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Mass Spectra of Diaryl Disulfides, Diaryl Thiolsulfinates and Diaryl Thiolsulfonates

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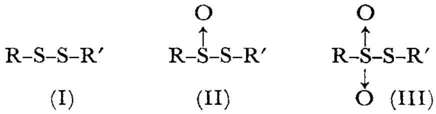
The mass spectra of diaryl disulfides, diaryl thiolsulfinates and diaryl thiolsulfonates have been studied by analyzing metastable peaks and mass numbers. The main fragmentation observed for the disulfides was the cleavage of the S–S bond while the fragmentation of thiolsulfinates was similar to that of disulfides after elimination of oxygen. In the case of thiosulfonates, however, no such deoxygenation was observed, formation of sulfonium ion and one oxygen migration from the sulfone sulfur to the thiol sulfur were observed. Formation of thiabenzonium ion was observed in the mass spectra of sulfinates and sulfonates.

The mass spectra of organic sulfur compounds have been investigated considerably in recent years, and those of alkyl and diaryl sulfides,[1-4] sulfoxides[2,5,6] and sulfones[5-7] have been well understood.

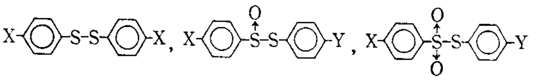
However, the mass spectra of the aromatic compounds containing S–S bond, *i.e.*, disulfides (I), thiolsulfinates (II), and thiolsulfonates (III) have received rather scant attention except for diphenyl disulfide.[4]



$$R\text{-}S\text{-}S\text{-}R' \quad (I) \qquad R\text{-}\overset{\overset{O}{\uparrow}}{S}\text{-}S\text{-}R' \quad (II) \qquad R\text{-}\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}\text{-}S\text{-}R' \quad (III)$$

(R, R'=aryl)

This paper describes a detailed study on the electron impact fragmentation of these three types of sulfur compounds where R and R' are aryl groups. The following compounds were subjected to mass spectrometric analysis.



Ia $X=H$
b $X=CH_3$
c $X=Cl$
d $X=OCH_3$
e $X=NO_2$

IIa $X=H, Y=H$
b $X=H, Y=CH_3$
c $X=CH_3, Y=CH_3$
d $X=H, Y=OCH_3$

IIIa $X=H, Y=H$
b $X=CH_3, Y=CH_3$
c $X=H, Y=NO_2$
d $X=H, Y=Cl$

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[1] P. Natalis and J. L. Franklin, *J. Phys. Chem.*, **69**, 2943 (1965).

[2] R. G. Gills and J. L. Occolowits, *Tetrahedron Lett.*, **1966**, 1997.

[3] J. H. Bowie, S.-O. Lawesson, J. O. Madsen, C. Nolde, G. Schroll and D. H. Williams, *J. Chem. Soc.*, *B*, **1966**, 946.

[4] J. H. Bowie, S.-O. Lawesson, J. O. Madsen, C. Nolde and D. H. Williams, *ibid.*, *B*, **1966**, 951.

[5] J. O. Madsen, C. Nolde, S.-O. Lawesson, G. Schroll, J. H. Bowie and D. H. Williams, *Tetrahedron Lett.*, **1965**, 4377.

[6] J. H. Bowie, D. H. Williams, S.-O. Lawesson, J. O. Madsen, C. Nolde and G. Schroll, *Tetrahedron*, **22**, 3515 (1966).

[7] S. Meyerson, H. Drews and E. K. Fields, *Anal. Chem.*, **36**, 1294 (1964).

Results and Discussion

Diaryl Disulfides. Of first group of compounds (Ia—Ie), the mass spectrum of only the unsubstituted compound (Ia)[4] has been reported. The substituent effect on the fragmentation has not been investigated. The main spectra of these compounds are summarized in Table 1.

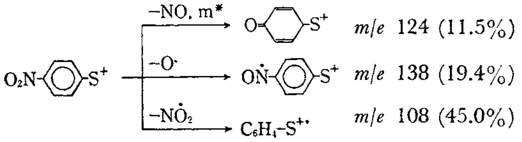
TABLE 1. RELATIVE ABUNDANCE OF MAJOR PEAKS AND METASTABLE PEAKS OF DIARYL DISULFIDES

Compd. / Ion	Ia	Ib	Ic	Id	Ie
M	86	75.8	42	38.6	100
M-(S)	4.7	1.9	0.1	0.2	9.4
M-(SH)	14.1	3.2	0.2	trace	trace
M-(S_2)	20	7.7	2.3	0.3	0.3
M-(S--X)	100	100	100	100	5.7
M-(C_6H_4X)	4.1	1.3	1.0	0.6	1.5
C_6H_4X	15.1	12.8	1.8	0.3	1.0
M-(X)	—	trace	0.4	0.2	3.1
C_6H_4S	—	5.1	44.4	1.6	45
Metastable peak					
M→M-(SH)	present	present	—	—	—
M→M-(S_2)	present	present	—	—	present

A few characteristic features of these spectra may be summarized as follows.

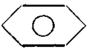
1) All the compounds give prominent parent peaks.

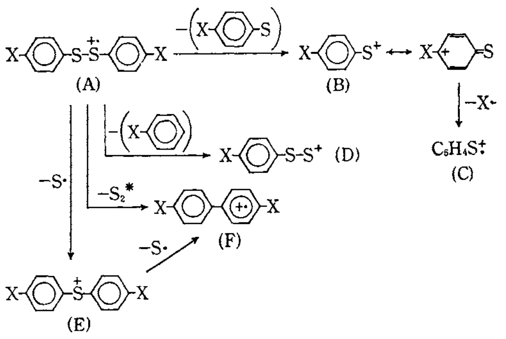
2) The largest peaks for the compounds are fragment peaks formed by cleavage of the S–S bond except in the case of the nitro compound. The anomaly of the nitro compound may be due to the facile decomposition of the ion formed by cleavage of the S–S bond. In this case, three distinctive peaks observed (*i.e.*, *m/e*, 138, 124 and 108) suggest the succeeding decomposition of the daughter ions.



Scheme 1

3) Elimination of S or S_2 from the parent ions was observed, although the process was minor.

4) The relatively high intensity of the fragment having mass number 108 is to be noted. This ion is probably formed by the subsequent cleavage of the X–C bond of the X--S^+ ion. The intensities of these ions are apparently affected by the substituent X and decrease in the order $-NO_2 > -Cl > -CH_3 > -OCH_3$. This order is consistent with the relative stability of the precursor ions. These observations suggest the fragmentation scheme of of these diaryl disulfides as shown below:

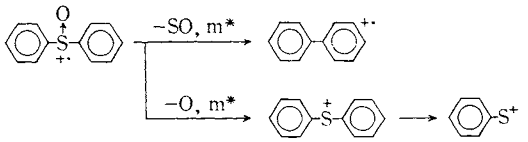


Scheme 2

The main fragmentation process for these compounds is (A)→(B)→(C) and a small portion of the parent ion undergoes decomposition through other pathways.

Ion (F) may be formed either by the direct desulfurization of the parent ion or through ion (E). The direct process is confirmed by the aid of the metastable peak. However, the pathway giving (F) from (E) is also not unreasonable in view of the similar fragmentation of diarylsulfides.[6]

Diaryl Thiol Sulfinates. The mass spectra of diaryl sulfides were investigated by Natalis *et al.*[1,4,5] and the main fragment peaks reported corresponded to those of the diaryl cation and the sulfenium ion formed by the loss of one aryl group. On the other hand, diaryl sulfoxides are known to give the following fragmentation.



These results suggest that the oxidation of sulfur atom of diaryl sulfides does not give rise to any distinctive difference in mass spectra of these compounds. Thus, it is interesting to compare the mass spectra of diaryl thiolsulfinates with those of the corresponding disulfides.

The main spectra of the sulfinates are summarized in Table 2.

As was expected, all the sulfinates give no parent peak or a very small one and the spectra are similar to those of disulfides, hence the general fragmentation patterns for these compounds are initial elimination of oxygen followed by cleavage of the S–S bond or the elimination of sulfur, similar to the fragmentation of the disulfides.

A question arises as to whether the spectra were simply from the sulfinates, since the thiolsulfinates are known to undergo thermal disproportionation to

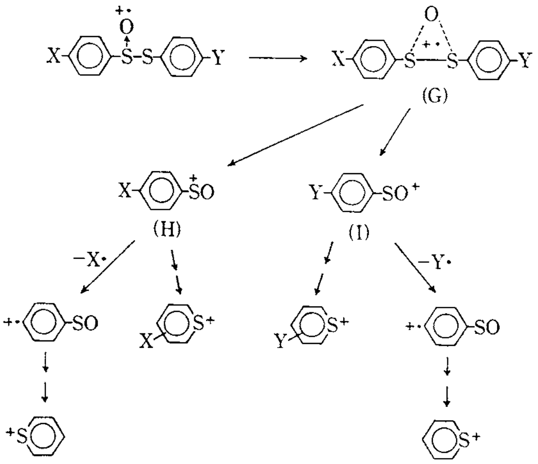
TABLE 2. RELATIVE ABUNDANE OF MAJOR PEAKS AND METASTABLE PEAKS OF DIARYL THIOLSULFINATES

Compd. / Ion	Relative abundance IIa	IIb	IIc	IId
M	—	5	trace	trace
M-(O)	89	42	66	12
M-(SO)	7.0	2.8	2.7	2.4
M-(S_2O)	4.7	5	8.1	3.6
X-⌬-SO	22.6	14.2	8.1	9.7
Y-⌬-SO		14.2		6.1
X-⌬-S	100	100	100	23.2
Y-⌬-S		34		100
m/e 97 ⌬S	4.6	4.0	5	6.1
X-⌬S			0.7	—
Y-⌬S		3.4		—
Metastable peak				
M-(O)→ M-(SOH)	present	present	present	—
M-(O)→ M-(SO)	present	present	present	—
M-(O)→ M-(φ-SO)	present	—	present	—
M-(O)→ M-(φ-S_2O)	present	—	present	—

give the corresponding thiolsulfonates and disulfides.[8]

In the present study, only small peaks corresponding to thiolsulfonates were observed.

The peaks are, however, too small to be expected from disproportionation and moreover the whole pattern of the spectra is quite different from the combined spectra of the equimolar mixture of the thiolsulfonate and the corresponding disulfide. Therefore it should be assumed that the spectra show just the fragmentation of thiolsulfinates.



Scheme 3

In addition to these processes, a fragmentation giving thiabenzonium ion was observed as in the case of diaryl sulfoxides,[6] shown in Scheme 3.

The path giving the thiabenzonium ion from diphenylsulfoxide was confirmed by the presence of the metastable peak and the component of the ion was also determined by means of high resolution mass spectrometry.[6] On the other hand, the ion of the mass number 97 in this work seems to be formed in a somewhat different way since these peaks appear at the same mass number even in methyl-substituted compounds, although there were also small peaks corresponding to the substituted thiabenzonium ion. Thus the process giving the thiabenzonium ion must include the elimination process of the substituent and hence is considered as a rearrangement ion.

Comparing these spectra with those of diaryl sulfoxides, a minor but noticeable difference is observed in deoxygenation. Although similar deoxygenation is observable in the case of diaryl sulfoxides the parent peaks are always observed quite clearly, unlike the case of the thiolsulfinates which undergo deoxygenation almost exclusively. The

TABLE 3. RELATIVE ABUNDANCE AND METASTABLE PEAKS OF DIARYL THIOLSULFONATES

Compd. / Ion	Relative abundance IIIa	IIIb	IIIc	IIId
M	39	33	7.8	40
M-(S)	1.2	1.5	0.8	2.7
M-(SO_2)	5.1	7.8	19.4	39.1
X-⌬-SO_2	33	30	65	63.3
X-⌬-SO	82	100	8.5	63.7
Y-⌬-S			0.2	46.9
X-⌬-S	48	37	—	13.1
Y-⌬-S			1.2	68.3
⌬S	12.2	2.6	3.4	9.1
X-⌬S		3		
Y-⌬S			—	2.2
X-C_6H_4	trace	46	trace	trace
Y-C_6H_4			trace	80.5
H-C_6H_4	100	18.2	100	100
Metastable peak				
M → X-⌬-SO	present	present	—	present
X-⌬-SO_2 → XC_6H_4	present	present	present	present
M → X-⌬-SO_2	—	—	present	present

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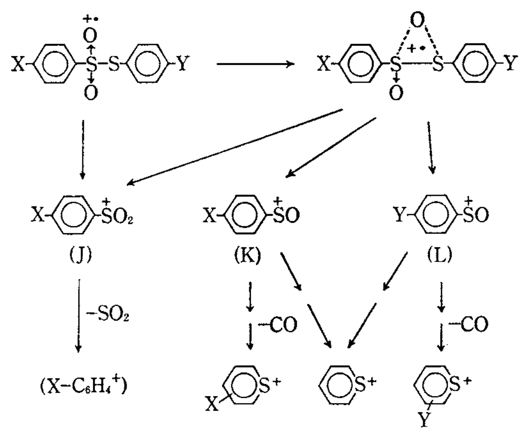
[8] D. Barnard, *J. Chem. Soc.*, **1957**, 4675.



Scheme 4

observation that thiolsulfinates undergo more facile deoxygenation than the sulfoxides seems to conflict with the strength of the S–O bonds of these compounds obtained from IR spectra.[9] The facile deoxygenation in diaryl thiolsulfinates, however, may be rationalized in terms of resonance stabilization of the daughter ions. Namely, although the S–O bond of thiolsulfinate is stronger than that of sulfoxide, the deoxygenation of the former gives disulfide ions which is undoubtedly much more stable than sulfide ions formed by the deoxygenation of sulfoxides. The initial ionization to introduce a positive charge on the oxygen atom of the S–O bond would be easier with thiolsulfinate than with sulfoxide since the positive charge on the sulfur atom can be delocalized to a greater extent more with the former than the latter. This resonance stabilization perhaps outweighs the small difference in the bond strength resulting in the more facile deoxygenation with thiolsulfinate than sulfoxide.

Diaryl Thiolsulfonates. Mass spectrometric analyses were also carried out with the sulfur compounds containing one more oxygen atom around the S–S bond *i. e.*, diaryl thiolsulfonates. The common spectral features of these compounds are summarized in Table 3. As the mass spectra of these thiolsulfonates give the matastable peaks corresponding to the path from the parent ions to the fragments (J), (K) and (L), an intermediate with three-membered ring containing oxygen may be postulated. The main fragmentation scheme for these sulfonates can be depicted as shown in Scheme 4. This includes the cleavage of the S–S bond before or after the migration of one oxygen atom from the sulfone sulfur to the thiol sulfur.

The oxygen migration at the two sulfur atoms appears to be an important process in the fragmentation of diaryl thiolsulfonates. This oxygen migration is also observed in the mass spectra of diaryl thiolsulfinates but minor since the initial elimination of the oxygen is the major process in the fragmentation of thiolsulfinates. On the other hand, the elimination of oxygen atom from the sulfonate linkage is not observed. This difference between the sulfonates and the sulfinates is in good accordance with the difference in the bond strength of the S–O bonds.[9] Similar observations have also been made for the mass spectra of diphenyl sulfoxide in which deoxygenation was found to be minor but no such process was found in that of diphenyl sulfone.[6]

Formation of the thiabenzonium ion is also found in these cases. It is suggested that the formation of the thiabenzonium ion is a common phenomenon with sulfur compounds having an S–O bond adjacent to phenyl group.

The common pattern of the cleavage for these sulfur compounds *i. e.*, disulfides, thiolsulfinates and thiolsulfonates is the cleavage of the S–S bond. Cleavage involving one oxygen migration is also a common process for the sulfinates and the sulfonates.

Experimental

The spectra were recorded with a Hitachi RMU-6E single focus mass spectrometer using 80 eV at the emission

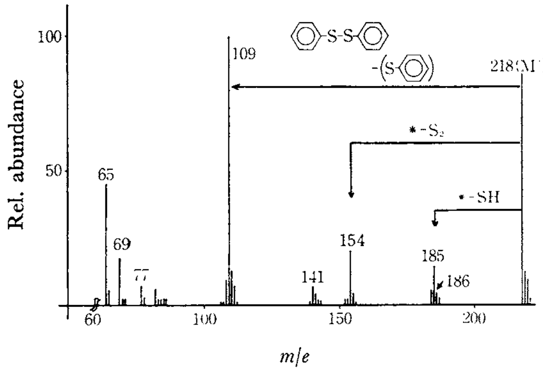


Fig. 1. The mass spectra of C_6H_5-S-S-C_6H_5.

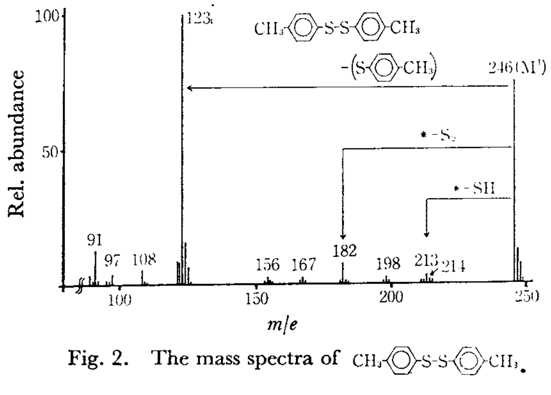


Fig. 2. The mass spectra of CH_3-C_6H_4-S-S-C_6H_4-CH_3.

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[9] S. Ghesretti and G. Modena, *Ann. Chim.* (Rome), **53**, 1083 (1963).

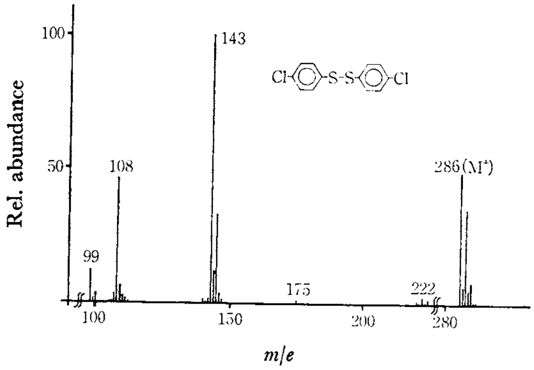
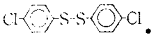


Fig. 3. The mass spectra of .

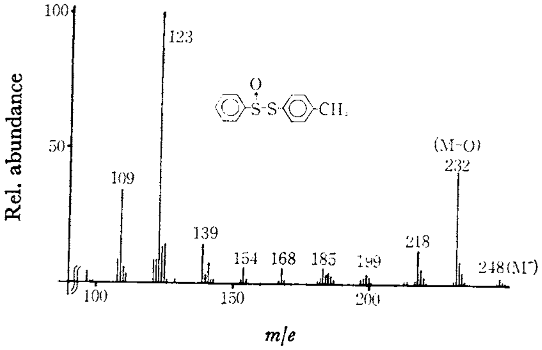
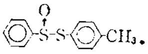


Fig. 6. The mass spectra of .

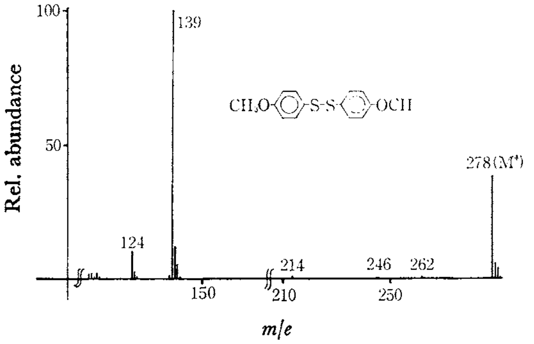
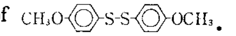


Fig. 4. The mass spectra of .

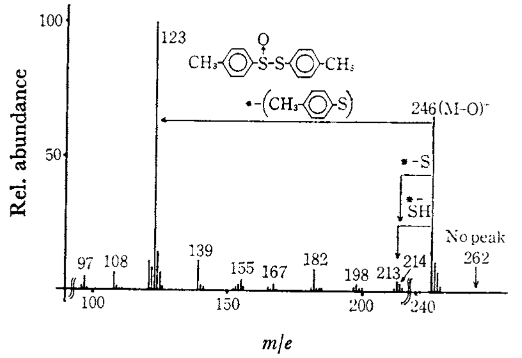
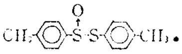


Fig. 7. The mass spectra of .

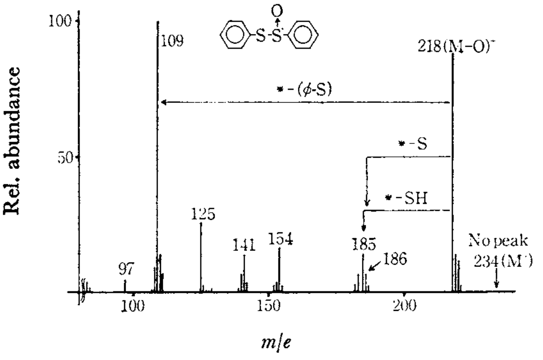
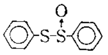


Fig. 5. The mass spectra of .

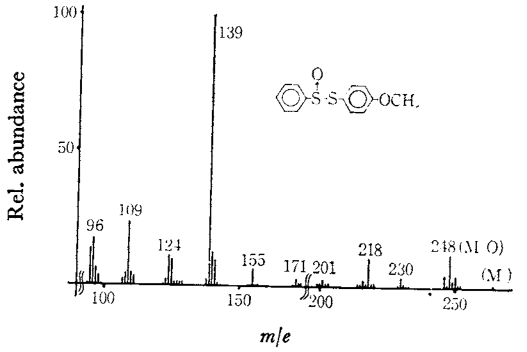
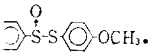


Fig. 8. The mass spectra of .

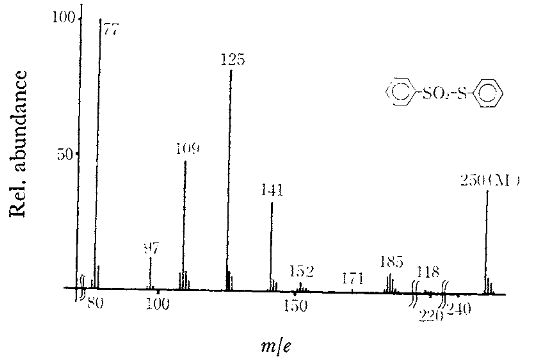
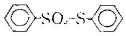


Fig. 9. The mass spectra of .

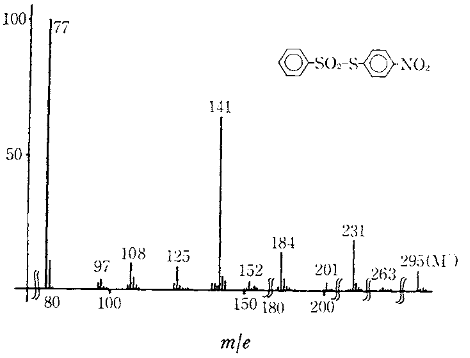
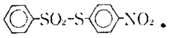


Fig. 11. The mass spectra of .

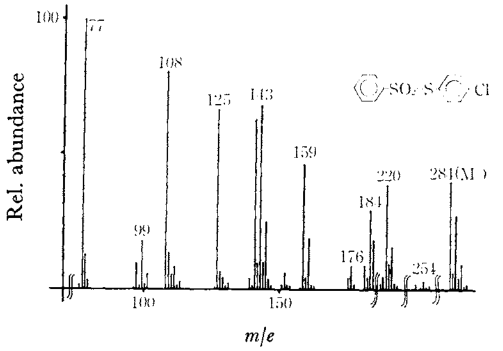
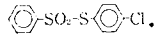


Fig. 12. The mass spectra of .

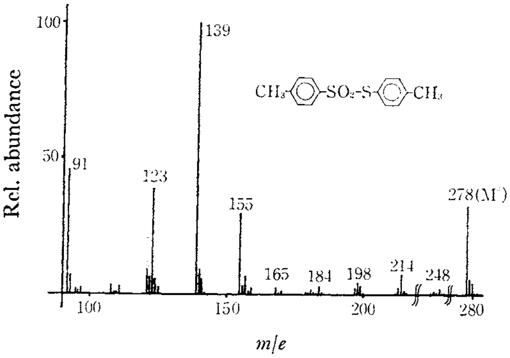
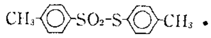


Fig. 10. The mass spectra of .

current of 110 μA. Samples were introduced into the ionization chamber through an all glass inlet system (141-B) heated up to approx. 200°C. These spectra are shown in Figs. 1—12.

Disulfides (Ia—e) were prepared by the iodine oxidation of the corresponding thiophenol.[10] Thiolsulfinates (IIa—d) were obtained by the reaction of thio phenol and sulfinyl chloride.[11] Thiolsulfonates (IIIa—d) were prepared from benzenesulfonyl chloride and benzenesulfinic acid.[12]

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[10] P. Klason, J. Carlson, *Ber.*, **39**, 738 (1906).

[11] D. Barnard and E. J. Peray, *J. Chem. Soc.*, **1962**, 1669.

[12] H. H. Gilman, L. H. Smith and H. H. Parker, *J. Amer. Chem. Soc.*, **47**, 851 (1925).