Ortho Effects in Organic Molecules on Electron Impact 17-Parallel Oxygen Transfers from Nitro Group to Olefinic Double Bond and Sulfur in α-(*o*-Nitrophenylthio)cinnamic Acids

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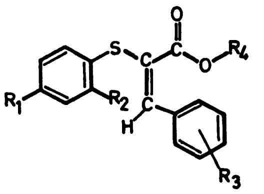
An oxygen transfer from the nitro group to the olefinic double bond followed by a simple cleavage affords intense fragment corresponding to *o*-nitrosophenylthio cation at *m*/*z* 138 during the mass spectral fragmentations of α-(*o*-nitrophenylthio)cinnamic acid. Single and double oxygen transfers from the nitro group to sulfur lead to concerted ejections of [$SO+CO_2$] and [SO_2+CO_2] from the molecular ion of this compound. The mechanisms proposed for these processes are supported by high-resolution data, CID linked scan spectra, D-labelling, and chemical evidence.

The nitro group is known to interact very effectively with the ortho substituent in aromatic systems by transfering oxygen atoms to multiple bonds[1–4] or heteroatoms[5,6] present in the side chain on electron impact. Sulfur in the form of a thiocarbonyl[7,8] and a sulfide[9,10] is known to interact with the nitro group by accepting one or more oxygen atoms with subsequent expulsions of neutral molecules.[11] The electron impact mass spectra of α-(*o*-nitrophenylthio)cinnamic acid derivatives **1**—**8** (Scheme 1) were undertaken in this work in order to study the ortho interaction of the nitro group with the side chain containing sulfur and an olefinic double bond with a carboxyl group.

Results and Discussion

The base peak in the mass spectrum of α-(*o*-nitrophenylthio)cinnamic acid (**1**) is at *m*/*z* 138, having an elemental composition of C_6H_4NOS (138.00095) (Scheme 2, Tables 1 and 4). Furthermore, examination of the B/E linked scan spectrum of the molecular ion of **1** (Table 2) revealed that the ion at *m*/*z* 138 is directly formed from the molecular ion. An *o*-nitrosophenylthio cation structure is assigned to the ion at *m*/*z* 138. This hypothesis is confirmed



	R_1	R_2	R_3	R_4
1	H	NO_2	H	H
2	NO_2	H	H	H
3	H	NO_2	H	D
4	NO_2	H	H	D
5	H	NO_2	o-OCH_3	H
6	H	NO_2	p-OCH_3	H
7	H	NO_2	o-Cl	H
8	H	NO_2	p-Cl	H

Scheme 1.

Table 1. Partial Mass Spectra of Compounds **1**—**8**

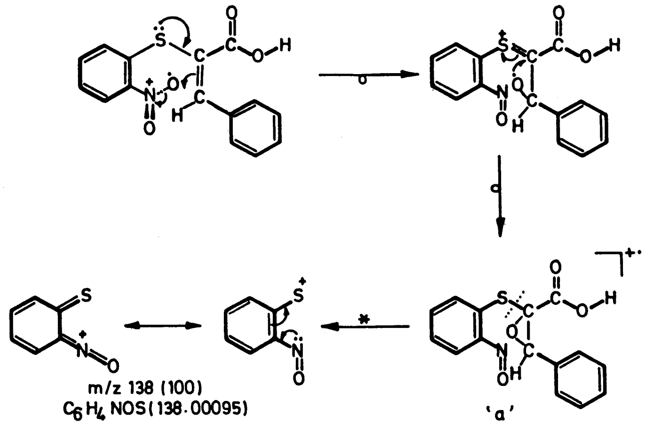
Compoud No.	Relative abundance of								
	$M^{+\cdot}$	*m*/*z* 138	$[M-92]^{+\cdot}$	$[M-93]^{+}$	f	e	*m*/*z* 208	*m*/*z* 192	*m*/*z* 165
1	39 (301)	100	18 (209)	16 (208)	11 (193)	12 (192)	16	12	27
2	100 (301)	—	17 (209)	17 (208)	—	—	17	—	35
3	31 (302)	100	17 (210)	15 (209)	10 (194)	9 (193)	12	12	28
4	100 (302)	—	66 (210)	28 (209)	—	—	28	—	59
5	29 (331)	100	2 (239)	3 (238)	5 (223)	3 (222)	9	2	16
6	21 (331)	100	3 (239)	2 (238)	5 (223)	2 (222)	11	1	70
7	29 (335)	100	2 (243)	2 (242)	7 (227)	4 (226)	54	16	53
8	18 (335)	100	6 (243)	3 (242)	5 (227)	3 (224)	15	4	17

The figures in parentheses indicate *m*/*z* values the ions.

Table 2. B/E Linked Scan Spectrum of $M^{+\cdot}$ at *m/z* 301, *m/z* 209, 208, and 192 of Compound **1**

Parent ion (*m/z*)	*m/z* values of daughter ions							
301	237 (58)	236 (10)	209 (23)	208 (5)	193 (9)	192 (10)	191 (10)	138 (100)
209	208 (100)	192 (16)	181 (38)	180 (75)				
208	193 (7)	192 (7)	181 (100)	180 (80)	179 (36)	178 (14)		
192	191 (100)	165 (82)	164 (29)					

The figures in parentheses indicate relative abundances of the ions.



Scheme 2.

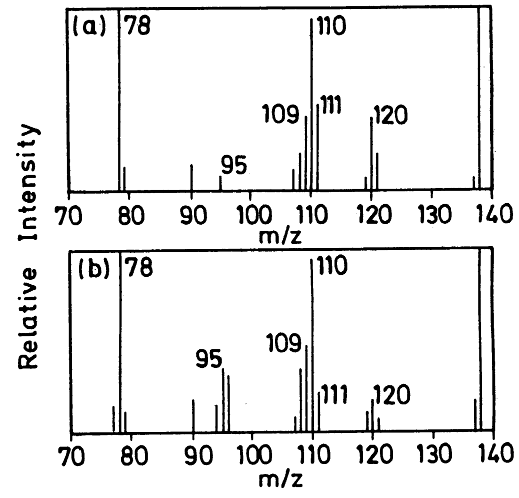
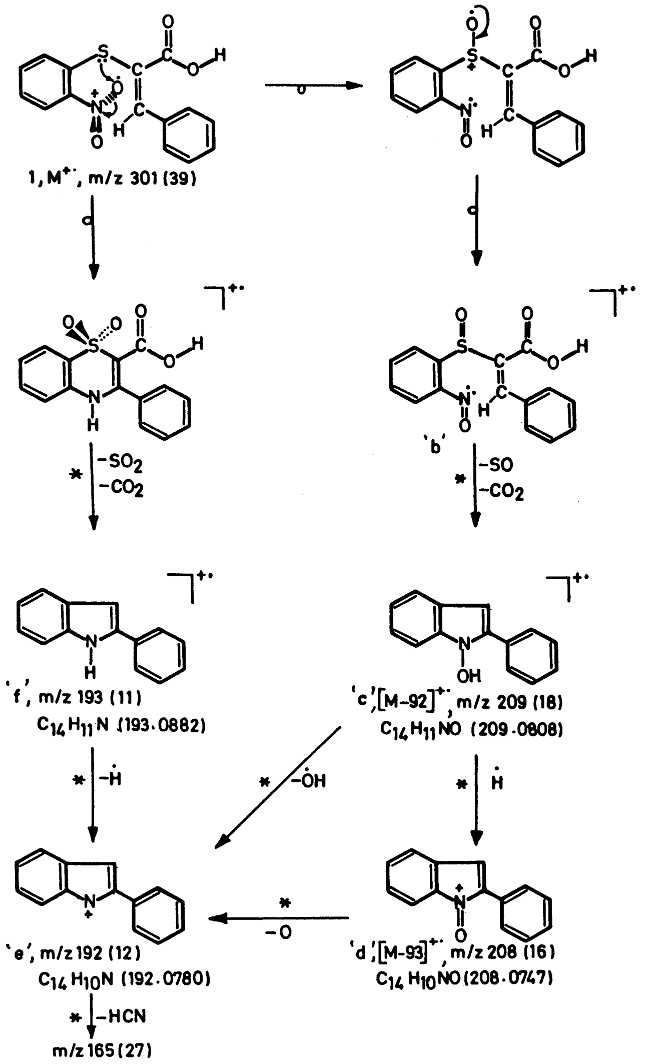


Fig. 1. CID B/E linked scan spectra of (a) *m/z* 138 of compound **1** and (b) *m/z* 138 of bis(*o*-nitrophenyl) disulfide.



Scheme 3.

from the fact that the collision induced dissociation B/E linked scan spectrum of *m/z* 138 ion from compound **1** is identical with that of the ion at *m/z* 138 (Fig. 1) obtained from bis(*o*-nitrophenyl)disulfide, having *o*-nitrosophenylthio cation structure.[12]

Based on these observations, an oxygen transfer from the nitro group to the double bond in the side chain of compound **1** is envisaged for the formation of the rearranged molecular ion 'a' where a simple cleavage of the C-S bond affords the base peak in the spectrum at *m/z* 138 (Scheme 2). The proposed mechanism is further supported by the fact that the mass spectra of the substituted compounds **3** and **5**—**8** also have the base peaks at *m/z* 138 without any shifts (Table 1). Moreover, this ion is totally absent in the mass spectrum of the para isomer (**2**) (Table 1).

Single and double oxygen transfers from the nitro group to the sulfur in the side chain have also been noticed in the mass specturm of compound **1** (Scheme 3). The single oxygen migration from the nitro group to sulfur leads to the rearranged molecular ion 'b'. Subsequent concerted ejection of SO and CO_2 from 'b' affords the ion 'c', $[M-92]^+$ at m/z 209 of 18% relative abundance. The extrusion of SO from 'b' can be visualized as the migration of the phenyl group from sulfur to the olefinic carbon followed by the expulsion of SO. Further loss of $\dot{H}$ from 'c' gives rise to an ion 'd' at m/z 208 (16) (Scheme 3). The elemental compositions $C_{14}H_{11}NO$ (209.0808) and $C_{14}H_{10}NO$ (208.0747) (Table 4) for 'c' and 'd' respectively obtained by high resolution technique, support the proposed elimination of SO and CO_2 from the molecular ion for the formation of 'c'. Both 'c' and 'd' lose $\dot{O}H$ and O respectively to give rise to a fragment 'e' at m/z 192.

The formation of 'e' at m/z 192 also takes place through another interesting parallel oxygen migration process. Initial double oxygen transfer from the nitro group to sulfur followed by concerted elimination of SO_2 and CO_2 directly from the molecular ion affords the interesting fragment ion 'f' at m/z 193 (11) (Scheme 3). An aryl migration from sulfur to the olefinic carbon after the initial double oxygen migration from the nitro group to sulfur can be proposed for the formation of 'f' $[M-SO_2]^{+\cdot}$. The expulsion of $\dot{H}$ from 'f' produces the ion 'e' at m/z 192. Also there is an evidence for the direct formation of 'e' from the molecular ion as seen in B/E linked scan spectrum of $M^{+\cdot}$ of **1** (Table 2). The elemental compositions $C_{14}H_{11}N$ (193.0882) and $C_{14}H_{10}N$ (192.0780) (Table 4) for 'f' and 'e' are in good agreement with the proposed elimination of SO_2 and CO_2 from the molecular ion for the formation of 'f'. The fragmentation pathways described in Scheme 2 are substantiated by linked scan B/E spectra of $M^{+\cdot}$, 'c', 'd', and 'e' (Table 2) of compound **1**. Similar single and double oxygen transfers from the nitro group to sulfur in the substituted compounds **5**—**8** lead to the formation of ions corresponding to 'c', 'd', 'f', and 'e' (Table 1). Also loss of substituent from 'e' in preference to loss of $\dot{H}$ leads to formation of the ion at m/z 208 and in turn to the formation of the fragment at m/z 192 in compounds **5**—**8** (Table 1).

Table 3. B/E Linked Scan Spectrum of $M^{+\cdot}$at m/z 301 and m/z 210 of Compound **2**

Parent ion (m/z)	m/z values of daughter ions					
301	256 (31)	255 (19)	240 (20)	210 (13)	195 (13)	163 (100)
210		209 (100)	178 (22)	166 (14)	165 (95)	

The figures in parentheses indicate relative abundances of the ions.

Table 4. High-Resolution Data

Compound	m/z	Formula	Observed	Calculated
1	138	C_6H_4NOS	138.0010	138.0030
	209	$C_{14}H_{11}NO$	209.0808	209.0841
	208	$C_{14}H_{10}NO$	208.0747	208.0762
	193	$C_{14}H_{11}N$	193.0882	193.0892
	192	$C_{14}H_{10}N$	192.0780	192.0813
2	210	$C_{14}H_{10}S$	210.0451	210.0520
	209	$C_{14}H_9S$	209.0409	209.0442
	208	$C_{14}H_8S$	208.0315	208.0364

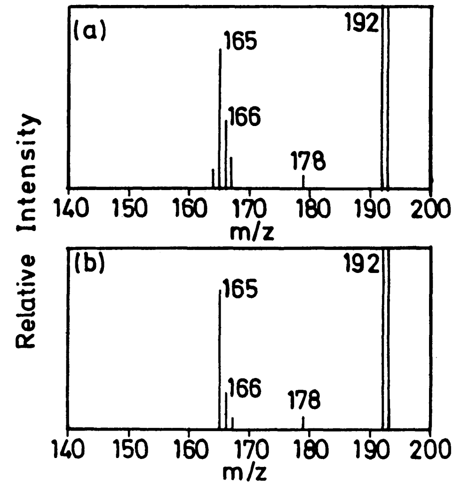
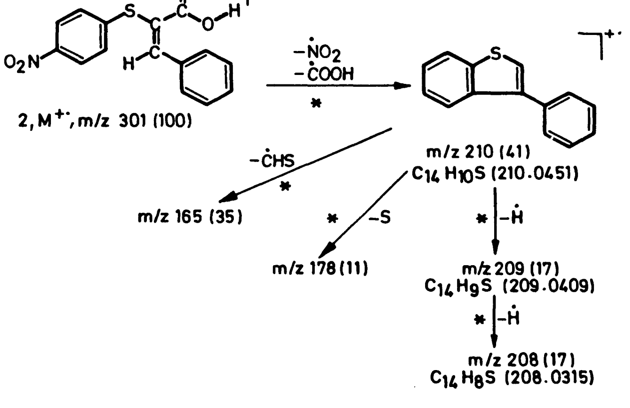


Fig. 2. CID B/E linked scan spectra of (a) ion 'f' and (b) m/z 193 from 2-phenylindole.

A cyclic structure is proposed for 'c' from which the secondary fragmentations as observed in the mass spectrum of this compound are better explained. A 2-phenylindole structure is visualized for the ion 'f' at m/z 193 in compound **1**, instead of an open chain structure with an electron deficient nitrogen after the oxygen transfers. Evidence for the proposed structure for 'f' is obtained from the observation that the collision induced dissociation B/E linked scan spectrum of 'f' is identical with that of the molecular ion of 2-phenylindole (Fig. 2) taken as a reference compound. Furthermore the elemental compositions of



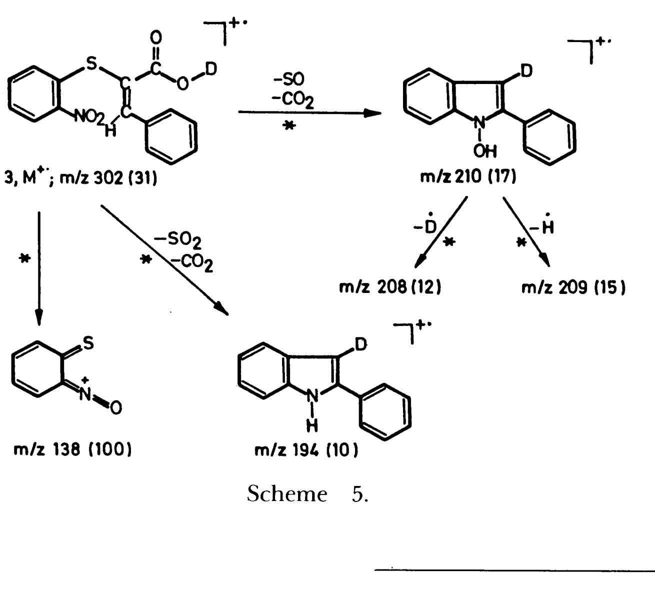
Scheme 4.

these ions as determined by the accurate mass measurements are also in agreement with those of the proposed structures.

However, the mass spectrum of the para isomer, **2**, also contains the peaks corresponding to $[M-92]^{+\cdot}$ and $[M-93]^{+}$ (Scheme 4) (Table 1). But the B/E linked scan spectra of $M^{+\cdot}$ and the abundant fragment ion at *m/z* 210 (Table 3) indicate that the mechanism of formation of the ions at *m/z* 209 and 208 in compound **2** is different from that noticed in compound **1**. A concerted elimination of $\dot{C}OOH$ and $\dot{N}O_2$ from the molecular ion affords the abundant ion at *m/z* 210. Two successive losses of $\dot{H}$ from the ion at *m/z* 210 produce the fragment ions at *m/z* 209 and *m/z* 208. The proposed mechanism is further supported by the elemental compositions $C_{14}H_{10}S$ (210.0451), $C_{14}H_9S$ (209.0409), and $C_{14}H_8S$ (208.0315) (Table 4) for the ions at *m/z* 210, 209, and 208 respectively.

Further evidence for the proposed ortho interactions are obtained from the mass spectra of deuterium analogues **3** and **4** (Scheme 4). The base peak in the mass spectrum of **3** is at *m/z* 138 since there is no involvement of the -COOH group in the formation of this ion. On the other hand, the concerted elimination of SO and CO_2 from the molecular ion affords the ion at *m/z* 210 which loses both $\dot{H}$ and $\dot{D}$ to give ions at *m/z* 209 and 208, respectively. Also the concerted ejection of SO_2 and CO_2 from the molecular ion of **3** produces an ion at *m/z* 194 (Scheme 5). These observations clearly indicate that the formation of 'c' and 'f' in compound **1** involves a decarboxylation process (elimination of SO and CO_2 or SO_2 and CO_2) and not an elimination of the $\dot{C}OOH$ as in the case of the para isomer, **2**. Moreover, the molecular ion of compound **4** undergoes, as expected, concerted expulsion of $\dot{N}O_2$ and $\dot{C}OOD$ giving rise to an abundant ion at *m/z* 210 as in compound **2** (Table 1).

It is evident from this study that the oxygen transfer to the olefinic double bond is more predominent, whereas the oxygen transfer to the sulfur is associated with the decarboxylation process.



Scheme 5.

Experimental

Compounds **1**,**2**, and **5**—**8** were prepared[13,14] by condensation reactions of (2-nitrophenylthio)acetic acid or (4-nitrophenylthio)acetic acid with the appropriate substituted benzaldehyde, according to the procedure reported in literature for the preparation of these compounds. Compounds **3** and **4** were synthesized by refluxing 50 mg each of **1** or **2** with one ml of D_2O for 120 h followed by usual workup. The D-incorporation is found to be 76% in **3** and 62% in **4**. The purity of the compounds was checked by TLC and was characterized by IR and NMR spectral data.

The low-resolution spectra were taken on a Varian MAT CH-7 mass spectrometer. The spectra were run at 70 eV with an emission current of 100 μA. All the compounds were introduced into the mass spectrometer through the direct probe insertion at a probe temperature varying between 70 and 110 °C. The high-resolution data (at a resolution of 5000, 10% valley) were recorded on a Finnigan MAT 8230 mass spectrometer at an ionization energy of 70 eV and an acceleration voltage of 3 kV. The linked scan spectra were run on a Finnigan MAT 90 mass spectrometer.

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