Cyclic Meso-ionic Compounds. Part 20.[1] Mass Spectra of Meso-ionic Heterocycles

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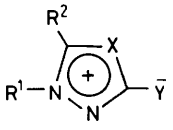
The mass spectra of ten related meso-ionic systems have been recorded and analysed in terms of a general fragmentation scheme. Mass spectrometry is particularly useful for distinguishing between pairs of meso-ionic isomers.

In a previous study of the mass spectra of meso-ionic heterocycles,[2] we have shown that the fragmentation of the nine meso-ionic systems with the structure (1; X or Y = O, S, or NR) can be rationalised in terms of a general



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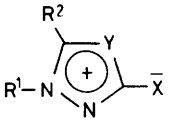

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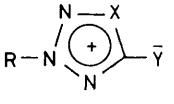

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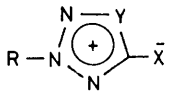

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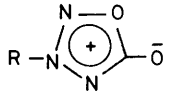

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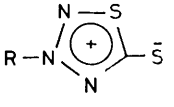

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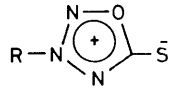

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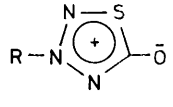

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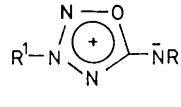

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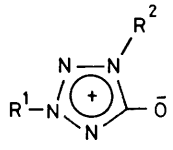

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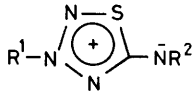

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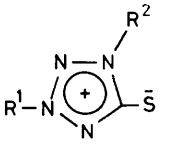

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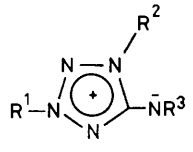

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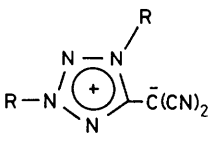

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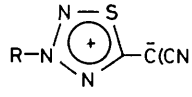
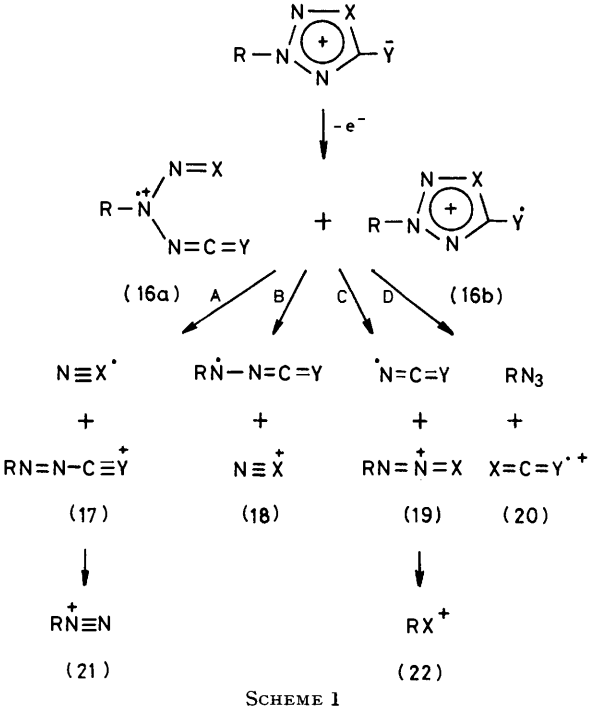


(15)

fragmentation scheme. In subsequent studies, we have investigated the chemistry of new meso-ionic systems which have the general structure (3; X or Y = O, S, or NR). In principle, there are nine possible meso-ionic systems of the type (3; X or Y = O, S, or NR) and we have synthesised and characterised derivatives of eight of these systems (5)—(12).[3-6] A method of preparing derivatives of the remaining member of this class, the 1,2,3,4-tetrazolium-5-aminides (13), has not been reported. In addition, we have prepared derivatives of the related meso-ionic systems (14) and (15).[1,6]

As in our study of meso-ionic systems of the general type (1),[2] we have found mass spectrometry to be an invaluable tool for structure determination, particularly for distinguishing between pairs of isomers of the general type (3) and (4). The discussion of the fragmentation of the meso-ionic systems (5)—(12) is based upon a general fragmentation pattern (Scheme 1), which is fully supported by the observation of metastable ions. Accurate mass measurements gave the elemental composition of the ions, but structures drawn for fragment ions are intended to represent constitutions rather than molecular geometries. Peaks of intensity <5% of that of the base peak have been neglected except in cases of special significance.

The fragmentation patterns of the meso-ionic systems (5)—(12) are easily correlated. The molecular ion (16) (Scheme 1) can apparently fragment by four pathways (A, B, C, and D). The major fragmentation pathway varies with structural type (5)—(12), but simultaneous fragmentation *via* all four pathways is never observed. Pathway A gives the fragment ion (17) by loss of NX· radical from the molecular ion (16). Further fragmentation gives the ion $RN\overset{+}{\equiv}N$ and its daughter ion (R^+). Pathway B is closely related to pathway A and



Scheme 1

gives the fragment ion (18). This type of cleavage predominates in the mass spectrum of the meso-ionic tetrazoles (10 and 12), the product being the relatively stable aryl arenediazonium cation (18; X = NR^2). Pathway C corresponds to loss of ·N=C=Y radical from the molecular ion (16) giving a fragment ion whose constitution is consistent with the structure (19). We have only observed this type of cleavage in cases where the heteroatom X is sulphur (3; X = S). Further fragmentation of the ion (19; X = S) gives the daughter ion RS^+ together with a corresponding metastable ion.

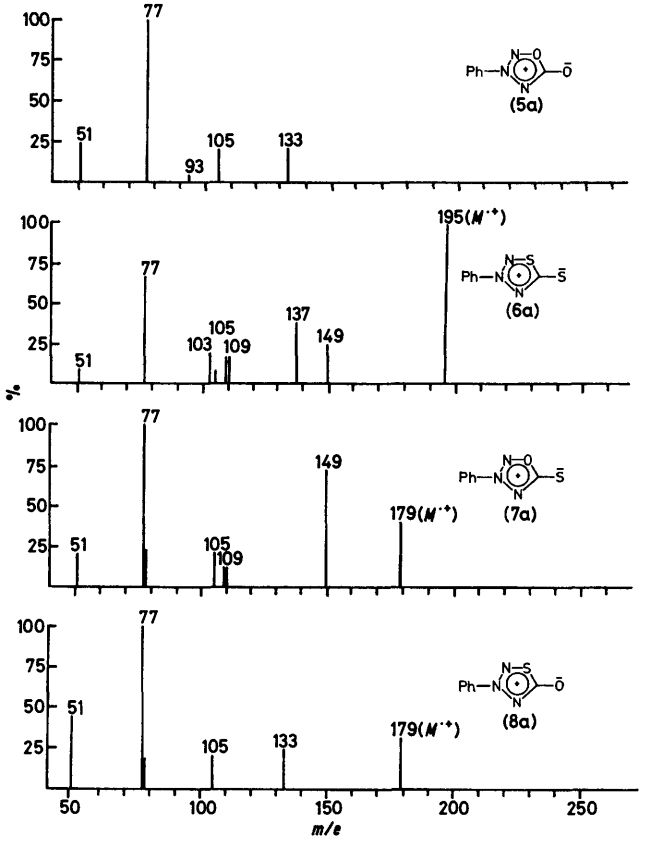


FIGURE 1 Comparison of the mass spectra of four meso-ionic systems [Table 1, compounds (5a) and (6a); Table 2, compounds (7a) and (8a)]

Pathway D is a minor pathway giving a heterocumulene radical cation (20) and is observable only in a few cases.

The Mass Spectra of the 1,2,3,4-*Oxatriazolium-5-olates* (5) *and* 1,2,3,4-*Thiatriazolium-5-thiolates* (6).—We have recorded the mass spectra of the four meso-ionic oxatriazoliumolates (5a—d) (Table 1); the spectrum of the 3-phenyl compound (5a) is typical (Figure 1). A molecular ion is not observed in any of the spectra that we have recorded for compounds (5a—d), but the fragment ion (17; Y = O) corresponding to loss of nitroxyl radical (·NO) from the molecular ion (Scheme 1, pathway A) is observed. Further fragmentation of this ion (17; Y = O) gives carbon monoxide and an arenediazonium ion ($R\overset{+}{N}\equiv N$); this process ($RN{=}N{-}C{\equiv}O^+ \longrightarrow R\overset{+}{N}\equiv N$) is fully supported by the observation of metastable ions.

In all the mass spectra of compounds (5a—d) the base peak is the aryl cation (R^+) formed by loss of nitrogen from the arenediazonium ion ($R\overset{+}{N}\equiv N$).

No evidence of fragmentation by pathways B, C, or D (Scheme 1) is observed in the mass spectra of compounds (5a—d) but a weak fragment ion corresponding to the structure RO^+ is observed in each case. It is possible that this ion (RO^+) is formed *via* the ion (19; X = O) (Scheme 1, pathway C).

In contrast to compounds (5), the mass spectra of compounds (6a—c) (Table 1) show an intense molecular ion. The spectra are exemplified by that of the 3-phenyl compound (6a) (Figure 1). In a process analogous to that for the compounds (5), compounds (6) undergo fragmentation by pathway A (Scheme 1), losing thionitroxyl radical (NS·), and form the daughter ion (17; Y = S) (Scheme 1). This ion (17; Y = S) undergoes further cleavage giving the arenediazonium ion ($R\overset{+}{N}\equiv N$) which loses nitrogen forming the aryl cation (R^+). The molecular ion (16) (Scheme 1) also undergoes cleavage *via* pathway C (Scheme 1), losing the thiocyanate radical (·N=C=S) and giving a fragment ion corresponding to the structure (19; X = S). The loss of nitrogen from this ion ($RN{=}\overset{+}{N}{=}S$) probably accounts for the observation of the weak ions corresponding to the structure RS^+ (Table 1).

Mass spectrometry has been shown to be invaluable for distinguishing between pairs of meso-ionic isomers of the types (1) and (2) [2] and it is equally informative for

TABLE 1

Relative intensities (%) of the principal ions in the mass spectra of the meso-ionic 1,2,3,4-oxatriazolium-5-olates (5) and 1,2,3,4-thiatriazolium-5-thiolates (6)

Cpd.	R	$M^{\cdot+}$	$RN{=}N{\cdot}C{\equiv}O^+$	$RN{=}\overset{+}{N}{=}O$	$R\overset{+}{N}\equiv N$	R^+	RO^+
(5a)	Ph	–	21	–	15	100	5
(5b)	*p*-MeC_6H_4	–	22	–	12	100	8
(5c)	*p*-ClC_6H_4	–	39	–	32	100	5
(5d)	*p*-$MeOC_6H_4$	–	87	–	96	100	5
		$M^{\cdot+}$	$RN{=}N{\cdot}C{\equiv}S^+$	$RN{=}\overset{+}{N}{=}S$	$R\overset{+}{N}\equiv N$	R^+	RS^+
(6a)	Ph	100	18	32	8	68	20
(6b)	*p*-MeC_6H_4	32	3	10	2	100	7
(6c)	*p*ClC_6H_4	88	10	37	14	100	12

TABLE 2

Relative intensities (%) of the principal ions in the mass spectra of the meso-ionic 1,2,3,4-oxatriazolium-5-thiolates (7) and 1,2,3,4-thiatriazolium-5-olates (8)

Cpd.	R	$M^{\cdot+}$	$RN{=}N{\cdot}C{\equiv}S^+$	$R\overset{+}{N}\equiv N$	R^+	RS^+
(7a)	Ph	33	73	17	100	13
(7b)	*p*-MeC_6H_4	22	65	6	100	5
(7c)	*p*-ClC_6H_4	26	45	17	100	2
(7d)	*p*-$MeOC_6H_4$	6	100	16	75	9
(7e)	*p*-$EtOC_6H_4$	6	100	8	93	2
		$M^{\cdot+}$	$RN{=}N{\cdot}C{\equiv}O^+$	$R\overset{+}{N}\equiv N$	R^+	RO^+
(8a)	Ph	27	23	12	100	–
(8b)	*p*-MeC_6H_4	33	28	9	100	–
(8c)	*p*-ClC_6H_4	31	35	24	100	–
(8d)	*p*-$MeOC_6H_4$	75	84	32	100	–
(8e)	*p*-$EtOC_6H_4$	42	54	32	100	–

TABLE 3

Relative intensities (%) of the principal ions in the mass spectra of the meso-ionic 1,2,3,4-oxatriazolium-5-aminides (9) and 1,2,3,4-tetrazolium-5-olates (10)

Cpd.	R^1	R^2	$M^{\cdot+}$	$R^1N{=}N{\cdot}C{\equiv}NR^2$	$R^2\dot{N}{=}C{=}O$	$R^1\overset{+}{N}{\equiv}N$	R^{1+}	R^{2+}	$R^1\overset{+}{N}{\equiv}CR^2$
(9a)	Ph	Ph	18	10	32	49	100		11
(9b)	Ph	*p*-MeC_6H_4	44	<1	8	85	100	26	5
(9c)	Ph	*p*-ClC_6H_4	7	<1	2	35	100	5	–
(9d)	*p*-MeC_6H_4	Ph	11	1	–	44	100	16	1
(9e)	*p*-ClC_6H_4	Ph	16	2	4	70	100	25	–
(9f)	*p*-$NO_2C_6H_4$	Ph	15	<1	3	40	100	30	–

			$M^{\cdot+}$	$R^1N{=}N{\cdot}C{=}O^+$	$R^2\dot{N}{=}C{=}O$	$R^1\overset{+}{N}{\equiv}N$	$R^2\overset{+}{N}{\equiv}N$	R^{1+}	R^{2+}
(10a)	Ph	Ph	10	–	<1	48		100	
(10b)	Ph	*p*-MeC_6H_4	16	–	–	<1	93	34	100
(10c)	Ph	*p*-ClC_6H_4	8	–	<1	<1	54	19	100
(10d)	*p*-MeC_6H_4	Ph	6	–	–	–	56	21	100
(10e)	*p*-MeC_6H_4	*p*-MeC_6H_4	8	–	<1	42		100	
(10f)	*p*-ClC_6H_4	Ph	8	<1	<1	<1	69	11	100
(10g)	*p*-ClC_6H_4	*p*-ClC_6H_4	9	–	<1	53		100	

discriminating between pairs of meso-ionic isomers of the general types (3) and (4).

The Mass Spectra of 1,2,3,4-*Oxatriazolium-5-thiolates* (7) *and* 1,2,3,4-*Thiatriazolium-5-olates* (8).—The spectra of compounds (7a—e) and (8a—e) (Table 2) are simple and are illustrated by the spectra of the 3-phenyl compounds (7a) and (8a) (Figure 1). Both systems show a moderately intense molecular ion (16) which fragments by pathway A (Scheme 1). The oxatriazolium-thiolates (7) are characterised by their loss of nitroxyl radical giving the fragment ion (17; Y = S) (Scheme 1, pathway A), whereas the thiatriazoliumolates (8) lose thionitroxyl radical giving the fragment ion (17; Y = O) (Scheme 1, pathway A). In both cases, further fragmentation gives the daughter ions $R\overset{+}{N}{\equiv}N$ and R^+.

Although fragmentation by pathway C (Scheme 1) is not observed for the oxatriazoliumthiolates (7a—e), all the spectra show a weak ion corresponding to the structure RS^+. This may well be formed by loss of nitrogen from the unobserved fragment ion (19; X = S).

The Mass Spectra of 1,2,3,4-*Oxatriazolium-5-aminides* (9) *and* 1,2,3,4-*Tetrazolium-5-olates* (10).—The mass spectra of the meso-ionic compounds (9a—f) (Table 3), illustrated by that of the diphenyl derivative (9a) (Figure 2), show a moderately strong molecular ion. Fragmentation occurs *via* pathway A (Scheme 1) and, although the daughter ion (17; Y = NR^2) is very weak, the fragmentation process ($M^{\cdot+} \longrightarrow R^1N{=}N{\cdot}C{\equiv}\overset{+}{N}R^2$) (Scheme 1, pathway A) is supported by the observation of strong metastable ions. Further fragmentation of the ion $R^1N{=}N{\cdot}C{\equiv}\overset{+}{N}R^2$ gives the arenediazonium ion ($R^1\overset{+}{N}{\equiv}N$) and the aryl cation ($R^{1+}$) which in all the derivatives (9a—f) that we have studied is the base peak. A relatively weak fragment ion due to the aryl cation R^{2+} is also observed. This may well be formed from the fragment ion (17; Y = NR^2).

An aryl isocyanate radical cation ($R^2\dot{N}{=}C{=}O$) is observed in each of the spectra of compounds (9a—f) and this corresponds to cleavage of the molecular ion by pathway D (Scheme 1). There is no evidence for fragmentation by pathways B and C. A weak ion whose constitution corresponds to the structure $R^1C{\equiv}NR^2$ is sometimes observed and its formation corresponds to the loss of nitrogen from the fragment ion (17; Y = NR^2).

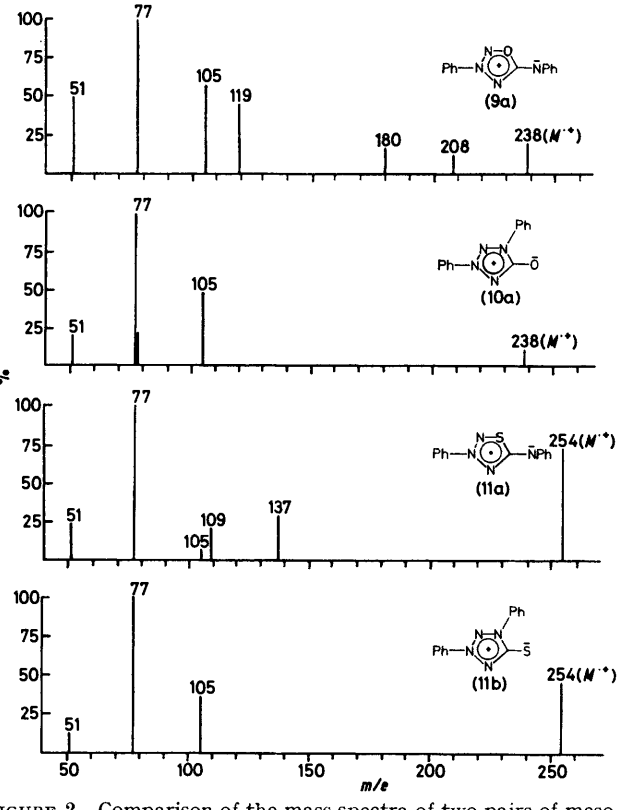


FIGURE 2 Comparison of the mass spectra of two pairs of meso-ionic isomers [Table 3, compounds (9a) and (10a); Table 4, compounds (11a) and (12a)]

The mass spectra of the tetrazoliumolates (10a—g) (Table 3) are even simpler than those of the isomeric compounds (10). The spectrum of the diphenyl derivative (10a) is typical. All the tetrazoliumolates (10a—g) show a molecular ion (16) (Scheme 1), but a daughter ion corresponding to cleavage *via* pathway A is not

observed. Extremely weak fragment ions having the arenediazonium ion structure $R^1\overset{+}{N}\equiv N$ are observed suggesting that cleavage by pathway A (Scheme 1) is minor. However, very intense fragment ion peaks corresponding to the arenediazonium ion $R^2\overset{+}{N}\equiv N$ are recorded and the formation of these ions directly from the molecular ion (pathway D, Scheme 1) is confirmed by the observation of strong metastable ions. The ion $R^2\overset{+}{N}\equiv N$ fragments to the aryl cation R^{2+} which is the base peak.

It is significant that the mass spectra of the oxatriazoliumaminides (9a—f) do not show fragment ions corresponding to the structure $R^2\overset{+}{N}\equiv N$ and the intensity of the aryl cation R^{2+} is relatively weak. Thus, it is particularly straightforward to distinguish between the isomeric species (9) and (10).

The spectra of the tetrazoliumolates (10) show a weak aryl isocyanate radical cation (20; X = O, Y = NPh) which is due to cleavage by pathway D (Scheme 1). No fragmentation by pathway C is observed.

The Mass Spectra of 1,2,3,4-*Thiatriazolium-5-aminides* (11) *and* 1,2,3,4-*Tetrazolium-5-thiolates* (12).—The mass spectra of the thiatriazoliumaminides (11a—f) (Table 4) are very similar to those of the oxatriazoliumaminides (9). The spectrum of the diphenyl derivative (11a) is shown in Figure 2. The strong molecular ion (16) (Scheme 1) fragments *via* pathway C giving the daughter ion (19; X = S) which loses nitrogen giving the ion R^1S^+. This fragmentation sequence ($M^{\cdot+} \longrightarrow R^1N=\overset{+}{N}=S \longrightarrow R^1S^+$) is fully supported by the observation of strong metastable ions in the mass spectra of compounds (11a—f). Fragmentation by pathway A giving the ion $R^1N{=}N{\cdot}C{\equiv}\overset{+}{N}R^2$ (Scheme 1) does not occur and only in one case, compound (11f), was an aryl thiocyanate radical cation (20; X = S, Y = NPh) formed *via* pathway D observed. The most intense ion in the spectra is the aryl cation R^{1+}.

Like the mass spectra of the tetrazoliumolates (10), the mass spectra of the tetrazoliumthiolates (12a—e) (Table 4) are extremely simple. The spectrum of the diphenyl derivative (12a) is typical. The molecular ion (16) (Scheme 1) is strong and does not appear to undergo fragmentation by pathways A, C, or D. Fragmentation by pathway B gives a moderately strong arenediazonium ion ($R^2\overset{+}{N}\equiv N$) which loses nitrogen giving the aryl cation R^{2+}. The latter is the base peak.

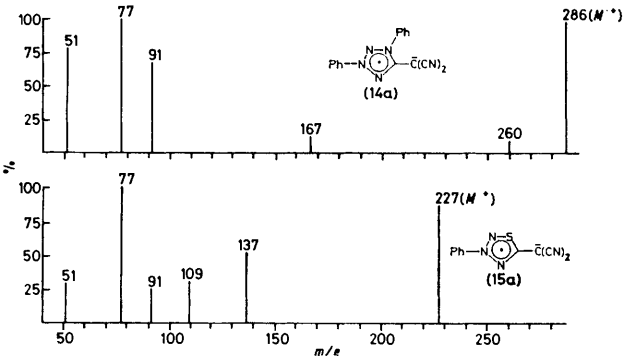


FIGURE 3 Comparison of the mass spectra of two meso-ionic compounds [Table 5, compounds (14a) and (15a)]

TABLE 4

Relative intensities (%) of the principal ions in the mass spectra of the meso-ionic 1,2,3,4-thiatriazolium-5-aminides (11) and 1,2,3,4-tetrazolium-5-thiolates (12)

Cpd	R^1	R^2	$M^{\cdot+}$	$R^1N=\overset{+}{N}=S$	$R^2\dot{\overset{+}{N}}=C=S$	$R^1\overset{+}{N}\equiv N$	R^{1+}	R^{2+}	R^1S^+
(11a)	Ph	Ph	78	29	–	5	100		18
(11b)	Ph	*p*-MeC_6H_4	72	30	–	10	100	9	18
(11c)	Ph	*p*-ClC_6H_4	32	26	–	5	100	2	18
(11d)	*p*-MeC_6H_4	Ph	37	12	–	2	100	–	5
(11e)	*p*-MeC_6H_4	*p*-MeC_6H_4	39	20	–	3	100		9
(11f)	*p*ClC_6H_4	Ph	22	12	7	12	100	–	5

			$M^{\cdot+}$	$R^1N=\overset{+}{N}=NR^2$	$R^2\dot{\overset{+}{N}}=C=C$	$R^1\overset{+}{N}\equiv N$	$R^2\overset{+}{N}\equiv N$	R^{1+}	R^{2+}
(12a)	Ph	Ph	43	–	–	36		100	
(12b)	Ph	*p*-ClC_6H_4	38	–	–	14	54	42	100
(12c)	*p*-MeC_6H_4	*p*-MeC_6H_4	21	–	–	24		100	
(12d)	*p*-ClC_6H_4	Ph	18	–	–	2	33	10	100
(12e)	*p*-ClC_6H_4	*p*-ClC_6H_4	33	–	–	40		100	

The Mass Spectra of 1,2,3,4-*Tetrazolium-5-dicyanomethylides* (14) *and* 1,2,3,4-*Thiatriazolium-5-dicyanomethylides* (15).—The mass spectra of the meso-ionic tetrazolium dicyanomethylides (14a and b) (Table 5),

TABLE 5

Relative intensities (%) of the principal ions in the mass spectra of the meso-ionic 1,2,3,4-tetrazolium-5-dicyanomethylides (14) and 1,2,3,4-thiatriazolium-5-dicyanomethylides (15)

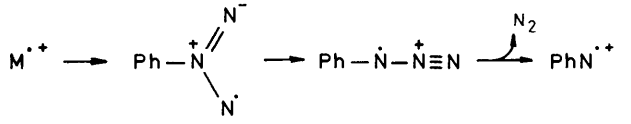
Cpd.	R	$M^{\cdot+}$	$M^{\cdot+}-CN$	RN^+	$R\dot{\overset{+}{N}}=C=C(CN)_2$	RS^+
(14a)	Ph	85	8	60	10	100
(14b)	*p*-MeC_6H_4	100	6	29	–	65

		$M^{\cdot+}$	$M^{\cdot+}-CN$	RN^+	$RN=\overset{+}{N}=S$	RS^+	R^+
(15a)	Ph	94	–	25	56	31	100
(15b)	*p*-MeC_6H_4	60	–	–	–	–	100

show a strong molecular ion, but its fragmentation into daughter ions is not easy to rationalise in terms of the pathways shown in Scheme 1. The spectrum of the diphenyl derivative (14a) is shown in Figure 3. The

molecular ion loses a nitrile radical giving a weak daughter ion and some fragmentation *via* pathway D does occur. A strong fragment ion corresponding to the constitution RN^+ is observed and this may well be formed directly from the molecular ion.

The spectra of two meso-ionic thiatriazolium dicyanomethylides (15a and b) (Table 5) have been recorded and that of the phenyl derivative (15a) is shown in Figure 3.



SCHEME 2

The intense molecular ion fragments *via* pathway C (Scheme 1) giving the ion (19; X = S) which undergoes further fragmentation to the ion (22; X = S). An ion corresponding to the structure RN^+ is observed. This may well be formed by loss of nitrogen from a phenyl azide radical cation (Scheme 2)1

The analysis of the mass spectra of 45 compounds belonging to ten meso-ionic systems presented in this paper is excellently correlatable to the general modes of fragmentation proposed earlier for nine different meso-ionic systems. This is very reassuring support for the general features of mass spectral fragmentation proposed earlier.[2] The usefulness of mass spectrometry to distinguish between pairs of meso-ionic isomers [7] is clearly demonstrated and its application for differentiation between other pairs of isomers of either meso-ionic or traditional heterocycles may be equally rewarding.

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.

[6/1148 *Received*, 15*th June*, 1976]

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