10-Methyl-4-phenyl-3,5-dioxopyrimido[5,6-c]-1'-azaquinolizine (IVb). To a 0.75-g portion (2.5 mmoles) of compound Ib was added 1.7 g (25 mmoles) of a 25% aqueous ammonia solution, and the mixture was refluxed for 40 min. After cooling, the resulting precipitate of IVb was filtered off. Yield 0.3 g (40%), mp >350°C (DMF). Found: C 66.2; H 5.0; N 18.1%. $C_{17}H_{12}N_4O_2$. Calculated: C 67.1; H 3.9; N 18.4%.

1-Methyl-5-formyl-6-aminouracil (IX). To a 1.2-g portion (5 mmoles) of 1-methyl-6-(1'-pyridinio)-5-formyluracil-2-oleate was added 3.4 g (50 mmoles) of a 25% aqueous ammonia solution, and the mixture was refluxed for 40 min. After cooling, the precipitated compound IX was filtered off. Yield 0.59 g (68%), mp >330°C (DMF). Found: C 42.9; H 4.4; N 24.8%. $C_6H_7N_3O_3$. Calculated: C 42.6; H 4.1; N 24.8%.

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MASS-SPECTROMETRIC STUDY OF ISOMERIC 5-AMINO-1,2,3-THIADIAZOLES AND 5-MERCAPTO-1,2,3-TRIAZOLES

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The behavior of the isomeric 5-amino-1,2,3-thiadiazoles and 5-mercapto-1,2,3-triazoles under electron impact was studied. It was shown that mass spectrometry can serve as a rapid and reliable method for the identification of these compounds. Key factors in the assignment of a compound to one or the other class are the peaks of the $[M - N_2]^+$ ions, which are more intense in the case of the thiadiazoles, and the ions determined by the decomposition of the prototropic forms of the triazoles. The compositions of the ions were determined by the high-resolution mass spectra.

Either 5-amino-1,2,3-thiadiazoles or the isomeric 5-mercapto-1,2,3-triazoles are formed in the reaction of thioamides, containing acidic methylene hydrogen atoms in the α-position to the thioamide group, with tosylamides.* The structural determination of the products of this cyclization is performed by chemical methods. However, it is known that the interconversion of aminothiadiazoles and mercaptotriazoles proceeds at raised temperatures [2] and under acid-base catalysis [3]; this makes the results of the chemical proof of the structure of these heterocyclic compounds inconclusive. The mass-spectrometric experiment

*It was shown that the final stage of this reaction is the cyclization of the intermediate α-diazothioamides [1].

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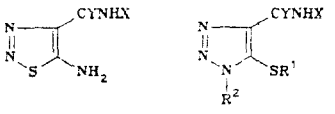
permits the determination of the structure of organic compounds under conditions where intermolecular interactions and the effects of the solvent are absent. When the substance is sufficiently volatile, a qualitative reproducible mass spectrum can be obtained without heating, or with the insignificant warming up of the substance.

The mass spectra of the isomeric 5-amino-1,2,3-thiadiazoles (I) and 5-mercapto-1,2,3-triazoles (II) were studied:



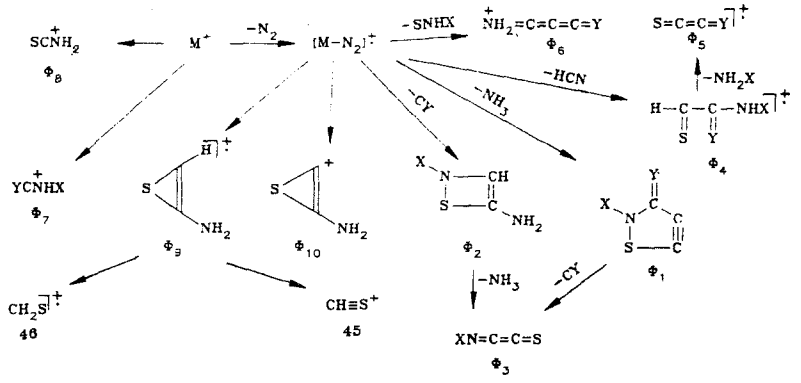
I a-e II a-c,f-j

a,c,g,h,j X=H; b,d X=CH_3; e X=$CH_2COOC_2H_5$; f,i X=NH_2; a,b,~~e~~ i Y=O; c,d,j Y=S; a-f, j R^1=H; g,i R^1=CH_3; h R^1=C_2H_5; a-i R^2=H; j R^2=CH_3

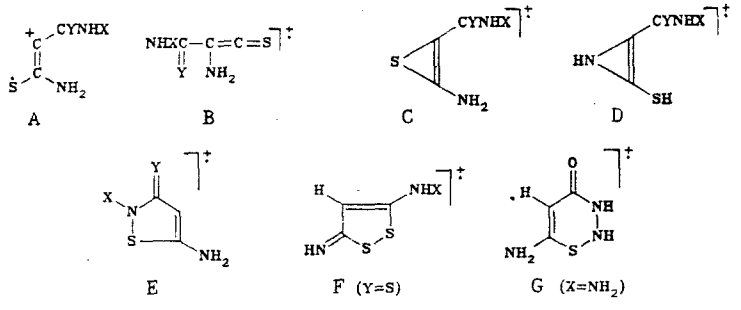
The direct comparison of the spectra of the compounds (I) and (II) permits the conclusion that there are principal differences in the routes of the decomposition of these isomers. The main characteristics of the route of the decomposition of the thiadiazoles (Ia-e) can be described by a general scheme.*

According to the intensity of the peaks in the mass spectra of all the thiadiazoles (I), the main peaks are those of the molecular ions (M^+). The peaks of the $[M - N_2]^{+\cdot}$ ions also have adequate intensity (see Table 2). It is necessary to emphasize that the relative intensities of the peaks of the $[M - N_2]^{+\cdot}$ ions are more than tenfold lower in the spectra of the isomeric mercaptotriazoles (II) (see Table 2); this permits the reliable assignment of a compound to one or the other class on the basis of the relative intensity of the peak of the given fragment. The structure of this ion, which determines the subsequent decomposi-

Scheme 1



tion, may be described by several structural formulas. As was previously shown [4-6], the linear form of the $[M - N_2]^{+\cdot}$ ion (A), which is formed right after the cleavage of the nitrogen molecule, is stabilized on account of the rearrangement to the thioketene (B) if an alkyl substituent occurs at the 5 position of the thiadiazole ring, or the rearrangement to the thiirene (C) if an amino group occurs at this position.



The amino group at the 5 position may also participate in the cyclization (accompanied by the migration of a hydrogen atom) of the $[M - N_2]^{+\cdot}$ ion to the azirine (D). It was noted

*The elemental compositions of the ions were determined by the high-resolution mass spectra (see Table 1).

TABLE 1. High-Resolution Mass Spectra of the Compounds (I) and (II)

Compound	Accurate ion mass		Elemental composition of the ion	Ratio of intensities of the peaks of isobaric ions
	determined	calculated		
1	2	3	4	5
Ia 99	98,9781	98,9779	C_3HNOS (Φ_1)	
89	88,9936	88,9935	C_2H_3NOS (Φ_4)	
88	88,0100	88,0095	$C_2H_4N_2S$ (Φ_2)	
73	72,9988	72,9986	C_2H_3NS (Φ_9)	
72	71,9674	71,9669	C_2OS (Φ_5)	1
	71,9904	71,9908	C_2H_2NS (Φ_{10})	6
71	70,9829	70,9830	C_2HNS (Φ_3)	
68	68,0135	68,0138	C_3H_2NO (Φ_6)	
44	44,0136	44,0136	CH_2NO (Φ_7)	
Ib 113	112,9940	112,9935	C_4H_3NOS (Φ_1)	
103	103,0100	103,0092	C_3H_5NOS (Φ_4)	
102	102,0257	102,0252	$C_3H_6N_2S$ (Φ_2)	
85	84,9982	84,9986	C_3H_3NS (Φ_3)	
72	71,9902	71,9908	C_2H_2NS (Φ_{10})	
68	68,0136	68,0138	C_3H_2NO (Φ_6)	
Ic 115	114,9558	114,9550	C_3HNS_2 (Φ_1)	
105	104,9700	104,9706	$C_2H_3NS_2$ (Φ_4)	
88	87,9437	87,9441	C_2S_2 (Φ_5)	
84	83,9907	83,9908	C_3H_2NS (Φ_6)	
72	71,9908	71,9908	C_2H_2NS (Φ_{10})	
71	70,9828	70,9830	C_2HNS (Φ_3)	
68	68,0379	68,0375	$C_3H_4N_2$ [M—N_2, —S_2]	
67	67,0303	67,0297	$C_3H_3N_2$ [M—N_2, —S_2H]	
66	66,0221	66,0219	$C_3H_2N_2$ [M—N_2, —S_2H_2]	
Id 129	128,9710	128,9707	$C_4H_3NS_2$ (Φ_1)	
88	87,9440	87,9441	C_2S_2 (Φ_5)	
85	84,9985	84,9986	C_3H_3NS (Φ_3)	
84	83,9910	83,9908	C_3H_2NS (Φ_6)	
82	82,0531	82,0532	$C_4H_6N_2$ [M—N_2, —S_2]	
81	81,0460	81,0454	$C_4H_5N_2$ [M—N_2, —S_2H]	
79	79,0299	79,0297	$C_4H_3N_2$ [M—N_2, —S_2H_3]	
Ie 202	202,0153	202,0161	$C_5H_6N_4O_3S$ [M—C_2H_4]	
185	185,0130	185,0133	$C_5H_5N_4O_2S$ [M—C_2H_5O]	
157	157,0181	157,0184	$C_4H_5N_4OS$ [M—$COOC_2H_5$]	
128	127,9937	127,9939	$C_3H_2N_3OS$ [M—$NHCH_2COOC_2H_5$]	
Ik 117	117,0245	117,0248	C_4H_7NOS (Φ_4)	
116	116,0412	116,0408	$C_4H_8N_2S$ (Φ_2)	
100	100,0226	100,0221	C_4H_6NS (Φ_3)	
72	72,0448	72,0449	C_3H_6NO (Φ_7)	8
	71,9909	71,9908	C_2H_2NS (Φ_{10})	1
68	68,0141	68,0136	C_3H_2NO (Φ_6)	
Iℓ 114	114,0001	114,0000	$C_2H_2N_4S$ (Φ_2)	
72	71,9676	71,9670	C_2OS (Φ_5)	1
	71,9909	71,9908	C_2H_2NS (Φ_{10})	8
70	70,0035	70,0041	CON_3 (Φ_7)	1
	69,9749	69,9752	C_2NS	5
IIa 28	127,9914	127,9918	$C_3H_2N_3OS$ [M—NH_2]	
127	126,9844	126,9840	C_3HN_3OS [M—NH_3]	
126	126,0001	126,0000	$C_3H_2N_4S$ [M—H_2O]	
99	98,9781	98,9779	C_3HNOS (Φ_1)	
89	88,9937	88,9935	C_2H_3NOS (Φ_4)	
88	88,0100	88,0095	$C_2H_4N_2S$ (Φ_2)	
71	70,9825	70,9830	C_2HNS (Φ_3)	3
	71,0236	71,0245	$C_2H_3N_2O$	2
67	67,0175	67,0171	C_2HN_3	
68	68,0140	68,0136	C_3H_2NO (Φ_6)	1
	68,0245	68,0249	$C_2H_2N_3$	1
IIb 128	127,9921	127,9919	$C_3H_2N_3OS$ [M—CH_3NH]	
127	126,9848	126,9841	C_3HN_3OS [M—CH_3NH_2]	
140	140,0151	140,0157	$C_4H_4N_4S$ [M—H_2O]	
113	112,9941	112,9935	C_4H_3NOS (Φ_1)	
103	103,0094	103,0092	C_3H_5NOS (Φ_4)	
102	102,0254	102,0252	$C_3H_6N_2S$ (Φ_2)	
85	84,9994	84,9986	C_3H_3NS (Φ_3)	
68	68,0247	68,0249	$C_2H_2N_3$	1
	68,0138	68,0136	C_3H_2NO (Φ_6)	1

TABLE 1 (Continued)

1	2	3	4	5
IIc 126	126,0002	126,0000	$C_3H_2N_4S$ [M−H_2S]	
115	114,9559	114,9550	C_3HNS_2 (Φ_1)	
105	104,9703	104,9706	$C_2H_3NS_2$ (Φ_4)	
88	88,0100	88,0095	$C_2H_4N_2S$ (Φ_2)	1
	87,9451	87,9441	C_2S_2 (Φ_5)	6
84	83,9906	83,9908	C_3H_2NS (Φ_6)	
68	68,0372	68,0375	$C_3H_4N_2$ [M−N_2, −S_2]	1
	68,0245	68,0249	$C_2H_2N_3$	1
67	67,0292	67,0297	$C_3H_3N_2$ [M−N_2, −S_2H]	
IIf 128	127,9922	127,9919	$C_3H_2N_3OS$ [M−$NHNH_2$]	
102	102,0021	102,0014	C_3H_4NOS [M−N_2, −N_2H]	
68	68,0252	68,0249	$C_2H_2N_3$	
IIg 142	142,0072	142,0075	$C_4H_4N_3OS$ [M−NH_2]	
141	140,9987	140,9997	$C_4H_3N_3OS$ [M−NH_3]	
128	127,9925	127,9919	$C_3H_2N_3OS$ [M−CH_3NH]	
125	125,0468	125,0463	$C_4H_5N_4O$ [M−SH]	
103	103,0097	103,0092	C_3H_3NOS (Φ_4)	
102	102,0244	102,0252	$C_3H_6N_2S$ (Φ_2)	
72	71,9900	71,9908	C_2H_2NS [Φ_9−CH_3]	8
	71,9673	71,9670	C_2OS (Φ_5)	1
68	68,0245	68,0249	$C_2H_2N_3$	1
	68,0138	68,0136	C_3H_2NO (Φ_6)	4
47	46,9952	46,9935	CH_3S	
IIh 155	155,0151	155,0153	$C_5H_5N_3OS$ [M−NH_2]	
144	144,0355	144,0357	$C_5H_8N_2OS$ [M−N_2]	1
	144,0104	144,0106	$C_3H_4N_4OS$ [M−C_2H_4]	8
139	139,0623	139,0620	$C_5H_7N_4O$ [M−SH]	
61	61,0111	61,0112	C_2H_5S	
IIi 142	142,0071	142,0075	$C_4H_4N_3OS$ [M−N_2H_3]	
116	116,0173	116,0170	C_4H_6NOS [M−N_2, −N_2H]	
101	101,0175	101,0173	$C_3H_5N_2S$ (Φ_3)	
72	71,9909	71,9908	C_2H_2NS [Φ_9−CH_3]	10
	71,9673	71,9670	C_2OS (Φ_5)	1
68	68,0141	68,0136	C_3H_2NO (Φ_6)	
IIj 129	128,9710	128,9707	$C_4H_3NS_2$ (Φ_1)	
117	116,9712	116,9707	$C_3H_3NS_2$ [M−CH_3N_3]	
105	104,9698	104,9707	$C_2H_3NS_2$ (Φ_4)	
88	87,9437	87,9441	C_2S_2 (Φ_5)	
85	84,9976	84,9986	C_3H_3NS (Φ_3)	
81	81,0452	81,0452	$C_4H_5N_2$ [M−N_2, −S_2H]	
80	80,0382	80,0374	$C_4H_4N_2$ [M−N_2, −S_2H_2]	
79	79,0301	79,0296	$C_4H_3N_2$ [M−N_2, −S_2H_3]	
74	74,0056	74,0064	C_2H_4NS	

TABLE 2. Intensities of the Peaks of the Characteristic Fragment Ions in the Mass Spectra of the Compounds (I) and (II) in Percentages of the Complete Ion Current

Compound	M^+	[M − N_2]	[M − NHX]	M − NH_2X	M − H_2Y	Φ_1	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6	Φ_7	Φ_8	Φ_9	Φ_{10}	46	45
Ia	23,3	3,9	—	—	—	3.6	2.2	1,5	2,2	0,4	2,2	9,9	3,1	11,5	2,4	15,1	6,6
Ib	9.6	3,0	—	—	—	11,7	1,3	1,4	1,4	—	2,3	17,8	2,3	9,6	2,9	9,6	4,3
Ic	21,9	7,2	—	—	0,2	1.1	—	1.3	7,1	2,9	1,8	13,0[a]		1,7	2.9	8,6	5,4
Id	21,4	3,4	—	—	—	3.5	—	1,4	2,2	3,6	1,6	6,8	10.2	9,0	3,4	3,6	4,8
Ik	12,9	1,8	—	—	—	0,1[b]	2.0	2,9[b]	1,9	—	1,4	25,4	1.8	1.5	3.2	1,0	2.1
Il	6,5	6,2	0,4[c]	—	—	—	0.2	—	0.2	1,0	1,7	0,8	13,4	0,5	7,6	1,7	5,6
IIa	21.7	0,3	1,7	22,6	0,8	1.0	0,5	1,7	1,1	0,5	1,1	10,5	1,4	4,4	0.9	2,9	6,8
IIb	28,6	0,2	6,7	8,2	3,3	1.3	0,4	1.1	0,4	—	1.0	12,2	1,4	3.3	1.6	2,4	4,8
IIc	33,4	0,8	0,6	5,5	2.6	0,5	0,1	1.5	1,8	1,1	1,2	7,7[a]		2,0	3.3	3,2	5,3
IIf	28,0	—	28.9	1,5	0,5	—	0.1	0,3	0,1	—	—	0,8	2,7	1,2	3,0	0,9	4,7
IIg	13.5	0,1	1.8	14,9	0.3	3.1[d]	1,5	1,0[d]	0,7	0,5	1,8	7,0	1.3	6,1[d]	7,3[d]	1,4	6,4
IIi	16,3	—	23.9	0,6	—	0.4[b]	—	1,3[b,d]	—	0.2	2,8	1,4	1,4	3,0[d]	11,0[d]	1,1	3,5
IIj	32 5	0,2		—	0.5	0,2	—	1.5	3,3	3,0	—	4,6	2,7	4,7[d]	2,5[d]	2,7	3,5

[a]The ions have the same elemental composition. [b]The NH_2 radical, and not the NH_3 molecule, is eliminated. [c]The $[M - N_3]^+$ ion. [d]The structure of the ion differs from that presented in the scheme. [e]The total contribution of the Φ_9 + [Φ_9 − CH_3] and Φ_{10} + [Φ_{10} − CH_3] ions.

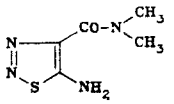
in the work [7] that the carboxamide group leads to the emergence of more complex structures for the $[M - N_2]^{+\cdot}$ ion. The thiocarboxamide group leads to the appearance of the form (F) (cf. below). It should be noted that the formation of the structures (D-F) assumes the rearrangement of the atoms; the intermediates formed at the early stages of the formation of these ions may decompose in some cases. A large amount of the isomeric forms of the $[M - N_2]^{+\cdot}$ ion leads to a variety of routes for the further decomposition of these ions; the structural formulas of the $[M - N_2]^+$ ion are not therefore presented in the Schemes 1 and 2.

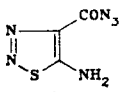
The Φ_1 ion is formed by the cleavage of an ammonia molecule. The 5-amino group of the investigated thiadiazoles, and not the amide nitrogen atom, participates in this, since a molecule of ammonia, and not methylamine, is eliminated with the $[M - N_2]^+$ ion in the decomposition of the compounds (Ib, d) (X = CH_3).

It should be noted that there was not a single case where the process of decomposition, determined by the ortho effect of the substituents, were registered; this agrees with the data of other investigators [7].

The introduction of a more complex radical at the 4 position [compound (Ie) (X = CH_2COOEt)] leads to the appearance of the intense peaks of the $[M - C_2H_4]^+$, $[M - OC_2H_5]^+$, $[M - COOC_2H_5]^+$, and $[M - CH_2COOC_2H_5]^+$ fragments in the spectrum; the decomposition of the heterocyclic nucleus is thereby suppressed. It is for this reason that the intensities of the peaks of fragments, which are common with other thiadiazoles, are not presented in Table 1.

The thiadiazoles (Ik, ℓ) are also characterized by routes of decomposition which are very similar to those presented in Scheme 1.


Ik


Iℓ

However, the stabilization of the $[M - N_2]^+$ ion with the formation of the five-membered heterocyclic ion (E) (cf. Scheme 1) is impossible when the hydrogen atom is absent from the amide group of these compounds. Structures of the type (B-D) are evidently formed in the given case. It is impossible to exclude more complex rearrangements.

The main difference in the decomposition of the isomeric triazoles (II) from the decomposition of thiadiazoles considered above, besides the low intensities of the peaks of the $[M - N_2]^+$ ions, is the high intensity of the peaks of the $[M - NHX]^+$ and $[M - NH_2X]^+$ fragments (see Table 2). It is logical to propose that the formation of these ions is determined by the ortho-effect [8]. However, such fragments are not formed at all in the decomposition of the isomeric thiadiazoles (I), and the geometry of the molecules is the same. Consequently, the moving force for this process is the possibility of the tautomeric conversions of the triazole ring due to the availability of the hydrogen atom at the $N_{(1)}$ nitrogen atom which is capable of free migration through the entire heterocyclic ring [9-11]. The tautomeric form of M^+ with the hydrogen atom at the $C_{(4)}$ carbon atom leads to the elimination of the H_2X or H_2Y molecules (see Scheme 2). For the confirmation of this hypothesis, the mass spectrum of the compound (IIj) with the fixed tautomeric form was studied. As was also to be expected from the proposed mechanism, the $[M - NH_3]^+$ and $[M - H_2O]^+$ ions are not formed in the given case. An insignificant ortho-effect is observed in the decomposition of the triazoles (II); this is indicated by the peaks of the $[M - R^1NH]^{+\cdot}$ ions which are observed in the spectra of the compounds (IIg-i). However, the intensities of these fragments do not exceed 0.5% of the complete ion current. The tautomeric conversions in the triazole ring lead to the appearance of some other routes (not presented in the scheme) of the decomposition of M^+, e.g., the formation of the NH-N=C-SH and NH=N=C=C=Y ions with the peak intensities at around 1% of the complete ion current. They are caused by the tautomeric form of the M^+ in which the hydrogen atom occurs at the central $N_{(2)}$ atom.

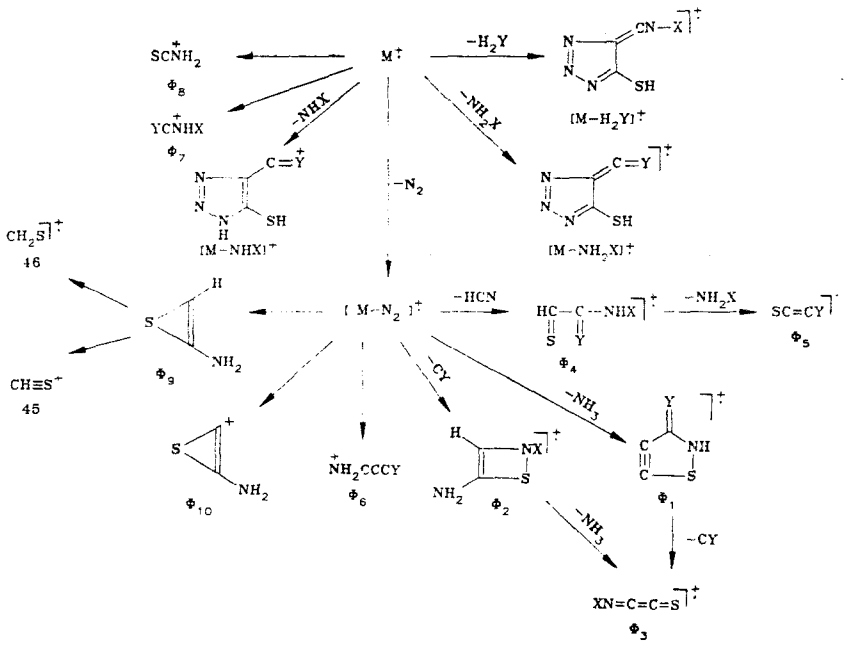
The main routes of the decomposition of the compounds (IIa-c, f) are presented in Scheme 2.

If the geometrical rearrangement of the molecule with the turning of the groups of atoms by 180° around the C–C bond is required for the formation of the structure (E) of the

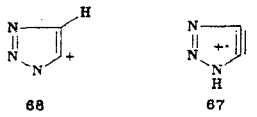
TABLE 3. Relative Intensity of the Peaks of the Fragments which are Formed in the Decomposition of the $[M - N_2]^+$ Ion of the Structure (F)

Compound	$M-N_2$, $-S_2$	$M-N_2$, $-S_2H$	$M-N_2$, $-S_2H_2$	$M-N_2$, $-S_2H_3$
Ic	3,8	5,3	1,7	0,1
Id	3,8	8,2	1,0	1,8
IIc	1,7	2,6	1,1	—
IIj	0,6	4,1	0,7	1,0

Scheme 2



$[M - N_2]^+$ ion in the case of the thiadiazoles, then there is no requirement for such a rearrangement in the case of the triazoles (II). The bond between the atoms of sulfur and nitrogen is possibly formed even before the elimination of the nitrogen molecule from the heterocycle. In fact, the 1,5-electrocyclization reaction proceeds; all the compounds (I) and (II) investigated in the present work were obtained by analogy with it [12]. Indirect confirmation of the possibility of such an isomerization is the formation of the ions 67 and 68 (2-3% of the complete ion current).*



The thiocarboxamide group in the compounds (Ic, d) and (IIc, j) leads to the appearance of one structure – (F) – for the $[M - N_2]^+$ ion. It is this form which causes the elimination of the S_2, S_2H, S_2H_2, and S_2H_3 molecules in one or several stages. The composition of these ions was determined with the aid of the high-resolution mass spectra. The relative intensities of the indicated fragments are presented in Table 3.

The methyl substituent R^2 in the triazole (IIj) leads to a significant change in the routes of decomposition, as was also noted previously [11]. This is first of all associated with the impossibility of the tautomerization of the M^+. In consequence, the peaks of the $[M - NH_2]^+$ and $[M - NH_3]^+$ ions disappear completely. The [M – SH] and $[M - SH_2]$ fragments

*The elemental composition of these ions was established with the aid of the high-resolution mass spectra (see Table 1).

TABLE 4. Mass Spectra of the Compounds (I) and (II)

Compound	Value of m/z, % (intensity of the peaks of the ions as a percentage of the maximal)*
Ia	144 (100), 116 (17,5), 99 (15,9), 73 (50.0), 72 (12,7), 68 (10,3), 60 (14,3) 46 (66,7), 45 (28,6), 44 (46,8)
Ib	158 (50,0), 130 (15,8), 113 (61,9), 73 (54,5), 72 (16,5), 68 (12,7), 60 (12,9) 58 (100), 46 (55,3), 45 (24,8)
Ic	160 (100), 132 (33,0), 105 (33.0), 88 (13,2), 72 (14,9), 68 (18,8), 67 (26,6) 60 (64,4), 46 (43,4), 45 (27,8)
Id	174 (100), 146 (14,7), 129 (18,8), 88 (19,7), 81 (45,2), 74 (37,6), 73 (50,0). 60 (55,9), 46 (20,0), 45 (26,8)
Ie	230 (42,0), 185 (81,2), 157 (72,5), 128 (36,5), 100 (28,5), 74 (38,5), 73 (100). 72 (57,0), 46 (34,5), 45 (28,5)
Ik	172 (41,2), 117 (6,4), 115 (6,7), 101 (18,3), 100 (10,0), 73 (6,8), 72 (100), 45 (7,4), 44 (45,8), 42 (27,5)
Il	170 (45.0), 142 (43,8), 86 (31,5), 72 (67,5), 70 (36,3), 60 (100), 59 (45,0), 53 (57,5), 45 (45,0), 44 (67,5)
IIa	144 (94,2), 128 (12,7), 127 (100), 73 (20,7), 71 (13,1), 70 (16,2), 67 (12,9), 46 (13,6), 45 (31,9), 44 (50,0)
IIb	158 (100), 140 (11,0), 128 (25,4), 127 (29,7), 74 (12,1), 73 (12,0), 70 (8,6), 58 (47,0), 46 (9,0), 45 (18,1)
IIc	162 (9,8), 160 (100), 143 (16,1), 127 (19,6), 72 (11,4), 70 (9,8), 67 (9,3), 60 (24,3), 46 (10,8), 45 (17,5)
IIf	159 (96,4), 128 (100), 127 (6,0), 102 (11,3), 72 (11,3), 70 (10,1), 69 (11,3), 68 (14,3), 60 (9,5), 45 (17,9)
IIg	158 (90,4), 142 (19,2), 141 (100), 113 (22,2), 72 (32,7), 71 (38,5), 70 (24,6), 68 (17,5), 45 (48,1), 44 (51,3)
IIh	172 (72,0), 155 (46,0), 144 (67,5), 139 (41,4), 127 (100), 122 (57,6), 73 (34,2), 72 (28,0), 45 (84,6), 44 (81,0)
IIi	173 (68,4), 142 (100), 116 (12,3), 86 (23,7), 75 (10,2), 71 (25,4), 70 (13,2), 68 (12,6), 47 (12,0), 45 (16,7)
IIj	176 (9,5), 174 (100), 105 (10,0), 81 (15,0), 74 (9,6), 72 (16,0), 60 (16,5), 46 (9,5), 45 (12,5), 42 (19,0)

*The 10 most intense peaks in the spectrum are presented.

are observed, but the low intensity of their signals (~0.5%) permits the proposition that the sulfur atom is cleaved from the 5 position – a process which proceeds for all of the considered triazoles (II).* The peaks of the ions, the formation of which is determined by the tautomeric conversions of the M^+ (cf. above), are also not observed in the spectrum. Moreover, for some characteristic ions presented in Table 2, they accompany the fragments corresponding with the loss of the methyl radical. The peaks of the $[M - CH_3N_3]^+$ ion also possesses high intensity (2.4%). The intensity of the analogous $[M - HN_3]^+$ fragments in the mass spectra of the other triazoles (II) did not exceed 0.3%. The R^2 substituent also causes the redistribution of the contributions of the different structures of the $[M - N_2]^+$ ion to the total current of this ion. The azirine form (D) [5, 6], as well as the form (F) or its intermediate (see above), evidently acquire the greatest significance in the given case. A large number of specific routes for the decomposition of the $[M - N_2]^+$ ion arises in connection with this: the elimination of the ammonia molecule on account of the ortho-effect of the SH group, the appearance of the series of ions $[M - N_2, - S_nH_m]$ (Table 3), etc. The total contribution of these specific ions to the complete ion current thereby proves to be adequately high (15%).

The R^1 alkyl substituents [compounds (IIg-i)] lead to the appearance of the sufficiently intense $[M - SR]^+$ and SR^+ fragments, as well as the $[M - SH]^+$ ion, which is characteristic of the decomposition of aromatic thioethers. The expansion of the aromatic ring thereby proceeds (to six-membered in the given case) due to the introduction of a carbon atom into it [13]. The intensity of the $[M - SH]^+$ fragment in the spectrum of the compounds (IIg-i) comprises 1.5, 4.4, and 0.1% correspondingly. On the whole, the R^1 substituent does not lead to a noticeable change in the fragmentation scheme of the triazole (see Scheme 2 and Table 2). The elimination of an ethylene molecule from the compound (IIh) ($R^1 = C_2H_5$) leads to the formation of the pseudomolecular ion of the triazole (IIa), and we are virtually dealing with the decomposition of two homologs, the spectra of which overlap in many respects. The decomposition of both homologs may be described by Scheme 2; therefore, in many cases it is difficult to determine whether a particular fragment is determined by the decompo-

*The SR^1 radical is cleaved in the case of the triazoles (IIg-i) with the alkyl substituent R^1. The fragments with the corresponding intensities of 1.2, 0.8, and 2.6% thereby arise.

sition of the relevant compound – (IIa) or (IIh). Therefore, the intensities of the peaks of the fragments in the mass spectrum of compound (IIh) are not presented in Table 2.

When X = NH_2 [compounds (IIf, i)], the peak of the $[M - NHNH_2]^+$ ion becomes maximal; this ion is formed on account of the simple breaking of the bond in the M^+. The formation of the form (G) of the $[M - N_2]^+$ ion permits an explanation of the synchronous elimination of the hydrogen atom and the nitrogen molecule from this ion; this leads to the $[M - N_4H]^+$ fragments with the intensities of 3.2% (IIf) and 2.8% (IIi).

Therefore, the analysis of the mass spectra, under electron impact, of the 5-amino-1,2,3-thiadiazoles (I) and 5-mercapto-1,2,3-triazoles (II) showed that these isomeric compounds can be readily identified by mass spectrometry. The $[M - N_2]^+$, $[M - NHX]^+$, $[M - NH_2X]^+$, and $[M - H_2Y]^+$ ions are key ions in the assignment of a compound to one or the other class. The $[M - N_2]^+$ ion in the spectra of the thiadiazoles is approximately tenfold more intense, and comprises 3-7% of the complete ion current. The intensity of this fragment comprises less than 0.5% in the mass spectra of the triazoles (II). The remaining fragments indicated are not observed in the spectra of the thiadiazoles (I), whereas the intensities of the peaks of these ions are very high (up to 30% of the complete ion current) in the case of the triazoles with an unsubstituted hydrogen atom at the ring nitrogen atom, and are determined by the tautomerism of the M^+. The substitution of the hydrogen atom by the alkyl group leads to the complete suppression of such processes.

EXPERIMENTAL

The compounds were synthesized in the Urals Polytechnical Institute by the methods of [12]. The mass spectral experiment and the accurate measurement of the mass fragments were performed on a Finnigan MAT-212 instrument using the system of the direct introduction of the substance into the ion source. The energy of the ionizing electrons was 70 eV; the exposure temperature was 30-100°C depending on the volatility of the sample. The determination of the accurate ion mass was performed manually.

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