Benzothiazole compounds XXXVI. Reactions of benzothiazole and its derivatives with bis(bromomethyl)benzenes

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Dedicated to Professor P. Hrnčiar, DrSc., in honour of his 60th birthday

Xylylenebis(3-benzothiazolium bromides) and 3-(bromomethylbenzyl)-benzothiazolium bromides were prepared by the reaction of benzothiazole, 6-methyl-, 6-methoxy-, 6-bromo-, 2-methyl-, 4-methyl-, and 2-styrylbenzothiazole with 1,2-, 1,3-, and 1,4-bis(bromomethyl)benzene. The formation of not typical tricyclic compounds has been proved by the reaction of 3-methyl-2-benzothiazolinethione with 1,2- and 1,3-bis(bromomethyl)benzene. Using 1,4-bis(bromomethyl)benzene, 2-methylthio-3-methylbenzothiazolium bromide is formed. The mechanisms of these reactions are proposed. The structure has been proved by the ^{1}H NMR spectra.

Бромиды ксилиленбис(3-бензотиазолия) и 3-(бромметилбензил)-бензотиазолия были получены посредством реакции бензотиазола, 6-метил-, 6-метокси-, 6-бром-, 2-метил-, 4-метил- и 2-стирилбензотиазола с 1,2-, 1,3- и 1,4-бис(бромметил)бензолом. Образование нетипичных трициклических соединений было доказано путем взаимодействия 3-метил-2-бензотиазолинтиона с 1,2- и 1,3-бис(бромметил)-бензолом. При использовании 1,4-бис(бромметил)бензола образуется бромид 2-метилтио-3-метилбензотиазолия. Предлагаются механизмы указанных реакций. Строение соединений подтверждено их ^{1}H ЯМР спектрами.

This paper is a continuation in the study of syntheses of benzothiazolium salts [1, 2] and their biological activity in the area of plant growth regulators. Our target was to study the reaction of benzothiazole and its derivatives with 1,2-, 1,3-, and 1,4-bis(bromomethyl)benzene, where we expected the formation of corresponding disalts.

It was found that the reaction of benzothiazole with 1,2-bis(bromomethyl)-benzene proceeds only to the first stage to give 3-(2-bromomethylbenzyl)benzothiazolium bromide (*I*). Corresponding xylylenebis(benzothiazolium salt) has not been formed even by using large excess of benzothiazole, prolonging the

reaction time and increasing temperature. It can be supposed that the reason for reactivity of *I* to the second stage is caused by the possible interaction of bromine of bromomethylene group with acidic hydrogen in the position 2 or with thiazole ring; owing to this fact, hindering of the rotation of 2-bromomethylbenzyl can appear. Corresponding xylylenebis(benzothiazolium salts) *II*, *III* are formed by the reaction of 1,3- and 1,4-bis(bromomethyl)benzene with benzothiazole.

The same results were also obtained in the case of the reaction of 6-methylbenzothiazole. It was shown that methyl group in the position 6 does not influence essentially electronic conditions in the molecule of benzothiazole because by the action of 1,2-bis(bromomethyl)benzene, monoderivative *IV* is again formed. By the reaction with 1,3-bis(bromomethyl)benzene, 1,3-xylylenebis(6-methyl-3-benzothiazolium bromide) (*V*) is formed. By the reaction with 1,4-bis(bromomethyl)benzothiazole in DMF—acetone medium faintly soluble 3-(4-bromomethylbenzyl)-6-methylbenzothiazolium bromide (*VI*) is formed. When this compound was dissolved in methanol and allowed to react with 6-methylbenzothiazole, 1,4-xylylenebis(6-methyl-3-benzothiazolium bromide) (*VII*) was isolated.

Methoxy group of 6-methoxybenzothiazole increases by its mesomeric effect nucleophilicity of nitrogen and enables progress of the reaction with 1,2- and 1,3-bis(bromomethyl)benzene to the second stage giving *VIII*, *IX* in high yields. During the reaction with 1,4-bis(bromomethyl)benzene, a mixture of mono- and disalts is formed. Isolation in pure condition using crystallization from methanol was successful only in the case of 3-(4-bromomethylbenzyl)-6-methoxybenzothiazolium bromide (*X*).

Reactions of 1,3- and 1,4-bis(bromomethyl)benzenes with 6-bromobenzothiazole afforded disalts *XI*, *XII*. Lower yields are caused by the electron-withdrawing effect of bromine. Reaction of 6-bromobenzothiazole with 1,2-bis(bromomethyl)benzene was not successful. At the temperatures of 40—80 °C, the reaction did not proceed even to the first stage and at 85—110 °C, unidentified decomposition products were formed. That means, this reaction takes undesirable course. On the basis of this fact and additional knowledge obtained during this work it can be supposed that the reaction to the first stage can partly proceed, but in the following, the second bromomethyl group after initial interaction with strongly acidic hydrogen of benzothiazole in the position 2 reacts under separation of HBr, which can easily react with 6-bromobenzothiazole. With regard to the extremely acidic hydrogen in the position 2, resulting 6-bromobenzothiazolium bromide is anticipated to react with 1,2-bis(bromomethyl)benzene. It is necessary to take into account also possible oxidation in the position 2 of considered quaternary salts.

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By the reaction of 2-methylbenzothiazole with 1,2-bis(bromomethyl)benzene, decomposition products were formed. 1,3-Bis(bromomethyl)benzene afforded 2-methyl-3-(3-bromomethylbenzyl)benzothiazolium bromide (*XIII*) and 1,4-bis(bromomethyl)benzene reacted under formation of 1,4-xylylenebis(2--methyl-3-benzothiazolium bromide) (*XIV*). From this finding it is evident that the reaction is influenced by the steric hindrances. 2-Methyl-3-(3-bromomethylbenzyl)benzothiazolium bromide (*XIII*) was formed only in acetonic medium. In the mixture of DMF—acetone ($\varphi_r = 2:1$) at the same conditions, a mixture of decomposition products having red colour resulted. Reaction mixture has turned red also in DMF medium. In this case we suppose that more polar reaction medium enables faster oxidation of methyl group in the resulting product to the first stage. Interaction of bromomethyl group with methyl group increasing acidity of hydrogens also supports oxidation. We suppose that oxidation results in the formation of dimers which can be liable to the further changes. Reaction performed in a sealed tube without solvent afforded a mixture of mono- and disalts and 2-(bromomethyl)benzothiazolium bromide. By the reaction of 2-methylbenzothiazole with 1,3-bis(bromomethyl)benzene in methanol, only 2-methylbenzothiazolium bromide was formed. Its structure was proved, in addition to the elemental analysis, by ^{1}H NMR spectrum.

The reactions of 4-methylbenzothiazole with bis(bromomethyl)benzenes proceeded by the same way as in the case of 2-methylbenzothiazole, *i.e.* using 1,3-bis(bromomethyl)benzene, 4-methyl-3-(3-bromomethylbenzyl)benzothiazolium bromide (*XV*) was formed and with 1,4-bis(bromomethyl)benzene, 1,4--xylylenebis(4-methyl-3-benzothiazolium bromide) (*XVI*) was formed with an exception that red colour of the reaction medium did not appear.

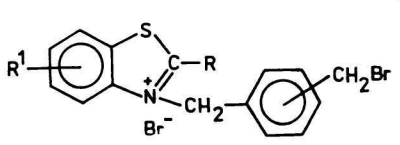
Steric factors were even more expressively demonstrated in the case of the reaction of 2-styrylbenzothiazole with bis(bromomethyl)benzenes where products only of the first stage resulted, *i.e.* 2-styryl-3-(2-, 3-, and 4-bromomethylbenzyl)benzothiazolium bromide (*XVII*, *XVIII*, resp. *XIX*). The reactions were performed in acetone where monosalts are little soluble. In the medium of DMF and DMSO, the salts have decomposed even at 50 °C. From acetonitrile or methanol even after addition of benzothiazole phase, monosalts were again isolated but more contaminated. All synthesized compounds are given in Table 1 and the course of discussed reactions is represented in Scheme 1.

3-Methyl-2-benzothiazolinethione afforded pure 1,2-, 1,3-, and 1,4--xylylenedithiobis(3-methyl-2-benzothiazolium bromides) (*XX*, *XXI*, resp. *XXII*) with all isomers of bis(bromomethyl)benzene (Table 2). In compounds *XX* and *XXI*, bromide anions were exchanged for perchlorate anions (*XXIII*, *XXIV*).

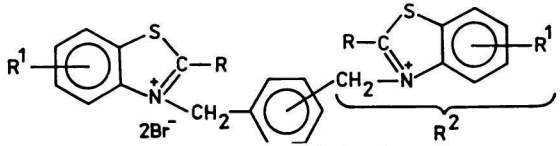
Interesting reactions were observed between 2-(methylthio)benzothiazole and individual isomers of bis(bromomethyl)benzene. In acetone or nitrometh-

Table 1

Characterization of the synthesized benzothiazolium salts



Series *A*

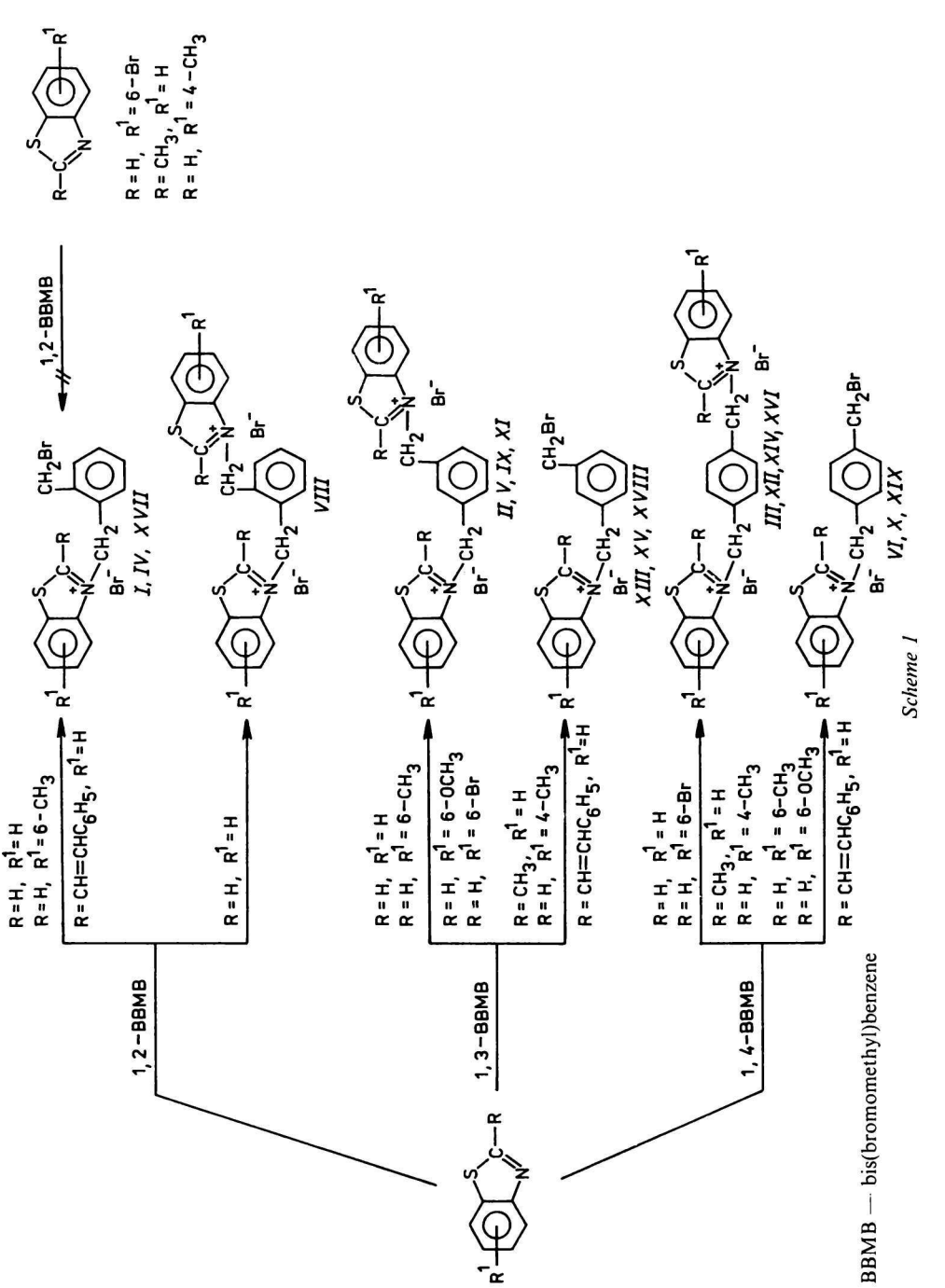


Series *B*

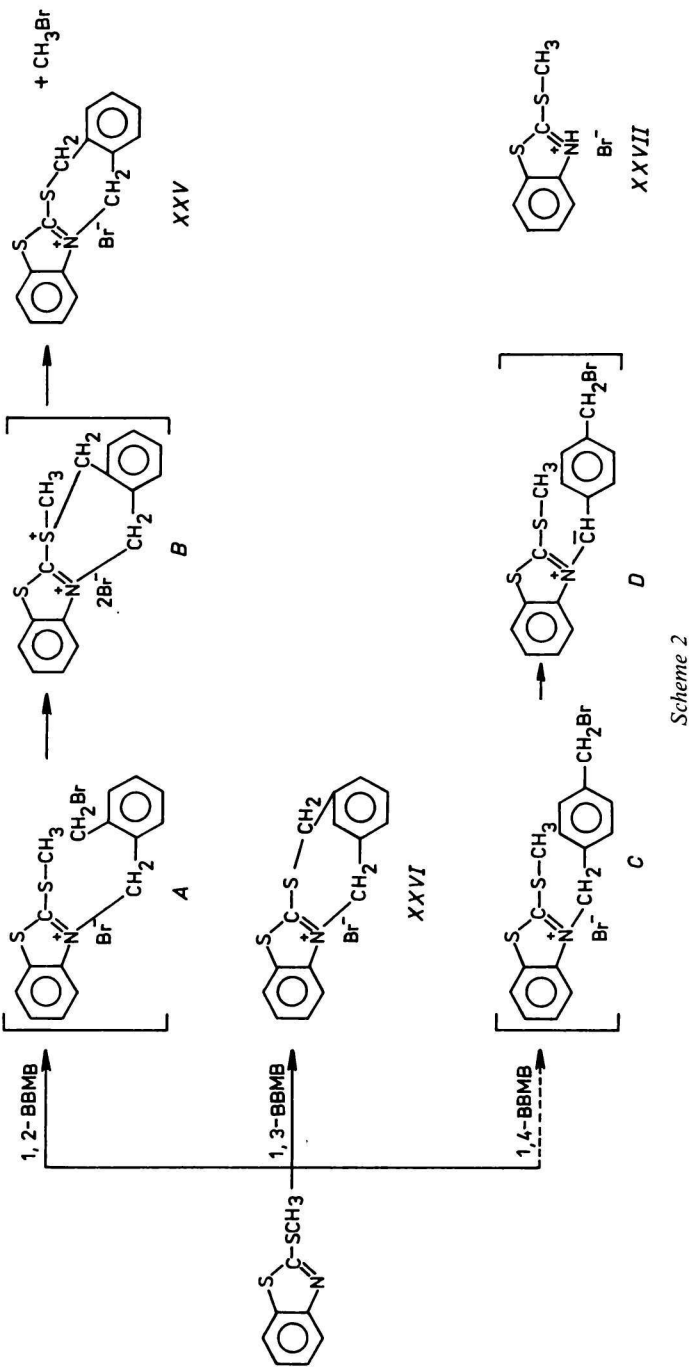
Compound	Series	R	R^1	Position $-CH_2Br$	Position R^2	Formula	M_r	w_i(calc.)/% w_i(found)/%				Yield	M.p.
								C	H	N	S	%	°C
I	*A*	H	H	2		$C_{15}H_{13}Br_2NS$	399.16	45.19	3.09	3.56	8.03	68	202—204
								45.52	3.20	3.78	8.34		
II	*B*	H	H		3	$C_{22}H_{18}Br_2N_2S_2$	534.34	49.45	3.39	5.24	12.00	69	204—206
								49.18	3.45	5.03	11.89		
III	*B*	H	H		4	$C_{22}H_{18}Br_2N_2S_2$	534.34	49.45	3.39	5.24	12.00	68	288—290
								49.12	3.41	4.96	11.95		
IV	*A*	H	6-CH_3	2		$C_{16}H_{15}Br_2NS$	413.19	46.51	3.66	3.39	7.76	83	248—250
								46.99	3.73	3.48	7.93		
V	*B*	H	6-CH_3		3	$C_{24}H_{22}Br_2N_2S_2$	562.40	51.24	3.90	4.97	11.40	83	246—248
								50.90	3.81	4.75	11.05		
VI	*A*	H	6-CH_3	4		$C_{16}H_{15}Br_2NS$	413.19	46.51	3.66	3.39	7.76	87	237—239
								46.58	3.65	3.40	7.81		
VII	*B*	H	6-CH_3		4	$C_{24}H_{22}Br_2N_2S_2$	562.40	51.24	3.90	4.97	11.40	45	237—240
								50.80	3.82	4.75	11.17		
VIII	*B*	H	6-OCH_3		2	$C_{24}H_{22}Br_2N_2O_2S_2$	594.40	48.50	3.73	4.71	10.79	71	233—235
								48.21	3.73	4.60	10.49		
IX	*B*	H	6-OCH_3		3	$C_{24}H_{22}Br_2N_2O_2S_2$	594.40	48.50	3.73	4.71	10.79	67	232—234
								48.23	3.65	4.59	10.70		
X	*A*	H	6-OCH_3	4		$C_{16}H_{15}Br_2NOS$	429.19	44.77	3.52	3.26	7.47	41	278—280
								45.10	3.39	3.45	7.62		

Table 1 (Continued)

Compound	Series	R	R^1	Position —CH_2Br	Position R^2	Formula	M_r	w_i(calc.)/% w_i(found)/%				Yield	M.p.
								C	H	N	S	%	°C
XI	*B*	H	6-Br		3	$C_{22}H_{16}Br_4N_2S_2$	692.14	38.18	2.33	4.05	9.26	31	195—196
								38.51	2.39	4.02	9.47		
XII	*B*	H	6-Br		4	$C_{22}H_{16}Br_4N_2S_2$	692.14	38.18	2.33	4.05	9.26	34	248—250
								38.00	2.52	3.98	9.04		
XIII	*A*	CH_3	H	3		$C_{16}H_{15}Br_2NS$	413.19	46.51	3.66	3.39	7.76	35	243—244
								46.44	3.65	3.38	7.82		
XIV	*B*	CH_3	H		4	$C_{24}H_{18}Br_2N_2S_2$	562.37	51.24	3.91	4.97	11.40	41	281—283
								50.88	3.83	4.75	11.14		
XV	*A*	H	4-CH_3	3		$C_{16}H_{15}Br_2NS$	413.19	46.51	3.66	3.39	7.76	23	171—173
								46.80	3.64	3.48	7.80		
XVI	*B*	H	4-CH_3		4	$C_{24}H_{18}Br_2N_2S_2$	562.37	51.24	3.91	4.97	11.40	35	223—225
								50.97	3.76	4.68	11.20		
XVII	*A*	CH=CHC_6H_5	H	2		$C_{23}H_{19}Br_2NS$	501.30	55.11	3.72	2.75	6.35	24	211—214
								55.49	3.91	2.90	6.55		
XVIII	*A*	CH=CHC_6H_5	H	3		$C_{23}H_{19}Br_2NS$	501.30	55.11	3.72	2.75	6.35	25	198—199
								54.92	3.76	2.78	6.16		
XIX	*A*	CH=CHC_6H_5	H	4		$C_{23}H_{19}Br_2NS$	501.30	55.11	3.72	2.75	6.35	28	220—221
								55.08	3.79	2.76	6.27		


1,2-BBMB
1,3-BBMB
1,4-BBMB
R = H, R¹ = H
R = H, R¹ = 6-CH₃
R = CH=CHC₆H₅, R¹ = H
R = H, R¹ = H
R = H, R¹ = 6-CH₃
R = H, R¹ = 6-OCH₃
R = H, R¹ = 6-Br
R = CH₃, R¹ = H
R = H, R¹ = 4-CH₃
R = CH=CHC₆H₅, R¹ = H
R = H, R¹ = H
R = H, R¹ = 6-Br
R = CH₃, R¹ = H
R = H, R¹ = 4-CH₃
R = H, R¹ = 6-CH₃
R = H, R¹ = 6-OCH₃
R = CH=CHC₆H₅, R¹ = H
R = H, R¹ = 6-Br
R = CH₃, R¹ = H
R = H, R¹ = 4-CH₃
I, IV, XVII
VIII
II, V, IX, XI
XIII, XV, XVIII
III, XII, XIV, XVI
VI, X, XIX
R = H, R¹ = 6-Br
R = CH₃, R¹ = H
R = H, R¹ = 4-CH₃
BBMB — bis(bromomethyl)benzene

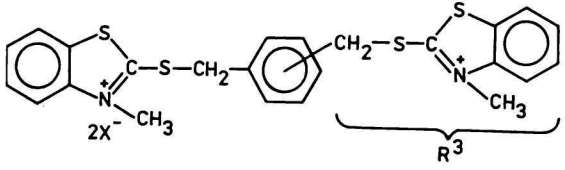
Scheme 1



Scheme 2

Table 2

Characterization of the synthesized benzothiazolium salts



Compound	Position R^3	$2X^-$	Formula	M_r	w_i(calc.)/% w_i(found)/%				Yield	M.p.
					C	H	N	S	%	°C
XX	2	Br	$C_{24}H_{22}Br_2N_2S_4$	626.50	46.13	3.54	4.47	20.47	58	113—115
					46.00	3.62	4.29	20.19		
XXI	3	Br	$C_{24}H_{22}Br_2N_2S_4$	626.50	46.13	3.54	4.47	20.47	63	150—152
					46.18	3.47	4.39	20.49		
XXII	4	Br	$C_{24}H_{22}Br_2N_2S_4$	626.50	46.13	3.54	4.47	20.47	70	135—136
					45.80	3.42	4.28	20.09		
XXIII	2	ClO_4	$C_{24}H_{22}Cl_2N_2O_8S_4$	665.61	43.31	3.33	4.21	19.27	82	288—290
					43.11	3.16	4.40	19.51		
XXIV	3	ClO_4	$C_{24}H_{22}Cl_2N_2O_8S_4$	665.61	43.31	3.33	4.21	19.27	77	222—225
					43.02	3.34	4.38	19.60		
XXV			$C_{15}H_{12}BrNS_2$	351.17	51.34	3.65	4.00	18.31	18	150—153
					50.89	3.46	4.05	18.62		
XXVI			$C_{15}H_{12}BrNS_2$	351.17	51.34	3.65	4.00	18.31	19	178—180
					51.70	3.46	4.34	18.54		
XXVII			$C_8H_8BrNS_2$	262.19	36.67	3.07	5.34	24.46	30	164—168
					36.41	3.21	5.11	24.09		

ane, a mixture of compounds with m.p. = 150—180 °C resulted whereas from acetonitrile, cyclic benzothiazolium salts were isolated. Their structure was proved spectroscopically. It can be assumed that 2-methylthio-3-(2--bromomethylbenzyl)benzothiazolium bromide (*A*) formed from 1,2-bis-(bromomethyl)benzene and analogically 2-methylthio-3-(3-bromomethylbenzyl)benzothiazolium bromide formed from 1,3-bis(bromomethyl)benzene, react through bromomethyl group with sulfur in methylthio group to form sulfonium cation of the type *B* (Scheme 2). Subsequent separation of methyl bromide results in the formation of tricyclic compounds *XXV* and *XXVI*.

Reaction of 2-(methylthio)benzothiazole with 1,4-bis(bromomethyl)benzene afforded 2-(methylthio)benzothiazolium bromide (*XXVII*). In its ^{1}H NMR spectrum, singlets of protons of —CH_3 group in the region of $\delta = 2.625$ ppm were observed. The signals of four aromatic protons of benzothiazole were observed in the region of $\delta = 7.1$—7.9 ppm. The signals of protons of $\overset{+}{N}$—CH_2— group were absent in the spectrum. Elemental analysis proved the isolated compound *XXVII*. We suppose that the reaction proceeds to the first stage but cyclization, with regard to the remote —CH_2Br group, does not proceed. Resulting 2-methylthio-3-(4-bromomethylbenzyl)benzothiazolium bromide (*C*) is unstable, proton is separated from the methylene group, and internal betaine (*D*) is formed which we were unsuccessful to isolate. The released HBr reacts with the starting 2-(methylthio)benzothiazole to give 2-(methylthio)benzothiazolium bromide (*XXVII*). The ^{1}H NMR spectra of the synthesized compounds are given in Table 3.

Experimental

Melting points were determined on Kofler hot-stage and analytical data of the synthesized compounds are given in Tables 1 and 2. The ^{1}H NMR spectra shown in Table 3 were measured on a Tesla 487 instrument operating at 80 MHz, in deuterotrifluoroacetic acid with hexamethyldisiloxane as internal standard. 2-Methylbenzothiazole was prepared from 2-aminothiophenol and acetic anhydride [3], 2-styrylbenzothiazole by the condensation of 2-methylbenzothiazole with benzaldehyde [4], 4- and 6-substituted benzothiazoles by deamination of corresponding 2-aminobenzothiazoles prepared from *o*- and *p*-substituted anilines *via* thioureas and by the cyclization using bromine [5], 3-methyl-2-benzothiazolinone by the thermal rearrangement of 2-(methylthio)benzothiazole [6].

3-(2-Bromomethylbenzyl)benzothiazolium bromide (I)

Benzothiazole (2.7 g; 0.02 mol) and 1,2-bis(bromomethyl)benzene (2.6 g; 0.01 mol) in dry acetone (20 cm^3) were heated under reflux for 6 h. After cooling, crystalline product was washed with dry acetone and crystallized from methanol.

Table 3

^{1}H NMR data of the synthesized benzothiazolium salts

Compound	δ/ppm			
	H_{arom}	$\overset{+}{N}—CH_2—$	$—CH_2—$	$—CH_3$
I	6.80—8.00 (m, 8H)	5.77 (s, 2H)	4.19 (s, 2H)	
II	6.75—8.00 (m, 12H)	5.74 (s, 4H)		
III	6.75—8.00 (m, 12H)	5.74 (s, 4H)		
IV	6.80—7.87 (m, 7H)	5.75 (s, 2H)	4.16 (s, 2H)	2.18 (s, 3H)
V	7.05—7.82 (m, 10H)	5.67 (s, 4H)		2.20 (s, 6H)
VI	6.92—7.92 (m, 7H)	5.60 (s, 2H)	4.03 (s, 2H)	2.20 (s, 3H)
VII	7.05—7.70 (m, 10H)	5.62 (s, 4H)		2.20 (s, 6H)
VIII	6.82—7.85 (m, 10H)	5.94 (s, 4H)		3.65 (s, 6H)
IX	6.92—7.73 (m, 10H)	5.68 (s, 4H)		3.57 (s, 6H)
X	7.17—7.77 (m, 7H)	5.55 (s, 2H)	4.02 (s, 2H)	3.55 (s, 3H)
XI	6.57—8.10 (m, 10H)	5.74 (s, 4H)		
XII	6.67—8.25 (m, 10H)	5.70 (s, 4H)		
XIII	6.57—7.50 (m, 12H)		5.10 (s, 4H)	
XIV	6.75—7.87 (m, 12H)	5.63 (s, 4H)		2.82 (s, 6H)
XV	6.73—7.77 (m, 7H)	5.87 (s, 2H)	4.03 (s, 2H)	2.51 (s, 3H)
XVI	6.83—7.80 (m, 10H)	5.96 (s, 4H)		2.49 (s, 6H)
XVII	6.68—7.82 (m, 15H)	5.72 (s, 2H)	4.04 (s, 2H)	
XVIII	6.55—7.92 (m, 15H)	5.69 (s, 2H)	4.01 (s, 2H)	
XIX	6.75—7.85 (m, 15H)	5.65 (s, 2H)	3.97 (s, 2H)	
XX	6.87—7.77 (m, 12H)		4.75 (s, 4H)	3.83 (s, 6H)
XXI	7.07—7.75 (m, 12H)		4.50 (s, 4H)	2.80 (s, 6H)
XXII	7.00—7.72 (m, 12H)		4.43 (s, 4H)	3.77 (s, 6H)
XXIII	6.90—7.75 (m, 12H)		4.73 (s, 4H)	3.82 (s, 6H)
XXIV	7.05—7.70 (m, 12H)		4.48 (s, 4H)	3.78 (s, 6H)
XXV	6.82—8.12 (m, 8H)	5.71 (s, 2H)	4.61 (s, 2H)	
XXVI	7.07—7.75 (m, 8H)	5.70 (s, 2H)	4.55 (s, 2H)	

Using the same procedure, 1,3- and 1,4-xylylenebis(3-benzothiazolium bromide) (*II*, resp. *III*) were prepared from 1,3- and 1,4-bis(bromomethyl)benzene, respectively.

1,3-Xylylenebis(6-methyl-3-benzothiazolium bromide) (V)

A mixture of 6-methylbenzothiazole (3.0 g; 0.02 mol) and 1,3-bis(bromomethyl)benzene (2.6 g; 0.01 mol) in DMF and acetone ($\varphi_r = 2:1$, 20 cm^3) was heated at 60—70 °C for 2 h. After cooling to room temperature, crystalline portion was washed with dry acetone, ether or THF.

The same procedure was used for preparation of 3-(2- and 4-bromomethylbenzyl)-6--methylbenzothiazolium bromide (*IV*, resp. *VI*) from 1,2- and 1,4-bis(bromomethyl)benzene, respectively.

1,4-Xylylenebis(6-methyl-3-benzothiazolium bromide) (VII)

6-Methylbenzothiazole (1.1 g; 7.5 mmol) in dry methanol (5 cm^3) was added to *VI* (2.06 g; 5 mmol) dissolved in hot dry methanol (50 cm^3). After 2 h, the reaction mixture was cooled and crystalline product was filtered off and washed with acetone.

1,2- and 1,3-xylylenebis(6-methoxy-3-benzothiazolium bromide) (VIII, resp. IX)

A mixture of 6-methoxybenzothiazole (3.3 g; 0.02 mol) and 1,2-, resp. 1,3-bis-(bromomethyl)benzene (2.6 g; 0.01 mol) in dry DMF and acetone ($\varphi_r = 1:1$, 20 cm^3) was heated at 60 °C for 3 h. After cooling and 2 h of standing at room temperature, crystalline product was filtered off, washed with acetone and crystallized from methanol.

Using the same conditions, 1,4-bis(bromomethyl)benzene afforded only 3-(4--bromomethylbenzyl)-6-methoxybenzothiazolium bromide (*X*).

1,3- and 1,4-xylylenebis(6-bromo-3-benzothiazolium bromide) (XI, resp. XII)

6-Bromobenzothiazole (2.1 g; 0.01 mol) and 1,3-, resp. 1,4-bis(bromomethyl)benzene (1.3 g; 5 mmol) in dry DMF and acetone ($\varphi_r = 1:1$, 20 cm^3) were heated under reflux for 12 h. After cooling, ether (2 cm^3) was added and crystalline portion was washed with acetone.

2-Methyl-3-(3-bromomethylbenzyl)benzothiazolium bromide (XIII)

A mixture of 2-methylbenzothiazole (3.0 g; 0.02 mol) and 1,3-bis(bromomethyl)benzene (2.6 g; 0.01 mol) in dry acetone (20 cm^3) was refluxed for 24 h. After 2 h of standing at room temperature, the product was filtered off and washed with dry acetone.

The same method was used for preparation of 2-styryl-3-(2-, 3-, and 4-bromomethylbenzyl)benzothiazolium bromide (*XVII*, *XVIII*, resp. *XIX*) from 2-styrylbenzothiazole and 1,2-, 1,3-, resp. 1,4-bis(bromomethyl)benzenes.

1,4-Xylylenebis(2- and 4-methyl-3-benzothiazolium bromide) (XIV, resp. XVI)

2-, resp. 4-methylbenzothiazole (3.0 g; 0.02 mol) and 1,4-bis(bromomethyl)benzene (2.6 g; 0.01 mol) in a mixture of DMF—acetone ($\varphi_r = 2:1$, 25 cm^3) were heated at 75—80 °C for 24 h. Reaction mixture stood at room temperature for additional 8 h.

Crystalline product of *XVI* was washed with dry acetone, *XIV* was recrystallized from a mixture of methanol and water ($\varphi_r = 1:1$).

Using the same method and 1,3-bis(bromomethyl)benzene as a starting material, 4-methyl-3-(3-bromomethylbenzyl)benzothiazolium bromide (*XV*) was prepared.

1,2-, 1,3-, and 1,4-xylylenedithiobis(3-methyl-2-benzothiazolium bromide) (XX, XXI, resp. XXII)

A mixture of 3-methyl-2-benzothiazolinethione (3.6 g; 0.02 mol) and 1,2-, 1,3-, resp. 1,4-bis(bromomethyl)benzene (2.6 g; 0.01 mol) in dry acetonitrile (20 cm^3) was left to stand at room temperature for 3 days. Then, it was heated at 50—60 °C for 2 h. After cooling, crystalline product was washed with dry acetone.

By the same procedure, 2-(methylthio)benzothiazolium bromide (*XXVII*) was prepared from 2-(methylthio)benzothiazole and 1,4-bis(bromomethyl)benzene.

1,2- and 1,3-xylylenedithiobis(3-methyl-2-benzothiazolium perchlorate) (XXIII, resp. XXIV)

XX, resp. *XXI* (3.3 g; 5 mmol) was dissolved in a mixture of methanol—water ($\varphi_r = 1:1$, 40 cm^3) preheated to 50—60 °C. To this solution, $KClO_4$ (2.7 g; 0.02 mol) in water (30 cm^3) preheated to 40—50 °C was gradually added under stirring. Crystalline product was washed with cold water and then with acetone.

Tricyclic compounds XXV and XXVI

A mixture of 2-(methylthio)benzothiazole (3.6 g; 0.02 mol) and 1,2-, resp. 1,3-bis(bromomethyl)benzene (2.6 g; 0.01 mol) in dry acetonitrile (20 cm^3) was heated under reflux for 24 h. After cooling, crystalline product was washed with dry acetone.

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