October, 1989] © 1989 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 62, 3349—3354 (1989) 3349

Ortho Effects in Organic Molecules on Electron Impact. 20. Parallel Oxygen Transfers from Nitro Group to Sulfur and Acetylenic Triple Bond in 3-(*o*-Nitrophenylthio)-1-propynes

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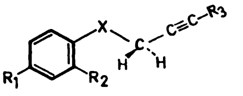
(Received January 5, 1989)

Oxygen transfers from nitro group to both the sulfur and acetylenic triple bond are noticed in parallel fragmentation pathways during the electron impact induced decompositions of 3-(*o*-nitrophenylthio)-1-propynes. Single oxygen transfer from nitro group to sulfur leads to abundant ions corresponding to *o*-nitrosobenzenesulfinyl cation and $[M-SO]^{+\cdot}$ while a concerted double oxygen transfer to sulfur followed by ejection of SO_2 from the rearranged molecular ion affords intense quinoline radical cation. Further, a single oxygen transfer to acetylenic triple bond, followed by a simple cleavage produces intense fragments corresponding to *o*-nitrosobenzenethiol radical cation at *m/z* 139 and *o*-nitrosophenylthio cation at *m/z* 138. The proposed fragmentation pathways and ion structures are established through high-resolution data, collision-induced dissociation (CID) mass-analyzed ion kinetic energy (MIKE) spectra, B/E linked scan spectra and chemical substitution.

The nitro group in the ortho position is a powerful interacting function in aromatic compounds during mass spectral decompositions. It is capable of transferring oxygens to the double bond,[1—3] heteroatoms[4,5] and activated carbon[6] in the side chain of aromatic ortho-disubstituted compounds. Recently the ortho interaction of nitro group with acetylenic triple bond is described[7] through an oxygen transfer producing abundant aroyl cations in (*o*-nitrophenyl)phenylacetylenes. Sulfur in the form of a thiocarbonyl[8,9] and a sulfide[10,11] is known to interact with the nitro group by accepting one or more oxygen atoms with the subsequent expulsions of SO and SO_2. It is also shown[12] that the oxygen transfer from the nitro group to the acetylenic triple bond is more predominant than to the sulfur when both were present together in the side chain as in (*o*-nitrophenylthio)phenylacetylenes. In the present study the mass spectral decompositions of 3-(*o*-nitrophenylthio)-1-propynes have been undertaken to assess the relative interacting abilities of sulfur and carbon-carbon triple bond to accept oxygens from ortho nitro group under electron impact conditions when a methylene group is inserted between sulfur and acetylenic moiety (Scheme 1).



Compd.	X	R1	R2	R3
1.	S	H	NO2	H
2.	S	NO2	H	H
3.	S	Cl	NO2	H
4.	S	H	NO2	Ph
5.	S	NO2	H	Ph
6.	SO2	H	NO2	H
7.	SO2	H	NO2	Ph
8.	O	H	NO2	H
9.	O	NO2	H	H

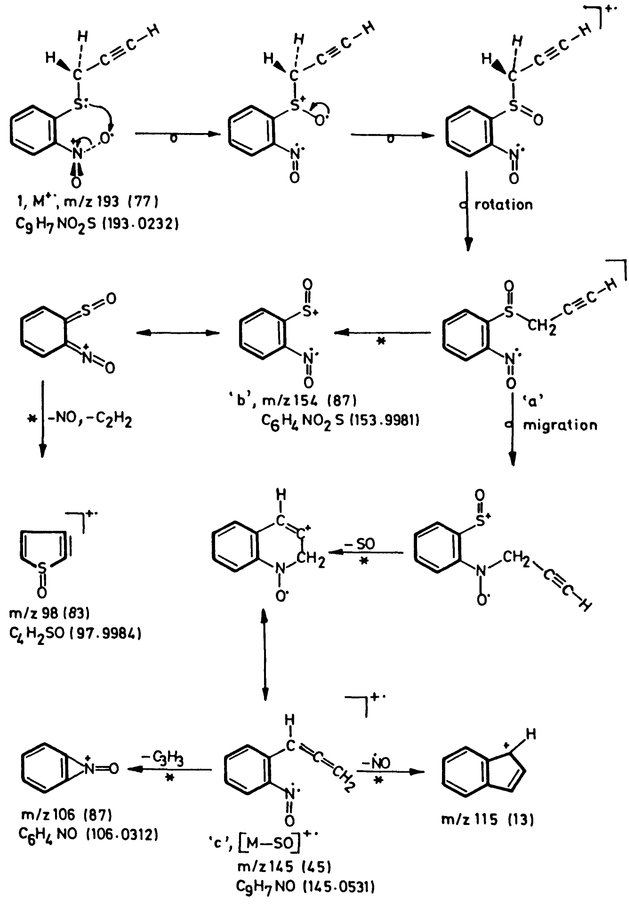
Scheme 1.

Results and Discussion

Evidence for the oxygen transfers from the nitro group to both the sulfur and acetylenic triple bond in parallel pathways is adduced from the mass spectral fragmentations of 3-(*o*-nitrophenylthio)-1-propyne (**1**). The molecular ion rearranges to 'a' after the initial single oxygen transfer from the nitro group to the sulfur (Scheme 2). An α-cleavage with respect to sulfur in 'a' affords 'b' at *m/z* 154 (87). The accurate mass of this fragment, as determined by high-

Table 1. High-Resolution Data

Compound	*m/z*	Observed	Calculated	Elemental composition
1	193	193.0232	193.0214	$C_9H_7NO_2S$
	154	153.9981	153.9979	$C_6H_4NO_2S$
	145	145.0531	145.0527	C_9H_7NO
	139	139.0149	139.0108	C_6H_5NOS
	138	138.0070	138.0030	C_6H_4NOS
	129	129.0524	129.0578	C_9H_7N
	128	128.0445	128.0500	C_9H_6N
	108	108.0042	108.0050	C_6H_4S
	106	106.0312	106.0292	C_6H_4NO
	98	97.9984	97.9843	C_4H_2SO
6	225	225.0077	225.0112	$C_9H_7NO_4S$
	186	185.9876	185.9878	$C_6H_4NO_4S$
	170	169.9916	169.9928	$C_6H_4NO_3S$
8	177	177.0327	177.0426	$C_9H_7NO_3$
	123	123.0239	123.0320	$C_6H_5NO_2$
	122	122.0231	122.0242	$C_6H_4NO_2$



Scheme 2.

Table 2. B/E Linked Scan Spectra

Parent ion	Daughter ions with relative abundances in parentheses
$M^{+\cdot}$, m/z 193 of compound **1**	176(5), 163(5), 154(58), 147(3), 145(100), 139(82), 138(78), 129(65), 128(75), 122(34), 96(20).
c, m/z 145 of compound **1**	144(100), 115(60), 106(21).
i, m/z 139 of compound **1**	138(32), 120(8), 111(40), 106(50), 95(8), 78(36).
$M^{+\cdot}$, m/z 225 of compound **6**	186(30), 170(65), 106(100).
$M^{+\cdot}$, m/z 177 of compound **8**	160(50), 131(40), 123(80), 122(100).

resolution technique is 153.9981 (Table 1) which corresponds to an elemental composition of $C_6H_4NO_2S$. Furthermore, examination of the B/E linked scan spectrum of $M^{+\cdot}$ of **1** (Table 2) revealed that the ion 'b' at m/z 154 is directly formed from the molecular ion. The ion at m/z 154 could also arise by a simple α-cleavage with respect to the sulfur in the molecular ion prior to the oxygen transfer. However, such a cleavage can, in principle, occur in the para-isomer (**2**) as well. But the intensity of the ion at m/z 154 in the mass spectrum of para-compound (**2**) is insignificant (Table 3). Therefore an ortho interaction is invoked for the formation of this fragment at m/z 154. Further the collision-induced dissociation (CID) mass-analyzed ion kinetic energy (MIKE) spectrum of the ion 'b' at m/z 154 from **1** is found to be identical (Fig. 1) with that of the ion at m/z 154 derived from bis(*o*-nitrophenyl) disulfide (reference compound). Since the fragment at m/z 154 in the reference compound is obtained as a result of a simple cleavage, an *o*-nitrosobenzenesulfinyl cation structure can be assigned to it. By the comparative study of the CID MIKE spectra of (Fig. 1) the ion 'b' from **1** and the fragment at m/z 154 from the reference compound an *o*-nitrosobenzenesulfinyl cation structure is proposed for the ion 'b' at m/z 154 in **1**.

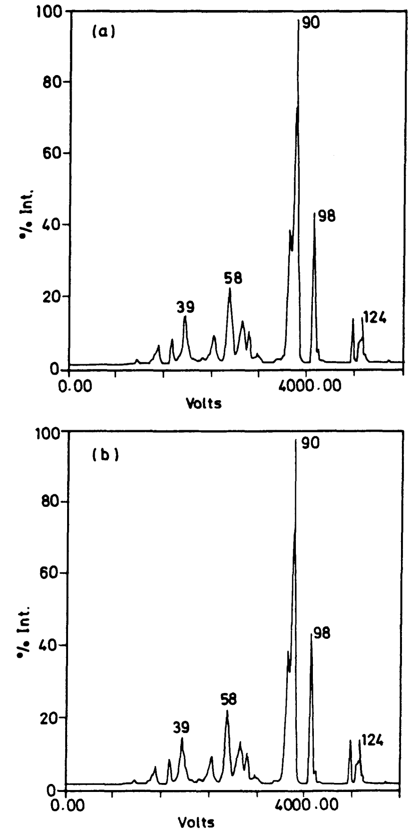
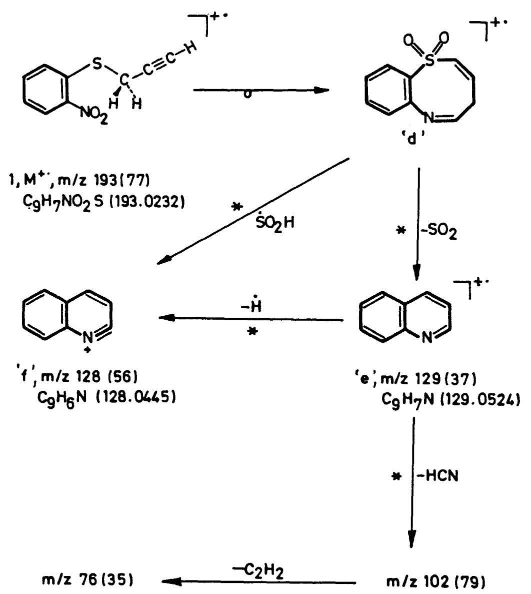


Fig. 1. CID MIKE spectra of ions at (a) m/z 154 of compound **1**, (b) m/z 154 of bis(*o*-nitrophenyl) disulfide.

The other characteristic ion resulting from the single oxygen transfer to sulfur in the mass spectrum of **1** is at m/z 145(45). Loss of 'SO from the rearranged molecular ion 'a' produces the $[M-SO]^{+\cdot}$ ion 'c' at m/z 145 (Scheme 2). The elemental composition C_7H_7NO (145.0531) for 'c' is in good agreement with the proposed elimination of 'SO' from the molecular ion and its direct formation is supported by the B/E linked scan spectrum of $M^{+\cdot}$ of **1** (Table 2). A 1-nitroso-2-(1,2-propadienyl)benzene radical cation structure is proposed for 'c' at m/z 145 in **1**, based upon the accurate mass measurements and secondary fragmentations of 'c'.



Scheme 3.

The most interesting decomposition mode in the mass spectrum of **1** is the expulsion of SO_2 and SO_2H radical in parallel fragmentation pathways from the molecular ion giving rise to intense ions at *m*/*z* 129(37) and 128(56), respectively (Scheme 3). The transfer of two oxygens from nitro group to sulfur followed by cyclization leading to the rearranged molecular ion 'd' is envisaged as an intermediate for this process. The rearranged molecular ion 'd' on ejection of SO_2 affords the abundant ion 'e' at *m*/*z* 129(37) (Scheme 3). Further loss of $\dot{H}$ from 'e' gives rise to an ion 'f' at *m*/*z* 128 (Scheme 3). The formation of 'f' at *m*/*z* 128 also takes place through a concerted elimination of SO_2H radical from 'd' as evidenced from the B/E linked scan spectrum of $M^{+\cdot}$ of **1** (Table 2). The elemental compositions C_9H_7N (129.0524) and C_9H_6N (128.0445) for 'e' and 'f' obtained by high-resolution technique, support the proposed elimination of SO_2 and $\dot{S}O_2H$ from the molecular ion for the formation of 'e' and 'f', respectively. Based on these facts a quinoline radical cation structure to 'e' and a dehydroquinolinium cation structure to 'f' are postulated (Scheme 3). Evidence for the proposed quinoline radical cation structure for 'e' is obtained from the observation that the CID MIKE spectra of 'e' from **1** and that of the molecular ion of quinoline, taken as a reference compound, at *m*/*z* 129 are superimposable (Fig. 3).

Another novel ortho interaction noticed in the mass spectrum of **1** is the formation of fragments initiated by the single oxygen migration from the nitro group to the acetylenic triple bond leading to the rearranged molecular ion 'g' (Scheme 4). An α-cleavage with respect to sulfur in 'g' affords 'h' at *m*/*z* 138(91) while the ion 'i' at *m*/*z* 139(61) is derived from a similar cleavage with an α-hydrogen migration. An *o*-nitrosophenylthio cation structure to 'h' and an *o*-

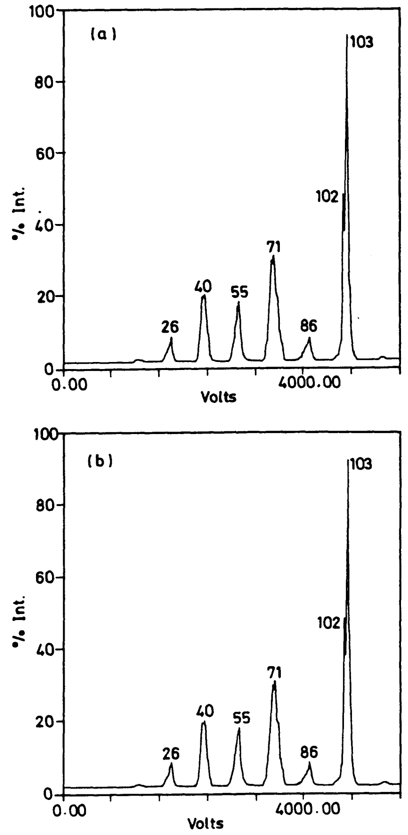


Fig. 2. CID MIKE spectra of ions at (a) *m*/*z* 129 of compound **1**, (b) $M^{+\cdot}$, *m*/*z* 129 of quinoline.

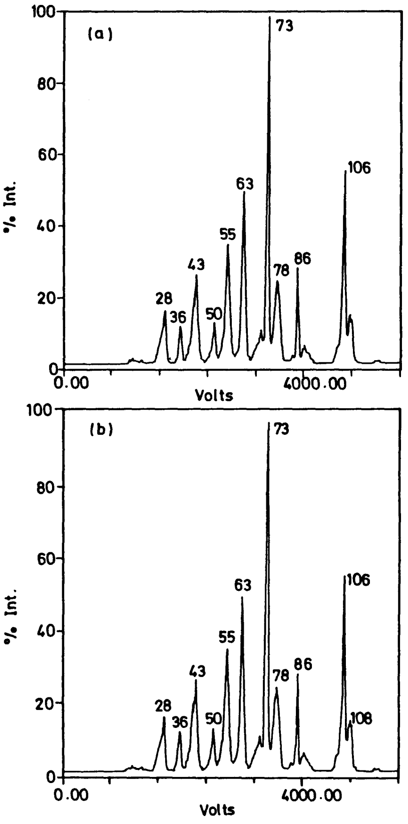
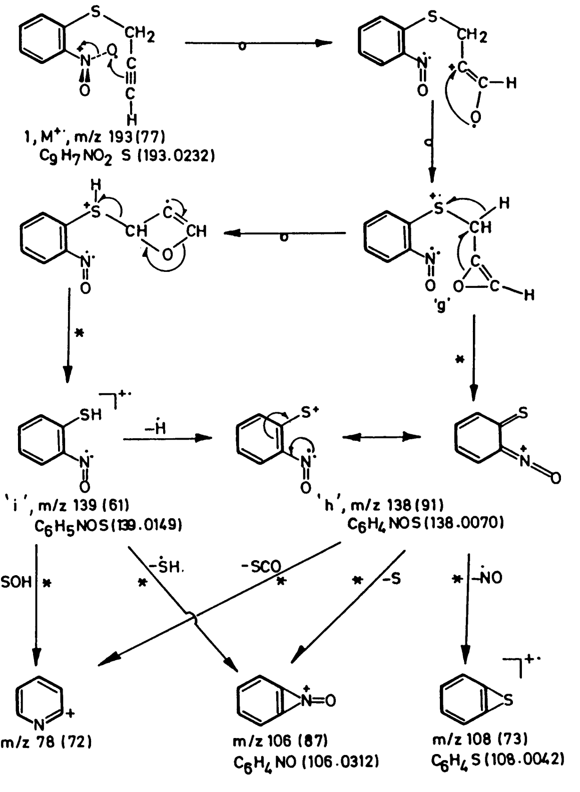


Fig. 3. CID MIKE spectra of ions at (a) *m*/*z* 138 of compound **1**, (b) *m*/*z* 138 of bis(*o*-nitrophenyl) disulfide.

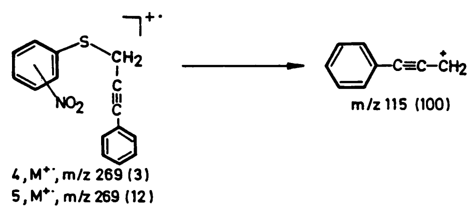
nitrosobenzenethiol radical cation structure to 'i' are assigned. The elemental compositions C_6H_4NOS (138.0076) and C_6H_5NOS (139.0149) for 'h' and 'i' respectively, obtained by high-resolution technique agree with the elemental compositions of the structures proposed for the ions 'h' and 'i'. The *o*-nitrosophenylthio cation structure envisaged for 'h' at *m/z* 138 is supported by the fact that the CID MIKE spectrum of 'h' is identical (Fig. 3) with that of the CID MIKE spectrum of the ion *m/z* 138, obtained from bis(*o*-nitrophenyl) disulfide, having *o*-nitrosophenylthio cation structure.[13] The fragmentation pathways described in Scheme 4 are substantiated by B/E linked scan spectra of $M^{+\cdot}$, 'h', and 'i' (Table 2) of compound **1**. All the ions noticed in the mass spectrum of **1** as a result of ortho interaction are also present in the substituted derivative (Compound **3**) with the corresponding shifts in the *m/z* values of the ions (Table 3).

Table 3. Partial Mass Spectra of Compounds **1** to **9**

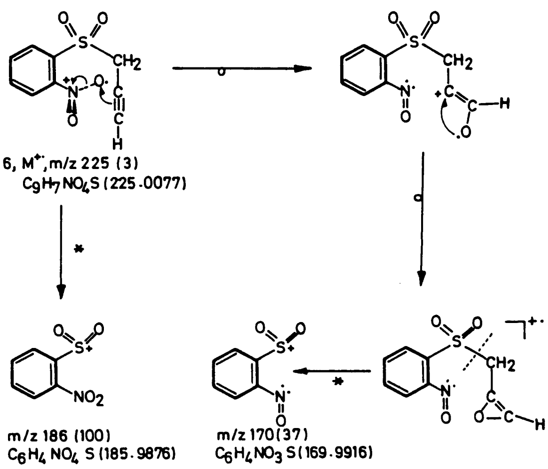
Compound	*m/z* values with relative abundances in parentheses
1	193(77), 154(87), 147(8), 145(45), 139(61), 138(91), 129(37), 128(56), 108(73), 106(87), 98(83), 96(100).
2	193(60), 176(21), 163(5), 154(3), 147(100), 146(42), 122(9), 96(6).
3	227(30), 188(83), 181(8), 179(16), 173(19), 172(65), 163(6), 162(12), 142(48), 140(55), 132(62), 130(55), 95(100).
4	269(3), 252(6), 221(3), 139(20), 115(100), 105(6).
5	269(12), 115(100), 89(5).
6	225(3), 186(100), 170(37), 107(28), 103(10).
7	301(6), 220(5), 195(9), 186(8), 170(3), 115(100).
8	177(42), 160(8), 131(30), 123(84), 122(100), 106(40), 94(22), 92(42).
9	177(74), 176(40), 160(54), 131(96), 130(100), 103(32).



Scheme 4.



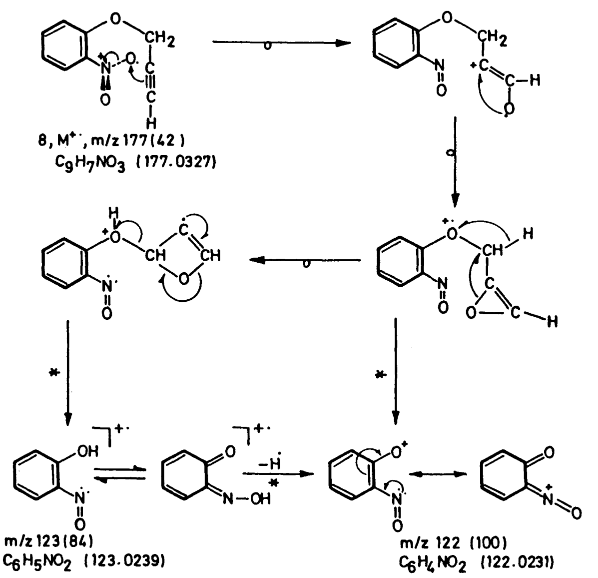
Scheme 5.



Scheme 6.

When this study is extended to 3-(*o*-nitrophenylthio)-1-phenyl-1-propyne (**4**) and its corresponding para-isomer (**5**), the chief fragment ion observed in the mass spectra of these two compounds is due to simple α-cleavage with respect to sulfur producing the stable 3-phenyl-2-propynyl cation at *m/z* 115 (Scheme 5) (Table 3). However no fragment ions corresponding to oxygen transfers from the nitro group either to sulfur or to the acetylenic triple bond are noticed in the ortho-isomer (**4**).

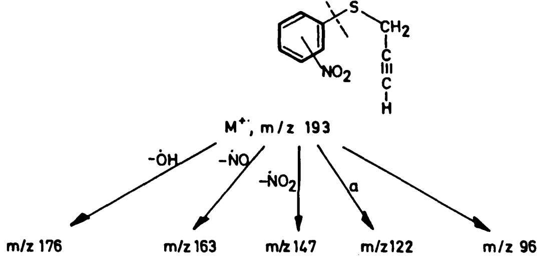
The mass spectrum of 3-(*o*-nitrophenylsulfonyl)-1-propyne (**6**) is also studied in this work to evaluate the feasibility of ortho interaction of nitro group with the side chain containing acetylenic triple bond and a sulfonyl group. The base peak in the mass spectrum of **6** is due to simple α-cleavage with respect to sulfonyl group producing the ion at *m/z* 186(100) (Scheme 6). Another intense ion observed in the mass spectrum of this compound is due to an oxygen transfer from nitro group to acetylenic triple bond followed by simple cleavage affording the ion at *m/z* 170(37) (Scheme 6). The oxygen analogue of compound **1** i.e., 3-(*o*-nitrophenoxy)-1-propyne (**8**), shows in its mass spectrum, the base peak at *m/z* 122(100) corresponding to oxygen migration from nitro group to acetylenic triple bond followed by simple cleavage



Scheme 7.

(Scheme 7). The same migration process leads to another intense ion at m/z 123(84) by an α-hydrogen transfer followed by simple cleavage from the rearranged molecular ion (Scheme 7). The fragmentation pathways described in Schemes 6 and 7 are substantiated by B/E linked scan spectra (Table 2) and accurate mass measurements (Table 1). It can be noticed from this comparative study of sulfur and oxygen compounds that the ortho interactions of nitro group are noticed with both sulfur and acetylenic triple bond as expected in compound **1** while fragments corresponding to the ortho interaction of the nitro group with the triple bond only are noticed in oxygen analogue (Compound **8**). These fragmentations due to the ortho interactions are of either negligible abundance or totally absent in the corresponding para-isomers (**2** and **9**) (Table 3). In the absence of these ortho interactions, the para-isomers (**2** and **9**) show almost similar fragmentation process (Table 3). The other common fragments observed in **1** and **2** are shown in Scheme 8.

It can be inferred from this study that the oxygen transfers from the nitro group to both sulfur and acetylenic triple bond are equally facile even when a methylene group is interjected between sulfur and acetylenic moiety. It can also be noticed that the carbon–carbon triple bond continues to act as a good oxygen acceptor even when placed one carbon atom away from sulfur. Another interesting aspect observed in this study is that while the sulfur is accepting two oxygens from nitro group, the acetylenic function is able to take only one oxygen, perhaps due to the unfavorable transition states required for the transfer of both the oxygens. Further, it can also be observed that if sulfur already possess oxygens as in the case of sulfone **6**, or if the sulfur is replaced by an oxygen as in the case of ether **8**, the oxygen transfer to the acetylenic triple bond is still noticed.



Scheme 8.

Experimental

Compounds **1** to **3** were prepared from the appropriate nitrobenzenethiol and 3-bromo-1-propyne by mechanically stirring for 6 hours in *N,N*-dimethylformamide solvent in the presence of potassium carbonate according to the general procedure reported in the literature.[14] Compounds **4** and **5** were synthesized by the same general procedure using appropriate nitrobenzenethiol and 3-bromo-1-phenyl-1-propyne. The 3-bromo-1-phenyl-1-propyne used in these reactions was prepared from phenylethyne, paraformaldehyde and phosphorus tribromide according to the literature[15] reported procedure. Compounds **6** and **7** were obtained through oxidation of **2** and **4** respectively using hydrogen peroxide in acetic acid at room temperature. Compounds **8** and **9** were prepared from the appropriate nitrophenol and 3-bromo-1-propyne using the same procedure reported for **1** to **3**.

All the compounds studied were recrystallized to constant melting point and their purity was checked by thin-layer chromatography (TLC). The compounds were characterized by nuclear magnetic resonance (^{1}H NMR) and infrared (IR) spectral data. Table 4 gives the yield, melting point (uncorrected), and microanalytical data for the hitherto unreported compounds discussed in this work. The low-resolution mass spectra were taken on a Varian MAT CH-7 and Finnigan MAT 8230 mass spectrometers. The spectra were run at 70 eV or with an emission current of 100 μA. All the compounds were introduced into the mass spectrometer through the direct probe insertion at probe temperatures varying between 30 and 110 °C.

Accurate mass measurements were carried out at a resolution of 7000 (10% valley) with Finnigan MAT 8230 double focussing mass spectrometer using peak-matching technique and PFK was used as reference. The B/E linked scan spectra in the first field free region were investigated with VG micromass 7070-H and Finnigan MAT 8230 mass spec-

Table 4. Characterization Data for Unknown Compounds

Compound	Yield	Mp[a]	Microanalytical data			
			Calcd (%)		Obsd (%)	
	%	°C	C	H	C	H
6	80	163—164	48.00	3.11	47.71	3.31
7	65	115—116	59.80	3.65	59.91	3.92

a) Solvent used for crystallization is benzene-hexane.

trometers. The collision-induced dissociation (CID) mass-analyzed ion kinetic energy (MIKE) spectra were measured using VG analytical ZAB 2F double focussing mass spectrometer with the following conditions: electron energy 70 eV, electron trap current 200 μA, accelerating voltage 6 kV and ion source temperature 200—300 °C. The ions of interest were focussed magnetically into the 2nd FFR and the MIKE spectrum obtained by scanning the ESA voltage. The collision was achieved by introducing 'He' gas into the collision cell of the 2nd FFR at such a rate that the intensity of the main beam was reduced to 50%.

The authors thank Prof. J. H. Beynon and Mr. Dipankar Ghosh, University College of Swansea, Swansea, UK for providing CID MIKE spectra and RRL, Hyderabad, India for few B/E linked scan spectra. Acknowledgements are due to RSIC, IIT, Madras, for high-resolution data. One of us (NVSRK) thanks CSIR, India for a research fellowship.

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