c. To the mixture, obtained analogously (Experiment 6), was added 1 g of NHEt_2 in 1 ml of water; the mixture was stirred for 2.5 h. According to the data of the ¹⁹F NMR spectrum, (XVIII) not containing (XIX) was obtained.

Interaction of 2-Aminoperfluoro-3-ethylindene (VIII) with Dry NHMe₂. Into the ampul for the recording of the NMR spectra were sealed 0.25 g of (VIII) in 0.25 ml of MeCN and 0.21 g of 30% NHMe₂ in MeCN; the mixture was held at ~20°C for 17 h. According to the data of the ¹⁹F NMR spectrum, the mixture containing a small amount (<20%) of the initial (VIII) together with unidentified products was obtained.

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REACTION OF ORGANYLTHIOCHLOROACETYLENES WITH ORGANYLSELENOLS

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The reaction of organylthiochloroacetylenes $RSC^{\alpha} \equiv C^{\beta}Cl$ with selenols in a DMSO solution containing KOH leads to organylthio(organylseleno)acetylenes $RSC \equiv CSeR'$. When the reaction of organylthiochloroacetylenes with selenols was carried out in diethyl ether, the previously unknown 1-organylthio-2-organyl-seleno-2-chloroethenes RSCH=CClSeR' were obtained in the form of Z- and E-isomers. The hydrochlorination of organylthio(organylseleno)acetylenes results in Z- and E-1-organylthio-2-organylseleno-1-chloroethenes RSCCI=CHSeR'.

Organylthiochloroacetylenes RSC $\alpha \equiv C^{\beta}C1$ (I) have a unique distribution of the electron density, enabling the preparation from them of both the products of the nucleophilic substitution of the Cl atom, and products of the nucleophilic substitution at the α -C and β -C atoms [1], depending on the "rigidness" and "mildness" of the nucleophile. Thus, the "rigid" alcoholates can add to both the α -C and the β -C atom of alkyl sulfides (I). The less "rigid" phenolates give only the addition products at the β -C atom and the substitution products, while the most "rigid" alcoholates form an entire spectrum of possible products. The "milder" thiols do not react with sulfides (I) without a catalyst, but in the presence of an alkali, addition takes place at the β -C atom with the formation of 1,2-bis(organylthio)-1chloroethenes RSCH=CC1SR' and substitution of the chlorine atom with the formation of bis-(organylthio)acetylenes RSC=CSR' [2, 3].

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Com- pound	Bp, °C (p, mm Hg)	n ²⁰ _D	d ₂₀ 4	IR spectrum (v, cm^{-1})	PMR spectrum (δ , ppm in CDC1 ₃)
(IIa)	140-143 (3)	1,6443	1,3966	3067, 3053 (=CH), 2964, 2923, 2864 (CH), 2070 (C≡C)	1.25 t (3H, CH ₃), 2,83 q (2H, CH ₂), 7,22 m, 7,43 m (5H, C_6H_5)
(II Þ)	137-140(2)	1,6232	1 ,39 82	3046(=CH), 2953, 2940, 2848(CH), 2053(C≡C)	1,27 ^d (6H, CH _s), 3,07 ^m (1H, CH), 7,13 ^m , 7,36 ^m (5H, C ₆ H _s)
(IIc)	151–153(3)	1,6278	1,1936	2925, 2830 (CH)	0,92t (3H, CH ₃), 1,72 m (2H, CH ₂), 2,61t (2H, CH ₂), 7,22 m, 7,43 m (5H, C ₆ H ₅)
(II d)	mp 115-117	-	-	3042(=CH), 1567(C ₈ H ₅)	7,29-7,40 m (C ₆ H ₅)
(I]e)	125–130(5)	1,5485	1,0865	2935, 2900, 2845(CH), 2040(C≡C)	0,99 d.t(6H, CH ₃), 1,70-1,52 m (6H, CH ₂), 2,66t (2H, CH ₂ S), 2,93t (2H, CH ₂ Se)

TABLE 1. Physicochemical Constants and IR and PMR Spectroscopy Data for Organylthio(organylseleno)acetylenes (II)

In continuation of studies on the reactivity of organylthiochloroacetylenes (I), we examined their reaction with organyl selenols, the "mildest" analogs of alcohols. Under alkaline conditions, selenols, similarly as thiols, react regioselectively with sulfides (I) - at the β -C atom only with the formation of organylthio(organylseleno)acetylenes (IIa-e)

$$\begin{array}{rcl} \text{RSC} \equiv \text{CCl} + \text{R'SeH} & \xrightarrow{\text{KOH. DMSO}} & \text{RSC} \equiv \text{CS}_{\theta}\text{R'} \\ & (\text{Ia-d}) & (\text{II} \text{a} - \text{e}) \\ \text{R} = \text{C}_{2}\text{H}_{5}, \text{R'} = \text{C}_{6}\text{H}_{5} & (\text{II}\text{a}); \text{R} = i\text{-}\text{C}_{3}\text{H}_{7}, \text{R'} = \text{C}_{6}\text{H}_{5} & (\text{II}\text{b}); \\ \text{R} = n\text{-}\text{C}_{3}\text{H}_{7}, \text{R'} = \text{C}_{6}\text{H}_{5} & (\text{II}\text{c}); \text{R} = \text{R'} = \text{C}_{6}\text{H}_{5} & (\text{II}\text{d}); \\ \text{R} = n\text{-}\text{C}_{3}\text{H}_{7}, \text{R'} = n\text{-}\text{C}_{4}\text{H}_{9} & (\text{II}\text{e}). \end{array}$$

The structure of compounds (IIa-e) is confirmed by IR spectra in which absorption bands of the triple bond are recorded, the PMR spectra (Table 1) and data of elemental analysis.

Compounds (II) of the aliphatic series were previously obtained by nucleophilic substitution of the halogen in alkyl halides by selenolates of the formula RSC=CSeNa in liquid NH_3 [4].

 $\begin{array}{c} \mathrm{RSC} \equiv \mathrm{CNa} + \mathrm{Se} \xrightarrow{\mathrm{NH}_3} \mathrm{RSC} \equiv \mathrm{CSeNa} \xrightarrow{\mathrm{R'X}} \mathrm{RSC} \equiv \mathrm{CSeR'} \\ \mathrm{R} = \mathrm{CH}_3, \ \mathrm{C}_3\mathrm{H}_7; \ \mathrm{R'} = \mathrm{CH}_3; \ \mathrm{X} = \mathrm{I}. \end{array}$

However, in this case it is virtually impossible to obtain compounds of the aromatic series, since monohaloaromatic compounds ArX are fairly stable to nucleophilic substitution, and are converted by the action of strong bases into arenes.

In the course of further investigations, we found that in contrast to alcohols and thiols, selenols react vigorously with organylthiochloroacetylenes in diethyl ether in the absence of any catalysts. As a result, the previously unknown l-organylthio-2-organylseleno-2-chloroethenes (III) are obtained in the form of Z- and E-isomers in an approximately 1:1 ratio (Table 2).

$$\begin{array}{c} \text{RSC} \equiv \text{CCl} + \text{R'SeH} \xrightarrow{\text{Et}_{2}\text{O}, \ 20^{\circ}} \mathbb{Z}, \ E\text{-RSCH} = \text{CClSeR'} \\ (1) & (111a - d) \\ \text{R} = \text{C}_{2}\text{H}_{5}, \ \text{R'} = \text{C}_{6}\text{H}_{5} \ (\text{IIIa}); \ \text{R} = i\text{-}\text{C}_{3}\text{H}_{7}, \ \text{R'} = \text{C}_{6}\text{H}_{5} \ (\text{IIIb}); \\ \text{R} = n\text{-}\text{C}_{4}\text{H}_{9}, \ \text{R'} = \text{C}_{6}\text{H}_{5} \ (\text{IIIc}); \ \text{R} = \text{C}_{2}\text{H}_{5}, \ \text{R'} = n\text{-}\text{C}_{4}\text{H}_{9} \ (\text{IIId}). \end{array}$$

The composition of the compounds obtained was confirmed by elemental analysis, and their structure was proved by the IR and PMR spectral data (Table 2) and by chemical transformations. In the IR spectra of compounds (IIIa-d), in particular, absorption bands were observed at 1512-1566 cm⁻¹ and 3040-3070 cm⁻¹, which are assignable to the stretching vibra-

Com- pound	Bp, °C (p, mm Hg)	n_D^{20}	IR spectrum $(\vee, \text{ cm}^{-1})$	PMR spectrum (δ , ppm in CDC1 ₃)
(IIIa)	142—145 (5)	1,6424	3070, 3053 (=CH), 2970, 2923, 2867 (CH), 1566, 1523 (C=C)	7,44 m, 7,29 m (5H, CeH ₅), 6,90 s, 6,77 s (45:55) a (1H, =CH), 2,72 d,32 (2H, CH ₂), 1,27 t (3H, CH ₃)
(IIIb)	126–132(5)	1,6251	3048 (=CH), 2956, 2913, 2855 (CH), 1556, 1518 (C=C)	7,48 m, 7,27 m (5H, C ₆ H ₅), 6,95 s, 6,82 s (37,5:62,5) = (1H, ==CH), 3,17 m (1H, CH), 1,28 d (6H, CH ₃)
(IIIc)	160–165(5)	1,6000	3047 (=CH), 2947, 2916, 2860 (CH), 1560, 1515 (C=C)	7,47m, 7,25m (5H, C ₀ H ₅), 6,87s, 6,76 s (43:57) ° (1H, =CH). 2,66m (2H, CH ₂), 1,49m (4H, C ₂ H ₄), 0,85t (3H, CH ₃)
(IIId)	123–125(5)	1,5692	3042 sh (=CH), 2930, 2900, 2844(CH), 1512(C=C)	6,70 s, 6,63 s (50 : 50) • (1H, ==CH), 2,91 q (2H, SCH ₂), 2,81 m (2H, SeCH ₂), 1,63 m (4H, C ₂ H ₄), 1,30 t (3H, CH ₃), 0,90 t (3H, CH ₃)
(IVa)	136–143(3)	1,64 78	3022(=CH), 2932, 2893, 2832(CH), 1550, 1520(C=C)	7,53 m, 7,28-7,24 m (5H, $C_{e}H_{5}$), 7,05 s, 6,90 s (70:30) a (1H, =CH), 2,77 q, 2,89 q (2H, CH ₂), 1,24 t, 1,32 t (3H, CH ₃)
(IVb)	165-168(3)	1 ,63 56	3037 (=CH), 2937, 2900, 2842 (CH), 1565 (C=C)	7,56 m, 7,23 m (5H, C ₆ H ₅), 7,10 s, 6,96 s, 6,76 s (58 : 19 : 23) ^a , 3,36' q (1H, CH), 1,27 d (6H, CH ₃)

TABLE 2. Physicochemical Constants and IR and PMR Spectroscopy Data for 1-Organylthio-2-organylseleno-2-chloroethenes (III) and 1-Organylthio-2-organylseleno-1-chloroethenes (IV)

aRatio of integral intensities.

tions of the C=C and H-C= bonds, respectively. There are signals in the PMR spectra of the vinyl protons at δ 6.76-6.82 (s) and 6.87-6.95 (s) ppm. In the case of R = i-C₃H₇, the predominance of one isomer (δ 6.82 s) was observed, possibly due to the preferential trans substitution. From a comparison of these data, the signals of the vinyl protons of compounds (III) at δ 6.76-6.82 ppm can be assigned to the E-isomers and the signals at δ 6.87-6.95 ppm to the Z-isomers.

On the basis of the possible regio- and stereodirectivity of the addition in this reaction, the formation of four different isomers is possible - the Z- and E-l-organylthio-2organylseleno-2-chloroethenes and Z- and E-l-organylthio-l-organylseleno-2-chloroethenes.

Attempts to reduce the chlorine atom in compounds (III) by means of LiAlH₄, NaBH₄, and Zn in HCl to obtain organylthio(organylseleno)ethenes RSCH=CHSeR' or RS(R'Se)C=CH₂ were unsuccessful. For a stricter confirmation of the proposed structures of compounds (III), mixtures of Z- and E-isomers of 1-ethylthio- (IIIa), 1-isopropylthio-2-phenylseleno-2-chloroethene (IIIb), and 1-ethylthio-2-butylseleno-2-chloroethene (IIIe) were treated with pyridine in benzene, KOH in DMSO, and t-BuOK. Pyridine was thus found practically not to cause the dehydrochlorination of compounds (III), while KOH and t-BuOK led to the formation of acetylenic compounds (II)

 $\begin{array}{rcl} \operatorname{RSCH}=\operatorname{CClSeR'} & \xrightarrow{t-\operatorname{BuOK}/t-\operatorname{BuOH} & \operatorname{or} & \operatorname{KOH}/\operatorname{DMSO}} & \operatorname{RSC}\cong\operatorname{CSeR'} \\ & & (\operatorname{II1a}, b, e) & & (\operatorname{IIa}, b, f) \\ \operatorname{R} & = \operatorname{C_2H_5}, & \operatorname{R'} & = n-\operatorname{C_4H_9}(\operatorname{Ilf}). \end{array}$

This fact can serve as a direct proof for the vicinal disposition of the organylthioand organylseleno groups in compounds (III).

It is of interest to note that during the dehydrochlorination of compound (IIIe) by the action of KOH in DMSO, together with ethylthio(butylseleno)acetylene (IIf), unreacted Z-1-ethylthio-2-butylseleno-2-chloroethene (IIIe) was isolated in a low yield (~10%). In the PMR spectrum of the mixture of the products obtained, the signal of the vinyl proton at δ 6.63 (s) ppm corresponded to this compound. This result, on the one hand, indicates the ex-

TABLE 3. Comparison of the Chemical Shifts of Vinyl Protons in the PMR Spectra of Compounds E-(III) and Z-(III) and Isomeric and Related Compounds

			^δ calc, ppm		
Compound	Structure	δ _{exp} , ppm	A	B	
E-(III) Z-(III) E-(III d) Z ¹ (III d)	E-PhSeCCl=C(H)SR Z-PhSeCCl=C(H)SR E-BuSeCCl=C(H)SEt Z-BuSeCCl=C(H)SEt Z-PhSe(RS)C=CHCl E-PhSe(RS)C=CHCl Z-RSCCl=CHSR' E-RSCCl=CHSR' RS(R'S)C=CHCl	$\begin{array}{c} 6,76-6,82\\ 6,87-6,95\\ 6,70\\ 6,63\\ -\\ -\\ 6,35-6,37\\ 6,52-6,54\\ [3]\\ -\\ -\end{array}$	6,70 6,54 6,70 6,53 5,94 6,41 6,20 6,41 5,95	6,64 ^a 6,93 ^a 6,68 ^b 6,53 ^b 6,18 ^c 6,41 ^c -	

Note. A - Calculated by the additive scheme [5]. B - Calculated from the values of chemical shifts of the vinyl protons of the selenides:

^aPhSeCC1=CH¹H² (δ_{H^1} 5.50 d, δ_{H^2} 5.82 d [6]); ^bBuSeCC1=CHC1 (δ_E 6.65 s, δ_Z 6.50 s [7]); ^cPhSeCC1=CHC1 (δ_E 6.67 s, δ_Z 6.44 s [8]).

pected lower activity of the Z-isomer of compound (III) with the cis disposition of the H and Cl in the vinyl group in the dehydrochlorination reaction, and, on the other hand, it indicates an Ad-E-mechanism of the substitution of the chlorine atom in the organylthiochloroacetylenes by the organylseleno group.

Since the data presented above still leave the possibility of an alternative treatment of structures of the obtained compounds (III) as 1-organylthio-1-organylseleno-2-chloro-ethenes RS(R'Se)C=CHC1, whose behavior under dehydrochlorination conditions is unknown, we carried out a comparison of the chemical shifts of the vinyl protons in the PMR spectra of compounds (III) obtained by us with analogous values in the PMR spectra of related compounds and with calculated values of the chemical shifts of vinyl protons in all the possible isomers of adducts of RSC=CC1 and R'SeH (Table 3). In the latter case, the calculations were carried out by the known additive scheme [5], or by replacing the increment of the Cl atom by the corresponding increment of the RS group [5] in the selenides PhSeCC1=CH₂, PhSeCH=CHC1 and RSeCC1=CHC1 [6-8]. The increments of the RSe group for the calculations according to the scheme [5] were obtained from the data for the above-listed 1- and 2-chloro- and 1,2-dichlorovinyl selenides [6-8]. The calculations gave the values z_{gem} (RSe) 1.41, z_{cis} (RSe) 1.19-1.21, z_{trans} (RSe) -0.1. The data in Table 3 show that the structures of Z- and E-1-organylthio-2-organylseleno-2-chloroethenes to a great extent conform with the experimental values of the chemical shifts of the vinyl protons in compounds (III).

It was reported in [4] that 1-organylthio-2-organylseleno-1-chloroethenes (IV), isomeric with compounds (III), are formed as a result of the addition of HCl to alkylthio(alkylseleno)acetylenes

$$RSC \equiv CSeR' + HCl \xrightarrow{CHCl_3, -40^{\circ}} RSCCl = CHSeR'$$

$$(IV)$$

$$R = CH_3, n-C_3H_7, R' = CH_3(IV).$$

However, the structure of these products was determined only on the basis of the fact that in unsaturated compounds the H atom present in the α -position to the Se atom is descreened, and its signal is shifted to a weaker field, compared with the sulfur analogs [4]. At the same time, for the compounds (III) that we obtained, for which the alternative structure (IV) is impossible, the chemical shifts of the vinyl protons in the α -position to the S atom are also present in a weaker field, and even to a greater extent (Table 2), compared with the sulfur analogs. This fact raises certain doubts concerning the correctness of the identification by the authors of [4] of the products of the addition of HCl to alkylthio(alkylseleno)-acetylenes as compounds (IV) and not their isomeric compounds (III). To settle this question, we carried out the hydrochlorination of ethylthio(phenylseleno)acetylene (IIa) and isopropyl-thio(phenylseleno)acetylene (IIb) in chloroform

$$\begin{array}{rcl} \text{RSC} \equiv \text{CSeR'} + \text{HCl} & \xrightarrow{\text{CHCl},} & \text{RSCCl} = \text{CHSeR'} \\ & & (\text{IIa, b)} & (\text{IVa, b}) \\ \text{R} = \text{C}_2\text{H}_5, & \text{R'} = \text{C}_6\text{H}_5 & (\text{IVa}); & \text{R} = i\text{-}\text{C}_3\text{H}_7, & \text{R'} = \text{C}_6\text{H}_5 & (\text{IVb}). \end{array}$$

Two compounds are formed by this reaction, whose PMR spectra show two singlet signals of the vinyl protons at δ , ppm: 7.05 and 6.90 (IVa) and 7.10 and 6.96 (IVb) (Table 2). Comparison of the GLC data and the PMR spectra for these products and compounds (III) indicates that Z- and E-1-organylthio-2-organylseleno-1-chloroethenes (IVa, b) are formed in the course of the reaction, which confirms the regiodirectivity of the addition to organylthio-(organylseleno)acetylenes proposed by the authors of [4]. Thus, the signals of the vinyl protons at δ 7.05-7.10 ppm in the PMR spectra correspond to the Z-isomers of compounds (IVa, b), and signals of the vinyl protons at δ 6.90-6.96 ppm correspond to the E-isomers.

EXPERIMENTAL

The IR spectra were run in a thin layer or in KBr tablets [compound (IId)] on a "Specord IR-75" spectrophotometer. The PMR spectra were recorded using 5-10% solutions of the compounds in $CDCl_3$ on a "Tesla BS-487B" spectrometer (80 MHz), relative to HMDS. The GLC was carried out on a LKhM-8MD chromatograph, using a catharometer detector, a 2000 × 3 mm column, and system 1: Chromaton N-AW (0.200-0.250 mm), 15% Silicone DC-550; system 2: Chromaton N-AW DMCS (0.200-0.250 mm) 5% Silicone XE-60, 160-200°C, helium, flow rate 40-50 ml/min.

Organylthiochloroacetylenes (Ia-f) were obtained by dehydrochlorination of organyl-2,2dichlorovinyl sulfides with a concentrated solution of alkali in the presence of DMSO [9].

<u>Preparation of Organylthio(organylseleno)acetylenes (IIa-e)</u>. A KOH powder was added to a solution organylthiochloroacetylene in DMSO, and then selenol was added dropwise with stirring. The mixture was thus warmed up to 60-65°C. The mixture was stirred for 7 h at 20-22°C, and poured into water. The oil that separated out was extracted with ether, and the extract was dried over CaCl₂. After the evaporation of the ether, the residue was either distilled in vacuo, or was recrystallized from MeOH [compound (IId)]. The ratio of the reagents, the yields of the products and the data of the elemental analysis are given in Table 4; the physicochemical characteristics and the IR and PMR spectroscopy data are given in Table 1.

<u>Preparation of 1-Organylthio-2-organylseleno-2-chloroethenes (IIIa-d)</u>. An equimolar amount of butane- or benzeneselenol was slowly added dropwise to the absolute ether solution of the organylthiochloroacetylene. After the cessation of the exothermal reaction, the mixture was stirred for 6 h at 20-22°C, was then washed with a 5% aqueous sodium carbonate solution to effect removal of the unreacted selenol, and the ether solution was dried over CaCl₂. After evaporation of the ether, the residue was distilled under vacuum. The ratio of the reagents, the yields of the products, and the data of the elemental analysis are given in Table 4; the physicochemical characteristics and the IR and PMR spectroscopy data are given in Table 2.

<u>Dehydrochlorination of 1-Ethylthio-2-phenylseleno-2-chloroethene (IIIa)</u>. A 2.38 g portion of (IIIa) was added to 30 ml of a solution obtained by dissolving 1.18 g of K in 30 ml of tert-butanol. The mixture was stirred for 3 h at ~20°C, was then diluted with an equal amount of water, extracted with ether, and the extracts were washed with water and dried over CaCl₂. After removal of the ether, the residue was distilled under vacuum. Yield, 0.95 g (46%) of ethylthio(phenylseleno)acetylene (IIa), bp 155-165°C (7 mm), n_D^{20} 1.6305. IR spectrum (v, cm⁻¹): 3056, 2973, 2930, 2860, 2070 (C=C), 1570. According to the GLC data, the product is identical with compound (IIa) obtained by the reaction of ethylthiochloroacetylene with benzeneselenol in DMSO/KOH.

<u>Dehydrochlorination of 1-Isopropylthio-2-phenylseleno-2-chloroethene (IIIb)</u>. In a similar way, from 4.02 g of a mixture of Z- and E-1-isopropylthio-2-phenylseleno-2-chloroethenes (IIIb) in a solution of 3 g of K in 30 ml of tert-butanol, after 1.5 h, 2.31 g (65) of isopropylthio(phenylseleno)acetylene (IIb) was obtained, bp 128-130°C (3 mm), n_D^{20} 1.6285. IR spectrum (v, cm⁻¹): 3026, 2938, 2900, 2836, 2044 (C=C), 1557. According to the GLC data, the product obtained was identical to compound (IIb), obtained by the reaction of isopropyl-thiochloroacetylene with benzeneselenol in DMSO/KOH.

Dehydrochlorination of 1-Ethylthio-2-butylseleno-2-chloroethene (IIId). A 1 g portion of finely crushed KOH was introduced into 8.5 ml of dry DMSO and 0.84 g of a mixture of Z- and E-isomers (1:1) of compound (IIId) was dissolved in this solution. The mixture was

Reaction Conditions of Organylthiochloroacetylenes with Selenols, Yields of Products, and Elemental Analysis TABLE 4. Data

-	Empirical formula	C10H10SSe	C ₁₁ H ₁₂ SSe	C ₁₁ H ₁₂ SS ₈	C ₁₄ H ₁₀ SSe	C,H,SSe	C ₁₀ H ₁₁ ClSSe	C ₁₁ H ₁₃ CISSe	C ₁₂ H ₁₅ ClSSe	C ₈ H ₁₅ ClSSe
	s	$\frac{32,33}{32,74}$	30,97 30,98	30,88 30,98	27,53 27,34	33,84 33,61	28,10 28,44	$\frac{27,40}{27,10}$	25,42 25,85	30,68 30,68
ulated, %	~~~	13,50 13,30	12,40 12,55	<u>12,51</u> 12,56	11,14	<u>13,75</u> 13,60	<u>11,40</u> 11,55	10,84 10,97	10,31 10,47	12,54
Found/ Calc	G	1	I		I	l	12,52	12,10 12,18	11,42 11,62	<u>13,65</u> 13,79
	H	4,40 4,18	4,81 4,70	4,68	3,59	7,20	3,78	4,65	5,18 4,91	5,79 5,82
	υ	49,86 49,80	51,20 51,76	51,76	58,61 58,13	<u>45,52</u> 45,95	<u>42,11</u> 43,26	45,00 45,28	<u>46,21</u> 47,13	37,00 37,28
	Yield, g (%)	5,88 (60)	4,98(60)	3,2 (56)	3,4 (60)	2,77 (42)	4,8(47)	4,86 (78)	4,8 (80)	4,6(82)
	Product	(IIa)	(411)	(IIc)	(PII)	(IIe)	(IIIa)	(9111)	(111c)	(PIII)
	Et ₂ 0, ml	1	I	I	1	1	20	20	20	20
RVN	g (mole)	3,4 (0,06)	2,7 (0,045)	1,87 (0,03)	1,65 (0,03)	2,32 (0,04)	1	I	I	I
	DMSO, m1	20		20	20	20	1	I	1	I
	Selenol, g (mole)	PhSeII	(PhSeH PhSeH 5 0 (0 03)	PhSeH 35(0.02)	PhSeH	BuSeH	PhSeH	PhSeH	PhSeH 3 31 (0.09)	BuSeH 3,48(0,02)
Oreany1+hio-	chloroace- tylene, g (mole)	EtSC=CCl	i-PrSC = CCl $i = 0.03$	n-PrSC≡CCI 3.0(0.02)	PhSC=CCI	n-PrSC = CCI	EtSC=CCI	i-PrSC≡CCl	$\frac{1}{2} \frac{1}{2} \frac{1}$	EtSC=CCI 3,06(0,02)

stirred for 5 h at ~20°C, and was then diluted with water, and extracted with ether. The ether extracts were washed with water, and dried over CaCl₂. After evaporation of the ether, 0.53 g of ethylthio(butylseleno)acetylene (IIf) (90%, according to GLC data) and Z-1-ethylthio-2-butylseleno-2-chloroethene (IIId) (10%, according to GLC data), n_D^{20} 1.5566 were obtained. The yield of compound (IIf) was 66%. IR spectrum (ν , cm⁻¹): 2932, 2898, 2845, 2065 (C=C). PMR spectrum (δ , ppm): 6.63 s, 0.93 t, 1.37 t, 1.73 q, 2.66 m, 2.74 m, 2.83 m.

<u>l-Ethylthio-2-phenylseleno-1-chloroethene (IVa)</u>. Hydrogen chloride was passed for 2.5 h, with stirring and cooling to 5°C into a solution of 8.0 g of acetylene (IIa) in 50 ml of dry chloroform. After evaporation of CHCl₃, the residue was distilled under vacuum. Yield, 4.41 g (55%) of Z- and E-isomers of compound (IVa), bp 136-145°C (2 mm), n_D^{20} 1.6478. IR spectrum (v, cm⁻¹): 3022 (=CH), 2932, 2893, 2832 (CH), 1550, 1520 (C=C). PMR spectrum (δ , ppm): 7.53 m, 7.28-7.24 m (5H, C₆H₅), 7.05 s, 6.90 s (1H, =CH) (70:30), 2.77 q, 2.89 q (2H, CH₂), 1.24 t (3H, CH₃).

<u>1-Isopropylthio-2-phenylseleno-1-chloroethene (IVb)</u>. In a similar way, from 0.8 of acetylene (IIb) in 15 ml of dry chloroform, after 7 h at 0 to -5° C, 0.53 g (58%) compound (IVb) was obtained, bp 165-168°C (3 mm), np²⁰ 1.6356. IR spectrum (v, cm⁻¹): 3037 (=CH), 2937, 2900, 2842 (CH), 1565 (C=C). PMR spectrum (δ , ppm): 7.56 m, 7.23 m (5H, C₆H₅), 7.10 s, 6.96 s, 6.76 s (58:19:23) (1H, =CH), 3.36 q (1H, CH), 1.27 d (6H, CH₃).

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