

Cyclic Meso-ionic Compounds. Part XIII.¹ Mass Spectra of Meso-ionic Heterocycles

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The mass spectra of nine related meso-ionic systems are discussed in terms of a general fragmentation scheme. Mass spectrometry is shown to be particularly useful for distinguishing between isomers.

WHEN the concept of meso-ionic heterocycles was introduced, the structural types (I)—(III) were recognised²⁻⁴ as belonging to this general class. These included the known 1,3,4-triazolium-2-aminides (V), 1,3,4-triazolium-2-olates (VIII), 1,3,4-triazolium-2-thiolates (IX), and 1,3,4-thiadiazolium-2-thiolates (VI). In addition, it was predicted^{2,3} that meso-ionic systems such as (IV),

(VII), and (X)—(XII) might also be preparable. The isosydnones (IV) are now well characterised,⁵ and recently methods for the synthesis of compounds (VII),⁶ (X),⁶ (XI),¹ and (XII)⁷ have been developed. Thus derivatives of the nine meso-ionic systems (IV)—

¹ Part XII, W. D. Ollis and C. A. Ramsden, preceding paper.

² W. Baker, W. D. Ollis, and V. D. Poole, *J. Chem. Soc.*, 1949, 307.

³ W. Baker and W. D. Ollis, *Quart. Rev.*, 1957, **11**, 15.

⁴ W. Baker, W. D. Ollis, A. Phillips, and T. Strawford, *J. Chem. Soc.*, 1951, 289.

⁵ A. R. McCarthy, W. D. Ollis, A. N. M. Barnes, L. E. Sutton, and C. Ainsworth, *J. Chem. Soc. (B)*, 1969, 1185; Part VIII, A. R. McCarthy, W. D. Ollis, and C. A. Ramsden, *J.C.S. Perkin I*, 1974, 624.

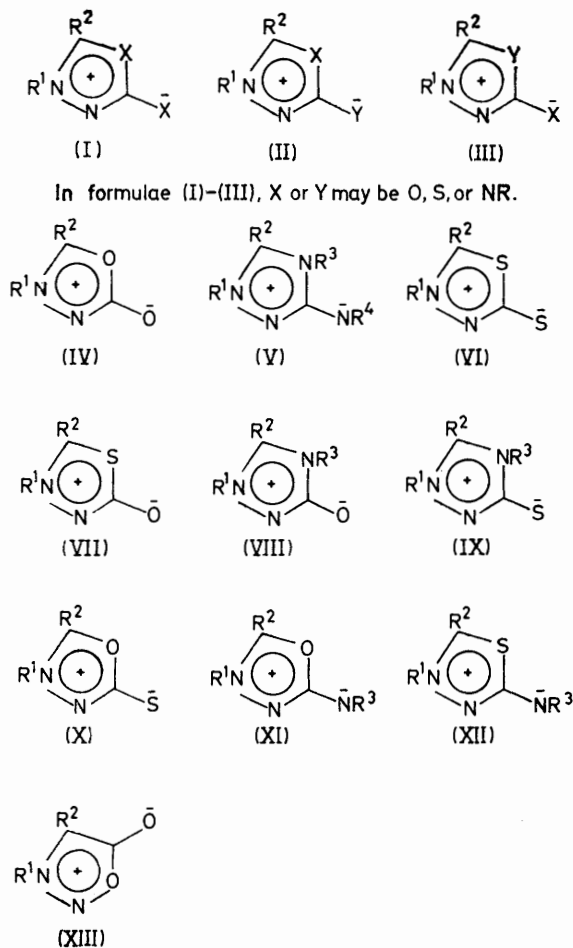
⁶ A. R. McCarthy, W. D. Ollis, and C. A. Ramsden, *Chem. Comm.*, 1968, 499; Part IX, *J.C.S. Perkin I*, 1974, 627.

⁷ W. D. Ollis and C. A. Ramsden, *Chem. Comm.*, 1971, 1222; Part X, *J.C.S. Perkin I*, 1974, 633.

(XII) are available;^{1,4-8} we now report a comparative study of their mass spectra.

The mass spectra of the sydnones⁹ and of an assortment of meso-ionic types¹⁰ have already been reported. Certain common aspects of mass spectral behaviour have been mentioned, but it is possible on the basis of the studies now reported to discuss fragmentation patterns in general terms (Scheme 1).

Our discussion of the fragmentation of the meso-ionic systems (IV)—(XII) is based upon a general empirical fragmentation pattern (Scheme 1), fully supported by the observation of metastable ions and the results of



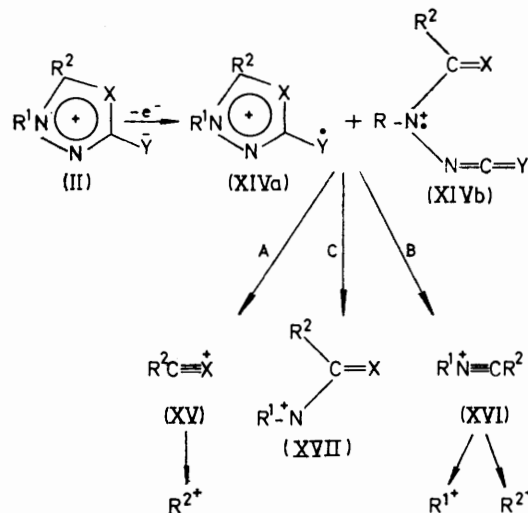
defocusing experiments.¹¹ Accurate mass measurements gave the elemental compositions of the ions, but the structures drawn for fragment ions are intended to represent constitutions rather than molecular geometries. Peaks of intensity less than 10% of that of the base peak have been neglected except in cases of special significance.

The fragmentation patterns of the meso-ionic systems (IV)—(XII) are simple. They show a molecular ion

⁸ W. D. Ollis and C. A. Ramsden, *Chem. Comm.*, 1971, 1224; Part XI, *J.C.S. Perkin I*, 1974, 638.

⁹ J. H. Bowie, R. A. Eade, and J. C. Earl, *Austral. J. Chem.*, 1968, **21**, 1665; R. S. Goudie, P. N. Preston, and M. H. Palmer, *Org. Mass Spectrometry*, 1969, **2**, 953.

(XIV) (Scheme 1) which apparently fragments by two major pathways (A and B). Pathway A gives the fragment ion $R^2C\equiv X^+$ (XV), which undergoes the usual



SCHEME 1

further fragmentation giving $(R^2)^+$; pathway B gives the fragment ion $R^1N\equiv CR^2+$ (XVI), which gives daughter ions $(R^1)^+$ and $(R^2)^+$. An additional minor pathway (C), giving the ion (XVII) or the rearranged ion $R^1N\equiv C-XR^2+$, is also observable in some cases.

Spectra of the Isosydones (IV), 1,3,4-Triazolium-2-aminides (V), and 1,3,4-Thiadiazolium-2-thiolates (VI).—The mass spectrum of 4,5-diphenylisosydnone (IV; $R^1 = R^2 = Ph$) has been reported.¹⁰ We have recorded the mass spectra of twelve isosydones (IV) (Table 1;

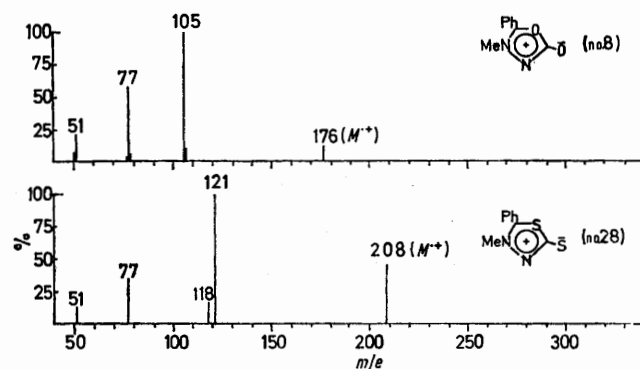


FIGURE 1 Comparison of the mass spectra of the isosydnone (no. 8, Table 1) and the 1,3,4-thiadiazolium-2-thiolate analogue (no. 28, Table 3)

compounds 1–12) of which that of 4-methyl-5-phenylisosydnone (IV; $R^1 = Me$, $R^2 = Ph$) is typical (Figure

¹⁰ T. Shima, A. Ouchida, and Y. Asahi, *Shikuryo Bunseki*, 1969, **17**, 661 (*Chem. Abs.*, 1970, **73**, 87,149j); R. C. Dougherty, R. L. Foltz, and L. B. Kier, *Tetrahedron*, 1970, **26**, 1989; W. K. Anderson and A. E. Friedman, *Org. Mass Spectrometry*, 1972, **6**, 797; K. T. Potts, R. Armbruster, E. Houghton, and J. Kane, *ibid.*, 1973, **7**, 203.

¹¹ K. R. Jennings, *J. Chem. Phys.*, 1965, **43**, 4176; 'Some Newer Physical Methods in Structure Chemistry,' United Trade Press, London, 1967, p. 105.

1). The low intensities of the molecular ion peaks (Table 1) indicate that these ions have little stability.

TABLE 1

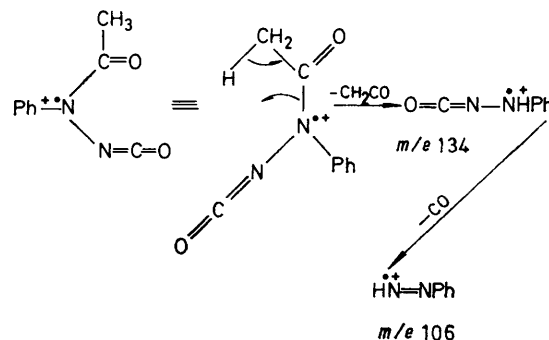
Cpd no.	Derivative		$M^{+\cdot}$	$R^2C\equiv O^+$	$R^1N\equiv CR^2$	$(R^1)^+$ $(R^2)^+$	
	R^1	R^2					
1	Ph	Ph	6	100	-	40	
2	Ph	<i>p</i> -ClC ₆ H ₄	8	100	-	4	25
3	<i>p</i> -ClC ₆ H ₄	Ph	3	100	-	8	47
4	<i>p</i> -ClC ₆ H ₄	<i>p</i> -ClC ₆ H ₄	2	100	-	29	
5	Ph	<i>p</i> -MeC ₆ H ₄	3	100	-	4	37
6	<i>p</i> -MeC ₆ H ₄	Ph	6	100	-	6	26
7	<i>p</i> -MeC ₆ H ₄	<i>p</i> -MeC ₆ H ₄	5	100	-	31	31
8	Me	Ph	12	100	-	-	57
9	Me	<i>p</i> -ClC ₆ H ₄	11	100	-	-	44
10	Me	<i>p</i> -MeC ₆ H ₄	13	100	-	-	37
11	Me	PhCH ₂	17	7	-	-	100
12	Ph	Me	20	100	-	19	-

-, Peak absent

In general, the base peak of the isosydnone spectra (Table 1) is the fragment ion $R^2C\equiv O$ (XV; $X = O$) (Scheme 1) formed by pathway A. The ion $R^1N\equiv CR^2$ (XVI) (pathway B) was not observed in any of the spectra (Table 1). The intensity of the peak due to $PhCH_2-C\equiv O^+$ (XV; $R^2 = PhCH_2$, $X = O$) in the spectrum of 5-benzyl-4-methylisosydnone (IV; $R^1 = Me$, $R^2 = PhCH_2$) (Table 1, compound 11) is exceptionally weak compared with that of the corresponding ion in other isosydnone spectra. Presumably the ion $PhCH_2-C\equiv O^+$ readily loses carbon monoxide giving the tropylium cation. In addition to fragmentation by pathway A, the spectrum of 5-methyl-4-phenylisosydnone (IV; $R^1 = Ph$, $R^2 = Me$) shows an intense peak at m/e 134 ($C_7H_6N_2O^{+\cdot}$). The observation of a metastable ion at m/e 102 indicates that the ion m/e 134 is formed directly from the molecular ion, and its formation can be rationalised by a proton transfer mechanism (Scheme 2). The occurrence of another metastable ion

at m/e 83.9 shows that the fragment ion at m/e 106 (Scheme 2) is formed from the ion $C_7H_6N_2O^{+\cdot}$.

In contrast to the isosydnone (IV) (Table 1), the most intense peak in the mass spectra of the eleven meso-ionic 1,3,4-triazolium-2-aminides (V) recorded in Table 2 is usually due to the molecular ion, which undergoes fragmentation by both pathways A and B (Scheme 1). Generally the peak due to the fragment ion $R^2C\equiv NR^3$ (XV; $X = NR^3$) is more intense than that due to the ion $R^1N\equiv CR^2$ (XVI) (Table 2). A comparatively weak fragment ion (XVII) formed by pathway C (Scheme 1) is often observed.



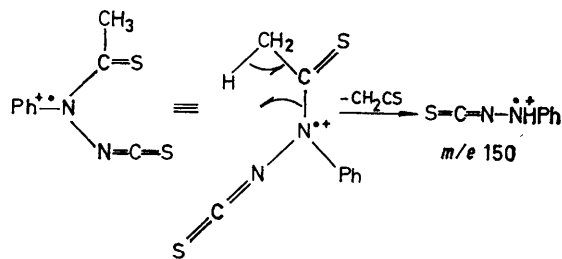
The spectra (Figure 2) of the isomeric *p*-tolyl-1,3,4-triazoles (V; $R^1 = Me$, $R^2 = R^3 = Ph$, $R^4 = p\text{-MeC}_6\text{H}_4$) and (V; $R^1 = Me$, $R^2 = R^4 = Ph$, $R^3 = p\text{-MeC}_6\text{H}_4$) are typical of the 1,3,4-triazolium-2-aminides (V). The physical and chemical properties of this pair of meso-ionic isomers (Table 2, compounds 17 and 18) are almost identical, but mass spectrometry provides an unambiguous method of distinguishing between them. Both show a molecular ion at m/e 340 and fragment ions at m/e 118 corresponding to $MeN\equiv CPh$ (XVI; $R^1 = Me$, $R^2 = Ph$) formed by pathway B (Scheme 1). The cleavage of the molecular ion by pathway A (Scheme 1)

TABLE 2

Relative intensities (%) of the principal ions in the mass spectra of the 1,3,4-triazolium-2-aminides (V)

Cpd. no.	Derivative				$M^{+\cdot}$	$R^2C\equiv NR^3$	$R^1N\equiv CR^2$	$(R^1)^+$	$(R^2)^+$ $(R^3)^+$ $(R^4)^+$		
	R^1	R^2	R^3	R^4							
13	Me	Ph	Ph	Ph	100	56	28	-	80		
14	Me	Ph	Ph	<i>p</i> -ClC ₆ H ₄	85	73	33	-	100		
15	Me	Ph	<i>p</i> -ClC ₆ H ₄	Ph	100	90	57	-	86	67	86
16	Me	Ph	<i>p</i> -ClC ₆ H ₄	<i>p</i> -ClC ₆ H ₄	100	84	24	-	24	52	
17	Me	Ph	Ph	<i>p</i> -MeC ₆ H ₄	100	47	20	-	100		
18	Me	Ph	<i>p</i> -MeC ₆ H ₄	Ph	100	92	56	-	52	100	52
19	Me	Ph	<i>p</i> -MeC ₆ H ₄	<i>p</i> -MeC ₆ H ₄	100	55	28	-	20	33	
20	Me	Ph	<i>p</i> -MeOC ₆ H ₄	Ph	100	94	63	-	58	-	58
21	Ph	Ph	Ph	Ph	63	94	94	-	100		
22	Ph	Ph	Ph	<i>p</i> -ClC ₆ H ₄	100	47	47	-	44	-	
23	Ph	H	Ph	Ph	100	22	≡ 22	81	-	81	

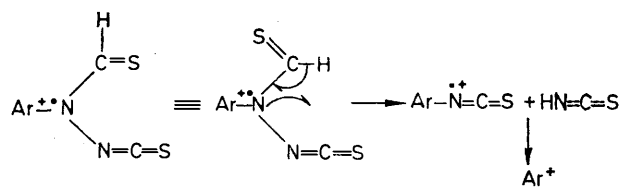
discriminates between the isomeric compounds 17 and 18. Compound 17 gives a fragment ion at m/e 180 ($\text{PhC}\equiv\text{N}^+\text{Ph}$) (XV; $\text{R}^2 = \text{Ph}$, $\text{X} = \text{NPh}$), whereas compound 18 gives an ion at m/e 194 ($\text{PhC}\equiv\text{N}^+\text{C}_6\text{H}_4\text{Me}-p$) (XV);



SCHEME 3

$\text{R}^2 = \text{Ph}$, $\text{X} = \text{N}\cdot\text{C}_6\text{H}_4\text{Me}-p$). Formation of the ion $\text{R}^2\text{C}\equiv\text{X}^+$ (XV) (Scheme 1) distinguishes between meso-ionic isomers (II) and (III).

The mass spectra of a number of 1,3,4-thiadiazolium-2-thiolates (VI) have been discussed.¹⁰ We have recorded the mass spectra of nine derivatives (VI) (Table 3). The spectrum (Figure 1) of the 4-methyl-5-phenyl derivative (VI; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Ph}$) (Table 3, compound 28) is typical. All the derivatives which we have studied (Table 3, compounds 24–32) show a molecular ion which fragments by both pathways A and B (Scheme 1). Unlike the 1,3,4-triazolium-2-aminides (V), the relative intensities of the peaks due to ions (XV) and (XVI) (Scheme 1) do not show a general trend (Table 3). Like 5-methyl-4-phenylisosydnone (IV; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$), 5-methyl-4-phenyl-1,3,4-thiadiazolium-2-thiolate (VI; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$) shows an additional fragmentation mode (Scheme 3). A moderately strong peak at m/e 150 has been shown by high resolution measurements to be derived from two fragment ions with the constitutions $\text{C}_7\text{H}_6\text{N}_2\text{S}^+$ and $\text{C}_8\text{H}_8\text{NS}^+$ and in the ratio 3:1, respectively.¹⁰ The more intense ion is probably formed (Scheme 3) by a process analogous to the corresponding isosydnone fragmentation (Scheme 2). The minor ion ($\text{C}_8\text{H}_8\text{NS}^+$) corresponds with the ion (XVII; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$, $\text{X} = \text{S}$) (Scheme 1) formed by fragmentation of the molecular ion by pathway C.



SCHEME 4

The 5-unsubstituted 1,3,4-thiadiazolium-2-thiolates (VI; $\text{R}^2 = \text{H}$) which we have studied (Table 3, compounds 30, 31, and 32) demonstrate exceptional fragmentation patterns showing an intense peak due to the aryl isothiocyanate radical cation (Scheme 4).

Mass Spectral Differentiation between Meso-ionic Isomers.—Mass spectrometry has been invaluable in our

study of the isomeric meso-ionic systems (VII) and (X),⁶ (VIII) and (XI),¹ and (IX) and (XII),⁷ which exhibit highly characteristic fragmentation patterns (Scheme 1).

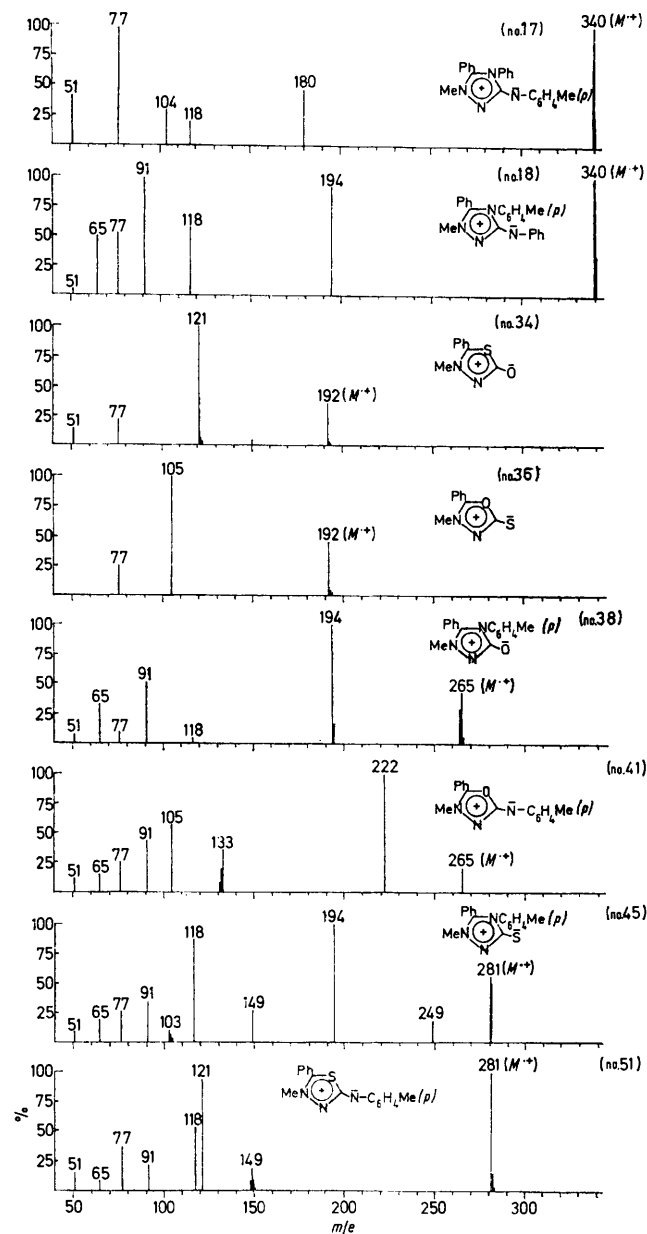


FIGURE 2 Comparison of the mass spectra of four pairs of meso-ionic isomers (Table 2, nos. 17 and 18, Table 4, nos. 34 and 36, Table 5, nos. 38 and 41, and Table 6, nos. 45 and 51)

The mass spectra of two 1,3,4-thiadiazolium-2-olates (VII) and two 1,3,4-oxadiazolium-2-thiolates (X) (Table 4) are shown in Figure 2. The 1,3,4-thiadiazolium-2-olates (VII) give the ion $\text{PhC}\equiv\text{S}^+$ (XV; $\text{R}^2 = \text{Ph}$, $\text{X} = \text{S}$) (Scheme 1), whereas the 1,3,4-oxadiazolium-2-thiolates (X) yield the ion ($\text{PhC}\equiv\text{O}^+$) (XV; $\text{R}^2 = \text{Ph}$, $\text{X} = \text{O}$) (Scheme 1). These ions correspond to fragmentation by pathway A and provide the most intense peaks in the

spectra. No fragmentation by pathway B (Scheme 1) was observed.

TABLE 3

Relative intensities (%) of the principal ions in the mass spectra of the 1,3,4-thiadiazolium-2-thiolates (VI)

Cpd. no.	Derivative			M^+	$R^2C\equiv S^+$	$R^1N^+\equiv CR^3$	$(R^1)^+$	$(R^2)^+$
	R^1	R^2	R^3					
24	Ph	Ph		39	100	29	48	48
25	Ph	<i>p</i> -ClC ₆ H ₄		19	82	95	100	17
26	<i>p</i> -ClC ₆ H ₄	Ph		5	26	100	40	25
27	<i>p</i> -ClC ₆ H ₄	<i>p</i> -ClC ₆ H ₄		26	100	57	29	29
28	Me	Ph		45	100	17	-	35
29	Ph	Me		43	100	49	80	-
30	Ph	H		30	7	20	100	-
31	<i>p</i> -ClC ₆ H ₄	H		2	-	-	42	-
32	<i>p</i> -MeC ₆ H ₄	H		3	-	-	45	-

The mass spectra of the 1,3,4-triazolium-2-olates (VIII) and the 1,3,4-oxadiazolium-2-aminides (XI) are illustrated by the spectra (Figure 2) of the *p*-tolyl derivatives (Table 5, compounds 38 and 41). For the 1,3,4-triazolium-2-olates (VIII), cleavage of the molecular ion occurs predominantly by pathway A (Table 5), but in the 1,3,4-oxadiazolium-2-aminides (XI) cleavage occurs exclusively by pathway A (Table 5). The

absence of fragmentation by pathway B is a common feature of all the meso-ionic 1,3,4-oxadiazole systems (IV), (X), and (XI) which we have studied. The 1,3,4-triazolium-2-olates (VIII) are readily distinguished from 1,3,4-oxadiazolium-2-aminides (XI) by the formation of

TABLE 4

Relative intensities (%) of the principal ions in the mass spectra of the meso-ionic 1,3,4-thiadiazoles (VII) (a) and 1,3,4-oxadiazoles (X) (b)

Cpd. no.	Derivative		M^+	$R^2C\equiv S^+$	$R^1N^+\equiv CR^2$	$(R^1)^+$	$(R^2)^+$
	R^1	R^2					
(a) 33	Ph	Ph	16	100	-	-	20
34	Me	Ph	36	100	-	-	22
			M^+	$R^2C\equiv O^+$	$R^1N^+\equiv CR^2$	$(R^1)^+$	$(R^2)^+$
(b) 35	Ph	Ph	8	100	-	-	48
36	Me	Ph	45	100	-	-	25

different fragment ions (XV) by pathway A (Scheme 1), the former (VIII) giving $R^2C\equiv NR^3$, whereas the latter (XI) give $R^2C\equiv O^+$. The 1,3,4-oxadiazolium-2-aminides also show a fragment ion corresponding to the aryl isocyanate radical cation ($ArN^+=C=O$). An unusual

TABLE 5

Relative intensities (%) of the principal ions in the mass spectra of the meso-ionic 1,3,4-triazoles (VIII) (a) and 1,3,4-oxadiazoles (XI) (b)

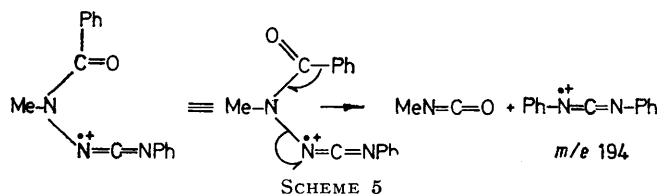
Cpd. no.	Derivative			M^+	$R^2C\equiv NR^3$	$R^1N^+\equiv CR^2$	$(R^1)^+$	$(R^2)^+$	$(R^3)^+$
	R^1	R^2	R^3						
(a) 37	Me	Ph	Ph	28	50	10	-	-	100
38	Me	Ph	<i>p</i> -MeC ₆ H ₄	43	100	4	-	10	50
39	Me	Ph	Me	42	100		-	33	-
				M^+	$R^2C\equiv O^+$	$R^1N^+\equiv CR^2$	$(R^1)^+$	$(R^2)^+$	$(R^3)^+$
(b) 40	Me	Ph	Ph	26	100	-	-	-	43
41	Me	Ph	<i>p</i> -MeC ₆ H ₄	20	57	-	-	26	43
42	Me	Ph	<i>p</i> -ClC ₆ H ₄	16	71	-	-	30	10
43	Me	Ph	Me	10	100	-	-	50	-

TABLE 6

Relative intensities (%) of the principal ions in the mass spectra of the meso-ionic 1,3,4-triazoles (IX) (a) and 1,3,4-thiadiazoles (XII) (b)

Cpd. no.	Derivative			M^+	$R^2C\equiv NR^3$	$R^1N^+\equiv CR^2$	$(R^1)^+$	$(R^2)^+$	$(R^3)^+$
	R^1	R^2	R^3						
(a) 44	Me	Ph	Ph	4	46	100	-	-	63
45	Me	Ph	<i>p</i> -MeC ₆ H ₄	50	100	87	-	26	35
46	Me	Ph	<i>p</i> -ClC ₆ H ₄	37	78	100	-	75	45
47	Me	Ph	Me	25	100		-	28	-
48	Ph	Ph	Ph	32	100		-	99	-
49	Ph	H	Ph	56	80	80	100	-	100
				M^+	$R^2C\equiv S^+$	$R^1N^+\equiv CR^2$	$(R^1)^+$	$(R^2)^+$	$(R^3)^+$
(b) 50	Me	Ph	Ph	65	65	35	-	-	100
51	Me	Ph	<i>p</i> -MeC ₆ H ₄	100	94	53	-	37	22
52	Me	Ph	<i>p</i> -ClC ₆ H ₄	52	49	40	-	100	52
53	Me	Ph	Me	67	100	30	-	40	-

observation in the mass spectrum of 4-methyl-5-phenyl-1,3,4-oxadiazolium-2-anilide (XI; $R^1 = \text{Me}$, $R^2 = R^3 = \text{Ph}$) is the intense fragment ion at m/e 194 ($\text{C}_{13}\text{H}_{10}\text{N}_2^+$). This may well be the diphenylcarbodi-imide radical cation, formed (Scheme 5) by a process similar to that of Scheme 4. The spectrum of the *p*-tolyl-1,3,4-oxadiazol-2-aminide (XI; $R^1 = \text{Me}$, $R^2 = \text{Ph}$, $R^3 = p\text{-MeC}_6\text{H}_4$) (Figure 2, compound 41) shows exceptional behaviour in that an intense peak is observed at m/e 222 ($\text{C}_{15}\text{H}_{12}\text{NO}^+$), corresponding to $M^{+\cdot} - \text{MeN}=\text{N}$.



The 1,3,4-triazolium-2-thiolates (IX) and the isomeric 1,3,4-thiadiazolium-2-aminides (XII) are readily distinguished by mass spectrometry. The spectra of a number of derivatives of both these systems (Table 6) show fragmentation by both pathways A and B. The nature

of the fragment ion (XV) (Scheme 1) readily distinguishes the two systems (IX) and (XII). The 1,3,4-triazolium-2-thiolates (IX) give the fragment ions $\text{R}^2\text{C}=\text{N}^+\text{R}^3$ (XV; $\text{X} = \text{NR}^3$), whereas the 1,3,4-thiadiazolium-2-aminides (XII) give the ions $\text{R}^2\text{C}=\text{S}^+$ (XV; $\text{X} = \text{S}$). The spectra (Figure 2) of the *p*-tolyl isomers (Table 6, compounds 45 and 51) are typical. In addition to the normal fragment ions, both show a fragment ion (m/e 149) which corresponds to the *p*-tolyl isothiocyanate radical cation ($p\text{-MeC}_6\text{H}_4\text{-N}^+=\text{C}=\text{S}$). However, aryl isothiocyanate radical cations are not always observed in the mass spectra of the meso-ionic systems (IX) and (XII).

EXPERIMENTAL

The mass spectra were recorded on A.E.I. MS 9 and MS 12 spectrometers (direct inlet systems; source temperature *ca.* 200–240°). An ionising voltage of 70 eV was used.

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