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ELECTRON IMPACT STUDIES—IX[1]

MASS SPECTRA OF ARYLSULPHINYLAMINES SKELETAL REARRANGEMENT ON ELECTRON IMPACT

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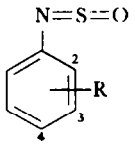
Abstract—The mass spectra of sixteen arylsulphinylamines are reported and discussed. The spectra exhibit pronounced molecular ions and large skeletal rearrangement fragments. The fragmentation modes have been substantiated by high resolution measurements, appropriate metastable ions and deuterium labelling studies. In several cases 'ortho effects' enable the determination of both the position and nature of the ortho substituent in substituted sulphinylanilines.

THE MASS spectra of thiophenols,[2] arylthioethers,[3] disulphides,[4] sulphones[5-8] and sulphoxides[5,6] have been reported. Large rearrangement ions are observed in the spectra of diaryl disulphides, arylsulphones and arylsulphoxides. Although the mass spectra of two perfluoroalkyl sulphinylamines have recently been determined,[9] no study of arylsulphinylamines has been reported.

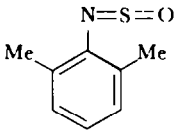
Because of our interest in the skeletal rearrangement processes which are observed in the spectra of sulphones[5-8] and sulphoxides[5,6] we have synthesized a series of sulphinylamines and have determined their mass spectra. This paper is concerned with the investigation of the mass spectra (Figs 1–8 and Table 1) of the sulphinylamines I–XVI. Although exact mass measurements (Table 2) establish the compositions of many fragment ions in the spectra, specific structures written for fragment

[1] Part VIII. J. H. Bowie, R. G. Cooks and G. E. Lewis, *J. Chem. Soc.* (B), in press.
[2] J. H. Bowie, S.-O. Lawesson, J. Ø. Madsen, G. Schroll and D. H. Williams, *Acta. Chem. Scand.* in press.
[3] J. H. Bowie, S.-O. Lawesson, J. Ø. Madsen and D. H. Williams, *J. Chem. Soc.* (B), 951 (1966).
[4] J. H. Bowie, D. H. Williams, S.-O. Lawesson, J. Ø. Madsen, C. Nolde and G. Schroll, *J. Chem. Soc.* (B), 946 (1966).
[5] S. Meyerson, H. Drews and E. K. Fields, *Analyt. Chem.* **36**, 1294 (1964).
[6] J. Ø. Madsen, C. Nolde, S.-O. Lawesson, G. Schroll, J. H. Bowie and D. H. Williams, *Tetrahedron Letters* 4377 (1965).
[7] J. H. Bowie, D. H. Williams, S. O. Lawesson, J. Ø. Madsen, C. Nolde and G. Schroll. *Tetrahedron* **22**, 3515 (1966).
[8] E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.* **88**, 2836 (1966).
[9] M. Lustig, *Inorg. Chem.* **5**, 1317 (1966).

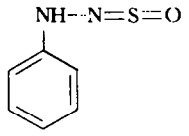
ions are nominal only, but serve to relate the fragmentation modes to the structure of the molecule in the ground state.[10,11] The presence of an asterisk either in the text or a figure represents the presence of an appropriate metastable ion for the process indicated.



	R
I	H
II	2-Cl
III	3-Cl
IV	4-Cl
V	2-CO_2Me
VI	3-CO_2Me

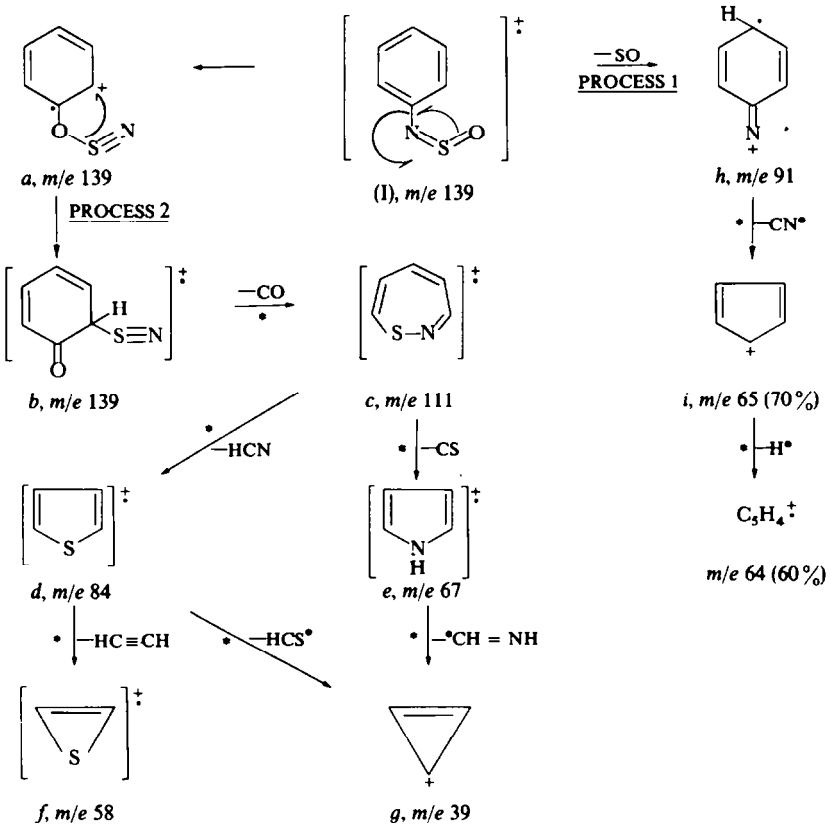


VII	2-Me
VIII	3-Me
IX	4-Me
X	2-OMe



XI	2-OCD_3
XII	3-OMe
XIII	4-OMe
XIV	3-NSO

Scheme 1



[10] J. Monigny, L. Brakier and L. D'or, *Bull. Classe, Sci. Acad. roy. Belg.* **48**, 1002 (1962).
[11] W. H. Pirkle, *J. Am. Chem. Soc.* **87**, 3022 (1965).

TABLE 1. MASS SPECTRA OF SULPHINYLAMINES*

III *m/e*	37	38	39	45	48	49	50	51	52	61	62	63	64	73	74	75	83	89	90	98
I(%)	19	24	33	25	14	7	12	9	6	13	21	48	24	10	8	16	7	13	52	7
	99	101	110	111	112	118	120	125	127	138	139	140	145	173(M^+)						
	24	12	56	8	4	11	4	13	13	100	12	6	4	63						
	174	175(M^+)																		
	4	24																		
IV *m/e*	37	38	39	45	48	49	50	51	52	61	62	63	64	65	73	74	75	83	89	90
I(%)	15	19	31	15	13	6	15	9	4	12	23	54	29	8	12	8	14	6	12	54
	91	92	98	99	100	101	110	111	118	120	125	127	129	138	139	140	145			
	4	4	5	15	4	7	49	6	12	3	20	23	6	100	7	5	6			
	173(M^+)	174	175(M^+)																	
	54	4	20																	
VI *m/e*	15	29	37	38	39	45	48	50	51	52	59	62	63	64	69	75	76	77	78	80
I(%)	18	9	10	12	47	12	13	20	13	8	13	11	54	30	6	8	10	8	12	21
	83	90	92	110	111	138	139	166	167	168	182	197(M^+)	198	199						
	14	30	11	34	13	68	6	100	16	7	10	58	8	4						
VIII *m/e*	37	38	39	45	48	50	51	52	53	62	63	64	65	66	75	77	78	79	80	81
I(%)	5	11	57	13	13	18	34	24	9	8	18	13	30	10	12	36	38	18	12	11
	85	91	92	97	98	104	105	110	124	125	126	136	137	138	139	152				
	10	18	38	16	19	24	6	16	24	19	6	8	5	38	6	8				
	153(M^+)	154	155																	
	100	9	5																	
XI† *m/e*	26	27	28	30	37	38	39	44	45	48	50	51	52	53	54	62	63	64	65	66
I(%)	10	24	12	15	12	19	30	18	9	10	40	76	47	16	8	18	58	50	22	20
	67	75	76	77	78	79	80	93	94	95	96	97	98	106	107	108	110	120	121	
	7	8	10	10	96	24	18	20	17	12	12	8	28	100	10	6	8	25	51	
	122	123	124	138	139	169	170	171	172	$d_0 = 14$, $d_1 = 33$,										
	40	31	19	18	8	10	25	27	14	$d_2 = 36$, $d_3 = 17\%$.										
XIV *m/e*	37	38	39	45	48	50	51	52	64	65	75	76	77	78	90	91	92	96	97	98
I(%)	25	34	47	22	100	26	26	26	26	15	15	29	52	20	6	16	14	8	26	18
	104	110	123	124	125	126	138	152	167	172	200(M^+)									
	20	6	8	55	8	8	21	32	3	3	20									
XV *m/e*	38	39	48	50	51	52	53	63	64	65	76	77	78	89	90	91	92	104	106	
I(%)	5	16	7	7	10	7	6	9	5	14	5	12	5	6	4	36	12	10	7	
	117	118	134	135	139	146	148	150	151	152	167(M^+)	168								
	19	11	7	5	5	6	8	100	10	13	46	5								
XVI *m/e*	38	39	48	49	50	51	52	63	65	74	76	77	78	105	154(M^+)					
I(%)	6	12	10	9	22	47	10	5	8	8	6	100	16	16	5					

* All peaks greater than 2% of the base peak (arbitrarily 100%) are recorded.

† Because of the complexity of this spectrum only peaks greater than 5% of the base peak are recorded.

TABLE 2. EXACT MASS MEASUREMENTS IN THE SPECTRA OF I–XV

Compound	*m/e*	Composition	Compound	*m/e*	Composition
I	62	C_5H_2	IX	91	C_7H_7 (40%)
	63	C_5H_3 (95%)			C_6H_5N (60%)
		C_4HN (5%)		92	C_6H_6N
	64	C_5H_4 (60%)		98	C_5H_6S
		C_4H_2N (40%)		104	C_7H_6N
	65	C_5H_5 (70%)		105	C_7H_7N
		C_4H_3N (30%)		110	C_5H_4NS
	67	C_4H_5N		124	C_6H_6NS
	84	C_4H_4S		125	C_6H_7NS
	91	C_6H_5N		136	C_7H_6NS
	111	C_5H_5NS		138	C_6H_4NOS
II	63	C_4HN (15%)	X	66	C_5H_6 (50%)
		C_5H_3 (85%)			C_4H_4N (50%)
	73	C_3H_2Cl		78	C_5H_4N
	75	C_3H_2Cl (25%)		93	C_6H_7N (70%)
		C_6H_3 (75%)			C_6H_5O (30%)
	83	C_4H_3S		98	C_4H_4NS
	90	C_6H_4N		110	C_5H_4NS
	98	C_5H_3Cl (60%)		106	C_6H_4NO
		C_4H_2OS (40%)		120	C_7H_6NO
	99	C_5H_4Cl		121	C_7H_7NO
	110	C_5H_4NS		138	C_6H_4NOS
	125/			139	C_6H_5NOS
	127	C_6H_4NCl			
	138	C_6H_4NOS	XII	141	C_6H_7NOS
V	63	C_5H_3	XIII	64	C_5H_4 (50%)
	78	C_5H_4N			C_4H_2N (30%)
	83	C_4H_3S			SO_2 (20%)
	90	C_6H_4N		66	C_4H_4N (50%)
	110	C_5H_4NS			C_5H_6 (50%)
				69	C_3HS
				78	C_5H_4N

The spectrum (Fig. 1) of sulphinylaniline (I)† is remarkable for its skeletal rearrangement ions, and these are summarized in Scheme 1. Exact mass measurements (Table 2) confirm the compositions of all major fragment ions, but it is stressed that the structures drawn for fragment ions are nominal.

Sulphinylaniline (I) fragments by two distinct pathways on electron impact. Loss of SO (by N–S cleavage) from the molecular ion I, (*m/e* 139) gives an ion *h*, *m/e* 91 which fragments by loss of $CN^{\bullet}$ to produce the cyclopentadienyl cation *i* (*m/e* 65) (Process 1). However, the major features of the spectrum are produced by a molecular ion rearrangement, which is a low energy process, even occurring at a nominal 10 eV. Loss of carbon monoxide from the molecular ion (Process 2) necessitates C—O bond formation, possibly of the type I → *a* (similar processes have been observed in the spectra of sulphones and sulphoxides.[5,6] The loss of carbon monoxide from *a* is then

† Since this paper went to press, the spectrum of sulphinylaniline has been reported; see B. E. Job, *Chem. Commun.* 44 (1967).

no more unusual than the loss of carbon monoxide from diaryl ethers.[12,13] The structure of *m/e* 111 (produced by elision of carbon monoxide from the molecular ion) must be cyclic (possibly *c*), as it may decompose by loss of either HCN or CS to the thiophene and pyrrole ion radicals (*d*, *m/e* 84 and *e*, *m/e* 67 respectively). The structures of *d* and *e* are supported by their characteristic fragmentation patterns (Scheme 1).[14,15]

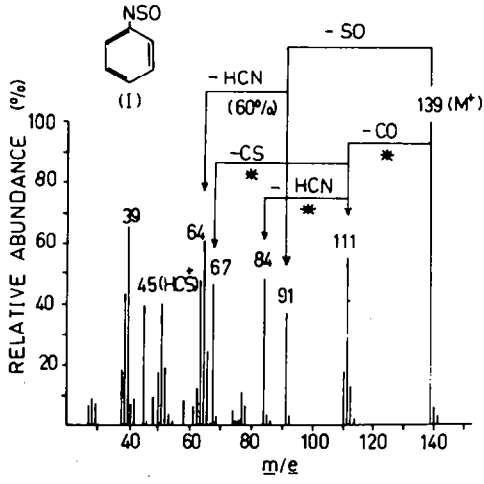


FIG. 1.

The spectra of the substituted sulphinylanilines II–XV retain some of the features of the spectrum of sulphinylaniline, but in general, the fragmentations will also involve the substituent. These features are illustrated by the mass spectra (Fig. 2 and Table 1) of the three chlorosulphinylanilines (II–IV). In the spectrum (Fig. 2) of 2-chlorosulphinylaniline (II), processes 1 and 2 (Scheme 1) are modified by the presence of the chloro substituent, viz. Process 1, M^+—SO—Cl$^\bullet$—HCN [instead of M^+—SO—CN$^\bullet$—H$^\bullet$ (Scheme 1)]; process 2, M^+—Cl$^\bullet$—CO [instead of M^+—CO (Scheme 1)]. The compositions of the major fragment ions in this spectrum have been determined by exact measurements (Table 2). It is of interest to note that the spectra of the three chloro compounds are very similar, a further illustration that halogen substituents seldom give rise to "ortho-effects" in mass spectrometry.

A different modification to Scheme 1 may be seen in the very similar spectra (Fig. 3 and Table 1) of the 2- and 3-methoxycarbonylsulphinylanilines (V, VI). Here, the loss of the entire ester group precedes the fragmentations by processes 1 and 2, and it can now be seen that these two processes may originate from either an odd electron (Fig. 1) or an even electron species (Fig. 3).

[12] J. H. Beynon, G. R. Lester and A. E. Williams, *J. Chem. Phys.* **63**, 1861 (1959).

[13] J. H. Beynon, *Mass Spectrometry and its Applications to Organic Chemistry* pp. 272–273. Elsevier, Amsterdam, (1960).

[14] H. Budzikiewicz, C. Djerassi and D. H. Williams, *Interpretation of Mass Spectra of Organic Compounds* p. 231. Holden-Day, San Francisco (1964).

[15] H. Budzikiewicz, C. Djerassi, A. H. Jackson, G. W. Kenner, D. J. Newman and J. M. Wilson, *J. Chem. Soc.* 1949 (1964).

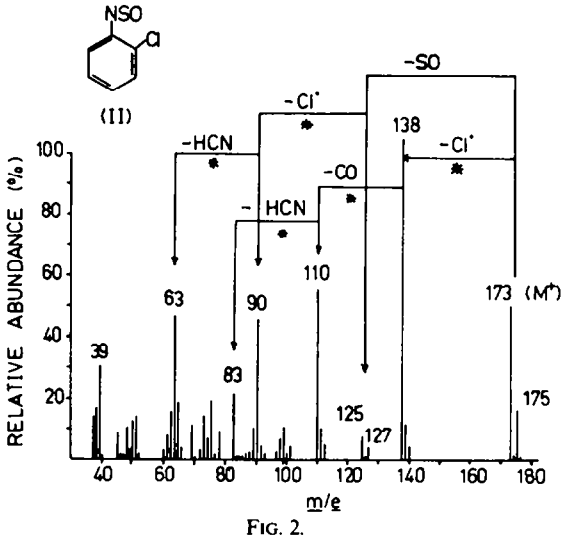


FIG. 2.

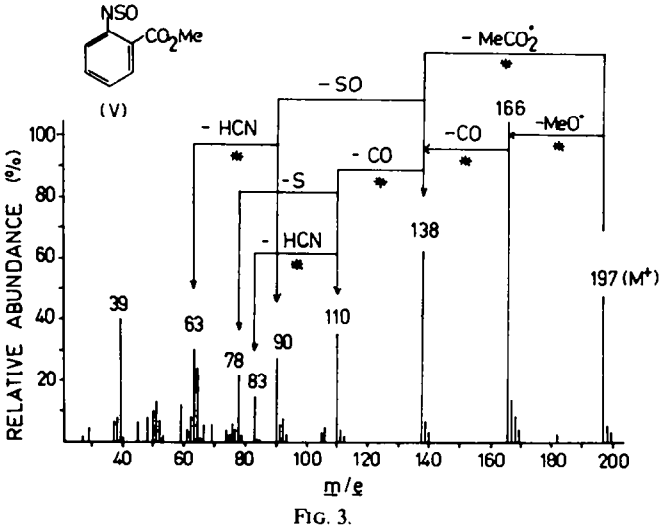


FIG. 3.

The spectra (Figs. 4 and 5, Table 1) of the methylsulphinylanilines differ markedly depending on the position of the substituent. The spectra (Fig. 4, Table 1) of the 3- and 4-methyl derivatives VIII and IX follow the general fragmentation patterns of substituted sulphinylanilines and the fragmentation modes are illustrated in Fig. 4. The major difference between the two spectra lies in the loss of the methyl radicals from the various molecular ions, viz. 83% of the base peak in the spectrum of IX, 37% in that of VIII. This observation reflects the enhanced stability of the cation *j*, *m/e* 138 produced on elimination of a methyl radical from the *p*-position. Similar effects are observed in the spectra of methylanisoles[16,17] and methylthioanisoles.[3]

[16] C. S. Barnes and J. L. Occolowitz, *Austral. J. Chem.* **15**, 219 (1963).
[17] Z. Pelah, J. M. Wilson, M. Ohashi, H. Budzikiewicz and C. Djerassi, *Tetrahedron* **19**, 2233 (1963).

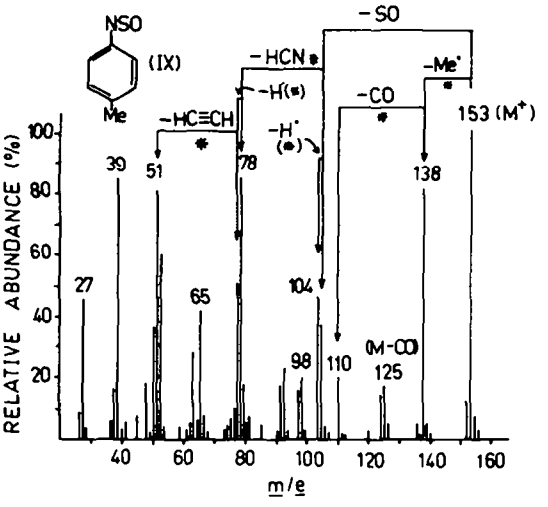


FIG. 4.

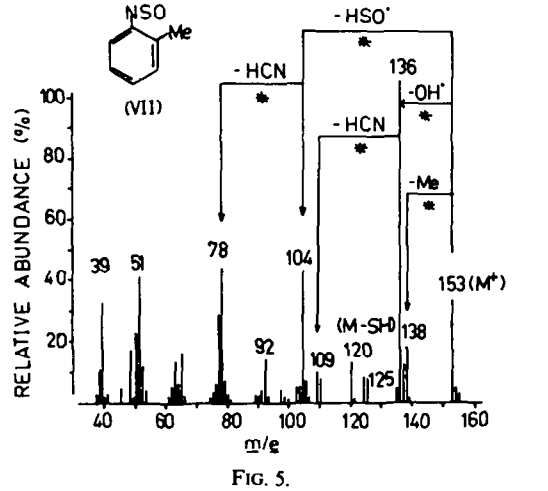
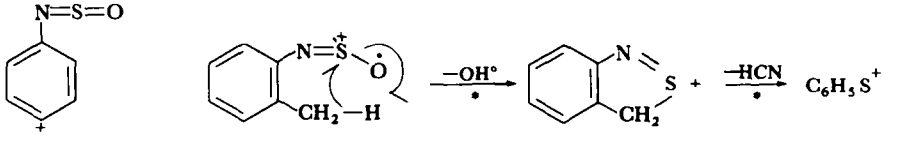


FIG. 5.



i, *m/e* 138 VII *k*, *m/e* 136 *m/e* 109

Although the spectrum (Fig. 5) of 2-methylsulphinylaniline (VII) retains the features of those of the other methyl isomers, an additional process is observed. Here, a specific "ortho-effect"[18] enables the immediate detection of the *ortho* methyl substituent. Loss of an hydroxyl radical from the molecular ion produces the base peak of the spectrum (possibly *k*, *m/e* 136) which fragments further by loss of HCN to an ion

[18] F. W. McLafferty in *Mass Spectrometry of Organic Ions* p. 337. Academic Press, N.Y. (1963).

$C_6H_5S^+$ (*m/e* 109). An M^+—$SH^\bullet$ ion (*m/e* 120 is also a feature of this spectrum. The genesis of this rearrangement process (which is substantiated by a metastable ion at *m/e* 94·1) is not clear, but it is an "ortho-effect", as analogous processes are not observed in the mass spectra of other sulphinylanilines.

An M—CO rearrangement ion (*m/e* 125, 8% of the base peak) is still observed in the spectrum (Fig. 5) of 2-methylsulphinylaniline (VII) even though the spectrum exhibits a large "ortho-effect". If both the 2 and 6 positions in sulphinylaniline were blocked by methyl substituents, an M—CO ion should still be observed in the mass spectrum provided that the rationalization in Scheme 1 is valid, and that the rearrangement process is not swamped by an enhanced "ortho-effect". The rationalization assumes that the oxygen is attached to C-1 and that the SN group migrates to either of the electron deficient ortho positions. The mass spectrum (Table 1) of 2,6-dimethylsulphinylaniline (XV) does contain a small M—CO ion (*m/e* 139, 5% of the base peak). This observation is consistent with, but does not prove the mechanism outlined in Scheme 1.

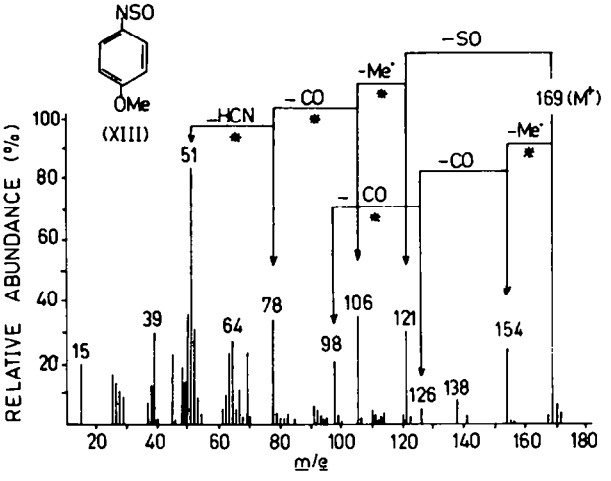


FIG. 6.

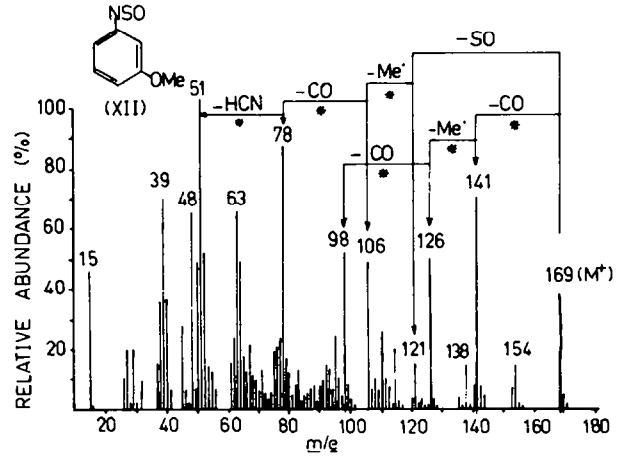


FIG. 7.

The mass spectra (Fig. 6–8) of the three methoxysulphinylanilines X, XII and XIII are very different from one another. The difference between the mass spectra (Figs. 6 and 7) of the 4-methoxy and 3-methoxy derivatives XIII and XII, is explained by the observation[3] that skeletal rearrangement processes become more prominent when simple reactions (e.g. the formation of M^+—Me$^\bullet$ or M^+—MeO$^\bullet$ fragments) are not particularly favourable. Consequently, substituent orientation plays a large part in the relative occurrence of skeletal rearrangement ions in the spectra of XII and XIII. In the spectrum (Fig. 6) of the *p*-isomer XIII, the simple processes M^+—Me$^\bullet$ (to *m/e* 154) and M^+—MeO$^\bullet$ (to *m/e* 138) predominate, whilst the M—CO rearrangement ion (*m/e* 141) constitutes only 3% of the base peak. When the methoxy substituent is *meta*, the processes M—Me$^\bullet$ and M—MeO$^\bullet$ will not be as favored,[3,16] therefore the rearrangement process (M—CO) may predominate. The M—CO ion in the spectrum (Fig. 7) of XII is now 72% of the base peak. Further fragmentation processes are outlined in Figs. 6 and 7; high resolution data is summarized in Table 2.

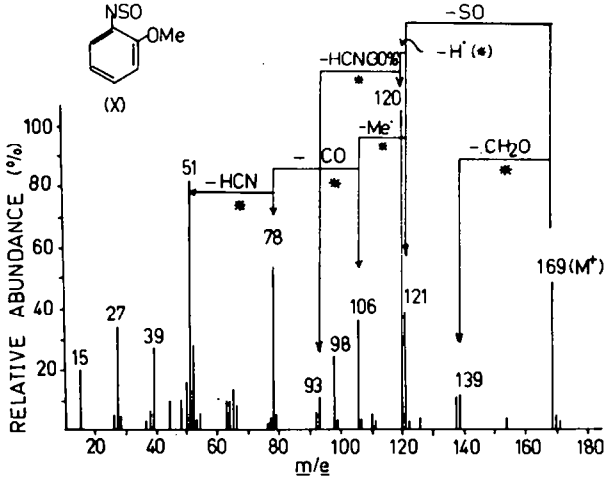
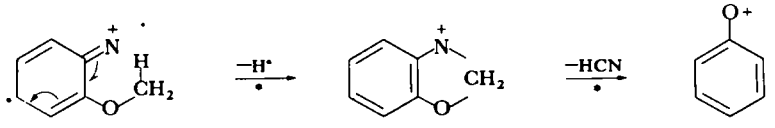


FIG. 8.

When the methoxyl substituent occupies the ortho position, as in X, the fragmentation (Fig. 8) takes a different course. The M^+—SO ion (*l*, *m/e* 121, cf. Process 1 in Scheme 1) may now lose a hydrogen atom to yield an ion *m/e* 120, which fragments further by loss of HCN possibly to *n*, *m/e* 93. Further fragmentations are illustrated in Fig. 8, and the spectrum (Table 1) of the d_3 derivative (XI) supports the above fragmentation schemes. It is therefore possible to identify all three methoxysulphinylanilines by mass spectrometry.



l, *m/e* 121 *m*, *m/e* 120 *n*, *m/e* 93

The mass spectrum (Table 1) of XIV exhibits *m/e* 48 (SO) as the base peak, and shows two separate decomposition patterns viz. M^+—SO—SO—HCN—HCN and M^+—SO—CO—HCN. Again large rearrangement ions are observed;

the M^+—SO—CO ion (*m/e* 124) constitutes 55% of the base peak. A very different situation is observed when the sulphinyl group is not directly attached to the aromatic ring. The spectrum (Table 1) of XV is a very simple one. No rearrangement ions are observed, instead the fragmentation proceeds by the process M^+— HSO—N_2—HC ≡ CH.

A series of other sulphinylamines were also investigated (e.g. nitrosulphinylanilines and aliphatic sulphinylamines) but because of their facile decomposition to the corresponding amines, their mass spectra contained peaks due to the fragmentation of the amine. Consequently they are not reported. This is a serious problem with all sulphinylamines and all spectra reported were determined with carefully purified samples.

The results presented in this paper illustrate that aromatic sulphinylamines decompose characteristically by well defined skeletal reorganisation on electron impact. This conclusion limits both the *a priori* prediction of fragmentation modes and the application of the element mapping technique[19, 20, 21] to this class of compound.

EXPERIMENTAL

All spectra were measured with a Hitachi–Perkin Elmer R.M.U. 6D mass spectrometer operating at 75 eV, and with the inlet system at approximately 100°. High resolution measurements were performed with an A.E.I. MS 9 mass spectrometer using a resolution of 14,000 (10% valley definition). Heptacosafluorotributylamine provided the reference masses and all exact mass measurements were correct to within 15 ppm.

Previously published procedures were used for the preparation of I[22], II[23], III[22], IV[22], VI[23], VII[22], VIII[23], IX[22], X[23], XII[24], XIII[25], XIV[23], XVI[26]. V was prepared from methyl anthranilate by the usual method.[27] Yield 77%. Bp. 149–150°C/12 mm Hg. n_D^{25} = 1·5844 (Anal. Rec.: C, 48·86; H, 3·54; N, 7·16; S, 16·64. Calc.: C, 48·88; H, 3·63; N, 7·12; S 16·59%.) XV was prepared as above.[27] Yield 84%, b.p. 102°C/11 mm Hg. n_D^{25} = 1·5778 (Anal.: Rec. C, 57·82; H, 5·52; N, 8·39; S, 19·29. Calc.: C, 57·48; H, 5·43; N, 8.38; S, 19·15%.) XI was prepared from *ortho*-nitrophenol by alkylation (diazomethane + D_2O)[28], reduction of the nitroanisole to *ortho*-anisidine followed by the treatment with thionylchloride.[27]

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