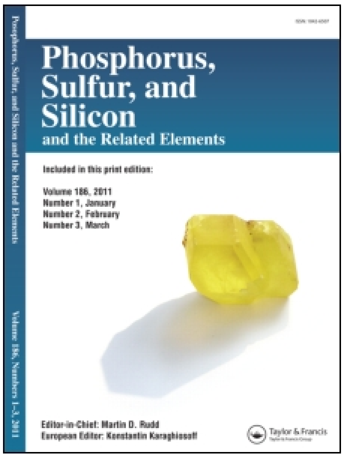

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THE MASS SPECTRAL FRAGMENTATION OF SULFENAMIDES AND RELATED COMPOUNDS

David N. Harpp[a]; Thomas G. Back[a]; James P. Snyder[b]
[a] Department of Chemistry, McGill University, Montreal, Canada [b] Department of General and Organic Chemistry, University of Copenhagen, Copenhagen, Denmark

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THE MASS SPECTRAL FRAGMENTATION OF SULFENAMIDES AND RELATED COMPOUNDS

by

David N. Harpp* and Thomas G. Back

Department of Chemistry, McGill University, Montreal, Canada

James P. Snyder

Department of General and Organic Chemistry, University of Copenhagen, 2100 Copenhagen, Denmark

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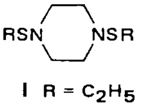
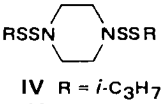
ABSTRACT

Plausible mechanistic interpretations of the major ions formed in the mass spectrometric fragmentation of a number of sulfenamides and related derivatives are presented. High resolution mass spectrometry was used to determine the composition of most of the ions investigated.

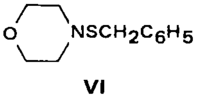
In recent years the behavior of certain sulfenyl compounds in the mass spectrometer has been extensively studied. In particular, the fragmentation modes of thiols,[1a] thioethers,[1a-c] thioketals,[1a] and disulfides[1a,c,d] have received much attention. However, to the best of our knowledge, the electron-impact fragmentation of compounds containing divalent sulfur bonded to nitrogen has not yet been investigated.[2] In view of the importance of compounds containing this structural moiety, we obtained high resolution spectra of the N,N′-bisalkylthiopiperazines I-III, N,N′-bisalkyldithiopiperazines IV and V, sulfenamide VI, N-aminothiophthalimide VII and N,N′-thiobisamines VIII and IX. In addition, the low resolution spectrum of the 1,2,5-thiadiazolidine X was recorded.



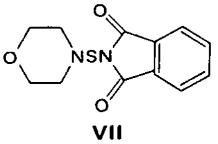
I R = C_2H_5
II R = t-C_4H_9
III R = $C_6H_5CH_2$



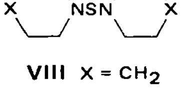
IV R = i-C_3H_7
V R = t-C_4H_9



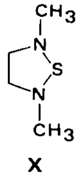
VI



VII



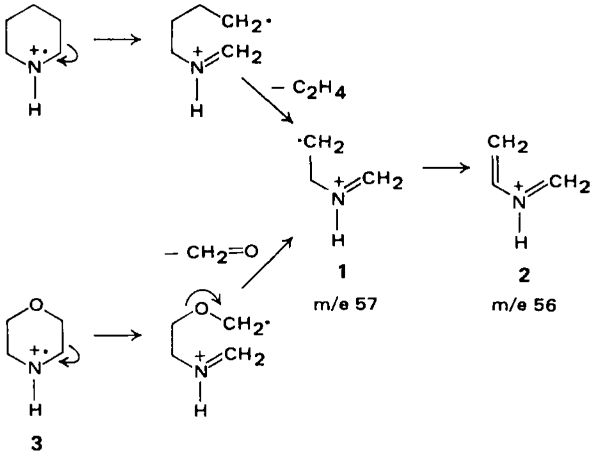
VIII X = CH_2
IX X = O



X

The fragmentation of these compounds is, in most cases, quite complex, particularly due to the presence of many strong ions derived from the saturated ring of the cyclic amine moiety in I-IX. Since the mass spectra of piperazine and piperidine derivatives have been studied in considerable detail,[3,4] a discussion of fragments derived therefrom will be limited to 1 and 2.

It is interesting to note that the spectra of the morpholine derivatives VI, VII, and IX display abundant ions corresponding to $C_3H_7N^+$ (**1**) and $C_3H_6N^+$ (**2**) at m/e 57 and 56 respectively. Djerassi and co-workers[3] also reported the presence of these



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* Author to whom correspondence may be addressed.

fragments in the mass spectrum of piperidine and invoked the mechanism involving ethylene expulsion depicted above to rationalize their formation. A similar process likely occurs in compounds VI, VII and IX where loss of formaldehyde from 3 results in the genesis of 1.

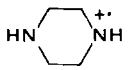
High Resolution Spectra of N,N′-Bisalkylthiopiperazines I-III

Sulfenamides I-III all produce intense molecular ions with that of the ethyl derivative I comprising the base peak. In the case of the *t*-butyl and benzyl derivatives II and III, cleavage of the carbon-sulfur bond results in the formation of the highly stable *t*-butyl cation and tropylium ion, thus providing base peaks at m/e 57 and 91 respectively. The ethyl cation however, appears in the spectrum of I to the extent of only 8.2% of the base peak presumably due to its lower stability.

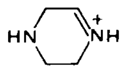
The presence of ion $C_{11}H_{16}N_2S^+$ in the spectrum of III indicates a nitrogen-sulfur bond cleavage process. A likely structure for this fragment is **4**, and there are two possible pathways for its formation. N-S cleavage of the parent ion with concomitant transfer of a hydrogen atom from the benzyl group to the nitrogen gives **4** and thiobenzaldehyde. The transferred hydrogen atom could also originate from the ortho position of the aromatic ring giving **4**, benzyne and thioformaldehyde. Loss of a hydrogen atom from **4** is indicated by the presence of the ion $C_{11}H_{15}N_2S^+$ (**5**). Alternately, formation of **5** might occur *via* simple cleavage of the sulfenamide linkage (N-S), followed by a tautomeric shift of an α-hydrogen. Unfortunately, the lack of appropriate metastable peaks in the low-resolution spectrum precludes determination of which of the two processes ($P^+ \rightarrow 5$ or $4 \rightarrow 5$) is, in fact, operative.

It is also interesting to note that the ethyl analog of species **4** is totally absent in the spectrum of I whereas that of **5** has a relative intensity of 71.1%, thus becoming the peak of penultimate strength. The *t*-butyl analogs of **4** and **5** appear only to a very minor extent in the spectrum of II.

In addition, rupture of the second nitrogen-sulfur bond occurs readily as evidenced by the presence of ions $C_4H_{10}N_2^+$ (**6**) and $C_4H_9N_2^+$ (**7**) in the spectra of compounds II and III. In the case of the ethyl derivative I, **6** is completely absent indicating that transfer of a hydrogen atom from the ethyl group to the amine nitrogen is not a favored process.

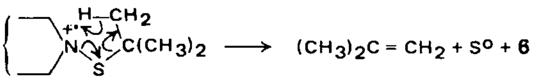


6 m/e 86

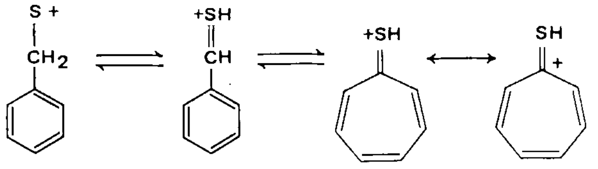


7 m/e 85

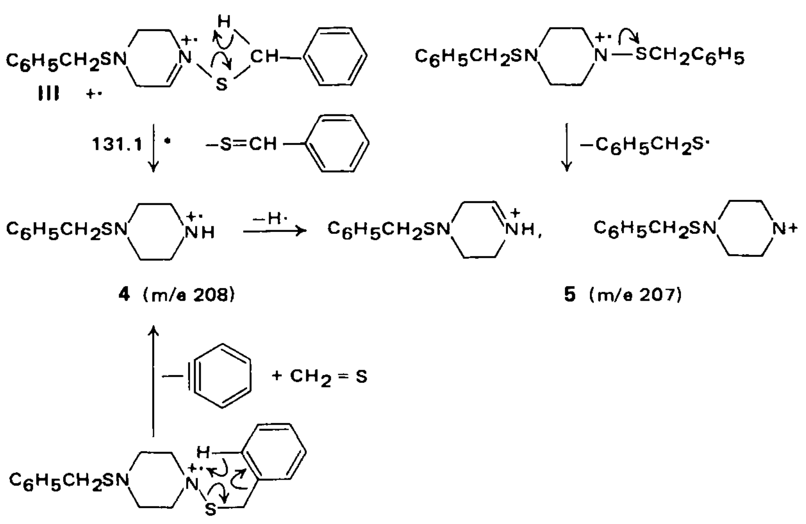
Formation of ion **6** in the *t*-butyl compound may be formulated to occur *via* the expulsion of isobutylene along with a neutral sulfur atom as shown below.



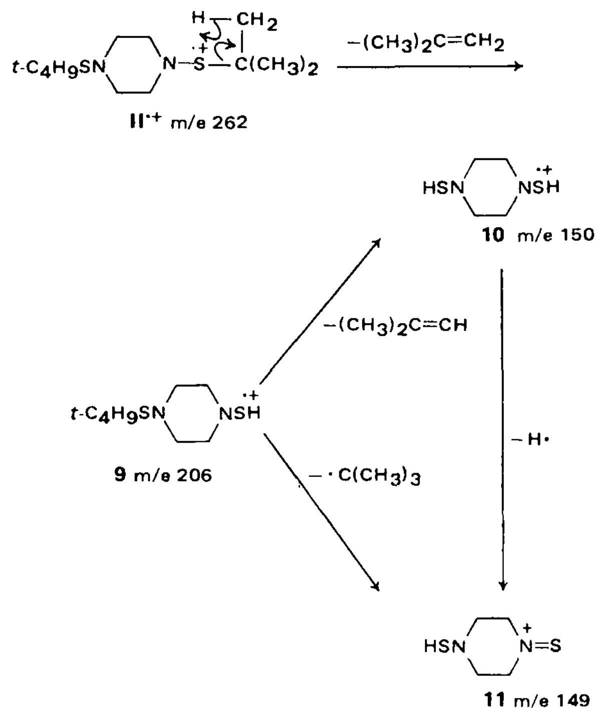
Retention of positive charge by the sulfur-containing hydrocarbon fragment upon scission of the sulfenamide linkage can also be observed. However, the process is significant only for benzyl derivative III where ion $C_7H_7S^+$ has a relative intensity of 43.7%. The prominence of this peak is best rationalized by assuming the existence of the resonance-stabilized tautomers of **8**.[5]



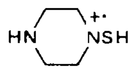
8 m/e 123



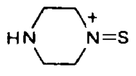
t-Butyl compound **II** also appears to undergo facile carbon-sulfur cleavage with charge retention on sulfur. For example, the presence of the $C_8H_{18}N_2S_2^+$ ion having a relative intensity of 21.4% indicates rupture of the alkyl-sulfur bond with transfer of a hydrogen atom from the *t*-butyl group to the adjacent sulfur atom to give moiety **9**. When the process is repeated on the other sulfur functionality, the formation of the abundant ion $C_4H_{10}N_2S_2^+$ (**10**) results. Genesis of species **9** and **10** assumes the expulsion of isobutylene as a neutral fragment; however, scission of the carbon-sulfur bond may also occur without hydrogen transfer, thereby producing the *t*-butyl radical. The presence of the ion $C_4H_9N_2S_2^+$ **11** in the spectrum of **II** may thus be rationalized (4.6%). Alternately, **11** could be produced by loss of a hydrogen atom from **10**. These mechanisms are illustrated as follows:



Fission of the carbon-sulfur bond may also occur in conjunction with cleavage of the sulfenamide linkage, thereby accounting for the presence of ions $C_4H_{10}N_2S^+$ **12** and $C_4H_9N_2S^+$ **13** in the spectrum of compound **II**.

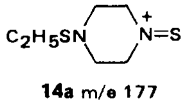


12 m/e 118

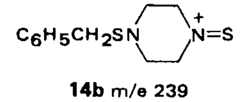


13 m/e 117

It thus appears that rupture of the carbon-sulfur bond with positive charge being retained by sulfur is prominent only in the case of the *t*-butyl derivative, a fact attributable to the relief of steric hindrance in the *t*-butyl group by expulsion of isobutylene or by generation of the *t*-butyl radical. In the ethyl and benzyl derivatives, however, only the presence of ions $C_6H_{13}N_2S_2^+$ and $C_{11}H_{15}N_2S_2^+$ (**14a, b**; 1.5, 10.3% respectively) indicates carbon-sulfur scission of any significance in which carbon is part of the neutral fragment. The existence of this latter fragment may be rationalized by loss of the tropylium radical from the molecular ion of **III**.

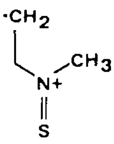


14a m/e 177

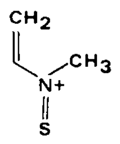


14b m/e 239

In addition, compounds **I** and **II** display peaks of moderate intensity resulting from the ions $C_3H_7NS^+$. and $C_3H_6NS^+$. The latter ion is also found in the spectrum of the benzyl derivative **III**. These species most likely arise from fission of the piperazine ring and are best represented by structures **15** and **16**.



15 m/e 89



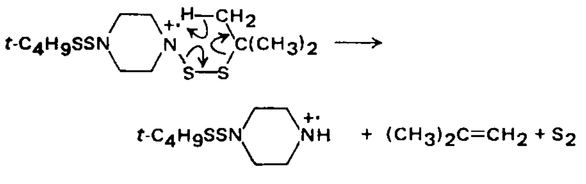
16 m/e 88

Finally, the moiety $HC{\equiv}S^+$ appears as a strong peak in the spectrum of **III**, possibly as an artifact resulting from further fragmentation of ion **8**.

High Resolution Spectra of N,N′-Bisalkyldithiopiperazines IV and V

The mass spectra of the *i*-propyl and *t*-butyl derivatives **IV** and **V** reveal strong molecular ions at m/e 298 and 326 respectively. In addition, these spectra are dominated by the presence of *i*-propyl and *t*-butyl cations which provide the penultimate and base peaks in **IV** and **V**.

As in the case of the monothio derivatives **I-III**, a favored site for fragmentation in bisdisulfides **IV** and **V** appears to be the nitrogen-sulfur bond. Cleavage of this linkage in the latter compounds results in charge retention exclusively by the nitrogen-containing fragment. Once again transfer of hydrogen from the *t*-butyl group to the nitrogen atom is indicated by the presence of the ion $C_8H_{18}N_2S_2^+$ (**17**). This fragment may be generated by loss of isobutylene and S_2 from the molecular ion.



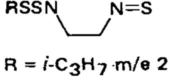
17 m/e 206

Loss of a hydrogen atom from **17**, or alternately, simple fission of the sulfenamide bond in the molecular ions of **IV** and **V**, also results in formation of ion **18**. Similarly, cleavage of the second nitrogen-sulfur bond provides strong peaks attributed to ions **6** and **7** as was also observed in the monothio derivatives.

18a R = i-C_3H_7 m/e 191
18b R = t-C_4H_9 m/e 205

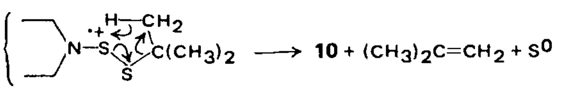
It is of interest to note that the two processes involving hydrogen transfers (*i.e.*, $p^+ \rightarrow$ **17** and **17** → **6**) were significantly more pronounced in the t-butyl derivative than in the i-propyl analog, most likely due to the greater relief of steric hindrance in the former as well as greater alkene stability.

The spectra of dithiopiperazines thus closely resemble those of the monothio compounds in that both undergo facile scission of the nitrogen-sulfur and carbon-sulfur bonds. In addition to these processes, however, disulfide cleavage contributes significantly to the spectra of the former compounds. This is not unexpected in view of the fact that fission of the S–S bond in dithiopiperazines (**IV** and **V**) produces similar fragments to those obtained by alkyl-sulfur cleavage in the monothio compounds. Thus, the presence of the ions $C_7H_{15}N_2S_3^+$ and $C_8H_{17}N_2S_3^+$ in the spectra of **IV** and **V** respectively implies formation of moieties **19a** and **b** *via* scission of the disulfide linkage.



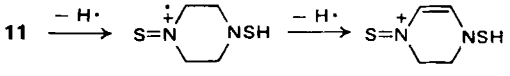
19a R = i-C_3H_7 m/e 223
19b R = t-C_4H_9 m/e 237

Furthermore, fission of the sulfur-sulfur bond can occur in much the same way as nitrogen-sulfur bond cleavage in that transfer of a hydrogen atom from the alkyl group to the charge-bearing fragment can take place. Thus, formation of ion **10** in compound **V** can be postulated to occur as shown below.



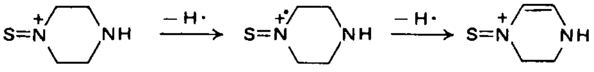
m/e 150

In addition, fragment **11** is abundant in the spectrum of **V** and faint in that of **IV**, having relative intensities of 29.5 and 1.5% respectively. Ion **11** then appears to lose two consecutive hydrogen atoms to generate ions **20** and **21**.



20 m/e 148 **21** m/e 147

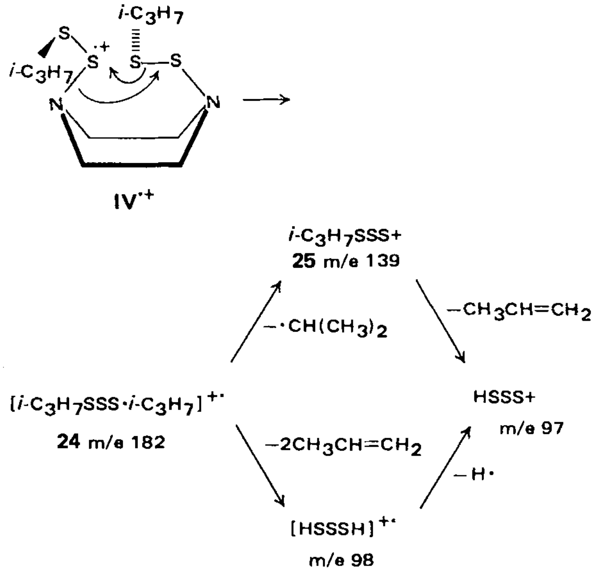
Finally, the process of disulfide cleavage can occur in conjunction with fission of the sulfenamide bond on the opposite side of the molecule, thereby producing ions **13**, **22**, and **23** in the spectra of **IV** and **V**.



13 m/e 117 **22** m/e 116 **23** m/e 115

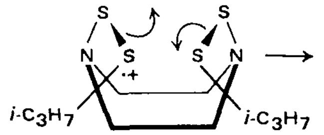
Thus it can be seen that the chief modes of fragmentation in the N,N′-bisalkyldithiopiperazines **IV** and **V** result from cleavage of the three principal bonds in the N–S–S–C group. Also, abundant ions are derived from the piperazine ring itself (*e.g.*, $C_4H_7N_2^+$ in **IV** furnishes the base peak).

In addition, we observed certain fragments of minor intensity in the spectrum of the i-propyl derivative **IV** that we feel are nevertheless worthy of comment due to the intriguing mechanisms by which they appear to be generated. For example, the formation of the ion $C_6H_{14}S_3^+$, **24**, could only arise from the transfer of an i-propylthio group to the sulfur atom **a** to the piperazine ring on the opposite side of the molecule. Models clearly demonstrate that the α and β sulfur atoms of the two respective i-propyldithio groups are in sufficiently close proximity for this rearrangement



to occur (providing that the piperazine ring assumes the boat conformation). Loss of an *i*-propyl radical from moiety **24** then generates fragment **25** which provides a moderately strong peak with a relative intensity of 10.7%. Faint peaks are also observed from the ions $H_2S_3^+$ and HS_3^+. These processes are illustrated on the previous page.

Similarly, fragments $C_6H_{14}S_2^+$ **26**, $C_3H_8S_2^+$ **27**, as well as the ion $H_2S_2^+$ **28** can be envisioned to form by cleavage of the two disulfide bonds with the formation of a new linkage between the two sulfur atoms β to the piperazine ring.



$IV^{\cdot+}$

$$[i\text{-}C_3H_7SS\cdot i\text{-}C_3H_7]^{+\cdot} \xrightarrow{-CH_3CH=CH_2}$$

26 m/e 150

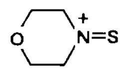
$$[i\text{-}C_3H_7SSH]^{+\cdot} \xrightarrow{-CH_3CH=CH_2} [HSSH]^{+\cdot}$$

27 m/e 108 **28** m/e 66

Analogous processes in the *t*-butyl derivative V appear to be insignificant or totally absent, possibly because of the greater hindrance of the two *t*-butyl groups which effectively prevent sufficient proximity of the two nitrogen substituents.

High Resolution Spectrum of N-Benzylthiomorpholine VI

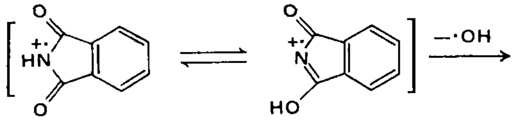
The relatively simple spectrum of the sulfenamide VI is dominated by the parent peak and by the tropylium ion which furnishes the base peak. Other ions observed include **8** and the fragments $HC{\equiv}S^+$ and $CH_2{=}N^+{=}S$ having relative intensities of 3.3, 4.9 and 2.3% respectively. Cleavage of the benzyl-sulfur bond also generates **2b**; however, this ion is faint as a result of the more favorable retention of charge by the tropylium ion. Finally, rupture of the morpholine ring produces ions **1** and **2** at m/e 57 and 56 as well as the moiety $CH_2{=}N^+{=}CH_2$.



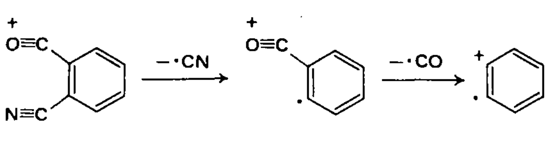
29b m/e 118

High Resolution Spectrum of N-Morpholinothiophthalimide VII

The molecular ion in the thiophthalimide VII is weak, comprising only 4.3% of the base peak. The presence of two different nitrogen-sulfur bonds in this compound accounts for the major fragments observed, with the imide-sulfur linkage being by far the more labile. Thus, cleavage of the latter bond with transfer of a hydrogen atom from the morpholine ring to the phthalimide group produces ion $C_8H_5NO_2^+$ (**30**) at m/e 147 which provides the base peak of the spectrum. Further fragmentation of **30** results in strong ions at m/e 130, 104 and 76 attributed to the structures **31**, **32** and **33** respectively as shown below. These fragments have also been reported in the spectra of other thiophthalimides,[6,7] as well as in alkyl phthalimide disulfides[8] and in sulfinylphthalimides,[9] Other prominent ions at m/e 103, 75, 74 and 50 ($C_7H_5N^+$, $C_6H_3^+$, $C_6H_2^+$, and $C_4H_2^+$ respectively) are also attributable to breakdown products of **30**.



30 m/e 147



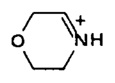
31 m/e 130 **32** m/e 104 **33** m/e 76

Alternately, scission of the imide-sulfur bond may result in formation of **29a**; however, the relative intensity of this latter fragment is only 6.1%, thus indicating that charge retention by the imide group is the favored process.

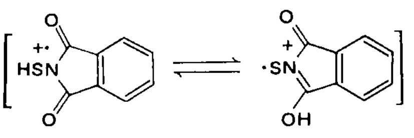
Furthermore, rupture of the amine-sulfur bond may also take place as evidenced by the presence of moderately strong peaks at m/e 87 and 86 due to the ions $C_4H_9NO^+$ (**3**) and $C_4H_8NO^+$ (**34b**) respectively. The existence of the former necessitates the transfer of a hydrogen atom from the phthalimide group to the amine nitrogen atom; the latter may be formed either by loss of a hydrogen atom from **3** or directly from the molecular ion.

Retention of positive charge by the sulfur-containing fragment upon cleavage of the amine-sulfur linkage also occurs, again with an accompanying hydrogen transfer from the morpholine ring to the sulfur atom. This process results in the formation of a minor peak at m/e 179 due to the ion $C_8H_5NO_2S^+$ (**35**). The latter fragment has also been observed in the spectra of certain alkyl phthalimido disulfides.[10]

Finally, abundant ions at m/e 57 and 56 may be attributed to fission of the morpholine ring, *vide supra.*



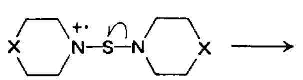
34b m/e 86



35 m/e 179

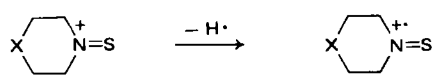
High Resolution Spectra of N,N′-Thiobisamines VIII and IX

The spectra of the two thiobisamines investigated display strong parent peaks and are once again dominated by scission of the sulfenamide bond. However, the variety of fragments obtained by cleavage of this linkage is more limited than in the case of the aminothiophthalimide VII as a result of the symmetry about sulfur in compounds VIII and IX. Upon rupture of this bond, retention of charge by either fragment is possible. When it occurs on the sulfur-bearing moiety, ions **29a** and **b** result, from which loss of hydrogen generates **36a** and **b**.



VIII$^{+\cdot}$ X = CH_2; m/e 200

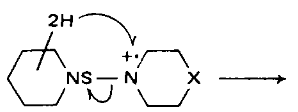
IX$^{+\cdot}$ X = O; m/e 204

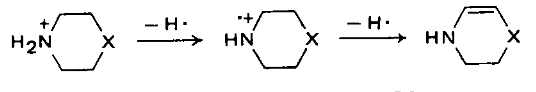


29a X = CH_2; m/e 116 **36a** X = CH_2; m/e 115

29b X = O; m/e 118 **36b** X = O; m/e 117

Alternately, the amine cation may be formed when the sulfur atom remains in the neutral fragment produced by the cleavage. It is interesting to note that a double hydrogen transfer to the amine cation may occur as evidenced by the prominent presence of the ions $C_5H_{12}N^+$ and $C_4H_{10}NO^+$ in the spectra of VIII and IX respectively. These fragments **37** may then consecutively lose two hydrogen atoms to form **38** and **34** with the latter comprising the base peak of the piperidine derivative VIII. It should be pointed out, however, that the possibility of genesis of 38 and 34 directly from the molecular ion cannot be eliminated.





37a X=CH_2 m/e 86 **38a** X=CH_2 m/e 85 **34a** X=CH_2 m/e 84

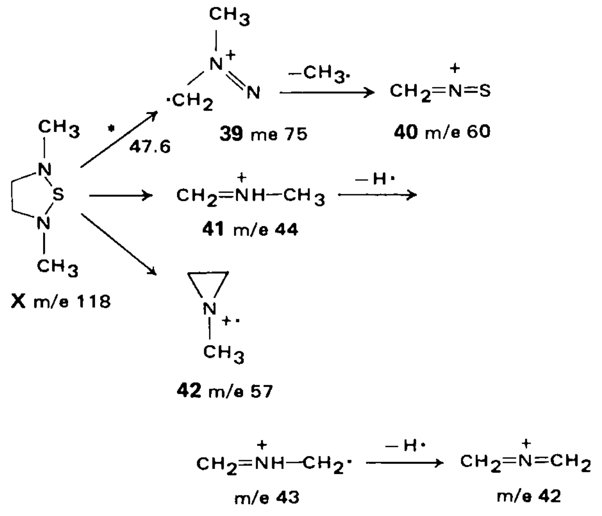
37b X=O m/e 88 **38b** X=O m/e 87 **34b** X=O m/e 86

In addition, ion **16** appears in the spectra of compounds VIII and IX with a relative intensity of 1.1 and 5.0% respectively. The ions CH_4NS^+, CH_3NS^+ and CH_2NS^+ are also prominent in the spectra of the thiobisamines; the first two being stronger in the piperidine derivative VIII and the latter being more abundant in the morpholine compound IX. Finally, the fragments **1** and **2** are again observed in the spectra of both compounds with **2** providing the base peak in that of IX.

Low Resolution Spectrum of 2,5-Dimethyl-1,2,5-thiadiazolidine X

Since thiadiazolidine X is in essence a cyclic thiobisamine, it might be expected that nitrogen-sulfur bond cleavage would again play a dominating role in the fragmentation of this compound. Our investigations revealed that the principal mode of decomposition on electron impact results from fission of this linkage in conjunction with cleavage of the C–C bond. Alternately, nitrogen-sulfur scission in the 1-position may occur together with rupture of the 4-carbon-nitrogen bond.

The former process produces the ion **39** at m/e 75 which then proceeds to lose a methyl radical, thus giving **40** at m/e 60. The genesis of **39** from the molecular ion is confirmed by a metastable peak at m/e 47.6. The alternate route, which also involves transfer of a hydrogen atom from the neutral to the charged fragment, produces ion **41** at m/e 44. Consecutive loss of two hydrogen atoms from the latter ion results in strong peaks at m/e 43 and 42 respectively with the latter comprising the base peak. In addition, the spectrum of X displays an intense molecular ion as well as a minor fragment at m/e 57 attributed to **42**. These processes are depicted below.



39 me 75

40 m/e 60

41 m/e 44

X m/e 118

42 m/e 57

m/e 43

m/e 42

TABLE I

The Mass Spectra of Sulfenamide Derivatives

Ion Formula[a]	Mass	I	II	III	IV	V	VI	VII	VIII	IX
$C_{18}H_{22}N_2S_2$	330	–	–	22.9	–	–	–	–	–	–
$C_{12}H_{26}N_2S_4$	326	–	–	–	–	17.3	–	–	–	–
$C_{10}H_{22}N_2S_4$	298	–	–	–	44.5	–	–	–	–	–
$C_{12}H_{12}N_2O_3S$	264	–	–	–	–	–	–	4.3	–	–
$C_{12}H_{26}N_2S_2$	262	–	45.5	–	–	–	–	–	–	–
$C_{11}H_{15}N_2S_2$	239	–	–	10.3	–	–	–	–	–	–
$C_8H_{17}N_2S_3$	237	–	–	–	–	1.7	–	–	–	–
$C_7H_{15}N_2S_3$	223	–	–	–	7.1	–	–	–	–	–
$C_{11}H_{15}NOS$	209	–	–	–	–	–	28.5	–	–	–
$C_{11}H_{16}N_2S$	208	–	–	5.5	–	–	–	–	–	–
$C_{11}H_{15}N_2S$	207	–	–	15.7	–	–	–	–	–	–
$C_8H_{18}N_2S_2$	206	100.0	21.4	–	–	17.3	–	–	–	–
$C_8H_{17}N_2S_2$	205	–	0.9	–	–	3.7	–	–	–	–
$C_8H_{16}N_2O_2S$	204	–	–	–	–	–	–	–	–	60.3
$C_{10}H_{20}N_2S$	200	–	–	–	–	–	–	–	81.1	–
$C_{10}H_{12}N_2S$	192	–	–	–	–	6.2	–	–	–	–
$C_7H_{15}N_2S_2$	191	–	–	–	–	43.7	–	–	–	–
$C_6H_{14}S_3$	182	–	–	–	–	1.1	–	–	–	–
$C_4H_8N_2S_3$	180	–	–	–	–	–	3.0	–	–	–
$C_8H_5NO_2S$	179	–	–	–	–	–	–	3.7	–	–
$C_8H_{18}S_2$	178	–	–	–	–	0.3	–	–	–	–
$C_{10}H_{12}NS$	178	–	–	1.1	–	–	–	–	–	–
$C_6H_{13}N_2S_2$	177	1.5	–	–	–	–	–	–	–	–
$C_8H_{18}N_2S$	174	–	0.2	–	–	–	–	–	–	–
$C_8H_{17}N_2S$	173	–	1.3	–	–	–	–	–	–	–
$C_7H_7S_2$	155	–	–	0.2	–	–	–	–	–	–
$C_4H_9S_3$	153	–	–	–	–	0.4	–	–	–	–
$C_6H_{14}S_2$	150	–	–	–	4.0	–	–	–	–	–
$C_4H_{10}N_2S_2$	150	–	50.5	–	–	8.6	–	–	–	–
$C_6H_2N_2O_3$	150	–	–	–	–	–	–	6.3	–	–
$C_4H_9N_2S_2$	149	–	4.6	–	1.5	29.5	–	–	–	–
$C_4H_8N_2S_2$	148	–	0.2	–	12.0	1.3	–	–	–	–
$C_8H_5NO_2$	147	–	–	–	–	–	–	100.0	–	–
$C_4H_7N_2S_2$	147	–	–	–	0.5	6	–	–	–	–
$C_6H_{13}N_2S$	145	71.1	–	–	–	–	–	–	–	–C
$C_3H_7S_3$	139	–	–	–	10.7	–	–	–	–	–
C_8H_4NO	130	–	–	–	–	–	–	12.5	–	–
C_7H_7S	123	–	–	43.7	–	–	3.3	–	–	–
$C_4H_{10}S_2$	122	0.9	–	–	–	–	–	–	–	–
$C_4H_{10}S_2^{++}$	122	7.9	–	–	–	–	–	–	–	–
$C_4H_9S_2$	121	–	–	–	–	0.1	–	–	–	–
$C_4H_{10}N_2S$	118	–	6.3	–	–	0.6	–	–	–	–
C_4H_8NOS	118	–	–	–	–	–	2.4	6.1	–	21.2
$C_4H_9N_2S$	117	0.4	53.5	2.1	11.7	4.6	–	–	–	–
C_4H_7NOS	117	–	–	–	–	–	0.3	3.3	–	5.6
$C_5H_{10}NS$	116	3.6	–	–	–	–	–	–	53.6	–
$C_4H_8N_2S$	116	–	0.6	0.9	9.8	8.4	–	–	–	–
C_4H_6NOS	116	–	–	–	–	–	–	3.3	–	0.3
C_5H_9NS	115	–	–	–	–	–	–	–	11.7	–

TABLE I continued

Ion Formula[a]	Mass	I	II	III	IV	V	VI	VII	VIII	IX
$C_4H_7N_2S$	115	0.2	0.4	1.1	3.5	1.9	–	–	–	–
$C_3H_8S_2$	108	–	–	–	3.1	–	–	–	–	–
$C_4H_{10}NS$	104	1.4	–	–	–	–	–	–	–	–
C_7H_4O	104	–	–	–	–	–	–	88.5	–	–
C_7H_5N	103	–	–	–	–	–	–	30.7	–	–
H_2S_3	98	–	–	–	0.7	–	–	–	–	–
HS_3	97	–	–	–	1.4	–	–	–	–	–
C_6H_4O	92	–	–	–	–	–	–	2.2	–	–
C_7H_7	91	–	–	100.0	–	–	100.0	–	–	–
$C_4H_{10}S$	90	–	–	–	–	1.1	–	–	–	–
C_4H_9S	89	–	0.4	–	–	–	–	–	–	–
C_3H_7NS	89	2.9	2.5	–	–	0.1	–	–	–	–
$C_4H_{10}NO$	88	–	–	–	–	–	–	–	–	6.8
C_3H_6NS	88	6.4	9.4	5.9	2.2	0.6	0.7	–	1.1	5.0
C_4H_9NO	87	–	–	–	–	–	1.3	11.1	–	8.6
$C_5H_{12}N$	86	–	–	–	–	–	–	–	5.4	–
$C_4H_{10}N_2$	86	–	9.0	4.1	1.9	47.1	–	–	–	–
C_4H_8NO	86	–	–	–	–	–	1.5	14.1	–	54.2
C_4H_7NO	85	–	–	–	–	–	0.1	1.5	–	0.9
$C_4H_9N_2$	85	26.4	41.4	25.7	33.6	67.5	–	–	–	–
$C_5H_{11}N$	85	–	–	–	–	–	–	–	20.8	–
C_4H_6NO	84	–	–	–	–	–	0.4	1.5	–	1.8
$C_4H_8N_2$	84	1.6	0.6	0.9	27.3	2.6	–	–	–	–
$C_5H_{10}N$	84	–	–	–	–	–	–	–	100.0	–
C_5H_9N	83	–	–	–	–	–	–	–	4.9	–
$C_4H_7N_2$	83	4.5	1.4	4.4	100.0	8.5	–	–	–	–
C_5H_8N	82	–	–	–	–	–	–	–	9.3	–
$C_4H_6N_2$	82	–	–	–	2.6	0.6	–	–	–	–
$C_4H_5N_2$	81	–	–	–	2.3	0.7	–	–	–	–
C_6H_7	79	–	–	2.0	–	–	–	–	–	–
C_6H_5	77	–	–	3.6	–	–	–	–	–	–
C_3H_8S	76	–	–	–	3.5	–	–	–	–	–
C_6H_4	76	–	–	3.1	–	–	–	91.6	–	–
C_2H_6NS	76	–	3.3	–	–	–	–	–	–	–
C_3H_7S	75	2.8	–	–	2.3	–	–	–	–	–
C_6H_3	75	–	–	–	–	–	–	10.9	–	–
C_2H_5NS	75	–	–	–	–	–	–	–	0.6	1.2
C_6H_2	74	–	–	–	–	–	–	10.5	–	–
C_2H_4NS	74	–	3.2	–	–	–	0.4	–	0.8	2.4
C_6H	73	–	–	–	–	–	–	2.1	–	–
C_4H_8N	70	–	–	–	–	–	0.1	–	3.9	0.3
C_4H_2O	66	–	–	–	–	–	–	3.0	–	–
H_2S_2	66	0.4	–	–	0.9	–	–	–	–	–
C_5H_5	65	–	–	8.1	–	–	4.5	–	–	–
S_2	64	–	–	–	1.5	0.3	–	–	–	–
CH_4NS	62	–	–	–	–	–	0.1	–	4.6	0.5
C_2H_5S	61	–	–	–	2.4	–	–	–	–	–
CH_3NS	61	–	–	–	–	–	0.2	–	2.6	1.0
CH_2NS	60	–	4.2	3.3	2.5	0.8	2.3	2.2	2.1	11.0

TABLE I continued

Ion Formula[a]	Mass	I	II	III	IV	V	VI	VII	VIII	IX
C_2H_3S	59	–	–	–	3.1	–	–	–	–	–
C_3H_8N	58	3.7	–	11.9	2.3	–	–	–	0.6	0.3
C_4H_9	57	–	100.0	–	–	100.0	0.1	–	4.2	–
C_3H_7N	57	6.0	–	3.2	9.1	–	2.4	11.1	4.6	10.8
C_3H_6N	56	79.6	44.6	24.2	71.1	13.7	6.6	19.5	15.3	100.0
C_4H_7	55	–	–	–	–	–	–	0.9	38.4	–
C_3H_5N	55	6.6	5.0	4.8	29.5	7.1	0.5	2.6	4.2	–
C_3H_4N	54	3.6	1.7	1.9	6.8	2.0	0.5	0.7	1.2	2.4
C_4H_3	51	–	–	2.3	–	–	–	–	–	–
C_4H_2	50	–	–	–	2.5	–	–	37.0	–	–
C_4H	49	–	–	–	–	–	–	2.2	–	–
CHS	45	3.0	–	26.8	1.7	0.5	4.9	–	–	–
C_2H_6N	44	3.6	–	4.8	1.8	–	0.6	1.4	–	–
CH_4N_2	44	–	–	–	–	–	–	–	–	2.6
C_3H_7	43	–	–	2.7	96.5	–	–	–	–	–
C_2H_5N	43	0.2	–	1.8	1.8	–	0.1	–	–	4.0
C_2H_4N	42	16.9	–	–	–	–	2.0	–	–	–
C_3H_3	39	–	–	–	–	–	2.2	–	–	–
CH_4N	30	6.1	–	–	–	–	2.1	–	–	–
C_2H_5	29	8.2	–	–	–	15.3	–	–	–	–
CH_2N	28	7.2	–	–	–	2.7	3.5	–	–	–
C_2H_3	27	7.7	–	–	–	3.1	–	–	–	–

[a] Unless otherwise indicated, all ions are singly charged.

Summary

Our investigations of the mass spectrometry of several compounds containing divalent sulfur linked to nitrogen have revealed their principal modes of fragmentation.

In the spectra of monothiopiperazines **I-III** rupture of both the sulfenamide and alkyl-thio bonds generally dominates the fragmentation. The relative importance of these two processes, as well as the degree of charge retention by the two halves formed in each cleavage is highly dependent on the exact nature of the alkyl substituent. Furthermore, transfer of a hydrogen atom from the neutral fragment to either sulfur or nitrogen appears prominent only in the *t*-butyl derivative.

Similar processes occur in the dithiopiperazines **IV** and **V** where scission of the disulfide bond may also take place. Of particular interest are certain group transfers occurring chiefly in the isopropyl derivative **IV**. The process is characterized by migration of an isopropylthio group to the α or β sulfur atoms on the opposite side of the piperazine ring.

In the spectra of compounds **VII-IX** the presence of the N-S-N moiety again results in facile nitrogen-sulfur cleavage. When the structure is symmetrical about sulfur, charge retention by either fragment is possible. However, when sulfur is linked to both an amine function and an imide group, the sulfur-imide bond proves to be by far the more labile and positive charge is preferentially retained on the imide moiety. Also of interest is the double transfer of hydrogen from the neutral, sulfur-containing fragment to the amine cation in thiobisamines **VIII** and **IX**.

Finally, it was observed that fission of the piperazine, piperidine and morpholine moieties in compounds **I-IX** generated certain ions such as $C_3H_7N^+$ and $C_3H_6N^+$ which were common to all or nearly all of the spectra. This similarity in behavior of these cyclic amine functions implies that neither the presence nor the type of heteroatom in the 4-position significantly influences their modes of fragmentation.

Experimental

The compounds **I-X** were prepared by the methods of Harpp and Back.[11,12] Purification *via* recrystallization was performed as necessary.

All high resolution spectra were recorded on a model AEI-MS-902 spectrometer utilizing a source temperature of

200°, an ionizing voltage of 500 V and an accelerating voltage of 8 kV. The samples were introduced with a direct insertion probe at temperatures between 40 and 110°. Nominal resolving power of the instrument was 10 K. All ions having relative intensities greater than 2% of the base peak are listed in Table I except for those containing heavy isotopes. In addition, many ions of lower intensity have been included due to particular interest or in order to correlate their presence in several spectra. Selection of elemental compositions was performed by computer according to the "best fits" of the measured masses.

The low resolution spectrum of compound X was obtained on a similar instrument, also using a direct insertion probe at a temperature of 145°.

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