

BROMOCYCLIZATION OF 1,1-DIOXO-3-THIOLEN-3-YL ESTERS OF
N,N-DIALKYLDITHIOCARBAMIC ACIDS

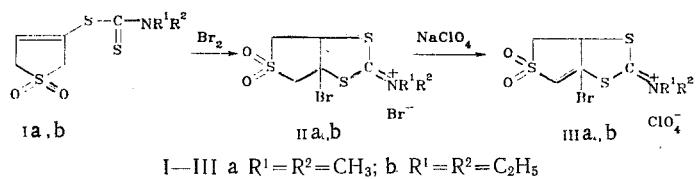
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Bicyclic 1,3-dithiolan-2-iminium salts were obtained by bromocyclization of 1,1-dioxo-3-thiolen-3-yl esters of N,N-dialkyldithiocarbamic acids.

It is known that on bromination, vinyl esters of N,N-dimethyldithiocarbamic acid undergo cyclization into 1,3-dithiolan-2-iminium salts [1, 2]. Hence, it could be expected that bicyclic 1,3-dithiolanes can be prepared from the corresponding derivatives of thiolane-1,1-dioxide already described in [3].

In the present work, we studied the bromination of 1,1-dioxo-3-thiolen-3-yl esters of N,N-dialkyldithiocarbamic acids Ia, b, and found that when the reaction is carried out in chloroform or acetic acid, bicyclic salts IIa, b are formed in a yield of 52-83%.



By treating aqueous solutions of compounds IIa, b with sodium perchlorate, sparingly soluble perchlorates IIIa, b are obtained.

Compounds IIa, b and IIIa, b are white powderlike substances, which are soluble in water, dimethyl sulfoxide, and hot acetic acid, and are insoluble in alcohols, ketones, and nonpolar organic solvents.

The structure of compounds IIa, b, IIIa, b was confirmed by the data of IR and UV spectroscopy (Table 1). The values of $\nu_{C=N}$ and also of λ_{max} and ϵ_{max} of compounds IIa, b, IIIa, b practically do not differ from the corresponding values for monocyclic 1,3-dithiolane-2-iminium salts [1, 2, 4]. The elemental composition of all the compounds obtained corresponds to the calculated values.

EXPERIMENTAL

The IR spectra of compounds II, III were run on the UR-20 spectrophotometer in KBr tablets. The UV spectra of aqueous solution (pH 5) were run on the SF-16 spectrophotometer.

TABLE 1. Spectral Characteristics of Compounds IIa, b, IIIa, b

Compound	IR spectrum, cm^{-1}			UV spectrum	
	$\nu_{SO_2^*}$, sym	$\nu_{SO_2^*}$, asym.	$\nu_{C=N}^+$	λ_{max} , nm	$\lg \epsilon$
IIa	1130	1318	1600	254	4.23
IIb	1130	1320	1570	254	4.14
IIIa	—*	1315	1605	253	4.26
IIIb	—*	1330	1580	255	4.14

*The vibrations of ClO_4^- are superimposed.

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1a-Bromo-5,5-dioxo-2-(N,N-dimethylimino)thiolano[3,4-d]-1,3-dithiolane Bromide (IIa). A 0.54-ml (0.01 mole) portion of bromine is added dropwise, slowly and with stirring, to a suspension of 2.37 g (0.01 mole) of 1,1-dioxo-3-thiolen-3-yl ester of N,N-dimethyldithiocarbamic acid Ia in 90 ml of CHCl₃. The orange precipitate is filtered, transferred into a beaker, soaked with 3-5 ml of acetone, and ground with a glass rod until a white powder is obtained. The precipitate is filtered, washed with acetone, and dried. Yield 2.1 g (52%), mp 196-198°C (from acetic acid). Found, %: Br 40.6; N 3.8; S 23.9. C₇H₁₁Br₂NO₂S₃. Calculated, %: Br 40.3; N 3.5; S 24.2.

When the reaction was carried out in acetic acid, compound IIa was obtained in a yield of 2.4 g (59%).

1a-Bromo-5,5-dioxo-2-(N,N-diethylimino)thiolano[3,4-d]-1,3-dithiolane Bromide (IIb). A 0.54-ml (0.01 mole) portion of bromine is added dropwise, slowly and with stirring, to a solution of 2.65 g (0.01 mole) of 1,1-dioxo-3-thiolen-3-yl ester of N,N-diethyldithiocarbamic acid Ib in 15 ml of CHCl₃. The precipitate is treated as described above. Yield 3.5 g (83%), mp 201-202°C (from acetic acid). Found, %: Br 37.4; N 3.4; S 22.2. C₉H₁₅Br₂NO₂S₃. Calculated, %: Br 37.7; N 3.3; S 22.6.

Preparation of Perchlorates IIIa, b. A solution of 0.02 mole of NaClO₄ in 5 ml of H₂O is added to a saturated solution of 0.01 mole of bromides IIa, b in water. The precipitate is filtered, washed with water, and dried in air.

LITERATURE CITED

1. K. Hirtani, H. Shiano, and M. Okawara, Chem. Lett., 867 (1973).
2. Y. Ueno, A. Nakayama, and M. Okawara, Synthesis, No. 4, 277 (1975).
3. T. É. Bezmenova, G. I. Khaskin, V. I. Slutskii, P. G. Dul'nev, L. N. Zakharov, V. I. Kulishov, and Yu. T. Struchkov, Khim. Geterotsikl. Soedin., No. 7, 907 (1981).
4. T. Nakai and M. Okawara, Bull. Chem. Soc. Jpn., No. 6, 1864 (1970).

COMPARATIVE STUDY OF RING-CHAIN ISOMERIC TRANSITIONS OF 2-CYANO-SUBSTITUTED BENZAMIDES AND BENZENESULFAMIDES*

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The rate constants of cyclization and the constant of ring-chain equilibrium of N-isopropyl-2-cyano-substituted benzamide and benzamide and benzenesulfamide by the methods of PMR and IR spectroscopy, and it was shown that in the transition from 2-cyanobenzamides to 2-cyanobenzenesulfamides a sharp destabilization of the cyclic isomeric form is observed; however, the cyclization of 2-cyanobenzenesulfamides proceeds at a higher rate than the cyclization of 2-cyanobenzamides.

N-Monosubstituted-2-cyanobenzamides (I) and their ring isomers - 3-iminoisoindolines (II) - are not interconverted in dioxane at room temperature [2]. N-Monosubstituted-2-cyanobenzenesulfamide (III) and 3-iminobenzisothiazoline-1,1-dioxides (IV) behave analogously in dioxane; however, the equilibrium III \rightleftharpoons IV was detected in a solution of dioxane +10% triethylamine, where the ring-chain equilibrium constants were measured by the method of IR spectroscopy.

*Communication 4 of the series "Ring-Chain Conversions with the Participation of the C≡N Group"; for communication 3, see [1].

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