which it was filtered, and the solvent was removed from the filtrate by partial distillation. The residual amine V was washed with water and recrystallized from alcohol.

2-Chloro-3-aziridinobenzo[b]thiophene 1,1-Dioxide (IIIa). This compound was obtained by the method used to prepare amine V. It was isolated by complete removal of the solvent by distillation and addition of 5 ml of ethanol to the residue.

2-Chloro-3-(β-chloroethylamino)benzo[b]thiophene 1,1-Dioxide (IV). A 1-g sample of aziridine derivative IIIa was dissolved in ethanol, and 10 ml of alcohol saturated with HCl was added. The solvent was removed by distillation, and the residue was washed with water and recrystallized from ethanol.

3-Oxo-2-chloro-2,3-dihydrobenzo[b]thiophene 1,1-Dioxide (VI). This compound was obtained by hydrolysis of II-V in 6 N H_2SO_4 and had mp 154-155°. IR spectrum: 1740 cm^{-1} (CO).

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ORGANIC COMPOUNDS OF SELENIUM AND TELLURIUM

I. REACTION OF SELENIUM TETRAHALIDES WITH 1,5- AND 1,6-DIOLEFINS AND THEIR DERIVATIVES

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Heterocyclic compounds containing a selenium(IV) atom as the heteroatom were obtained by the action of selenium tetrahalides on 1,5- and 1,6-diolefins and their derivatives.

One of the methods for the synthesis of selenium-containing heterocyclic compounds is cyclization of diolefins under the influence of selenium monochloride [1]. The literature does not contain data on the use of selenium tetrahalides in these reactions, whereas it is known [2] that selenium tetrachloride, as an electrophilic reagent, is capable of adding to olefinic carbon atoms to give bis(β-chloroalkyl)selenium dichlorides.

In the present research we studied the addition of selenium tetrahalides to diolefins 1,5-hexadiene – (I), diallyl ether (IIa), diallyl sulfide (IIb), diallylamine (IIc), ethyldiallylamine (IId), and phenyldiallylamine (IIe). It was found that the addition of selenium tetrahalide to the appropriate hydrohalic acid in an ether solution of I under mild conditions is accompanied by the formation of a crystalline substance, in which, according to the IR

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TABLE 1. Physical Constants, Spectral Characteristics, and Yields of the Products of Reactions of Selenium Tetrahalides with Diolefins

Compound	Reaction product	Isomer	mp, °C	R_f (system)	Empirical formula	Found, %					Calc., %					IR spectrum, cm^{-1}	PMR spectrum, δ	Yield, %
						C	H	Hal	Se	N	C	H	Hal	Se	N			
IIIa	1,1-Dibromo-2,5-bis(bromomethyl)-selenolane	cis trans[b]	158—159 153—154	0,86(E) 0,75(E)	$C_6H_{10}Br_4Se$	14,9 14,9	2,1 2,1	66,4 66,5	— —	— —	15,0 15,0	2,1 2,1	66,5 66,5	— —	— —	2940 1420 730 525	m 2,25—2,70 (4H, 3-H)[a] m 4,05—4,90 (6H, 2-H and α-H)	77
IIIb	1,1-Dichloro-2,5-bis-(chloromethyl)selenolane	cis trans	144—145 107—109	0,79(E) 0,69(E)	$C_6H_{10}Cl_4Se$	23,6 23,6	3,2 3,2	46,5 46,3	— —	— —	23,8 23,8	3,3 3,3	46,2 46,2	— —	— —	2950 1420 740 530	m 2,13—2,85 (4H, 3-H) m 3,85—4,50 (4H, α-H) m 4,65—5,10 (2H, 2-H)	77
Va	1,1-Dibromo-2,6-bis-(bromomethyl)-1,4-selenoxane	cis trans	124—124,5 105—106	0,83(B) 0,71(B)	$C_6H_{10}Br_4OSe$	14,5 14,3	2,1 2,3	64,5 64,5	15,8 15,9	— —	14,5 14,5	2,0 2,0	64,4 64,4	15,9 15,9	— —	2945 1420 730 530	m 3,50—4,80	99
Vb	1,1-Dibromo-2,6-bis-(bromomethyl)-1,4-selenothiane[c]	cis trans	116—118 104—105	0,61(E) 0,48(E)	$C_6H_{10}Br_4SSe$	14,1 13,9	1,9 1,5	62,4 62,3	— —	— —	14,0 14,0	1,9 1,9	62,0 62,0	— —	— —	2940 1425 730 530	m 3,35—4,40	99
Vc	1,1-Dibromo-2,6-bis-(bromomethyl)perhydro-1,4-selenazine[e]	—	94—96	0,73(E)	$C_6H_{11}Br_4NSe$	22,5	3,1	64,2	—	2,7	22,6	3,1	64,5	—	2,8	2945 1420 1110 530	m 3,75—4,65 (10 H), Broad signal centered at 8.4 ppm[d] (1H, NH)	56
Vd	1,1-Dibromo-2,6-bis-(bromomethyl)-4-ethylperhydro-1,4-selenazine[e]	—	112—113		$C_8H_{15}Br_4NSe$			61,2	—	2,8	—	—	60,9	—	2,8	2940 1430 730 530		75
Ve	1,1-Dibromo-2,6-bis-(bromomethyl)-4-phenylperhydro-1,4-selenazine	cis trans	180—181 165—166	0,37(D) 0,65(D)	$C_{12}H_{15}Br_4NSe$			55,8 55,7	— —	2,3 2,4	— —	— —	55,9 55,9	— —	2,4 2,4	2945 1430 730 525	m 3,70—4,60 (10 H), m Centered at 6,65 (5H, C_6H_5) ppm	91
Vf	1,1-Dichloro-2,6-bis-(chloromethyl)-1,4-selenoxane	cis trans	140—141,5 71,5—72,5	0,79(B) 0,64(B)	$C_6H_{10}Cl_4OSe$			44,1 44,3	24,5 24,8	— —	— —	— —	44,2 44,2	24,7 24,7	— —	2950 1420 730 525	—	30

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[a] In $(CD_3)_2SO$ solution with hexamethyldisiloxane as the external standard.

[b] The trans isomers were recrystallized from the system that was used for chromatography.

[c] Found: S 6.6%. Calculated: S 6.2%.

[d] In $CDCl_3$ solution with hexamethyldisiloxane as the internal standard.

[e] The isomers could not be separated.

TABLE 2. Physical Constants and Yields of IVa and VIa-f

No.	Compound	mp, °C	R_f (system)	Empirical formula	Found, %			Calc., %			IR spectrum, cm^{-1}	Yield, %
					C	H	Hal	C	H	Hal		
IVa	2,5-Bis(bromomethyl)selenolane[a]		0,25 C	$C_6H_{10}Br_2Se$			49,6			49,8	527, 645, 665, 740, 900, 970, 1075, 1130, 1230, 1300, 1422	40
VIa	2,6-Bis(bromomethyl)-1,4-selenoxane[b]	61,5–62[c]	0,57 B	$C_6H_{10}Br_2OSe$[d]	21,3	2,9	47,2	21,4	3,0	47,5	520, 560, 730, 890, 955, 1045, 1130, 1170, 1230, 1265, 1385, 1475	62
VIb	2,6-Bis(bromomethyl)-1,4-selenothiane[e]	92–93[f]	0,91 F	$C_6H_{10}Br_2SSe$[g]	20,4	2,8	45,4	20,4	2,9	45,3	520, 720, 740, 830, 850, 900, 990, 1150, 1200, 1235, 1320, 1385, 1470	82
VIc	2,6-Bis(bromomethyl)perhydro-1,4-selenazine	47[c]	—	$C_6H_{11}Br_2NSe$	21,4	3,3	47,6	21,5	3,3	47,6	—	89
VId	1-Ethyl-2,6-bis(bromomethyl)-1,4-selenazine	103–104[f]	—	$C_8H_{15}Br_2NSe$[h]			43,9			43,9	—	87
VIe	1-Phenyl-2,6-bis(bromomethyl)-perhydro-1,4-selenazine	63–64	0,31 C	$C_{12}H_{15}Br_2NSe$			38,8			38,8	—	92
VIf	2,6-Bis(chloromethyl)-1,4-selenoxane	75–77[i]	0,83 B	$C_6H_{10}Cl_2OSe$[j]			24,6			24,8	522, 570, 660, 730, 1100, 1140, 1220, 1290, 1330, 1420	87

[a] This compound had bp 120° (10 mm).

[b] PMR spectrum (in benzene, δ): 2.10-2.50 m (2H, 2-H), 3.05-3.70 m (6H, 3-H_a, α-H), 4.13 doublet of doublets (2H, 3-He, J_{ae} = 13 Hz, J_{2a3e} = 3 Hz).

[c] From carbon tetrachloride.

[d] Found: Se 23.4%. Calculated: Se 23.7%.

[e] PMR spectrum (in chloroform, δ): 3.05-4.45 m.

[f] From benzene.

[g] Found: S 9.0%. Calculated: S 9.0%.

[h] Found: N 3.8%. Calculated: N 3.8%.

[i] From methanol (mp 75-77.5° [1]).

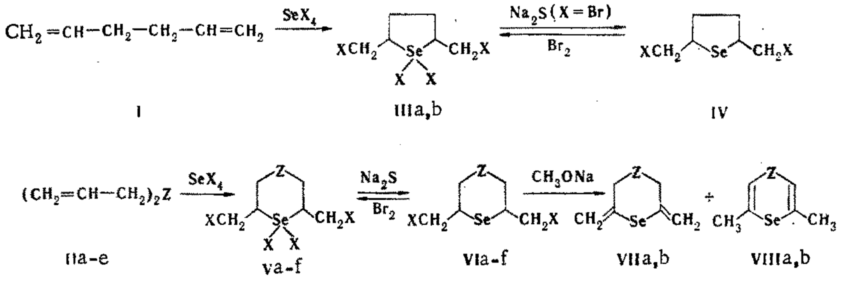
[j] Found: Se 31.6%. Calculated: Se 31.7%.

spectral data and the results of qualitative reactions with bromine water, multiple bonds are absent. 1,1-Dibromo-2,5-bis(bromomethyl)- (IIIa) and 1,1-dichloro-2,5-bis(chloromethyl)selenolane (IIIb) structures, respectively, were proposed for the substances obtained from selenium tetrabromide and tetrachloride. Their structures were also confirmed by the results of analysis and the PMR spectra. Six-membered selenium(IV)-containing heterocyclic compounds (Va-f) were similarly obtained from 1,6-diolefins IIa-e with a heteroatom in the chain.

According to the results of thin-layer chromatography (TLC), the reaction products are, as a rule, a mixture of two substances (in a ratio of 2 : 1 after separation by chromatography with a column filled with Al_2O_3 or fractional crystallization from chloroform) (see Table 1). On the basis of the fact that the substances obtained from a single experiment had identical elementary compositions and practically identical IR spectra, we assumed that they are geometrical isomers. It was impossible to use the PMR spectra for a detailed analysis, since the chemical shifts of all of the protons were found to be quite close and complex overlapping of the multiplets were always observed. Considering the fact that the cis isomers of 1,3-disubstituted heterocyclic compounds are thermodynamically more stable [3], the isomers formed in greater amounts can be assigned to the cis series. An additional confirmation of this assumption is the fact that cis-Vf undergoes dechlorination on treatment with sodium sulfide and is converted to VIf, the physical constants of which are in agreement with the literature data for cis-VIf.

Dehalogenation of the cis isomers of IIIa and Va-f with sodium sulfide is also accompanied by splitting out of the halogen atoms bonded to selenium and leads to selenium(II)-containing heterocyclic compounds IV and VIa-f, the individuality of which was confirmed by chromatography and the compositions and structure of which were confirmed by the results of elementary analysis and the IR spectra (see Table 2).

Dibromo derivatives IV and VIa-e, by treatment with bromine, can be converted to tetrabromides IIIa and Va-e, which, according to the IR spectral data and the absence of a melting-point depression, were found to be identical to the cis isomers of compounds obtained by reaction of selenium tetrabromide with the appropriate diolefins.



IIa, VIIa, VIIIa Z=O; IIb, VIIb, VIIIb Z=S; IIc Z=NH; IId $Z=NC_2H_5$; IIe $Z=NC_6H_5$; IIIa X=Br, b X=Cl; V—VIa Z=O, X=Br; V—VIb Z=S, X=Br; V—VIc Z=NH, X=Br; V—VIId $Z=NC_2H_5$, X=Br; V—VIe $Z=NC_6H_5$, X=Br; V—VIf Z=O, X=Cl

The dehydrohalogenation of cis-VIa or cis-VIf with sodium methoxide is accompanied by the formation of a mixture of isomeric unsaturated VIIa and VIIIa in a ratio of 1 : 2. We were able to separate these substances by chromatography with a column filled with Al_2O_3 and establish their structures by means of their PMR spectra.

The conversion of dibromide VIa and dichloride VIf to VIIa can be explained by assuming the initial formation of structure VIIa, which is isomerized to the more stable VIIIa under the reaction conditions. Compound VIIb also forms a mixture of VIIb and VIIIb when hydrogen halide is split out.

EXPERIMENTAL

The individuality of the compounds obtained in this research was monitored in a thin layer of activity II aluminum oxide in the following systems: chloroform–ethanol (1 : 1) (A), (11 : 1) (B), and (19 : 1) (C); chloroform–methanol (2 : 1) (D) and (14 : 1) (E); chloroform (F); hexane–ether (2 : 1) (G) and (1 : 5) (I); ether–chloroform (5 : 1) (J); ether–petroleum ether (1 : 1) (K). The IR spectra of KBr pellets and mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. The PMR spectra were obtained with a Varian ST-60 spectrometer with tetramethylsilane as the internal standard. The UV spectra of 10^{-5} M solutions of the compounds in ethanol ($l = 1$ cm) were obtained with an SF-4A spectrophotometer.

Diallyl-, ethyldiallyl-, and phenyldiallylamines were obtained by known methods [4]. Selenium tetrabromide and tetrachloride were obtained in the form of solutions from selenium dioxide and hydrobromic and hydrochloric acids, respectively, in twofold excess amounts.

Reaction of Selenium Tetrahalides with 1,5- and 1,6-Diolefins. An equimolar amount of a solution of selenium tetrahalide obtained from selenium dioxide and the appropriate hydrohalic acid (in a twofold excess amount) was added dropwise with vigorous stirring at 0° to a solution of 0.01 mole of the diolefin in 100 ml of ether, and the crystalline precipitate was removed by filtration. Evaporation of the ether from the organic layer yielded an additional amount of substance. The cis and trans isomers were separated by fractional crystallization from chloroform or by chromatography with a column filled with aluminum oxide (see Table 1).

2,5-Bis(bromomethyl)selenolane (IVa). A 0.079-mole sample of sodium sulfide nonahydrate was added with stirring to a solution of 0.015 mole of cis-IIIa in 150 ml of benzene. After the reaction mixture became colorless, the organic layer was separated and dried with calcium chloride. The solvent was vacuum evaporated, and the residue was distilled.

Crystalline VIa-f, which were purified by recrystallization, were obtained by a similar method from the appropriate Va-f (see Table 2).

Reaction of IVa and VIa-e with Bromine. An equimolar amount of bromine was added to a solution of dibromo derivative IVa or VIa-e in carbon tetrachloride, and the resulting precipitate was removed by filtration to give the corresponding tetrabromo derivatives IIIa or Va-f in quantitative yields.

2,6-Dimethyl-1,4-selenoxine (VIIIa) and 2,6-Dimethylidene-1,4-selenoxane (VIIa). A solution of 0.92 g of sodium in 50 ml of ethanol was added with stirring and cooling to 0° to a solution of 0.02 mole of VIa in 50 ml of benzene. At the end of the reaction, the benzene solution was washed successively with hydrobromic acid and water and dried with sodium sulfate. The solvent was evaporated, and the residue was vacuum distilled to give a product with bp 137° (2 mm). The product began to crystallize after distillation to give a solid with mp 54-55° [1.9 g (54.3%)] and R_f 0.67 and 0.15 (system K). Chromatography with a column filled with Al_2O_3 in system K initially yielded VIIIa with mp 57° and R_f 0.67. PMR spectrum, δ: 1.56 s (3H, CH_3) and 4.02 s (1H, CH). UV spectrum, λ_{max}, nm (log ε): 230 (3.42) and 265 (3.00). Found: Se 45.0%. C_8H_8OSe. Calculated: Se 45.1%. Subsequent elution yielded VIIa with mp 64° and R_f 0.15. PMR spectrum, δ: 2.95 s (2H, α-H) and 4.05 s (2H, OCH_2). Found: Se 45.2%. C_8H_8OSe. Calculated: Se 45.1%.

Compounds VIIIa and VIIa were obtained in 55% overall yield by a similar method from dichloro derivative VIf.

2,6-Dimethyl-1,4-selenothiine (VIIIb) and 2,6-Dimethylidene-1,4-selenothiane (VIIb). These compounds, with mp 77-79° (from benzene) and R_f 0.83 and 0.08 (system K), were obtained in 90% overall yield by the method presented above from VIb. Chromatography with a column filled with Al_2O_3 in system K initially yielded VIIIb with mp 81-82° (from ether) and R_f 0.83. PMR spectrum, δ: 1.50 s (3H, CH_3) and 3.78 s (1H, CH). Found: Se 41.0; S 16.6%. C_6H_8SSe. Calculated: Se 40.5; S 16.4%. Subsequent elution yielded VIIb with mp 93-94° (from benzene) and R_f 0.08 (system K). PMR spectrum, δ: 2.88 d (2H, SCH_2, J = 3.7 Hz) and 3.53 s (2H, α-H). Found: Se 40.5; S 16.2%. C_6H_8SSe. Calculated: Se 40.5; S 16.4%.

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