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THE MASS SPECTRA OF NITRONES

C—O BOND FORMATION UPON ELECTRON IMPACT[1]

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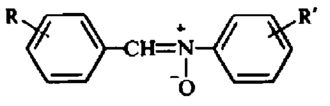
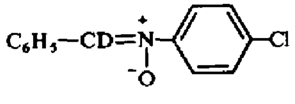
Abstract—The mass spectra of a series of nitrones are reported and discussed. All spectra contain molecular ions, and the majority of fragment ions owe their genesis to skeletal-reorganization of the molecular ion. Fragmentation modes have been substantiated by high-resolution data and appropriate metastable ions. Deuterium labelling has been used to elucidate the $M—H^{\bullet}$ process which is observed in many spectra.

THE mass spectra of pyridine N-oxides,[2] quinoline N-oxides,[3–5] Δ^1-pyrroline N-oxides,[2] phenazine and benzo[a]phenazine N-oxides[6] and aromatic azoxy compounds[7,8] have been reported. Skeletal-rearrangement fragments (produced by C—O bond formation) are observed in the mass spectra of N-oxides[4–6] and azoxy compounds.[7,8]

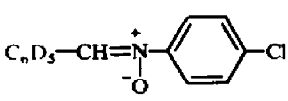
As a logical extension of the work on N-oxides[6] and azoxy compounds,[7,8] we have synthesized a series of nitrones (I–XV) and have measured their mass spectra.



	R	R′
I:	H	H
II:	*p*-Me	H
III:	*p*-Cl	H
IV:	H	*p*-Cl
V:	*m*-OH	H
VI:	*o*-OH	H
VII:	*o*-OD	H
VIII:	*p*-OMe	H
IX:	*m*-NO$_2$	H
X:	*p*-Cl	*p*-Cl
XI:	*o*-OH	*p*-Cl
XII:	*o*-OMe	*p*-Cl
XIII:	*p*-NO$_2$	*p*-Cl



XIV



XV

This study was also prompted from the knowledge[9] that nitrones undergo photochemical cyclization to oxaziridines. The spectra are recorded in Table 1 or Figs 1–8, exact mass measurements are listed in Table 2. The presence of an appropriate

Table 1. Mass spectra of V–VII, and X–XIII*

V *m/e*	26	27	28	29	38	39	40	41	43	44	45	46	50	51	52	53	55	57	63	64
I(%)	6	20	13	16	13	40	8	18	23	13	16	8	16	51	8	8	7	7	16	16
	65	66	68	72	74	75	76	77	78	91	92	93	94	104	105	107				
	41	13	8	16	6	6	6	100	9	24	6	36	13	16	8	8				
	109	121	122	141	167	184	196	197	198	213(M)										
	7	47	36	6	8	7	65	70	11	18										
VI *m/e*	28	39	50	51	52	65	64	65	66	76	77	78	91	92	93	94	104	105	120	
I(%)	7	12	9	38	8	9	15	17	8	6	86	14	100	16	24	12	11	7	10	
	121	141	167	168	184	185	196	197	212	213(M)	214									
	15	6	15	12	13	19	76	41	6	61	14									
VII *m/e*	27	28	38	39	40	50	51	52	63	64	65	66	76	77	78	91	92	93	94	
I(%)	10	8	8	24	6	12	62	11	12	21	18	12	6	88	14	100	13	13	22	
	95	104	105	120	121	122	167	168	185	186	196	197	198	213	214(M$^+$)					
	11	8	7	6	11	11	9	6	8	7	35	24	14	15	23					
	$d_0 = 38; d_1 = 62\%$																			
X *m/e*	38	39	50	51	62	63	64	73	74	75	76	77	87	89	90	99	111	112	113	
I(%)	6	14	24	20	9	25	8	7	12	57	16	7	4	18	35	14	86	10	25	
	125	126	127	128	138	139	140	141	152	248	249	250	251	252	253	264				
	100	12	44	9	8	26	8	16	5	18	25	19	16	7	6	8				
	265(M)	266	267(M)																	
	13	7	8																	
XI *m/e*	27	38	39	40	50	51	52	53	61	62	63	64	65	66	73	74	75	76	77	78
I(%)	10	10	31	7	16	26	12	8	6	8	20	12	26	8	7	11	54	17	21	14
	85	90	91	92	93	94	111	112	113	120	121	122	125	126	127	128	129			
	6	17	10	7	10	7	58	10	21	15	32	18	100	11	43	10	10			
	138	139	140	141	166	167	168	219	230	231	232	233	247(M)	248						
	12	9	8	16	10	15	7	8	54	52	26	16	35	6						
	249(M)																			
	11																			
XII *m/e*	27	37	38	39	50	51	52	62	63	64	65	66	75	76	77	78	89	90	91	92
I(%)	10	10	16	35	43	46	9	12	30	13	30	12	71	11	58	7	12	32	62	23
	93	94	104	105	107	111	112	113	118	119	120	121	125	126	127	128				
	7	7	13	13	10	76	7	27	16	69	10	10	61	8	63	11				
	129	135	136	138	141	143	166	167	214	230	232	245	261(M)	263(M)						
	16	31	36	7	27	10	6	6	6	33	12	8	9	3						
XIII *m/e*	39	50	51	63	75	90	111	113	125	126	127	128	150	151	152	166	260			
I(%)	6	6	6	9	12	18	14	6	100	9	43	13	8	9	8	6	8			
	276(M)	278(M)																		
	18	6																		

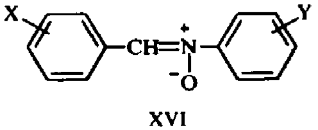
* All peaks greater than 5% of the base peak are recorded.

TABLE 2. COMPOSITIONS OF SOME IONS IN THE MASS SPECTRA OF I-XIII

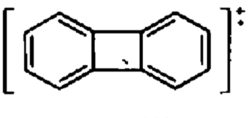
Compound	m/e	Composition
I	91	C_6H_5N (60%) C_7H_7 (40%)
	104	C_7H_6N
	105	C_7H_5O
	168	$C_{12}H_{10}N$
	169	$C_{12}H_{11}N$
	180	$C_{13}H_{10}N$
	181	$C_{13}H_{11}N$
II	91	C_7H_7
	119	C_8H_7O
	165	$C_{12}H_{10}N$
	183	$C_{13}H_{13}N$
III	105	C_7H_5O
	127	$C_6H_4NCl^{37}$ (90%) $C_6H_6NCl^{35}$ (10%)
	152	$C_{12}H_8$
IV	139	$C_7H_4OCl^{35}$ (95%) $C_{11}H_7$ (5%)
	141	$C_7H_4OCl^{37}$
	203/205	$C_{12}H_{10}NCl$
V	121	$C_7H_5O_2$
	122	$C_7H_6O_2$
	167	$C_{12}H_9N$
	185	$C_{12}H_{11}NO$
VIII	91	C_6H_5N
	150	$C_8H_8NO_2$
	167	$C_{12}H_9N$
	184	$C_{12}H_{10}NO$
	198	$C_{13}H_{10}O_2$
	199	$C_{13}H_{13}NO$ (50%) $C_{13}H_{11}O_2$ (50%)
IX	91	C_6H_5N
	150	$C_7H_4NO_3$ (80%) $C_{12}H_6$ (20%)
	167	$C_{12}H_9N$
	195	$C_{13}H_9NO$
X	125	$C_6H_4NCl^{35}$
	127	$C_6H_4NCl^{37}$ (95%) $C_6H_6NCl^{35}$ (5%)
	139/141	C_7H_4OCl
XI	121	$C_7H_5O_2$
	127	$C_6H_4NCl^{37}$ (90%) $C_6H_6NCl^{35}$ (10%)
	129	$C_6H_6NCl^{37}$
XII	127	$C_6H_4NCl^{37}$ (30%) $C_6H_6NCl^{35}$ (70%)
	129	$C_6H_6NCl^{37}$
	135	$C_8H_7O_2$
	136	$C_8H_8O_2$
	167	$C_{12}H_9N$
XIII	150	$C_7H_4NO_3$ (55%) $C_{12}H_6$ (45%)
	151	$C_7H_5NO_3$ (55%) $C_{12}H_7$ (45%)

metastable ion for any process is indicated, both in the text and in Figs, by an asterisk. Structures drawn for fragment ions are nominal only [work in many laboratories has shown that molecular ion rearrangements are no longer rare (cf. Ref. 10)] but relate the decomposition patterns to the structure of the intact molecule.

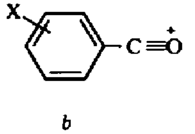
Many fragment ions observed in the mass spectra of the nitrones I–XV are produced by skeletal-rearrangement processes (Figs 1–8). These are all low energy processes and occur at 10 eV. The relative abundances of many ions produced by the major rearrangement processes are summarized in Table 3. Five specific classes of skeletal-rearrangements are observed. Consider the general cases XVI:



XVI



a: m/e 152



b

(1) M—CHNO—X$^{\cdot}$—Y$^{\cdot}$ or M—CHNO—H_2 (or other variations) to produce either the biphenylene radical ion (*a*) or substituted biphenylene radical ions. These processes are observed in most spectra, and are of the general type $[ABC]^{\cdot+} \rightarrow [AC]^{\cdot+} + B$.(11) A compendium of such processes is available.[10]

(2) M—CO, together with additional fragmentation through the substituents. This process is observed in the spectra (Figs 1–3 and 7) of I, II, III and VIII and demands C—O bond formation. M—CO ions are also present in the spectra (Table 1) of V, VI and XI, but as these compounds are phenolic, it is likely that at least some of the CO lost originates from the phenol moiety.[12]

(3) A process observed in all spectra is M—Y $C_6H_5N^{\cdot}$, which produces a species X $C_7H_4O^+$, best represented as the substituted benzoyl cation *b*. The formation of *b* necessitates C—O bond formation. This rearrangement has been reported previously.[13]

(4) The process M—X·C_7H_5O (to produce Y $C_6H_4N^{\cdot+}$) is noted in all spectra except that of II [where *m*/*e* 91 corresponds exclusively to the tropylium cation (Fig. 2, Table 2)].

(5) Skeletal-rearrangements involving the M—O ion. These are not observed in all spectra, but are of the general type $[ABC]^{\cdot+} \rightarrow [AC]^{\cdot+} + B$, e.g. M—O—Cl$^{\cdot}$—HCN to produce *a*, is observed in Fig. 4.

Table 3. Relative abundances (%) of some fragment ions in the spectra of I–VI and VIII–XIII*

Compound	M^+	M—1	M—O	M—CO	X $C_6H_4CO^+$	Y $C_6H_4N^+$	Y $C_6H_4^+$	X $C_6H_4^+$
I	23	19	9	5	21	60	X = Y	Total = 41
II	21	20	7	6	18	0	28	100
III	16	9	17	2	12	100	39	32
IV	18	6	6	0	24	100	38	7
V	17	4	70	5	47	23	100	35
VI	61	6	41	19	16	100	86	24
VIII	30	18	9	4	27	30	46	6
IX	8	1	6	0	4	100	34	0
X	13	7	25	0	26	100	X = Y	Total = 87
XI	35	2	52	8	32	100	59	11
XII	9	2	7	0	31	61	76	11
XIII	18	1	8	0	8	100	15	0

* Where the fragment ion contains Cl, the relative abundance of the ^{35}Cl isotope is recorded.

Before considering the rearrangement types 2–5 in detail, it is convenient to discuss several of the normal decompositions of nitrones, as a knowledge of these is necessary for the understanding of two of the rearrangement modes. Two processes observed in all spectra are M—O and M—H$^{\cdot}$. M—O ions are of diagnostic value in the spectra of many compounds containing the —N^+—O^- group.[2–8] It is noteworthy that in no case does the intensity of the M—O ion (Table 3) vary more than 10% when the 'heated' and 'direct' spectra are compared, indicating that this process (which does not have an appropriate metastable ion) is mainly electron-impact induced. The general species produced will be *c*, and this representation is supported by the spectra

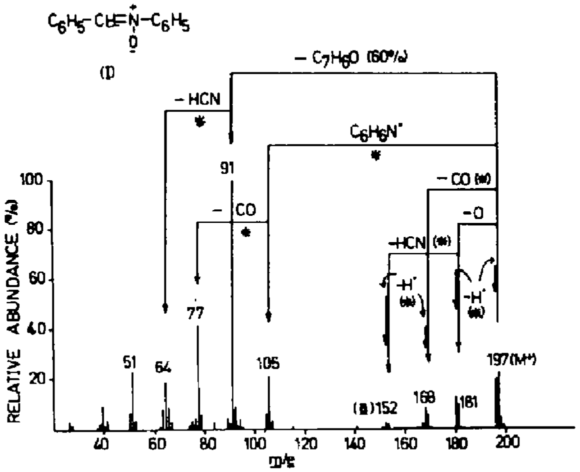


FIG. 1

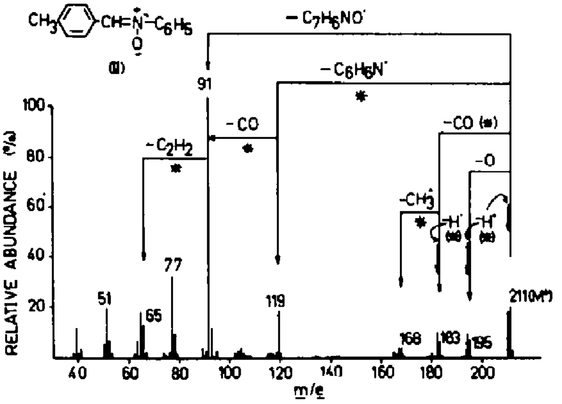


FIG. 2

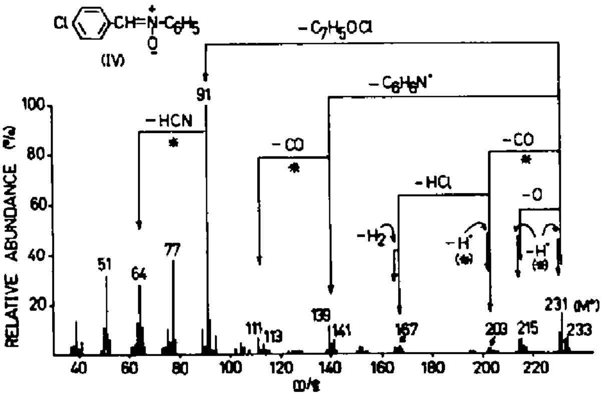


FIG. 3

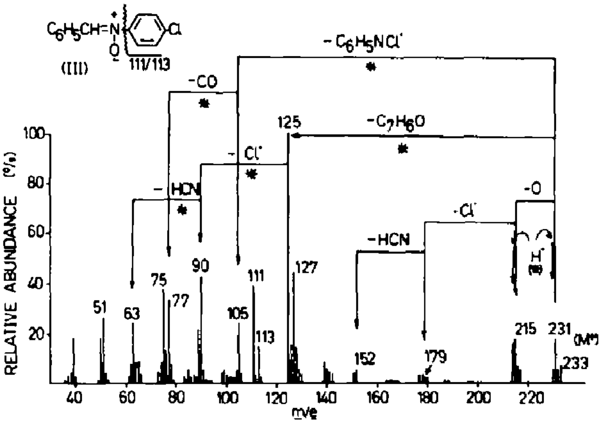


Fig 4

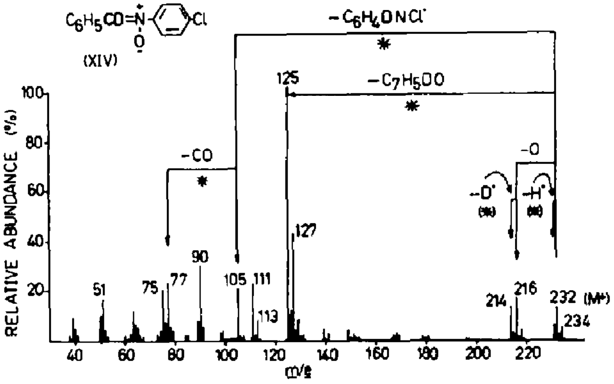


Fig 5

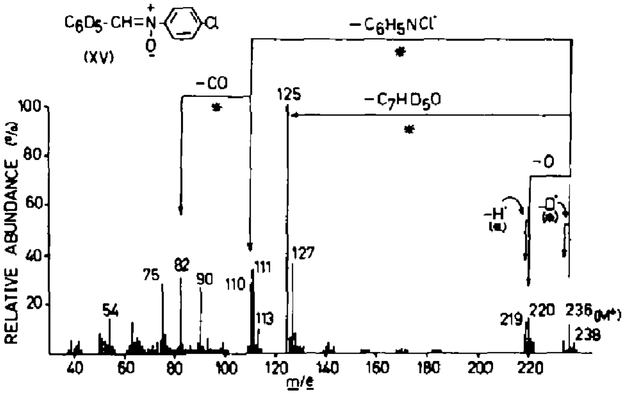


Fig. 6

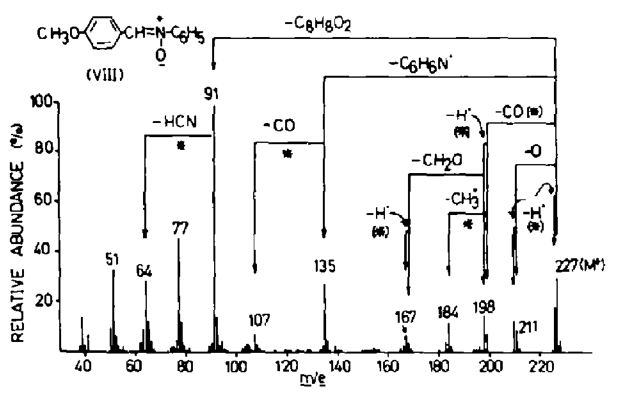


FIG. 7

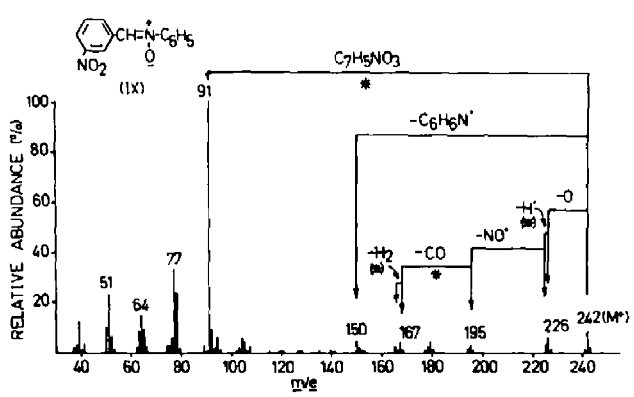
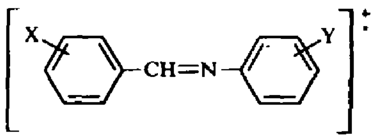
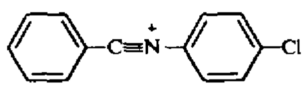


FIG. 8

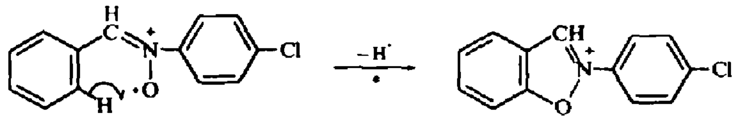
(Figs 4–6) of III and the labelled derivatives XIV and XV, where it can be seen that the process M—O—H$^{\cdot}$ of III becomes M—O—D$^{\cdot}$ in XIV. The ion produced is probably *d* (*m/e* 214/216). It has been shown[14] that the M—1 ion in the spectra of diaryl Schiffs' bases corresponds mainly (>85%) to ions analogous to *d*. Moreover, both the molecular ions and M—1 ions of Schiffs' bases undergo skeletal-reorganization reactions of the type ABC → AC + B,[14] thus clarifying the rearrangement process 5.



c

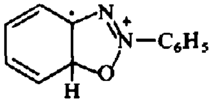


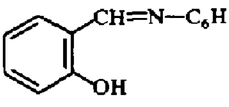
d: *m/e* 214/216

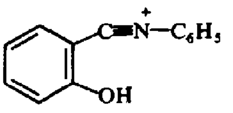


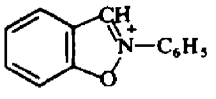
e: *m/e* 231/233 *f*: *m/e* 230/232

However, the hydrogen lost in the M—1 process of nitrones, does not originate from the methine position. Figures 4–6 show that the hydrogen comes from the aromatic ring furthest from the N—O group. The deuterium labelling studies are consistent with the formation of the stable cation *f* by an intermolecular aromatic substitution reaction, viz. *e* → *f*. The presence of a strongly electron withdrawing nitro substituent on the ring from which the hydrogen atom is lost, reduces the proclivity of the M—1 process (Table 3 and Fig. 8). Intermolecular aromatic substitution reactions involving C—O bond formation have been reported previously,[15–17] and it has been shown[16] that the hydrogens attached to any one aromatic ring become equivalent during this reaction.


g


XVIII

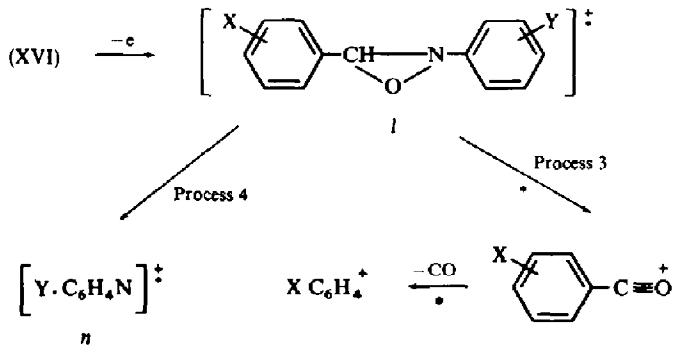

h: *m*/*e* 196


i: *m*/*e* 196

The skeletal-rearrangement fragments in the spectrum of azoxybenzene do not owe their genesis to the intermediacy of the *o*-hydroxyazobenzene radical ion, and breakdown of *g* has been invoked to rationalize the rearrangements.[8] Similarly, the M—CO process of the nitrone (I) cannot be explained by the formation of the molecular ion of the Schiffs base XVIII. The rearrangement modes in I are M—CO—H$^{\bullet}$ and M—H$^{\bullet}$—CO and in XVIII,[14] M—H$^{\bullet}$—CO and M—CHO$^{\bullet}$ (metastable ions substantiate all processes). Although two of these processes seem identical, they are not, as the M—1 ions are different in each spectrum, viz. *h* and *i* respectively. Moreover, several prominent ions in the spectrum[14] of XVIII are absent in that (Fig. 1) of I. The benzanilide radical ion is also not the reactive intermediate as this species does not exhibit an M—CO ion. An ion which best explains the M—CO process is *k* (analogous to *g* and *i*) which could originate by the process *j* → *k*.

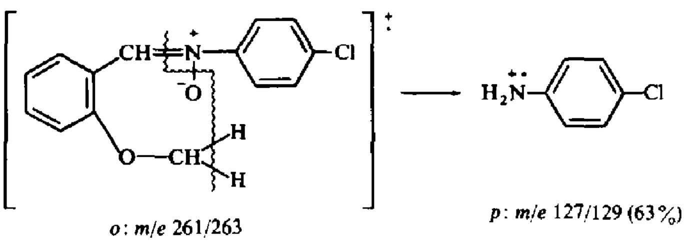

j: *m*/*e* 197 *k*: *m*/*e* 197

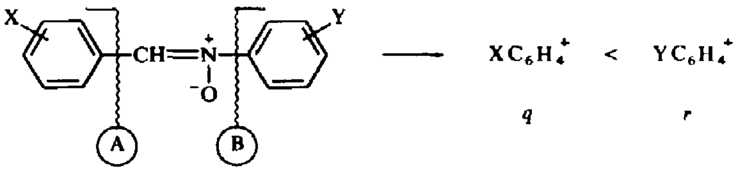
Processes 3 and 4 can be best explained by the formation of an oxaziridine intermediate. Although such a supposition is speculative, it has photochemical analogies.[9] An investigation of the mass-spectral breakdown of the oxaziridines postulated, would probably not be meaningful because of the relative instability of such systems.[9] The formation of the substituted benzoyl cations [metastable ions usually substantiate the $M \rightarrow X{-}C_6H_4{-}C{\equiv}\overset{+}{O}$ process (Ref. 13 and Figs 1–8] could come from the intermediate *l*. Similarly, the ion *n* (Process 4) could arise from *l*.



It is clear that these processes may be further complicated by the presence of substituents (X and Y), e.g. when X is hydroxy, o-methoxyl or nitro (e.g. V, VI, IX–XIII) ions due to both $X{\cdot}C_6H_4{\cdot}CHO^{\cdot+}$ and $X{\cdot}C_6H_4\ C{\equiv}O^+$ are observed. When Y is *p*-chloro (IV, X–XIII), high resolution (Table 2) indicates that as well as $Y{-}C_6H_4N^{\cdot+}$ species (*n*), small amounts of $Y{-}C_6H_4NH_2^{\cdot+}$ are also formed. A different hydrogen rearrangement is observed in the spectrum of I. 40% of *m/e* 91 (base peak) corresponds to the tropylium cation ($C_7H_7^+$), which can only be produced by a hydrogen rearrangement from the aromatic ring (adjacent to —N—O) to the methine group.

The fragmentations so far described have been due to reorganization of the molecular ion, which although of mechanistic interest, are of little use for structure elucidation. However, there are several processes which may be used for structure determination. The first of these is a specific hydrogen transfer process observed in the spectrum (Table 1) of XII (viz. *o* → *p*). These processes have been noted previously in the





spectra of azoxybenzenes[8] and Schiffs bases[14,18] and have been substantiated by deuterium labelling studies.[8] Processes of more general applicability are shown in XVII. In all cases [except for II (Fig. 2) where the formation of the exceptionally stable tropylium cation preponderates all other processes] cleavage B gives a more abundant ion than cleavage A, i.e. the relative abundance of X $C_6H_4^+$ (*q*) is less than that of Y $C_6H_4^+$ (*r*). The abundances of these ions are summarized in Table 3 and their relative intensities may be used to determine the position of the —$\overset{+}{N}$—$\overset{-}{O}$ group.

In summary, nitrones, in common with other compounds containing the N-oxide group, undergo complex reorganization on electron impact. As it is not possible to predict the presence of such processes with any certainty, only *a posteriori* statements may be made concerning them. Cleavage α to the —N—O moiety allows the determination of the position of this group, in compounds where alkyl groups are not attached to the aromatic rings.

EXPERIMENTAL

All spectra were determined by the direct-insertion procedure with an R.M.U. 6D double focusing mass spectrometer operating at 75 eV, and with a source temp between 100 and 150°. Exact mass measurements were performed with an A.E.I. MS 9 mass spectrometer, using a resolution of 10,000 (10% valley definition) with heptacosafluorotributylamine providing reference masses. All measurements were correct to within 10 ppm.

The spectra of VII was obtained by inserting VI into the source with D_2O.[19]

The following nitrones were synthesized by reported procedures;[20] I, II, IV–VI, VIII, and IX. Compounds III, VII, X and XI were prepared from arylaldehydes and N-arylhydroxylamines in ethanolic solution (cf. 20). The arylaldehydes were purified commercial samples, whereas the N-arylhydroxylamines were freshly prepared from the corresponding nitro compounds by reduction with zinc and ammonium chloride.[21,22]

Compound	m.p. (°C)	Found			Calculated		
		C	H	N	C	H	N
III	95–96	79·8	6·1	6·6	79·6	6·2	6·6
VII	178	67·7	4·2	5·9	67·4	4·4	6·0
X	126–127	64·9	4·7	5·3	64·3	4·6	5·4
XI	192–193	56·3	3·5	9·8	56·4	3·3	10·1

Microanalyses by Mrs. B. Rasmussen, Aarhus University.

The deuterated nitrone (XIV) was prepared from commercial C_6H_5CDO, while (XV) was prepared from C_6D_5CHO (synthesized from commercial C_6D_5Br).[23]

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