9. G. Wittig and F. Bangert, Chem. Ber., 58, 2636 (1925).
10. P. Venturella and A. Bellino, Ann. Chim., 58, 145 (1968).
11. F. Eiden and W. Lowe, Tetrahedron Lett., 1439 (1970).
12. L. G. Grishko, I. P. Kupchevskaya, and V. P. Khilya, Dokl. Akad. Nauk Ukr. SSR. B, No. 6, 518 (1978).
13. V. Szabo, J. Borda, and L. Losonczi, Magy. Kem. Flyrt., No. 6, 278 (1977).
14. W. Basinski and Z. Jermanowska, Reczn. Chem., 48, 989, 2217 (1974).

SYNTHESIS OF cis- AND trans-PERHYDROTHIENO[3,4-d]IMIDAZOLE-2-THIONE 5,5-DIOXIDES

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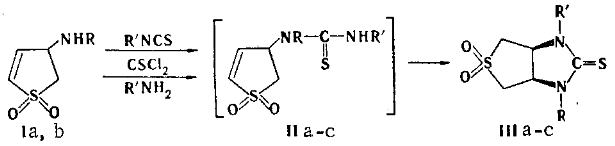
541.634

It is shown that the cis and trans isomers of perhydrothieno[3,4-d]imidazole-2-thione 5,5-dioxides can be obtained in good yields from the accessible derivatives of thiolane and 2-thiolene 1,1-dioxides.

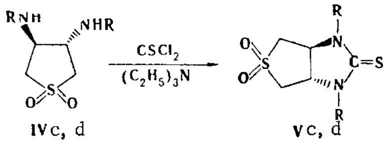
In the course of developing research on the synthesis of new two-ring compounds with potential biological activity from derivatives of thiolane and 2-thiolene 1,1-dioxides [1] we synthesized a number of perhydrothieno-[3,4-d]imidazole-2-thione 5,5-dioxides.

We established that sulfones Ia, b react with isothiocyanates or with thiophosgene and amines to give thioureas IIa-c, which undergo cyclization in the same way as ureas [2, 3] to give two-ring compounds IIIa-c:



Ia $R=C_6H_5$; b $R'=C_6H_5CH_2$; II, III a $R=R'=C_6H_5$; b $R=C_6H_5$, $R'=C_6H_5CH_2$; c $R=R'=C_6H_5CH_2$

It has previously been demonstrated [1, 2] that the intramolecular cyclization of N-(1,1-dioxo-2-thiolen-4-yl)ureas and N-monosubstituted 1,1-dioxo-2-thiolen-4-yl esters of dithiocarbamic acids leads to cis-fused two-ring compounds. The reaction under consideration in this paper proceeds similarly, and we therefore assigned a cis structure to IIIa-c. We obtained their trans isomers by the action of thiophosgene on trans-3,4-diaminothiolane 1,1-dioxides IVc, d (obtained by the method in [4]) in the presence of tertiary amines.



IV, V c $R=C_6H_5CH_2$; d $R=CH_3$

A melting-point depression is observed for a mixture of IIIc and Vc, and the IR (Table 1) and PMR spectra of these compounds differ: The α protons of the 1,1-dioxothiolane rings of IIIa, c give multiplets with widths of, respectively, 8 Hz (3.48 ppm, trifluoroacetic acid) and 13 Hz (3.4 ppm, deuteropyridine). A group of signals from 2.75 to 3.8 ppm is observed for the α protons of the 1,1-dioxothiolane ring of Vc in deuteropyridine. It has been reported that similar differences are observed in the spectra of cis- and trans-perhydrothieno[3,4-d]-imidazol-2-one 5,5-dioxides [2, 5] and cis and trans 3,4-disubstituted thiolane 1,1-dioxides [6]. Taking these data into account, we assigned cis and trans structures to III and V, respectively.

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TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp, °C	IR spectrum, cm^{-1}	Found, %			Empirical formula	Calc., %			Yield, %
			C	H	S		C	H	S	
IIIa	236—237	3010 w, 2860 w, 1490 w, 1435 m, 1395 m, 1290 s, 1265 s, 1165 m, 1120 m, 1070 w, 890 w., 660 m	59,1	4,6	18,7	$C_{17}H_{16}N_2O_2S_2$	59,3	4,7	18,6	98
IIIb	229—230	3010 w, 2930 w, 2860 w, 1490 m, 1450 m, 1400 m, 1300 m, 1265 s, 1240 m, 1160 m, 1115 m, 705 m, 660 w	60,5	5,0	18,10	$C_{18}H_{18}N_2O_2S_2$	60,4	5,1	17,9	91
IIIc	222—223	3025 w, 2930 w., 2860 w 1470 m, 1460 m, 1415 w, 1400 w, 1300 s, 1220 s, 1160 m, 1110 m, 1060 w, 950 w., 760 s	61,2	5,4	17,3	$C_{19}H_{20}N_2O_2S_2$	61,2	5,4	17,3	31[a]
Vc	218	3030 w., 2920 w, 2860 w, 1335 s, 1305 s, 1215 m, 1110 s, 990 w., 730 m, 470 m			17,0	$C_{19}H_{20}N_2O_2S_2$[b]			17,3	47
Vd	316	3015 m, 2935 w, 2880 w, 1450 w, 1430 m, 1335 s, 1310 s, 1220 s., 1115 s, 1085 m, 750 m, 465 s	38,5	5,4	29,3	$C_7H_{12}N_2O_2S_2$	38,2	5,5	29,2	85

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[a] By method A; the compound was obtained in 60% yield by method B.

[b] Found: N 7.5%. Calculated: N 7.5%.

We found that sulfone IVc is converted to IIIc when it is heated with carbon disulfide in the presence of triethylamine. The formation of a two-ring compound with an inverted configuration can be explained in the following way. Compound IVc reacts with CS_2 at one of the amino groups to give an inner salt of a dithiocarbamic acid, which in the presence of a tertiary amine eliminates RNH_2 as a consequence of the increased C−H acidity of the α-methylene groups of the 1,1-dioxothiolane ring [7]. The resulting salt of N-benzyl-N-(1,1-dioxo-2-thiolen-4-yl)dithiocarbamic acid is converted to thiourea IIc, which undergoes cyclization to IIIc.

Thus we have shown that cis- and trans-isomeric two-ring ureas can be obtained in good yields from accessible derivatives of thiolane and 2-thiolene 1,1-oxides by various synthetic methods.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of the compounds were recorded with a Tesla BS 487B spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard.

cis-1,3-Diphenylperhydrothieno[3,4-d]imidazole-2-thione 5,5-Dioxide (IIIa). A 1.4-g (0.01 mole) sample of phenyl isothiocyanate was added to a solution of 2.1 g (0.01 mole) of 4-anilino-2-thiolene 1,1-dioxide in 20 ml of benzene and 10 ml of pyridine, and the mixture was refluxed for 1-2 h. The benzene and pyridine were removed by distillation, and the residue was washed with ether and crystallized from 50% aqueous acetone to give 3.4 g (98%) of IIIa (Table 1).

cis-1-Phenyl-3-benzylperhydrothieno[3,4-d]imidazole-2-thione 5,5-Dioxide (IIIb). This compound was similarly obtained from 4-benzylamino-2-thiolene 1,1-dioxide.

cis-1,3-Dibenzylperhydrothieno[3,4-d]imidazole-2-thione 5,5-Dioxide (IIIc). A) A solution of 0.7 ml (9 mmole) of thiophosgene in 10 ml of tetrahydrofuran (THF) was added to a solution of 1.8 g (8.5 mmole) of 4-benzylamino-2-thiolene 1,1-dioxide in 25 ml of dry THF, and the mixture was stirred for 3 h. A 2.8-ml sample of triethylamine and 1 ml (9 mmole) of benzylamine were then added, and the solution was stirred at 50°C for 4 h. The THF and excess triethylamine were evaporated, and the residue was washed with water and crystallized from aqueous acetone. The yield was 0.93 g (31%).

B) A 3-g (0.04 mole) sample of CS_2 was added dropwise at room temperature to a solution of 6.6 g (0.02 mole) of trans-3,4-dibenzylaminothiolane 1,1-dioxide in 30 ml of THF and 5 ml of triethylamine, and the mixture was allowed to stand for 8 h, after which it was heated at 50-60°C for 4 h. The solution was evaporated, and the residue was washed with methanol and crystallized from 50% aqueous THF. The yield was 4.5 g (60%). No melting-point depression was observed for a mixture of this product with the compound obtained by method A.

trans-1,3-Dibenzylperhydrothieno[3,4-d]imidazole-2-thione 5,5-Dioxide (Vc). A 1.5-ml (0.02 mole) sample of thiophosgene was added at room temperature to a solution of 6.6 g (0.02 mole) of trans-3,4-dibenzylaminothiolane 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

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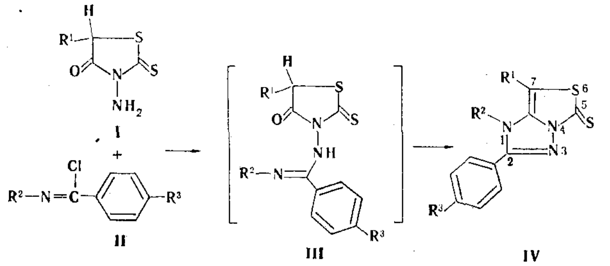
UDC 547.789'792.9.07

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

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*See [1] for Communication 3.

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