Mass Spectra I. Mass Spectra of 1,2,4-Thiadiazoles

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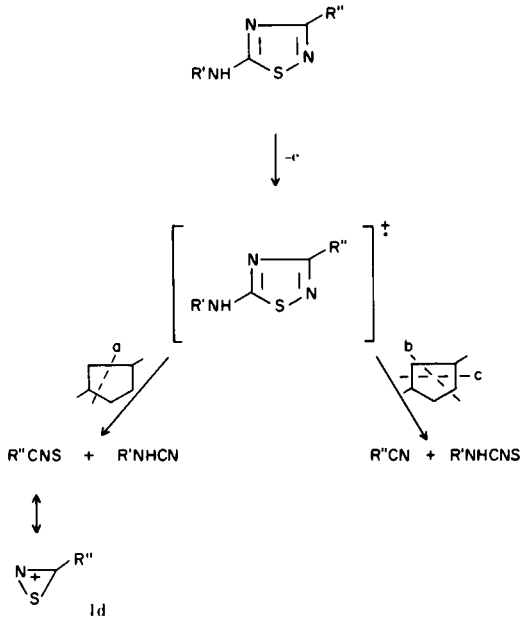
While a number of investigations concerning the mass spectra of thiophenes (1,2), pyrroles (3,4), furans (5,6), and more limited studies of imidazoles (9), thiazoles (8) and isothiazoles (9,10) have been reported, little information pertaining to the related 1,2,4-thiadiazoles has appeared. For some time we have been concerned with the chemical properties of a number of compounds containing the 1,2,4-thiadiazole ring system. This interest coupled with the lack of available information about their mass spectral properties prompted us to initiate an investigation of their dissociation behavior upon electron impact. This paper gives details of the low resolution mass spectra (Table I) and high resolution mass spectra (Table II) of variously 3-substituted 5-amino-1,2,4-thiadiazoles and discusses possible fragmentation pathways.

The fragmentation patterns of the examined 5-amino-1,2,4-thiadiazoles are quite consistent. All compounds exhibited intense parent ions. Fragmentation of the parent ion (Scheme I) occured *via* loss of fragments corresponding to R'NHCN (path a) and R''CN (path b or c) with major retention of charge by the sulfur containing fragments. Compounds having aliphatic side chains > CH_3 displayed substantial decomposition of the parent ion *via* loss of methyl or ethyl groups. Three compounds I, III and VI, exhibited metastable transitions corresponding to ejection of alkyl or alkyl CN groups.

The mass spectrum of 3-methyl-5-amino-1,2,4-thiadiazole (I) exhibited a strong molecular ion m/e 115 (base peak) and strong ion fragments formed *via* breakdown of the heterocyclic ring. Ions corresponding to the loss of a proton (m/e 114), methyl group (m/e 100), sulfur (m/e 83) or amino group (m/e 99) were not significant. Cleavage of I across the 3,4 and 1,5 bonds (path a), analogous to the 1,2 and 3,4 bond fragmentation reported in the mass spectra of thiazoles (8), gave rise to a major ion fragment appearing at m/e 73 and a somewhat weaker peak at m/e 42. Although the structure of the m/e 73 fragment is not known a nominal structure the thiazirine cation (1d), has been postulated.

Decomposition of I *via* cleavage across the 1,2 and 3,4 bonds (path b) or across the 2,3 and 4,5 bonds (path c) would account for the strong peak at m/e 74 and a weak peak at m/e 41. The metastable ion, appearing at m/e 47.65

SCHEME I



(Table II) results from the transition 115 → 74 + 41 and lends support for either path b or c as one of the fundamental fragmentation routes. The higher abundance of the m/e 73 and 74 ions versus the m/e 42 and 41 ions can be attributed to the major retention of charge by sulfur containing fragments. Similarly the approximate equal abundance of the m/e 73 and 74 ions indicates that there is no preference of one path over another.

The low resolution mass spectrum of 3-phenyl-5-amino-1,2,4-thiadiazole (II) exhibited a strong parent ion at m/e 177 and a base ion m/e 135 (ϕCNS) arising from cleavage along path a. Significantly weaker ions m/e 103 (ϕCN) and m/e 74 (CH_2N_2S) were identified as arising *via* path b or c.

As was expected 3-*n*-propyl-5-amino-1,2,4-thiadiazole (III) and 3-isopropyl-5-amino 1,2,4-thiadiazole (IV) provided mass spectra that were more complex than those of either I or II. The base peaks appearing at m/e 115 (P-C_2H_4) and at m/e 128 (P-CH_3) respectively arise from cleavage of the side chains of the appropriate molecular

TABLE I

Mass Spectra of 5-Amino-1,2,4-thiadiazoles

All peaks greater than 5% of the base peak (100%) and peaks due to rearrangements and metastable transition less than this value are recorded.

I 3-Methyl-5-amino-1,2,4-thiadiazole

m/e	26	29	28	29	32	33	38	39	40
I (%)	5	21	13	3	10	7	10	14	9
m/e	41	42	43	44	45	46	47	53	58
I (%)	9	20	22	5	26	19	50	10	9
m/e	59	60	72	73	74	75	76	86	115
I (%)	10	28	15	90	95	25	13	8	100
m/e	116	117							
I (%)	22	15							

II 3-Phenyl-5-amino-1,2,4-thiadiazole

m/e	47	51	74	76	77	91	103	104	108	135
I (%)	3	2	8	4	11	5	20	7	3	100
m/e	136	137	177							
I (%)	11	6	80							

III 3-Propyl-5-amino-1,2,4-thiadiazole

m/e	27	41	42	43	45	46	47	55
I (%)	31	33	10	24	14	17	8	9
m/e	59	60	70	72	73	74	75	86
I (%)	20	33	13	27	66	56	24	17
m/e	100	101	115	116	117	128	142	143
I (%)	14	49	100	18	15	82	18	75

IV 3-Isopropyl-5-amino-1,2,4-thiadiazole

m/e	41	42	43	46	59	68	70	74
I (%)	8	4	10	5	5	7	6	25
m/e	86	100	101	115	128	129	130	
I (%)	15	13	10	11	100	8	5	
m/e	143	144	145					
I (%)	78	13	5					

V 3-Benzyl-5-amino-1,2,4-thiadiazole

m/e	39	42	51	63	74	77	89	70	91
I (%)	5	3	5	5	8	5	5	6	57
m/e	92	116	117	118	121	132	148		
I (%)	6	42	21	6	4	13	4		
m/e	149	190	191	192	193				
I (%)	22	19	100	11	5				

TABLE I (Continued)

VI 3-Propyl-5-methylamino-1,2,4-thiadiazole

m/e	27	41	42	46	57	72
I (%)	6	6	4	4	9	6
m/e	73	74	88	89	101	129
I (%)	16	6	40	8	8	100
m/e	142	157				
I (%)	18	24				

TABLE II

High Resolution Studies of 5-Amino-1,2,4-thiadiazoles

Mass Measurements on Compound I R′-H R″=CH_3

Measured Mass	Formula	Theoretical	Proposed Structure
115.0196	$C_3H_5N_3S$	115.0205	Parent ion (P)
73.9940	CH_2N_2S	73.9939	P-(CN-CH_3)
72.9982	C_2H_3NS	72.9982	P-(NH_2-CN)
59.9914 (large)	CH_2NS	59.9908	P-(NC-CH_3-N)
59.9676 (small)	COS	59.9670	Impurity or oxidation product
46.9828	NSH	46.9830	
45.9752	NS	45.9752	
45.9884 (large)	CH_2S	45.9877	
42.0225 (medium)	CH_2N_2	42.0218	(NH_2-CN)
42.0344 (large)	C_2H_4N	42.0344	
41.9880 (small)	CON	41.9880	Impurity
41.0264	C_2H_3N	41.0265	(CN-CH_3)

Metastable Ions

47.65 ± 0.05:
($73.9940^2/115.0196 = 47.60$) $C_3H_5N_3S^+ \rightarrow CH_2N_2S^+ + CNCH_3$

Mass Measurements on Compound III R′=H R″=C_3H_7

143.0512	$C_5H_9N_3S$	143.0517	Parent (P)
115.0185	$C_3H_5N_3S$	115.0205	P-(C_2H_4)
101.0040 (small)	$C_2H_3N_3S$	101.0048	P-(C_3H_6)
101.0280 (large)	C_4H_7NS	101.0299	P-(NH_2-CN)
74.0196 (small)	C_3H_6S	74.0190	
73.9941 (large)	CH_2N_2S	73.9939	P-(CN-CH_2-CH_2-CH_3)
42.0464 (medium)	C_3H_6	42.0469	(C_3H_6)
42.0331 (medium)	C_2H_4N	42.0344	
42.0211 (largest)	CH_2N_2	42.0218	(NH_2-CN)
41.3880 (small)	CON	41.9880	
41.0271 (medium)	C_2H_3N	41.0265	
41.0394 (large)	C_3H_5	41.0391	(C_3H_5)

TABLE II (Continued)

Metastable Ions

92.43 ± 0.05: $C_5H_9N_3S \rightarrow C_3H_5N_3S^+ + C_2H_4$ $\left(\frac{115.0205^2}{143.0517} = 92.48\right)$

52.75 ± 0.05: $C_4H_7NS^+ \rightarrow C_2H_3NS^+ + C_2H_4$ $\left(\frac{72.9982^2}{101.0280} = 52.72\right)$

Mass Measurements on Compound VI $R'=CH_3$ $R''=C_3H_7$

157.0657	$C_6H_{11}N_3S$	157.0674	Parent (P)
129.0354	$C_4H_7N_3S$	129.0361	P-(CH_2-CH_2)
101.0278	C_4H_7NS	101.0299	P-(CH_3NH-CN)
88.0092	$C_2H_4N_2S$	88.0095	P-(CH-CH_2-CH_2-CH_3)
56.0510	C_3H_6N	56.0500	
56.0360	$C_2H_4N_2$	56.0374	(CH_3-NH-CN)

Metastable Ions

106.00 ± 0.05: $C_6H_{11}N_3S^+ \rightarrow C_4H_7N_3S^+ + C_2H_4$ $\left(\frac{129.0361^2}{157.0674} = 106.00\right)$

61.34 ± 0.05: $C_4H_7N_3S^+ \rightarrow C_2H_5N_2S^+ + C_2H_2N$ $\left(\frac{89.0170^2}{129.0354} = 61.40\right)$

52.72 ± 0.05: $C_4H_7NS^+ \rightarrow C_2H_3NS^+ + C_2H_4$ $\left(\frac{72.9982^2}{101.0278} = 52.72\right)$

ion. Fragmentation by path a for III and IV was supported by the appearance of fragments at m/e 101 (C_4H_7NS) and at m/e 42 (CH_2N_2). While ions having m/e 74 for both III and IV indicated cleavage along path b or c neither gave the corresponding m/e 69 (RCN) fragment.

The metastable ions m/e 52.75 and m/e 92.43 result respectively from the decomposition of the m/e 101 ion and of the parent ion by loss of C_2H_4.

The mass spectrum of 3-benzyl-5-amino-1,2,4-thiadiazole (V) was unexceptional showing a strong parent molecular ion m/e 191 (base peak) and the usually strong tropylium cation m/e 91. Dissociation *via* paths a and b was supported by moderate ion peaks m/e 149 and m/e 117 respectively.

3-*n*-Propyl-5-methylamino-1,2,4-thiadiazole (VI) like that of III and IV displayed side chain cleavage as the principal mode of decay giving rise to fragments m/e 129 (p-C_2H_4) and m/e 148 (p-CH_3). The latter ion is analogous to the m/e 128 fragment observed in the spectra of III and may be stabilized as a ring expanded aminodihydrothiadiazepine cation. Cleavage of the parent ion m/e 157 *via* path a and path b (or c) leads to ions having m/e 101 and m/e 88 respectively. The high resolution spectra of VI displayed three fragments having m/e 106.00 m/e 52.72 and m/e 61.40 corresponding to the metastable transitions; parent ion minus C_2H_4, m/e 101 minus C_2H_4 and m/e 129 minus C_2H_2N.

EXPERIMENTAL

The 5-amino-1,2,4-thiadiazoles (I-VI) were prepared by previously described procedures (11) and were analytically pure.

Medium resolution spectra of all compounds were measured on a CEC 21-110 mass spectrometer using a direct solids introduction system. Source temperature was 50° and the samples were readily vaporized without applying heat to the solids probe. High resolution measurements and metastable ion transitions were recorded using an AEI MS9. Samples for the MS9 were introduced through the standard batch inlet system. All spectra were obtained at 70 ev and the psectra measured on both instruments were in good agreement.

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