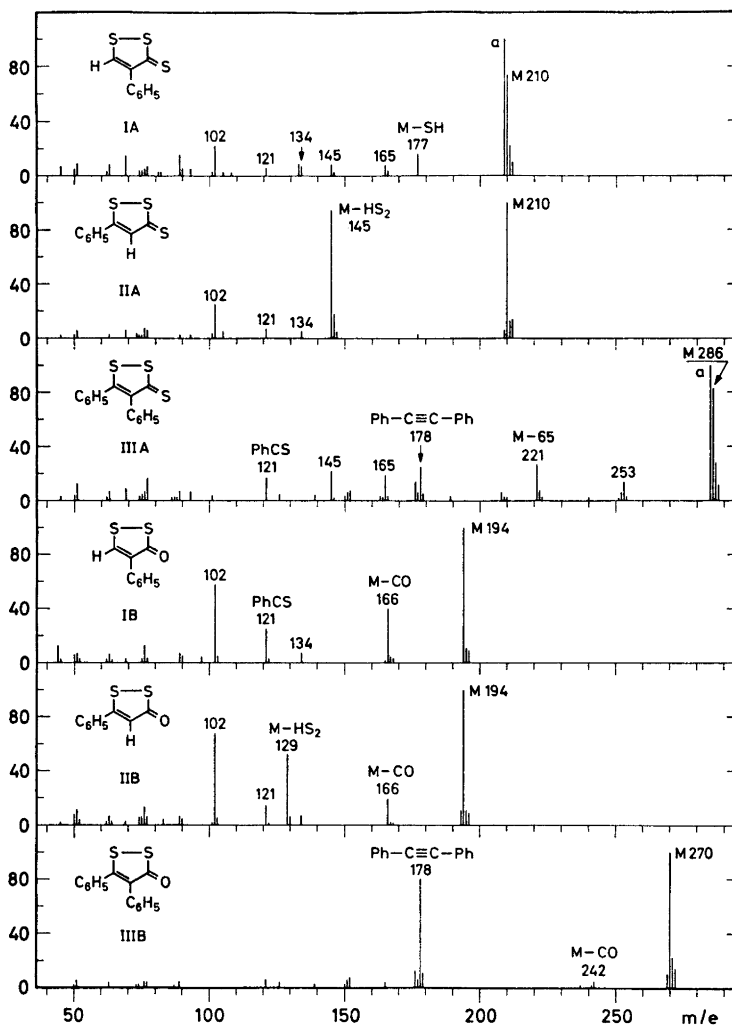


Fig. 1. Mass spectra of phenyl-substituted 1,2-dithiole-3-thiones and 1,2-dithiole-3-ones.

A general feature of the mass spectra of most of the 1,2-dithiole-3-thiones and 1,2-dithiole-3-ones investigated is that the base peak is often due to the molecular ion. The aromatic character of the above-mentioned compounds has been discussed on basis of their NMR spectra. Saquet and Thuillier¹ have concluded that the abnormally low chemical shifts of the ring protons are the consequence of a pseudoaromatic character of the systems, whereas Brown *et al.*² claim that it is not necessary to assume an aromatic character to explain the chemical shifts of the ring protons and the low allylic coupling constant between the ring proton and the methyl group in monomethyl de-

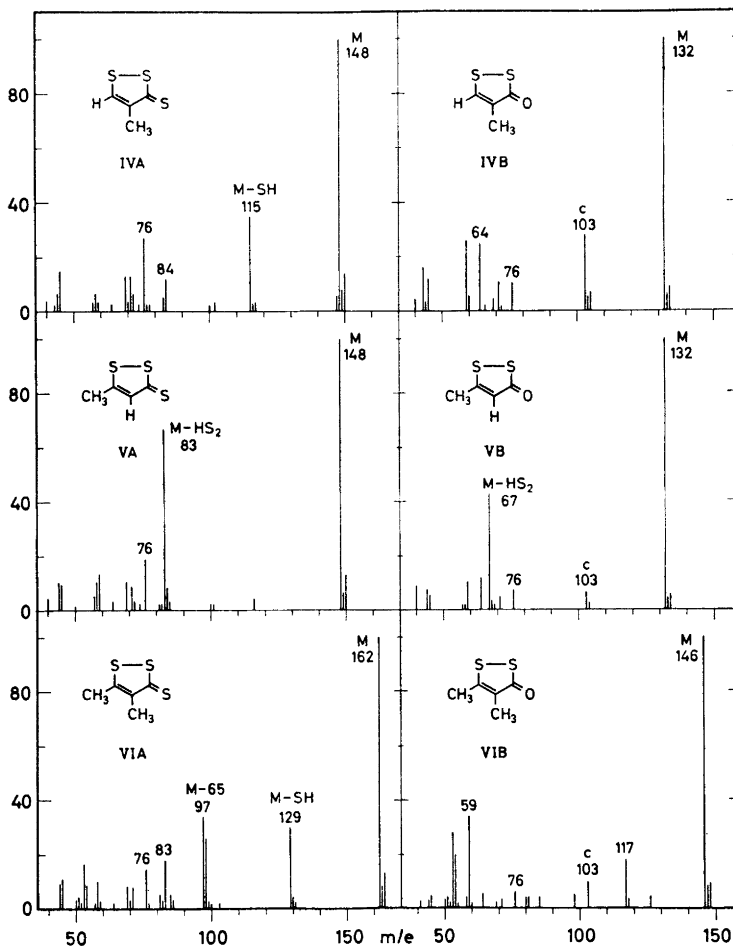


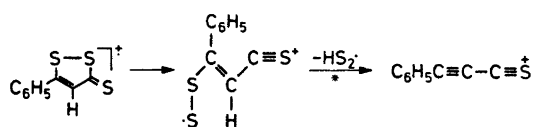
Fig. 2. Mass spectra of methyl-substituted 1,2-dithiole-3-thiones and 1,2-dithiole-3-ones.

rivatives. Without drawing any definite conclusions in this matter it can be said that the mass spectra of the methyl-substituted compounds were also very like mass spectra of aromatic compounds.

5-Substituted compounds. A general feature in the fragmentation pattern upon electron impact for all 5-substituted compounds investigated is the formation of prominent peaks appearing at masses corresponding to $M - HS_2$. These peaks are also found in the mass spectra of some of the disubstituted compounds. When peaks corresponding to $M - HS_2$ are present in the spectra of the 4-substituted analogues it is only with low intensities.

The modes of formation of these ions may be different depending on the nature and number of substituents present. In the case of IIA it has been shown by comparison with the mass spectrum of 5-pentadeuteriophenyl-1,2-dithiole-

3-one that the hydrogen atom involved in the abstraction of the HS_2 comes exclusively from the 4-position of the dithiole nucleus. Furthermore, a metastable peak corresponding to the process $\text{M}^+ \rightarrow \text{M} - 65^+$ is present in the mass spectra of IIA, and the low energy spectra support the assumption that the loss of HS_2 is a one-step reaction. The loss of HS_2 is observed in the mass spectra of other polysulfur compounds.³⁻⁵ Bowie and White⁴ have found an $\text{M} - \text{HS}_2$ peak in the mass spectra of 1,3-dithianes and 1,3-dithiolanes, which indicates that this fragment is formed very easily in polysulfur compounds even if the two sulfurs are not neighbours. For the compounds under investigation we will suggest that the disulfide sulfur atoms are expelled together with H-4 according to the following Scheme 1.

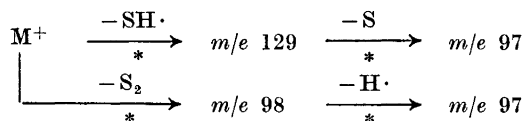


Scheme 1.

Similar fragmentation pathways may be written for the corresponding ions in the other 5-substituted compounds.

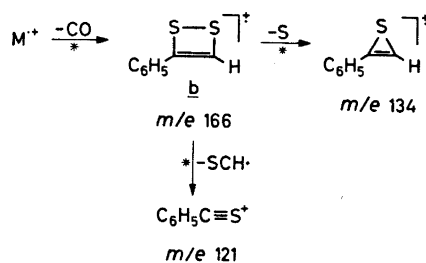
An $\text{M} - 65$ peak is found too in the mass spectrum of IIIA. In this case the corresponding ion, as shown by metastable defocusing technique is formed in two ways, loss of S_2 from the $\text{M} - 1$ ion and loss of S from the $\text{M} - \text{SH}$ ion.

Application of the metastable defocusing technique in the case of VIA has given the following pathway for the formation of the $\text{M} - 65$ ion (Scheme 2):



Scheme 2.

In the mass spectrum of IIA the only significant peaks in the higher mass range are the molecular ion base peak, the $\text{M} - 65$ peak, a peak at m/e 102



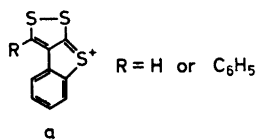
Scheme 3.

corresponding to $\text{Ph}-\text{C}\equiv\text{CH}^+$ and some minor peaks at m/e 121 (PhCS), m/e 134 ($\text{M}-\text{CS}_2$) and m/e 177 ($\text{M}-\text{SH}$).

In the corresponding oxygen analogue IIB the loss of CO from the molecular ion initiates the fragmentation depicted in Scheme 3.

This sequence gives rise to fragment ions of the same masses as in the case of IIA, except for m/e 166.

4-Substituted compounds. In the mass spectra of IA and also in the case of IIIA the $\text{M}-1$ peak is the base peak. The $\text{M}-\text{H}$ ion most probably has the structure *a*, which is supported by labelling experiments. In the mass spectrum of IA' an $\text{M}-2$ peak is present instead of an $\text{M}-1$ peak.



The difference between the mass spectrum of IA and that of the corresponding oxygen analogue IB is very marked especially with respect to the ease of formation of *a*. While the $\text{M}-\text{H}$ peak is the base peak in the spectrum of IA, the $\text{M}-\text{H}$ peak is only 1 % of the molecular ion peak in the spectrum of IB.

In none of the mass spectra of the methyl compounds abundant peaks corresponding to $\text{M}-\text{H}$ were observed, which supports the formulation of *a* given above.

Loss of SH from the molecular ions gives rise to important peaks in the spectra of 4-substituted 1,2-dithiole-3-thiones, most prominent in the methyl-substituted compounds, whereas the only 5-substituted compound that exhibits an $\text{M}-\text{SH}$ peak (3 %) is IIA. The mass spectrum of IA' shows that the hydrogen lost together with the sulfur does not originate from the dithiole nucleus in IA.

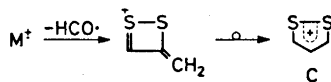
Loss of CO from the molecular ion in IB initiates a fragmentation pathway similar to the one observed in the mass spectrum of IIB. The common structure *b* (Scheme 3) can thus be ascribed to the $\text{M}-\text{CO}$ ion in the two spectra, explaining the great similarity between the mass spectra of the two isomers, aside from the $\text{M}-65$ peak that is present only in the mass spectrum of IIB.

The stability of the ion analogous to *b* is probably much smaller for IIIB because the formation of the stable $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5^+$ ion (m/e 178) may facilitate the loss of S_2 from this ion. The ion with m/e 178 is the only fragment with high abundance in this spectrum, and it was shown by metastable defocusing technique that it is also formed directly from the molecular ion, most probably by a concerted loss of $\text{S}_2 + \text{CO}$.

The corresponding sulfur analogue IIIA also exhibits a peak at m/e 178 but only with an intensity of 16 % (cf. 81 % in the case of IIIB). This might be due to the often reported higher stability of sulfur-containing ions over the corresponding oxygen analogues giving the possibility of other fragmentation routes. Thus IIIA exhibits prominent $\text{M}-1$, $\text{M}-33$, and $\text{M}-65$ peaks.

The methyl-substituted 1,2-dithiole-3-ones differ from the corresponding phenyl-substituted compounds by eliminating $\text{HCO}\cdot$ instead of CO from the molecular ion.

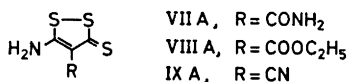
In the mass spectrum of IVB this $\text{M} - \text{HCO}$ peak has an intensity of 28 % of the molecular ion base peak, and is most probably due to the stable aromatic 1,2-dithiolylium ion *c*, which is isosteric with the tropylium ion. Ion *c* is probably formed by skeletal rearrangement in conjunction with $\text{HCO}\cdot$ loss as shown in Scheme 4.



Scheme 4.

In the spectrum of VB the same ion has an intensity of 8 % reflecting the more difficult formation of the ion in this compound, probably via ring expansion followed by concerted loss of $\text{CO} + \text{H}$. An additional reason for the small intensity of the 1,2-dithiolylium ion is the competitive elimination of S_2H from the molecular ion, which gives rise to the only intense fragment ion in this spectrum.

In a recent paper Yokoyama⁶ has reported some selected peaks of the mass spectra of 1,2-dithiole-3-thiones bearing functional groups such as VIIA – IXA.



In the case of VIIA and IXA these compounds show loss of S_2 directly from the molecular ion, as we have found for disubstituted 1,2-dithiole-3-thiones.

EXPERIMENTAL

Mass spectra were obtained on an MS 902 mass spectrometer using the direct sample insertion system and the lowest feasible ion source temperature. Unless otherwise stated, 70 eV electrons were used. High resolutions mass measurements were carried out under the same conditions. Peaks of lower abundance than 2 % are omitted. ^1H NMR spectra were recorded on a Varian A-60A spectrometer with *ca.* 5 % solutions in CDCl_3 . The chemical shifts are given as δ values.

5-Phenyl, 4,5-diphenyl, 5-methyl, and 4,5-dimethyl-1,2-dithiole-3-thiones were prepared from the appropriate ketones by the method of Thuillier and Vialle.⁷⁻⁹

4-Phenyl-1,2-dithiole-3-thione.¹⁰

4-Methyl-1,2-dithiole-3-thione.¹¹

4-Pentadeuteriophenyl-1,2-dithiole-3-thione was prepared analogously to the non-deuterated compound from 2-pentadeuteriophenyl-1-propene and sulfur; m.p. 120.0–121.5°C. NMR δ 8.27 (S). M^+ measured 214.9942, calc. for $\text{C}_6\text{HD}_5\text{S}_3$ 214.9945. Deuteration grade 89 % (NMR).

5-Pentadeuteriophenyl-1,2-dithiole-3-one was prepared analogously to the non-deuterated compound¹² from ethyl 3-pentadeuteriophenyl-2-propenoate and sulfur; m.p. 114.0–115.0°C. NMR δ 6.72 (S). M^+ measured 199.0171, calc. for $\text{C}_6\text{HD}_5\text{S}_2\text{O}$ 199.0174. Deuteration grade 95 % (NMR).

4-Phenyl, 5-phenyl, 4,5-diphenyl, 4-methyl, and 5-methyl-1,2-dithiole-3-ones were prepared from the corresponding thiones by oxidation with mercuric acetate.^{13,14}

4,5-Dimethyl-1,2-dithiole-3-one was prepared from the corresponding thione by oxidation with potassium permanganate in acetone.¹⁵

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