observed for a mixture of this product with the substance obtained by the method in [10]. The product has R_f 0.6 (B).

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MASS SPECTRA OF 4,5-DISUBSTITUTED 1,2,3-THIADIAZOLES

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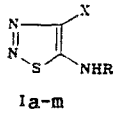
UDC 543.51:547.794.3

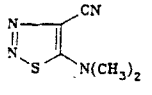
The schemes of the fragmentation of 4-substituted 5-arylamino-1,2,3-thiadiazoles were established on the basis of electron-impact mass spectra and high-resolution mass-spectrometric data, and the effect of substituents on the fragmentation pathways was analyzed. It is shown that the cyclization of the $[M - N_2]^+$ ions formed in the fragmentation of compounds that contain a thiocarboxamido group in the 4 position proceeds with the participation of the most nucleophilic heteroatom.

The 1,5-electrocyclization of diazo thioamides leads to 5-aminothiadiazoles or 5-mercaptotriazoles [1]. In [2] it was shown that mass spectrometry is the fastest and most reliable method for the identification of compounds of these classes.

In the present paper we present the results of a mass-spectrometric study of 4-cyano- and 4-thiocarboxyamido-5-aryl(alkyl)amino-1,2,3-thiadiazoles Ia-i.*



Ia-m



II

I a-d X=CN; e-g X=$CSNH_2$; h, i X=$CSNHCH_3$; a,e R=C_6H_5; b,f R=4-$CH_3C_6H_4$; c,g R=4-$CH_3OC_6H_4$; d R=4-$C_2H_5OC_6H_4$; h R=H; i R=CH_3

*The mass spectrum of Ih was presented in [2]. For the purposes of our investigation it was rerecorded under conditions that were identical for the entire series.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 118-122, January, 1988. Original article submitted July 8, 1986.

0009-3122/88/2401-0099$12.50

TABLE 1. Intensities of the Peaks of the Characteristic Fragment Ions in the Mass Spectra of Ia-i (% Σ_{40})*

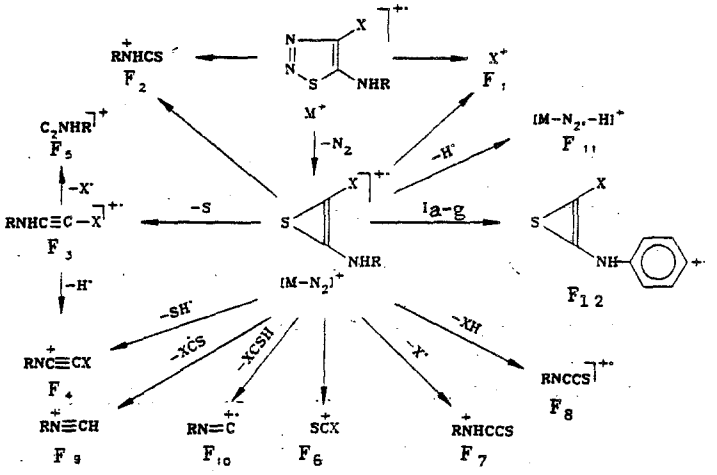
Compound	M^+	$[M-N_2]^+$	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	F_9	F_{10}	F_{11}	F_{12}
Ia	8,1	19,6	—**	0,1	8,6	2,0	1,7	0,8	1,9	1,9	2,6	4,1	3,4***	
Ib	7,9	14,4	—**	0,1	1,4	8,5	1,2	1,1	0,2	1,2	4,0	2,8	6,8	6,8
Ic	9,4	3,4	—**	0,1	1,7	1,2	0,8	1,7	1,3	0,9	13,9	4,0	0,4	2,5
Id	15,9	3,4	—**	0,1	0,5	0,1	0,3	0,8	0,1	0,3	6,9	0,7	0,2	0,4
Ie	19,9	1,0	2,2	1,3	0,1	4,9	1,0	0,3	4,2	0,8	2,6	0,8	1,0***	
If	19,3	1,1	1,1	0,4	2,4	4,2	1,2	0,3	3,1	0,8	2,8	0,9	1,2	1,0
Ig	14,9	0,7	2,0	0,7	3,1	2,7	0,3	0,3	1,7	0,5	4,2	1,5	1,0	1,0
Ih	13,6	2,9	5,5	4,0	0,3	1,3	—**	0,5	1,8	1,9	—**	—**	—	—
Ii	25,8	4,7	8,0***		0,3	2,1	0,4	0,7	5,5	0,8	3,1	0,7	—	—

*The ions due to fragmentation of the corresponding aromatic amine or hydrocarbon (for example, $ArNH_2^{+\cdot}$, $[ArNH_2 - CHN]^{+\cdot}$, $ArH^{+\cdot}$, etc.) constitute from 15% to 25% of the total ion current.

**The ion has an m/z value below 40 and does not enter into the range of recordable masses.

***The ions have identical elemental compositions.

The molecular ions of thiadiazoles Ia-i are stable, and the M^+ peaks constitute 8-26% of the total ion current (Table 1).

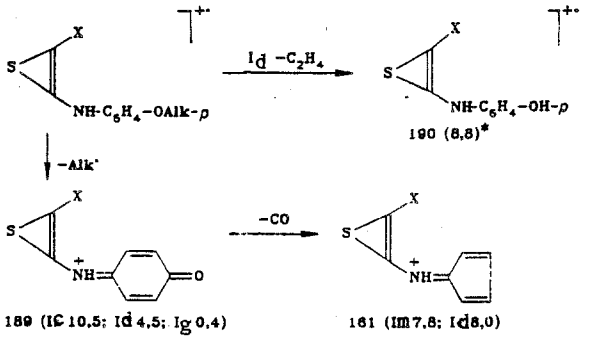


One of the principal processes in the fragmentation of the M^+ ions of 1,2,3-thiadiazoles is the elimination of a molecule of nitrogen. The resulting $[M - N_2]^+$ ions can exist in several isomeric forms; this is responsible for the entire variety of the pathways of their subsequent fragmentation [2-8]. The presence of an alkyl substituent in the 5 position of thiadiazoles leads to a thioketene form of the $[M - N_2]^+$ ion [4, 5], while the presence of an alkylamino group in the 5 position leads to a thiirene form [3-8]. The presence in the 4 position of the thiadiazole of a substituent that contains heteroatomic groupings may lead to more complex structures of this ion [2, 3]. In the case of thiadiazoles Ia-i the principal form of the $[M - N_2]^+$ ions is evidently the thiirene form.

The elimination of a sulfur atom or an SH radical is probably due to the linear form of the $[M - N_2]^+$ ions, which develops in the first instant after splitting out of a molecule of nitrogen from M^+. Ejection by the $[M - N_2S]^+$ ion (fragment F_3) of radical X leads to ion F_5. Radical X or molecule XH may also be eliminated directly from the $[M - N_2]^+$ ion. These processes lead to fragments F_7 and F_8, which have rather intense signals. Ions F_6, the formation of which is associated with fragmentation of $[M - N_2]^+$ ions with a thiirene structure, are also characteristic [6-8]. The intensities of the peaks of fragment F_6 are somewhat higher in the case of cyano derivatives Ia-d, probably as a consequence of the fact that the presence of a thiocarboxamido group in the 4 position of the other thiadiazoles (Ie-i) is responsible for the possibility of further fragmentation of F_6 ions with the formation of stable fragments. The peaks of F_9 and F_{10} ions are also intense in the mass spectra of thiadiazoles Ia-i. The F_6 and F_9 ions are isobaric in the case of Ie. High-resolution mass-spectrometric data showed that the ratio of the intensities of the peaks of these ions is

1:8; ion F_6 has elementary composition $C_2H_2NS_2$ (calculated 103.9629; determined 103.9634), while ion F_9 has elementary composition C_7H_6N (calculated 104.0500; determined 104.0503).

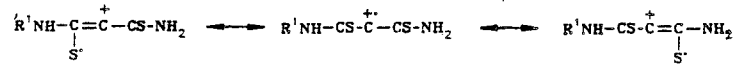
Another characteristic process in the fragmentation of the $[M - N_2]^+$ ions of Ia-g is the elimination of a hydrogen atom or a substituent in the benzene ring with the formation of fragments F_{11} and F_{12}, respectively. The splitting out of a hydrogen atom may be realized from the amino nitrogen atom or from the ortho position of the benzene ring, while in the case of Ib and If (R = 4-$CH_3C_6H_4$) splitting out of a hydrogen atom from the methyl group of the tolyl substituent with the formation of a substituted tropylium cation is also possible. The presence of an alkoxyphenyl substituent in the 5 position (Ic, d, g) leads to the development of yet another pathway for the fragmentation of $[M - N_2]^+$ ions, which was previously described in [8]:



*The m/z values (peak intensities in percent of the total ion current).

The F_3 ions may also undergo similar fragmentation processes involving the alkoxy group. Fragments with masses of 158, 157, and 129 are formed as a result. The intensities of the peaks of these ions are 2.1%, 3.5%, and 2.1%, respectively, in the case of Id, as compared with 0%, 1.3%, and 0.8%, respectively, in the case of Ic.

The presence of a thiocarboxamido substituent in the 4 position (Ie-i) leads to suppression of the indicated fragmentation pathways and creates additional possibilities for transformation of the initially formed $[M - N_2]^+$ ions [2, 3]. If one turns to the possible structure of these linear ions, it is apparent that their stabilization may be realized by cyclization to an azirine or thiirene ring with the inclusion of any of the four heteroatoms. In addition, the formation of large rings is also possible [2].



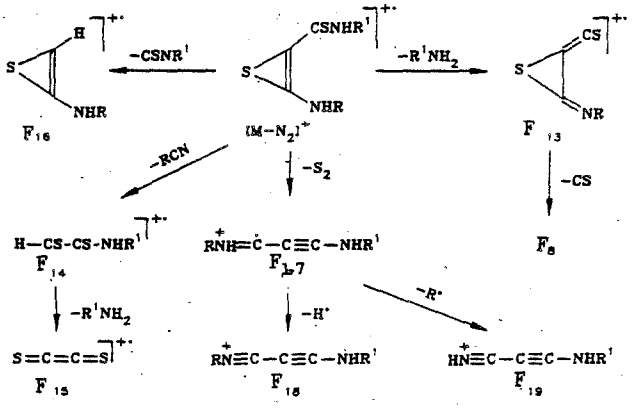
An analysis of the mass spectra of Ie-i made it possible to conclude that cyclization takes place primarily at the sulfur atom of the substituted thioamide group. In fact, the principal pathways of fragmentation of $[M - N_2]^+$ ions that have a thiirene structure are ejection of R^1NH_2 (due to the ortho effect) and R^1CN molecules [2, 3]. Cyclization at the unsubstituted thioamido group should lead to the loss of HCN and R^1NH_2 molecules, while cyclization at the substituted thioamido group should lead to the loss of NH_3 and R^1CN molecules. The intensities of the peaks of the second pair of ions (F_{13} and F_{14}) are substantially (by more than an order of magnitude) higher; this indicates that cyclization takes place primarily at the substituted thiocarboxamido group. This process is in conformity with principle, since electron-donor aryl and alkyl substituents R in Ie-i increase the electron density on the corresponding sulfur atom, making it more nucleophilic as compared with the second atom. This specific cyclization of the $[M - N_2]^+$ ion does not make it possible to determine whether the thiocarboxamido group enters into the composition of the heteroring or is a substituent in the 4 position. The answer to this question can be obtained by comparing the relative intensities of the peaks of fragments F_1 and F_2. The formation of a thiocarboxamide ion by cleavage of the exocyclic C–C bond in the 4 position is substantially more favorable than in the case of opening of the heteroring with cleavage of the C=C and S–N bonds. As a result, the intensity of the peaks of fragment F_1 is higher than that of fragment F_2, even in those cases in which the energy of ionization of the latter is lower (see Table 1). Thus, of the two ions of a common nature ($RNHCS^+$), the peak of the fragment formed by simple cleavage of the $C_{(4)}$–C bond will be more intense. This fact makes it possible to reliably identify isomeric 4,5-disubstituted thiadiazoles with various hydrocarbon substituents attached to the nitrogen atoms in the 4 or 5 position.

TABLE 2. Intensities of the Peaks of the Characteristic Fragment Ions in the Mass Spectra of Ie-i ($\% \Sigma_{40}$)

Compound	F_{13}	F_{14}	F_{15}	F_{16}	F_{17}	F_{18}	F_{19}
Ie	13,0	4,6	4,1	2,8	1,6	3,7	1,0
If	10,0	3,3	2,7	1,7	1,1	3,9	0,5
Ig	8,3	3,2	2,9	1,6	0,8	4,2	0,5
Ih	2,7	4,9	3,0	1,2	1,7	2,9	3,6
Ii	1,6	4,9	2,2	0,5	1,1	2,2	3,5

Among other pathways for the fragmentation of thiadiazoles Ie-i one should single out some processes involving the fragmentation of $[M - N_2]^+$ ions that lead to fragments that give intense peaks in the mass spectra.

The formation of F_{17} ions is associated with the successive or simultaneous splitting out of two sulfur atoms; the simultaneous route requires the realization of a five-membered heterocyclic form of the $[M - N_2]^+$ ion with an S–S bond [2]. The F_{17} ion subsequently loses a hydrogen atom or an aromatic radical. The intensities of the peaks of fragment ions F_{13}–F_{19} are presented in Table 2.



The pathways of the fragmentation of thiadiazole II remain the same; four principal ions – M^+ (14.1), $[M - N_2]^+$ (15.1), $NC{-}CS{-}C{\equiv}\overset{+}{N}{-}CH_3$ (18.9), and $NC\overset{+}{C}S$ (21.7%) – constitute ~70% of the total ion current. The elementary compositions of the last two ions were confirmed by means of high-resolution mass spectrometry. For the first ion the calculated value was 111.0018, and the value found was 111.0013; for the second ion the calculated value was 69.9752, and the value found was 69.9759. The intensities of the peaks of the $[M - N_2, - S]^+$ and $[M - N_2, - SH]^+$ ions are 1.8% and 2.4%, respectively.

Thus, the basic principles in the fragmentation of 4-cyano- and 4-thiocarboxamido-5-aryl(alkyl)amino-1,2,3-thiadiazoles under electron impact were found as a result of our investigation. On the basis of a comparison of the intensities of the peaks of the characteristic fragment ions we found a method for the determination of the positions of the radicals attached to the nitrogen atoms of amino groups in the 4 or 5 position of the thiadiazole ring. It was established that stabilization of the $[M - N_2]^+$ ion proceeds through cyclization to a thiirene with inclusion of the sulfur atom of the substituted thioamido group.

EXPERIMENTAL

Compounds Ia-i and II were synthesized in the Ural Polytechnical Institute [1]. The mass spectra were obtained with an MKh-1320 spectrometer with direct introduction of the samples into the ion source. The ionization energy was 50 eV. The recording temperature was varied from 50°C to 150°C, depending on the volatility of the compounds. Appreciable changes in the relative intensities of the ion peaks were not observed when the temperature of admission of the samples was changed; this constitutes evidence for the absence of thermal destruction. The total ion current was computed manually over the mass range from m/z 40 to M^+. The high-resolution mass spectra were obtained with an MAT-311A spectrometer. The precise masses of the ions were determined manually with the use of perfluorinated kerosene

as the mass standard. The 10 principal ions in the mass spectrum of II, m/z (relative intensity, %): 154 (61), 126 (66), 125 (8), 111 (84), 94 (9), 93 (11), 72 (7), 70 (100), 67 (10), 42 (22).

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REACTION OF METHYL PROPIOLATE WITH THIOSEMICARBAZONES

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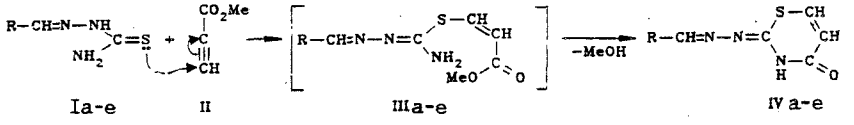
UDC 547.371'497.1'869.07

Methyl propiolate reacts with thiosemicarbazones in methanol in the presence of triethylamine to give 2-benzylidene(thenylidene, or furfurlidene)azino-3H-1,3-thiazin-4-ones.

Continuing a study of the reactions of nitrogen and sulfur-containing ambifunctional compounds with activated acetylenes [1], we have now examined the reactions of thiosemicarbazones with methyl propiolate.

1-Acetylthiosemicarbazide is known to react with methyl propiolate in methanol on warming to give a mixture of cis,cis- and cis,trans-dimethyl β-thiodiacrylic ethers [55% yield). Similar compounds have been obtained by reacting thiobenzamide and thioacetamide with methyl propiolate in methanol at 20°C, the yields being 77 and 70% respectively. However, the reaction of ethyl propiolate with thiobenzamide in the absence of a solvent on heating proceeds vigorously to give 2-phenyl-1,3-thiazin-4-one [4]. Arylthiohydrazides react with methyl propiolate on heating in methanol to give 60-65% of substituted 1,3,4-thiadiazoles [5, 6]. The reaction of propiolate esters with thiourea and its derivatives affords 1,3-thiazin-4-ones [7-9].

We have now examined the reaction of thiosemicarbazones (I) of various types with methyl propiolate (II) in equimolar amounts, in methanol at 60°C in the presence of catalytic amounts of triethylamine, to give 2-benzylidene (thenylidene, or furfurylidene)azino-3H-1,3-thiazin-4-ones (IVa-e).



Ia-e II IIIa-e IV a-e

III—IV a R=Ph; b R=*p*-Br—C_6H_4; c R=*p*-NO_2—C_6H_4; d R=α-C_4H_3S; e R=α-C_4H_3O

The reaction clearly involves the intermediate formation of the S-monoadducts, which cyclize readily to (IVa-e) with the removal of a molecule of alcohol. The intermediate

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 123-125, January, 1988. Original article submitted August 5, 1986; revision submitted May 28, 1987.