SYNTHESIS AND REACTIONS OF 3-AMINOTHIAZOLIDINE-2-THION-4-ONE DERIVATIVES.

3. *REACTION OF 3-[N-(α-METHYLTHIO)ETHYLIDENE] AMINOTHIAZOLIDINE-2-THION-4-ONE WITH AMINES

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It is shown that cyclization leading to the formation of 1,3,4-thiadiazole derivatives occurs in the reaction of 3-[N-(α-methylthio)ethylidene]aminothiazolidine-2-thion-4-one with amines. The structures of the compounds obtained were established by spectral methods and were confirmed by alternative synthesis.

Continuing our research on the reactions of 3-aminothiazolidine-2-thion-4-one derivatives [1] we have studied the reaction of 3-[N-(α-methylthio)ethylidene]aminothiazolidine-2-thion-4-one (I) with ammonia and aniline; the formation of diverse products is possible in this case, since there are three electrophilic centers in the starting compound. Since rhodanine I can be regarded as a substituted thioimino ester from which amidines are formed by the action of amines [2], in our case one might have expected the production of derivatives of the II type or their transformation products.

\[
\begin{align*}
&\text{I} \quad \text{IIa, b} \\
&\text{a R=H; b R=C}_6\text{H}_5
\end{align*}
\]

In fact, we found from the results of elementary analysis that the methylthio group is replaced by an amine residue in the compounds obtained. The same conclusion also follows from the PMR spectra, in which singlets of C-methyl and methylene groups (2.67 and ~4.0 ppm), as well as signals of protons of amino or phenylamino groups, are observed (see the experimental section).

*See [1] for Communication 2.

TABLE 1. Mass Spectra of the Products of the Reaction of Rhodanine I with Ammonia and Aniline

<table>
<thead>
<tr>
<th>Compound</th>
<th>m/e values (relative intensities in percent)</th>
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<tbody>
<tr>
<td>IIa (I+NH₃)</td>
<td>40 (8,6), 41 (23,6), 42 (39,0), 43 (2,9), 44 (39,1), 45 (23,3), 46 (75,2), 47 (13,0), 48 (3,6), 56 (6,2), 57 (2,3), 58 (13,9), 59 (40,7), 60 (61,1), 61 (2,3), 64 (2,1), 69 (5,8), 72 (8,7), 73 (6,5), 74 (2,0), 75 (2,3), 76 (2,2), 78 (6,5), 88 (5,5), 90 (2,5), 99 (8,2), 101 (5,4), 105 (18,1), 113 (3,6), 117 (24,1), 144 (3,2), 145 (11,6), 146 (100), 147 (9,2), 148 (9,3), 172 (11,7), 189 (11,6)</td>
</tr>
<tr>
<td>IIb (I+C₆H₄NH₂)</td>
<td>38 (3,7), 39 (29,2), 40 (5,9), 41 (17,8), 42 (29,7), 43 (5,5), 45 (15,3), 46 (48,2), 47 (5,1), 48 (2,2), 50 (2,4), 51 (15,5), 52 (4,2), 55 (2,3), 56 (6,3), 57 (2,1), 58 (6,8), 59 (30,0), 60 (7,7), 63 (5,9), 64 (8,3), 65 (45,2), 66 (9,8), 69 (50,4), 70 (2,1), 72 (6,0), 73 (2,3), 75 (2,7), 77 (57,1), 78 (5,2), 79 (6,5), 80 (2,1), 88 (4,4), 91 (8,2), 92 (14,9), 93 (58,4), 94 (4,7), 97 (16,1), 99 (7,3), 101 (5,6), 104 (4,2), 105 (21,2), 106 (20,5), 113 (4,6), 119 (4,4), 120 (3,5), 124 (7,4), 132 (3,0), 133 (8,3), 142 (3,6), 145 (14,0), 146 (65,7), 147 (5,7), 148 (5,9), 172 (42,0), 173 (100), 174 (16,8), 175 (14,5), 265 (14,0), 266 (2,0)</td>
</tr>
</tbody>
</table>

*The peaks of ions with intensities ≥ 2% are presented.

However, the chemical properties of the synthesized products did not correspond to the II structure. Thus, in contrast to ordinary 3-substituted rhodanines [3], these compounds do not react with p-dimethylaninobenzaldehyde but do react readily with it after prior heating with dimethyl sulfate.

On the basis of the UV spectra it may be concluded that the products of the reaction of thiazolidine I with amines do not contain a rhodanine ring, since the absorption maxima of their solutions (265 and 250 nm) are considerably higher than in the case of solutions of the starting rhodanine [1] or 3-aminorhodanine (295 nm) [4]. Absorption bands of an amide carbonyl group at 1690 cm⁻¹ and of an N–H bond (3080–3360 cm⁻¹), as well as bands characteristic for a substituted thiadiazole ring [5] (1250, 1390, and 1505 cm⁻¹), are observed in the IR spectrum of the compound obtained by the action of aniline on rhodanine I, and this indicates the possibility of the formation of thiadiazoles IIIa,b.

The mass-spectral data (Table 1) also are in good agreement with the assumption of a thiadiazole structure for the reaction products. The results of a study of the effect of electron impact on 2-ureido-1,3,4-thiadiazoles [6] were taken into account in the interpretation of these spectra.

Fragment ions formed by cleavage of the amide bond or by cleavage of the exocyclic C–C bond, which proceeds both with transfer of a hydrogen atom to the charged fragment and without it, are clearly recorded in the spectra:

\[
\begin{align*}
\text{CH}_3\text{N} & \text{SCH}_2\text{CO} \\
\text{CH}_3\text{N} & \text{SCH}_2 \\
\text{CH}_3 & \text{SCH}_3 \\
\text{CH}_3 & \text{SCH}_3
\end{align*}
\]

The charge in the molecular ions may also be localized on the part of the molecule that includes the amino group. Then, for example, in the case of IIb, C₆H₄NH⁺, C₆H₅N⁺, C₆H₅NCO⁺, and C₆H₅NCO²⁺ ions (92, 93, 119, and 120, respectively) are formed as a result of the bonds indicated above. The elementary compositions of the ions with m/e 119 and 120 were confirmed by precise measurements of their masses (Table 2), and their formation serves as absolute proof that the investigated product cannot have rhodanine structure IIb. Evidence for this is also provided by the absence in the examined spectra of ion peaks with masses M-28 and M-72, which could arise in the case of successive ejection of CO and CS molecules from the rhodanine ring.

Other ions that are common to the reaction products (99, 132, 105, and 106) evidently have the following structures:

*Here and subsequently, the numbers that characterize the ions are the mass-to-charge ratios.