tion turned green and a precipitate formed, which was then filtered and dried to give 0.46 g of compound IX.

Dibromodibenzo[b,i]phenoxazine (X). To 3.3 g (12 mmole) of compound I in 100 ml glacial acetic acid was added dropwise 1.2 ml (24 mmole) bromine, and the mixture was stirred for 3 h; the resulting precipitate was filtered and recrystallized from xylene to give 3.2 g of compound X; M^+ 441.

Dibromo-2(3),9(10)-di-tert-butyldibenzo[b,i]phenoxazine (XI). To 0.5 g (1.3 mmole) of compound V in 20 ml glacial acetic acid was added dropwise at 20°C 0.13 ml (2.6 mmole) of bromine, and the mixture was stirred for 1 h; the resulting precipitate was filtered and recrystallilzed from benzene to give 0.5 g of compound XI; M^+ 553.

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CONDENSED THIOLANE 1,1-DIOXIDE SYSTEM.

1. SYNTHESIS AND REARRANGEMENT OF trans-2-IMINOPERHYDROTHIENO[3,4-d]-OXAZOLE 5,5-DIOXIDES

T. É. Bezmenova,* A. B. Rozhenko, G. I. Khaskin, A. F. Bratunets, and and A. M. Shakhnvorost

UDC 547.727'735'785.5'787.3.07

Alkylation of trans-N-alkyl(or aryl)-N'-(3-hydroxy-1,1-dioxothiolan-4-yl) thioureas with ethyl p-toluenesulfonate, and the reaction of cyanogen bromide wiht an ethyl p-toluenesulfonate, and the reaction of cyanogen bromide with trans-3-hydroxy-4-aminothiolan-1,1-dioxides have given salts of trans-2-iminoperhydrothieno[3,4-d]-oxazole 5,5-dioxides. Rearrangement of these oxazolidines in the presence of bases afford perhydrothieno[3,4-d]imidazole-2-one 5,5-dioxides.

Some recently-synthesized bicyclic thiolan-1,1-dioxides are intermediates in the synthesis of biologically active compounds [1, 2]. We had earlier assumed that decomposition of the hydroiodides of N-substituted trans-N'-(3-hydroxy-1,1-dioxothiolan-4-yl)-S-methylthioureas would afford the hydroiodides of trans-2-alkylarylperhydrothieno[3,4-d]oxazole 5,5-dioxides [3, 4]. These compounds could not, however, be isolated. Treatment of the reaction mixture

*Deceased.

Department of Petroleum Chemistry, Institute of Physical Organic and Carbon Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252160.

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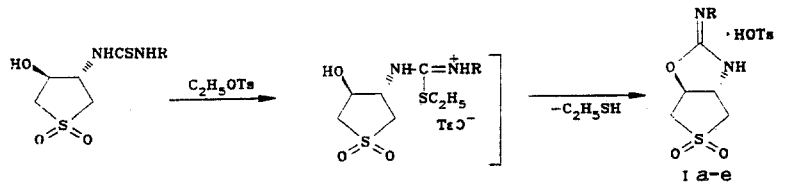
TABLE 1. Properties of Compounds Obtained

Compound	T_{mp}, °C*	IR spectrum, cm^{-1}	Found, %		Empirical formula	Calc., %		Yield, %
			N	S		N	S	
Ia	195—196	3320, 1690, 1330, 1220, 1200, 1180, 1155, 1120, 1030, 1010, 685, 565	6,6	15,1	$C_{18}H_{20}N_2O_6S_2$	6,6	15,1	47,1
Ib	177	3180, 1720, 1335, 1215, 1160, 1130, 1110, 1035, 740, 700, 675, 570	6,4	14,8	$C_{19}H_{22}N_2O_6S_2$	6,4	14,6	68,5
Ic	207	3180, 1735, 1335, 1235, 1170, 1140, 1040, 700, 570	7,3	16,3	$C_{15}H_{22}N_2O_6S_2$	7,2	16,4	62,3
Id	169	3300, 1715, 1320, 1220, 1200, 1170, 1125, 1040, 685, 570	7,1	16,6	$C_{15}H_{20}N_2O_6S_2$	7,2	16,5	43,8
Ie	217—219	3150, 1740, 1590, 1330, 1305, 1230, 1170, 1130, 1035, 1015, 685, 570	10,3	11,3	$C_{12}H_{12}N_2O_4S$	10,0	11,4	62,0
IIa	215	3270, 1700, 1510, 1440, 1315, 1265, 1195, 1140, 760, 700, 465, 440	11,1	12,6	$C_{11}H_{12}N_2O_3S$	11,1	12,7	95,1
IIb	232	3210, 1690, 1480, 1320, 1260, 1170, 1140, 700, 465, 430	10,6	11,9	$C_{12}H_{14}N_2O_3S$	10,5	12,0	81,5
IIc	192,5	3460, 3250, 1670, 1480, 1320, 1130, 700, 480, 435	12,7	14,5	$C_8H_{14}N_2O_3S$	12,8	14,7	80,0
IId	164	3230, 1725, 1500, 1435, 1410, 1320, 1280, 1150, 1110, 825, 745, 465	12,8	14,5	$C_8H_{12}N_2O_3S$	13,0	14,8	76,0
IIf	317	3330, 3270, 1690, 1670, 1530, 1500, 1470, 1300, 1270, 1230, 1110, 695, 630, 465, 445	16,2	18,2	$C_5H_8N_2O_3S$	15,9	18,2	79,5
V	226,5—228	3240, 1730, 1495, 1330, 1270, 1200, 1170, 1150, 705, 465, 435	10,3	11,3	$C_{12}H_{12}N_2O_4S$	10,2	11,3	86,4

*Crystallization solvents for (Ia) and (IIb, c), aqueous ethanol; for (Ib) and (IIf), water; for (Ic), aqueous acetone; for (Id), acetone; for (Ie) and (V), acetonitrile; for (IIa), aqueous DMF; and for (IId), ethanol.

with bases gave the isomeric cis-perhydrothieno[3,4-d]imidazole-2-one 5,5-dioxides, apparently formed by rearrangement. The object of the present investigation was to synthesize and identify the stable salts of trans-2-iminoperhydrothieno[3,4-d]oxazole 5,5-dioxides (I), and then confirm the rearrangement mechanism proposed previously [3]. We have found that at 120°C trans-N-(3-hydroxy-1,1-dioxothiolan-4-yl)thiorueas are readily alkylated by ethyl toluene-p-sulfonate followed by cyclodesulfurization of the intermediate isothiuronium salt, to give the stable tosylates of 2-iminoperhydrothieno[3,4-d]oxazole 5,5-dioxides (Ia-d, Table 1).



I a R=C_6H_5, b R=$C_6H_5CH_2$, c R=C_3H_7-*iso*, d R=CH_2=CH—CH_2, e R=COC_6H_5

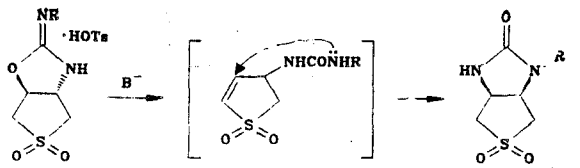
Alkylation of trans-N-benzoyl-N'-(3-hydroxy-1,1-dioxothiolan-4-yl)thiorueas occurs under more severe conditions (140°C). The bicyclic product (Ie) was isolated as the free base.

On boiling the sulfones (Ia-d) in protic solvents in the presence of base (triethylamine or sodium carbonate), the rearrangement products (N-substituted cis-perhydrothieno[3,4-d]imidazol-2-one 5,5-dioxides) (IIa-d) were obtained.

TABLE 2. ^{13}C NMR Spectral Data, ppm (363 K)

Comopurid	$-CH_2-$	$-\overset{|}{C}H-N$	$-\overset{|}{C}H-O$	$\overset{N}{\underset{O}{}}\!\!>C=N$
Ia	52,30; 52,30	54,97	81,37	160,36
Ib	52,42; 52,51	55,06	80,92	161,08
Ic	52,81; 52,91	55,02	80,85	160,34
Id	52,47; 52,55	55,00	80,78	161,09
IVc*	53,96; 55,40	60,97	83,15	164,30

*Obtained in CF_3COOD (303 K).

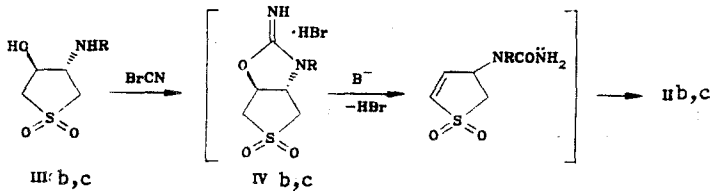


Ia-d IIa-d

II a R=C_6H_5, b R=$C_6H_5CH_2$, c R=C_3H_7-*iso*, d R=CH_2=CH—CH_2

The bicyclic ureas (IIb, c) were also synthesized from trans-3-hydroxy-4-aminothiolan 1,1-dioxides (IIIb, c) and cyanogen bromide in the presence of bases, via the intermediate formation of the trans-2-iminoperhydrothieno[3,4-d]oxazole 5,5-dioxides (IVb, c). We obtained the latter in admixture with the hydrobromides of the starting β-hydroxyamines (IIIb, c).

The structures of the bicyclic sulfones (Ia-d) and (IVc) were confirmed by their ^{13}C NMR spectra (Table 2).

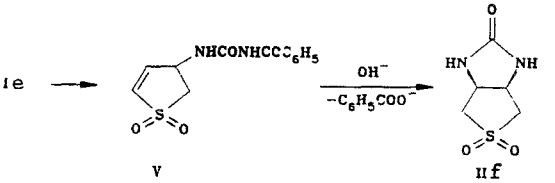


IIIb,c IVb,c IIb,c

III, IV b R=$C_6H_5CH_2$, c R=C_3H_7-*iso*

The formation of the condensed ureas (IIb, c) from the structurally isomeric sulfones (Ib, c) and (IVb, c) provides additional support for the previously-proposed [3, 4] mechanism for the rearrangement involving elimination and nucleophilic addition.

On boiling the oxazolidine (Ia) in alcoholic triethylamine, there was obtained only the product of the opening of the oxazolidine ring, namely N-benzoyl-N'-(1,1-dioxo-2-thiolen-4-yl)urea (V). Cyclization of (V) to give the imidazolone did not occur, apparently as a result of the reduced nucleophilicity of the nitrogen atom bonded to the benzoyl group.



Ie V IIf

The structure of the sulfone (V) was confirmed by ^{13}C NMR spectroscopy. On alkaline hydrolysis, it was converted into the known cis-perhydrothieno[3,4-d]imidazole-2-one 5,5-dioxide (IIf) [5].

The compositions and structures of the compounds obtained were confirmed by elementary analysis and IR spectroscopy (Table 1).

EXPERIMENTAL

IR spectra were obtained on a UR-20 instrument in KBr disks. ^{13}C NMR spectra were obtained on a Bruker CXP-200 spectrometer (50.33 MHz) in aqueous solution. Stabilization of

the resonance conditions was achieved in respect of the ^2H NMR signal for CD_3CN (3%), used simultaneously as internal standard. Assignment of the signals was made from spectra with incomplete decoupling from protons.

The properties of (Ia-e), (IIa-d, f) and (V) are given in Tables 1 and 2.

trans-2-Phenyliminoperhydrothieno[3,4-d]oxazole 5,5-Dioxide Tosylate (Ia). A mixture of 6.08 g (40 mmole) of 3-hydroxy-4-aminothiolan-1,1-dioxide and 7.5 g (55 mmole) of phenyl isothiocyanate in 200 ml was boiled until the starting material had completely dissolved. On cooling, the precipitated N-(3-hydroxy-1,1-dioxothiolan-4-yl)-N'-phenylthiourea was isolated, washed with ether, dried, and mixed with 33.00 g (165 mmole) of ethyl toxylate. The mixture was kept at 120°C until all the ethyl mercaptan had been removed, cooled, and the melt triturated with 50 ml of ethanol. The crystalline solid was isolated, washed with 100 ml of ether, and crystallized from ethanol–water (10:1) to give 7.40 g of (Ia). Tosylates (Ib-d) were obtained similarly.

trans-2-Benzoyliminoperhydrothieno[3,4-d]oxazole 5,5-Dioxide (Ie). To a solution of 1.51 g (10 mmole) of 3-hydroxy-4-aminothiolan 1,1-dioxide in 60 ml of ethanol was added a solution of 1.63 g (10 mmole) of benzoyl isothiocyanate in 20 ml of acetone. The mixture was boiled for 30 min, cooled, and the precipitated N-benzoyl-N'-(1,1-dioxo-3-hydroxythiolan-4-yl)thiourea isolated, and washed with 10 ml of ethanol and 25 ml of ether. This thiourea (2.41 g) was mixed without further purification, with 3.00 g (15 mmole) of ethyl tosylate, and the mixture kept for 2 h at 140-150°C until evolution of ethyl mercaptan had ceased. The cooled reaction mixture was triturated with 10 ml of ethanol, and the resulting solid isolated, and washed on the filter successively with 20 ml of acetone and 10 ml of ether to give 1.42 g (50.7%) of oxazolidine (Ie), calculated on the β-hydroxyamine taken.

cis-N-Phenylperhydrothieno[3,4-d]imidazole-2-one 5,5-Dioxide (IIa). A mixture of 20.00 g (471 mmole) of (Ia) and 6.00 g (318 mmole) of sodium carbonate in 250 ml of water was boiled for 20 min, cooled, the solid isolated, and washed with alcohol ether (100 ml of each). There was obtained 11.30 g of (IIa). The other ureas (II) were obtained similarly from the tosylates (I).

cis-N-Benzylperhydrothieno[3,4-d]imidazole-2-one 5,5-Dioxide (IIb). To 5.02 g (20 mmole) of trans-3-hydroxy-4-benzylaminothiolan 1,1-dioxide in 100 ml of ethanol was added a solution of 2.12 g (20 mmole) of cyanogen bromide in 50 ml of ethanol. The mixture was stirred for 3 h, 2.07 g (15 mmole) of K_2CO_3 in 100 ml of water added, kept at 90°C for 30 min, cooled, and the crystalline solid which separated filtered off, washed with 20 ml of water and 10 ml of ethanol, and dried. There was obtained 4.59 g (84.9%) of urea (IIb), identical in its IR spectrum and melting point with that obtained by reacting (Ib) with triethylamine in water. Urea (IIc) was obtained similarly, in 70.7% yield.

N-Benzoyl-N'-(1,1-dioxo-2-thiolen-4-yl)urea (V). A mixture of 2.80 g (10 mmole) of the oxazolidine (Ie) and 1.01 g (10 mmole) of triethylamine in 100 ml of ethanol was boiled for 2 h, cooled, and the solid filtered off, washed with ethanol and ether (20 ml of each) to give 2.42 g of the urea (V). ^{13}C NMR spectrum (in CF_3COOD): 52.52 (d); 56.80 (t); 131.00 (d), 132.14 (d); 133.92 (s); 135.92 (d); 137.42 (d); 143.98 (d); 161.60 (s); 173.23 ppm (s).

cis-Perhydrothieno[3,4-d]imidazol-2-one 5,5-Dioxide (IIf). A mixture of 2.80 (10 mmole) of urea (V), 1.06 g (10 mmole) of Na_2CO_3, and 100 ml of water was boiled for 3 h, cooled, and the solid isolated, washed with 20 ml of water and 10 ml of ethanol, and dried. Crystallization from water gave 1.12 g (63.6%) of (IIf). (IIf) was obtained similarly from (Ie) in 56.2% yield.

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