Mass Spectra of Some 1,2,4-Triazole Derivatives (1)

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Fragmentation of various 1,2,4-triazole derivatives occurs by two predominant pathways involving the loss of RCN originating from both C_3 and C_5 positions. The resulting diazirinium radical cation was observed to lose a nitrogen atom to give a nitrilium ion whose substitution pattern was dependent upon the original substituents in the nucleus.

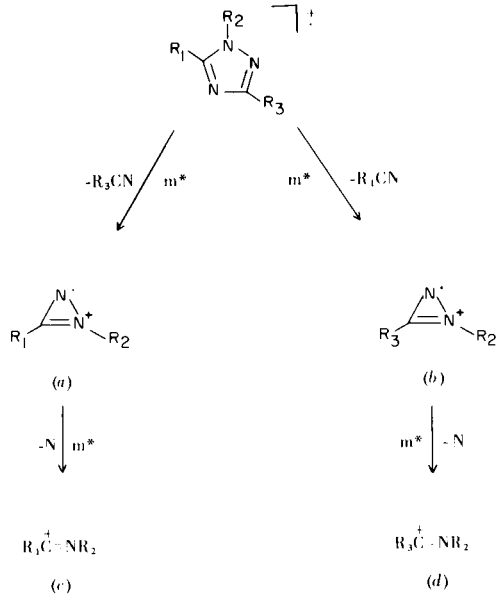
In recent years the mass spectra of numerous nitrogen containing five-membered heterocyclic ring systems have been studied (2-10) and their mass spectral fragmentation patterns established. A report (11) describing energetic metastable transitions in the mass spectrum of *s*-triazole itself indicated that this system was worthy of further study, and the availability of a representative series of derivatives of *s*-triazole prompted the investigation reported below. Other studies describing the fragmentation of 3-amino- and 4-amino-*s*-triazole (12a), as well as a series of *s*-triazolines (12b) and *s*-triazole-4-*N*-oxides (12c) have also been made. These collective data now provide a complete description of the fragmentation patterns of this ring system.

In the earlier study (11) of the mass spectrum of *s*-triazole, it was shown that the molecular ion lost HCN giving a major fragment ion, m/e 42. The spectrum was noticeable for the presence of two flat-topped metastable ions at m/e 24.4 and 18.7, corresponding to the transitions 69 → 41 + 28 and 42 → 28 + 14, respectively. These energetic metastable decompositions indicate the elimination of a small, stable molecule or radical and, with *s*-triazole, the transition 42 → 28 + 14 was shown to involve the loss of a nitrogen atom.

The spectra of the *s*-triazole derivatives I-XVII were very simple (Table I). In all those spectra showing an ion m/e 42, the characteristic flat-topped metastable ion at m/e 18.7 was present and these compounds were always unsubstituted at either the 3- or 5-position of the nucleus. A general fragmentation pattern (Scheme 1) may be written for the majority of the compounds studied, the major exceptions being those compounds with a 3-mercapto or a 3-methylthio substituent, together with 4-amino-3,5-diphenyl-*s*-triazole. Similar fragmentations were observed with the *s*-triazole-4-*N*-oxides after oxygen was eliminated from the molecular ion (12c).

It is particularly interesting that in all the *C*-methyl substituted compounds studied no $[M\text{-}1]^+$ ion was observed. This has also been reported with 3-methylthiazole (13) and is in direct contrast to the behavior of *C*-methyl substituted pyrroles (14), furans (15), thiophens (16), pyrazoles (6) and isothiazoles (17). However, with 3-benzyl- and 3-benzyl-5-methyl-*s*-triazoles, a hydrogen atom is readily lost and $[M\text{-}1]^+$ ions are formed with relative intensities of 83% and 92%, respectively (12c).

SCHEME I



In *s*-triazole itself an $[M\text{-}28]^+$ ion was attributed to the loss of N_2, but in the other compounds studied, only in 3,5-diphenyl-*s*-triazole was any appreciable loss of N_2 detected. In ring-fused *s*-triazole derivatives, such as *s*-

TABLE I

Mass Spectral Data for Derivatives of Some *s*-Triazoles

Compound Number	Substituents R_1	R_2	R_3																	
I	H	H	H	m/e	69	42	41	28												
				Rel. Int.	100	55	18	40												
II	H	H	Cl	m/e	105	103	78	76	48	47	42	41	40							
				Rel. Int.	25	78	12	42	10	12	100	10	8							
III	CH_3	H	Cl	m/e	119	117	78	76	62	56	54	42	41	40						
				Rel. Int.	24	78	10	32	14	64	18	100	22	12						
IV	H	H	Br	m/e	149	147	122	120	81	79	42									
				Rel. Int.	95	95	25	25	25	25	100									
V	CH_3	H	Br	m/e	163	161	122	120	56	42										
				Rel. Int.	24	24	10	10	100	60										
VI	H	H	NH_2	m/e	84	57	43	42	41											
				Rel. Int.	100	40	22	20	20											
VII	CH_3	H	NH_2	m/e	98	84	60	57	56	45	43	42	41	40						
				Rel. Int.	100	10	13	60	27	27	57	61	19	10						
VIII	Ph	NH_2	Ph	m/e	236	133	105	104	103	91	89	77	76	63	51	39				
				Rel. Int.	40	13	13	100	10	13	13	75	13	14	23	14				
IX	H	H	SH	m/e	101	74	69	43	42	41										
				Rel. Int.	100	22	40	12	45	8										
X	CH_3	H	SH	m/e	115	83	74	60	59	58	57	56	55	45	42					
				Rel. Int.	100	5	16	5	10	5	15	75	10	10	40					
XI	Ph	H	SH	m/e	177	145	119	118	104	103	91	77	76	74	63	51	39			
				Rel. Int.	100	11	14	47	38	21	25	32	13	10	10	21	10			
XII	H	H	SCH_3	m/e	115	114	88	83	82	76	74	73	71	70	59	58	47	46	45	44	43	42
				Rel. Int.	100	70	13	8	42	10	65	11	11	75	9	10	8	9	17	10	16	29
XIII	CH_3	H	SCH_3	m/e	129	128	115	114	96	88	84	74	73	59	58	56	45	43	42			
				Rel. Int.	26	11	10	7	11	32	45	17	12	10	15	100	14	14	27			
XIV	H	H	CH_3	m/e	83	56	42													
				Rel. Int.	95	40	100													
XV	H	H	Ph	m/e	145	118	104	91	77	63	51	42	39							
				Rel. Int.	100	23	48	15	20	13	10	15	10							
XVI	Ph	H	Ph	m/e	221	193	118	91	89	77	63	51	39							
				Rel. Int.	100	5	95	30	20	22	14	11	10							
XVII	H	Ph	Ph	m/e	221	194	91	77	64	51										
				Rel. Int.	85	19	100	11	21	9										

TABLE II

Metastable Ions Present in the Mass Spectra of Some *s*-Triazoles

Substituents			Compound	Transition	Calculated	Found	Fragment
R_1	R_2	R_3	Number		m*	m*	Expelled
H	H	H	I	42 → 28	18.7	19.0	N
H	H	Cl	II	103 → 76	56.1	56.0	HCN
H	H	Br	IV	147 → 120	98.0	98.0	HCN
				147 → 79	42.1	42.0	$C_2H_2N_3$
CH_3	H	Br	V	161 → 120	89.5	89.5	CH_3CN
H	H	NH_2	VI	84 → 57	37.8	37.8	HCN
CH_3	H	NH_2	VII	98 → 57	33.2	33.2	CH_3CN
				98 → 56	32.2	32.5	NH_2CN
Ph	NH_2	Ph	VIII	236 → 133	75.0	75.0	PhCN
				236 → 104	45.8	46.0	$C_7H_6N_3$
				236 → 103	44.7	45.0	$C_7H_7N_3$
				104 → 77	57.0	57.0	HCN
H	H	SH	IX	101 → 74	54.1	54.2	HCN
				101 → 43	18.3	18.3	SCN
				69 → 42	25.6	26.0	HCN
CH_3	H	SH	X	115 → 74	47.6	47.7	CH_3CN
				115 → 57	28.4	28.5	SCN
Ph	H	SH	XI	177 → 145	119.0	119.5	S
				177 → 119	80.0	80.0	SCN
				177 → 118	78.8	79.0	SHCN
				177 → 74	31.0	31.0	PhCN
				145 → 118	96.0	96.0	HCN
H	H	SCH_3	XII	115 → 114	113.0	113.0	H
				115 → 88	67.3	67.5	HCN
				115 → 82	58.3	58.0	SH
				115 → 70	42.5	42.5	SCH
CH_3	H	SCH_3	XIII	129 → 128	127.0	127.0	H
H	H	CH_3	XIV	83 → 56	37.8	38.0	HCN
H	H	Ph	XV	145 → 118	96.0	96.0	HCN
Ph	H	Ph	XVI	221 → 193	168.5	168.5	N_2
				221 → 118	63.0	63.0	PhCN
H	Ph	Ph	XVII	221 → 194	170.2	170.5	HCN

triazolo[4,3-*a*]pyridine (18a) and *s*-triazolo[4,3-*a*]pyrazine (18b), this loss of N_2 was also observed only in the parent members of the ring systems. In the corresponding 3-alkyl derivatives, the fragmentation was dominated by the initial loss of RCN from the molecular ion. However, the *s*-triazole-4-*N*-oxides have been reported (12c) to lose N_2, this being a minor fragmentation pathway of the molecular ion. These authors found that the loss of N_2 depended markedly on the inlet temperature utilized.

The *s*-triazole derivatives I-XVII all showed molecular ions, in many instances the most intense ion in the spectrum, reflecting the stability of this heteroaromatic system (19). In 3-chloro-*s*-triazole (compound II) loss of ClCN and HCN occurred, the former being the predominant fragmentation. Introduction of a 5-methyl substituent (compound III) did not alter the fragmentation pattern. Loss of a nitrogen atom from the ion, m/e 56 (*a*, Scheme 1) (20) gave m/e 42 (*c*, Scheme 1) and, similarly, loss of a nitrogen atom from m/e 76 (*b*, Scheme 1) (20) gave m/e 62 (*d*, Scheme 1). Replacement of the 3-chloro substituent with bromine (compounds IV and V) did not effect the above pattern. The $^{79}Br:^{81}Br \cong 1:1$, and the $^{37}Cl:^{35}Cl \cong 1:3$ isotope abundances were clearly evident in the respective fragment ions. However, with a 5-phenyl or a 5-benzyl substituent, the 3-bromo-*s*-triazoles show a much more diverse fragmentation pattern (12c). In addition to the loss of RCN, the molecular ion loses N_2 as well as the elements of BrCN which, in these cases, are lost in a two-

step process involving first elimination of Br· followed by CN·.

In 3-amino- and 3-amino-5-methyl-*s*-triazole (compounds VI and VII) an electron donating group has replaced the electron withdrawing halogen substituent. Though this did not effect the fragmentation pattern, it did have a significant effect on the relative intensities of the $[M\text{-}R_1CN]^+$ and $[M\text{-}NH_2CN]^+$ ions in that the former was now the more abundant ion. No fragmentation indicating the elimination of an NH_2 radical was observed.

Variation from the general fragmentation pattern (Scheme 1) was observed with an *N*-amino compound, 4-amino-3,5-diphenyl-*s*-triazole (compound VIII). In addition to the loss of PhCN from the molecular ion, it was observed to lose $C_7H_6N_3$ yielding m/e 104, most likely the protonated benzonitrilium ion, which then lost HCN. The molecular ion also lost $C_7H_7N_3$ giving m/e 103, in this case the benzonitrilium ion which then lost HCN. These transitions were supported by the appropriate metastable ions (Table II).

s-Triazole-3-thiol (compound IX) and its 3-methyl- (compound X) and 3-phenyl- (compound XI) derivatives followed the general pathway in Scheme 1. In addition, the molecular ions lost S and SCN· giving significant (15-25%) daughter ions (Table I). These fragmentations are analogous to those reported recently for the corresponding ring-fused *s*-triazole derivatives (18) and for the *s*-triazolines (12b) except that for the oxygen containing derivatives an additional fragmentation was observed in which the major portion of the *s*-triazole nucleus was lost.

Conversion of these thiols into their methylthio ethers resulted in several deviations from the general pathway being observed. 3-Methylthio-*s*-triazole (compound XII), in addition to losing HCN and CH_3SCN (Scheme 1) from the molecular ion, gave an $[M\text{-}1]^+$ ion, as well as an $[M\text{-}SH]^+$ ion, the last fragmentation being characteristic of aromatic methylthio ethers (21). The molecular ion also lost HCS·, a process which must have involved migration of the CH_3 group attached to the sulfur atom to the ring nitrogen atom with the concomitant loss of a hydrogen atom, giving an ion m/e 70. This may be represented in terms of a protonated *s*-triazole ion which would be expected to be an extremely stable species. The corresponding 5-methyl-3-methylthio-*s*-triazole (compound XIII) underwent fragmentation by a completely analogous pathway.

3-Methyl- and 3-phenyl-*s*-triazole (compounds XIV and XV) underwent fragmentation in the manner described in Scheme 1. 3,5-Diphenyl-*s*-triazole (compound XVI) lost PhCN from its molecular ion as well as N_2, the ion resulting from the latter decomposition being formed only to the extent of 5%. It has been suggested that the loss of N_2 from *s*-triazole is a symmetry forbidden process (22). This would account for the minor character of the decomposition in this case and for its not being detected in the other compounds studied. 1,3-Diphenyl-*s*-triazole (compound XVII) was only observed to lose HCN from its molecular ion giving ion m/e 194 which then lost PhCN to give m/e 91. This may be represented as an azatropylium ion.

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EXPERIMENTAL

The compounds studied were of analytical purity and were prepared by published procedures (19).

The mass spectra were determined with an Hitachi Perkin-Elmer RMU-6E mass spectrometer operating at an ionizing voltage of 70 eV using the direct insertion probe technique with a source temperature of *ca.* 120°. The indirect inlet was utilized for those compounds with low melting points and high volatility.

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