

## ***N*-Isothiocyanatoamines**

### **VIII. The Mass Spectra of an *N*-Isothiocyanatodimethylamine Dimer Containing the 1,2,4-Triazole Ring and of Seven Deuterium Labeled Analogs**

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The fragmentation under electron impact of one of the dimers of *N*-isothiocyanatodimethylamine, 4-dimethylamino-1-methyl-3-methylthio-1,2,4-triazol-2-ine-5-thione, has been analyzed with the aid of deuterium labeling and low-voltage spectroscopy. The major fragmentation pattern consists of initial removal of the dimethylamino group followed by degradation of the other substituents attached to the heterocyclic nucleus. The three pathways suggested for fission of the triazole ring system involve rupture both of C-N and of N-N bonds.

In an earlier paper<sup>1</sup> the mass spectrum of *N*-isothiocyanatodiisopropylamine was discussed. Other isothiocyanatoamines show a pronounced tendency to dimerize and supplementary information about the mass spectra of the dimers became necessary before investigations of the monomers could be extended. In paper IV of this series<sup>2</sup> it was shown that the dimerization of *N*-isothiocyanatodimethylamine proceeds *via* a linear dimer to give two crystalline dimers, both of which are triazole derivatives. Preliminary studies of the mass spectra made it clear that the synthesis of a series of isotopically labeled species was necessary to elucidate the observed fragmentation patterns. The more stable of the dimers, 4-dimethylamino-1-methyl-3-methylthio-1,2,4-

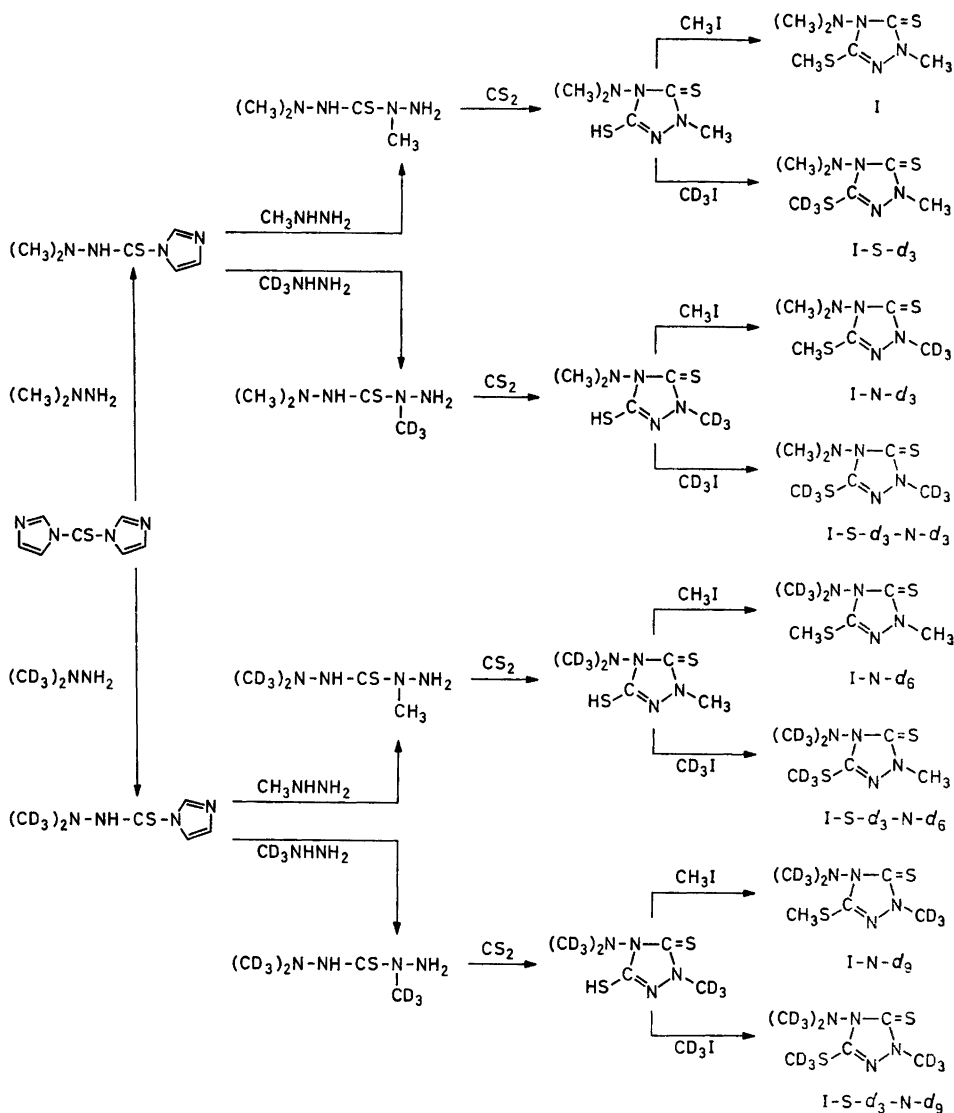


Fig. 1. Synthesis of 4-dimethylamino-1-methyl-3-methylthio-1,2,4-triazol-2-ine-5-thione (I) and its deuterated analogs.

triazol-2-ine-5-thione (I), could be synthesized by an independent route from methylhydrazine and dimethylhydrazine as outlined in Fig. 1. The analogous deuterium-labeled starting materials,  $d_3$ -methylhydrazine and  $d_6$ -1,1-dimethylhydrazine, have been reported in part I<sup>3</sup> of a series of papers concerning derivatives of hydrazine. Their conversion to the deuterated analogs of I is

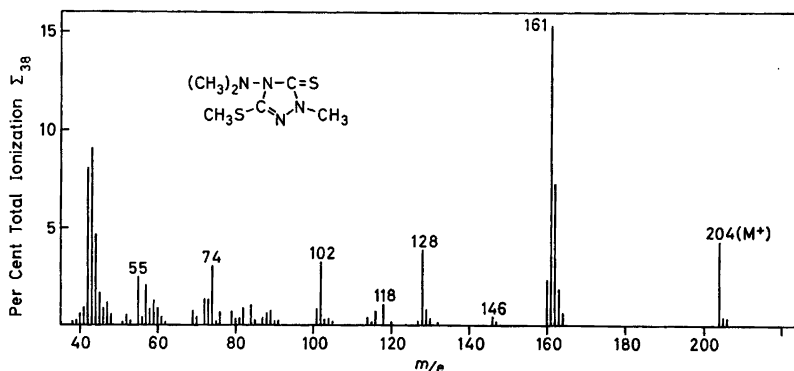


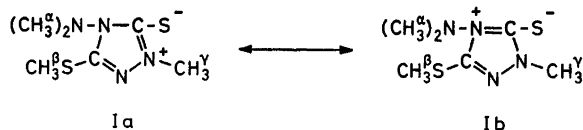
Fig. 2. Mass spectrum of 4-dimethylamino-1-methyl-3-methylthio-1,2,4-triazol-2-ine-5-thione (I).

summarized in Fig. 1. The experimental details of these reactions have been reported earlier<sup>2</sup> and only insignificant changes were necessary to adapt the procedures to a micro scale.

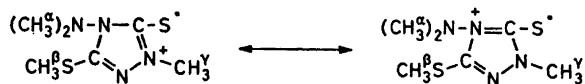
The mass spectrum of the undeuterated species (I), shown in Fig. 2, is representative for the eight compounds investigated. For convenience, each of the groups of peaks will be discussed separately below. Some of these are barely observable on the bar graph, but since they can be consistently explained by considering all eight compounds we feel that they contribute essentially to an understanding of the factors governing the fragmentation of I. All intensities in the tables and in the text are given in per cent  $\Sigma_{38}$  corrected for incomplete deuteration (0.5% per deuterium atom present) and for contributions from higher carbon, nitrogen, and sulfur isotopes. Transitions indicated by asterisks in figures or text are substantiated by the presence of appropriate metastable peaks.

#### THE STRUCTURE OF I AND THE MOLECULAR ION

Chemical and physical evidence supports the view<sup>2,4</sup> that (I) is extensively stabilized by thioureide resonance, *i.e.* by the dipolar structures Ia and Ib.



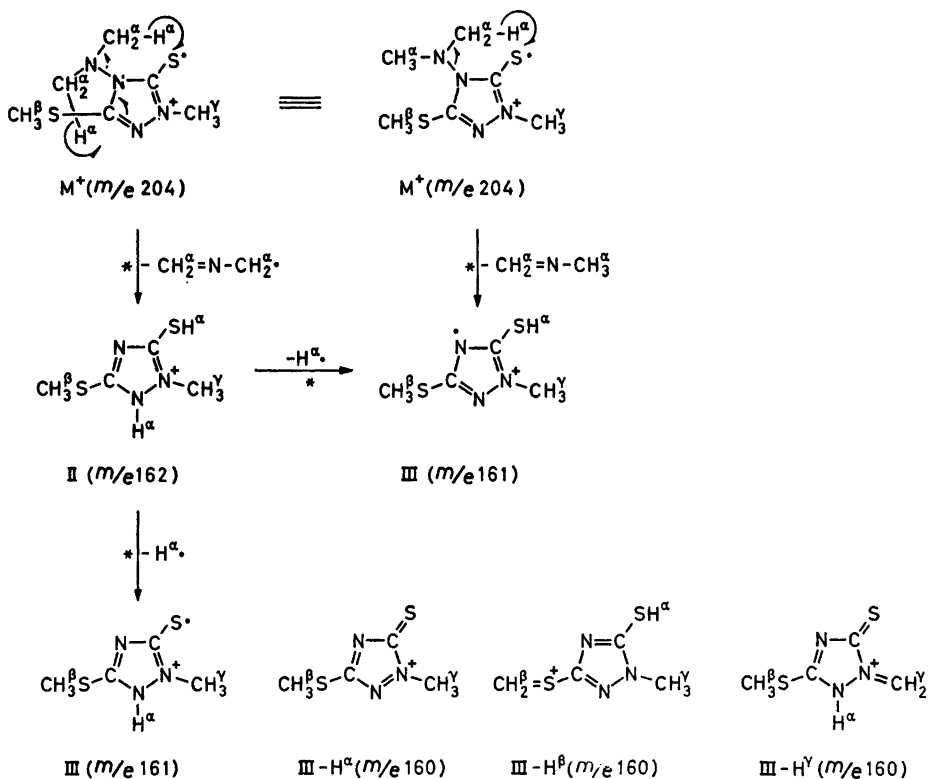
The most useful guide in predicting the structure of the molecular ion seems to be the resemblance to thiourea,<sup>5</sup> which suggests that the primary ionization process results in a molecular ion with the following preferred representations:



Though we are well aware of the dangers inherent in such a formulation it has proved meaningful from the standpoint of rationalizing the complicated fragmentation pattern of (I). With no better choice at hand it was therefore adopted in drawing Schemes 1—7. The hydrogen atoms have been labeled  $\text{H}^\alpha$ ,  $\text{H}^\beta$  and  $\text{H}^\gamma$  in order to facilitate their identification in the fragments.

### The peak group $m/e$ 160—170

The only adequate mechanistic rationalization of the results (Table 1) is set out in Scheme 1. In accordance with expectation the molecular ion,  $\text{M}^+$ , is of appreciable intensity (4—5 %). The base peak corresponding to the formulae III is generated from  $\text{M}^+$  exclusively by two pathways: a hydrogen rearrangement involving transfer of one  $\text{H}^\alpha$  from the dimethylamino group to



Scheme 1. Formation of the peak cluster in the range  $m/e$  160—170 from the molecular ion. (Values for  $m/e$  refer to the undeuterated species).

Table 1. Intensities \* exceeding 8.2% ( $\sum_{160}^{385}$ ) in the range  $m/e$  160–170 in the mass spectra of I and its deuterated species. The last five columns show the percentage contributions ( $\sum_{160}^{170}$ ) of the fragments (Scheme 1) to this region. (Figures in parentheses are combined values for two or more fragments).

	160	161	162	163	164	165	166	167	168	170	II	III	III-H $\beta$	III-H $\alpha$	III-H'
I	2.33	15.24	6.01								25.5	64.6	(9.9)	(9.9)	(9.9)
I-S-d <sub>3</sub>			0.81	1.92	16.15	6.51					25.6	63.6	3.2 <sup>a</sup>	(7.6)	(7.6)
I-N-d <sub>3</sub>			0.88	1.49	16.00	6.27					25.4	64.9	(6.0)	(6.0)	3.6 <sup>a</sup>
I-S-d <sub>3</sub> -N-d <sub>2</sub>						2.17	0.21	16.39	6.50		25.7	64.9	(8.6)	0.8 <sup>b</sup>	(8.6)
I-N-d <sub>4</sub>	0.32	2.45	17.16		5.88						22.8	66.5	(9.5)	1.2 <sup>a</sup>	(9.5)
I-S-d <sub>3</sub> -N-d <sub>4</sub>				1.19	1.85	17.21		5.97			22.8	65.6	(4.5)	(4.5)	7.1 <sup>b</sup>
I-N-d <sub>5</sub>				0.99	1.73	17.01		5.99			23.3	66.1	6.7 <sup>b</sup>	(3.8)	(3.8)
I-S-d <sub>3</sub> -N-d <sub>5</sub>						2.07	17.04	5.90			23.6	68.1	(8.3)	(8.3)	(8.3)

\* All values are corrected for incomplete deuteration and for contamination with <sup>13</sup>C, <sup>15</sup>N, <sup>33</sup>S, and <sup>34</sup>S. <sup>a</sup> Peak originating from loss of one deuterium atom only. <sup>b</sup> Peak originating from loss of one hydrogen atom only.

the radical site on sulfur; or alternatively a double hydrogen rearrangement leading to II followed by loss of  $H^\alpha$ . Because of this latter pathway III becomes a mixture of ions with  $H^\alpha$  attached to sulfur and nitrogen. The data in Table 1 show that deuteration of the dimethylamino group diminishes the intensity of II relatively to III. The discrimination against a double deuterium transfer in hydrogen rearrangements is not unexpected from mechanistic considerations and is consistent with other recent evidence.<sup>6</sup>

Subsequent loss of hydrogen or deuterium from III leads, respectively, to the peaks one or two mass units below the base peak. The further fragmentation of the ions formed is an unresolved problem and the location of  $H^\alpha$  in the structures shown should be considered tentative. Table 1 demonstrates that loss of  $H^\alpha$  from III contributes only *ca.* 1 % to the ions in this mass range, but loss of  $H^\beta$  and  $H^\gamma$  contributes a total of 7–10 %. At low electron energies these processes are quenched by energetically more favourable bond fissions, and they disappear below 12 eV. It should be noted (Table 1) that the loss of  $H^\beta$  relative to  $H^\gamma$  shows a pronounced isotope effect. Thus, when deuterium is substituted either for  $H^\beta$  or  $H^\gamma$  it will contribute only approximately one half of the intensity observed for loss of the original hydrogen.

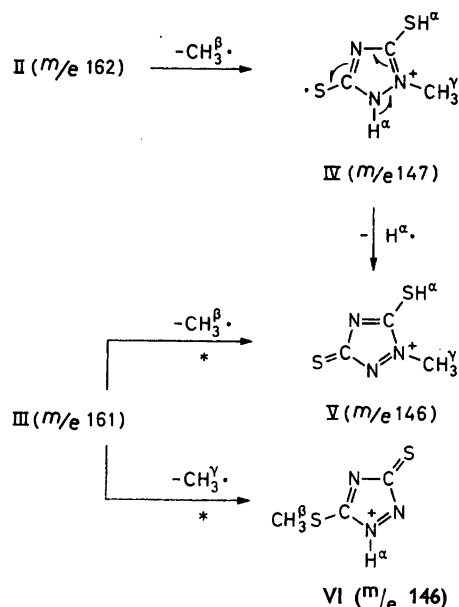
#### The peak group $m/e$ 146–152

The principal fragments in this region (Table 2) arise as shown in Scheme 2. It is not obvious why II exclusively (or, if the limits of accuracy are taken into account, to an extent exceeding 90 %) loses the  $CH_3$  group to give IV, whilst III loses both  $CH_3$  and  $CH_2$  with formation of V and VI. Expulsion of the methyl radical from the  $SCH_3$  group is a feature commonly encountered among aromatic thioethers, *e.g.* thioanisole.<sup>7</sup> The existence of the fragmentation process III  $\rightarrow$  VI can possibly be explained by assuming the precursor of VI to be the form of III bearing no  $H^\alpha$  on the sulfur atom. This view leads

Table 2. Intensities \* exceeding 0.1 % ( $\Sigma_{38}$ ) in the range  $m/e$  146–152 in the mass spectra of I and its deuterated species. The last three columns show the percentage contributions ( $\Sigma_{146}^{152}$ ) of the fragments IV–VI (Scheme 2) to this mass range. (Figures in parentheses are combined values for two or more fragments).

	146	147	149	150	152	IV	V	VI
I	0.49	0.21				30	(70)	(70)
I-S- $d_3$	0.23	0.18	0.24			28	35	37
I-N- $d_3$	0.27		0.18	0.21		32	27	41
I-S- $d_3$ -N- $d_3$			0.48	0.19		28	(72)	(72)
I-N- $d_6$		0.51	0.17			25	(75)	(75)
I-S- $d_3$ -N- $d_6$		0.21	0.16	0.29		24	32	44
I-N- $d_9$		0.35		0.17	0.16	24	25	51
I-S- $d_3$ -N- $d_9$				0.56	0.17	23	(77)	(77)

\* See footnote to Table 1.



Scheme 2. Formation of the peak cluster in the range  $m/e$  146–152 from II and III. (Values for  $m/e$  refer to the undeuterated species).

to the representation for VI shown in Scheme 2 which is expected to be quite stable. The genesis of V might to some extent be expected to follow from loss of  $\text{H}^\alpha$  from IV. However low-voltage spectra show that the peak due to V persists with only slightly diminished intensity at 12 eV though the rate constant for the step II — IV at 12 eV is negligible. Thus, it is tempting to conclude from the last two columns in Table 2 that a deuterated methyl group is split more easily off from III than an undeuterated one, especially if the relative stabilities of V and VI are accepted to be similar. In this connection the comparable effects of deuteration on the rupture of the C—O band in methanol can be invoked, but it is not clear to what extent such results can be generalized.<sup>8,9</sup>

#### The peak group $m/e$ 128–136

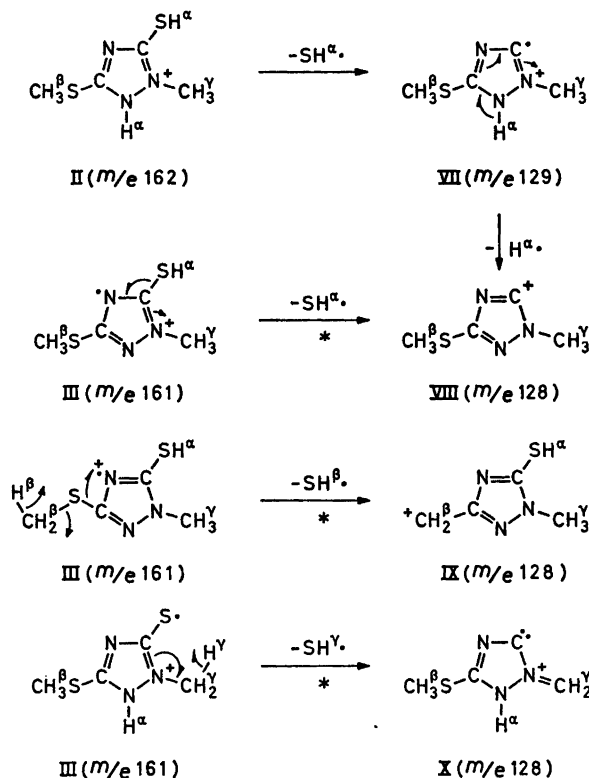
The stronger peaks in this range arise through loss of SH from II and III. Analysis of the results in Table 3 has established the elemental composition of the fragments VII—X shown in Scheme 3. The fact that they gain importance (in terms of percentage total ion current) at reduced energy (11–14 eV) suggests that the species IX and X which appear quite unstable as depicted in Scheme 3 are more properly formulated as the ring-expanded triazinyl ions which have the required electronic configuration for maximum stabilization. However, the absence of corroborative data confines this hypothesis to a speculative level at present.

Table 3. Intensities \* exceeding 0.25 % ( $\sum_{128}^{136}$ ) in the range  $m/e$  128 – 136 in the mass spectra of I and its deuterated species. The last four columns show the percentage contributions ( $\sum_{128}^{136}$ ) of the fragments VII – X (Scheme 3) to this mass range. (Figures in parentheses are combined values for two or more fragments).

	128	129	130	131	132	133	134	135	136	VII	VIII	IX	X
I	3.93	0.58								13	(87)	(87)	(87)
I-S-d <sub>3</sub>			2.66	0.99	0.56					13	(24)	63	(24)
I-N-d <sub>3</sub>			0.64	3.72	0.49					10	(77)	(77)	13
I-N-d <sub>3</sub> -S-d <sub>3</sub>						3.22	0.47	0.38		9	12	(79)	(79)
I-N-d <sub>6</sub>	0.67	4.20	0.33							6	13	(81)	(81)
I-S-d <sub>3</sub> -N-d <sub>6</sub>				3.79	0.66	0.31				6	14	(80)	(80)
I-N-d <sub>9</sub>				1.03	3.76	0.38				7	(20)	73	(20)
I-S-d <sub>3</sub> -N-d <sub>9</sub>							4.14		0.56	12	(88)	(88)	(88)

\* See footnote to Table 1.





Scheme 3. Formation of the peak cluster in the range  $m/e$  128–136 from II and III. (Values for  $m/e$  refer to the undeuterated species).

The elimination of  $\text{SH}^\alpha$  from II corresponds to a fragmentation pathway consistently observed for aromatic thiols<sup>7</sup> and agrees with the structure proposed for II (as does the fact that expulsion of  $\text{SH}^\gamma$  is not observed). The genesis of VIII, IX, and X can be adequately rationalized by invoking the double formulation of III pictured in Scheme 3. On the other hand it has recently been shown<sup>10</sup> that fragmentation processes of the type III  $\rightarrow$  IX proceed not only *via* an intermediate with a three-ring but also to a smaller extent by abstraction of neighbouring hydrogen atoms on the aromatic nucleus. If the premise is granted that  $\text{H}^\alpha$  is partly located at one of the nitrogen atoms next to the  $\text{C}-\text{SCH}^\beta$  moiety, some of the elimination of  $\text{H}^\alpha$  might proceed in this way and not only as shown in Scheme 3. Our results, therefore, do not constitute a proof of the twofold representation of III which would obviously require isotopic labeling of sulfur.

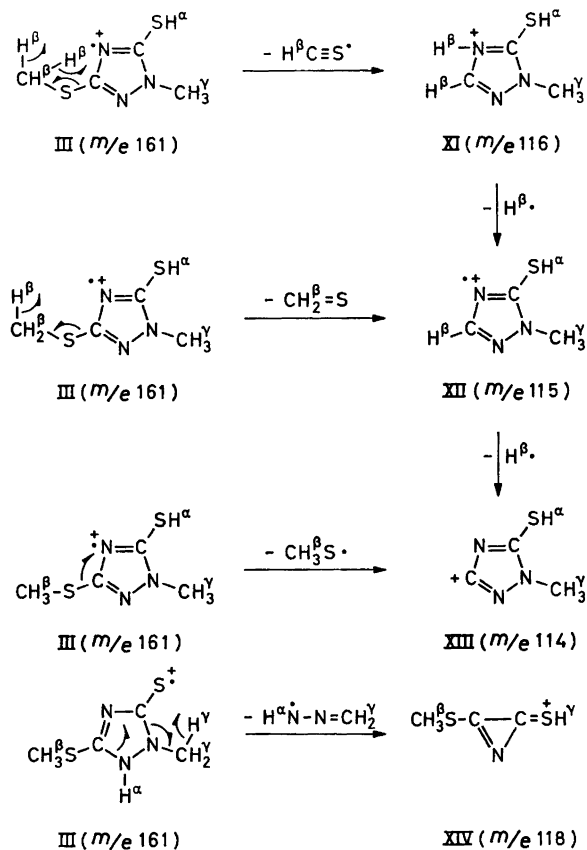
The figures for the percentage contributions of the fragments VII–X (Table 3) are consistent except for I-S- $d_3$ -N- $d_9$ . We have reasons to believe

that the one discrepancy is due to contributions from other low-intensity fragments to the peak at  $m/e$  136.

### The peak group $m/e$ 114–122

The peaks in this mass range (Table 4) are partly formed by degradation of the  $\text{CH}^\beta_3\text{S}-\text{C}$  group, partly by ring fission (Scheme 4). The elimination of thioformaldehyde from III to form XII parallels the analogous reaction of thioanisole,<sup>7</sup> and loss of the entire  $\text{CH}^\beta_3\text{S}$  group is a feature common to compounds containing this entity.<sup>7,11</sup>

In addition there is present a fairly intense peak due to an ion formed by loss of the thioformyl radical from III which is assigned the structure XI. The fact that this fragmentation is typical only of thioethers<sup>7</sup> with the sulphur in a ring suggests that the process proceeds *via* the intermediate III– $\text{H}^\beta$



Scheme 4. Formation of the peak cluster in the range  $m/e$  114–122 from III. (Values for  $m/e$  refer to the undeuterated species).

Table 4. Intensities \* exceeding 0.16 % ( $\sum_{as}$ ) in the range  $m/e$  114–122 in the mass spectra of I and its deuterated species. The last four columns show the percentage contributions ( $\sum_{114}^{122}$ ) of the fragments XI–XIV (Scheme 4) to this mass range. (Figures in parentheses are combined values for two or more fragments).

	114	115	116	117	118	119	120	121	122	XI	XII	XIII	XIV
I	0.43	0.18	0.72		1.10					30	7	18	45
I-S-d <sub>3</sub>	0.55		(0.09)		0.56			1.22		23	4	23	50
I-N-d <sub>3</sub>				0.42	0.22	1.77				(73)	9	17	(73)
I-N-d <sub>3</sub> -S-d <sub>3</sub>				0.53	0.11			0.63	1.14	26	5	22	47
I-N-d <sub>6</sub>		0.41	0.14	0.94	1.01					38	6	16	40
I-S-d <sub>3</sub> -N-d <sub>6</sub>		0.47		0.12		0.78		1.11		31	5	19	45
I-N-d <sub>9</sub>					0.34	1.01	0.91			40	(45)	15	(45)
I-S-d <sub>3</sub> -N-d <sub>9</sub>					0.46		0.18		1.71	(73)	8	20	(73)

\* See footnote to Table 1.

(Scheme 1), which might achieve such a structure through ring expansion. This pathway is, however, contradicted by low-voltage spectra showing the peak attributed to III—H<sup>β</sup> to disappear below 12 eV at which potential the peaks assigned to XI—XIII still remain with considerable intensity.

We may infer from Table 4 that XIII is more abundant relative to both XI and XII for a species of III carrying a deuterated methylthio group than for the corresponding species with an undeuterated methylthio group. A detailed discussion of arguments based on the figures in the table is, however, not warranted since the reaction sequence XI → XII → XIII proceeds to an unknown extent.

The formation of XIV from III can be rationalized as proceeding by cleavage of the C—N single bonds with simultaneous transfer of H<sup>γ</sup> to sulfur. A somewhat similar fragmentation has been reported for 3,5-dimethylpyrazole.<sup>12</sup> From the figures in the last column in Table 4 it cannot be decided to what extent deuteration of the CH<sub>3</sub> group influences this fragmentation but it is obvious that XIV is more abundant if CH<sub>3</sub> is deuterated.

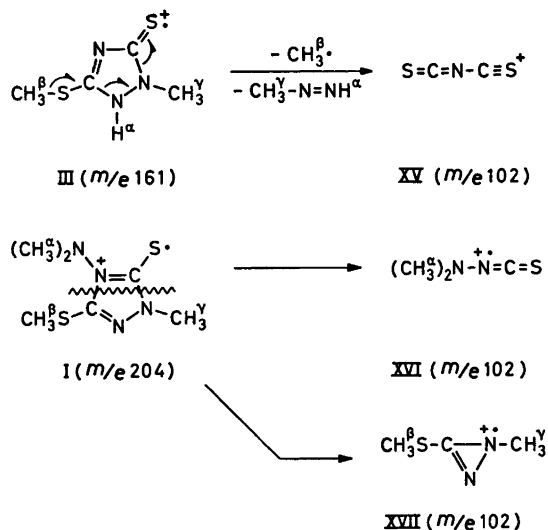
#### The peak group *m/e* 101—108

The figures calculated (Table 5) from the mass spectra only allow secure deductions to be made for the composition of three of the fragments contributing in this mass range (XV—XVII, Scheme 5). In addition to these ions the doubly charged molecular ion appears with an intensity of *ca.* 0.1 % ( $\Sigma_{38}$ ). The formation of XV may proceed by several different pathways but low-voltage data indicate that it is, at least to some extent, formed directly from III as shown. Thus at 11 eV the peaks from the other possible precursors IV, V, VI, and XIV have disappeared whilst the peak from XV persists though

Table 5. Intensities \* exceeding 0.2 % ( $\Sigma_{38}$ ) in the range *m/e* 101—108 in the mass spectra of I and its deuterated species. The last three columns show the percentage contributions ( $\Sigma_{101}^{108}$ ) of the fragments XV—XVII (Scheme 5) to this mass range. (Figures in parentheses are combined values for two or more fragments).

	101	102	103	104	105	106	107	108	XV	XVI	XVII
I	0.86	3.22							(79)	(79)	(79)
I—S—d <sub>3</sub>	0.27	2.40		0.59	1.13				(55)	(55)	26
I—N—d <sub>3</sub>	0.36	2.62	0.22	0.20	1.10				(58)	(58)	24
I—S—d <sub>3</sub> —N—d <sub>3</sub>	0.39	2.73			0.20	0.25	0.30	0.93	(57)	(57)	19
I—N—d <sub>3</sub>	0.55	2.80	0.20		0.23	0.49		0.26	(62)	6	(62)
I—S—d <sub>3</sub> —N—d <sub>3</sub>		2.34		0.56	1.26	0.46		0.40	47	8	25
I—N—d <sub>3</sub>		2.12	0.21		1.02	0.62		0.23	50	6	24
I—S—d <sub>3</sub> —N—d <sub>3</sub>		2.32				0.70		1.59	50	(35)	(35)

\* See footnote to Table 1. In the corrections for <sup>13</sup>C, <sup>15</sup>N, <sup>33</sup>S, and <sup>34</sup>S it has been assumed that *m/e* 101 in (I) and the corresponding fragments in the deuterated species are composed of XVI—H<sup>α</sup> and XVII—H<sup>γ</sup>. In this range corrections for the abundance of the doubly charged species of the molecular ion have also been applied.



Scheme 5. Formation of the peak cluster in the range  $m/e$  101–108 from I and III. (Values for  $m/e$  refer to the undeuterated species).

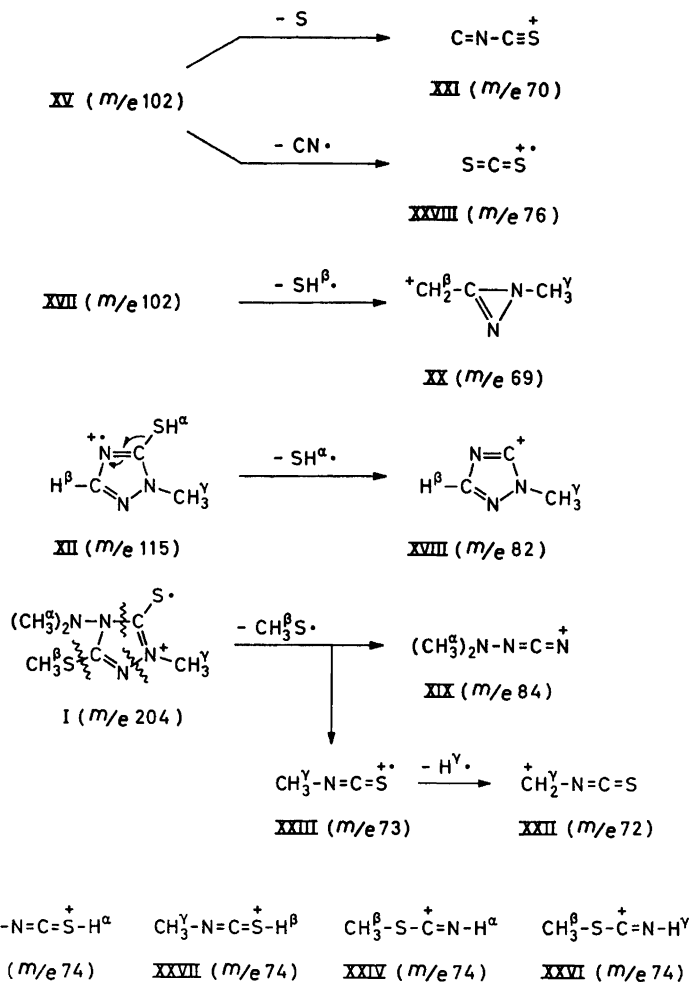
with lowered intensity. The conjoint appearance of XVI and XVII points to their formation by transannular cleavage of the C–N single bonds of the molecular ion, giving two fragments of the same elemental composition, both able to retain the positive charge.

The peak groups  $m/e$  82–90 and  $m/e$  69–78

Within the former mass range only the data listed in Table 6 supplied unambiguous structural information. The contributing ions XVIII and XIX are shown in Scheme 6. Since several unidentified ions fall in this range there was no interest in calculating the percentage contributions from the figures in Table 6. The situation is quite different for the range  $m/e$  69–78 (Table 7) in which nine fragments have been adequately characterized (XX–XXVIII) and all peaks with intensities exceeding 0.3 % ( $\sum_{38}$ ) explained.

It is a common rule<sup>7</sup> that cleavage of multiple bonds is an unfavourable process in mass spectroscopy. A corollary of this rule is that the fragmentation route XV  $\rightarrow$  XXI should be quenched by lower potentials as was indeed observed. It was rather unexpected that the alternate sequence III  $\rightarrow$  XV  $\rightarrow$  XXVIII is still observed at 11 eV but the reason must be sought in the unusual stability of the fragments involved. The ejection of SH <sup>$\beta$</sup>  from the part of the  $m/e$  102 peak corresponding to XVII gives rise to XX, and the analogous conversion of III has been discussed above (*cf.* Scheme 3).

The fragmentation leading to XVIII is completely suppressed at low electron voltage (11 eV) whilst XII gains significance. The formulation of the



Scheme 6. Formation of the peak clusters in the ranges  $m/e$  82–90 and  $m/e$  69–78. (Values for  $m/e$  refer to the undeuterated species).

process XII  $\rightarrow$  XVIII as a simple  $\alpha$ -cleavage with expulsion of  $\text{SH}^\alpha$  seems to account for these results and is noteworthy in the light of the previously discussed fragmentation of II to VII (Scheme 3).

The transannular fission of I leading to XIX is interesting in that it involves cleavage of the N–N bond. The intensity drops off slowly to half the initial value as the energy diminishes from 14 to 11 eV. Considering the presence of the dimethylamino group in XIX the proposed genesis from I seems to be reasonably well supported. The driving force for the process is probably the elimination of neutral methyl isothiocyanate; if so, we have a parallel to the

Table 6. Intensities \* exceeding 0.7 % ( $\Sigma_{98}$ ) in the range  $m/e$  82–90 in the mass spectra of I and its deuterated species. The contributing fragments XVIII and XIX are shown in Scheme 6.

	82	83	84	85	86	90
I	0.93		1.07			
I-S- $d_3$		0.81	0.72			
I-N- $d_3$			1.18	1.05		
I-S- $d_3$ -N- $d_3$			0.88		0.98	
I-N- $d_3$	1.06					0.90
I-S- $d_3$ -N- $d_6$		0.85				0.94
I-N- $d_6$				0.98		1.03
I-S- $d_3$ -N- $d_9$					1.12	1.45

\* See footnote to Table 1.

familiar eliminations of hydrogen cyanide and nitriles from heterocyclic nitrogen compounds, *e.g.* pyrazoles.<sup>12</sup>

Identification of the four ions composing the  $m/e$  74 peak (XXIV–XXVII) elucidates the rearrangements of hydrogen atoms in the fragmentation processes. The formation of XXIV and XXV is straightforward if the double identity of III is taken into account. The presence of XXVI serves to identify a rearrangement process involving transfer of  $H^+$  to a neighbouring nitrogen atom either in one of the ions containing the triazole ring or in an ion such as XIV. The latter case implies a subsequent elimination of CS, which seems a reasonable hypothesis. Another unexpected fragment is XXVII, but speculation about its origin is probably not warranted in the absence of isotopic labeling of sulfur.

In contrast to the peak at  $m/e$  74 which nearly disappears at an energy of 11 eV, the peak corresponding to XXIII is hardly diminished at 11 eV, which makes the molecular ion or one of the fragment ions III or IX the candidates for precursorship. The most reasonable pathway is that the collapse of I to XXIII may proceed with charge transfer to sulfur. The ion XXII becomes unimportant at 12 eV and is conveniently visualized as originating by allylic cleavage of  $H^+$  from XXIII.

#### Peaks below $m/e$ 69

From the mass spectrum reproduced in Fig. 2 it is evident that a large part of the ion current originates from fragments of low mass. A consistent analysis of this range is not possible without high-resolution data and is outside the scope of the present work. It must be realized that most of the fragmentations discussed above conceivably also proceed in such a way that the smaller of the fragments becomes the charge-bearing species. Under these circumstances a complete analysis would not be expected to contribute significant new fragmentation routes.

Table 7. Intensities \* exceeding 0.3% ( $\sum_{78}^{79}$ ) in the mass spectra of I and its deuterated species. The last nine columns show the percentage contributions ( $\sum_{78}^{79}$ ) of the fragments XX-XXVIII (Scheme 6) to this mass range. (Figures in parentheses are combined values for two or more fragments).

	69	70	71	72	73	74	75	76	77	78	XX XXI	XXII	XXIII	XXIV	XXV	XXVI	XXVII	XXVIII	
I	0.79	0.43	1.35	1.31	2.96	0.56					11	6	18	18	(40)	(40)	(40)	8	
I-S-d <sub>3</sub>		0.46	0.60	1.42	1.32	1.08	0.39	0.85	2.03		7	6	17	16	(25)	13	(25)	5	10
I-N-d <sub>3</sub>		0.51	0.97		2.28	0.50	1.95	1.53			13	7	(29)	(25)	(29)	(20)	6	(20)	(25)
I-S-d <sub>3</sub> -N-d <sub>3</sub>		0.44			1.79		1.89	2.42	0.87		(24)	6	(24)	(26)	(33)	(33)	(12)	(12)	(26)
I-N-d <sub>6</sub>	0.72	0.47	1.37	1.41	1.12	1.85	0.71				9	6	18	18	(24)	(24)	(15)	(15)	9
I-S-d <sub>3</sub> -N-d <sub>6</sub>		0.45	0.66	1.36	1.11	1.32	0.84	0.72	1.16		9	6	18	15	15	(17)	9	(17)	11
I-N-d <sub>9</sub>		0.44	0.93		1.29	1.26	1.90	0.46	0.96		13	6	18	(26)	(17)	13	(17)	6	(26)
I-S-d <sub>3</sub> -N-d <sub>9</sub>		0.44			2.08		2.09		3.04		(27)	6	(27)	(27)	(40)	(40)	(40)	(40)	(27)

\* See footnote to Table 1.



## EXPERIMENTAL

The mass spectra were obtained with an Atlas CH 4 instrument operating at 70 eV. The low voltage spectra were recorded at 11, 12, 13, and 14 eV. The compounds were introduced through an all-metal gas inlet system held at 150°C. The ion source temperature was 250°C and the ionizing current 35  $\mu$ A.

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