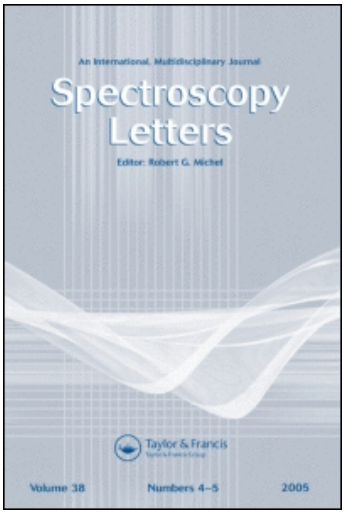

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Skeletal Rearrangements in 2,4-Dinitrophenyl-4'-Substituted Phenyl sulfides and Sulfones Upon Electron Impact

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Abstract

The mass spectral fragmentation patterns of a various 2,4-dinitrophenyl-4'-substituted phenyl sulfides and sulfones help define the role of substituent effects under electron impact, and subsequently determines the appearance of the base peak. These substituent effects correlated well with the Hammett σ-values. The mass spectral features arise from the elimination of the sulfur atom with recombination of the terminal end groups or with scission across 4'-substituted phenyl ring in sulfides, whereas in sulfones the most abundant ion is formed through the sci-ssion of the rearranged aryl sulfinate ester. A comparison between the spectra of the two types is discussed. The results

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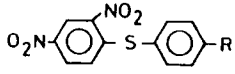
* This paper was represented at the 9th IUPAC conference on Physical Organic Chemistry, F.R.G (1988).

suggest that the skeletal rearrangement of the molecular ion occurring in these S-bridged compounds is a sensitive diagonstic tool in structure elucidation.

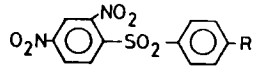
Introduction

In connection with a program devoted to synthesis of a number of aryl benzyl sulfur derivatives[1-3], the title compounds have not been studied previously with regard to their mass spectrometric behaviour, but closely related substituted diaryl, aryl pyridyl, aryl thiadiazole sulfides and unsubstituted diaryl sulfones have been examined[4-10].

This paper describes the decomposition pattern upon electron impact of 2,4-dinitrophonyl-4'-substituted phenyl sulfides **1-6** and the corresponding sulfones **7-12**.



1-6

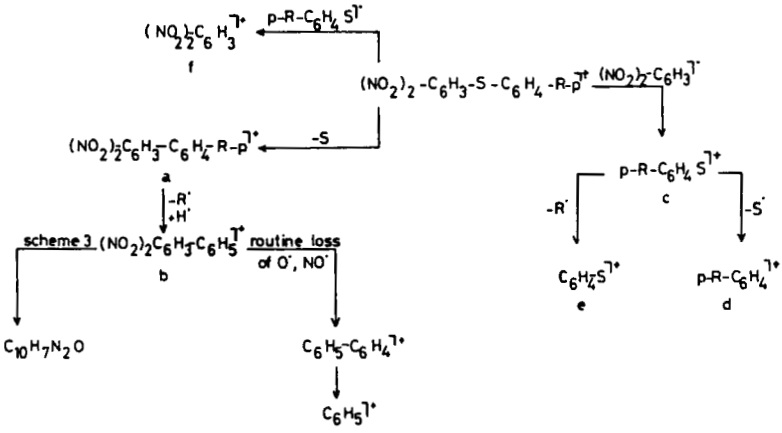


7 – 12

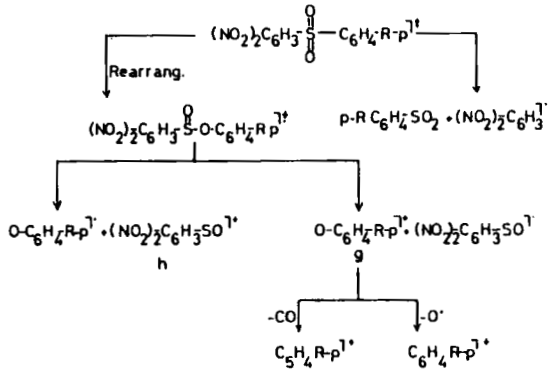
1,7, R = H ; **2,8**, R = OCH_3 ; **3,9**, R = CH_3 ; **4,10**, R = Br **5,11**, R = Cl ; **6,12**, R = NH_2

Results and Discussion

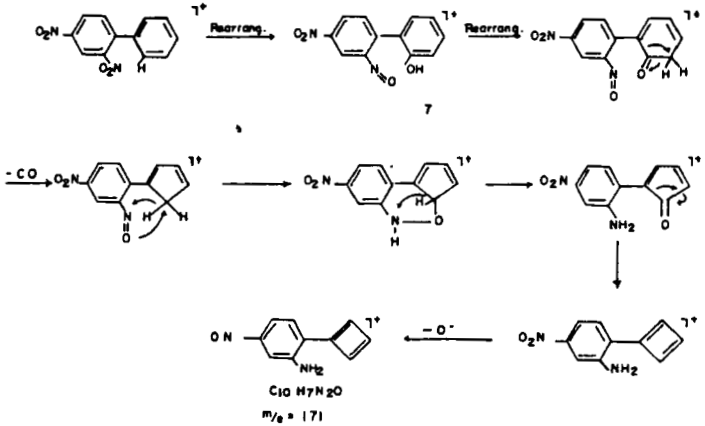
The general rationale for the electron-impact induced mass spectral fragmentation of the sulfides **1-6** and sulfones **7-12** is shown in scheme I and II. Additional spectral features arising from the decomposition of the rearranged 2(2'-nitroso-4-nitrophenyl) phenol are shown in scheme III.



Scheme (1)



Scheme (2)



Scheme (3)

Table (1) partial Mass Spectra of 2,4-Dinitrophenyl 4'-Substituted Phenyl Sulphides.

Comp.	Ion	1	2	3	4	5	6
M.wt		276	306	290	354	310	291
				Relative Abundance			
m/z	P+·	23.0	50.0	60.0	42.0	21.0	44.0
322	$(NO_2)_2$-C_6H_3-$C_6H_4Br^+$				4.0		
278	$(NO_2)_2$-C_6H_3-$C_6H_4Cl^+$					9.0	
274	$(NO_2)^2$-C_6H_3-$C_6H_4)OCH_3$		9.0				
259	$(NO_2)_2$-C_6H_3-$C_6H_4NH_2^+$						1.0
258	$(NO_2)_2$-C_6H_3-$C_6H_4CH_3^+$			5.0			
244	$(NO_2)_2$-C_6H_3-$C_6H_5^+$	5.0	3.0	2.0	4.0	2.0	2.0
227	$(NO_2)(NO)$-C_6H_3-$C_6H_4^+$		55.0	10.0			
212	$(NO)_2$-C_6H_3-$C_6H_5^+$	3.0	8.0	11.0	10.0	22.0	2.0
199	(NO_2)-C_6H_4-$C_6H_5^+$	8.0	8.0	2.0	9.0	10.0	16.0
198	(NO_2)-$C_6H_3C_6H_5^+$		45.0	37.0	100.0	100.0	
187	S-$C_6H_4Br^+$				10.0		
182	$(NO)C_6H_3$-$C_6H_5^+$	16.0	100.0	100.0	24.0	18.0	90.0
171	$(NO)(NH_2)$-$C_6H_3C_4H_2^+$	14.0	36.0	10.0	18.0	17.0	25.0
167	$(NO_2)_2$-$C_6H_3^+$	100.0	4.0	6.0	66.0	31.0	5.0
155	$C_6H_4Br^+$				12.0		
153	C_6H_5-$C_6H_4^+$	3.0	26.0	26.0	47.0	12.0	29.0
148	S-$C_6H_4Cl^+$					9.0	
139	S-$C_6H_4OCH_3^+$		20.0				
124	S-C_6H_4-NH_2^+						14.0
123	S-C_6H_4-CH_3^+			16.0			
111	$C_6H_4Cl^+$				14.0		
109	$C_6H_5S^+$	14.0					
108	$C_6H_4S^+$						100.0
92	$C_6H_4NH_2^+$						7.0
91	$C_7H_7^+$			28.0			
77	$C_6H_5^+$	37.0	14.0	12.0	21.0	13.0	6.0

N.B.: Decimal values approximated to zero.

Selected ions and their relative abundances are listed in tables (1) and (2).

Sulfides

The identification of the sulfides 1-6 from their mass spectra is not a simple matter. These sulfides are sensitive not only to molecular weight but also to structural differences in 4'-substituents. That such sensitivity and differentiation is possible implies that 4'-substitution plays an important role in its ionic decomposition.

Table (2):Partial Mass Spectra of 2,4-Dinitrophenyl 4'-substituted Phenyl Sulphones.

Comp.	Ion	7	8	9	10	11	12
M.wt.		308	338	322	386	342	323
		Relative Abundance					
m/z	$p^{+\cdot}$	2.0	3.0	3.0	5.0	9.0	6.0
219	$Br\text{-}C_6H_4\text{-}SO_2$				6.0		
215	$(NO_2)_2\text{-}C_6H_3\text{-}SO^{+}$	17.0	2.0	2.0	5.0	8.0	10.0
175	$Cl\text{-}C_6H_4\text{-}SO2$					12.0	
171	$OCH_3\text{-}C_6H_4\text{-}SO_2$		3.0				
177	$Br\text{-}C_6H_4\text{-}O^{+}$				100.0		
156	$NH_2\text{-}C_6H_4\text{-}SO_2$						8.0
155	$Br\text{-}C_6H_4^{+}$				50.0		
	$CH_3\text{-}C_6H_4\text{-}SO_2$			6.0			
143	$Br\text{-}C_6H_4^{+}$				14.0		
141	$C_6H_5\text{-}SO_2$	24.0					
127	$Cl\text{-}C_6H_4\text{-}O^{+}$					100.0	
123	$OCH_3\text{-}C_6H_4^{+}$		100.0				
111	$Cl\text{-}C_6H_4^{+}$					74.0	
108	$NH_2\text{-}C_6H_4\text{-}O^{+}$						100.0
107	$OCH_3\text{-}C_6H_4^{+}$		88.0				
	$CH_3\text{-}C_6H_4\text{-}O^{+}$			100.0			
99	$Cl\text{-}C_6H_4^{+}$					27.0	
93	$C_6H_5\text{-}O^{+}$	100.0					
92	$NH_2\text{-}C_6H_4^{+}$						66.0
77	$C_6H_5^{+}$	70.0	12.0	14.0	36.0	32.0	44.0

N.B.: Decimal values approximated to zero.

The sulfides **1-6** eliminate the sulfur atom and the terminal groups then combine to give ion **a** , $(NO_2)_2\text{-}C_6H_3\text{-}C_6H_4\text{-}R\text{-}p^{+}$ This ion fragments further by loss of R; to give ion **b**,this undergoes successive loss of oxygen , nitrogen oxide and nitrogen dioxide[11]. The molecular ion of the sulfides is not the base peak; it occurs at lower masses, and represented at m/z 198 for **4,5** or m/z 182 for **3,4**. Peaks associated with the fission across the 4'-substituted phenyl ring are of medium to low intensity. These fissions are illustrated in scheme I.

The spectra of the sulfides **1-6** exhibit through a different fragmention route ion **c**, corresponding to the loss

of $(NO_2)_2$-$C_6H_3^{\cdot}$ from the molecular ion, the intensity of ion **b** is comparatively low. It fragments further to produce ion **d** and the complimentary ion **e**. Ion **d** occurs with medium intensity in compounds **1** and **3**, while ion **e** is the source of the base peak in **6**.

Ion **f** arises by loss of R-$C_6H_4S^{\cdot}$ from the parent ion, it is of variable intensity, and represents the base peak in **1** and occurs with medium intensity in **4** and **5**, Table (1).

The prominant peak at m/z 171 observed in the spectra of compound **1** through sequential loss of two malecules of CO followed by oxygen radical from the rearranged form of ion **b** [2(2'-nitroso-4-nitrophenyl) phenol] resembles closely the reported loss of two CO from 2-nitrobiphenyl[11].

Sulfones

In the spectra of 2,4-dinitrophenyl-4'-substituted phenyl sulfones **7-12**, which are very similar (scheme III), the most abundant ion **g** is the same through **7-12** compounds, which fromed through the scission of the rearranged aryl sulfinate ester and in a manner different from that envisaged earlier[4]. This ion **g** fragments further with loss of O· radical and CO. Fragmentation of the molecular ion produces $(NO_2)_2$-C_6H_3-SO^{1+}, **h** , all other peaks in the spectra are small.

It is of some interest to note that in our case, scission of the sulfones, followed by the rupture of the S-OAr bond does not gives peaks corresponding to $(NO_2)_2$-$C_6H_3O]^+$ and R-$C_6H_4SO^{1+}$ ions . However, the absence of certain peaks corresponding to a process is not a proof that

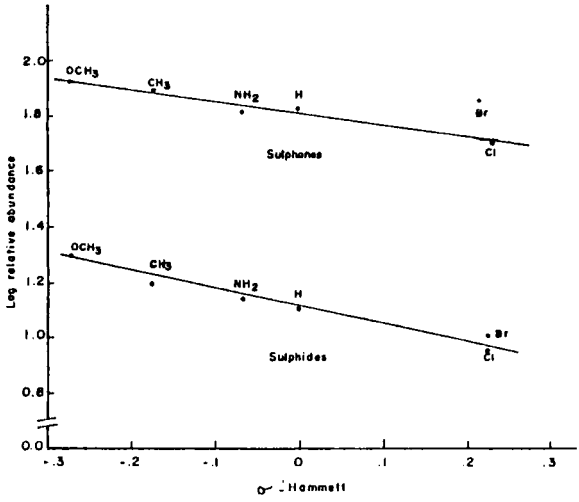


Figure (1)

this scission does not occur. On the other hand, fragmentation does occur in which neutral $R\text{-}C_6H_4SO_2$ is formed but observed at low abundance (table 2).

The ion $(NO_2)\text{-}C_6H_3SO^{1+}$ is also detected, but it is of much reduced abundance in sulfones. It is suggested that the function group-NH_2 assumes a certain geometry, its rupture leads to most abundant peak.

Comparison Between the Mass Fragmentation of sulfides 1-6 and sulfones 7-12

The mass spectra of sulfides 1-6 and sulfones 7-12 are strikingly different. That of the sulfides being +M, +I , and are characterized by abundant parent ions, all other peaks, except the base peak, in the spectra are intermediate to small. While in the case of sulfones 7-12 (-M,-I), the

intensity of the parent ions is small and assume a new fragmentation pattern. The $(NO_2)_2$-C_6H_3-$C_6H_4R^{1+}$ radical cation generally formed through elimination of sulfur radical in sulfides and would have assumed to be present in the spectra of the sulfones through elimination of SO_2 was not detected[12]. The sulfides cleavage showed a marked dependence upon the nature of the substituents whereas in decomposition of the sulfones, this was not affected.

Similar to alkyl sulfides[13-14], a substituent effect is present from the mass spectra of the twelve sulfides **1-6** and sulfones **7-12** and correlated with the Hammett σ-values. (isotopic peaks are accounted for Br,Cl). Such plots of the logarithmic abundance of the $SC_6H_4R^{1+}$ ions in the sulfides **1-6** and the C_6H_4-R^{1+} ions in the sulfones versus the σ-values are given in figure (1). This seems reasonable and can be rationalized in terms of inductive effect.

Experimental

The mass spectral analysis (electron impact) were measured on Varian MAT CH7, 70 eV., using direct probe method at 250°C.

2,4-Dinitrophenyl-4'-substituted phenyl sulfides **1-6** were obtained through nucleophilic displacement reactions starting from 2,4-dinitrochloro benzene and sodium salt of 4-substituted thiophenols in alcohol[15]. All the corresponding 2,4-dinitro-4'-substituted phenyl sulfones **7-12** were prepared by oxidising the sulfides with excess amount of H_2O_2(30%), in glacial acetic acid[15].

References

1- A. Kassem, and A. El-Bardan, J. Chem. Engn. Data, 1986 ,31(4), 496.

2- A Kassem, A. A. El-Bardan, and S. Mansour, ibid, 1987 ,32(4), 483.

3- A. A. El-Bardan, E. A. Hamed and E.F. Saad, ibid, 1989 ,34, 133.

4- S. Meyerson, H. Drews and E. K. Fields, Anal. Chem., 1964 , 36(7), 1294.

5- G. Madsen, J. C. Nolde, S. O. Lawesson and G. Schroll, Tetrahedron Lett, 1965 , 49, 4377.

6- G.Madsen, J. C. Nolde, S. O. Lawesson and G. Schorll, ibid, 1965 , 50, 4736; S. Meyerson, P. N. Rylander, E. L. Eilel and J.D. McCollum, J. Am. Chem, Soc., 1959 , 81, 2606

7- G. Schroll and S. O, Lawesson, Sulphur in Organic Chemistry and Inorganic Chemistry, 1972, Vol.2,Ch.17, p. 186, Marcel Dekker, New York.

8- F. Bottino, R. Fradullo and S. Pappalardo, Org. Mass Spectrom., 1981 , 16(4), 190.

9- F.Bottino, R. Fradullo and S. Pappalardo, ibid, 1981 , 16(7),289.

10- F. Bottino, R. Fradullo S. Caccamese and S. Pappalardo, ibid, 1982 , 17(7), 335.

11- S. Meyerson, I. Puskas and E. K. Fields, J. Am. Chem. Soc., 1966, 88, 4974.

12- H. Drews, E. K. Fields and S. Meyerson, Chem. Ind., 1961 , 1403.

13- M. M. Bursey and . W. McLafferty, J. Am. Chem . Soc., 1967 , 89, 1.

14- D. H. Williams, Mass Spectra of Organic Compounds. 1967 p.33, p.162, Holden Day San Francisico 1967 .

15- A. M. Ahmed, E. A. Hamed, A. A. El-Bardan and E. F. Saad, Alex. Eng. J., 1989 , 28(2), 577.

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