REACTION OF BENZOTHIAZOLINE-2-THIONE WITH 1-CHLORO-2,3-EPOXYPROPANE

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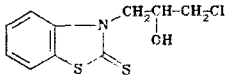
The reaction of 1-chloro-2,3-epoxypropane with benzothiazoline-2-thione leads to the formation of 2-(2-hydroxy-3-chloropropylthio)benzothiazole, while this epoxypropane reacts with the sodium salt of benzothiazoline-2-thione to form 3-(2,3-epithiopropyl)benzothiazolin-2-one.

Due to the ambident —NH—C=S system, benzothiazoline-2-thione may give two series of derivatives at the nitrogen and sulfur atoms, depending on the reaction conditions and nature of the reagent.

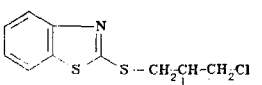
Previous work on the reaction of benzothiazoline-2-thione (I) with 1-chloro-2,3-epoxypropane (II) gave contradictory results. Grigoryan et al. [1] assigned structure III to the product obtained by heating the reagent in benzene solution at reflux on the basis of IR data. Later, Getmanchuk et al. [2] studied the UV spectra of this product and showed that it is the corresponding S-isomer IV. However, Sebast'yan et al. [3] reexamined the IR spectrum of this product obtained analogously to the previous work [1, 2] and concluded that it is a mixture of the S-isomer and N-isomer with predominance of the former.

In a continuation of a study of the reactions of thione I [4], we carried out an additional study of the structure of the product of the reaction of thione I with oxirane II.

Analysis of the PMR, UV, and IR spectra of the compound obtained under previously reported conditions [1-3] showed that it is 2-(2-hydroxy-3-chloropropylthio)benzothiazole (IV).



III

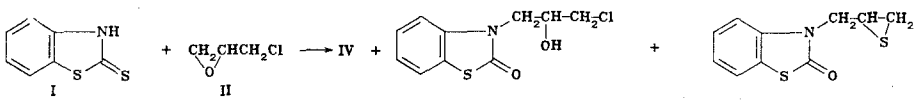


IV

The PMR spectrum of IV has signals for the aromatic ring protons as two multiplets at 7.22 and 7.67 ppm, which is characteristic for S-derivatives of thione I. The CH_2 group proton signal at 3.55 ppm also indicates that this group is attached to the sulfur atom [5]. The shape of the UV spectrum is identical to that described by Getmanchuk et al. [2] and characterizes the S-product.

The IR spectral data do not permit reliable characterization of the S- and N-structures. The statement of Sebast'yan et al. [3] that the band at 1670-1640 cm^{-1} characterizes IV as a derivative of addition to the sulfur atom is unjustified. This band is absent in the spectrum of carefully purified IV and in the spectra of several 2-alkylthiobenzothiazoles. The discovery of this band by Sebast'yan et al. [3] was apparently related to the presence of a trace of benzothiazolin-2-one (V) or its nitrogen derivative; the carbonyl group of these compounds absorbs in this region.

Of the products of the reaction studied, we isolated 3-(2-hydroxy-2-chloropropyl)benzothiazolin-2-one (IV) (2.2% yield) and 3-(2,2-epithiopropyl)benzothiazolin-2-one (1%).



I II VI VII

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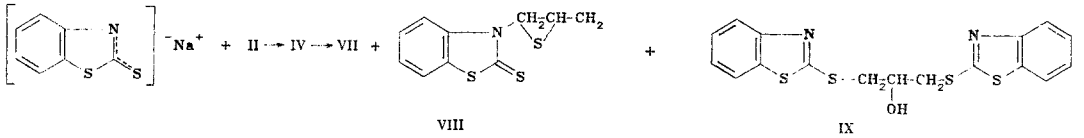
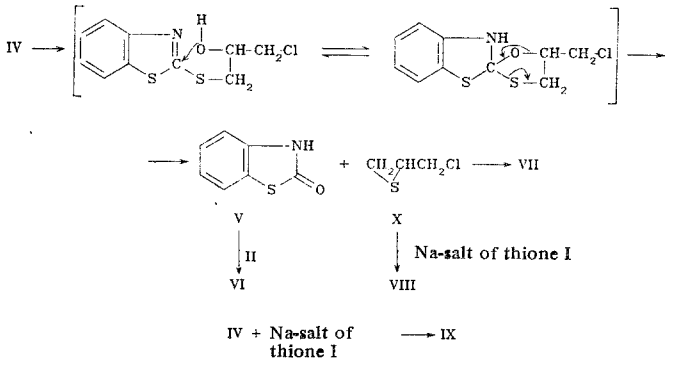
Sebast'yan et al. [3] concluded the presence of a trace of the N-isomer on the basis of the band at 1348 cm^{-1} which was assigned to the N—C bond of the $>N—C=S$ group. However, this presence of the band is not sufficient for assignment of the thione form of this compound since thiol derivatives also have bands in the range from 1380 to 1310 cm^{-1}. This band apparently corresponds to the deformation vibrations of the CH_2 group attached to the sulfur atom and of the chlorine [6].

The major product of the reaction of the sodium salt of thione I with oxirane II was VII and not 2-(2,3-epoxypropylthio)benzothiazole as reported in previous work [2, 3]. The other products of this reaction are 3-(2,3-epithiopropyl)benzothiazoline-2-thione (VIII) and 1,3-bis(benzothiazolyl-2-thio)propanol-2 (IX).



VIII IX

The formations of products VI-IX is the result of transformations of the initially isolated product IV, which was shown by special experiments. The reaction pathways are shown in the following scheme.



This scheme was confirmed by the preparation of VI and VII from V and oxirane II and 1-chloro-2,3-epithiopropane X, respectively, of VIII from the sodium salt of thione I and thiirane X, and of IX from the sodium salt of I and IV.

The PMR spectra of VII and VIII correspond to the proposed structures. Comparison of these spectra show a significant difference only for the $N—CH_2$ group protons, which appear as a broad doublet at 4.05 ppm in the spectrum of VII and as two quartets with J_{gem} = 15 Hz and J_{vic} = 5.5 and 6.5 Hz at 4.20-4.80 in the spectrum of VIII (Table 1). This pattern results from hindered internal rotation about the $C_{(1)}—C_{(2)}$ bond. Shologon et al. [7] came to a similar conclusion in a study of the conformation of the epoxide group in glycidyl derivatives. Support for this hypothesis is also found from significant diminution of the nonequivalence of the $N—CH_2$ protons in VIII at 180°C with nitrobenzene solvent and the increased nonequivalence of these protons in VII at −70°C with $CCl_4—CHCl_3$ as solvent. The factors accounting for the different extents of hindrance to rotation in VII and VIII will be the subject of an additional study.

EXPERIMENTAL

The IR spectra were taken in KBr pellets on a UR-20 spectrophotometer. The UV spectra were taken on a Hitachi EPS-3T spectrometer in ethanol. The PMR spectra were taken on a Jeol C-60 HL spectrometer with HMDS as internal standard. The purity and individual nature of the compounds were checked by thin-layer chromatography on Silufol UV-254 plates. The preparative separation was carried out on 20 × 20-cm plates coated with alumina having grade II activity. The preparative column separation was carried out on a column packed with silica gel L 100/160 with 1:2:1 benzene—hexane—chloroform as eluent.

Reaction of benzothiazoline-2-thione with 1-chloro-2,3-epoxypropane. The reaction was performed as described previously [2, 3]. After removal of oxirane II by preparative thin-layer chromatography, the residue with mp 74-78°C (1 g) was separated into three products with R_f 0.30, 0.18, and 0.82 (chloroform).

TABLE 1. PMR Spectral Data for IV, VI-IX

Compound	Chemical shifts						Aromatic protons	Solvent
	S–CH_2	N<H_α H_β	O–CH	Cl–CH_2	CH–CH_2 (S)	CH–CH_2 (S)		
IV	3,55 (m)	—	4,25 (m)	3,41 (M)	—	—	7,22; 7,67 (m)	$CDCl_3$
VI	—	3,92 (m)	4,12 (m)	3,35 (M)	—	—	6,90 (m)	CF_3COOH
VII	—	4,05 (d)	—	—	3,06 (m)	2,45 (m)	7,28 (m)	$CDCl_3$
VIII	—	4,20 (q); 4,80 (q)	—	—	3,55 (m)	2,51 (m)	7,23 (m)	$CDCl_3$
IX	3,55 (m)	—	4,22 (m)	—	—	—	7,13; 7,81 (m)	$CDCl_3$

The compound with R_f 0.30 is 2-(2-hydroxy-3-chloropropylthio)benzothiazole (IV) with mp 82-83°C (from hexane), 81-83°C [1-3]. The yield was 0.76 g (63%). UV spectrum, λ_{max} (log ε): 282 (3.98), 292 (3.94), 302 nm (3.84). IR spectrum: 3240 cm^{-1} (OH).

The compound with R_f 0.18 was isolated with a yield of 0.025 g (2.2%). It is 3-(2-hydroxy-3-chloropropyl)benzothiazolin-2-one (VI) with mp 108-109°C (from benzene), 108-110°C [3]. UV spectrum, λ_{max} (log ε) 282, 290 nm (3.84). IR spectrum 1650-1660 (C=O), 3435 cm^{-1} (OH). The identical product was obtained upon heating 0.75 g (0.005 mole) V and 1.38 g (0.015 mole) oxirane II at 100°C for 12 h. The yield in this case was 0.86 g (71%).

The compound with R_f 0.82 is 3-(2,3-epithiopropyl)benzothiazolin-2-one (VII) with mp 50-51°C (from hexane). The yield was 0.02 g (1%). UV spectrum, λ_{max} (log ε): 284, 292 nm (3.29). IR spectrum: 1680 cm^{-1} (C=O). Found: N, 6.41%. Calculated for $C_{10}H_9NOS_2$: N, 6.27%. The identical product was obtained in the reaction of 1.73 g (0.01 mole) sodium salt of V and 1.08 g (0.01 mole) thiirane X according to Getmanchuk [2]. The yield in this case was 0.9 g (42%).

Reaction of the sodium salt of benzothiazoline-2-thione with 1-chloro-2,3-epoxypropane. The reaction was carried out as described by Getmanchuk et al. [2]. The unpurified product is an oil which appears as three spots upon thin-layer chromatography with R_f 0.50, 0.87, and 0.10 using 1:1 benzene–chloroform as eluent. The column separation of 1 g of this product gave 0.65 g (48%) VII with R_f 0.50, mp 50-51°C; a mixed melting point with the sample described above was undepressed.

The compound with R_f 0.87 is 3-(2,3-epithiopropyl)benzothiazoline-2-thione (VIII), mp 114-115°C (from ethanol). The yield was 0.03 g (2%). UV spectrum, λ_{max} (log ε): 328 nm (4.39). Found: N, 5.78%. Calculated for $C_{10}H_9NS_3$: N, 5.78%. This product was also obtained in the reaction of 1.89 g (0.01 mole) sodium salt of thione I and 1.08 g (0.001 mole) thiirane X according to Getmanchuk et al. [2]. The yield in this case was 0.098 g (4%).

The compound with R_f 0.10 is 1,3-bis(benzothiazolyl-2-thio)propanol-2 (IX) with mp 91-92°C (from ethanol). The yield was 0.1 g (4%). UV spectrum, λ_{max} (log ε): 282 (4.37), 292 (4.32), 302 nm (4.25). IR spectrum: 3220-3330 cm^{-1} (OH). Found: N, 7.05%. Calculated for $C_{17}H_{14}N_2S_4O$: N, 7.18%. This product was also obtained in the reaction of the sodium salt of thione I and IV. A sample of 2.82 g (0.015 mole) sodium salt of thione I in 20 ml ethanol was added dropwise with stirring to a solution of 3.9 g (0.015 mole) IV in 30 ml absolute ethanol at 50°C. The reaction solution was stirred for 210 min at 50°C. After cooling, the precipitate was filtered off and the filtrate was evaporated. The residue was extracted with chloroform, washed with 5% aqueous sodium hydroxide and then with water, and dried over $CaCl_2$. After solvent removal, the residue was recrystallized from ethanol to yield 3.75 g (64%) IX.

Transformation of 2-(2-hydroxy-3-chloroprophylthio)benzothiazole (IV). A. Reaction with 1-chloro-2,3-epoxypropane. A mixture of 1.3 g (0.005 mole) IV and 0.925 g (0.01 mole) oxirane II was heated at 70°C for 2 h. Thin-layer chromatography showed the presence of V, VI, and VII.

B. Reaction with sodium hydroxide. The reaction was carried out as described by Getmanchuk et al. [2]. Column chromatography of 0.78 g of the unpurified product gave 0.46 g (44%) VII, 0.026 g (2%) VIII, and 0.1 g (5%) IX.

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SOME TRANSFORMATIONS OF 2-(2-HYDROXY-3-CHLOROPROPYLTHIO)BENZOTHIAZOLE

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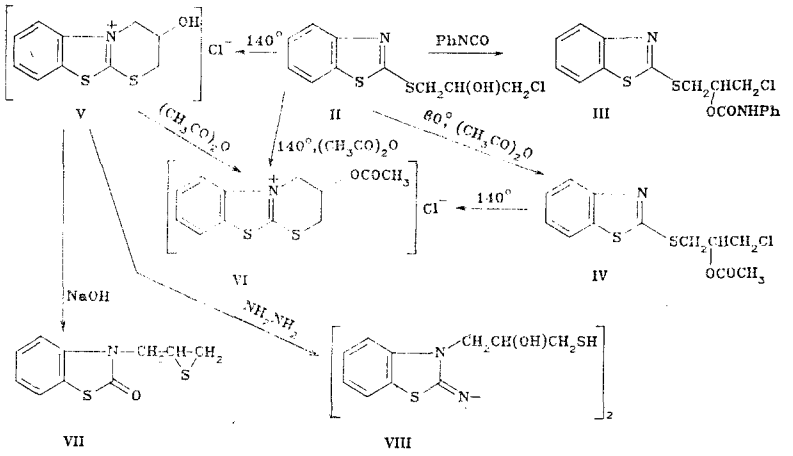
The reaction of phenyl isocyanate and acetic anhydride with 2-(2-hydroxo-3-chloropropylthio)benzothiazole was studied. At 140°C, this benzothiazole cyclizes with the formation of quaternary salt which readily reacts with hydrazine and alkali.

Many derivatives of benzothiazoline-2-thione (I) are biologically active which have, in particular, defoliating [1] and fungicide properties [2].

In a search for new pesticides, we studied some chemical transformations of 2-(2-hydoxy-3-chloropropylthio)benzothiazole (II) obtained in the reaction of thione I with 1-chloro-2, 3-epoxypropane [3].



The hydroxyl group of thiazole II reacts with phenyl isocyanate and acetic anhydride with the formation of 2-(2-phenylcarbamoyloxy-3-chloropropylthio)benzothiazole (III) and 2-(2-acetoxy-3-chloropropylthio)benzothiazole (IV), respectively. Heating thiazole II in xylene solution at reflux leads to cyclization and the formation of quaternary salt V. This salt reacts with acetic anhydride upon heating in glacial acetic acid at reflux and gives a quantitative yield of 5-acetoxy-4,5-dihydro-6H-benzothiazolo[2,3-b]thiazonium chloride (VI) which may also be obtained by the acetylation of thiazole II at 140°C or cyclization of acetoxy derivative IV.

Quaternary salt V readily reacts with alkali to form 3-(2,3-epithiopropyl)benzothiazolin-2-one (VII) and with hydrazine to form the azine of 3-(2-hydroxy-3-mercaptopropyl)benzazolin-2-one (VIII).

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