Molecular Ion Rearrangements of Benzenesulfonylhydrazides†

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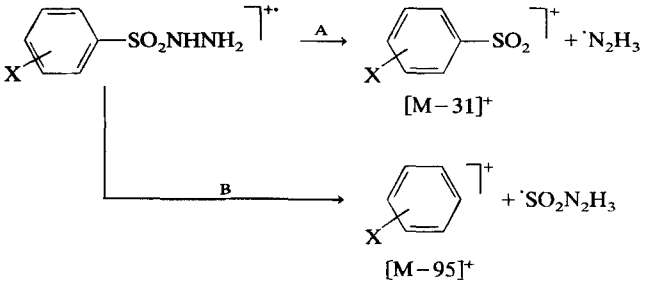
The mass spectra of a series of substituted benzenesulfonylhydrazides are discussed. The main fragmentation mode of these compounds corresponds to rearrangement of the molecular ion with subsequent loss of $N_2H^{\cdot}$ and/or N_2H_2. These fragmentations are confirmed by mass analysed ion kinetic energy spectra. Simple cleavage of the S—N bond with retention of the charge on nitrogen is observed for all the hydrazides studied but is favoured by electron withdrawing substituents. This latter fragmentation could not be confirmed by mass analysed ion kinetic energy spectra as it is probably very rapid and occurs mainly in the source.

INTRODUCTION

The electron impact (EI) induced fragmentation of several benzenesulfonylhydrazides has been reported.[2,3] However, these reports are not in agreement. For example, it has been indicated that phenylsulfonylhydrazide (**1**) lacks a molecular ion and has a base peak at *m/z* 78.[2] On the other hand, Balza and Duran reported that the mass spectra of phenylsulfonylhydrazide (**1**) as well as the 4-methyl (**2**), 4-methoxy (**3**) and 4-bromo (**6**) benzenesulfonylhydrazides contain molecular ions that cleave via two pathways.[3] The first (path A of Scheme 1) is simple rupture of the N—S bond producing a $[M-31]^+$ fragment and the second (path B) is breakage of the C—S bond resulting in the formation of an $[M-95]^+$ ion.[3]

In connection with our studies of α-ketosulfonylhydrazones[4] we felt it important to clarify the EI induced fragmentation of the precursor benzenesulfonylhydrazides. Thus, compounds **1–13** were prepared and an investigation of their mass spectra was undertaken. We report here the results of our study. The fragmentation proposed has been confirmed to a great extent by the mass analysed ion kinetic energy spectra (MIKES) of the molecular ions and of key fragments.



Scheme 1

† See Ref. 1.

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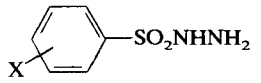

1: X = H
2: X = 4-CH_3
3: X = 4-OCH_3
4: X = 3-OCH_3
5: X = 2-OCH_3
6: X = 4-Br
7: X = 4-Cl
8: X = 4-$NHCOCH_3$
9: X = 2,4,6-trimethyl
10: X = 4-COOH
11: X = 4-NO_2
12: X = 3-NO_2
13: X = 2-NO_2

RESULTS AND DISCUSSION

The mass spectral abundance data for the benzenesulfonylhydrazides are shown in Table 1. All the compounds give molecular ions. In the case of the hydrazides with electron donating substituents this ion is moderately intense (10–28%), but it is very weak for those hydrazides that contain electron withdrawing substituents (<3%). Abundant ions corresponding to $[M-29]^+$ or $[M-30]^{+\cdot}$ are observed for compounds **1**, **2**, **3**, **4**, **5** and **8**. These peaks are of medium intensity for compounds **6**, **7**, **9** and **10**, and of low intensity for compounds **11**, **12** and **13**. An $[M-64]^{+\cdot}$ ion, is observed in the spectra of all the compounds studied, but is of significant intensity only in the case of the 4-carboxy (**10**), 4-nitro (**11**) and 3-nitro (**12**) derivatives. Scheme 2 presents a generalized sequence of fragmentation observed for the benzenesulfonylhydrazides. The structures indicated are speculative and are meant to aid in the visualization of the fragmentation process. Solid arrows indicate transitions confirmed by MIKES and broken arrows those that are unconfirmed.

Thermal effects

Benzenesulfonylhydrazides are not very thermally stable. This is undoubtedly the reason why some authors have not observed molecular ions for these compounds. It has been reported that condensed phase pyrolysis of benzenesulfonylhydrazides gives the corresponding thiosulfonate (**14**), disulfide (**15**), sulfonamide (**16**) and ammonium sulfonate (**17**) as shown

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Table 1. 70 eV mass spectral data for a number of benzenesulfonylhydrazides ($XC_6H_4SO_2NHNH_2$)[a]

X	$[M]^{+\cdot}$	$[M-29]^+$	$[M-30]^{+\cdot}$	$[M-31]^+$	$[M-47]^+$	$[M-64]^{+\cdot}$	$[M-78]^{+\cdot}$	$[M-79]^+$	$[M-93]^+$	$[M-94]^{+\cdot}$	$[M-95]^+$	m/z 31	Other ions above 10%
1, H	172(29)	143(78)	142(18)	141(3)	125(16)	108(1)	94(9)	93(3)	79(30)	78(83)	77(100)	(77)	51(47)
2, 4-CH_3	186(22)	157(58)	156(28)	155(7)	139(19)	122(0.6)	108(7)	107(10)	93(13)	92(58)	91(100)	(56)	107(10), 77(15), 65(36), 39(16)
3, 4-OCH_3	202(27)	173(24)	172(100)	171(36)	155(67)	138(0.7)	124(10)	123(78)	109(9)	108(57)	107(42)	(43)	92(69), 77(75), 64(39), 63(30), 51(11), 50(13)
4, 3-OCH_3	202(25)	173(18)	172(100)	171(2)	155(5)	—	124(67)	123(0.6)	109(4)	108(20)	107(38)	(43)	96(11), 92(47), 78(13), 77(56), 76(10), 65(10), 64(24), 63(15), 36(15)
5, 2-OCH_3	202(28)	173(8)	172(71)	171(2)	155(72)	138(2)	124(42)	123(5)	109(11)	108(46)	107(32)	(46)	125(22), 97(14), 92(46), 79(36), 78(51), 77(100), 65(20), 64(22), 63(17), 51(24)
6, 4-Br	250(10)	221(22)	220(8)	219(2)	203(10)	186(0.3)	172(6)	171(3)	157(33)	156(23)	155(32)	(100)	141(11), 77(33), 76(38),
	252(10)	223(21)	222(10)	221(22)	205(11)	188(0.6)	174(4)	173(3)	159(3)	158(23)	157(33)		75(50), 74(14)
7, 4-Cl	206(11)	177(22)	176(6)	175(3)	159(13)	142(0.5)	128(6)	127(3)	113(16)	112(40)	111(35)	(100)	77(15), 75(37), 51(10),
	208(4)	179(8)	178(4)	177(22)	161(5)	144(0.8)	130(2)	129(1)	115(2)	114(13)	113(16)		50(15)
8, 4-$NHCOCH_3$	229(21)	200(10)	199(72)	198(24)	182(2)	—	151(2)	150(2)	136(6)	135(67)	134(31)	(38)	157(57), 140(72), 108(52), 93(34), 92(38), 91(11), 65(52), 64(13), 63(15), 43(100)
9, 2,4,6-tri-CH_3	214(12)	185(17)	184(20)	183(2)	167(3)	150(0.4)	136(9)	135(17)	121(14)	120(84)	119(100)	(40)	117(15), 115(13), 105(31), 104(12), 103(17), 91(56), 79(13), 78(12), 77(30), 65(13), 41(24), 39(15), 36(14), 32(15)
10, 4-COOH	216(3)	187(5)	186(20)	185(2)	169(7)	152(14)	138(6)	137(2)	123(6)	122(55)	121(16)	(100)	105(17), 78(15), 77(13), 76(12), 65(36), 51(13), 50(14)
11, 4-NO_2	217(1)	188(1)	187(2)	186(1)	170(1)	153(22)	139(0.6)	138(0.2)	124(3)	123(25)	124(4)	(100)	77(14), 76(25), 75(15), 50(23)
12, 3-NO_2	217(1)	188(0.6)	187(2)	186(0.8)	170(2)	153(25)	139(0.7)	138(0.2)	124(8)	123(38)	122(3)	(100)	77(12), 76(40), 75(14), 50(25)
13, 2-NO_2	217(0.1)	188(1)	187(13)	186(3)	170(4)	153(2)	139(0.3)	138(0.5)	124(81)	123(31)	122(0.4)	(97)	94(17), 93(26), 92(11), 79(13), 78(45), 77(100), 76(71), 75(19), 74(19), 65(61), 64(20), 63(24), 52(66), 51(81), 50(84), 49(79), 39(34), 36(12), 30(42).

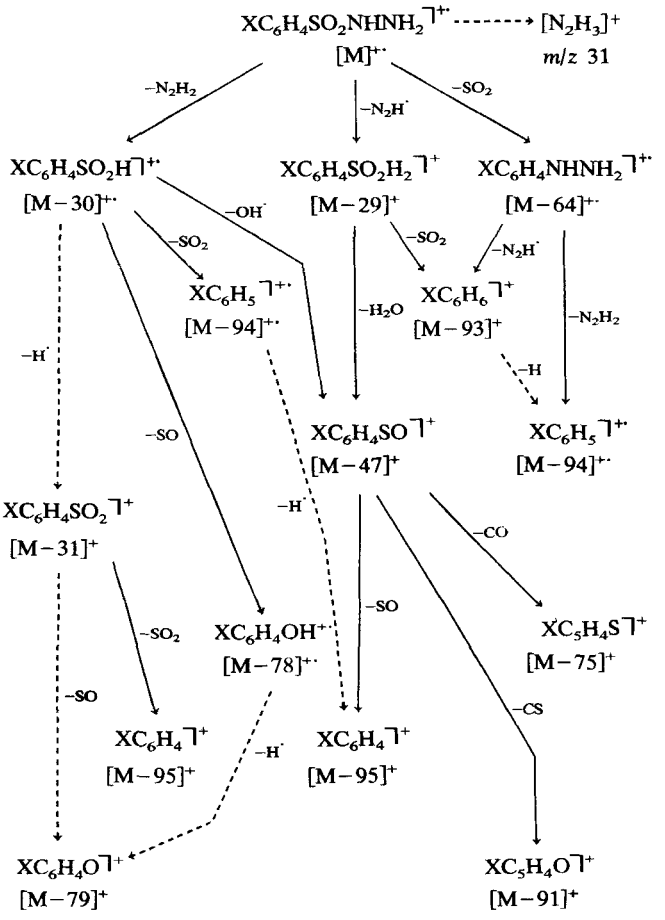
[a] *m/z* (%).

in Scheme 3.[4–6] We were able to confirm the formation of compounds **14** and **15** in the mass spectrometer by pyrolysing the benzenesulfonylhydrazides in the direct inlet probe. For example, in the case of X = 4-CH_3 (**2**) an increase in temperature causes the appearance of peaks at *m/z* 278 (**14**, X = 4-CH_3) and *m/z* 246 (**15**, X = 4-CH_3). A significant increase is also observed for the peaks at *m/z* 155 and *m/z* 123. With respect to the parent 4-toluenesulfonylhydrazide (**2**) the *m/z* 155 peak corresponds to $[M-31]^+$ which is normally less intense than the *m/z* 157 and *m/z* 156 peaks in the spectrum of this compound. All the compounds studied gave similar results. Thus, we considered that the spectrum was free of thermal decomposition if peaks corresponding to compounds **14** and **15** were not observed, or contained a minimum of decomposition if these peaks were less than 1%. Unless indicated, the spectra reported in Table 1 conform to these criteria.

To obtain MIKES, the time required to make measurements and the temperatures required to obtain sufficient ion intensity, made it impossible to completely avoid thermal decomposition. However, we were able to confirm that the MIKES of individual ions did not change with time or temperature. Thus, it would seem that ions such as *m/z* 155 in the spectrum of 4-toluenesulfonylhydrazide (**2**) probably have the same structure regardless of whether they result from fragmentation of **2** or of 4-ditolythiosulfonate (**14**, X = 4-CH_3).

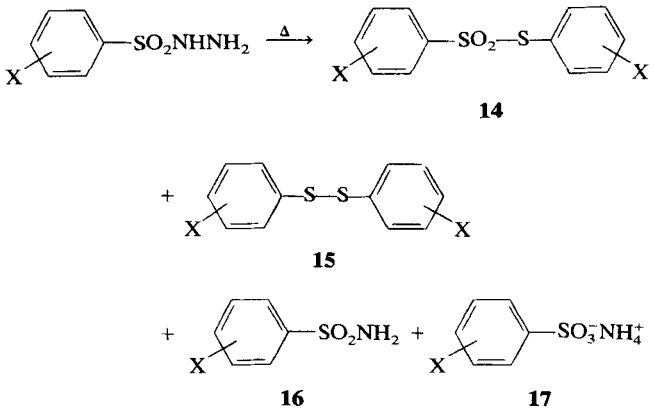
Rearrangements of the molecular ion

The $[M-29]^+$ ion, which we have shown as a protonated sulfinic acid, is present in the mass spectra of all the benzenesulfonylhydrazides. Formation of this ion requires rearrangement of the molecular ion. This rearrangement may involve simply an initial migration of a hydrogen atom to one of the sulfonyl oxygens, thus molecular ion *a* gives molecular ion *b*, or it may involve prior skeletal rearrangement (ions *c* and *d*) followed by migration of a hydrogen atom from nitrogen to oxygen (ions *e* and *f*) as shown in Scheme 4. Migration of a second atom of hydrogen is necessary in order to form $[M-29]^+$, and it is possible that this

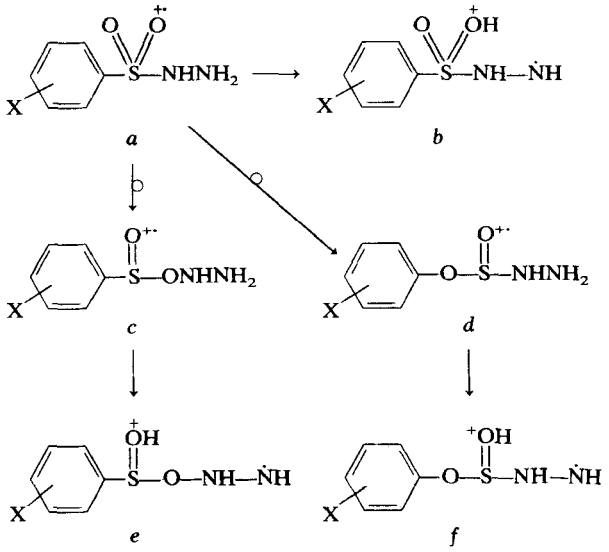


Scheme 2

takes place simultaneously with fragmentation resulting in the loss of $N_2H^{\cdot}$ and the formation of ions g and *h*. These ions can eliminate a molecule of water giving rise to a product ion *i*, which may rearrange and fragment subsequently by competitive losses of SO, CS and CO (Scheme 5). Ions *g* and *h* also may fragment via loss of SO_2. In both cases, this requires migration of two hydrogen atoms to the benzene ring. Again this probably involves migration of one hydrogen atom to the ring in the initial step, followed by simultaneous migration of the second hydrogen with elimination of SO_2. The third fragmentation of ions g

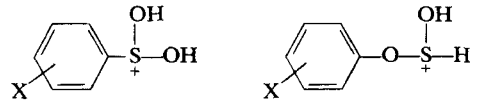


Scheme 3

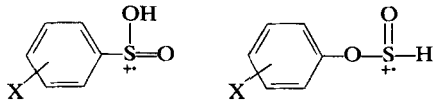


Scheme 4

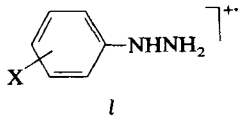
and *h* is loss of an atom of hydrogen to give the corresponding ions *j* and *k* which may also be formed directly from the molecular ion. Ion *k* can lose ·SOH



in one step by simple cleavage, whereas *j* requires skeletal rearrangement followed by cleavage.



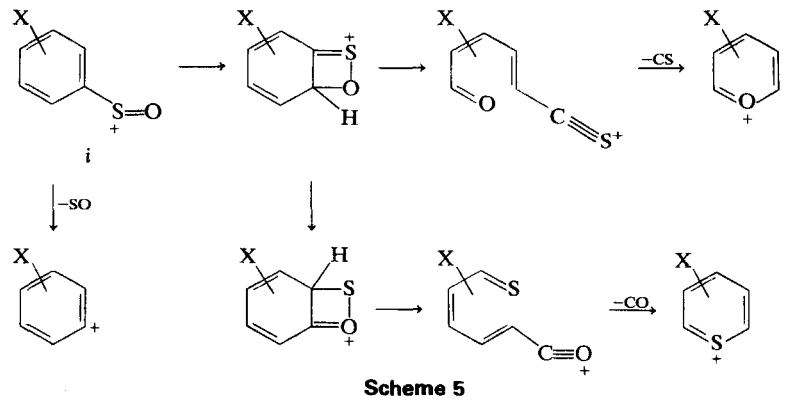
Another fragment of the molecular ion usually present in the mass spectra of the benzenesulfonylhydrazides is $[M-64]^{+\cdot}$ resulting from elimination of SO_2. This fragmentation also requires rearrangement of the molecular ion with formation of a carbon–nitrogen bond. Probably a cyclic intermediate is involved. In each case the product ion could be the ion of the corresponding phenylhydrazide (*l*). However,



the MIKES of the $[M-64]^{+\cdot}$ peak of 4-nitrobenzenesulfonylhydrazide (**11**) is significantly different from the MIKES of the molecular ion of 4-nitrophenylhydrazide (**18**) (Fig. 1). Thus, it appears that the structures also must be different.

Substituent effects

If the abundance of $[M]^{+\cdot}$ is considered as a fraction of the sum of the ten most intense ions (Σ_{10}), we can obtain an idea of the effect of the substituent on the stability of the molecular ion. Electron withdrawing groups such as 4-COOH (**10**, 1.0% of Σ_{10}) and NO_2 (**11**, 0.4%; **12**, 0.4% and **13**, 0.01% of Σ_{10}) destabilize



Scheme 5

the molecular ion relative to the unsubstituted compound (**1**, 6% of Σ_{10}). On the other hand, electron donating substituents do not seem to greatly affect the stability of the molecular ion. This is consistent with the presence of the positive charge on the ring and/or on the sulfonyl group in the molecular ion.

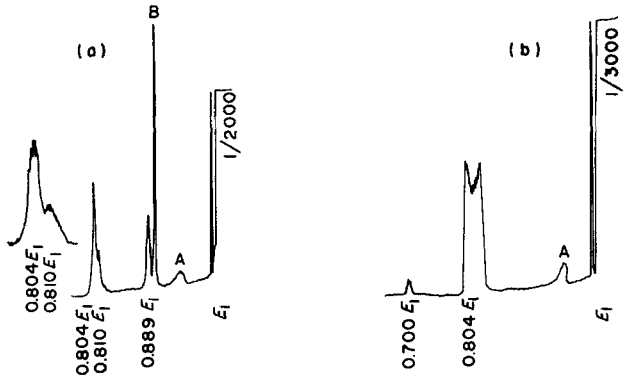


Figure 1. MIKES of (a) $[M-64]^{+\cdot}$, m/z 153, from *p*-nitrobenzenesulfonylhydrazide (**11**), (b) the molecular ion of *p*-nitrobenzenehydrazide (**18**). The peaks marked A and B are artefact peaks. Peak A appears in all the MIKES; its intensity depends on the quantity of sample being used. Peak B results from fragmentation in the first field free region of the instrument.

The opposite is observed with respect to the m/z 31 peak. This peak probably results from simple cleavage of the S—N bond with retention of the charge on the hydrazide portion of the molecule. Since the electron withdrawing groups favour localization of the charge on nitrogen rather than on the ring, it is reasonable that they favour formation of m/z 31. Thus, for the 4-COOH (**10**) derivative and the three NO_2 derivatives (**11**, **12**, **13**), m/z 31 is 33.3, 42.9, 37.5 and 12.7 of Σ_{10} respectively. The corresponding values of the three methoxy derivatives (**3**, **4**, **5**) are 6.8, 9.8 and 8.5% of Σ_{10}. In fact, a plot of σ values for the substituents vs log Z/Z_0 (Table 2) for m/z 31 shows a definite linear Hammett correlation with a $\rho = +0.52$ (Fig. 2). The σ values for the 3- and 4-methoxy substituents are off the line, but the σ^+ value for the 4-methoxy substituent falls on the curve. This is consistent with the above observations.

The nature of the substituent also affects the loss of SO_2 from the molecular ion. From the mass spectra (Table 1), it can be seen that this loss is abundant only for the 4-COOH (**10**) and the 4- and 3-nitrobenzenesulfonylhydrazides (**11**, **12**). This loss is also confirmed by the MIKES of the corresponding molecular ions (Table 3). Perhaps the rearrangement required for the elimination of sulfur dioxide involves

Table 2. Data for the log Z/Z_0 and σ plots for m/z 31

Compound	Σ_A[a]	Rel. int. of m/z 31	Ref. Int. of m/z 31 Σ_a	log Z/Z_0	σ[b]	σ^+[b]
1, H	Σ_5 528	78	$0.148 = Z_0$	0	0	
2, 4-CH_3	Σ_5 495	56	0.113	−0.117	−0.17	
3, 4-OCH_3	Σ_{10} 740	43	0.058	−0.407	−0.27	−0.78
4, 3-OCH_3	Σ_5 526	43	0.082	−0.258	0.12	
5, 2-OCH_3	—	—	—	—	—	
6, 4-Br	Σ_5 486	100	0.206	0.143	0.23	
7, 4-Cl	Σ_5 372	100	0.269	0.259	0.23	
8, 4-$NHCOCH_3$	—	—	—	—	—	
9, 2,4,6-trimethyl	—	—	—	—	—	
10, 4-COOH	Σ_5 381	100	0.263	0.250	0.36	
11, 4-NO_2	Σ_5 264	100	0.379	0.408	0.78	
12, 3-NO_2	Σ_5 296	100	0.338	0.359	0.71	
13, 2-NO_2	—	—	—	—	—	

[a] The sum of all ions above A%.
[b] H. H. Jaffé, *Chem. Rev.* **53**, 191 (1953).

an initial nucleophilic attack of nitrogen on the aromatic ring. This is the only fragmentation of the molecular ions of compounds **11** and **12** which can be confirmed by MIKES. Elimination of sulfur dioxide is also observed as one of the fragmentations in the metastable ion spectra of **10**, but is not observed in the MIKES of the molecular ions of any of the other compounds (Table 3).

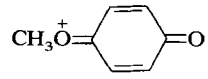
The other important cleavage of the molecular ion is the rearrangement of a hydrogen atom followed by elimination of N_2H_2 to give $[M-30]^{+\cdot}$ or by rearrangement of a second hydrogen atom with elimination of $N_2H^{\cdot}$ to give $[M-29]^{+}$. Either one or both of these fragmentations is observed in the MIKES of all the compounds except the three nitro derivatives (**11, 12, 13**). It can be seen from the mass spectra (Table 1) that these fragmentations are favoured by electron donating groups. This is not unexpected as these substituents may stabilize the charge on the ring, thereby permitting rearrangement of the hydrazide hydrogens either to the ring or to the oxygens of the sulfonyl group.

Ortho effects

In the compounds with an *ortho* substituent there exists the possibility of an interaction between the substituent and the sulfonylhydrazide group, which may affect the fragmentation. For example, 2,4,6-trimethylbenzenesulfonylhydrazide (**9**) loses $^{\cdot}N_2H_3$ and H_2O in one step from the molecular ion as confirmed by MIKES (Table 3). Presumably, the extra hydrogens involved are provided by an *ortho* methyl group. No such loss is observed in the spectrum of **2**. The losses of H_2O from the fragments $[M-30]^{+\cdot}$ and $[M-31]^{+}$ in the spectrum of **9** probably involve the *ortho* methyl groups as well.

Comparing the three nitro derivatives (**11, 12, 13**), it can be observed that in the spectrum of 2-nitrobenzenesulfonylhydrazide (**13**) the $[M-30]^{+\cdot}$ fragment is seven times more intense than in the spectra of the 4- and 3-nitro derivatives (**11, 12**). This may be due to a facile rearrangement of a hydrazide hydrogen to an oxygen of the nitro group. Another notable difference in the spectra of these three compounds is the low intensity of the $[M-SO_2]^{+\cdot}$ ion from 2-nitrobenzenesulfonylhydrazide (**13**) in comparison with that from **11** and **12**. This is possibly due to steric inhibition by the *ortho* nitro group since this rearrangement undoubtedly requires a cyclic transition state. The failure to observe this effect in the case of **9** and of **5** is due to the very low abundance of the $[M-SO_2]^{+\cdot}$ ion in the spectra of the *para* and *meta* derivatives as well.

In the case of the methoxy compounds, it is difficult to decide if there is an *ortho* effect on the basis of the mass spectra alone. For example, both the *ortho*- and *para*-methoxybenzenesulfonylhydrazides (**5**, **3**) contain intense peaks at *m/z* 155 $[M-N_2H^{\cdot}-H_2O]^{+}$ but the *meta* compound (**4**) does not. On the other hand, compounds **4** and **5** contain a relatively intense peak at *m/z* 124, while compound **3** has an intense peak at *m/z* 123. The latter is probably due to resonance stabilization of the ion *m* (*m/z* 123).



m

The MIKES of the molecular ions does, however, show definite evidence for an *ortho* effect. Thus, for compounds **3** and **4**, peaks for the losses of $N_2H^{\cdot}$ and N_2H_2 are observed (Table 3). For the *ortho* compound (**5**) these fragmentations are observed, as is a third one due to the loss of H_3N_2O probably as $N_2H^{\cdot}$ and H_2O giving rise, at least in part, to *m/z* 155. The driving force for this reaction may be the formation of a stable

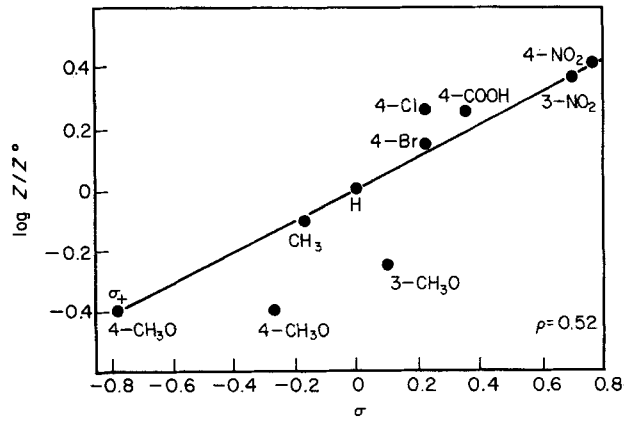


Figure 2. Hammett correlation for *m/z* 31 observed in the mass spectra of the benzenesulfonylhydrazides.

Table 3. Summary of MIKES of the molecular ions of substituted benzenesulfonylhydrazides at 70 eV

Precursor	$[M]^{+\cdot}$ *m/z* (rel.ab.%)[a]	Fragment ion *m/z* (rel.ab.%)[b]	Neutral fragment
1, X = H	172(29)	143(100)	N_2H
2, X = 4-CH_3	186(22)	157(100)	N_2H
3, X = 4-OCH_3	202(27)	173(67.6)	N_2H
		172(32)	N_2H_2
		155(0.4)	N_2H_3O
4, X = 3-OCH_3	202(25)	173(46.6)	N_2H
		172(53)	N_2H_2
		155(0.4)	N_2H_3O
5, X = 2-OCH_3	202(28)	173(26)	N_2H
		172(46)	N_2H_2
		155(28)	N_2H_3O
6, X = 4-Br	252(10)	223(100)	N_2H
	250(10)	221(100)	N_2H
7, X = 4-Cl	208(4)	179(100)	N_2H
	206(11)	177(100)	N_2H
8, X = NHAc	229(21)	199(100)	N_2H_2
9, X = 2,4,6-Trimethyl	214(12)	185(99)	N_2H
		165(1)	$N_2H_3+H_2O$
10, X = 4-COOH	216(3)	187(23)	N_2H
		186(25)	N_2H_2
		152(52)	SO_2
11, X = 4-NO_2	217(1)	153(100)	SO_2
12, X = 3-NO_2	217(1)	153(100)	SO_2
13, X = 2-NO_2	217(0.1)	—	—

[a] Precursor ion abundance in 70 eV EI spectrum relative to base peak.
[b] Abundances relative to total metastable intensity.

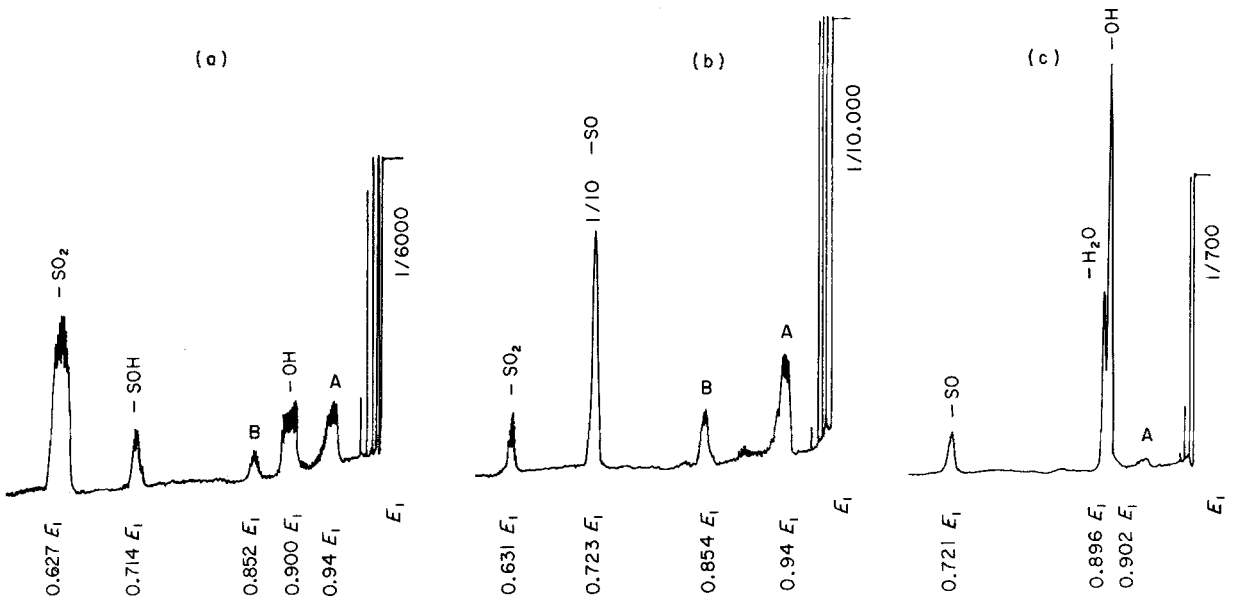
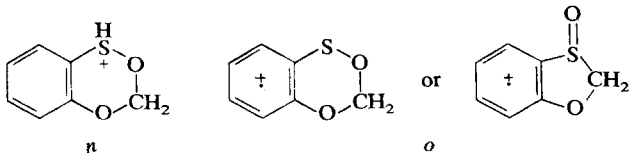


Figure 3. MIKES of *m/z* 172 from (a) *p*-methoxy (**3**) *m*-methoxy (**4**) and (c) *o*-methoxybenzenesulfonylhydrazide (**5**). The peaks marked A and B are artefact peaks. Peak A appears in all the MIKES; its intensity depends on the quantity of sample used. Peak B is due to the fragmentation of the molecular ion in the magnetic sector.

cyclic product ion such as *n*. The $[M-30]^{+\cdot}$ peak (*m/z* 172) also shows a definite *ortho* effect from the MIKES data (Fig. 3). Thus, in compound **5** the losses of OH$^{\cdot}$ and H_2O are of primary importance. This is probably due to the participation of the methoxy group in the formation of ion *n* (*m/z* 155) and ion *o*



n *o*

(*m/z* 154). Evidence for such a cyclic structure is found from the MIKES of *m/z* 155. When the ion is from compound **5**, the major fragmentation observed is loss of CH_2O. This loss is not observed for the other two isomers.

EXPERIMENTAL

The benzenesulfonylhydrazides were prepared by reaction of the appropriate benzenesulfonyl chloride with hydrazine.[8] All are known compounds whose melting points are in agreement with those reported previously. The mass spectra were recorded on a Varian MAT 311A spectrometer with a reverse Nier-Johnson geometry at a nominal voltage of 70 eV and an ion source temperature of 80 °C. Samples were introduced directly into the ion source and vaporized by careful heating. All the mass analysed ion kinetic energy spectra were obtained at a nominal electron energy of 70 eV, accelerating voltage of 3 kV and an initial electric sector voltage of 506–507 V. The spectra were stable over a reasonable period of time under the conditions reported.

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