Benzothiazole compounds XXIV. Synthesis of 2-alkylthio-3-alkylbenzothiazolium salts and their growth-regulating activity

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When studying the effect of the medium on methylation of 2-alkylthiobenzothiazoles with methyl iodide it was found that the alkyl group was eliminated and 2-methylthio-3-methylbenzothiazolium iodide was formed. From 3-alkyl-2-benzothiazolinethiones 2-methylthio-3-alkylbenzothiazolium iodide or 2-methylthio-3-methylbenzothiazolium iodide was formed in dependence on the chosen medium. The structures of the synthesized 2-alkylthio-3-alkylbenzothiazolium salts were proved by their ^{1}H NMR spectra. The synthesized compounds showed growth-regulating activities.

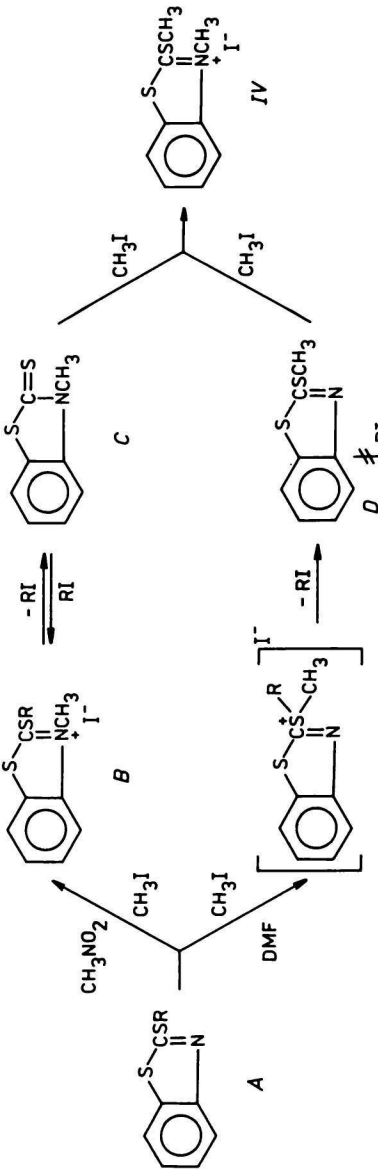
При изучении влияния среды на ход метилирования 2-алкилтиобензотиазолов метилиодидом было обнаружено, что алкильная группа отщепляется и образуется иодид 2-метилтио-3-метилбензотиазолия. Из 3-алкил-2-бензотиазолинтионов в зависимости от выбранной среды образуется иодид 2-метилтио-3-алкилбензотиазолия или иодид 2-метилтио-3-метилбензотиазолия. Строение синтезированных солей 2-алкилтио-3-алкилбензотиазолия было подтверждено измерением их ^{1}H ЯМР спектров. Синтезированные соединения по своей активности относятся к регуляторам роста растений.

In the previous work [1] we prepared 2-alkoxycarbonylmethylthio-3-alkylbenzothiazolium salts from 3-alkyl-2-benzothiazolinethiones by alkylation with esters of bromoacetic acid. Their stimulating and/or inhibiting effects on plant growth initiated the synthesis of 2-alkylthio-3-alkylbenzothiazolium salts. Of this type of compounds the authors in [2] prepared 2-methylthio-3-methylben-

zothiazolium iodide *IV*), 2-ethylthio-3-methylbenzothiazolium iodide, and 2-methylthio-3-ethylbenzothiazolium iodide by treatment of 2-ethylthiobenzothiazole with methyl iodide and studied the mechanism of their formation as well as their structures. It can be assumed that sulfur in the alkylthio group and nitrogen in the skeleton operate as nucleophilic centres and the formed intermediate sulfonium salt orders the alkyl groups to the position 2 and 3.

The aim of the present work was to study the effect of the medium on methylation of 2-alkylthiobenzothiazole and 3-alkyl-2-benzothiazolinone and on the basis of the obtained results suggest a reaction mechanism and compare it with those presented by other authors [3]. The further task was to prepare 2--methylthio-3-methylbenzothiazolium salts with various counterions and study the effect of the anion on biological activity as well as to prepare series of 2-methylthio-3-alkylbenzothiazolium and 2-alkylthio-3-methylbenzothiazolium salts and study the effect of the substituents in the positions 2 and 3 on biological activity.

2-Ethoxycarbonylmethylthiobenzothiazole was chosen as the starting substrate and treated with CH_3I in DMF, mixture of DMF and acetone (volume ratio = 2 : 1), acetone, THF, acetonitrile, dimethyl sulfoxide, and nitromethane under heating at 60—70 °C for 8 h. Based on the previous results it was assumed that 2-methylthio-3-methylbenzothiazolium iodide (*IV*) may be formed in two ways, depending on the chosen medium (Scheme 1). Analysis of the reaction mixture in DMF by gas chromatography and IR spectroscopy revealed the presence of 2-methylthiobenzothiazole (*D*) ($\tilde{\nu}(\delta_s(CH)) = 1422\ cm^{-1}$, $\tilde{\nu}(\delta_{as}(CH)) = 1455\ cm^{-1}$, skeletal vibrations at $\tilde{\nu} \sim 1000\ cm^{-1}$), traces of 3-methyl-2-benzothiazolinethione (*C*) [4], and 2-methylthio-3-methylbenzothiazolium iodide (*IV*) as the main product ($\tilde{\nu}(\delta_s(CH)) = 1455\ cm^{-1}$, $\tilde{\nu}(\delta_{as}(CH)) = 1375\ cm^{-1}$, $\tilde{\nu}(\nu(CH)) = 750\ cm^{-1}$). In addition, ethyl iodoacetate was proved by gas chromatography. We proved also trace amounts of another compound in the reaction mixture but have not identified it. The reaction mixture did not contain 2-methylthio-3-ethoxycarbonylmethylbenzothiazolium iodide (*E*). The reaction mixture in nitromethane was proved to contain 2-ethoxycarbonylmethylthio-3-methylbenzothiazolium iodide (*B*) ($\tilde{\nu}(\nu(C{=}O)) = 1720\ cm^{-1}$, $\tilde{\nu}(\delta_s(CH)) = 1395\ cm^{-1}$, $\tilde{\nu}(\delta_{as}(CH)) = 1440\ cm^{-1}$, $\tilde{\nu}(\delta(C{-}O)) = 1180\ cm^{-1}$, $\tilde{\nu}(\nu(CH)) = 760\ cm^{-1}$), compound *C*, and *IV*. The compound *D* was not present in this mixture, however, ethyl iodoacetate and traces of another compound were proved similarly as in the above-mentioned case. The compound *B* did not crystallize from the reaction mixture and addition of acetone and ether or petroleum ether brought about crystallization of the derivative *IV* (8—10 %) only. It means that nitromethane, due to its polarity, makes the compound *B* sufficiently soluble and thus enables the formation of the derivative *IV*. The compounds of the *B* type can be synthesized most advantageously from 3-substituted 2-benzothiazolinethiones [1]. The unreacted 2-ethoxycarbonyl-

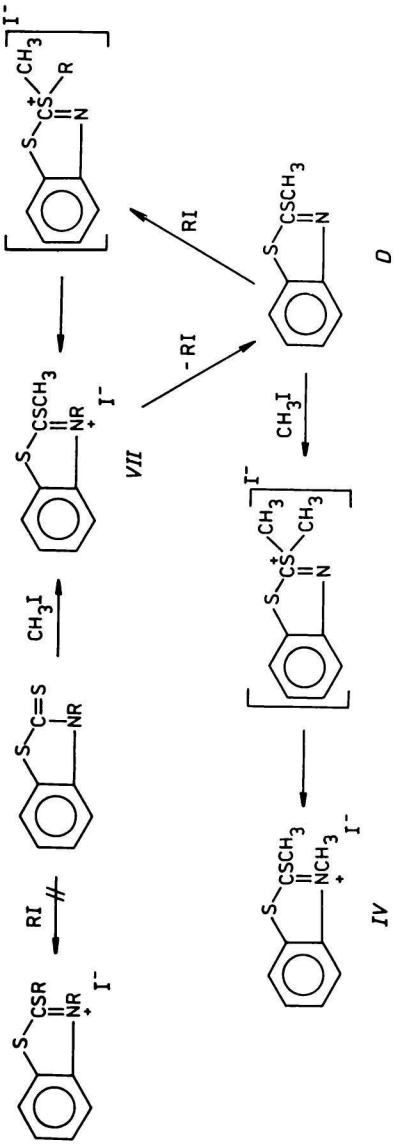

A
B
C
D
E
IV
CH3NO2
DMF
CH3I
CH3I
CH3I
CH3I
- RI
RI
- RI
RI
I⁻
R = CH2COOC2H5

Scheme 1

methylthiobenzothiazole (*A*) ($\tilde{\nu}(\nu(C{=}O)) = 1730\ cm^{-1}$, $\tilde{\nu}(\delta_s(CH)) = 1425\ cm^{-1}$, $\tilde{\nu}(\delta_{as}(CH)) = 1460\ cm^{-1}$, $\tilde{\nu}(\delta(C{-}O)) = 1295\ cm^{-1}$) was proved in both reaction media. Also other experiments were performed in DMF with CH_3I where the substrate was 2-allylthio-, 2-benzylthio- or 2-allyloxycarbonylmethylthiobenzothiazole. As the main product compound *IV* was isolated in all cases.

Morgan [3] excluded the possibility of formation of the intermediate sulfonium salt. He performed syntheses without solvents at 100 °C and assumed that from 2-alkylthiobenzotiazole a quaternary salt was formed first. This decomposed at the given temperature to thermodynamically more stable *N*-alkyl-2-benzothiazolinethione which reacted with methyl iodide. Our results obtained in DMF entitle us to presume the formation of the sulfonium salt since in the reaction mixture of 2-ethoxycarbonylmethylthiobenzothiazole and CH_3I besides *IV* also 2-methylthiobenzothiazole (*D*) (Scheme 1) was identified. In CH_3NO_2 this compound was not proved. By treating 3-ethoxycarbonylmethyl-2-benzothiazolinethione without solvent or in CH_3NO_2 with CH_3I, 2-methylthio-3-ethoxycarbonylmethylbenzothiazolium iodide (*VII*) was obtained as the main product. When the reaction was carried out in DMF the compound *IV* was isolated. The course of this reaction is illustrated in Scheme 2. The assumption of formation of *D* and the sulfonium salt is confirmed by the course of further reactions. Treating 2-dodecylthiobenzothiazole without solvent, in CH_3NO_2 or DMF with dimethyl sulfate resulted in 2-methylthio-3-methylbenzothiazolium iodide (*IV*). However, treating of 3-dodecyl-2-benzothiazolinethione without solvent or in nitromethane with dimethyl sulfate afforded 2-methylthio-3-dodecylbenzothiazolium sulfate (*IX*), while in DMF 2-methylthio-3-methylbenzothiazolium sulfate (*II*) was formed again. We assume that DMF as an aprotic polar solvent enables the formation of an unstable associate, sulfonium salt, and thus the replacement of the weaker electrophile by the stronger methyl iodide. Treatment of 3-allyl-2-benzothiazolinethione with methyl iodide in nitromethane at 60—70 °C resulted in *VI*, treatment of 3-methyl-2-benzothiazolinethione with allyl bromide in *XII* and with propargyl bromide in *XIII*, and treatment of 3-ethyl-2-benzothiazolinethione in *XIV*. The compound *XIII* was prepared also by 48 h standing without solvent. The synthesized compounds are presented in Table 1.

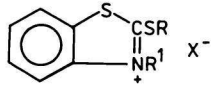
The structures of the synthesized compounds were proved by evaluation of their ^1H NMR spectra where multiplets of aromatic hydrogens of the benzothiazole heterocycle were observed in the region of $\delta = 7.9$—7.2 ppm. The spectra of the compounds with the methyl group bound on nitrogen atom revealed significant singlets at $\delta = 3.8$ ppm. The spectra of the compounds with other alkyls on the heterocyclic nitrogen showed the corresponding signals presented in Table 2. Singlets assigned to hydrogens of the SCH_3 groups were observed at $\delta = 2.7$ ppm.



Scheme 2

Table 1

Characterization of the synthesized benzothiazolium salts



Compound	R	R^1	X^-	Formula	M_r	w_i(calc.)/% / w_i(found)/%				Yield	M.p.
						C	H	N	S	%	°C
I	CH_3	H	HSO_4	$C_8H_9NO_4S_3$	279.35	33.31	3.24	5.01	34.41	73	198—201
						33.69	3.13	5.01	34.60		
II	CH_3	CH_3	CH_3SO_4	$C_{10}H_{13}NO_4S_3$	307.41	39.07	4.26	4.55	31.29	70	214—216
						39.01	4.27	4.63	31.09		
III	CH_3	CH_3	ClO_4	$C_9H_{10}ClNO_4S_2$	295.76	36.55	3.40	4.73	21.68	89	178—183
						36.42	3.46	4.81	21.49		
IV	CH_3	CH_3	I	$C_9H_{10}INS_2$	323.22	33.44	3.11	4.33	19.84	76	129—132
						33.29	3.07	4.25	20.00		
V	CH_3	$CH_2CH=CH_2$	CH_3SO_4	$C_{12}H_{15}NO_4S_3$	333.44	43.23	4.54	4.20	28.84	71	150—153
						42.98	4.52	4.37	29.08		
VI	CH_3	$CH_2CH=CH_2$	I	$C_{11}H_{12}INS_2$	349.25	37.83	3.46	4.01	18.37	88	102—104
						37.87	3.39	4.04	18.45		
VII	CH_3	$CH_2COOC_2H_5$	I	$C_{12}H_{14}INO_2S_2$	395.28	36.46	3.56	3.56	16.22	42	102—106
						36.23	3.37	3.47	16.18		
VIII	CH_3	$CH_2C_6H_5$	CH_3SO_4	$C_{16}H_{17}NO_4S_3$	383.50	50.11	4.46	3.65	25.08	68	193—196
						49.87	4.30	3.48	25.21		
IX	CH_3	$(CH_2)_{11}CH_3$	CH_3SO_4	$C_{21}H_{35}NO_4S_3$	461.70	54.63	7.63	3.03	20.82	68	107—111
						54.42	7.86	3.02	20.94		
X	C_2H_5	CH_3	CH_3SO_4	$C_{11}H_{15}NO_4S_3$	321.43	41.10	4.70	4.35	29.92	74	135—137
						41.11	4.67	4.40	29.53		

Table 1 (Continued)

Compound	R	R^1	X^-	Formula	M_r	w_i(calc.)/% w_i(found)/%				Yield	M.p.
						C	H	N	S	%	°C
XI	$CH_2CH=CH_2$	H	HSO_4	$C_{10}H_{11}NO_4S_3$	305.39	39.32 39.36	3.62 3.61	4.58 4.59	31.49 31.17	70	153—154
XII	$CH_2CH=CH_2$	CH_3	Br	$C_{11}H_{12}BrNS_2$	302.25	43.71 43.48	4.00 4.33	4.63 4.34	21.21 21.18	86	107—110
XIII	$CH_2C\equiv CH$	CH_3	Br	$C_{11}H_{10}BrNS_2$	300.24	44.01 44.00	3.35 3.26	4.66 4.66	21.36 21.30	65	133—127
XIV	$CH_2C\equiv CH$	C_2H_5	Br	$C_{12}H_{12}BrNS_2$	314.27	45.86 45.80	3.84 3.71	4.45 4.36	20.40 20.21	56	125—130
XV	$CH_2CH(CH_3)_2$	CH_3	CH_3SO_4	$C_{13}H_{19}NO_4S_3$	349.49	44.74 44.35	5.48 5.52	4.01 4.11	27.53 27.59	47	150—153

Table 2

Numerical values of ^{1}H NMR chemical shifts δ/ppm of the synthesized 2-alkylthio-3-alkylbenzothiazolium salts

Compound	
I	7.8—7.2 (ar, 4H, m); 2.66 (S—CH_3, 3H, s)
II	7.8—7.2 (ar, 4H, m); 3.78 ($\overset{+}{N}$—CH_3, 3H, s); 3.50 ($CH_3SO_4^-$, 3H, s); 2.70 (S—CH_3, 3H, s)
III	7.8—7.2 (ar, 4H, m); 3.75 ($\overset{+}{N}$—CH_3, 3H, s); 2.67 (S—CH_3, 3H, s)
IV	7.9—7.2 (ar, 4H, m); 3.78 ($\overset{+}{N}$—CH_3, 3H, s); 2.70 (S—CH_3, 3H, s)
V	7.8—7.2 (ar, 4H, m); 5.5 (=CH, 1H, m); 5.0 (=CH_2, 2H, m); 4.86 ($\overset{+}{N}$—CH_2, 2H, d); 2.71 (S—CH_3, 3H, s)
VI	7.9—7.2 (ar, 4H, m); 5.6 (=CH, 1H, m); 5.1 (=CH_2, 2H, m); 4.88 ($\overset{+}{N}$—CH_2, 2H, d); 2.73 (S—CH_3, 3H, s)
VII	7.9—7.2 (ar, 4H, m); 5.16 ($\overset{+}{N}$—CH_2, 2H, s); 4.00 (O—CH_2, 2H, q, J = 7.4 Hz); 2.75 (S—CH_3, 3H, s); 0.91 (C—CH_3, 3H, t)
VIII	7.9—7.2 (ar, 4H, m); 6.7—6.1 (Ph, 5H, m); 5.43 ($\overset{+}{N}$—CH_2, 2H, s); 3.46 ($CH_3SO_4^-$, 3H, s); 2.69 (S—CH_3, 3H, s)
IX	7.9—7.2 (ar, 4H, m); 4.23 ($\overset{+}{N}$—CH_2, 2H, t); 3.49 ($CH_3SO_4^-$, 3H, s); 2.68 (S—CH_3, 3H, s); 1.8—0.6 ($C_{11}H_{23}$, 23H, m)
X	7.8—7.2 (ar, 4H, m); 3.79 ($\overset{+}{N}$—CH_3, 3H, s); 3.48 ($CH_3SO_4^-$, 3H, s); 3.20 (S—CH_2, 2H, q); 1.28 (C—CH_3, 3H, t)
XI	7.8—7.2 (ar, 4H, m); 5.9—5.0 (—CH=CH_2, 3H, m); 3.75 (S—CH_2, 2H, d)
XII	7.8—7.2 (ar, 4H, m); 5.8—5.0 (—CH=CH_2, 3H, m); 3.80 (S—CH_2, 2H, d); 3.78 ($\overset{+}{N}$—CH_3, 3H, s)
XIII	7.9—7.2 (ar, 4H, m); 3.95 (S—CH_2, 2H, d); 3.82 ($\overset{+}{N}$—CH_3, 3H, s); 2.17 (=CH, 1H, t)
XIV	7.9—7.2 (ar, 4H, m); 4.34 ($\overset{+}{N}$—CH_2, 2H, q); 4.00 (S—CH_2, 2H, d); 2.19 (=CH, 1H, t); 1.23 (C—CH_3, 3H, t)
XV	7.8—7.2 (ar, 4H, m); 3.78 ($\overset{+}{N}$—CH_3, 3H, s); 3.03 (S—CH_2, 2H, d); 1.90 (CH, 1H, n); 0.80 (CH_3, 6H, d)

s — singlet, d — doublet, t — triplet, q — quartet, m — multiplet, n — nonet.

The spectra proved the structures of the synthesized 2-alkylthio-3-alkylbenzothiazolium salts unambiguously.

Growth-regulating activity was tested on *Vicia sativa* according to the method in [5]. The synthesized compounds having retained the CH_3 group in the position 3 or the SCH_3 group in the psition 2 enabled to study the influence of the anion on biological activity (Table 3). The anion in most of the compounds synthesized previously was bromine [1]. The finding that biological activity was influenced most intensively by the methyl group was confirmed also in this case. The compounds *IV*, *X*, and *XIII* showed stimulating activity comparable to that of β-indolylacetic acid (IAA) or 2,4-dichlorophenoxyacetic acid (2,4-D). The inhibiting activity with *I*, *V*, *IX*, *XIV*, and *XV* was better than that with 2-chloroethyltrimethylammonium chloride (CCC). It means that 8 out of the 15 compounds prepared in the present study showed good growth-regulating activity. The influence of the anion on biological activity is also interesting. We tested a compound with perchlorate anion the first time. The anion brought about a change from stimulating to inhibiting activity (comparison of the compounds *IV* and *III*). This relationship will be studied with further compounds. The methylsulfate anion reduced the stimulating

Table 3

Growth-regulating activity of benzothiazolium salts on *Vicia sativa*

Compound	Stimulation		Inhibition	
	Δl/mm	c/(mol dm^{-3})	$-\Delta l$/mm	c/(mol dm^{-3})
I			3.55	10^{-13}
II	3.85	10^{-7}		
III			22.40	10^{-3}
IV	4.40	10^{-11}		
V	3.60	10^{-7}	6.20	10^{-11}
VI			19.75	10^{-3}
VII			20.55	10^{-3}
VIII			14.40	10^{-3}
IX			3.15	10^{-13}
X	5.85	10^{-11}		
XI	3.35	10^{-7}		
XII	1.90	10^{-9}		
XIII	4.25	10^{-11}		
XIV			3.45	10^{-13}
XV			4.30	10^{-13}
IAA	3.10	10^{-12}	18.55	10^{-6}
2,4-D	4.95	10^{-9}	23.30	10^{-5}
CCC			3.85	10^{-3}

activity of the compound *II* when compared to that of *IV*. Replacement of methyl group in the position 2 with ethyl group in the compound *X* resulted in high stimulating activity. Further replacement with isobutyl group, when retaining the same anion, brought about a change to inhibiting activity. Replacement of methyl group in the position 3 by allyl, ethoxycarbonylmethyl, benzyl, and dodecyl groups in the compounds *V*—*IX* resulted in inhibiting activity. The results obtained necessitate further studies of the compounds synthesized so far, mainly their stability in aqueous medium where the respective 3-alkyl-2-benzothiazolinones may be formed at different rates and which may secondarily act as growth regulators, too.

Experimental

3-Alkyl-2-benzothiazolinethiones were synthesized from 2-alkylthiobenzothiazoles [4]. Melting points were determined on a Kofler block. Analytical data of the synthesized compounds are presented in Table 1. ^{1}H NMR spectra, presented in Table 2, were measured on a Tesla 487 apparatus at 80 MHz in deuterated trifluoroacetic acid using hexamethyldisiloxane as internal standard. IR spectra were measured with a Perkin—Elmer 180 spectrophotometer in nujol suspension. Gas chromatographic measurements were performed with a Chrom 4 apparatus using a column (150 cm × 0.3 cm) of 3 % Carbowax 20 M + 4 % KOH on Chromosorb W, nitrogen as carrier gas; inlet pressure 0.04 MPa, column temperature 150—200 °C. Growth stimulation of roots was determined according to [5].

2-Methylthiobenzothiazolium hydrogen sulfate (I)

2-Methylthiobenzothiazole (3.6 g; 0.02 mol) was dissolved in dry THF (15 cm^3) and H_2SO_4 (2.4 g; 0.025 mol) was added dropwise with stirring at room temperature. The reaction mixture was stirred for 1 h and the precipitate was filtered off and crystallized from ethanol.

2-Allylthiobenzothiazolium hydrogen sulfate (*IX*) was prepared in the same way.

2-Methylthio-3-methylbenzothiazolium methyl sulfate (II)

a) 2-Methylthiobenzothiazole (3.6 g; 0.02 mol) or 3-methyl-2-benzothiazolinethione was dissolved in dry acetone (10 cm^3) and dimethyl sulfate (3.1 g; 0.025 mol) was added. The reaction mixture was allowed to stand at occasional stirring for 2 h. The crystalline portion after washing with acetone recrystallized at 135—145 °C and melted at 214—216 °C. Yield = 70 %.

b) 2-Dodecylthiobenzothiazole (3.3 g; 0.01 mol) and dimethyl sulfate (1.9 g; 0.015 mol) were heated at 100—110 °C for 15 min. After cooling acetone or THF was added and the crystalline portion was washed with acetone to give a 59 % yield.

2-Methylthio-3-methylbenzothiazolium perchlorate (III)

To 2-methylthio-3-methylbenzothiazolium iodide (6.4 g; 0.02 mol) dissolved in water (50 cm^3) $NaClO_4$ (3.05 g; 0.025 mol) in water (20 cm^3) was added. The precipitate was washed with water.

2-Methylthio-3-methylbenzothiazolium iodide (IV)

a) To 3-methyl-2-benzothiazolinethione (3.6 g; 0.02 mol) or 2-methylthiobenzothiazole dissolved in nitromethane (10 cm^3) methyl iodide (3.5 g; 0.025 mol) was added. The reaction mixture was allowed to stand for 48 h. The crystalline portion was washed with dry acetone to give a 76 % yield.

b) To 3-methyl-2-benzothiazolinethione (3.6 g; 0.02 mol) or 2-methylthiobenzothiazole methyl iodide (9.9 g; 0.07 mol) was added and the mixture was heated on a water bath at 50—60 °C for 2 h. After dissolution of the starting compound the reaction mixture became solid. After addition of dry acetone, benzene, THF or ether and stirring, the crystalline portion was filtered off to give a 67—70 % yield.

c) 2-Allyloxycarbonylmethylthiobenzothiazole (2.6 g; 0.01 mol), 2-allylthiobenzothiazole (2.0 g; 0.01 mol), 2-ethyloxycarbonylmethylthiobenzothiazole (2.5 g; 0.01 mol) or 2-benzylthiobenzothiazole (2.2 g; 0.01 mol), DMF (7 cm^3), mixture of DMF and acetone (2 : 1; 10 cm^3), acetone, THF, acetonitrile, nitromethane or dimethyl sulfoxide, and methyl iodide (2.1 g; 0.015 mol) were heated at 60—70 °C for 8 h. Yield = 60—65 %. In nitromethane without heating 8—10 % *IV* was isolated.

d) To 3-ethoxycarbonylmethyl-2-benzothiazolinethione (2.5 g; 0.01 mol) dissolved in the mixture of DMF and acetone (volume ratio = 2 : 1; 10 cm^3) methyl iodide (2.1 g; 0.015 mol) was added and the mixture was heated at boiling for 10 h. After 48 h standing the crystalline portion was washed with dry acetone. Yield = 53 %.

2-Methylthio-3-allylbenzothiazolium methyl sulfate (V)

3-Allyl-2-benzothiazolinethione (2 g; 0.01 mol) and dimethyl sulfate (1.9 g; 0.015 mol) were heated on a boiling water bath for 10 min. The viscous oil became solid and after cooling it was crystallized from the mixture of ethanol and acetone (volume ratio = 3 : 1). The compounds *VIII*—*X* and *XV* were prepared similarly.

2-Methylthio-3-allylbenzothiazolium iodide (VI)

3-Allyl-2-benzothiazolinethione (2 g; 0.01 mol), nitromethane (8 cm^3), and methyl iodide (2.1 g; 0.015 mol) were heated at 60—75 °C for 8 h. The reaction mixture was

allowed to stand for 24 h. The crystalline compound was washed with dry acetone. The compounds *XII—XIV* were prepared by the same method. The compound *XIII* was prepared also by 48 h standing of the starting components without solvent at room temperature. It was boiled in acetone prior to isolation.

2-Methylthio-3-ethoxycarbonylmethylbenzothiazolium iodide (VII)

3-Ethoxycarbonylmethyl-2-benzothiazolinethione (2.5 g; 0.01 mol) and methyl iodide (2.1 g; 0.015 mol) were heated at 100—110 °C for 4 h. The formed solution on cooling became solid. After addition of acetone and stirring the compound was filtered off.

3-Ethoxycarbonylmethyl-2-benzothiazolinethione

The mixture of 2-methylthiobenzothiazole (30 g; 0.1 mol) and ethyl bromoacetate (41.7 g; 0.25 mol) was heated with stirring at 140—160 °C for 2 h. After cooling benzene and charcoal were added, the solution was filtered and then petroleum ether was added until the solution turned turbid. The compound isolated after cooling had m.p. = 115—120 °C. Yield = 68 %. For $C_{11}H_{11}NO_2S_2$ ($M_r = 253.34$) w_i(calculated): 25.34 % S, 5.53 % N; w_i(found): 25.08 % S, 5.62 % N.

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