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Effect of Chalcogenyl Substituent on the Course of Allyl Rearrangement at Chalcogenation of 1,3-Dichloropropene

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Abstract—Formation of 1,3-dichalcogenylpropene at the treatment of 1,3-dichloropropene with organic dichalcogenides in a redox system hydrazine hydrate–KOH is governed by the possibility of an allyl rearrangement. In the presence of bases this rearrangement proceeds via carbanion partially stabilized by the chalcogenyl substituent. The effectivity of the stabilization and consequently the probability of the rearrangement varies in the series of substituents PhS > BnS > PhSe. In the stage of the direct nucleophilic substitution of chlorine the anion $PhSe^-$ possesses the highest activity.

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Hetero-substituted allyl systems are important reagents in organic synthesis [1]. With the use of allyl chalcogenides the high temperature synthesis of benzothiophene and its analogs was performed [2], the possibility was studied of allyl rearrangement [3] and of Claisen rearrangement [4] in the allyl phenyl chalcogenide series.

The general preparation method of allyl monochalcogenides is the reaction of chalcogen-containing nucleophiles with allyl halides. In the majority of these reactions the conditions may be adjusted leading to high yields of target compounds.

Allyl derivatives with two chalcogenyl substituents in the positions *1*, *3* are far less understood, although their synthetic potential in many instances may be higher than that of monochalcogenides. A lithium derivative of 1,3-bis(methylsulfanyl)propene plays the role of a synthetic equivalent of a hypothetic acrolein β-anion which may underlie the preparation of versatile unsaturated structures [5]. Several approaches were suggested for the synthesis of 1,3-bischalcogenyl propene derivatives. 1,3-(Dibutylsulfanyl)- or 1,3-(diphenylsulfanyl)propene were obtained in 15–20% yields in reactions of 1,1-dichloroprop-2-ene with sodium butanethiolate or sodium thiophenolate [6]. In the reaction of enones with tris(phenylsulfanyl)borate 1,3-bis(phenylsulfanyl)propene formed in 35–78% yields [7].

1,3-Bisselanyl propene derivatives were obtained with the use of difficultly available selanylallyl alcohols and the corresponding selenols (yield 77–82%), and also from selanylacetic aldehyde and Wittig reagent (yield 60%) [8]. 1,3-Bis(phenylsulfanyl)-propene was obtained in 43% yield by the reaction of butyllithium with 2-methoxy-1,3-bis(phenylsulfanyl)-propane [9]. 1,3-Bis(phenylsulfanyl)propene (yield 85%) and 1,3-bis(phenylselanyl)propene (yield 90%) were obtained by the reaction of 1,3-dichloropropene with thiophenol in the presence of KOH or with diphenyl diselenide in the presence of rongalite and KOH respectively [10]. In both cases the reaction was carried out in highly basic medium with excess KOH. Reaction products are formed as a result of successive transformations, and the key stage is the allyl rearrangement of the primarily formed product of chlorine monosubstitution at the sp^3-hybridized carbon atom; the double bond shifts to the chalcogen atom. This rearrangement proceeds evidently through an intermediate formation of a carbanion whose stability is governed by the influence of the contiguous chalcogenyl groups [10]. This influence depends both on the nature of the chalcogen atom and on the

electronic properties of the organic substituent bound to it.

The allyl rearrangement in the series of allyl phenyl chalcogenides resulting in the migration of the double bond to the chalcogen atom under the same conditions occurs with sulfide to 95% and with the corresponding selenide only to 53% [3].

Reactions of chalcogenation of 2,3-dichloroprop-1-ene [11] and 1,4-dichlorobut-2-yne [12] include several stages, and some among them involve carbanions. The structure of formed compounds depends on the possibility of stabilization by a chalcogenyl substituent of the adjacent carbanion site.

In continuation of this research we studied the chalcogenation of commercially available 1,3-dichloropropene **1** with chalcogenolates **2a–2d** which were obtained by the reduction of organic dichalcogenides Ph_2Y_2 and Bn_2S_2 in the system hydrazine hydrate–KOH [13] (Scheme 1). The reduction products without isolation were used in the subsequent syntheses.

Scheme 1.

$$2R_2Y_2 + N_2H_4 \cdot H_2O + 4KOH \longrightarrow \underset{\textbf{2a–2d}}{4RYK} + N_2 + 5H_2O$$

R = Ph, Y = S (**a**), Se (**b**), Te (**c**); R = Bn, Y = S (**d**).

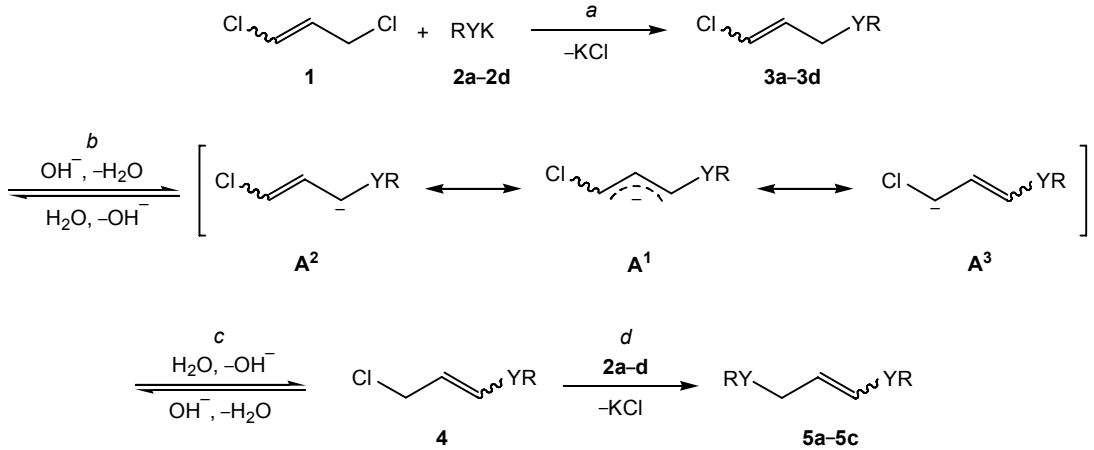
In keeping with [10] and the presumed mechanism of the allyl rearrangement [14] the reaction of 1,3-dichloropropene **1** with chalcogenolates **2a–2d** proceeds through several stages including the nucleophilic substitution of the allyl chlorine with the formation of [(3-chloroprop-2-en-1-yl)chalcogenyl]benzenes **3a–3d** (*a*), ionization of compounds **3** leading to carbanions $\mathbf{A^1}$ (*b*), allyl rearrangement in carbanions $\mathbf{A^1}$, resulting in the formation of [(3-chloroprop-1-en-1-yl)-chalcogenyl]benzenes **4** (*c*), fast replacement of the chlorine in the allyl position of compounds **4** to give (propene-1,3-diyldichalcogenanediyl)dibenzenes **5** (*d*) (Scheme 2).

In keeping with Scheme 2 the possibility of conversion **3**→**5** is governed by the occurrence of the allyl rearrangement (stages *b, c*), which in its turn depends on the rate of deprotonation of compounds **3** and on the stability of anion $\mathbf{A^1}$, whose structure may be represented as a resonance hybrid of anion forms $\mathbf{A^2}$ and $\mathbf{A^3}$. The deprotonation rate of compound **3** depends on the alkali concentration in the system (on the ratio R_2Y_2–KOH) and on the reaction temperature.

The selective formation of compound **3a** from thiolate **2a** (allyl rearrangement is absent) occurs only at 0°C (ratio Ph_2S_2–KOH 1 : 5, yield of compound **3a** 82%). However already at 25–35°C thiolate **2a** in the reaction with 1,3-dichloropropene **1** (Ph_2S_2–KOH, 1 : 5) forms a mixture of compounds **3a** and **5a** in a ratio 1 : 6 (yield of compound **5a** 67%). At the same temperature but at higher alkali concentration (Ph_2S_2–KOH, 1 : 10) the reaction product is exclusively 1,3-bis(phenylsulfanyl) propene derivative **5a** (yield 63%). At the ratio Ph_2S_2–KOH 1 : 5 the selective formation of compound **5a** (yield 62%) occurs at 60°C.

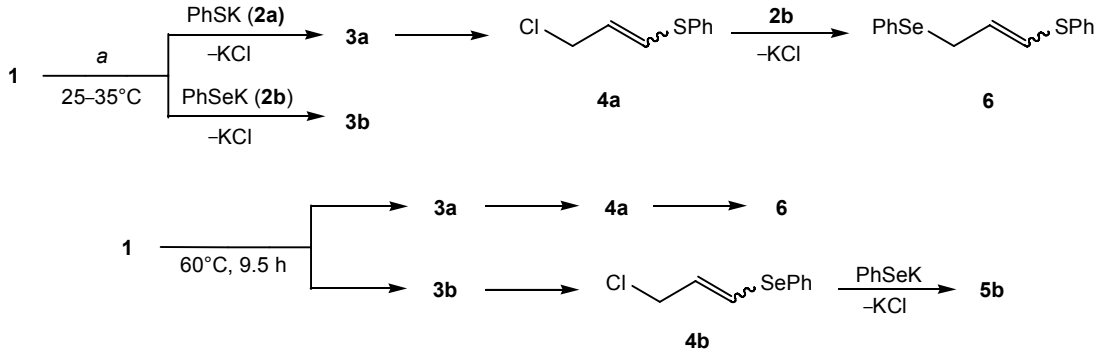
At the use of reagents **2b–2d** even at 25–35°C only the first stage of the reaction presented in Scheme 2

Scheme 2.



R = Ph, Y = S (**a**), Se (**b**), Te (**c**); R = Bn, Y = S (**d**).

Scheme 3.



occurs with the formation compounds **3b–3d** in 92, 68, 37% yields respectively. These results are well consistent with the data of [11, 12], where it has been demonstrated that the substituent PhS is the most efficient stabilizer of the adjacent carbanion site.

The increase in the temperature to 60°C makes it possible to obtain from 1,3-dichloropropene **1** and selenolate **2b** 1,3-bis(phenylselanyl) propene derivative (76%), and from thiolate **2d**, 1,3-bis(benzylsulfanyl) propene derivative (68%). Diphenyl ditelluride at this temperature affords a complex mixture of substances.

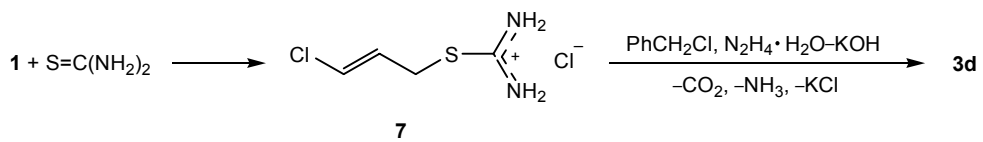
At simultaneous bringing into the reaction with 1,3-dichloropropene **1** two chalcogenolates **2a** and **2b** (25–35°C) compounds **3b** and **6** formed in the molar ratio 4.2 : 1.0 in 60 and 27% yields respectively calculated with respect to the reacted Ph_2Se_2 (^{1}H NMR data). Apparently under the reaction conditions 1,3-dichloropropene **1** in the stage *a* reacts predominantly with phenylselenolate **2b** and somewhat less effectively with thiolate **2a**. Yet the formed compounds **3a** and 3**b** behave further differently: compound **3b** does not undergo the allyl rearrangement and remains unchanged in the system, whereas sulfide **3a** isomerizes (stage *b*) into compound **4a** that quickly reacts prevailingly with PhSeK **2b** (Scheme 3).

At carrying out this concurrent reaction at 60°C (9.5 h) also a mixture formed of two compounds: bisselenide **5b** (yield 27%) and mixed chalcogenide **6** (yield 32%). Obviously in these conditions the both intermediate compounds **3a** and **3b** underwent the allyl rearrangement, and both isomerization products **4a** and **4b** reacted with selenolate **2b** (Scheme 3).

In the reactions represented in Schemes 2, 3 commercial 1,3-dichloropropene **1** was used composed of *E*- and *Z*-isomers with a small excess of *E*-isomer [*E*/*Z* (1.0–1.15) : 1.0, ^{1}H NMR data]. Compounds **3**, **5**, and **6** also are composed of the corresponding *E*- and *Z*-isomers with the prevalence of the *E*-isomer [*E*/*Z* (1.05–1.50) : 1.0], in agreement with the higher thermodynamic stability of *E*-isomers. Compounds of this type are not described in the literature. In [14] from *E*-1,3-dichloropropene was obtained only *E*-isomer of compound **3d** isolated by column chromatography.

The selective formation of compounds **3a–3c** (Scheme 2) makes it possible to regard them as initial compounds for the preparation of propene-1,3-diylbischalcogenides **5** and **6**. The independent occurrence of these reactions confirms the assumed mechanism of compounds **5** and **6** formation from 1,3-dichloropropene **1** (Scheme 2), provides a possibility to synthesize 1,3-dichalcogenyl propene derivatives with diverse chalcogenyl substituents and to acquire additional information on the effect of the substituent nature on the course of the allyl rearrangement. Compounds **3** with a single chalcogenyl fragment may be used in the organic synthesis, for instance, for the preparation of sulfonium methylides and a wide range of unsaturated structures based on them [15].

Scheme 4.



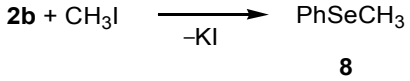
Compound **3c** formed with the smallest yield apparently because of the well-known instability of organotellurium compounds [16].

Since benzylsulfanyl derivative of chloropropene **3d** is also isolated in a low yield (68%), and its *E*-isomer is obtained from phenylmethanethiol, *E*-1,3-dichloropropene, and trimethylamine in ether (25°C, 12 h) in 52% yield [15], we have developed an alternative method of preparation of compound **3d** using isothiouronium salts with organic residue sensitive to the action of bases [17].

Isothiouronium salt **7** prepared from 1,3-dichloropropene **1** and thiourea was treated with benzyl chloride gradually adding the basic redox mixture $N_2H_4 \cdot H_2O$–KOH (Scheme 4). By this procedure compound **3d** was obtained in 87% yield.

In reaction of chlorosulfide **3a** with Ph_2Se_2 (25–35°C, Ph_2Se_2–KOH, 1 : 5, 5 h) compound **6** was obtained, yet the conversion of initial **3a** was only 47%, and the yield of mixed chalcogenide **6** was 74% (calculated with respect to reacted Ph_2Se_2) with a significant prevalence of *E*-isomer (*E*/*Z* 11.6 : 1.0). The increase in the temperature of the reaction between chlorosulfide **3a** and selenolate **2b** to 60°C (Ph_2Se_2–KOH, 1 : 5, 5 h) resulted in the formation of compound **6** in 81% yield (*E*/*Z* 1.9 : 1.0). At increased quantity of KOH (Ph_2Se_2–KOH 1 : 10) at 10–20°C (4 h) the conversion of compounds **3** (50%) and the yield of compound **6** (81% calculated with respect to reacted Ph_2Se_2) somewhat increased. The ratio of *E*- and *Z*-isomers of compound **6** under these conditions was 4.3 : 1.0. The conversion of Ph_2Se_2 was estimated by treating with methyl iodide the water-hydrazine layer remaining after extraction of compounds **3a** and **6** with dichloromethane and ether. Selenolate **2b** present in the water-hydrazine layer at methylation formed selenoanisole **8** (Scheme 5), the yield of which was used to calculate the quantity of PhSeK unreacted with chlorosulfide **3a**.

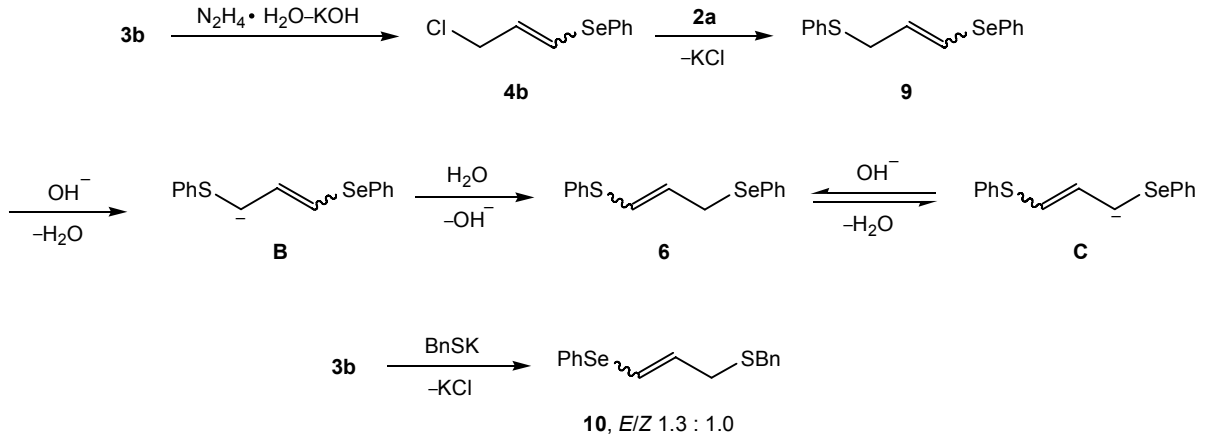
Scheme 5.



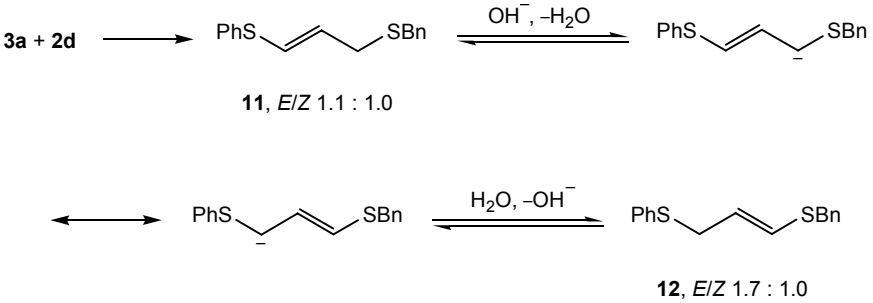
Chloroselenide **3b** at 25–35°C did not react with Ph_2S_2, and at 60°C (Ph_2S_2–KOH, 1 : 5, 10 h) it formed compound **6** in 72% yield (*E*/*Z* 1.3 : 1.0). In keeping with Scheme 2 the reaction product should be compound **9**, yet it was not found in the reaction mixture. Probably its formation along Scheme 3 is accompanied with allyl rearrangement proceeding through carbanion **B** stabilized with adjacent moiety PhS (Scheme 6). The reverse rearrangement **6**→**9** is less probable since carbanion **C** arising from compound **6** is located near the group PhSe which stabilizes the anion site less efficiently than the PhS group.

In the reaction of chloroselenide **3b** with thiolate **2d** (60°C, Bn_2S_2–KOH, 1 : 10, 10 h) the main reaction product (yield 63%) was mixed chalcogenide **10** (Scheme 6), whose structure was well consistent with the general Scheme 2 of the formation of compound **5**. Compound **10** was obtained in 22% yield in simultaneous reaction of Ph_2Se_2 and Bn_2S_2 with 1,3-dichloropropene **1** [60°C, 10 h, Ph_2Se_2–Bn_2S_2, 1 : 1, (Ph_2S_2 + Bn_2S_2)–KOH, 1 : 5]. The main reaction product was bisselenide **5b** (yield 45 %) that showed the higher reactivity of $PhSe^-$ anions compared with BnS^- anions.

Scheme 6.



Scheme 7.



In analogous conditions chlorosulfide **3a** with thiolate **2d** afforded a mixture of two compounds: that expected in conformity to Scheme 2 [3-(benzylsulfanyl)prop-1-en-1-yl]sulfanylbenzene **11** and the product of its allyl rearrangement **12** in ~1 : 1 ratio; each compound was a mixture of *E*- and *Z*-isomers, 1.1 : 1.0 (**11**), 1.7 : 1.0 (**12**). The overall yield of the mixture of compounds **11** and **12** was 76%. The possibility of the partial isomerization **11**→**12** is due to nearly equal stabilization of the carbanion site with the groups PhS and BnS (Scheme 7), yet in the reaction with 1,4-dichlorobut-2-yne [13] more efficient stabilization of carbanion with PhS is observed.

The attempt to prepare compounds **11** and **12** by the simultaneous reaction of Ph_2S_2 and Bn_2S_2 [60°C, 9 h, (Ph_2S_2 + Bn_2S_2)–KOH, 1 : 5] resulted in the formation of a complex mixture of substances where compounds (*E*,*Z*)-**11** and (*E*,*Z*)-**12** were detected by ^{1}H NMR spectroscopy. In the reaction of chlorosulfide **3d** with thiolate **2a** (Ph_2S_2–KOH, 1 : 10, 60°C, 10 h) a complex mixture of nonidentifiable substances was obtained.

Thus the reactions of 1,3-dichloropropene with diphenyl and dibenzyl dichalcogenides in the system hydrazine hydrate–KOH provide versatile unsaturated organic chalcogenides. The key stage of compounds formation containing two chalcogen atoms is the allyl rearrangement that most efficiently occurs in the case of PhS substituent, then BnS, and PhSe. Among the studied anions the highest reactivity is demonstrated by $PhSe^-$.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Bruker IFS-25 from thin films. ^{1}H, ^{13}C, ^{77}Se, ^{125}Te NMR spectra were registered on a spectrometer Bruker DPX-400 (400.13, 100.62, 76.31, and 126.2 MHz respectively) in $CDCl_3$, internal reference TMS (^{1}H, ^{13}C), Me_2Se (^{77}Se), $(CH_3)_2Te$ (^{125}Te). Mass spectra were measured on an GC-MS instrument Shimadzu GCMS–QP5050A (column SPB-5, 60000 × 0.25 mm), quadrupole mass analyzer, electron impact, 70 eV, temperature of ion source 190°C, range of detected masses 34–650 Da.

The monitoring of reaction progress and the analysis of liquid substances was carried out on a chromatograph LKhM 80-MD-2 (column 2000 × 3 mm, liquid phase DC-550, 5% on carrier Chromaton N-AW-HMDS, linear programming of temperature at the heating rate 12 deg/min, carrier gas helium).

1,3-Dichloropropene **1** was distilled prior to use. Due to the considerable difference in boiling points of isomers of compound **1** [112°C (*E*), 104.3°C (*Z*)] [18] in different distillation conditions fractions were obtained with various isomer ratio (^{1}H NMR data) with the prevalence of *E*-isomer.

Reactions of diphenyl and dibenzyl dichalcogenides R_2Y_2 with 1,3-dichloropropene. General procedure. To a solution of a calculated quantity of potassium hydroxide in hydrazine hydrate corresponding to the necessary ratio R_2Y_2–KOH was added R_2Y_2. The obtained mixture was heated at stirring for 2 h at 80–85°C, then it was cooled to desired temperature (0, 25, or 60°C) and 1,3-dichloropropene **1** was added dropwise. The reaction mixture was stirred at the temperature of the experiment for 4–21 h. The reaction products were extracted with CH_2Cl_2 (2 × 30–50 mL) and ethyl ether (2 × 30–50 mL). The combined extracts were dried with $MgSO_4$. The solvent was distilled off, the residue was studied by NMR, IR, and GC-MS spectroscopy, and subjected to further workup.

Compounds **3a**, **3b**, **3d**, **5a**, **5b**, **5d**, **6**, and **10** were obtained as mixtures of *E*- and *Z*-isomers. The other compounds were identified by ^{1}H, ^{13}C, ^{77}Se, and ^{125}Te NMR

spectroscopy in mixtures with the other reaction products. The attempts at vacuum distillation (1–2 mmHg) resulted in a fast decomposition of the mixtures components.

Anions **2a** and/or **2b** in water-hydrazine layer conserved after reaction products extraction were determined by converting them in thioanisole or selenoanisole by treating with methyl iodide [19].

[(3-Chloroprop-2-en-1-yl)sulfanyl]benzene (3a) was obtained from 8 g (0.037 mol) of Ph_2S_2, 10.36 g (0.185 mol) of KOH, 8.2 g (0.074 mol) dichloropropene **1** in 50 mL of hydrazine hydrate (from 0 to –3°C, 10 h). Yield 82% (*E*/*Z* 1.15 : 1.0). Colorless liquid, bp 98–100°C (2 mmHg) {132°C (3 mmHg) [6], 79–80°C (1 mmHg) [20]}. IR spectrum, ν, cm^{-1}: 1624 (C=C).

E-Isomer. ^1H NMR spectrum, δ, ppm: 3.45 m (2H, CH_2S), 5.93 m (2H, CH=CH), 7.19–7.35 m (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 34.86 (CH_2S), 120.36 (=CHCl), 126.96 (C^p), 128.97 (=$\underline{C}HCH_2$), 129.00 (C^o), 130.85 (C^m), 134.82 (C^i).

Z-Isomer. ^1H NMR spectrum, δ, ppm: 3.68 d.d (2H, SCH_2, ^2J 7.0, ^4J 1.2 Hz), 5.83 d.t (1H, =C$\underline{H}CH_2$, ^3J 7.0, J_{cis} 7.0 Hz), 6.06 d.t (1H, =CHCl, J_{cis} 7.0, ^4J 1.2 Hz), 7.19–7.35 m (5H, C_6H_5). Mass spectrum, *m/z*: 186 $[M]^+$ (^{37}Cl) and 184 $[M]^+$ (^{37}Cl). Found, %: C 58.78; H 4.93; Cl 19.06; S 17.40. C_9H_9ClS. Calculated, %: C 58.53; H 4.91; Cl 19.20; S 17.39.

[(3-Chloroprop-2-en-1-yl)selanyl]benzene (3b) was obtained from 2.2 g (0.007 mol) of Ph_2Se_2, 1.98 g (0.035 mol) of KOH in 9 mL of hydrazine hydrate and 0.782 g (0.007 mol) of 1,3-dichloropropene **1** at 25°C (2.5 h) and 30–35°C (2 h). Yield 92%, light-yellow liquid. Conversion of Ph_2Se_2 was estimated by the formation of selenoanisole **8** (0.9 g), 63%. Yield of compound **3b** calculated with respect to reacted Ph_2Se_2 87%, *E*/*Z* 1.06 : 1.0. IR spectrum, ν, cm^1: 1620 (C=C). At 25°C and the ratio Ph_2Se_2–**1** 1 : 2 yield of compound **3b** 91% at a complete conversion of Ph_2Se_2.

E-Isomer. ^1H NMR spectrum, δ, ppm: 3.39 d (2H, CH_2Se, ^3J 8.1 Hz), 5.76 d (1H, =CHCl, J_{trans} 13.2 Hz), 5.99 d.t (1H, =C$\underline{H}CH_2$, ^3J 8.1, J_{trans} 13.2 Hz), 7.23–7.50 m (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 27.47 (CH_2Se, $^1J_{CSe}$ 60.0 Hz), 120.05 (=CHCl), 127.71 (C^p), 129.00 (C^o), 129.80 (=$CHCH_2$), 131.79 (C^i), 134.19 (C^m). ^{77}Se NMR spectrum, δ, ppm: 346.3.

Z-Isomer. ^1H NMR spectrum, δ, ppm: 3.64 d (2H, CH_2Se, ^3J 7.7 Hz), 5.91 d.t (1H, =C$\underline{H}CH_2$, J_{cis} 7.1, ^3J 7.7 Hz), 5.97 d (1H, =CHCl, J_{cis} 7.1 Hz), 7.23 m (3H, $H^{p,m}$, C_6H_5), 7.46, 7.50 m (2H, H^o). ^{13}C NMR spectrum, δ, ppm: 22.99 (CH_2Se, $^1J_{CSe}$ 59.7 Hz), 119.30 (=CHCl), 127.38 (C^p), 128.18 (=$\underline{C}HCH_2$), 129.07 (C^o), 133.23 (C^i), 133.54 (C^m). ^{77}Se NMR spectrum, δ, ppm: 340.7. At GC-MS study two peaks are observed on the chromatogram that in the mass spectra correspond to clusters of molecular ions, *m/z* 232 $[M]^+$ (^{35}Cl, ^{80}Se). Found, %: C 46.24; H 3.99; Cl 14.86; Se 33.65. C_9H_9ClSe. Calculated, %: C 46.68; H 3.92; Cl 15.31; Se 34.09.

[(3-Chloroprop-2-en-1-yl)tellanyl]benzene (3c). In the reaction of 2.0 g (0.0049 mol) of Ph_2Te_2 with 1.08 g (0.01 mol) of dichloropropene **1**, 1.37 g (0.0244 mol) of KOH in 6 mL of hydrazine hydrate (2.5 h at 25°C, 2 h at 30–35°C) we obtained 2.38 g of dark red liquid containing according to ^1H and ^{125}Te NMR data Ph_2Te_2 and compound **3c** in a molar ratio 1 : 1. Yield 38% with respect to 1,3-dichloropropene **1** brought into reaction. According to NMR data a mixture of *E*- and *Z*-isomers, 2.5 : 1.0, yet in the mixture with diphenyl ditelluride it was impossible to identify the isomers. IR spectrum, ν, cm^{-1}: 1617 (C=C) (the absorption bands of nearly the same intensity were present at 1656 and 1680 cm^{-1}, which were not identified). ^1H NMR spectrum, δ, ppm: 3.44 m, 3.68 m (CH_2Te), 5.83 m, 5.99 m (CH=), 7.11–7.73 m (C_6H_5). ^{13}C NMR spectrum, δ, ppm: 2.88, 6.96 (CH_2Te), 117.61, 118.85 (=CHCl), 128.02, 129.21 (C^m), 128.25, 129.73 (C^p), 131.58, 139.67 (=$\underline{C}HCH_2$), 137.63, 139.37 (C^o), 129.73, 139.77 (C^i). ^{125}Te NMR spectrum, δ, ppm: 421.77 (Ph_2Te_2) [21], 596.29, 597.64 (intensity ratio 2.5 : 1).

We failed to obtain the mass spectrum of compound **3c** because of its complete decomposition in the chromatographic column of mass spectrometer.

{[(3-Chloroprop-2-en-1-yl)sulfanyl]methyl}benzene (3d). *a*. was obtained from 6.0 g (0.0244 mol) of Bn_2S_2, 6.84 g (0.122 mol) of KOH, 30 mL of hydrazine hydrate, and 5.42 g (0.0488 mol) of dichloropropene **1** (2.5 h at 25°C and 2 h at 30–35°C). Yield 68%, bp 114–116°C (2 mmHg). Colorless liquid, mixture of *E*- and *Z*-isomers, 1.1 : 1.0. IR spectrum, ν, cm^{-1}: 1624 s, 1602 w (C=C).

E-isomer. ^1H NMR spectrum, δ, ppm: 2.91 d.d (2H, SCH_2C=, ^3J 7.3, ^4J 0.9 Hz), 3.60 s (2H, SCH_2Ph), 5.84 d.t (1H, =C$\underline{H}CH_2$, ^3J 7.3, J_{trans} 13.2 Hz), 5.92 d.t (1H, =CHCl, J_{trans} 13.2, ^4J 0.9 Hz), 7.08–7.29 m (5H, C_6H_5) (cf. [9]). ^{13}C NMR spectrum, δ, ppm: 30.88 ($S\underline{C}H_2CH$=), 35.09 (SCH_2Ph), 119.73 (=CHCl), 127.06

(C^p), 128.51 (C^o), 128.90 (C^m), 129.64 (=<u>C</u>HCH$_2$), 137.69 (C^i).

Z-Isomer. ^{1}H NMR spectrum, δ, ppm: 3.19 d.d (2H, SCH$_2$C=, ^3J 7.5, ^4J 1.2 Hz), 3.64 s (2H, SCH$_2$Ph), 5.76 d.t (1H, =C<u>H</u>CH$_2$, ^3J 7.5, J_{cis} 7.2 Hz), 6.06 d.t (1H, =CHCl, J_{cis} 7.2, ^4J 1.2 Hz), 7.08–7.29 m (5H, C$_6$H$_5$). ^{13}C NMR spectrum, δ, ppm: 27.59 (S<u>C</u>H$_2$CH=), 35.75 (SCH$_2$Ph), 120.02 (=CHCl), 126.99 (C^p), 128.30 (=<u>C</u>HCH$_2$), 128.42 (C^o), 128.90 (C^m), 138.02 (C^i). In mass spectra of each isomer to the molecular ion correspond values of *m/z* 198 [M]$^+$ (^{35}Cl), 200 [M]$^+$ (^{37}Cl). Found, %: C 60.88; H 5.48; Cl 17.52; S 15.64. C$_{10}$H$_{11}$ClS. Calculated, %: C 60.44; H 5.58; Cl 17.84; S 16.13.

b. From 1.25 g (0.0067 mol) of isothiouronium salt **7** (prepared by procedure [22]), 0.85 g (0.0067 mol) of benzyl chloride, 0.75 g (0.0134 mol) of KOH, and 3 mL of hydrazine hydrate under the conditions described in [17]. Yield 87% (*E*/*Z* ~1 : 1). The spectral characteristics and elemental analysis data totally coincide with those mentioned above.

(Propene-1,3-diyldisulfandiyl)dibenzene (5a) was obtained from 4.0 g (0.0180 mol) of Ph$_2$S$_2$, 10.27 g (0.183 mol) of KOH, 2.0 g (0.0180 mol) of dichloropropene **1** in 45 mL of hydrazine hydrate. Yield 63%, bp 177–179°C (2 mmHg) {192–198°C (3.2 mmHg) [9]}, *E*/*Z* 1.5 : 1.0. IR spectrum, ν, cm^{-1}: 1606 w, 1583 s (C=C).

E-Isomer. ^{1}H NMR spectrum, δ, ppm: 3.54 d.d (2H, SCH$_2$, ^3J 7.2, ^4J 0.9 Hz), 5.86 d.t (1H, =C<u>H</u>CH$_2$, ^3J 7.2, J_{trans} 14.8 Hz), 6.11 d.t (1H, =CHSPh, J_{trans} 14.8, ^4J 0.9 Hz), 7.05–7.36 m (10H, C$_6$H$_5$). ^{13}C NMR spectrum, δ, ppm: 36.80 (SCH$_2$), 126.39, 126.61** (C^p), 127.72, 128.89** (C^i), 130.90, 129.07** (C^o), 128.83, 129.00** (C^m), 128.81 (=<u>C</u>HCH$_2$), 128.89 (=CHS).

Z-Isomer, ^{1}H NMR spectrum: 3.73 d.d (2H, SCH$_2$, ^3J 7.5, ^4J 0.7 Hz), 5.83 d.t (1H, =C<u>H</u>CH$_2$, ^3J 7.5, J_{cis} 9.2 Hz), 6.25 d.t (1H, =CHSPh, J_{cis} 9.2, ^4J 0.7 Hz), 7.05–7.36 m (10H, C$_6$H$_5$). ^{13}C NMR spectrum, δ, ppm: 31.95 (SCH$_2$), 125.53, 126.08** (C^p), 128.10, 129.62** (C^m), 128.72, 129.03** (C^o), 130.70, 127.51** (C^i), 126.48 (=<u>C</u>HCH$_2$), 129.01 (=CHS). In the mass spectra of both isomers molecular ion is observed, *m/z* 258. Found, %: C 70.09; H 5.44; S 24.81. C$_{15}$H$_{14}$S$_2$. Calculated, %: C 69.72; H 5.46; S 24.81.

** First the chemical shift of PhS at CH$_2$ is given, then of PhS at the double bond.

(Propene-1,3-diyldiselandiyl)dibenzene (5b) was obtained from 2.2 g (0.007 mol) of Ph$_2$Se$_2$, 1.98 g (0.035 mol) of KOH, 10 mL of hydrazine hydrate, and 0.78 g (0.007 mol) of 1,3-dichloropropene **1** (60°C, 19 h). After evaporation of solvents yield 76%, mixture of *E*- and *Z*-isomers, 1.25 : 1.0, yellow liquid, bp 120°C (0.12 mmHg) [8]. At the residual pressure 1–2 mmHg the substance suffers fast decomposition. IR spectrum, ν, cm^{-1}: 1599 w, 1578 s (C=C).

E-Isomer. ^{1}H NMR spectrum, δ, ppm: 3.50 d (2H, CH$_2$Se, ^3J 7.8 Hz), 6.06 d.t (1H, =C<u>H</u>CH$_2$, ^3J 7.8, J_{trans} 15.0 Hz), 6.23 d (1H, =CHSe, J_{trans} 15.0 Hz), 7.17–7.48 m (10H, C$_6$H$_5$) [8, 10]. ^{13}C NMR spectrum, δ, ppm: 30.96 (SeCH$_2$, $^1J_{CSe}$ 58.9 Hz), 120.14 (=CHSe). The rest of signals were not attributed to *E*- and *Z*-isomers. ^{77}Se NMR spectrum, δ, ppm: 345.5 (SeCH$_2$), 376.2 (SeCH=).

Z-Isomer. ^{1}H NMR spectrum, δ, ppm: 3.67 d (2H, CH$_2$Se, ^3J 7.8 Hz), 6.19 d.t (1H, =C<u>H</u>CH$_2$, J_{cis} 8.9, ^3J 7.8 Hz), 6.46 d (1H, =CHSe, J_{cis} 8.9 Hz), 7.17–7.48 m (10H, C$_6$H$_5$). ^{13}C NMR spectrum, δ, ppm: 27.44 (SeCH$_2$, $^1J_{CSe}$ 58.5 Hz), 123.66 (=CHSe). ^{77}Se NMR spectrum, δ, ppm: 327.1 (SeCH=), 343.8 (SeCH$_2$).

[Propene-1,3-diyl(bissulfandiylmethylene)]dibenzene (5c) was obtained from 2.46 g (0.01 mol) of Bn$_2$S$_2$, 2.81 g (0.05 mol) of KOH, 12 mL of hydrazine hydrate, and 1.11 g (0.01 mol) of dichloropropene **1** (60°C, 21 h). Mixture of *E*- and *Z*-isomers, 0.9 : 1.0, yield 58%. IR spectrum, ν, cm^{-1}: 1602 (C=C).

E-Isomer. ^{1}H NMR spectrum, δ, ppm: 2.96 d (2H, =CHC<u>H</u>$_2$S, ^3J 7.6 Hz), 3.50 s (2H, SCH$_2$Ph), 3.82 s (2H, SCH$_2$Ph), 5.52 d.t (1H, =C<u>H</u>CH$_2$S, ^3J 7.6, J_{trans} 14.9 Hz), 5.94 d (1H, =CHS, J_{trans} 14.9 Hz), 7.13–7.28 m (10H, C$_6$H$_5$). The signals in ^{13}C NMR spectrum of the isomers mixture were not unambiguously identified.

Z-Isomer. ^{1}H NMR spectrum, δ, ppm: 3.12 d (2H, =CHC<u>H</u>$_2$S, ^3J 7.5 Hz), 3.55 s (2H, SCH$_2$Ph), 3.82 s (2H, SCH$_2$Ph), 5.57 d.t (1H, =C<u>H</u>CH$_2$S, ^3J 7.5, J_{cis} 9.4 Hz), 6.05 d (1H, =CHS, J_{cis} 9.4 Hz), 7.13–7.28 m (10H, C$_6$H$_5$). Found, %: C 70.83; H 6.18; S 22.58. C$_{17}$H$_{18}$S$_2$. Calculated, %: C 71.28; H 6.33; S 22.38.

[3-(Phenylselanyl)prop-1-en-1-ylsulfanyl]benzene (6) *a*. was obtained from 1.18 g (0.0064 mol) of compound **3a**, 1.0 g (0.0032 mol) Ph$_2$Se$_2$, 1.8 g (0.032 mol) of KOH, (Ph$_2$Se$_2$–KOH 1 : 10) in 8 mL of hydrazine hydrate (10–20°C, 4 h), mixture of *E*- and *Z*-isomers, 4.3 : 1.0. Conversion of compound **3a** 60%, conversion of Ph$_2$Se$_2$ 47%. Yield 78% calculated with

respect to the reacted chloride **3a**, 98% calculated with respect to the reacted Ph_2Se_2. In 2.5 h at 20°C and 2 h at 30–35°C yield 74% calculated with respect to the reacted Ph_2Se_2. Conversion of Ph_2Se_2 68%, conversion of chloride **3a** 47%. Virtually complete conversion of compound **3a** was obtained at 60°C in 5 h, yield 81% calculated with respect to the Ph_2Se_2 taken in the reaction, the ratio of *E*- and *Z*-isomers 1.9 : 1.0). Isomers characterized in the mixture with unreacted chloride **3a**. IR spectrum, ν, cm^{-1}: 1601 w, 1580 s (C=C). Found, %: C 59.08; H 4.70; Se 25.96. $C_{15}H_{14}SSe$. Calculated, %: C 59.01; H 4.62; Se 25.86.

E-Isomer. ^{1}H NMR spectrum, δ, ppm: 3.51 d (2H, $C\underline{H}_2SePh$, ^3J 3.4 Hz), 5.93 d.t (1H, =$C\underline{H}CH_2$, ^3J 3.4, J_{trans} 14.4 Hz), 5.91 d (1H, =CHS, J_{trans} 14.4 Hz), 7.00–7.46 m (10H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 20.98 (CH_2Se, $^1J_{CSe}$ 58.9 Hz), the rest of signals were not unambiguously identified. ^{77}Se NMR spectrum, δ, ppm: 348.8.

Z-Isomer. ^{1}H NMR spectrum, δ, ppm: 3.65 d (2H, CH_2Se, ^3J 6.8 Hz), 5.92 d (1H, =$C\underline{H}CH_2Se$, ^3J 6.8, J_{cis} 7.9 Hz), 6.15 d.t (1H, =CHS, ^3J 6.8, J_{cis} 7.9 Hz), 7.00–7.46 m (10H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 25.27 ($SeCH_2$, $^1J_{CSe}$ 58.9 Hz). ^{77}Se NMR spectrum, δ, ppm: 345.5.

b. The compound was obtained from 1.5 g (0.0065 mol) of compound **3b**, 0.71 g (0.00325 mol) of Ph_2S_2 in the presence of 1.82 g (0.0325 mol) of KOH and 8 mL of hydrazine hydrate. Yield 72%, mixture of *E*- and *Z*-isomers, 1.3 : 1.0. Spectral characteristics are fully identical to those mentioned above.

c. The compound was obtained from 1.42 g (0.0128 mol) of compounds **1**, 1.4 g (0.0064 mol) of Ph_2S_2, and 2.0 g (0.0064 mol) of Ph_2Se_2 in 2.5 h at 25°C and 2 h at 30–35°C. Dichalcogenides were separately reduced in the system of 1.8 g (0.032 mol) of KOH and 8 mL of hydrazine hydrate, the solutions were combined and brought into the reaction with dichloropropene **1**. Conversion of Ph_2Se_2 87%, conversion of Ph_2S_2 66%. Yield of compound **6** 27% (calculated with respect to reacted Ph_2Se_2); compound **3b** was obtained in 60% yield (calculated with respect to reacted Ph_2Se_2). Spectral characteristics of compounds **6** and **3b** are fully identical to those mentioned above.

At 60°C (9.5 h) at virtually complete conversion of Ph_2Se_2 (97%) a mixture was formed of compound **6** (*E*/*Z* ~1.0 : 1.0) (yield 32% with respect to dichloropropene **1** taken in the reaction) and compound **5b** (*E*/*Z* ~1.0 : 1.0) (yield 27%). Spectral characteristics of compounds **6** and **5b** are fully identical to those mentioned above.

[3-(Benzylsulfanyl)prop-1-en-1-ylselanyl]benzene (10) *a*. was obtained from 1.1 g (0.0048 mol) of compound 3b and 0.59 g (0.0024 mol) of dibenzyl disulfide in 6 mL of hydrazine hydrate, and 1.34 g (0.024 mol) of KOH (60°C, 10 h). Yield 80% (*E*/*Z* 1.3 : 1.0). Light-yellow liquid. IR spectrum, ν, cm^{-1}: 1600 m, 1579 m (C=C). Found, %: C 60.00; H 5.14; S 10.47; Se 24.29. $C_{16}H_{16}SSe$. Calculated, %: C 60.18; H 5.05; S 10.04; Se 24.73.

E-Isomer. ^{1}H NMR spectrum, δ, ppm: 3.45 d (2H, =CCH_2S, ^3J 7.6 Hz), 3.72 s (2H, SCH_2Ph), 5.67 d.t (1H, =$C\underline{H}CH_2$, ^3J 7.6, J_{trans} 14.8 Hz), 5.80 d (1H, =CHSe, J_{trans} 14.8 Hz), 7.16–7.461 m (10H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 25.56 ($S\underline{C}H_2CH$=), 37.94 (SCH_2Ph), 125.94 (=$\underline{C}HCH_2$), 127.08 (=CHSe), 127.20, 126.95 (C^p), 128.88, 128.79 (C^m), 133.15, 128.54 (C^o), 132.64, 137.63 (C^i). ^{77}Se NMR spectrum, δ, ppm: 340.2.

Z-Isomer. ^{1}H NMR spectrum, δ, ppm: 3.60 d (2H, =$CHC\underline{H}_2S$, ^3J 8.1 Hz), 3.74 s (2H, SCH_2Ph), 5.69 d.t (1H, =$C\underline{H}CH_2$, ^3J 8.1, J_{cis} 9.3 Hz), 5.93 d (1H, =CHSe, J_{cis} 9.3 Hz), 7.16–7.47 m (10H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 30.32 ($S\underline{C}H_2CH$=), 37.09 (SCH_2Ph), 125.13 (=$\underline{C}HCH_2$), 125.93 (=CHSe), 127.29, 127.15 (C^p), 128.72, 128.51 (C^m), 133.91, 128.90 (C^o), 132.87, 137.22 (C^i). ^{77}Se NMR spectrum, δ, ppm: 347.2.

b. The compound was obtained from 1.08 g (0.0027 mol) of compound **3c** and 0.84 g (0.0027 mol) of Ph_2Se_2 in the presence of 1.51 g (0.027 mol) of KOH and 7 mL of hydrazine hydrate (60°C, 10 h). Yield 65%, the ratio of *E*- and *Z*-isomers 1.3 : 1.0. Spectral characteristics are fully identical to those mentioned above.

[3-(Benzylsulfanyl)prop-1-en-1-ylsulfanyl]benzene (11) and [3-(benzylsulfanyl)prop-2-en-1-ylsulfanyl]benzene (12) (1 : 1) were obtained in an overall yield 76% from 1.2 g (0.0065 mol) of compound **3a**, 0.8 g (0.00325 mol) of Bn_2S_2, 1.82 g (0.0325 mol) of KOH in 8 mL of hydrazine hydrate (60°C, 9.5 h). The ratios of *E*- and *Z*-isomers are given in the main text.

E-Isomer of compound **11**. ^{1}H NMR spectrum, δ, ppm: 3.06 d.d (2H, =$CHC\underline{H}_2$, ^3J 7.5, ^4J 1.1 Hz), 3.75 s (2H, CH_2Ph), 5.79 d.t (1H, =$C\underline{H}CH_2$, ^3J 7.5, J_{trans} 14.9 Hz), 6.18 d.t (1H, =CHS, ^4J 1.1, J_{trans} 14.9 Hz), 7.14–7.28 m (10H, C_6H_5).

Z-Isomer of compound **11**. ^{1}H NMR spectrum, δ, ppm: 3.26 d.d (2H, =CHC<u>H</u>$_2$, ^3J 7.5, ^4J 1.0 Hz), 3.70 s (2H, CH_2Ph), 5.80 d.t (1H, =C<u>H</u>CH_2, ^3J 7.5, J_{cis} 9.2 Hz), 6.31 d.t (1H, =CHS, J_{cis} 9.2, ^4J 1.0 Hz).

E-Isomer of compound **12**. ^{1}H NMR spectrum, δ, ppm: 3.47 d.d (2H, =CHC<u>H</u>$_2$, ^3J 7.2, ^4J 1.1 Hz), 3.65 s (2H, SCH_2Ph), 5.60 d.t (1H, =C<u>H</u>CH_2, ^3J 7.2, J_{trans} 15.0 Hz), 5.97 d.t (1H, =CHS, J_{trans} 15.0, ^4J 1.1 Hz).

Z-Isomer of compound **12**. ^{1}H NMR spectrum, δ, ppm: 3.59 d.d (2H, =CHC<u>H</u>$_2$, ^3J 7.3, ^4J 1.1 Hz), 3.77 s (2H, SCH_2Ph), 5.60 d.t (1H, =C<u>H</u>CH_2, ^3J 7.3, J_{cis} 9.3 Hz), 6.01 d.t (1H, =CHS, J_{cis} 9.3, ^4J 1.1 Hz). ^{13}C NMR spectrum of the mixture was impossible to unambiguously interpret.

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