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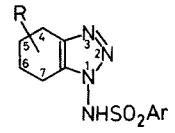
New Mass Spectra

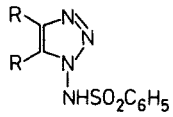
Electron Impact Induced Deamination of 1-Sulphonylamino-1,2,3-triazoles

While there are a number of reports on the mass spectrometry of 1,2,3-triazoles,[1–6] including a detailed study on 1,2,3-triazole itself,[3] very little is known on the mass spectrometric behaviour of derivatives of 1-amino-1,2,3-triazoles.[7]

As part of an investigation on the synthesis of heterocycles from α-diketones we have synthesized several novel 1-sulphonylamino-1,2,3-triazoles by acid-catalysed cyclization[8] of substituted 1,2-cyclohexanedione bis-sulphonylhydrazones.[9] In this paper we wish to report on the behaviour under electron impact (EI) of the fused triazoles **1–7**, obtained by this route, and of compounds **8** and **9** which were obtained by literature methods.[10,11] The mass spectrometric experiments were conducted on a VG 70/70 instrument operating in EI (70 eV, 200 μA); fragmentation pathways were investigated by way of exact mass measurements, *B/E* and B^2/E linked scans.[12] Triazoles **1–7** were analytically pure samples; triazoles **8** and **9** were purified to match the reported physical constants.

Unlike simple 1,2,3-triazoles, the 1-sulphonylamino derivatives **1–9** exhibit molecular ions of low abundance (Table 1), in nearly all cases accompanied by M + 1 ions of comparable relative abundance. The fragmentation of the fused triazoles **1–7** follows two main pathways (Scheme 1 and Table 1). The first (route 1) is initiated by loss of arylsulphonyl radicals, to give the cations *a*; these, in turn, eliminate N_2 giving ions *b* which are abundant in the spectra of all the fused triazoles. While it is likely that ions *b* possess initially either the azirinium structure b_1 or the isomeric structure b_2 with the charge localized on carbon, it appears that other structures also contribute to their fragmentation. Thus the diazonium ion b_3 or the cyclic structure b_4 would appear to be more consistent with the loss of a second nitrogen molecule; b_4 could also account for the observed loss of HCN leading to ions *e*, while the loss of ammonia to give *d* would be better explained by b_5 in which the six-membered ring is fully aromatic.



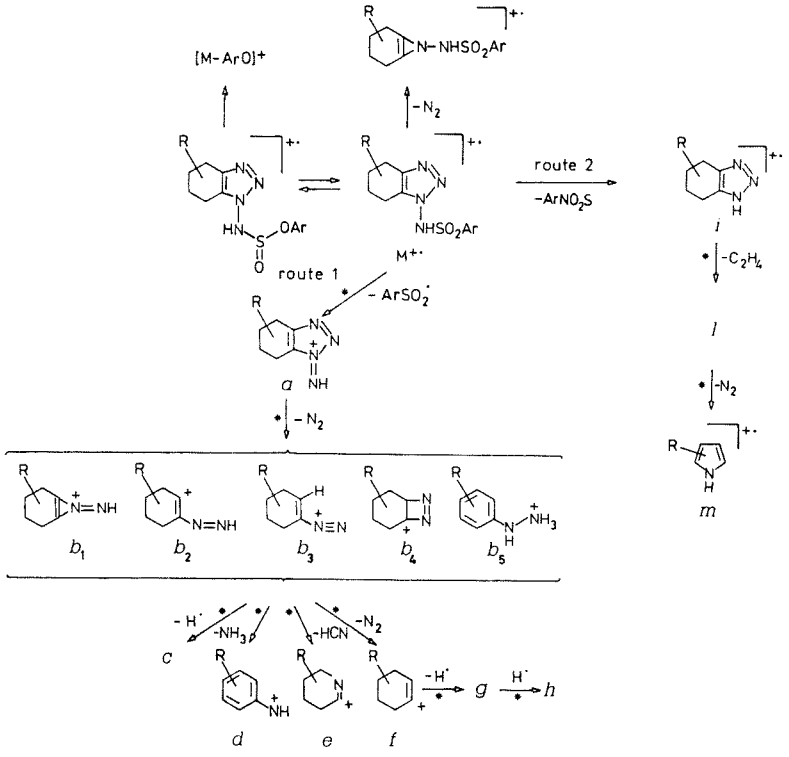


1 R = H; Ar = C_6H_5
2 R = H; Ar = *p*-$CH_3C_6H_4$
3 R = 4-CH_3; Ar = C_6H_5
4 R = 4-CH_3; Ar = *p*-$CH_3C_6H_4$
5 R = 5-CH_3; Ar = C_6H_5
6 R = 5-$C(CH_3)_3$; Ar = C_6H_5
7 R = 6-$C(CH_3)_3$; Ar = C_6H_5
8 R = CH_3
9 R = C_6H_5

The second fragmentation pathway (route 2) corresponds to the formal loss of $ArNO_2S$ fragments, accompanied by hydrogen migration, giving ions *i*. This unusual process corresponds to a formal reductive cleavage of the *N*-sulphonamido moiety, thus leading from the molecular ion of the 1-substituted triazoles to the molecular ion of the parent heterocycles. No metastable peaks were found for the formation of *i*.

Further fragmentation of ions *i* involves a double loss of 28 mass units (Table 1); accurate mass measurements showed that the first process corresponds to the loss of C_2H_4 fragments from the six-membered ring. This is then followed by loss of nitrogen to give ions *m*.

Both these pathways are followed also by triazoles **8** and **9**, although the abundances of some of the fragments along the



Scheme 1

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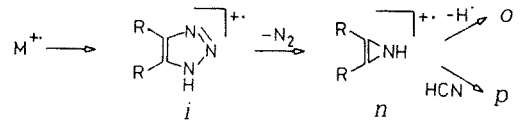
Table 1. 70 eV EI mass spectra of triazoles 1–9

	m/z (%)								
Ion	1	2	3	4	5	6	7	8	9
$[M + H]^+$	279 (2)	293 (3)	293 (0.1)	307 (0.2)	293 (1)		335 (1.4)		
$M^{+\cdot}$	278 (4)	292 (5)	292 (0.2)	306 (0.3)	292 (0.4)	334 (0.4)	334 (1)	252 (0.3)	
$[M - N_2]^{+\cdot}$	250 (3)	264 (2)	264 (0.3)	278 (0.8)	264 (0.4)		306 (0.3)		
$[M - ArO]^+$	185 (0.5)	185 (0.5)	199 (0.1)	199 (0.4)	199 (0.4)	241 (0.3)	241 (0.3)	159 (0.3)	
$a[M - ArSO_2]^+$	137 (6)	137 (5)	151 (0.4)	151 (0.5)	151 (0.9)	193 (0.3)	193 (0.5)	111 (0.5)	
$b[M - ArSO_2 - N_2]^+$	109 (88)	*109 (100)*	*123 (100)*	*123 (100)*	123 (44)	165 (25)	165 (74)	83 (8)	
$c[M - ArSO_2 - N_2 - H]^{+\cdot}$	108 (4)	108 (7)	122 (4)	122 (8)	122 (1)	164 (5)	164 (0.3)		206 (2)
$d[M - ArSO_2 - N_2 - NH_3]^+$	92 (10)	92 (11)	106 (12)	106 (16)	106 (2)	148 (1)	148 (0.5)	66 (4)	
$e[M - ArSO_2 - N_2 - HCN]^+$	82 (21)	82 (21)	96 (13)	96 (15)	96 (4)			56 (12)	
$f[M - ArSO_2 - 2N_2]^+$	*81 (100)*	81 (92)	95 (53)	95 (60)	95 (23)	137 (3)	137 (3)	55 (5)	*178 (100)*
$g[M - ArSO_2 - 2N_2 - H]^{+\cdot}$	80 (16)	80 (24)	94 (9)	94 (14)	94 (7)	136 (2)	136 (1)	54 (18)	177 (7)
$h[M - ArSO_2 - 2N_2 - H_2]^+$	79 (45)	79 (65)	93 (7)	93 (10)	93 (10)	135 (3)	135 (3)	53 (29)	176 (12)
$i[M - ArSO_2N]^{+\cdot}$	123 (1.5)	123 (3)	137 (0.5)	137 (1)	137 (1.5)	179 (6)	179 (3)	97 (15)	221 (63)
$l[M - ArSO_2N - C_2H_4]^{+\cdot}$	95 (13)	95 (13)	109 (4)	109 (5)	109 (9)	151 (4)	151 (5)		
$m[M - ArSO_2N - C_2H_4 - N_2]^{+\cdot}$	67 (27)	67 (27)	81 (31)	81 (35)	*81 (100)*	123 (52)	123 (8)		
$n[M - ArSO_2N - N_2]^{+\cdot}$								69 (2)	193 (11)
$o[M - ArSO_2N - N_2 - H]^+$								68 (70)	192 (17)
$p[M - ArSO_2N - N_2 - HCN]^{+\cdot}$									165 (33)
$ArSO_2NH_2^+$	157 (1)	175 (0.5)	157 (0.5)	171 (1)	157 (1)	157 (12)	157 (8)	157 (7)	157 (17)
$ArSO_2^+$	141 (3)	155 (4)	141 (2)	155 (3)	141 (2)	141 (13)	141 (2)	141 (9)	141 (10)
$ArSOH^{+\cdot}$	126 (16)	140 (32)	126 (5)	140 (10)	126 (10)	126 (10)	126 (11)	126 (4)	126 (4)
$ArSO^+$	125 (11)	139 (39)	125 (4)	139 (14)	125 (6)	125 (11)	125 (5)	125 (8)	125 (4)
Ar^+	77 (58)	91 (59)	77 (53)	91 (50)	77 (44)	*77 (100)*	77 (45)	*77 (100)*	77 (72)

Table 2. Relative percentage of routes 1 (fragments *a–h*) and 2 (fragments *i–p*)

Triazole	Route 1	Route 2
1	89	11
2	88	12
3	85	15
4	84	16
5	45	55
6	39	61
7	84	16
8	49	51
9	49	51

two routes are rather different (Table 1). This is particularly evident in the fragmentation of the diphenyl derivative **9**: route 1 is channelled through the double loss of N_2 which leads to ions *f*, while the precursors *a* and *b* and the alternative products *d* and *e* are absent. Both **8** and **9** give strong peaks for the formation of the 1*H*-1,2,3-triazole molecular ions *i* by the deamination process corresponding to route 2 (Scheme 2); the fragmentation of this species, in agreement with the behaviour of 1*H*-1,2,3-triazoles,[1–6] is diverted towards the loss of N_2, giving ions *n* followed by loss of hydrogen and of HCN.



Scheme 2

In addition to these major routes other fragmentation pathways found for triazoles **1–7** correspond to the loss of aryloxy radicals, following a sulphone–sulphinate rearrangement with aryl migration on oxygen (Scheme 1) and the loss of N_2 from the molecular ion which is characteristic of triazoles, being in general the first step in their fragmentation. The presence of the sulphonamido group is to be correlated with the fragments $ArSO_2NH_2^+$, $ArSO_2^+$, $ArSOH^{+\cdot}$, $ArSO^+$ and Ar^+.

Finally, in Table 2 are reported the relative percentages of all the ionic fragments corresponding to route 1 (*a–h*) and to route 2 (*i–p*); these values, which have been calculated neglecting all other minor fragmentations, represent the distributions between the two pathways for each compound. The data follow a well-defined trend: for the fused compounds **1–4** and **7** route 1 represents more than 80% of the whole fragmentation; for triazoles **5** and **6**, both substituted at the 5 position, route 2 is preferred over route 1; for triazoles **8** and **9** both routes equally contribute to the fragmentation. It thus appears that the distribution between the two pathways can be well correlated to the structure of the triazole; in particular, in the series of 1-sulphonylamino triazoles examined, the preference for the deamination corresponding to route 2 is diagnostic of substitution at the 5 position.

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