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Ortho Effects in Organic Molecules on Electron Impact

Part 22. Competing Oxygen Transfers from the Nitro Group to Sulphur and the Olefinic Double Bond in 2-Nitrophenyl Styryl Sulphides

D. V. Ramana,† N. Sundaram and M. George
Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

Double oxygen migration to sulphur from the *ortho*-nitro group leading to eliminations of SO_2 and $^{\bullet}SO_2H$ from the molecular ions and single oxygen transfer to the olefinic double bond in the side-chain giving rise to the most abundant ion at *m/z* 138 have been observed in 2-nitrophenyl styryl sulphides on electron impact. The proposed fragmentation mechanisms and the product ion structures were confirmed with the aid of high-resolution data, *B/E* linked scan and CID spectra.

INTRODUCTION

The nitro group, owing to the presence of two electron-rich oxygen atoms, its size and the possibility of a stable existence as a nitroso group after donating an oxygen atom to an acceptor site, is known to transfer oxygen atoms to multiple bonds[1–5] and heteroatoms such as nitrogen[6,7] and sulphur[8–13] by forming favourable transition states. In order to investigate the *ortho* interactions of the nitro group with the side-chain containing two competing oxygen acceptor sites, namely sulphur and an olefinic double bond, a mass spectral study of the styryl sulphides **1–4** was undertaken.

RESULTS AND DISCUSSION

Interesting oxygen transfer processes have been observed during the electron impact-induced decomposition of 2-nitrophenyl styryl sulphide (**1**). The migration of two oxygen atoms from the nitro group to sulphur in the side-chain in the molecular ion of **1** leads to the rearranged molecular ion *a* (Scheme 1). Subsequently, *a* undergoes fragmentation in two parallel pathways. Expulsion of SO_2 from *a* affords the fragment ion *b* at *m/z* 193, which eliminates a hydrogen radical to produce another fragment ion *c* at *m/z* 192 (15% abundance). Ion *c* is also formed directly from *a* by the ejection of $^{\bullet}SO_2H$. The proposed fragmentation pathways in Scheme 1 are supported by the *B/E* linked scan spectra of the molecular ion at *m/z* 257 and the ions *b*

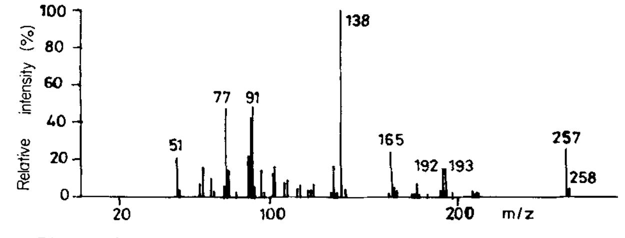
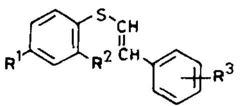
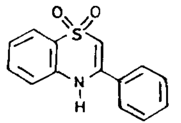


Figure 1. Electron impact mass spectrum of compound **1**.



	R^1	R^2	R^3
1	H	NO_2	H
2	NO_2	H	H
3	H	NO_2	o-OCH_3
4	H	NO_2	p-OCH_3



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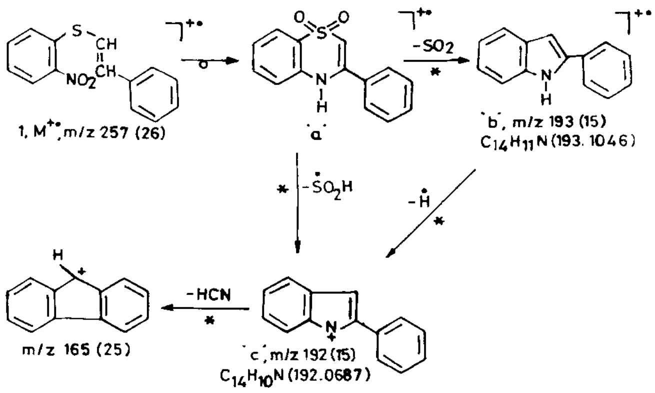

Scheme 1

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† Author to whom correspondence should be addressed.

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Table 1. B/E linked scan spectra of $M^{+\cdot}$ at m/z 257, 193 and 192 of compound 1

Parent ion m/z	m/z of daughter ions[a]				
257	193	192	138		
	(70)	(14)	(100)		
193	192	178	167	166	165
	(100)	(11)	(16)	(45)	(80)
192	166	165	164		
	(30)	(100)	(32)		

[a] Abundances in parentheses.

Table 2. Partial mass spectra of compounds 1–5

Compound	Relative abundances (%)[a] $M^{+\cdot}$	b	c	e	Other ions	
1	26	15	15	100	48	
	(257)	(193)	(192)	(138)	(91)	
2	100	—	—	—	42	
	(257)				(91)	
3	30	2	2	100	26	33
	(287)	(223)	(222)	(138)	(149)	(121)
4	19	2	—	32	100	70
	(287)	(223)		(138)	(149)	(121)
5	51	100	10	—		
	(257)	(193)	(192)			

[a] The figures in parentheses are m/z values of the ions.

and c of compound **1** (Table 1). In addition, the elemental compositions $C_{14}H_{11}N$ (193.1046) and $C_{14}H_{10}N$ (192.0687) for b and c, respectively, as determined by the high-resolution technique, confirm the formation of b by the ejection of SO_2 and the formation of c by the expulsion of $^{\cdot}SO_2H$ respectively, from the molecular ion.

A 2-phenylindole molecular ion structure is proposed for the ion b at m/z 193 of compound **1**. The proposed structure for b is supported by the fact that its collision-induced dissociation B/E linked scan spectrum (with characteristic fragment ions) is identical with that of the molecular ion of 2-phenylindole[14] (Fig. 2) taken as a reference compound.

A 3-phenyl[1,4]benzthiazene 1,1-dioxide structure is proposed for the rearranged molecular ion a. Hence 3-phenyl[1,4]benzthiazene 1,1-dioxide (**5**) was synthesized in this work and its mass spectral fragmentations (Table 2) are found to resemble those corresponding to the rearranged molecular ion of a of **1**, indicating that the cyclic sulphone structure a proposed for the rearranged $M^{+\cdot}$ for **1** is justified.

In another rearrangement process, the transfer of an oxygen atom from the nitro group to the olefinic double bond in the side-chain of **1** leads to the epoxide intermediate d. A simple cleavage of the C—S bond in d produces the ion e at m/z 138, which is the most abundant ion in this spectrum (Scheme 2). A hydrogen shift in d followed by bond reorganizations leads to another rearranged molecular ion f. A simple α-cleavage with respect to the carbonyl group in f affords the abundant tropylium cation at m/z 91. The B/E linked scan spectrum of $M^{+\cdot}$ at m/z 257 of **1** (Table 1) supports the envisaged direct formation of the ion at m/z 138 from the molecular ion. Further, the elemental composition C_6H_4NOS (138.0152) for e, as determined by high-resolution technique, is in good agreement with the elemental composition of the proposed *o*-nitrosothiophenoxy cation structure for e. Further support for the postulated structure for ion e is derived from the fact that its CID B/E linked scan spectrum (Fig. 3) (with characteristic fragment ions) is identical with that of the ion at m/z 138, having an *o*-nitrosothiophenoxy cation structure, obtained from 2,2′-dinitrodiphenyl disulphide[9] taken as a reference compound.

Further support for the proposed *ortho* interactions are obtained from the observation that the ions at m/z 193, 192 and 138 present in the mass spectrum of **1**, which are envisaged to be formed as a result of *ortho* interactions, are totally absent in the mass spectrum of the *para* isomer **2** (Table 2).

Another interesting observation in the mass spectra of the methoxy compounds **3** and **4** is the presence of the abundant ions at m/z 149 and 121. The transfer of an oxygen from the *ortho*-nitro group to the olefinic double bond in these compounds gives rise to an epoxy intermediate g, which undergoes a simple cleavage of the C—S bond with a hydrogen shift affording intense ions h at m/z 149 (Scheme 3, Table 2). In fact, the frag-

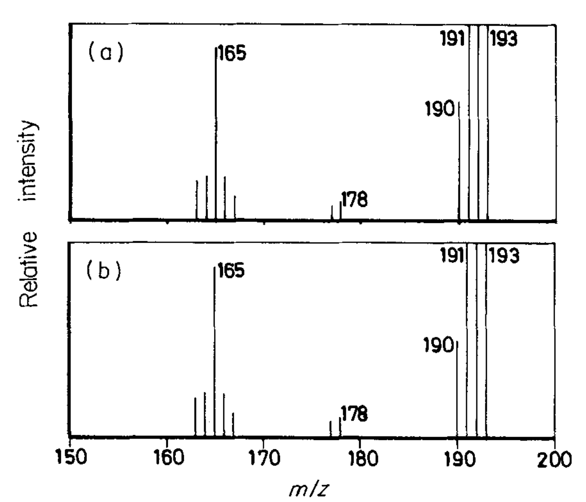
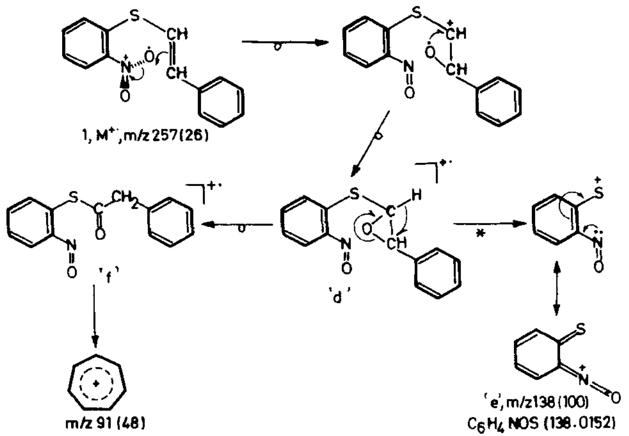


Figure 2. CID B/E linked scan mass spectra of ions at (a) m/z 193 of compound **1** and (b) m/z 193 from 2-phenylindole.



Scheme 2

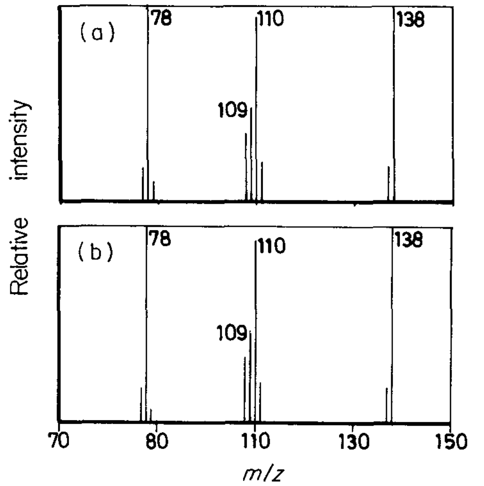
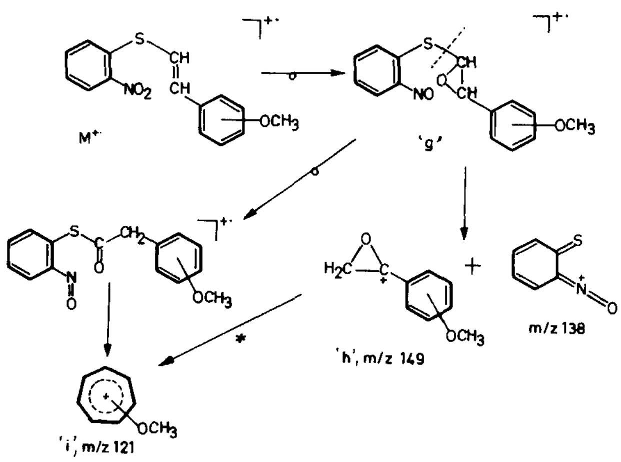


Figure 3. CID *B*/*E* linked scan mass spectra of ions at (a) *m*/*z* 138 of compound **1** and (b) *m*/*z* 138 from 2,2'-dinitrophenyl disulphide.

ment ion *h* happens to be the base peak in the mass spectrum of the *para*-methoxy compound **4**. The elemental composition $C_9H_9O_2$ (149.0610), as determined by the high-resolution technique, for the ion *h* is in good agreement with the elemental composition of the proposed structure for this ion. Another abundant fragment ion *i*, corresponding to the methoxy tropylium cation, is formed from both *h* (by the expulsion of CO) and the molecular ion directly. The ion *i* at *m*/*z* 121 has an elemental composition C_8H_9O (121.0654), which is in agreement with the elemental composition of the proposed structure for this ion. It can be noticed in the mass spectra of these compounds that the fragment ions corresponding to the expulsions of SO_2 and $^{\bullet}SO_2H$ from the molecular ions are of negligible abundances (Table 2).



Scheme 3

Table 3. High-resolution mass spectral and other data for the molecular ions of compounds 1–4

Compound	Yield (%)	M.p. (°C)	Data for M+· Observed mass	Calculated mass	Formula
1	72	125	257.0517	257.0527	$C_{14}H_{11}NO_2S$
2	66	80	257.0537	257.0527	$C_{14}H_{11}NO_2S$
3	74	94	287.0618	287.0633	$C_{15}H_{13}NO_3S$
4	73	107	287.0616	287.0633	$C_{15}H_{13}NO_3S$

Hence it can be inferred from this mass spectral study of nitrophenyl styryl sulphides that oxygen transfer from the *ortho*-nitro group to the olefin double bond is more favoured than that to sulphur when present together in the side-chain.

EXPERIMENTAL

Compounds **1–4** were hitherto unknown and were synthesised from the corresponding ω-(nitrophenylthio)-acetophenones[15] by reduction with sodium borohydride to the corresponding alcohols followed by dehydration with concentrated sulphuric acid. The compounds were purified by silica gel column chromatography using hexane as eluent and were recrystallized from benzene–hexane. Melting points and high-resolution mass spectral data for $M^{+\bullet}$ are given in Table 3.

Compound **5** was synthesized[16] by the reductive cyclization of ω-(2-nitrophenylsulphonyl)acetophenone with zinc and acetic acid and recrystallized from acetone; yield 30%, m.p. 265–266 °C.

All the compounds were characterized by IR, NMR and mass spectral data and their purities were checked by thin-layer chromatography.

The low-resolution mass spectra were recorded on a Varian-MAT CH-7 mass spectrometer at 70 eV electron energy, an emission current of 100 μA and an acceleration voltage of 3 kV. All the samples were introduced into the spectrometer by direct probe insertion at a probe temperature varying between 70 and 150 °C. The high-resolution data (at a resolution of 6000, 10% valley) were obtained using a Finnigan-MAT 8230 mass spectrometer. The linked scan spectra were measured on a VG-Micromass 7070H mass spectrometer.

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