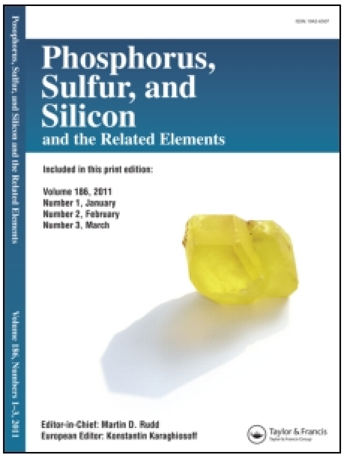

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MASS SPECTROMETRY OF SULFINAMIDES AND SULFINATE ESTERS

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MASS SPECTROMETRY OF SULFINAMIDES AND SULFINATE ESTERS

by

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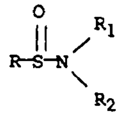
ABSTRACT

The low resolution mass spectra of alkyl and aryl sulfinamides containing alkyl, cycloalkyl, aryl and cyclic amine functions were recorded and the major fragmentation modes were elucidated with the aid of metastable peaks. In addition, the behavior of a variety of sulfinate esters upon electron-impact was similarly established.

In recent years many electron-impact studies of organo-sulfur compounds have appeared in the literature.[1] However, the investigation of sulfinyl compounds has hitherto been confined to sulfoxides,[1f] arylsulfinylamines,[2] thiosulfinates[3] and sulfinylphthalimides.[4] In addition, Baarschers and Krupay[5] have determined the mass spectra of two alkyl arenesulfinates and two aryl alkanesulfinates.

Our interest in the fragmentation modes of sulfinyl derivatives thus prompted us to obtain the mass spectra of sulfinamides **I-VII** as well as those of alkyl alkanesulfinates **VIII-XI** and the alkyl arenesulfinate **XII**.

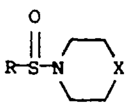


I $R = CH_3;\ R_1 = R_2 = C_2H_5$

II $R = i\text{-}C_3H_7;\ R_1 = CH_3;\ R_2 = n\text{-}C_4H_9$

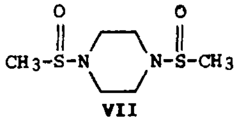
III $R = C_6H_5;\ R = C_6H_{11};\ R_2 = H$

IV $R = CH_3;\ R_1 = C_6H_5;\ R_2 = H$

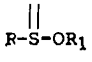


V $R = C_6H_5CH_2;\ X = O$

VI $R = C_2H_5;\ X = CH_2$



VII

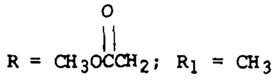


$R\text{-}S(=O)\text{-}OR_1$

VIII $R = n\text{-}C_4H_9;\ R_1 = CH_3$

IX $R = R_1 = i\text{-}C_3H_7$

X $R = C_6H_5CH_2;\ R_1 = C_2H_5$



XI $R = CH_3OC(=O)CH_2;\ R_1 = CH_3$

XII $R = C_6H_5;\ R_1 = C_2H_5$

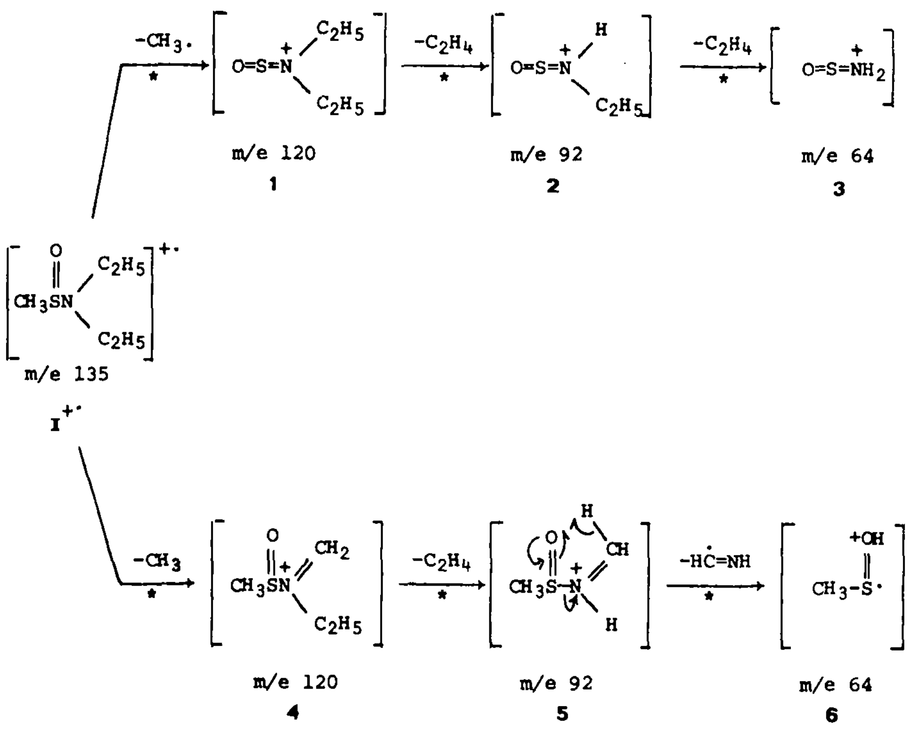
Mass Spectra of Sulfinamides I–VIII

Despite the wide variety of the sulfinamides studied, certain general features are nevertheless common to all. Compounds **I-VII** exhibit parent peaks varying in intensity from 60% in sulfinanilide **IV** to 1% in the morpholine derivative **V**. Furthermore, the spectra of these sulfinamides appear to be dominated by cleavage of the carbon–sulfur and nitrogen–sulfur bonds. However, the exact nature of these fragmentation processes is highly dependent on the type of nitrogen and sulfur substituents.

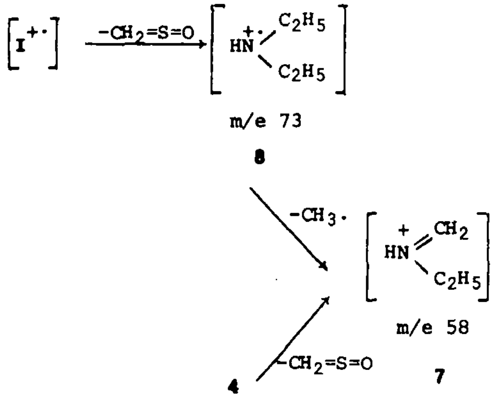
The spectrum of sulfinamide **I** displays a moderately intense parent peak at m/e 135. Cleavage of the methylsulfinyl bond generates ion **1** as evidence by the base peak at m/e 120. The loss of two consecutive ethylene molecules from the latter fragment then produces strong peaks at m/e 92 and 64 attributable to ions **2** and **3**, with appropriate metastable ions being observed for all of these processes.

However, loss of a methyl radical from the ethyl group of the molecular ion followed by expulsion of ethylene could generate species **4** and **5**, isomeric with **1** and **2**. Furthermore, ejection of the neutral fragment $H\dot{C}{=}NH$ from **5** might then produce **6** at m/e 64. These processes are illustrated below.

Further evidence for the existence of the mechanism $P^{+} \to$ **1** $\to$ **2** $\to$ **3** is suggested by the facile formation of fragments containing the $>N\overset{\pm}{-}S{=}O$ moiety in sulfinylphthalimides[4] and in other sulfinamides *vide infra*. On the other hand, a significant contribution of species **4** to the peak at m/e 120 is not unlikely in view of the fact that a process analogous to $P^{+} \to$ **4** has been reported in the spectrum of *N,N*-diethylacetamide.[6] In order to resolve this behavioral dichotomy, a high resolution spectrum of the peak at m/e 64 was obtained.

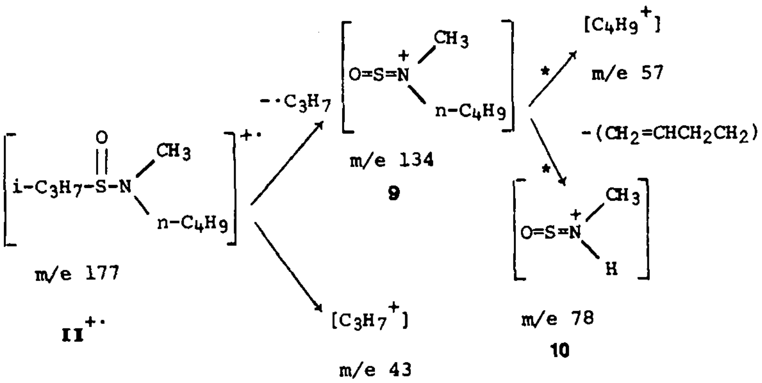


This showed the contributions of NH_2SO^+ and CH_4SO^+ to be in the ratio of 15 : 1, thereby confirming the process $P^+ \rightarrow 1 \rightarrow 2 \rightarrow 3$. However, the low abundance of 6 indicates that $P^+ \rightarrow 4 \rightarrow 5 \rightarrow 6$ is not a favored pathway. The latter fragment could also arise directly from the molecular ion.



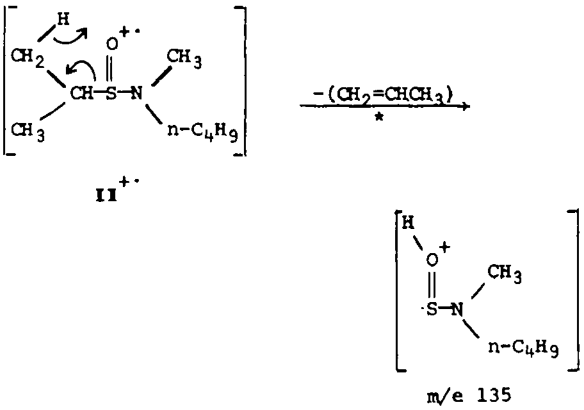
A moderately strong ion at m/e 58 was also observed in the spectrum of I. A similar peak has been attributed to fragment 7 in the spectrum of *N,N*-diethylacetamide[6], and was found to arise both *via* loss of ketene from the carbonyl analog of 4 and through formation of 8 from the molecular ion followed by loss of a methyl radical. Similar processes are likely operative in the sulfinamide I as shown below; however, lack of appropriate metastable ions precludes their confirmation.

The spectrum of sulfinamide II again reveals carbon-sulfur fission to be a key process. Unlike derivative I however, compound II permits charge retention by the alkyl fragment as well as by the sulfur-bearing moiety. Hence, although species 9 is prominent, it is not the base peak in II as 1 is in I. Furthermore, an abundant ion at m/e 43 indicates the presence of the *i*-propyl cation. Loss of butene from 9 then provides a strong peak at m/e 78, 10. In addition, $[CH_3NSO]\cdot$ can be



expelled from 9 as a neutral fragment, thereby generating the butyl cation. The latter two processes are accompanied by the presence of appropriate metastable peaks at m/e 45.4 and 24.2 respectively.

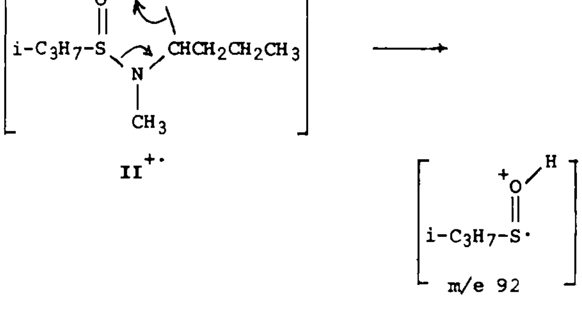
It is also possible for carbon-sulfur scission to be accompanied by the transfer of a hydrogen atom from the isopropyl group to the sulfinyl moiety, thus producing ion **11** along with a molecule of propene *via* the five-center McLafferty rearrangement[7] shown below. The process $P^+ \rightarrow$ **11** is confirmed by the presence of a metastable peak at m/e 103.0. It is interesting to note that a similar mechanism was found to be operative in the case of alkylsulfinylphthalimides[4] containing β-hydrogen atoms on the sulfur substituent.



$II^{+\cdot}$

11

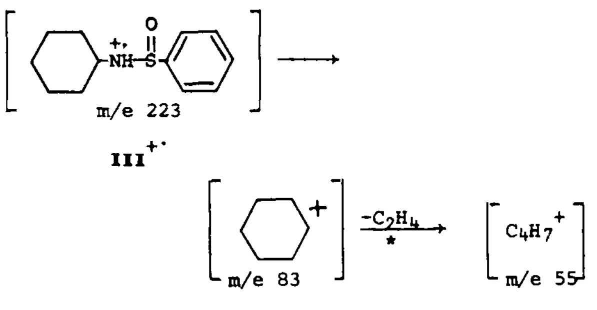
In addition to cleavage of the alkyl-sulfur bond, facile ruptures of the nitrogen-sulfur linkage occurs as evidenced by the base peak of the spectrum at m/e 92. Genesis of ion **12** likely proceeds by rearrangement of a β-hydrogen from the butyl group to the sulfinyl oxygen with concomitant elimination of the imine as shown below.



$II^{+\cdot}$

12

The complexity of the spectrum of sulfinamide III is largely due to the presence of the cyclohexyl group which undergoes a wide variety of bond fissions and rearrangements. The appearance of a moderately strong peak at m/e 83 is likely due to formation of the cyclohexyl cation **13** which then proceeds to lose ethylene to generate **14** as shown below. This process, which is confirmed to a metastable ion at m/e 36.4, has also been reported in the mass spectrum of methylcyclohexane by Meyerson.[8] These authors reported that ethylene is lost from the molecular ion of the latter compound in a complex fashion with the ethylene carbons originating in any of several positions. It is likely that the process **13** → **14** proceeds in a similarly equivocal manner in **III**.

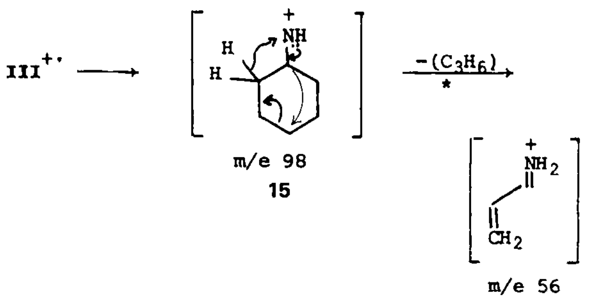


$III^{+\cdot}$

13 **14**

The penultimate and base peaks of III appear at m/e 43 and 41 respectively. The identity of these ions is most likely that of the isopropyl and allyl cations; however, the lack of appropriate metastable peaks precludes determination of their exact origin.

The site of initial bond cleavage in the molecular ion of **III** may also be the sulfinamide linkage (>N–S), thus producing ion **15** at m/e 98. Subsequent loss of a neutral fragment of 42 mass units is indicated by a strong peak at m/e 56 (**16**) and by a metastable peak at m/e 32.0. The mechanism depicted below may be invoked to rationalize this process. It is interesting to note that fragment **16** provides the base peak in the spectrum of cyclohexylamine[9] although its origin in that compound was postulated[1g] to be the parent ion rather than **15**.

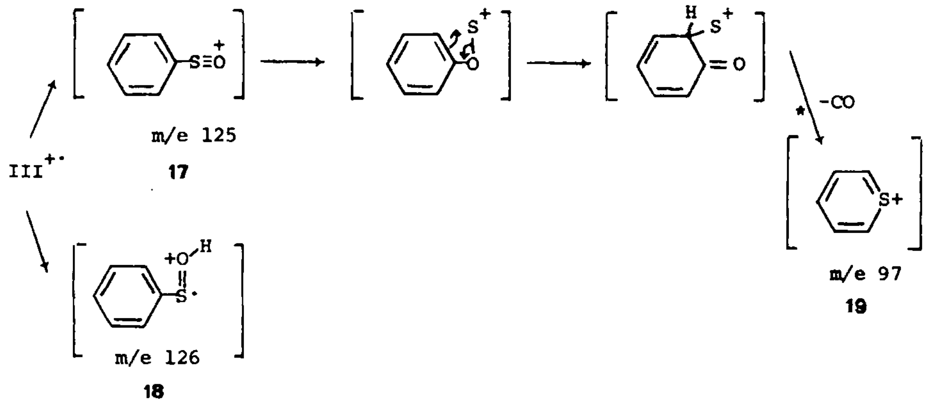


15

16

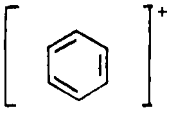
It is also possible that the peak at m/e 56 receives a significant contribution from the ion $C_4H_8^+$ as the latter moiety is prominent in the spectra of both cyclohexane and its methyl derivative.[8]

Scission of the nitrogen-sulfur bond also permits positive charge to remain on the sulfur-containing

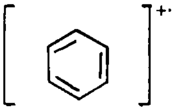


fragment. Thus, formation of species 17 and 18 results in moderately strong peaks appearing at m/e 125 and 126 with the presence of the latter indicating the possibility of a hydrogen rearrangement. Furthermore, a significant peak at m/e 97 together with a metastable ion at m/e 75.3 suggests formation of the thiapyrrylium ion 19 from 17. This rearrangement is well-known in certain sulfoxides[10] and sulfinate esters.[5]

The presence of abundant ions at m/e 77 and 78 (20 and 21) in the spectrum of sulfinamide III indicates that fission of the aryl-sulfur linkage is also a favored process with formation of 21 necessitating a hydrogen transfer to the aryl group.

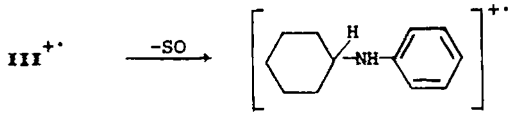

m/e 77

20


m/e 78

21

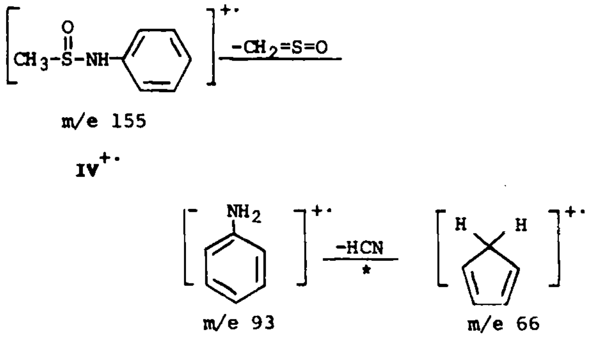
In addition to the fragments obtained by cleavage of the three principal bonds in the C–N–S–C unit, the spectrum of III revealed a moderate peak at m/e 175 (22). This species is likely due to loss of SO from the parent ion, a process which has previously been noted in the spectra of certain sulfoxides[11] and sulfinylphthalimides.[4]



m/e 175

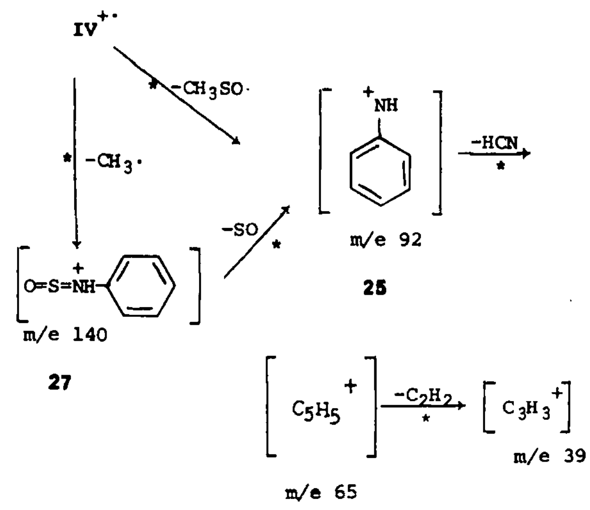
22

The spectrum of sulfinanilide IV has been investigated by Baarschers and Krupay.[5] However, comment was made on only one fragment, namely that of 23 which may be formed by ejection of $CH_2{=}S{=}O$ from the parent ion. Our own studies confirm the formation of this ion.[12] Furthermore, we found that loss of HCN from 23 generates 24 with an accompanying metastable peak at m/e 46.8. The process 23 → 24 has also been observed in the spectra of acetanilide[13] and aniline.[14]



23 **24**

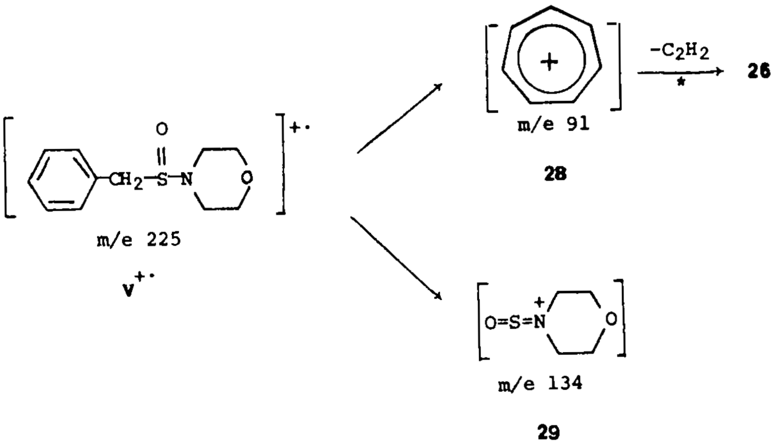
The spectrum of compound IV displays the strongest parent peak of all sulfinamides studied having a relative intensity of 60%. In addition, simple cleavage of the sulfinamide bond forms ion 25 which furnishes the base peak at m/e 92. Elimination of HCN from the latter



25

27

26



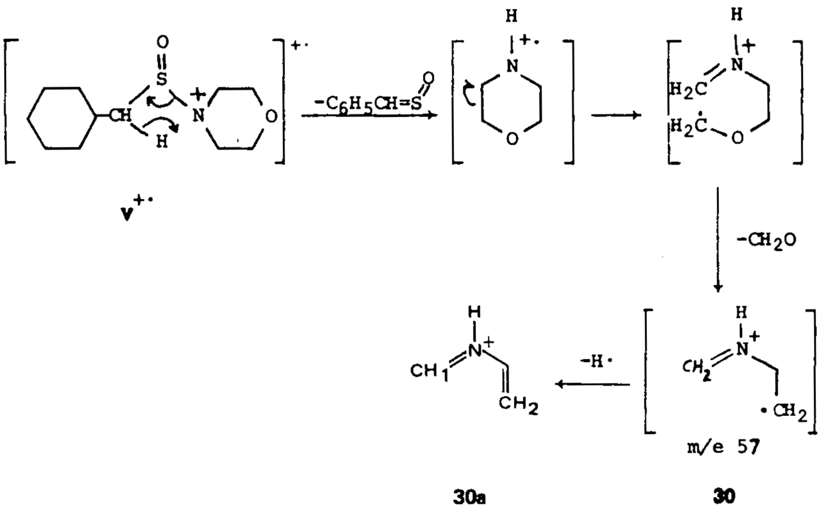
fragment produces the cyclopentadienyl cation **26** at m/e 65 which in turn loses acetylene to provide $C_3H_3^+$ at m/e 39.

Alternately, ion **25** may be generated *via* loss of a methyl radical from the molecular ion followed by expulsion of SO from fragment **27**. All of these processes are accompanied by metastable peaks.

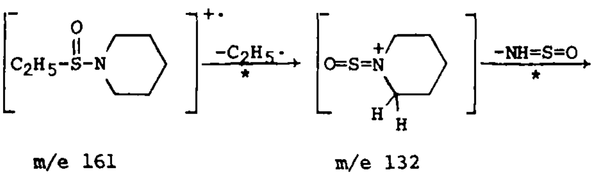
The mass spectrum of *N*-(benzylsulfinyl)-morpholine (**V**) displays a faint parent peak and is dominated by formation of the tropylium ion **28** which furnishes the base peak at m/e 91. Further fragmentation of the latter species produces the cyclopentadienyl ion **26** as evidenced by a metastable peak at m/e 46.4. Carbon–sulfur scission may also result in charge retention by the sulfur-bearing fragment thus generating **29**. However, the lower abundance of the latter ion demonstrates that retention by the tropylium ion[15] is the favored process.

The presence of intense peaks at m/e 57 and 56 is likely due to formation of ions **30** and **30a**. These fragments have also been observed in the mass spectra of morpholine-containing sulfenamides[16] where their identity was established through high resolution experiments. A reasonable mechanism for the genesis of **30** and **30a** appears below; however, it must be pointed out that expulsion of the neutral sulfine fragment prior to that of formaldehyde is arbitrary as the converse could likewise readily occur. The lack of strong peaks at m/e 87 (P^+-C_7H_6SO) and 195 (P^+–CH_2O) and of the corresponding metastable ions prevents resolution of this mechanistic dichotomy. Furthermore, the source of the rearranged hydrogen atom is equivocal as it could conceivably originate from the ortho position of the benzene ring.

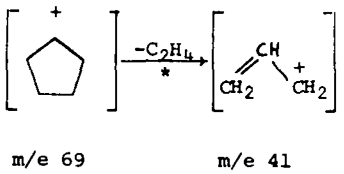
The spectrum of the piperidine derivative **VI** displays a strong parent peak and is dominated by rupture of the alkyl-sulfur bond. Thus, fragment **31** furnishes the base peak at m/e 132. Ring contraction in the latter species then proceeds with ejection of NH=S=O, thereby generating the cyclopentyl cation **32** which furnishes the penultimate peak at m/e 69. Loss of ethylene from **32** results in the formation of a strong peak at m/e 41 attributable to the allyl cation. These processes are all accompanied by metastable peaks.



The appearance of a strong peak at m/e 133 (**33**) also implies that carbon-sulfur scission may occur with rearrangement of hydrogen to the sulfinyl group with concomitant elimination of ethylene. An analogous process was found to be prominent only in compound **II** among the sulfinamides studied (*vide supra*).

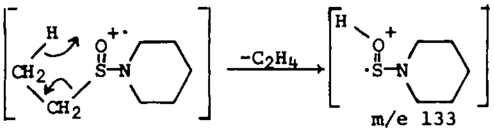


VI$^{+\cdot}$ **31**



32

This fact lends further support to the postulate that the transferred hydrogen originates in the β-position of the alkyl substituent on sulfur. It is also worthy of note that the intensity of **11** in **II** is considerably greater than that of **33** in **VI**. This may be a reflection of the greater stability of the alkene fragment and greater relief of steric hindrance in the former compound.



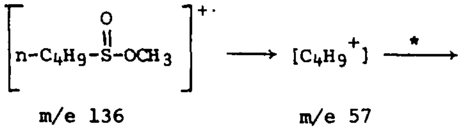
VI$^{+\cdot}$ **33**

The spectrum of *bis*sulfinamide **VII** is quite complex as a result of the presence of two sulfinamide functions each of which may undergo fragmentation. Major fragments result from cleavage of both S—N bonds. Also, many abundant ions result from fission of the piperazine ring.

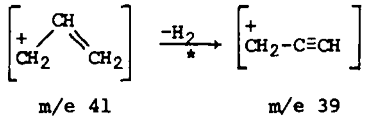
Mass Spectra of Sulfinate Esters VIII-XII

The chief fragmentation modes of sulfinate esters result from cleavage of the carbon-sulfur linkage or alternately by rupture of the sulfur-oxygen single bond. Rearrangement of hydrogen may also accompany the former process; however, in general, the spectra of compounds **VIII-XII** are simpler than those of the sulfinamides **I-VII**.

In methyl *n*-butanesulfinate (**VIII**), alkyl-sulfur scission generates the butyl cation which furnishes the base peak. Further decomposition of this fragment accounts for the presence of a strong peak at m/e 41, attributable to the allyl cation, which in turn produces ion **34** at m/e 39 through loss of a hydrogen molecule. The latter two processes are accompanied by appropriate metastable peaks.



VIII$^{+\cdot}$

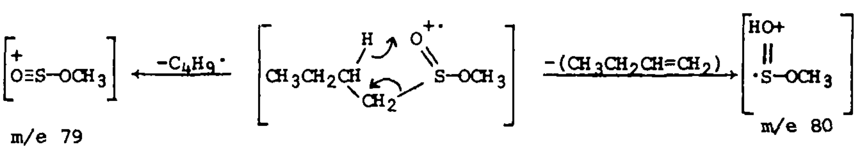


34

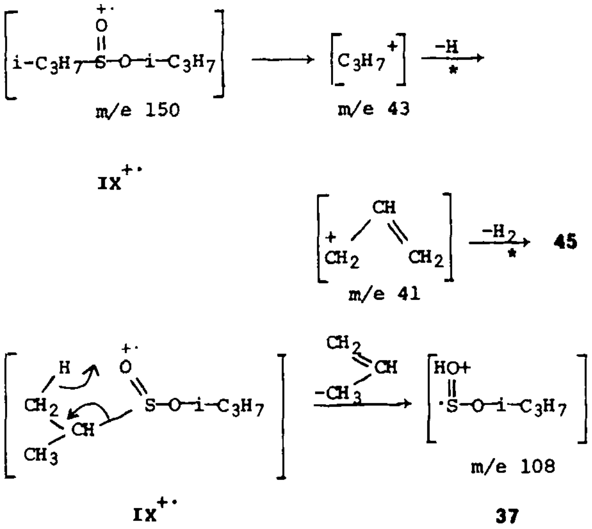
Alternately, carbon-sulfur cleavage may permit charge to reside on the sulfur-containing fragment, thus forming ions **35** and **36**. The existence of the latter suggests a hydrogen transfer, most likely from the β-position of the *n*-butyl group as follows. This process is analogous to the five-center McLafferty rearrangement observed in sulfinamides **II** and **VI**.

In sulfinate ester **IX** the base peak at m/e 43 indicates facile formation of the *i*-propyl cation. Although a small contribution to this peak from the oxygen substituent would be expected, we feel that the majority derives from the group on sulfur, particularly in view of the intensity of the butyl cation in **VIII**. Two hydrogen molecules are then lost consecutively to provide strong peaks at m/e 41 and 39 (metastable ions at m/e 39.1 and 37.1).

In addition, a process analogous to the formation of **36** in the spectrum of **VIII** provides the ion **37**; however, the abundance of the latter is considerably lower (9% *vs*. 45% for **36**).



35 VIII$^{+\cdot}$ **36**



Finally, cleavage of the sulfur-oxygen single bond generates fragment 38 at m/e 91.

$IX^{+\cdot} \longrightarrow [\ i\text{-}C_3H_7\text{-}S{\equiv}O^{+}\ ]$

m/e 91

38

The mass spectrum of ethyl benzylsulfinate (X) is exceedingly simple due to overwhelming domination by the tropylium ion 28.

Carbon-sulfur cleavage similarly is important in the spectrum of ester XI, but unlike the case of X, charge is retained almost exclusively by the sulfur-bearing fragment 35 which provides the base peak. Also, loss of $CH_3O\cdot$ from the molecular ion results in a minor peak at m/e 121. This behavior contrasts with that of diethyl malonate[17] in which analogous loss of an ethoxy radical furnishes the base peak of the spectrum.

In addition to the spectra of the alkyl alkanesulfinates VIII-XI, that of ethyl benzenesulfinate (XII) was also studied. The latter compound reveals a significantly more pronounced parent peak (relative intensity 60%) than derivatives VIII-XI. Furthermore, fragments 17, 19 and 20 are abundant in the spectrum of XII. Their occurence in that of methyl benzenesulfinate has also been recently reported.[5]

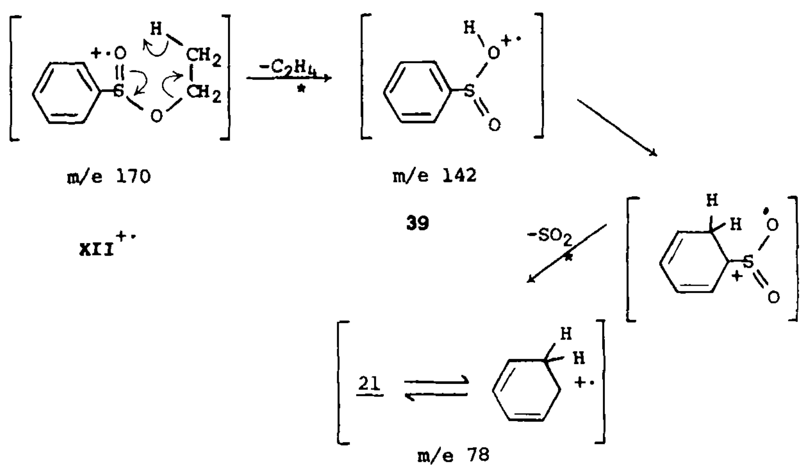
Furthermore, the spectrum of derivative XII displays a strong peak at m/e 142 (39) attributable to loss of ethylene from the parent ion. Fragment 39 in turn loses SO_2 to generate 21 as follows. The appropriate metastable peaks are observed for both processes.

Finally, the presence of an abundant ion at m/e 51 can be rationalized by expulsion of acetylene from 20 as evidenced by the metastable peak at m/e 33.8.

Summary

The low resolution mass spectra of alkyl and aryl sulfinamides containing alkyl, cycloalkyl, aryl and cyclic amine functions were recorded and the major fragmentation modes were elucidated with the aid of metastable ions. Moreover, the behavior of a variety of sulfinate esters upon electron-impact was similarly established.

It was found that parent peaks are observed in the spectra of all sulfinamides studied. However, the parent ions are generally considerably less intense in those derivatives having higher molecular weights. Cleavage of the carbon-sulfur bond plays a prominent role in the fragmentation of compounds I-VII. With the exception of III, all display strong peaks resulting from rupture of the carbon-sulfur linkage with retention of charge by the sulfur-containing fragment. Since facile hydrogen rearrangement accompanies this process only in II and VI, it appears that the availability of hydrogen in the β-position of an alkyl substituent on sulfur is necessary for such a transfer to take place.



Alternately, carbon–sulfur scission in sulfinamides may permit charge retention by carbon; however, such ions are prominent only in derivatives **II**, **III**, and **V** where the cation so formed possesses exceptional stability.

Cleavage of the sulfinamide bond is also indicated in certain cases. It occurs with charge retention by either half in **III** and **VII** and primarily by nitrogen in sulfinanilide **IV**. Rearrangement of a hydrogen atom to the amine function is also favorable in the latter compound and a similar transfer to the sulfinyl group in **II** provides the vase peak in its spectrum.

In addition, loss of SO from the molecular ion is significant in **III** and faint in **V**.

Parent peaks were also observed in all of the sulfinate esters studied with that of the aryl derivative **XII** being by far the most intense. The spectra of compounds **VIII-XII** are again dominated by cleavage of the crucial carbon–sulfur linkage, with the resulting alkyl or aryl fragments providing the base peaks in all of the esters except **XI**. The anomalous behavior of the latter is due to more favorable retention of charge by the sulfur-containing moiety.

Fragmentation of the sulfur–oxygen single bond is significant in ester **XII**, likely the result of resonance stabilization of the ion formed. This process also plays a minor role in the spectrum of compound **IX**.

Experimental Section

The sulfinamides **I-VII** and sulfinate esters **VIII-XII** were prepared by the method of Harpp and Back.[4] Mass spectra were recorded by Mr. W. Budd on a model AEI-MS-902 spectrometer using a direct insertion probe. All peaks whose relative intensity exceeds 10% of the base peak are listed in Table I.

Acknowledgment

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TABLE I[a] - Relative Intensities I-XII m/e(%)

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
P^+135(29)	P^+177(15)	P^+223(5)	P^+155(60)	P^+225(1)	P^+161(29)	P^+210(3)	P^+136(17)	P^+150(11)	P^+184(2)	P^+152(12)	P^+170(60)
132(54)	136(10)	175(16)	140(48)	134(26)	134(13)	195(18)	80(45)	110(10)	92(10)	79(100)	142(54)
120(100)	135(78)	159(11)	93(28)	92(12)	133(19)	147(61)	79(19)	91(18)	91(100)	58(14)	126(11)
92(80)	134(78)	126(18)	92(100)	91(100)	132(100)	131(28)	65(10)	43(100)	65(11)	44(12)	125(57)
69(20)	94(10)	125(23)	77(10)	90(19)	84(13)	85(97)	57(100)	42(16)		43(21)	110(17)
64(60)	92(100)	98(45)	66(12)	89(12)	83(12)	84(48)	55(25)	41(46)		42(14)	109(14)
58(13)	87(15)	97(11)	65(77)	77(10)	78(13)	83(100)	43(11)	39(22)			97(17)
56(31)	78(50)	81(22)	64(12)	76(10)	76(15)	76(10)	41(76)				78(66)
55(14)	76(10)	78(45)	63(15)	65(73)	69(87)	63(21)	39(15)				77(100)
44(17)	57(70)	77(37)	39(30)	63(38)	56(10)	58(16)					66(11)
43(14)	44(65)	56(88)		60(28)	55(55)	57(43)					65(14)
42(34)	43(40)	55(73)		57(26)	42(29)	56(98)					51(57)
41(17)	42(38)	51(13)		56(78)	41(50)	55(84)					50(20)
40(34)	41(38)	43(96)		55(30)	39(10)	54(21)					43(11)
	40(13)	41(100)		54(23)		47(11)					39(14)
	39(13)	39(11)		51(23)		45(10)					
				50(17)		43(10)					
				45(14)		42(98)					
				43(22)		41(16)					
				42(46)							
				41(28)							
				39(51)							

[a] Parent peak is denoted by P^+ and is followed by: m/e (relative intensity). All peaks > 10% are included.

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