tate (0.5 g) of compound IV was filtered off. IR spectrum: 3180, 2940, 1610, 1440, 1415, 1300, 1290, 1215, 890, 870 cm^{-1}.

LITERATURE CITED

1. I. K. Moiseev, M. I. Kalinina, M. N. Zemtsova, and P. L. Trakhtenberg, Zh. Org. Khim., 22, 2292 (1986).
2. L. I. Khmel'nitskii, T. I. Godovikova, N. A. Ruleva, B. N. Khasapov, and S. S. Novikov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2295 (1979).
3. J. V. Burakevich, A. M. Lore, and G. P. Volpp, J. Org. Chem., 36, 5 (1971).
4. J. V. Burakevich, R. S. Butler, and G. P. Volpp. J. Org. Chem., 37, 593 (1972).
5. A. R. Gagneux and R. Meier, Helv. Chim. Acta, 53, 1883 (1970).
6. G. Ponzio, Gazz. Chim. Ital., 53, 507 (1923).
7. L. I. Khmel'nitskii, S. S. Novikov, and T. I. Godovikova, Chemistry of Furoxans. Part 1. Structure and Synthesis [in Russian], Nauka, Moscow (1981), p. 120.

SYNTHESIS AND SPECTRAL LUMINESCENCE PROPERTIES OF DIBENZO[b,i]PHENOXAZINE AND SEVERAL OF ITS DERIVATIVES

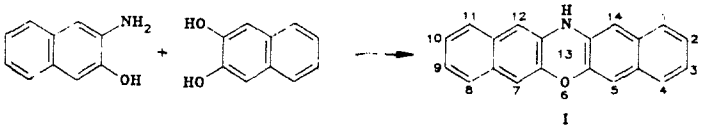
L. E. Marinina, V. I. Alekseeva, L. P. Savvina, and E. A. Luk'yanets

UDC 535.371:547.867.6.07

The synthesis of dibenzo[b,i]phenoxazine, its p-tert-butyl substituted analog, and a series of nitro-, amino-, and bromosubstituted derivatives, is described. The spectral luminescence properties of these newly synthesized compounds have been investigated.

Phenoxazine derivatives, in particular hydroxy- and aminophenoxazines, are efficient red heat (light) luminophores, and are thus widely used as generating compounds in tunable visible region lasers [1]. We have previously demonstrated [2] that 3,6-dinitrophenoxazine, in contrast to the majority of other nitro compounds, also exhibits luminescence in alkaline alcohol solutions (luminescence λ_{max} 760 nm). This may be rationalized in terms of its deprotonation to form a symmetrical anion which is an analog of phenoxazine dyes, except that it carries a negative charge. In this regard, therefore, it was of interest to us to study condensed phenoxazine analogs, especially its linearly annelated naphthalene analog, dibenzo[b,i]phenoxazine (I).

In the present paper we describe the synthesis and spectral luminescence properties of compound I and a series of its derivatives. Compound I was first reported as a side product (~2% yield) in the synthesis of 2,2'-binaphth[2,3-d]oxazole from 3-amino-2-naphthol and anhydrous oxalic acid, but was not adequately characterized [3]. We have prepared compound I, in analogy with phenoxazine [4], by treatment of 3-amino-2-naphthol with 2,3-dihydronaphthalene, with an overall yield of about 45%.



I

The electronic absorption spectrum of compound I in DMF contains, in addition to the two bands reported in [3], with maxima at 328 and 385 nm, another band with an absorption maximum at 278 nm.

The PMR spectrum of compound I (in DMSO-D_6) exhibits two broadened singlets at 6.74 and 7.08 ppm, corresponding to the protons at $C_{(12)}$ ($C_{(14)}$) and $C_{(5)}$ ($C_{(7)}$). The $C_{(1)}$($C_{(11)}$)

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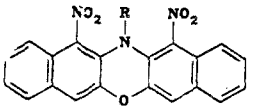
and $C_{(4)}$ ($C_{(8)}$) proton signals appear as broadened doublets with 8.3 Hz splitting, centered at 7.40 and 7.42 ppm; the $C_{(2)}$ ($C_{(10)}$) and $C_{(3)}$ ($C_{(9)}$) protons give rise to multiplets in the 6.98 -7.25 ppm region.

Treatment of comopund I with acetic anhdride results in the formation of its N-acetyl derivative (II).

Pursuant to the preparation of nitro- and aminosubstituted dibenzo[b,i]-phenoxazines, we have investigated the nitration of compounds I and II. Two methods are known for the preparation of nitrosubstituted phenoxazines: a) nitration of acetylphenoxazine protecting group in the nitration product [5], and b) treatment of phenoxazine with sodium nitrite and chloride in acetic acid, in which nucleophilic addition of nitrite anion to an intermediate phenoxazonium cation [6] is assumed to occur. In both cases the main reaction product is 3,6-dinitrophenoxazine.

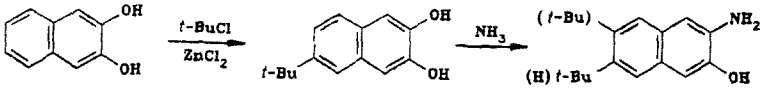
Nitration of the N-acetyl derivative II with concentrated HNO_3 in glacial acetic acid gave the dinitroderivative III in excellent yield; subsequent workup with alcoholic base gave the corresponding dinitrodibenzo[b,i]phenoxazine (IV).



III, IV
III R=CCCH$_3$; IV R=H

This same compound could also be prepared, but in significantly lower yield, according to method b. The most efficient method for its preparation, however, proved to be nitration with sodium nitrite in glacial acetic acid in the absence of iron chloride; this gave compound IV in almost quantitative yield. At attempt to determine the position of the nitro groups in compound IV using PMR spectroscopy was unsuccessful, due to its inadequate solubility.

In order to increase the solubility of dibenzo[b,i]phenoxazine and its nitro derivatives, and also in order to establish the structures of the latter, we synthesized the tert-butyl substituted dibenzo[b,i]phenoxazine analog V and carried out the nitration reactions. Compound V could be synthesized in approximately 20% yield by fusion of 2,3-dihydroxy-6-tert-butylnaphthalene (VI) with 3-amino-6(7)-tert-butyl-2-2-napthol (VIII). Compound VI was prepared by alkylation of 2,3-dihydroxynaphthalene with tert-butyl chloride in the presence of zinc chloride. The tert-butyl group is introduced in this manner in the only sterically unhindered position in the molecule, position 6 (in 2-naphthanol the tert-butyl group is introduced only in the 3- and 6-positions [7]).



VI VII

Compound VII was prepared by amination of compound VI at 200°C in an autoclave [8], and consists of a mixture of two isomers, differing in the position of the tert-butyl group; this fact predetermines the existence of compound V as a mixture of isomers as well: 2,9-, 2,10-, and 3,9-di-tert-butyl-dibenzo[b,i]phenoxazine. The liquid chromatogram of this product contained two well resolved peaks, with an intensity ratio of 2:1. The higher intensity peak apparently corresponds to a mixture of the 3,9- and 2,10-isomers, which are not resolved chromatographically.

The PMR spectrum of compound V in DMSO-D_6 (250 MHz) contains a singlet signal for the tert-butyl groups at 1.50 ppm, and a complex multiplet for the aromatic protons, at 7.0-7.7 ppm; this confirms its existence as a mixture of isomers. In this case, however, the presence of tert-butyl groups in the molecules (compound V) and their positions are not expected to exert a substantial influence on the character of the resulting substitution products or on their spectral luminescence properties. Thus, in fact, nitration of compound V under different conditions resulted in the formation of compound VIII, which contains two nitro groups based on elemental analysis (Table 1), and which appears to be an analog of compound IV based on its electronic spectrum (Table 2). Compound VIII is apparently formed as a mixture of isomers differing in the positions of the tert-butyl groups, but these isomers cannot be differentiated or separated by liquid chromatography.

TABLE 1. Characteristics of Dibenzo[b,i]phenoxazine Derivatives I-XI

Compound	T_{mp} °C*	Found, %			Molecular formula	Calculated, %			Yield, %
		C	H	N (Br)		C	H	N (Br)	
I	360	84,6	4,9	5,0	$C_{20}H_{13}NO$	84,8	4,6	4,9	46
II	224	81,0	4,7	4,0	$C_{22}H_{15}NO_2$	81,2	4,6	4,3	65
III	282—283	63,3	3,3	10,4	$C_{22}H_{13}N_3O_6$	63,6	3,2	10,1	62
IV	280decomp.	64,0	3,1	10,9	$C_{20}H_{11}N_3O_5$	64,3	3,0	11,3	97
V	320	84,8	7,4	3,5	$C_{28}H_{29}NO$	85,0	7,4	3,5	21
VI	159—160	77,4	7,4		$C_{14}H_{16}O_2$	77,4	7,4		77
VII	179	72,3	7,8	5,6	$C_{14}H_{17}NO \cdot H_2O$	72,1	7,5	6,0	54
VIII	250	68,9	5,5	8,5	$C_{28}H_{27}N_3O_5$	69.2	5,6	8,6	61
IX	>350	72,8	6,6	8,7	$C_{28}H_{30}ClN_3O$	73,1	6,6	9,1	75
X	296—297	54,5	2,5	3,3 (36,1)	$C_{20}H_{11}Br_2NO$	54,4	2,5	3,2 (36,2)	73
XI	223—224	61,0	4,9	2,3 (28,8)	$C_{28}H_{27}Br_2NO$	60,8	4,9	2,5 (28,9)	83

*Solvent for compounds I and V was DMF, for II glacial CH_3COOH, for III and IV chlorobenzene, for VI CCl_4, for VII H_2O—ethanol, 5:1, for VIII heptane, for X xylene, and for XI benzene.

TABLE 2. Spectral Luminescence Characteristics of Newly Synthesized Compounds

Compound	Solvent	Absorption λ_{max}, nm (log ε)	Luminescence* λ_{max}, nm (φ)
I	DMF	282 (4,74), 328 (4,30), 385 (4,17)	398 sh., 408 (0,46)
II	DMF	265 (4,70), 332 (3,84), 378 (3,30)	408 (0,35)
III	DMF	276 (4,87), 408 (4,39), 436 (4,43)	420 (0.05)
IV	DMF	274 (4,71), 382 (4,00), 483 (4,17)	Absent
	0.1 N KOH in ethanol	280 (4,68), 378 (4,25), 557 (4,07)	Absent
V	DMF	282 (4,87), 328 (4,34), 385 (4,30)	398sh., 408 (0,44)
VIII	Chloroform	270 (4,82), 375 (3,90), 485 (4,16)	Absent
	0.1 N KOH in ethanol	280 (4,74), 378 (4,32), 557 (4,16)	Absent
IX†	Ethanol	268 (4,88), 375 (3,95), 477 (4,17)	Absent
	Ethanol	289 (4,58), 432 (3,95), 740 (4,04)	790 (weak luminescence)
	0.1 N KOH in ethanol	289 (4,57), 570 (4,04)	640 (0,05)
	Chloroform	290 (4,51), 430 (3,97), 685 (4,03)	770 (weak luminescence)
X	Chloroform	282 (4,94), 327 (4,30), 365 (4,20), 382 (4,41)	401 (0,05)
XI	Chloroform	282 (4,79), 327 (4,30), 365 (4,16), 382 (4,23)	401 (0,05)

*Excitation λ_{max} is superimposable on absorption λ_{max}.
†In the case of compound IX the luminescence spectrum is presented without correcting for the spectral sensitivity of the instrument.

The PMR spectrum of compound VIII (DMSO-D_6, 250 MHz) is shown in Fig. 1. Comparison of this with the spectrum of compound I reveals that two low-field signals are present: 8.28 (d, J = 1.5 Hz) and 8.27 ppm (d, J = 9 Hz). The downfield shift of these proton signals (of about 0.9 ppm) relative to compound I, as well as the magnitude of J = 9 Hz for one of these signals, indicates that these protons are located in positions peri to the substituent.

The small chemical shift difference observed for the $C_{(5)}$ and $C_{(7)}$ protons (7.28 and 7.32 ppm), as seen in the PMR spectrum of compound VIII, suggests that the most preferred structures are 12, 14-substituted dibenzo[b,i]-phenoxazines with tert-butyl groups in the 7,9-, 2,10-, and 3,10-positions.

Upon reduction of compound VIII with tin dichloride under conditions analogous to those used in the reduction of nitrophenoxazines [5], a diamine was formed, which was isolated in the form of its corresponding phenoxazonium dye IX.

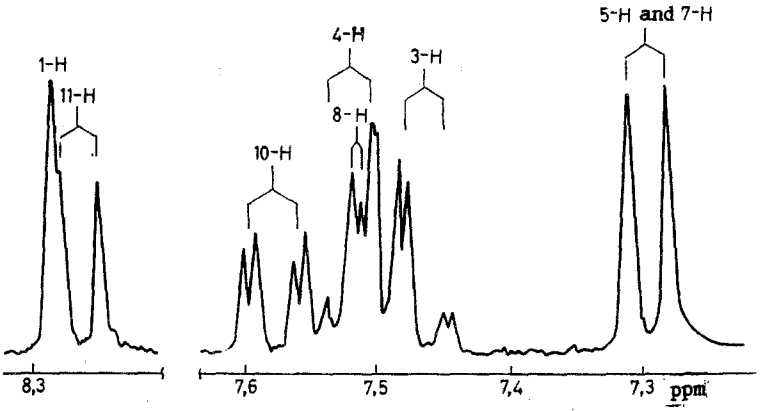
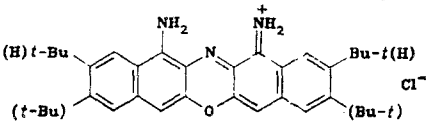


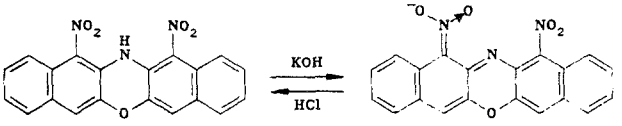
Fig. 1. PMR spectrum of compound VIII in DMSO-D_6 (the spectral assignment is given for the structure of the 2,9-isomer; the symmetrical 2,10- and 3,9-isomers contain protons with analogous immediate surroundings).



IX

Bromination of compound I and its tert-butyl derivative V gave the respective dibromo derivatives X and XI, containing bromine atoms preferentially in the 12 and 14-positions; their structures have not been examined in detail.

The spectral luminescence characteristics of the newly synthesized compounds I-XI are given in Table 2. The introduction of nitro groups to the phenoxazine molecule in compounds I and V leads, in contrast to bromine atoms, to a substantial (~100 nm) bathochromic shift of the long wavelength absorption bands, a further bathochromic shift (~80 nm) is observed in alcoholic base, indicative of deprotonation analogous to that observed in 3,6-dinitrophenoxazine [2]. In contrast to the latter, however, in this case the deprotonated form is not luminescent.



IV

The diamino dibenzophenoxazonium dye IX luminesces in the 735-800 nm region. In alcoholic base solution a significant hypsochromic shift of both the absorption and luminescence spectra is observed, due to the formation in basic media of the base dye form of IX, in analogy with the known phenoxazine dye Nile blue [9].

EXPERIMENTAL

PMR spectra were recorded on a Bruker WM-250 spectrometer (at 250 MHz) using DMSO-D_6 and $CDCl_3$ solutions versus TMS as internal standard. Solution absorption spectra of the compounds under investigation were measured on a Hitachi-356 spectrophotometer, while luminescence spectra were obtained on SDL-1 and Hitachi MRF-2A instruments. Quantum yields of compounds I-III, V, X, and XI were measured relative to 3-aminophthalimide (φ = 0.60 [10]) as standard; that of compound IX in 0.1 N KOH solution in ethanol was measured relative to cresol violet (φ = 0.56 [11]). Chromatographic analyses were carried out on a Waters liquid chromatograph equipped with a UV detector (λ280 nm). The column was 250 × 4.5 mm filled with Silasorb-600 sorbent (particle size 5 μm, column efficiency 20,000 theoretical plates). Programmed elution was used, from 20% CH_2Cl_2 in hexane to 100% CH_2Cl_2 (10 min), with a sample size of 2 μliter. Mass spectra were recorded on a LKB-9000 spectrometer at an ionizing electron energy of 70 eV.

Dibenzo[b,i]phenoxazine (I). A mixture of 4.8 g (30 mmole) 2-hydroxy-3-aminophthalene [7] and 4.8 g (30 mmole) 2,3-dihydroxynaphthalene was fused at 230°C for 4 h. The resulting fusion was ground up, washed with water and alcohol, dried, and recrystallized from DMF to give 3.9 g of compound I; M^+ 283.

N-Acetyldibenzo[b,i]phenoxazine (II). A mixture of 5.6 g (20 mmole) of compound I, 60 ml acetic anhydride, and 0.1 g fused $ZnCl_2$ was refluxed for ~1 h, cooled, and the resulting precipitate removed by filtration and recrystallized from glacial acetic acid to give 3.7 g of compound II; M^+ 325.

N-Acetyl-12,14-dinitrodibenzo[b,i]phenoxazine (III). To a solution of 3.7 g (11 mmole) of compound II in 350 ml glacial acetic acid was added dropwise a mixture of 4.5 ml conc. HNO_3 and 6 ml glacial acetic acid. The mixture was stirred for 3 h at 20°C. The resulting dark red precipitate was recrystallized from chlorobenzene to give 1.8 g of compound III as dark red needles with a gold shine. An analytically pure sample was prepared by chromatography of 0.2 g of compound III on a column (d 30 mm, h 50 cm) filled with 40/100 μm silica gel (chloroform eluent), R_f 0.57 (chloroform).

12,14-Dinitrodibenzo[b,i]phenoxazine (IV). A. Compound III (1.6 g, 4 mmole) was dissolved in 200 ml alcohol upon heating, 16 ml of 20% NaOH solution was added, and the resulting violet solution was treated dropwise with dilute H_2SO_4 until the solution was red, then with 600 ml water. The resulting red precipitate was recrystallized from chlorobenzene to give 1.1 g (91%) of compound IV; M^+ 373.

B. A mixture of 1.0 g (3.5 mmole) compound I, 1.0 g (14 mmole) $NaNO_2$, and 300 ml glacial acetic acid was allowed to stand for 18 h at 20°C. The resulting red precipitate was washed with chloroform and recrystallized from chlorobenzene, Yield 1.0 (97%) of compound IV.

C. A mixture of 1.0 g (3.5 mmole) compound I, 0.75 g (10.5 mmole) $NaNO_2$, 3.5 g (11.5 mmole) $FeCl_3$ and 50 ml glacial acetic acid was allowed to stand for 3 h at 20°C. The resulting red precipitate was washed with chloroform and recrystallized from chlorobenzene to give 0.4 g (30%) of compound IV.

6-tert-Butyl-2,3-dihydroxynaphthalene (VI). To a mixture of 50 g (0.31 mole) 2,3-dihydroxynaphthalene and 3.5 g $ZnCl_2$ in 200 ml CCl_4 was added dropwise with stirring 40 ml (0.38 mole) of tert-butyl chloride. The mixture was refluxed 4 h, cooled, and the resulting precipitate filtered and recrystallized from CCl_4 to give 52 g of compound VI.

6(7)-tert-Butyl-3-amino-2-hydroxynaphthalene (VII). A mixture of 5.4 g (25 mmole) of compound VI and 2 g NaOH in 50 ml of 17% NH_4OH solution was heated for 2 h in an autoclave at 200°C, then cooled and filtered. The filtrate was neutalized with conc. HCl to pH 7, and the resulting precipitate was recrystallized from a water–alcohol mixture (5:1 by volume) and dried at 100°C to give 2.9 g of compound VII.

2(3),9(10)-Di-tert-butyldibenzo[b,i]phenoxazine (V). A mixture of 2.9 g (3 mmole) compound VI and 3.0 g (13 mmole) compound VII was ground in a mortar and then fused at 190°C for 2 h. The substance was recrystallized from chlorobenzene and then from DMF to give 1.1 g of compound V; M^+ 395.

12,14-Dinitro-2(3),9(10)-di-tert-butyldibenzo[b,i]phenoxazine (VIII). A. To a mixture of 0.23 g (0.6 mmole) compound V and 0.8 g of $FeCl_3$ in 10 ml glacial acetic acid was added gradually with stirring 0.23 g (3 mmole) $NaNO_2$ over 1 h. The resulting red precipitate was removed by filtration and recrystdallized from heptane. Yield 0.1 g (35%) of compound VIII: M^+ 485.

B. To 0.16 g (0.4 mmole) of compound V in 10 ml glacial acetic acid was added 0.16 g (2.3 mmole) $NaNO_2$ with stirring; the mixture was then allowed to stand overnight. The resulting precipitate was filtered and recrystallized from heptane. Yield 0.2 g (61%) of compound VII.

C. To 0.3 g (7.5 mmole) of compound V in 10 ml glacial acetic was added a solution of 0.2 ml fuming HNO_3 in 0.4 ml glacial acetic acid; a red precipitate formed immediately and was filtered and recrystallized from heptane. Yield 0.2 g (55%) of compound VII.

12,14-Diamino-2(3),9(10)-di-tert-butyldibenzo[b,i]phenoxyzonium chloride (IX). To a solution of 0.65 g (1.34 mmole) compound VIII in 75 ml alcohol was added 4.2 g of $SnCl_2 \cdot 6\ H_2O$, 7.5 ml conc. HCl, and the mixture was refluxed until it was colorless; the solution was then diluted with 100 ml of water. The resulting precipitate was filtered, treated with 100 ml of 10% NaOH solution and an air stream was passed through the solution until it was dark violet-colored; the solution was then extracted with chloroform (3 × 50 ml), and the chloroform was evaporated. The residue was refluxed with 50 ml heptane, and the insoluble portion was removed by filtration, while the solution was treated with 1 ml conc. HCl. The solu-

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.

LITERATURE CITED

1. B. M. Krasovitskii and B. M. Bolotin, Organic Luminophores [in Russian], Khimiya, Moscow (1984), p. 225.
2. L. E. Marinina, V. I. Alekseeva, and E. A. Luk'yanets, Abstracts of Proceedings, All-Union Conference on Molecular Luminescence and Its Application, Khar'kov (1982). p. 153.
3. H. X. Kaempfen, J. Heterocycl. Chem., 9, 303 (1972).
4. A. Bernthsen, Chem Ber., 20, 942 (1877).
5. F. Kehrmann and A. Saager, ibid., 36, 475 (1903).
6. L. S. Karpishchenko, A. V. Prosyanik, and S. V. Burmistrov, Khim. Geterosikl. Soedin., No. 5, 616 (1977).
7. R. B. Contractor, A. T. Peters, and F. M. Rorge, J. Chem. Soc., No. 8, 1993 (1949).
8. V. V. Kozlov and I. K. Vaselovskaya, Zh. Obshch. Khim., 31, 3030 (1961).
9. V. I. Alekseeva, S. A. Lebedev, E. A. Luk'yanets, L. E. Marinina, L. P. Savvina, and L. K. Slivka, Abstracts of Proceedings, All-Union Conference on Organic Luminophores and Their Application in Algorithm and Their Applications in Agriculture, Khar'kov (1984), p. 8.
10. J. N. Demas and G. A. Crosby, J. Phys. Chem., 75, 1010 (1971).
11. R. Sens and K. H. Drexhage, J. Luminesc., 24/25 710 (1981).

CONDENSED THIOLANE 1,1-DIOXIDE SYSTEM.

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

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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.

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