2,2,5,5-Tetrathiofulvalene (TTF). A 1-g sample of CaO and 0.3 g of acid II were ground in a mortar, and the mixture was heated in vacuo (1 mm) at 300°. The sublimed tetrathiofulvalene was collected to give the product in 15% yield. Yellow crystals with mp 100-102° (mp 98-102° [7]) were obtained after chromatography on silica gel (elution with benzene) and slow evaporation of the solvent in an inert atmosphere.

7,7,8,8-Tetracyanoquinonedimethane – 2,2,5,5-Tetrathiofulvalene (TCQD – TTF) Complex. The TTF was vacuum sublimed twice prior to the synthesis of this complex. The TCQD was crystallized twice from acetonitrile and vacuum sublimed twice to give a product with mp 298-299.5°. Solutions of 1 g of TTF in 60 ml of hot benzene and 1 g of TCQD in 100 ml of hot acetonitrile were poured together, and the resulting mixture was allowed to cool for 4 h in a nitrogen atmosphere. The resulting precipitate was removed by filtration to give 1.6 g (80%) of the complex. A 1 : 1 complex was formed at all reagent ratios. Found: C 52.8; H 2.0%. $C_{12}H_4N_4 \cdot C_6H_4S_4$. Calculated: C 52.9; H 2.0%. Single crystals of the complex were grown by slow cooling of a solution of the complex in acetonitrile in an inert atmosphere.

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SYNTHESIS AND STRUCTURES OF 1-METHYL-2,1,3-BENZOTHIA(SELENA)DIAZOLIUM SALTS

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Mixtures of quaternary salts with isomeric structures, the ratio between which depends on the nature of the substituent, are obtained by dimethyl sulfate alkylation of derivatives of 2,1,3-benzothia(selena) diazoles containing a substituent in the benzene ring. Individual 1-methyl-2,1,3-benzothia(selena)diazolium salts are obtained in good yields by treatment of 4(5)-substituted N-methyl-o-phenylenediamine dihydrochlorides with thionyl chloride or selenious acid.

It is known [1] that benzothia(selena)diazolium salts are formed when 2,1,3-benzothia(selena)diazole is heated with dimethyl sulfate. The alkylation of 5(6)-substituted benzothia(selena)diazole has not yet been investigated. The introduction of a substituent in the condensed benzene ring of these heterocycles renders the nitrogen atom in them nonequivalent, and one might therefore have assumed that the alkylation of such substituted compounds could proceed in two directions to give isomers II and III.

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TABLE 1. 1-Methyl-2,1,3-benzothia(selena)diazolium Salts (II, III)

Compound*	Chemical shifts of the N-methyl protons, Hz	mp, °C (dec.)	Empirical formula	Found, %		Calc., %		Yield, %
				N	Hal	N	Hal	
IIIa	328,4	158—159	$C_7H_6Cl_2N_2S$	12,5	32,4	12,7	32,1	83
IIIe	326,3	185—187	$C_7H_6Cl_2N_2Se$	10,6	26,6	10,4	26,5	68
IIa	333,4	188—189	$C_7H_6Cl_2N_2S$	12,8	29,9	12,7	32,1	77
IIe	335,2	200—202	$C_7H_6Cl_2N_2Se$	10,3	26,7	10,4	26,5	85
IIIb	327,8	143—145	$C_7H_6BrClN_2S$	10,7	43,6	10,6	43,4	74
IIIf	326,0	182—183	$C_7H_6BrClN_2Se$	8,7	36,8	9,0	36,9	79
IIb	333,7	185—186	$C_7H_6BrClN_2S$	10,7	43,3	10,6	43,4	72
IIf	334,8	196—197	$C_7H_6BrClN_2Se$	8,7	37,2	9,0	36,9	87
IIIc	325,0	179—181	$C_8H_9ClN_2S$	14,1	17,9	14,0	17,7	91
IIIg	325,9	199—200	$C_8H_9ClN_2Se$	11,6	14,2	11,3	14,3	69
IIc	332,1	180—181	$C_8H_9ClN_2S$	13,8	17,6	14,0	17,7	73
IIg	331,5	206—208	$C_8H_9ClN_2Se$	11,1	14,1	11,3	14,3	64
IIId	311,0	149—150	$C_8H_9ClN_2OS$	12,7	16,6	12,9	16,4	73
IIIh	312,7	180—181	$C_8H_9ClN_2OSe$	10,4	13,3	10,6	13,4	79
IId	327,0	163—164	$C_8H_9ClN_2OS$	13,2	16,5	12,9	16,4	96
IIh	327,9	195—196	$C_8H_9ClN_2OSe$	10,6	13,6	10,6	13,4	89

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*$y^- = Cl^-$.

TABLE 2. Characteristics of Mixtures of Isomers Isolated in the Alkylation of Substituted 2,1,3-Benzothia(selena)diazoles

Mixture of isomers*	Isomer ratio, %	Empirical formula	Found, %		Calc., %		Yield of the mixture, %
			N	Hal	N	Hal	
IIa+IIIa	48 : 52	$C_8H_9ClN_2O_4S_2$	9,5	11,9	9,4	11,9	83
IIb+IIIb	43 : 57	$C_8H_9BrN_2O_4S_2$	8,1	23,5	8,2	23,4	87
IIc+IIIc	45 : 55	$C_9H_{12}N_2O_4S_2$	10,2	—	10,1	—	76
IId+IIId	33 : 67	$C_9H_{12}N_2O_5S_2$	9,5	—	9,6	—	84
IIe+IIIe	45 : 55	$C_8H_9ClN_2O_4SSe$	8,0	10,2	8,2	10,3	89
IIf+IIIf	45 : 55	$C_8H_9BrN_2O_4SSe$	7,1	20,4	7,2	20,6	88
IIg +IIIg	45 : 55	$C_9H_{12}N_2O_4SSe$	8,5	—	8,7	—	79
IIh+IIIh	32 : 68	$C_9H_{12}N_2O_5SSe$	8,2	—	8,3	—	92

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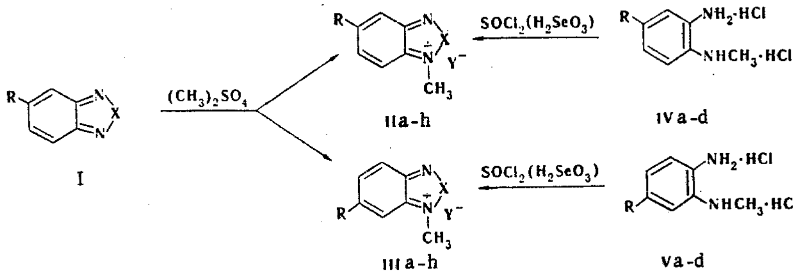
*$y^- = CH_3SO_4^-$.

The alkylation of 5(6)-substituted 2,1,3-benzothiadiazoles was accomplished by the method described for the unsubstituted compounds [1]. In the case of the selenium derivatives, carrying out the reaction in toluene makes it possible to obtain the desired salts in purer form and in better yields. The PMR spectra of the alkylation products contain two signals of protons of N-methyl groups, in contrast to the benzene ring-unsubstituted quaternary salts. When the substituents are CH_3 and CH_3O groups one also observes splitting of the signals of the protons of these substituents. This confirms our assumption of the formation of a mixture of two isomers in the alkylation of I.

The previously undescribed individual isomeric 2,1,3-benzothiadiazolium salts (II, IIIa-d) were obtained by refluxing the corresponding N-methyl-o-phenylenediamine dihydrochlorides (IV, V) with a small excess of thionyl chloride in dry benzene. Their selenium analogs (II, IIIe-h) are formed smoothly by treatment of salts IV and V with selenious acid in glacial acetic acid (Table 1).



I—III a R=Cl, X=S; b R=Br, X=S; c R=CH_3, X=S; d R=CH_3O, X=S; e R=Cl, X=Se; f R=Br, X=Se; g R=CH_3, X=Se; h R=CH_3O, X=Se; IV, V a R=Cl; b R=Br; c R=CH_3; d R=CH_3O

Multiplets of aromatic protons of the ABC type and singlets of protons of N-methyl groups are observed in the PMR spectra of the 1-methyl-2,1,3-benzothia(selena)diazolium salts, and this unambiguously confirms the structure of these compounds.

Inasmuch as the chemical shifts of the signals of the protons of the N-methyl groups in isomers IIa-h and IIIa-h are close to one another, the assignment of their signals in mixtures obtained by alkylation was made by comparison of the intensities of the corresponding signals after the addition to the mixture of an isomer with a known structure. On the basis of this comparison we concluded that the signals of the protons of the N-methyl groups of the 6-substituted isomers are found at stronger field than the signals of the protons of the N-methyl groups of the 5-substituted isomers. The chemical shifts of the protons of the N-methyl groups are given in Table 1. Data on the ratios of the isomers obtained by alkylation are presented in Table 2. In all cases the 6-substituted isomers (III) are formed in greater amounts than the 5-substituted isomers (II), and this is evidently explained by the electron-donor effect of the substituents. In conformity with this, the compounds with a methoxy group, which is the strongest electron donor of the substituents studied, give the greatest amount of the 6-substituted isomer. Replacement of the sulfur by selenium in the starting diazoles has practically no effect on the ratio of the isomers obtained.

EXPERIMENTAL

The PMR spectra of trifluoroacetic acid solutions of the compounds were recorded with a Varian HA-100 spectrometer with cyclohexane as the internal standard.

The starting benzothia(selena)diazoles were obtained by known methods [1-4]. The starting N-methyl-o-phenylenediamines were obtained by the methods in [5-7].

Substituted 1-Methyl-2,1,3-benzothiadiazolium Chlorides (IIa-d and IIIa-d, Table 1). A 1.2-ml sample of thionyl chloride was added to 3.1 mmole of the dihydrochloride of the appropriate N-methyl-o-phenylenediamine in 10 ml of dry benzene, after which the mixture was refluxed for 2 h. The resulting precipitate was removed by filtration, dried, and recrystallized from methanol.

Substituted 1-Methyl-2,1,3-benzoselenadiazolium Chlorides (IIe-h and IIIe-h, Table 1). A 0.5-g sample of selenious acid was added to a solution of 2.8 mmole of the dihydrochloride of the appropriate N-methyl-o-phenylenediamine in 15 ml of glacial acetic acid, and the resulting precipitate was removed by filtration, dried, and recrystallized from methanol.

Alkylation of Substituted 2,1,3-Benzothiadiazoles. A mixture of 8.6 mmole of substituted 2,1,3-benzothiadiazoles (Ia-d) and 1 ml of dimethyl sulfate was heated on a glycerol bath at 90-100° for 4-6 h, after which the melt was triturated, washed with toluene and ether, and vacuum dried. The yield and results of elementary analysis of the mixture of isomers, as well as the isomer ratio from the PMR spectral data, are presented in Table 2.

Alkylation of Substituted 2,1,3-Benzoselenathiazoles. A mixture of 9.4 mmole of the appropriate 2,1,3-benzoselenathiazole (Ie-h), 3 ml of toluene, and 1.5 ml of dimethyl sulfate was heated at 80-90° for 2-4 h, and the resulting crystals were removed by filtration, washed with toluene and ether, and vacuum dried. The characteristics of the products are presented in Table 2.

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