

R. Zugazagoitia, R. Martínez and E. Cortés* (2)

Instituto de Química, Universidad Nacional Autónoma de México (3),
Circuito Exterior, Ciudad Universitaria, México 20, D.F.

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The mass spectral fragmentation patterns of thirteen 2',3' and 4'-*R-trans*-2,4-dinitrostilbenes obtained by electron impact have been studied. The main routes of fragmentation involves loss from the molecular ion due to the *ortho* effects of the 2-nitro substituents. Substitution on positions 2',3' and 4' of stilbene moiety does not influence the fragmentation patterns.

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In previous electron impact mass spectrometry studies (4) of two 2,4-dinitrostilbenes, it was found that their dominant fragmentation route involved a rearrangement of the molecular ion to corresponding epoxide intermediate by oxidation of the olefinic double bond by the *ortho*-nitro group. Likewise, since the *ortho*-nitro group has an appreciable influence on the fragmentation patterns of some monosubstituted-2-nitrostilbene derivatives (5), we would like to analyze their behaviour under electron impact of 2,4-dinitrostilbene compounds with a *R*-substituent on positions 2',3' and 4' with a view to observed if only the 2-nitro group influences the fragmentation patterns in these compounds; 2',3' and 4'-*R-trans*-2,4-dinitrostilbenes of type I (Scheme I) represent a series of compounds which have these characteristics. In addition, antifertility properties of some stilbenes have been described (6).

In this paper we describe the *ortho* effects of the 2-nitro group in I on electron impact. The main fragments are different from those into which the 2-nitrostilbenes fragment and although some of the fragments mentioned earlier are observed, their relative abundances are quite different (see Table 1, ‡). Most of the ions in the mass spectra of I arise from cleavage of the N-O bond of the 2-nitro group in addition to cleavage of the carbon-carbon double bond of the stilbenes. The relative abundance of the main fragments are shown in Table 1.

Loss of H to form the $M^+ - 1$ ion occurs in all the mass spectra analyzed. The species responsible for the $M^+ - 1$ peak is depicted as a 1,2-benzoxazine *N*-oxide derivative (Scheme 2). These species may be formed by the loss of the α -hydrogen of the styryl group and formation of a bond between one oxygen from the nitro group and the α -carbon atom of the styryl moiety. The driving force for such a process is undoubtedly the production of this stable ion.

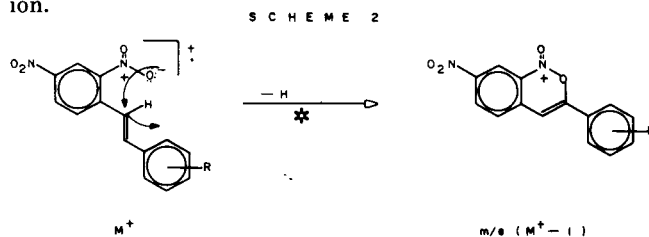
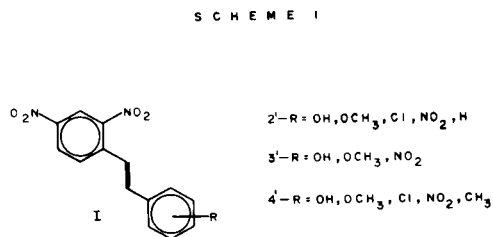


Table 1

Relative Abundance of the Principal Fragments

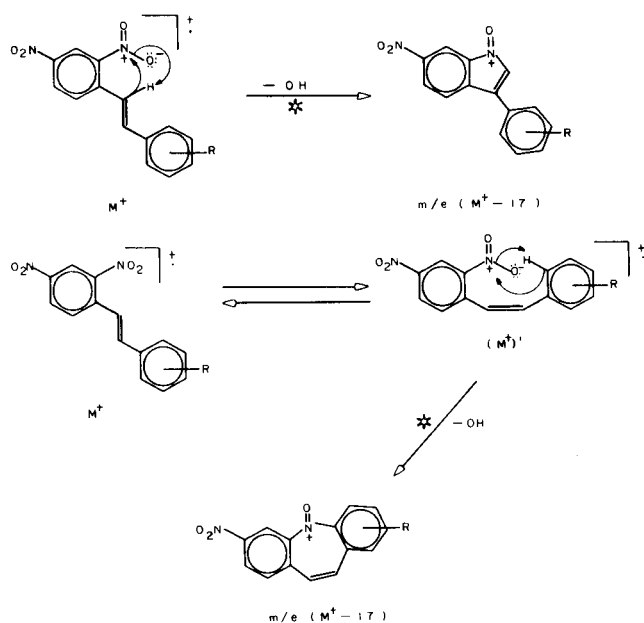
m/e	Substituents of R													
	H	4'-Me	2'-Cl	3'-Cl	2'-OH	3'-OH	4'-OH	2'-OMe	3'-OMe	4'-OMe	2'-NO ₂	3'-NO ₂	4'-NO ₂	
M^+	3.0	16.03	6.15	16.66	7.05	24.24	19.69	18.18	13.80	18.18	2.30	4.60	3.05	
$M^+ - 1$	2.20	1.52	2.2	3.78	0.15	3.03	3.00	1.50	1.53	1.51	0.46	0.76	0.61	
$M^+ - 17\ddagger$	13.60	19.84	13.63	15.15	13.60	12.12	19.19	9.09	7.69	9.09	3.84	12.30	6.10	
$M^+ - 29\ddagger$	7.50	6.87	6.06	5.30	3.00	7.57	6.06	12.12	4.61	4.54	3.84	4.61	5.34	
$M^+ - 46$	7.50	4.58	6.06	6.81	19.60	7.57	10.60	6.06	6.15	4.54	4.61	4.61	4.58	
$M^+ - 75$	15.15	6.87	5.30	9.09	6.06	7.57	9.09	6.06	4.61	4.54	2.30	4.61	3.05	
$M^+ - 92$	25.70	10.60	7.57	15.90	15.15	10.60	10.60	6.06	6.92	4.54	4.61	6.15	5.34	
$105 + R\ddagger$	28.78	22.90	22.72	31.06	95.4	100	46.96	46.96	100	68.18	46.15	18.46	53.43	
$104 + R\ddagger$	87.8	100	71.21	67.42	100	84.84	100	56.06	13.84	100	69.24	36.92	58.77	
$165\ddagger$	42.42	19.84	37.87	34.84	45.45	63.63	45.45	30.30	20.00	22.72	21.53	23.07	100	
$164\ddagger$	50.0	19.08	100	100	22.72	19.69	16.66	22.72	13.84	15.15	27.69	100	35.87	
$118\ddagger$	37.8	54.19	43.93	56.06	18.18	16.66	15.15	51.15	6.16	4.54	15.38	37.69	22.90	
91	100	29.0	12.12	20.45	12.12	7.57	10.60	100	7.69	7.57	69.23	10.76	9.16	
77	74.2	9.92	15.15	12.12	40.90	18.18	16.66	28.78	7.69	12.12	50.76	11.53	9.92	

Table 2

Compound R	Mp °C	Yield %	Formula	Calcd./Found C %		Calcd./Found H %		Calcd./Found N %	
3'-OH	195-197	56	C ₁₄ H ₁₀ O ₃ N ₂	58.74	58.65	3.52	3.50	9.78	9.71
4'-OH	150-152	10	C ₁₄ H ₁₀ O ₃ N ₂	58.74	58.62	3.52	3.51	9.78	9.69
3'-OMe	133-135	40	C ₁₅ H ₁₂ O ₃ N ₂	59.99	60.06	4.02	4.00	9.33	9.23
4'-Cl	140-142	28	C ₁₄ H ₉ ClO ₃ N ₂	55.18	55.02	2.97	3.00	9.19	9.20

One major fragmentation route from the molecular ion of all the compounds studied involves the loss of an OH group which gives rise to an ion at m/e ($M^+ - 17$). This ion is depicted either as a 3-(*o,p* or *m*-R-phenyl)indole *N*-oxide or a dibenzazepine *N*-oxide derivatives, and is obtained either by the loss of the α -hydrogen atom of the styryl group and one oxygen atom from the 2-nitro substituent or by the loss of the *ortho*-hydrogen of the phenyl group and the same oxygen (Scheme 3). A similar *ortho*-nitro interaction has been reported for 4-nitrostyrylisoxazoles (7).

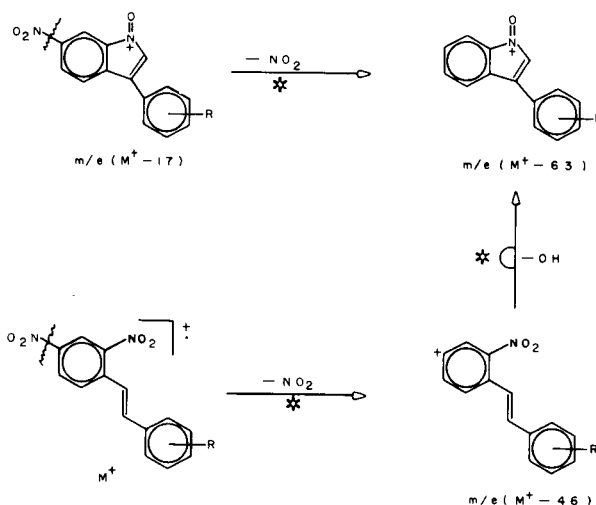
SCHEME 3



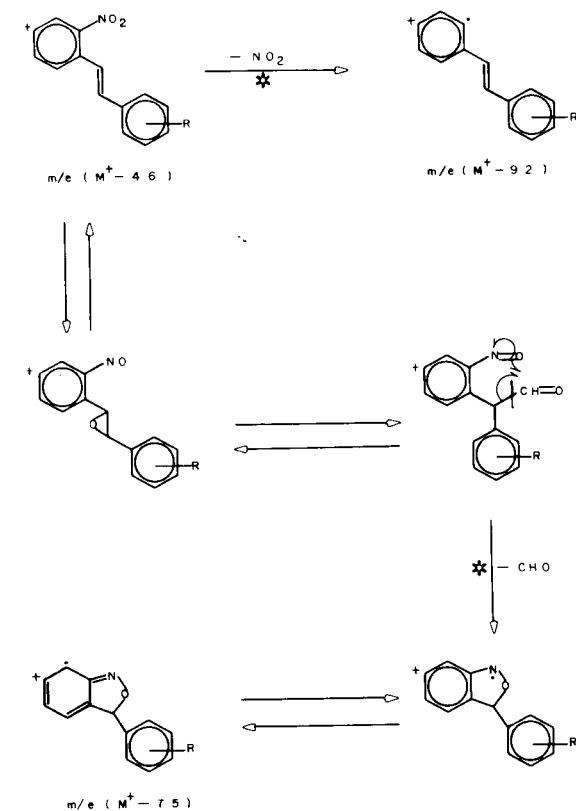
The $M^+ - 17$ ion may lose 46 mass units (NO_2) to form an ion at m/e ($M^+ - 63$). This ion is also afforded by the ejection of an NO_2 group from the molecular ion leading to the ion at m/e ($M^+ - 46$) which in turn loses 17 mass units (OH) to give the m/e ($M^+ - 63$) ion (Scheme 4). The m/e ($M^+ - 46$) ion also may lose a CHO moiety to afford an ion at m/e ($M^+ - 75$) or an NO_2 group to afford an ion at m/e ($M^+ - 92$) (Scheme 5). Also this fragmentation has been observed on other nitro compounds (8).

In addition to the fragments discussed above, the mass spectra of I has also exhibited characteristic fragments at m/e ($M^+ - 29$), $105 + R$, $104 + R$, 165 , 164 , 118 and 91 whose structure has been elucidated by mass spectrometry

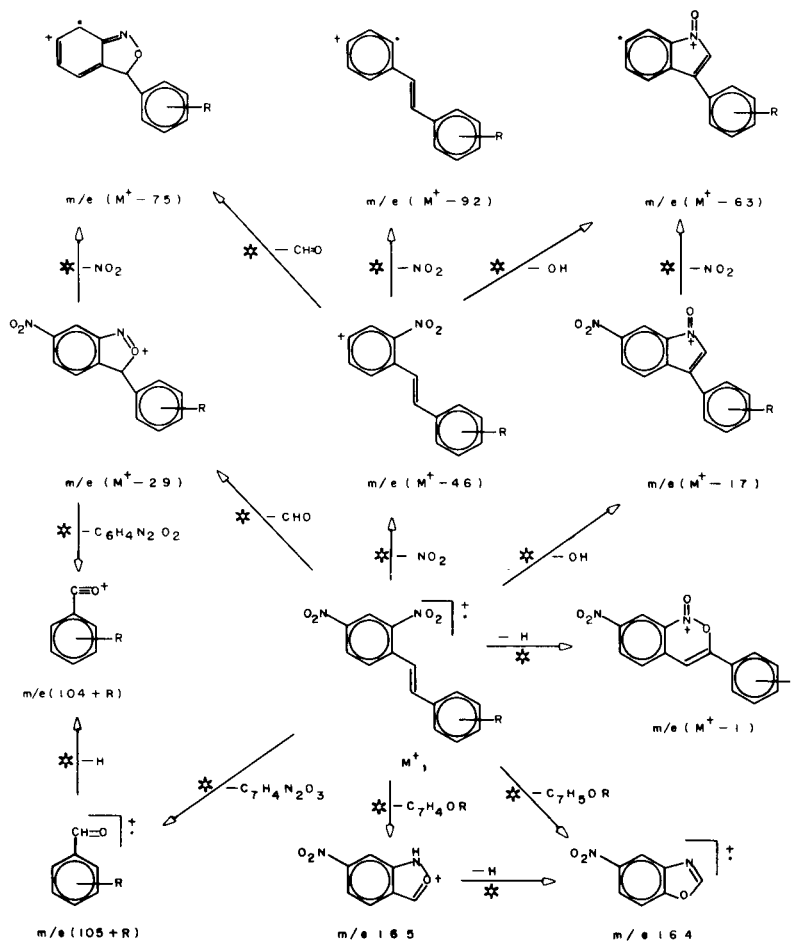
SCHEME 4



SCHEME 5



S C H E M E 6



studies of 2,2'-nitrostilbene and 2-nitrostilbazoles (5,9) and, therefore, they are not discussed in detail. These fragmentation patterns are summarized in Scheme 6.

In view of these results, we can say that the fragmentation patterns of I on electron impact are influenced only by the 2- NO_2 substituent and not by substituents in the 2',3' and 4' position of the stilbene framework.

All fragmentation pathways are supported by the corresponding metastable transitions which are depicted by an asterisk in the figures.

EXPERIMENTAL

The compounds were synthesized according to literature methods (10). All the compounds investigated gave satisfactory elemental analyses and the majority have been reported (10,11,12). The balance of these are described in Table 2. The mass spectra were measured on a Hitachi-Perkin Elmer RMU-7H double focusing mass spectrometer using the

direct inlet system. The samples were recorded at an ionization chamber temperature of 190° .

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