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SYNTHESIS AND TRANSFORMATIONS OF S- AND N-SUBSTITUTED 2-MERCAPTOBENZOTHIAZOLES

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2-Mercaptobenzothiazole reacts with alkyl halides and hydrazine hydrate in the thiol form, and with formaldehyde in the thione form. The alkylation of 2-mercaptobenzothiazolidin-3-yl-methanol has been performed with sulfoalkyl halides and with propan-1,3-sultone. A number of new 2-hydrazinobenzothiazoles derivatives have been synthesized.

The existence of 2-mercaptobenzothiazole (I) in the thiol and thione tautomeric forms [1] explains its capacity for forming derivatives substituted at the sulfur or the nitrogen atoms. The aim of the present investigation was to find luster-imparting additives for the electrolytic deposition of metals, in connection with which methods have been developed for obtaining some derivatives of the thiazole (I) of various types and studying their reactivities.

The thiazole (I) reacts with formalin in the thione form, giving rise to 2-thioxobenzothiazolidin-3-yl-methanol (II) [1], which is alkylated by sulfoalkyl halides or propan-1,3-sultone in the presence of caustic potash to form salts of the (2-thioxobenzothiazolidin-3-yl-methoxy)alkanesulfonic acids (III-V) (Table 1).

TABLE 1. Characteristics of the Compounds (III-V), (VII-XI), and (XIII-XXI)

Compound	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	S		C	H	S	
III	210—212[a]	35,2	3,1	25,4	$C_{11}H_{12}KNO_5S_3$	35,4	3,2	25,8	48
IV	240[a]	36,5	3,2	29,4	$C_{10}H_{10}NNaO_5S_3$	36,7	3,1	29,4	92
V	271[a]	36,8	3,5	27,0	$C_{11}H_{12}KNO_4S_3$	37,0	3,4	26,9	60
VII	125—127	47,7	4,9	39,3	$C_{13}H_{16}N_2S_4$	47,6	4,9	39,0	88
VIII	92—94	52,8	6,1	33,0	$C_{17}H_{24}N_2S_4$	53,1	6,3	33,3	51
IX	208[a]	34,9	3,0	28,3	$C_{10}H_{10}KNO_4S_3$	35,0	2,9	28,0	54
X	71—72	50,2	4,0	27,1	$C_{10}H_9NO_2S_2$	50,2	3,8	26,8	61
XI	159—160	45,3	4,0	27,0	$C_9H_9N_3OS_2$	45,2	3,8	26,8	73
XIII	193—194[b]	56,1	4,7	16,5	$C_9H_9N_3S$	56,2	4,7	16,7	71
XIV	144—145	60,0	5,8	14,4	$C_{11}H_{13}N_3S$	60,2	6,0	14,6	72
XV	216—217[c]	66,2	4,3	12,6	$C_{14}H_{11}N_3S$	66,4	4,4	12,7	84
XVI	191—192	62,8	5,8	11,3	$C_{15}H_{13}N_3OS$	62,7	6,0	11,1	78
XVII	285[a]	34,2	2,8	22,8	$C_8H_8N_3NaO_3S_2$	34,1	2,9	22,8	58
XVIII	101—102	55,0	4,8	14,3	$C_{10}H_{10}N_4S$	55,0	4,6	14,7	56
XIX	76—79	54,6	4,9	14,3	$C_{10}H_{11}N_3OS$	54,5	5,0	14,5	77
XX	141—142	62,7	4,7	13,7	$C_{12}H_{11}N_3S$	62,8	4,8	14,0	52
XXI	171—172[d]	54,8	2,9	18,4	$C_8H_5N_3S$	54,9	2,9	18,3	86

[a] Melts with decomposition. [b] According to [4], mp 194-195°C. [c] According to [4], mp 221-222°C. [d] According to [2], mp 174.5-177°C.

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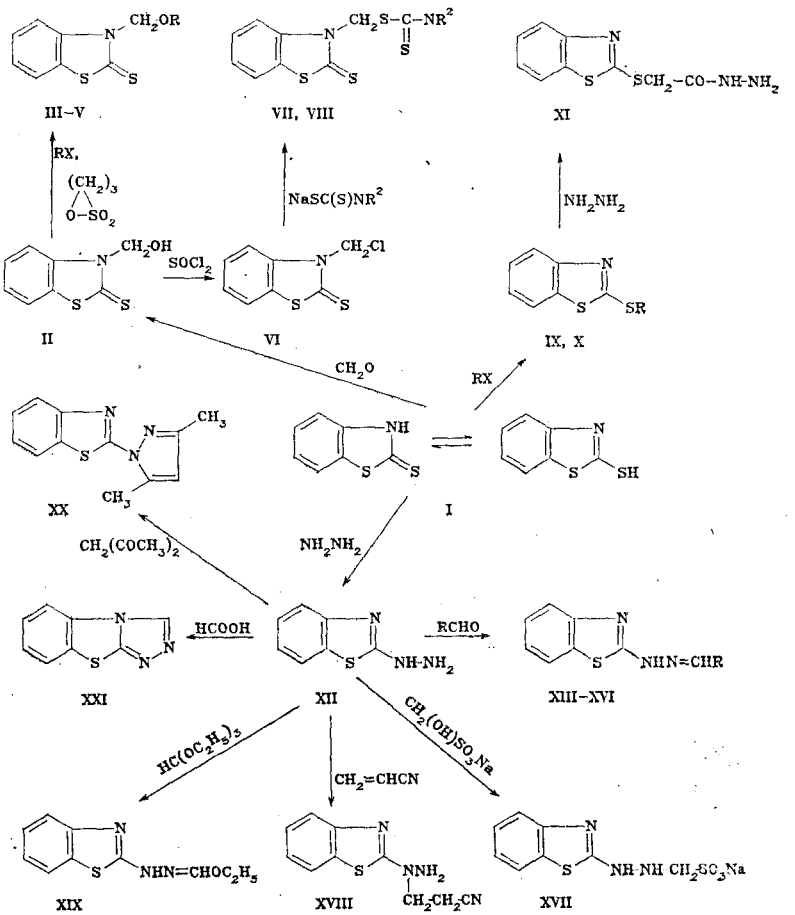
TABLE 2. Details of the PMR Spectra of Compounds (VII), (VIII), (XIII-XXI)

Compound	Solvent	Chemical shifts, ppm
VII	C_6D_6	0,47 (3H, t, CH_3); 0,75 (3H, t, CH_3); 2,77 (2H, q, $\mathbf{CH_2}CH_3$); 3,42 (2H, q, $\mathbf{CH_2}CH_3$); 6,26 (2H, s., $\mathbf{CH_2}S$)
VIII	C_6D_6	3,02 (2H, t, $\mathbf{CH_2}C_3H_7$); 3,60 (2H, t, $\mathbf{CH_2}C_3H_7$); 6,24 (2H, s, CH_2S)
XIII	Py—D_5	1,69 (3H, d, CH_3)
XIV	Py—D_5	0,69 (3H, t, CH_3); 1,29 (2H, m $\mathbf{CH_2}CH_3$); 2,01 (2H, q, $\mathbf{CH_2}C_2H_5$)
XV	Py—D_5	8,24 (1H, s, N=CH)
XVI	Py—D_5	8,22 (1H, s, N=CH)
XVII	D_2O	3,84 (2H, s, CH_2)
XVIII	$(CD_3)_2CO$	2,89 (2H, t, CH_2CN); 4,04 (2H, t, $\mathbf{CH_2}CH_2CN$); 5,06 (2H, s, NH_2)
XIX	$(CD_3)_2CO$	1,06 (3H, t, CH_3); 4,02 (2H, q, $\mathbf{CH_2}CH_3$); 6,71 (1H, s, —NH—N); 9,24 (1H, s, N=CH)
XX	$CDCl_3$	2,04 (3H, s, N=C—$\mathbf{CH_3}$); 2,62 (3H, d, $\mathbf{CH_3}$—C=CH); 5,84 (1H, s, CH_3—C—$\mathbf{CH}$)
XXI	Py—D_5	9,55 (1H, s, N=CH—N)

The alkylation of sodium N,N-dialkyldithiocarbamates with the chloride (VI) took place on heating in DMFA with the formation of the dithiocarbamates (VII) and (VIII). The PMR spectra of compounds (VII) and (VIII) show hindered rotation about the C—N bond (Table 2).

The reaction of the thiazole (I) with alkyl halides in the presence of caustic potash led to the formation of the benzothiazol-2-yl thioethers (IX) and (X). On being boiled with hydrazine hydrate, methyl benzothiazol-2-yl-thioacetate (X) was converted into the hydrazide (XI).



III, IX R=$CH_2CH(OH)CH_2SO_3K$; IV R=$CH_2CH_2SO_3Na$; V R=$(CH_2)_3SO_3K$; VII R=C_2H_5; VIII R=C_4H_9; X R=CH_2COOCH_3; XIII R=CH_3; XIV R=C_3H_7; XV R=C_6H_5; XVI R=p-$CH_3OC_6H_4$

The thiazole (I) reacted with hydrazine hydrate with the elimination of hydrogen sulfide and the formation of 2-hydrazinobenzothiazole (XII), the condensation of which with aliphatic and aromatic aldehydes led to the hydrazones (XIII-XVI).

On reaction with sodium hydroxymethanesulfonate monohydrate in ethanol the hydrazine (XII) formed the sodium hydrazinomethanesulfonate (XVII). The nucleophilic addition of acrylonitrile to the hydrazine (XII) took place at the monosubstituted nitrogen atom with the formation of the hydrazine (XVIII), as was confirmed by its PMR spectrum, in which the signals of the protons of the NH_2 group appeared in the form of a singlet at 5.60 ppm, and also by its IR spectrum, having the absorption of a C≡N bond at 2230 cm^{-1}.

By condensing the hydrazine (XII) with ethyl orthoformate, the ethoxymethylenehydrazine (XIX) was obtained, its structure being confirmed by the presence in its PMR spectrum of the signal of the protons of a methyl group in the form of a triplet at 1.06 ppm, the signal of a proton of a NH—N group in the form of a singlet at 6.71 ppm, and the signal of the proton of a —N=CH group in the form of a singlet at 9.24 ppm. It is stated in a patent [2] that the performance of this reaction in xylene leads to the formation of 1,2,4-triazolo[4,3-b]benzothiazole (XXI). We isolated compound (XXI) after the condensation of formic acid with the hydrazine (XII).

The condensation of acetylacetone with the hydrazine (XII) led to 2-(3,5-dimethylpyrazol-1-yl)benzothiazole (XX).

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrometer in KBr tablets. PMR spectra were taken on a Hitachi R-22 (90 MHz) spectrometer with HMDS as internal standard or, in the case of compound (VII), external standard.* The characteristics of the compounds obtained and details of their spectra are given in Tables 1 and 2.

2-Thioxobenzothiazolidin-3-yl-methanol (II) and 3-chloromethyl-2-thioxobenzothiazolidine (VI) [1] and 2-hydrazinobenzothiazole (XII) [3] were obtained as described in the literature.

Salts of (2-Thioxobenzothiazolidin-3-yl-methoxy)alkanesulfonic Acids (III-V). A solution of 4.2 g (75 mmole) of KOH and 13.6 g (75 mmole) of compound (II) in 70 ml of ethanol was treated with 75 mmole of 1-chloro-2-hydroxypropane-3-sulfonic acid or 1-bromoethanesulfonic acid and 5 ml of H_2O, the mixture was boiled for 4 h, the hot solution was decanted, the ethanol was distilled off, and the residue was filtered off and recrystallized from ethanol—water (5:1). Compounds (III) and (IV) were obtained in this way.

To a solution of 4.2 g (75 mmole) of KOH in 5 ml of H_2O were added a solution of 13.6 g (75 mmole) of the thiazole (I) in 70 ml of dioxane and 9.1 g (75 mmole) of propan-1,3-sultane, and the mixture was heated at 70°C for 4 h, cooled, and diluted with acetone, and the resulting precipitate of compound (V) was filtered off and recrystallized from ethanol—water (5:1).

2-Thioxobenzothiazolidin-3-yl-methyl Dithiocarbamates (VII and VIII). A mixture of 5 g (25 mmole) of the chloride (VI) and 25 mmole of the appropriate sodium N,N-dialkyldithiocarbamate in 50 ml of ethanol was heated at 50°C for 2 h and diluted with water, and the precipitate was filtered off and washed with water.

Potassium 3-(Benzothiazol-2-yl-thio)-2-hydroxypropanesulfonate (IX). A solution of 2.8 g (50 mmole) of KOH in 50 ml of methanol was treated with 8.4 g (50 mmole) of the thiazole (I), 9 g (50 mmole) of potassium 3-chloro-2-hydroxypropane-1-sulfonic acid, and 5 ml of H_2O, the mixture was boiled for 4 h, the hot solution was decanted off, the methanol was distilled off, and the residue was recrystallized from ethanol—water (5:1).

Methyl (Benzothiazol-2-yl-thio)acetate (X). This was obtained in a similar manner to the preceding compound from 2.8 g (50 mmole) of KOH, 8.4 g (50 mmole) of the thiazole (I), and 5.4 g (50 mmole) of methyl monochloroacetate in 100 ml of acetone.

(Benzothiazol-2-yl-thio)acethydrazide (XI). A solution of 4.8 g (20 mmole) of compound (X) in 50 ml of methanol was treated with 4 g (80 mmole) of hydrazine hydrate, the mixture was boiled for 5 h, and cooled, and the precipitate was filtered off and washed with methanol.

Benzothiazol-2-yl-hydrazones (XII-XVI). A solution of 8.3 g (50 mmole) of compound (XII) in dioxane was treated with 50 mmole of the appropriate aldehyde and the mixture was

*We express our gratitude to S. P. Plevokas for recording and interpreting the PMR spectra.

heated for 2 hours at 40°C (for compounds (XIII) and (XIV)) or at 80°C (for compounds (XV) and (XVI)), and cooled, and the precipitate was filtered off and recrystallized from propanol.

Sodium Benzothiazol-2-yl-hydrazinomethanesulfonate (XVII). A mixture of 7.6 g (50 mmole) sodium hydroxymethanesulfonate monohydrate and 8.3 g (50 mmole) of compound (XII) in 70 ml of aqueous ethanol (5:2) was heated at 80°C for 5 h, the ethanol was distilled off, and the precipitate was filtered off and washed with ether.

N-(Benzothiazol-2-yl)-N-(2-cyanoethyl)hydrazine (XVIII). A solution of 8.3 g (50 mmole) of compound (XII) in dioxane was treated with 0.5 ml of 40% aqueous KOH solution and 2.65 g (50 mmole) of acrylonitrile in 10 ml of dioxane, and the mixture was kept for 2 h and was purified by chromatography on a column of Al_2O_3 (with dioxane as eluent). After the addition of hexane, the precipitate was filtered off.

N-(Benzothiazolyl)-N'-(ethoxymethylene)hydrazine (XIX). A mixture of 8.3 g (50 mmole) of compound (XII) and 19.8 g (150 mmole) of ethyl orthoformate was heated at 120°C for 3 h with the simultaneous elimination of ethanol, and then the excess of ethyl orthoformate was distilled off, the residue was treated with hexane, and the precipitate was filtered off and washed with hexane.

2-(3,5-Dimethylpyrazol-1-yl)benzothiazole (XX). A mixture of 5 g (30 mmole) of compound (XII) and 50 ml of acetylacetone was heated at 125°C for 3 h and was cooled, and the precipitate was filtered off and recrystallized from propanol—water (2:1).

1,2,4-Triazolo[4,3-b]benzothiazole (XXI). A mixture of 8.3 g (50 mmole) of compound (XII) and 40 ml of formic acid was heated at 100°C for 2 h 30 min, cooled, and poured into 500 ml of water, and the precipitate was filtered off and washed with water.

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AN INVESTIGATION OF THE TRANSFORMATIONS OF 2-AMINO-2-THIAZOLIN-4-ONE AND ITS DERIVATIVES IN AQUEOUS SOLUTIONS

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It has been shown by thin-layer radiochromatography that the action of an aqueous solution of alkali on 2-amino-2-thiazolin-4-one and its 5-alkyl derivatives leads predominantly to the opening of the ring by a mechanism similar to the opening of lactams in an alkaline medium.

2-Amino-2-thiazolin-4-one and its 5-alkyl derivatives possess a radioprotective action [1]. In aqueous solutions at pH > 7 these compounds decompose with the formation of urea and thiourea and of 2-hydroxy and 2-mercapto carboxylic acids [2-5]. This composition of the reaction products presupposes that an opening of the initial heterocycle at the $S—C_{(5)}$ or $S—C_{(2)}$ bond first takes place (scheme, pathways 1 and 3). The presence of a lactam grouping in the 2-amino-2-thiazolin-4-one molecule permits the assumption that, under the conditions considered, opening of the heterocycle at the $N_{(3)}—C_{(4)}$ bond is also possible (scheme, pathway 2) [6]. We have therefore made a quantitative investigation of the behavior of 2-amino-2-thiazolin-4-one derivatives in aqueous alkaline solutions.

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