

thiolane 1,1-dioxide in 50 ml of dioxane, and the mixture was stirred for 3 h. Pyridine (10 ml) was added dropwise, and the mixture was stirred for another 2 h. The solvent was evaporated, and the residue was washed with water and crystallized from 50% aqueous dioxane. A mixture of Vc and IIIc melted at 211°C.

trans-1,3-Dimethylperhydrothieno[3,4-d]imidazole-2-thione 5,5-Dioxide (Vd). This compound was similarly obtained.

LITERATURE CITED

1. T. É. Bezmenova, P. G. Dul'nev, G. I. Khaskin, and V. I. Kulishov, Summaries of Papers Presented at the 9th International Symposium on the Chemistry of Organic Sulfur Compounds [in Russian], Zinatne, Riga (1980), p. 297.
2. F. Ellis and P. G. Sammes, J. Chem. Soc., Perkin Trans. I, No. 22, 2866 (1972).
3. P. I. Parkhomenko, T. A. Ovcharenko, S. M. Lukashev, and T. É. Bezmenova, Summaries of Papers Presented at the 13th Scientific Session on the Chemistry and Technology of Organic Sulfur Compounds and Sulfurous Petroleum Oils [in Russian], Zinatne, Riga (1974), p. 238.
4. H. Kotake, K. Inomata, I. Murata, H. Kinoshita, and M. Katsuragawa, Chem. Lett., No. 10, 1073 (1976).
5. F. Ellis, P. G. Sammes, M. B. Hursthouse, and S. Neidle, J. Chem. Soc., Perkin I, No. 12, 1560 (1972).
6. L. V. Spirikhin, R. A. Sadykov, B. V. Flekhter, N. N. Novitskaya, A. A. Topasenko, and T. A. Tolstikov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1029 (1980).
7. T. É. Bezmenova and P. G. Dul'nev, Khim. Geterotsikl. Soedin., No. 5, 622 (1974).

SYNTHESIS AND REACTIONS

OF 3-AMINOTHIAZOLIDINE-2-THION-4-ONE DERIVATIVES.

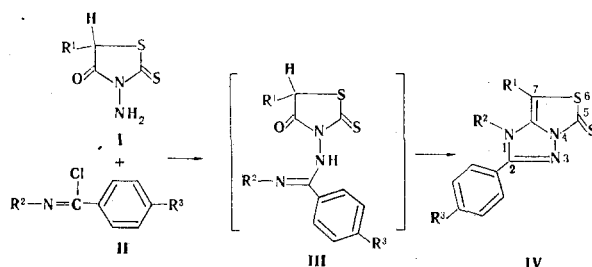
4.* THIAZOLO[3,4-b][1,2,4]TRIAZOLE DERIVATIVES

E. K. Mikitenko and N. N. Romanov

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It is shown that derivatives of a new heterocyclic system, viz., thiazolo[3,4-b][1,2,4]triazole, the structure of which was established by means of their IR and PMR spectra, are formed in the reaction of 5-substituted 3-aminorhodanines with imidoyl chlorides.

In [2] it was shown that the synthesis of condensed heterocyclic thiazole systems on the basis of N-aminorhodanine is extremely promising. We studied the reaction of 5-methyl- and 5-phenyl-3-aminothiazolidine-2-thion-4-ones (I) with N-substituted benzimidoyl chlorides II.



It is known that aminorhodanines react with electrophilic agents such as acid anhydrides and chlorides to give N-acylaminorhodanines [3]. Since amidines are usually formed in the reaction of amines with imidoyl chlorides [4], one might have also expected the formation of thiazolidinyl-substituted amidines of the III type in the case under consideration. However, we found that the reaction does not stop at this step but proceeds further

*See [1] for Communication 3.

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskih Soedinenii, No. 3, pp. 331-333, March, 1982. Original article submitted January 16, 1981.

TABLE 1. Thiazolo[3,4-b][1,2,4]triazole-5-thiones IV

Compound	R ¹	R ²	R ³	mp, * °C	λ_{\max} , nm (lg ϵ)	Found, %		Empirical formula	Calc., %		Yield, %
						N	S		N	S	
IVa	CH ₃	CH ₃	H	249—250	239 (3,38), 302 (2,18), 388 (3,13)	16,0	23,9	C ₁₂ H ₁₁ N ₃ S ₂	16,1	24,5	24
IVb	CH ₃	C ₆ H ₅	H	241—242	244 (3,32), 310 (2,40), 390 (3,22)	13,0	19,8	C ₁₇ H ₁₃ N ₃ S ₂	13,0	19,8	47
IVc	C ₆ H ₅	CH ₃	H	252—253	240 (3,32), 257 (3,23), 315 (2,76), 400 (3,20)	12,9	19,6	C ₁₇ H ₁₃ N ₃ S ₂	13,0	19,8	50
IVd	C ₆ H ₅	C ₆ H ₅	H	274—275	242 (3,34), 257 (3,33), 320 (2,77), 400 (3,24)	11,0	16,6	C ₂₂ H ₁₅ N ₃ S ₂	10,9	16,6	64
IVe	C ₆ H ₅	C ₆ H ₅	OCH ₃	206—207	281 (3,47), 397 (3,27)	10,0	15,5	C ₂₃ H ₁₇ N ₃ OS ₂	10,1	15,4	52
IVf	C ₆ H ₅	C ₆ H ₅	NO ₂	279—280	276 (3,37), 360 (3,12), 405 (2,87)	13,2	14,8	C ₂₂ H ₁₄ N ₄ O ₂ S ₂	13,2	14,9	20

*The compounds were crystallized: IVa-c from alcohol, IVd from dimethylformamide (DMF), and IVe, f from alcohol-MDF (1 : 1).

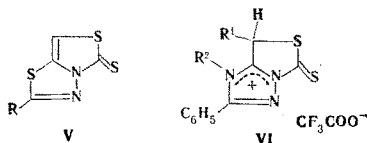
TABLE 2. Chemical Shifts (δ , ppm) of the Protons in the PMR Spectra of Thiazolotriazoles IV and Aminorhodanines I

Compound	d ₆ -DMSO			CF ₃ COOH			
	C—CH ₃	N—CH ₃	Ph	C—CH ₃	N—CH ₃	CR ¹ —H	Ph
IVa	2,65	4,06	8,00	1,70 (d)	3,77	5,16 (q)	7,33
IVb	1,98	—	7,66—7,95	1,27 (d)	—	5,17 (q)	7,09—7,50
IVc	—	3,77	7,67—8,20	—	3,37	6,27	7,05—7,40
IVd	—	—	7,00—8,00	—	—	6,02	6,70—7,11
I (R' = CH ₃)	—	—	—	1,35 (d)	—	4,07 (q)	—
I (R' = Ph)	—	—	—	—	—	5,03	7,00

to give derivatives of a new heterocyclic system that was previously unknown in the condensed thiazolo-S-triazole series [5], viz., thiazolo[3,4-b][1,2,4]triazoles IV (see Table 1).

The IR spectra of the condensation products do not contain absorption bands of the C=O and N—H groups of starting rhodanines I (1680–1710, 3150–3280 cm⁻¹) but do not contain absorption bands of a C=N bond at 1580–1612 cm⁻¹. Only signals of aromatic protons and singlets of protons of methyl groups are observed in the PMR spectra of IV (Table 2) recorded in d₆-DMSO. Three maxima are noted in the electronic spectra of condensation products IV (Table 1).

As in the case of starting rhodanines I, signals that are characteristic for the —CHR¹— grouping are observed in the PMR spectra of solutions of the compounds obtained in this research in trifluoroacetic acid, and the substances are isolated unchanged when these solutions are diluted. These data indicate that, in contrast to thiazolothiadiazoles of the V type, which are protonated at the sulfur atom of the thiono group [2, 6], a proton evidently adds to the carbon atom in the 7 position to give salts with structure VI in the case of thiazolotriazoles:



The reason for this different behavior of thiazolotriazoles and thiazolothiadiazoles with respect to trifluoroacetic acid may be the greater basicity of the triazole fragment of IV as compared with the thiadiazole fragment in compounds of the V type. In addition, steric hindrance exists between the hydrogen atoms in the ortho positions of the phenyl groups, and the hydrogen atoms of the methyl group (IVb, c). The rather wide interval (Table 2) in the PMR spectra of the signals of the aromatic protons [7] indicates the existence of this interaction. In the VI cation formed by protonation the repulsion between the unbonded hydrogen atoms is smaller than in the starting thione. This phenomenon should additionally increase the basicities of thiazolotriazoles IV as compared with thiazolothiadiazoles V, i.e., it should promote C rather than S protonation [8].

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were obtained with a UR-10 spectrometer. The UV spectra of solutions of the compounds in CH₃OH were obtained with an SF-8 spectrophotometer. The PMR spectra of solutions of the compounds in CF₃COOH [with hexamethyldisiloxane (HMDS) as the internal standard] and d₆-DMSO (with HMDS as the external standard) were recorded with a Tesla BS-467 spectrometer (60 MHz).

5H-1,7-Dimethyl-2-phenylthiazolo[3,4-b][1,2,4]triazole-5-thione (IVa). A mixture of 0.32 g (2 mmole) of 5-methyl-3-aminothiazolidine-2-thion-4-one and 0.30 g (2 mmole) of N-methylbenzimidoyl chloride was fused at 80°C in the course of an hour. The crystallized melt was triturated with CH₃CN, and the reaction product was removed by filtration and crystallized (Table 1).

5H-1,2,7-Triphenylthiazolo[3,4-b][1,2,4]triazole-5-thione (IVd). A mixture of 0.22 g (1 mmole) of 5-phenyl-3-aminothiazolidine-2-thion-4-one and 0.21 g (1 mmole) of N-phenylbenzimidoyl chloride was fused at 120°C in the course of an hour, after which the melt was triturated with acetone, and the reaction product was removed by filtration and crystallized.

Compounds IVb-f were similarly obtained from the corresponding aminorhodanines and benzimidoyl chlorides.

LITERATURE CITED

1. E. K. Mikitenko, N. N. Romanov, and I. S. Shpileva, *Khim. Geterotsikl. Soedin.*, No. 3, 339 (1981).
2. E. K. Mikitenko and N. N. Romanov, *Khim. Geterotsikl. Soedin.*, No. 4, 564 (1981).
3. F. Brown, *Chem. Rev.*, **61**, 463 (1961).
4. H. Ulrich, *The Chemistry of Imidoyl Halides*, Plenum Press, New York (1968), p. 85.
5. U. Tamura, H. Hayashi, J. Kim, and M. Ikeda, *J. Heterocycl. Chem.*, **10**, 947 (1973).
6. E. D. Sych, E. K. Mikitenko, and M. Yu. Kornilov, *Khim. Geterotsikl. Soedin.*, No. 6, 778 (1976).
7. M. Yu. Kornilov, L. M. Shulezhko, and A. I. Tolmachev, *Teor. Éksp. Khim.*, **10**, 508 (1974).
8. N. N. Romanov, F. S. Babichev, Yu. L. Slominskii, and A. I. Tolmachev, *Dokl. Akad. Nauk Ukr. SSR, Ser. B*, No. 1, 43 (1977).

MASS-SPECTROMETRIC STUDY OF THE CYCLIZATION OF DIAZO KETONES.

1. CYCLIZATION OF 1-DIAZO-3-SULFONYLAMINOPROPAN-2-ONES TO N-SULFONYLAZETIDIN-3-ONES

P. A. Sharbatyan, A. T. Lebedev,
A. M. Sipyagin, V. G. Kartsev,
and V. S. Petrosyan

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A comparison of the mass spectra of 1-diazo-3-sulfonylaminopropan-2-ones and N-sulfonylazetid-3-ones makes it possible to conclude that under the conditions of electron impact and chemical ionization the molecular ions of diazo ketones lose a molecule of nitrogen and undergo partial cyclization to the corresponding azetidines without undergoing the Wolff rearrangement.

It was recently shown [1] that 1-diazo-3-sulfonylaminopropan-2-ones (I) are converted to N-sulfonylazetid-3-ones (II) by the action of concentrated sulfuric acid. In order to investigate the possibility of the occurrence of similar processes in the gas phase we studied the mass spectra of two series of compounds (Ia-k and IIIa-j) under the conditions of electron impact and chemical ionization.

M. V. Lomonosov Moscow State University, Moscow 117234. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 3, pp. 334-342, March, 1982. Original article submitted July 9, 1981.