h. The reaction mixture was passed through Al_2O_3, the dioxane distilled off and the oily product triturated with cold hexane. VIf (0.6 g) was obtained as a white powder.

1,3-Thiazinoazoles VIIf and VIIIf were obtained similarly.

Benzimidazol-2-ones (IX). A mixture of VIa (0.3 g, 0.0012 mmoles) and KOH solution (20%, 0.06 g) in dioxane (10 ml) was stirred at 20°C. After 3 days only VIa was found (by TLC in chloroform). Heating the mixture at 90-100°C for 5 h, cooling, passage through an Al_2O_3 column, removal of dioxane, washing of the crystalline residue with ether (2 × 3 ml) and drying gave benzimidazolone IX (0.1 g, 65%) with mp 317°C (alcohol); literature data [9], mp 308°C. The IR spectrum was identical to that of a known sample.

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SYNTHESIS AND MASS-SPECTROMETRIC STUDY OF 2-AMINO- and 2-CHLORO-5-ARYL-1,3,4-THIADIAZOLES

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The cyclization of aldehyde thiosemicarbazones with ferric chloride yielded 2-amino-5-aryl-1,3,4-thiadiazoles, forming 2-chloro-5-aryl-1,3,4-thiadiazoles in the Sandmeyer reaction. The mass-spectrometric behavior of the 2-amino- and 2-chloro-5-aryl-1,3,4-thiadiazoles was studied; the typical routes of fragmentation characteristic of each group of compounds were found.

Substances with a varying spectrum of biological action have been found among the derivatives of 1,3,4-thiadiazoles, the chemistry of which is developing intensively at the present time [1]. The broad practical application of derivatives of 1,3,4-thiadiazoles in agriculture and medicine requires their reliable and rapid identification. Mass spectrometry is one of the methods permitting the solution of the given undertaking.

We obtained the thiosemicarbazones from the corresponding aromatic aldehydes and thiosemicarbazide [2]; the cyclization of the thiosemicarbazones with ferric chloride led to the 2-amino-5-aryl-1,3,4-thiadiazoles (I)-(IX) [3]. Under the conditions of the Sandmeyer

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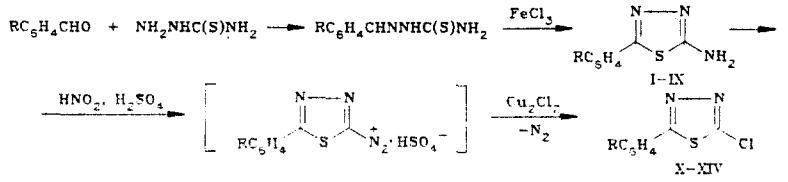
TABLE 1. Properties of the 2-Amino- and 2-Chloro-5-aryl-1,3,4-thiadiazoles (IV), (V), (X), (XII), and (XIII)

Compound	mp, °C	R_f	Found, %				Empirical formula	Calculated, %				Yield, % [A]
			C	H	N	S		C	H	N	S	
IV	201—202	0,44	37,4	2.3	16,7	12,4	$C_8H_6BrN_3S$ [a]	37,5	2,4	16,4	12.5	52
V	220	0.52	37.3	2,3	16.3	12,6	$C_8H_6BrN_3S$	37.5	2.4	16.4	12.5	89
X	154—156	0,44	40.1	2,1	17,9	13,4	$C_8H_4ClN_3O_2S$ [b]	39,8	1.7	17,4	13.3	80
XII	117	0,46	35,1	1,7	9.8	11,5	$C_8H_4BrClN_2S$ [b]	34.9	1,5	10.2	11,6	91
XIII	161	0,47	34,4	1,2	10,6	11,3	$C_8H_4BrClN_2S$	34,9	1,5	10,2	11,6	90

[a] Found, %: BR 30.9. Calculated, %: Br 31.2.
[b] Found, %: Br 28.5; Cl 12.7. Calculated, %: Br 29.0; Cl 12.9.

reaction, the compounds (II), (III), (V), (VI), and (IX) formed the 2-chloro-5-aryl-1,3,4-thiadiazoles (X)-(XIV), which are crystalline substances. The analytical data for the previously undescribed compounds (IV), (V), (X), (XII), and (XIII) are presented in Table 1; the melting points of the substances (I)-(III), (VI)-(IX), (XI), and (XIV) agree with the values presented in the literature.

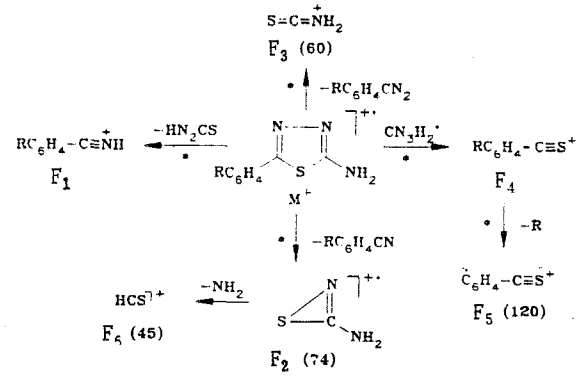
Scheme 1



I R=2-NO_2; II, X R=3-NO_2; III, XI R=4-NO_2; IV R=2-Br; V, XII R=3-Br; VI, XIII R=4-Br; VII R=2-F; VIII R=4-F; IX, XIV R=4-Cl

The analysis of the mass spectra (Table 2) permitted the determination of the main features of the decomposition of the compounds (I)-(XIV) on electron impact, and the construction of fragmentation schemes characteristic of each group of the compounds.

Scheme 2



The decomposition of 2-amino-5-phenyl-1,3,4-thiadiazole (XV) under electron impact was previously studied [4]; the decomposition proceeds with the cleavage of the HCNS and HN_2CS molecules, and the formation of ions having peak intensities 3 and 35% of the maximal value, respectively. The process of the fragmentation of the compounds (I)-(IX) differs somewhat from the fragmentation of compound (XV). The decomposition of the molecular ions (M^+) of the compounds (I)-(IX) is associated with some competing processes, confirmed by metastable transitions. One route for the fragmentation of M^+ relates to the breaking of the $S-C_{(2)}$ bond and the cleavage of the CN_3H_2 fragment (the F_4 ion, Scheme 1). The removal of the RC_6H_4CN fragments, which is characteristic of five-membered heterocycles with three heteroatoms con-

TABLE 2. Mass Spectra* of the 2-Amino- and 2-Chloro-5-aryl-1,3,4-thiadiazoles

Compound	Values of m/z (relative intensity as the % of the maximum peak)
I	222 (46), 195 (12), 149 (8), 134 (44), 120 (6), 104 (33), 76 (15), 75 (5), 74 (23), 60 (24), 45 (100)
II	222 (100), 176 (4), 163 (5), 149 (4), 134 (12), 120 (14), 76 (6), 75 (5), 74 (41), 60 (7), 45 (29)
III	222 (97), 195 (7), 163 (4), 149 (10), 134 (10), 120 (20), 76 (4), 75 (6), 74 (43), 60 (18), 45 (100)
IV	255 (100), a200 (12), a183 (30), 135 (18), 120 (17), 102 (10), 76 (9), 75 (7), 74 (52), 60 (12), 45 (31)
V	a255 (63), a200 (7); a183 (9), 135 (9), 120 (19), 102 (11), 76 (15), 75 (13), 74 (100), 60 (13), 45 (21)
VI	a255 (100), a200 (12), a183 (15), 135 (9), 120 (17), 102 (11), 76 (10), 75 (9), 74 (65), 45 (12)
VII	195 (100), 153 (8), 139 (14), 136 (5), 122 (16), 120 (8), 95 (5), 94 (3), 75 (4), 74 (27), 60 (3)
VIII	195 (100), 153 (21), 139 (88), 136 (15), 122 (73), 120 (46), 95 (64), 94 (21), 75 (36), 74 (76), 60 (18)
IX	b211 (100), b156 (22), b139 (22), b138 (12), 120 (5), b111 (17), 102 (6), 76 (5), 75 (10), 74 (54), 60 (9)
X	b241 (100), 206 (11), b195 (10), 180 (82), 166 (4), 134 (33), 120 (18), 102 (17), b93 (23), 76 (12), 75 (15)
XI	b241 (100), 206 (12), 195 (6), 180 (31), 166 (4), 134 (39), 120 (25), 102 (26), b93 (92), 76 (22), 75 (27)
XII	c274 (67), a239 (11), a213 (40), a199 (15), a181 (29), 134 (25), 120 (33), 102 (47), c93 (100), 76 (31), 75 (40)
XIII	c274 (76), a239 (10), a213 (44), a199 (12), a181 (37), 134 (20), 120 (20), 102 (37), c93 (51), 76 (22), 75 (29)
XIV	d230 (100), b195 (20), b169 (58), b155 (20), b137 (61), 134 (5), 120 (5), 102 (17), b93 (61), 76 (8), 75 (27)

*The peaks of M^+ and the 10 most intense ones in the mass spectrum are presented. For the chlorine- and bromine-containing compounds, the mass numbers of the ions containing the appropriate isotopes are presented as follows: a(^{79}Br), b(^{35}Cl), c(^{35}Cl, ^{79}Br), and d($^{35}Cl_2$).

taining the structural element $R^1-\underset{|}{C}=N$ [5], HN_2CS, and $RC_6H_4CN_2$, is associated with the cleavage of the $S-C_{(5)}$ bond. The second stage in the formation of the F_1-F_3 ions is distinct: the N–N bond breaks for the first two, and the $C_{(2)}$–N bond breaks for the F_3 ion. The proposed path for the formation of the F_1-F_4 ions is confirmed by measuring their accurate mass for compound (II). The values are as follows: F_1) Found: 149.0339. $C_7H_5N_2O_2$. Calculated: 149.0352; F_2) Found: 73.9951. CN_2H_2S. Calculated: 73.9940; F_3) Found: 59.9929. CNH_2S. Calculated: 59.9909; F_4) Found: 165.9923. $C_7H_4NO_2S$. Calculated: 165.9963. The total intensity of the peaks of the M^+ ions and F_1-F_4 in the mass spectra of compounds (II)-(IX) exceeds 40% of the complete ion current; this indicates the high selectivity of the decomposition. Consideration of the relative intensities of the peaks of the F_2 ions (Table 3) for the compounds (I)-(IX) shows that a decrease of the electron-acceptor character of the substituents in the phenyl ring assists the cleavage of the $S-C_{(5)}$ bond, and the fragmentation with the formation of the F_2 ion becomes preferable. Therefore, the comparison of the processes of fragmentation of compounds (I)-(IX) and (XV) on electron impact shows that the introduction of substituents into the phenyl ring not only influences the probability of single-type decompositions (cleavage of the HN_2CS fragment – the F_1 ion, Table 3), but also causes the appearance of new routes for the fragmentation of M^+ with the formation of the F_2-F_4 ions.

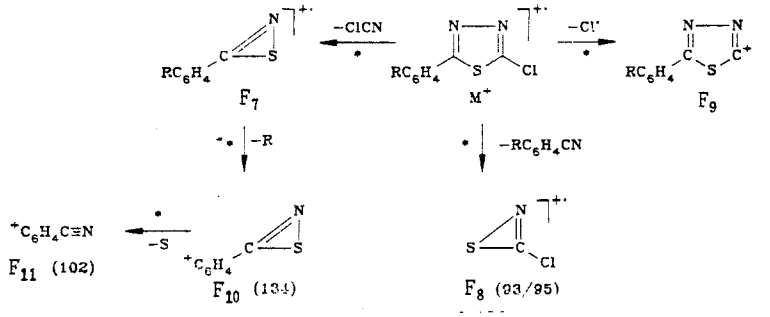
The analysis of the mass spectra of the compounds (X)-(XIV) shows that their molecular ions undergo decomposition on fragmentation, which is analogous to the ions of the aminothiadiazoles (I)-(IX), with the loss of the RC_6H_4CN fragment (the F_8 ion, Scheme 2, Table 4). The other primary processes of the dissociative ionization of the compounds (X)-(XIV) differ from the decomposition of the compounds (I)-(IX). These are the elimination of the ClCN molecule from M^+ (the F_7 ion) and the loss of the chlorine atom with the formation of the F_9 ion.

The mass spectra of the compounds (I)-(XIV) were studied for the first time, and present practical interest for the identification of similar compounds and their isoelectronic analogs.

TABLE 3. Intensity of the Peaks of the Characteristic Ions of the 2-Amino-5-aryl-1,3,4-thiadiazoles in a Complete Ion Current (% Σ_{45})

Compound	M^+	F_1	F_2	F_3	F_4	F_5	F_6
I	9,1	1,7	4,5	4,7	0,2	1,2	19,7
II	35,1	1,4	14,4	2,6	1,9	4,7	10,3
III	22,9	2,4	10,3	4,4	0,7	4,7	23,7
IV	36,0	1,8	9,4	2,2	4,4	3,1	5,6
V	27,7	1,4	22,5	3,0	3,4	4,2	4,6
VI	42,9	2,0	14,4	1,8	5,4	3,7	2,7
VII	48,4	7,7	13,1	1,5	6,6	4,0	0,7
VIII	13,3	9,7	10,1	2,3	11,7	6,1	0,6
IX	36,8	4,5	13,9	2,2	7,9	1,3	—

Scheme 3



EXPERIMENTAL

The low-resolution mass spectra of the compounds (I)-(XIV) were taken on an LKB-2091 instrument applying the system of direct sample input and the energy of the ionizing electrons of 70 and 20 eV. The spectra were registered by means of a light-trace oscillograph. The high-resolution mass spectra were taken on an MKh-1320 instrument with direct input. The resolving capacity of the instrument comprised 10,000-12,000 with the value of the accelerating voltage of 2.5 kV and the energy of the ionizing electrons of 70 eV. The control of the purity of the compounds obtained was carried out by the method of TLC on plates of Silufol UV-254; the development was performed using UV light, and the eluent was the 2:1 mixture of acetone—hexane [for compounds (IV, V)] the chloroform [for (X), (XII), XIII)].

The aldehyde thiosemicarbazones were obtained according to the method of [2] from the corresponding aromatic aldehydes and thiosemicarbazide.

2-Amino-5-(2-bromophenyl)-1,3,4-thiadiazole (IV) [3]. The solution of 12.9 g (0.05 mole) of 2-bromobenzaldehyde thiosemicarbazone and 54.1 g (0.2 mole) of $FeCl_3 \cdot 6H_2O$ in 450 ml of ethanol is boiled for 45 min. A large part of the solvent is removed; the residue is cooled and treated with 40 ml of concentrated HCl. The mixture is cooled for 2 h in a bath with ice and salt. The precipitated crystalline residue is filtered off and washed with 40 ml of cold concentrated HCl. Aqueous ammonia is added to the residue; the mixture is heated on a water bath for 15 min. The precipitated crystalline residue is filtered off and recrystallized from ethanol.

The thiadiazoles (I)-(III) and (V)-(IX) are obtained analogously.

2-Chloro-5-(3-nitrophenyl)-1,3,4-thiadiazole (X). A. The solution of 2.2 g (10 mmoles) of 2-amino-5-(3-nitrophenyl)-1,3,4-thiadiazole (II) in 20 ml of acetic acid is added to the solution of 0.8 g of sodium nitrite in 8 ml of concentrated H_2SO_4 at −5°C so that the temperature does not exceed 0°C. The resulting bright yellow solution of the diazonium salt is poured into an ice-cooled solution of Cu_2Cl_2 in 20 ml of concentrated HCl at −10°C in the course of 5 min. The mixture is heated to 80°C; it is cooled. An equal volume of water is added, and the precipitated crystalline residue is filtered off.

TABLE 4. Intensity of the Peaks of Characteristic Ions of the 2-Chloro-5-aryl-1,3,4-thiadiazoles in the Complete Ion Current (% Σ_{45})

Compound	M^+	F_7	F_8	F_9	F_{10}	F_{11}
X	24,6	5,1	5,7	1,9	5,9	3,0
XI	16,6	3,8	15,5	1,5	4,9	3,2
XII	15,6	7,0	11,9	2,2	2,2	4,1
XIII	20,4	8,8	7,2	2,4	2,0	3,7
XIV	23,1	11,5	10,3	3,3	0,6	2,1

B. To the solution of 1.1 g (5 mmoles) of the thiadiazole (II) in 120 ml of concentrated HCl at −10°C is added 0.85 g of sodium nitrite in 6.5 ml of water; the mixture is stirred for 2 h. The mixture is heated to 70°C; it is cooled, and the residue is filtered off. The substances obtained by the methods A and B are identical according to the melting points, the TLC, and the mass spectra.

The compounds (XI)-(XIV) were obtained by the method A.

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10-ALKENYLPHENOTHIAZINES.

2.* SYNTHESIS AND MECHANISM OF ACIDIC HYDROLYSIS OF cis- AND trans-10-2-PHENYLVINYL)PHENOTHIAZINES

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The addition of phenothiazine to phenylacetylene in super-base media proceeds regio- and stereoselectively and leads to the predominant formation of cis-10-(2-phenylvinyl)phenothiazine, which is completely converted to its trans-isomer at 200°C. Kinetic analysis of the acidic hydrolysis of the cis- and trans-isomers has allowed us to assign to it an AS_E2 reaction mechanism, similar to the mechanism of hydrolysis of vinyl alkyl ethers.

The reaction of phenothiazine with acetylene is used for the preparation of 10-vinylphenothiazine (I) [2, 3]. The reaction of phenothiazine with acetylene homologs has not been described in the literature, although it is obvious that these reactions would represent a straightforward method for the synthesis of a wide variety of 10-alkenylphenothiazines. In

*For Communication No. 1, see [1].

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