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New Approaches to Synthesis of Unsaturated Organochalcogen Compounds with Two Different Chalcogen Atoms

E. P. Levanova, V. S. Vakhrina, V. A. Grabel'nykh, I. B. Rozentsveig, N. V. Russavskaya, A. I. Albanov, E. R. Sanzheeva, and N. A. Korchevin

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: venk@irioch.irk.ru

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Abstract—Two approaches to synthesis of bis-chalcogenyl derivatives of propene with two different chalcogen atoms are proposed. Reaction of 2,3-dichloro-1-propene with two different chalcogen nucleophiles PhY^- (Y = S, Se) results in a mixture of two products with two identical chalcogen atoms and two products with different ones. The reactivity of PhY^- anions under the reaction conditions (60°C) practically does not depend on the Y nature. Reaction of anions RY^- (Y = S, Se, Te) with the products of the reaction of 2,3-dichloro-1-propene and organic chalcogenides in the hydrazine hydrate–alkali medium affords the target unsaturated chalcogen-containing compounds with two different chalcogen atoms, 1,2-bis(organylchalcogenyl)propenes in up to 73% yield.

Keywords: 2,3-dichloro-1-propene, organic dichalcogenide, hydrazine hydrate–alkali, 1,2-bis(organylchalcogenyl)propenes

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Organochalcogen compounds are important reactants in organic synthesis [1–3]. Unsaturated organochalcogen compounds are especially promising [4, 5]. The presence of two or more of chalcogen atoms in the molecule expands their use in organic synthesis and opens possibilities for design of new chelating ligands capable of complex formation with transition metal ions [6–9]. Introduction of two different chalcogen atoms in the molecule is of special interest since such compounds are attractive in view of mutual interaction of atoms in the molecule, reactivity features, and formation of coordination bonds.

Preparation of unsaturated organochalcogen compounds with two different chalcogen atoms can be performed via photoinduced two-step radical addition of two different radicals $PhY^{\cdot}$ (Y = S, Se, Te) to various unsaturated compounds [10–12], or via nucleophilic addition of anions RY^- (Y = Se, Te) to phenylthioacetylenes [13, 14]. The first method provides high regioselectivity of the reaction due to the different reactivity of the $PhY^{\cdot}$ radicals depending on the nature of the chalcogen atom, both at the stage of addition of the radical to the multiple bond and at the stage of subsequent recombination of the formed radical-adduct with another radical $PhY^{\cdot}$. However, this method is limited to preparation of phenylchalcogenated derivatives. The second approach is limited by poor availability of phenylthioacetylenes and their analogs.

Recently, we have discovered the domino-type reaction of 2,3-dichloro-1-propene **I** with diphenyldisulfide [15], diphenyldiselenide [16], and dibenzyldichalcogenides [17] occurring as sequential substitution of allylic chlorine atom with chalcogen-containing nucleophile, dehydrochlorination of the product to form allenylchalcogenide, the allene–acetylene rearrangement, and addition of the nucleophile to the triple bond. The final product was 1,2-dichalcogenyl-substituted propene of *Z*-configuration [15–17].

Extending those studies, we tried to synthesize unsaturated organochalcogen compounds with two different chalcogen atoms, first via the reaction of 2,3-

dichloro-1-propene **I** with two different chalcogenide anions: PhO^- (**IIa**) and PhS^- (**IIb**); PhO^- and $PhSe^-$ (**IIc**); or PhS^- and $PhSe^-$. The $PhTe^-$ (**IId**) anion was not used since it reacted with compound **I** in a different manner [18].

Anions PhO^- **IIa** were obtained by dissolving phenol in the hydrazine hydrate–KOH medium.

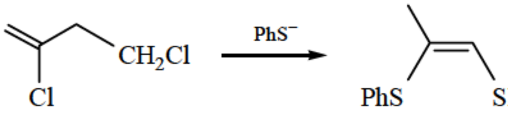
$$PhOH + KOH \rightarrow PhOK + H_2O. \quad (1)$$

Anions **IIb**–**IId** were obtained by reductive splitting of diphenyldichalcogenides in the same medium [19].

$$\begin{gathered}2Ph_2Y_2 + N_2H_4{\cdot}H_2O + 4KOH \\ \rightarrow \underset{\textbf{IIb–IId}}{4PhYK} + N_2 + 5H_2O, \quad (2) \\ Y = S\ (\textbf{b}),\ Se\ (\textbf{c}),\ Te\ (\textbf{d}).\end{gathered}$$

According to the earlier reported data [15–19] the excess of alkali (KOH : Ph_2Y_2 = 5 : 1) was required for complete conversion of Ph_2Y_2 via reaction (2). By analogy, the ratio of KOH : PhOH = 1.0 : 2.5 was used in reaction (1). Reagents **II** prepared by reactions (1) and (2) were introduced in further reactions without isolation.

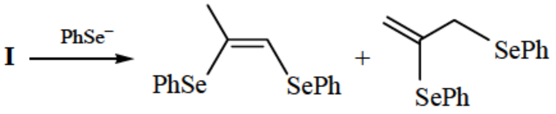
When using the mixtures **IIa** + **IIb** or **IIa** + **IIc**, no oxygen-containing products were detected. The reaction of dichloropropene **I** with the mixture of PhO^- and PhS^- (60°C, 19 h) led to *Z*-1,2-bis(phenylsulfanyl)-propene (*Z*-**IIIa**) as the only product with 72% yield. That was consistent with a lower reactivity of PhO^- anions in nucleophilic substitution reactions as compared to that of PhS^- and $PhSe^-$ [20].



I *Z*-**IIIa**

(3)

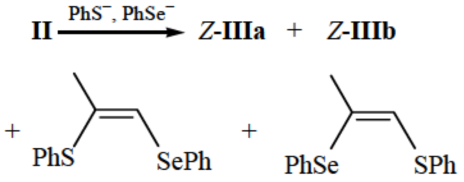
In the reaction with the mixture of PhO^- and $PhSe^-$ under the same conditions, two selenium-containing products, *Z*-1,2-bis(phenylselanyl)propene (*Z*-**IIIb**) and 2,3-bis(phenylselanyl)-1-propene (**IV**) were obtained with total yield of 81%, in the ratio of 10 : 1 (^{1}H NMR).



Z-**IIIb** **IV**

(4)

In the reaction with the mixture of PhS^- and $PhSe^-$, four major products were formed: (*Z*-**IIIa**) (19%), (*Z*-**IIIb**) (18%), 1-phenylselanyl-2-phenylsulfanyl-1-propene (**Va**) (21%) and 1-phenylsulfanyl-2-phenylselanyl-1-propene (**Vb**) (21%).



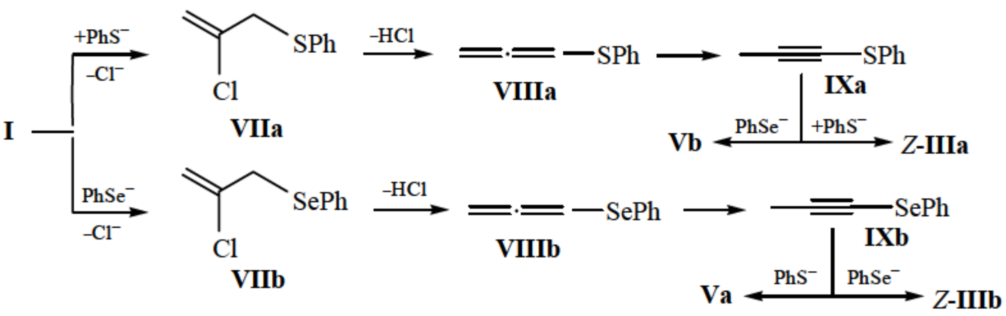
Va **Vb**

(5)

The yields of the products of reaction (5) were indicative of the fact that reactivity of anions PhS^- and $PhSe^-$ under the reaction conditions was nearly the same. That was confirmed by treatment with methyl iodide of the water-hydrazine layer after extraction of the products of reaction (5). This reaction the mixture of thioanisole **VIa** and selenoanisole **VIb** in molar ratio of 1 : 1 gives.

$$\underset{\textbf{IIb, IIc}}{PhY^-} + CH_3I \rightarrow \underset{\textbf{VIa, VIb}}{PhYCH_3}, \quad (6)$$
$$Y = S, Se.$$

Taking into account our earlier results [15–17], the formation of compounds *Z*-**IIIa**, *Z*-**IIIb**, **Va**, and **Vb** could be represented by the scheme (7).



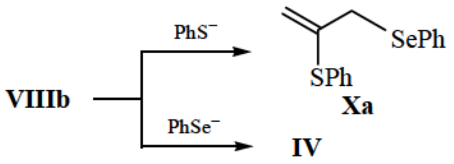
(7)

Table 1. Yields of products of reaction (9)

Reaction product	Y^1	R^1	Y^2	R^2	*Z*-**Va**–**Vf**, %	*E*-**Va**–**Vf**, %	**Xa**–**Xf**, %
a	Se	Ph	S	Ph	51	13	Traces
b	S	Ph	Se	Ph	69	Traces	"
c	S	Ph	Se	Me	58	23	–
d	S	Ph	Te	Ph	73	–	7[a]
e	Se	Ph	Te	Ph	32	Not identified	
f	S	Bn	Se	Me	59	5	16

[a] The reaction mixture contained 0.034 g of Ph_2Te_2 (conversion 97%).

^1H, ^{13}C, and ^{77}Se NMR spectroscopy revealed that traces of bisselenide **IV** and 2-phenylsulfanyl-3-phenylselanyl-1-propene **Xa** were formed (total yield of ca. 3%) in reaction (5) besides the above-mentioned compounds. Formation of those compounds could be due to different rate of isomerization of the allenyl compounds **VIII** into the acetylene chalcogenides **IX**. For the corresponding selenide, the **VIIIb** → **IXb** transformation was substantially slower [16, 17], so selenide **VIIIb** existed long enough to add anions PhS^- or $PhSe^-$ at the allene bond.

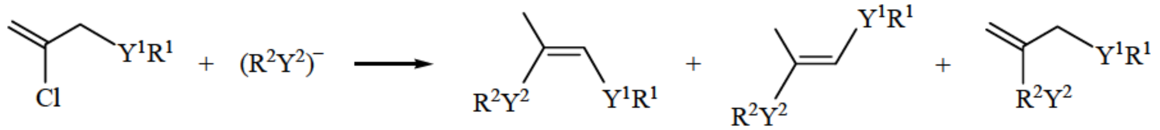


(8)

When using larger excess of alkali in reaction (5) (KOH : Ph_2Y_2 = 10 : 1), a more complex mixture of products was formed. By-products **IV** and **Xa** were formed in trace amounts, but *E*-isomers of compounds **IIIa, IIIb, Va, Vb** were detected (*E*-**IIIa** ~1%, *E*-**IIIb** 3%, *E*-**Va** 2%, and *E*-**Vb** 7%). Yields of the *Z*-isomers were as follows: *Z*-**IIIa** 16%, *Z*-**IIIb** 33%, *Z*-**Va** 17%, and *Z*-**Vb** 2%. However, reactivity of PhS^- and $PhSe^-$ anions was again nearly equal, as indicated by formation of equimolar mixture of thioanisole **VIa** and selenoanisole **VIb** the yield being of 28% by treatment with methyl iodide [Eq. (6)] of the water-hydrazine layer after extraction of the products of reaction.

Another approach to synthesis of unsaturated derivatives containing two different chalcogen atoms is based on the use of the easily prepared [15–17] products of the first stages of the domino-type reaction: 2-chloro-3-phenylchalcogenyl-1-propenes (**VIIb, VIIc**), phenylchalcogenylpropadienes-1,2 (**VIIIb, VIIIc**) and 1-phenylchalcogenyl-1-propynes (**IXb, IXc**).

Compounds **VII** were selectively formed via the reaction of dichalcogenides Ph_2Y_2, Bn_2Y_2 with dichloropropene **I** at –5 to –20°C [15–17]. Those products of the first step of the domino-type reaction were introduced in the reaction with chalcogenolate ions **IIb**–**IIe**[1] at 60°C. In all the cases, the major products of the reaction were the *Z*-isomers (*Z*-**Va**–**Vf**) of the unsaturated dichalcogenides containing two different chalcogen atoms. As by-products, the corresponding *E*-isomers (*E*-**Va**–**Vf**) and 2,3-dichalcogenyl-1-propenes (**Xa**–**Xf**) were identified in some of the batches (Table 1).



VIIa–**VIIc** **IIb**–**IIe** *Z*-**Va**–**Vf** *E*-**Va**–**Vf** **Xa**–**Xf**

(9)

R^1 = Ph, Y^1 = S (**VIIa**), Se (**VIIb**); R^1 = Bn, Y^1 = S (**VIIc**); R^2 = Ph, Y^2 = S (**IIb**), Se (**IIc**), Te (**IId**); R^2 = Me, Y^2 = Se (**IIe**); **Va**–**Vf**, **Xa**–**Xf** see Table 1.

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[1] Anion CH_3Se^- (**IIe**) was generated via reductive splitting of Me_2Se_2.

Table 2. ^{77}Se chemical shifts of compounds **IIIb, IV, V,** and **X** ($CDCl_3$)

Comp. no.	δ_{Se}, ppm	Comp. no.	δ_{Se}, ppm
Z-**IIIb**	386.9 (=CHSePh)[a] 429.2 (=CMeSePh)	**Xb**	431.6 (=CSePh)
E-**IIIb**	371.0 (=CHSePh) 493.7 (=CMeSePh)	*Z*-**Vc**	215.2 (=CMeSeMe)[b]
IV	338.5 (CH_2SePh) 433.0 (=CSePh)	*E*-**Vc**	269.2 (=CMeSeMe)
Z-**Va**	386.2 (=CHSePh)[c]	*Z*-**Ve**	395.3 (=CHSePh)[d]
E-**Va**	361.9 (=CHSePh)	*Z*-**Vf**	203.8 (=CMeSeMe)[e]
Xa	343.1 (CH_2SePh)	*E*-**Vf**	265.4 (=CMeSeMe)[f]
Z-**Vb**	421.1 (=CMeSePh)	**Xf**	210.0 (=C-SeMe)
E-**Vb**	483.4 (=CMeSePh)		

[a] $^3J_{Se-Se}$ 91.4 Hz. [b] $^2J_{Se-H}$ 48.1 Hz. [c] $^2J_{CH3-Se}$ 11.9 Hz; $^3J_{Se-H}$ 11.9 Hz. [d] δ, ppm, ^{125}Te 676.6. [e] $^3J_{Se-C=C-H}$ 12.4 Hz, $^2J(CH_3–Se)$ 11.9 Hz, $^3J(CH_3–C–Se)$ 1.9 Hz. [f] $^3J_{Se-C=CH}$ 10.7 Hz.

The products shown in scheme (9) were apparently formed similarly to the mechanism behind schemes (7) and (8). However, the presence of anions $(R^2Y^2)^-$ resulted in high selectivity of the process.

The *E*-isomers of compounds **Va–Vf** were likely the products of the *Z* → *E* isomerization of the corresponding *Z*-isomers, the degree of isomerization being dependent on the reaction time. Hence, we assumed the possibility of further optimization of the yields of the *Z* or *E*-isomers. Formation of compounds **X**, as shown in scheme (8), involved nucleophilic addition of anions $(R^2Y^2)^-$ to the allene derivatives **VIII**, the products of the second step of the domino reaction. Their yield depended on the rate of isomerization of the allenyl chalcogenide into the acetylene isomer **VIII** → **IX**, the rate of isomerization being in turn dependent on the nature of the chalcogenyl group (R^1Y^1) and alkali concentration in the reaction mixture.

Possibility of using the products of the second and the third steps of the domino-type reaction (formed with much lower selectivity and hardly separable [15–17]) in the synthesis of bischalcogenyl derivatives with two different chalcogen atoms was demonstrated using a mixture of allenyl **VIIIa** and acetylene derivative **IXa** in the reaction with anions $MeSe^-$ as an example. The reaction was analogous to chalcogenation of phenylthioacetylenes described in [13, 14].

$$\underset{1\,:\,9}{\mathbf{VIIIa} + \mathbf{IXa}} \xrightarrow{\mathbf{IIe}} \underset{70\%}{Z\text{-}\mathbf{Vc}} + \underset{13\%}{E\text{-}\mathbf{Vc}} \qquad (10)$$

As follows from scheme (10), using the products of the second and the third steps of the domino-type reaction led to more selective formation of adducts **V** (total yield 83%). However, degree of the *Z* → *E* isomerization was higher under those conditions (60ºC, 18 h).

Structure of the synthesized compounds was confirmed by IR, ^{1}H, ^{13}C, ^{77}Se, and ^{125}Te NMR spectroscopy and chromato-mass spectrometry. Assignment of the *Z* or *E*-isomers of compounds **Va–Vf** was performed using NOESY technique [21]. The spectra of the *Z*-isomers contained a cross peak of the CH_3 protons and the vinyl proton =CH. The ^{77}Se NMR parameters of the synthesized compounds are given in Table 2.

To conclude, 2,3-dichloro-1-propene **I** can be used as convenient reagent for synthesis of unsaturated organochalcogen compounds containing two different chalcogen atoms, the latter being promising ligands and reagents for organic synthesis.

EXPERIMENTAL

IR spectra of thin films were recorded using a Bruker IFS-25 spectrometer. ^{1}H, ^{13}C, ^{77}Se, and ^{125}Te NMR spectra were registered with a Bruker DPX-400 spectrometer (400.13, 100.62, 76.31, and 126.2 MHz, respectively) in $CDCl_3$ solution, chemical shifts were referenced to TMS (^{1}H, ^{13}C), Me_2Se (^{77}Se), and $(CH_3)_2Te$ (^{125}Te). Mass spectra were obtained with a Shimadzu GCMS–QP5050A chromato-mass spectrometer (column SPB-5, 60000 × 0.25 mm), quadruple mass analyzer, electron impact 70 eV, temperature of ionic source 190°C, range of detected masses 34-650 Da.

The reactions were monitored and the liquid products analyzed by GLC on a LKhM 80-MD-2 device (column 2000 × 3 mm, liquid phase DC-550, 5% on Chromaton N-AW-HMDS, linear temperature prog-ramming 12 deg/min, gas carrier helium).

Reaction of phenol and diphenyldisulfide with 2,3-dichloro-1-propene I in hydrazine hydrate–KOH. Phenol (4.31 g, 0.046 mol) was added to a solution of KOH (6.42 g, 0.114 mol) in 30 mL of hydrazine hydrate at 45–50ºC. Diphenyldisulfide (5.0 g, 0.023 mol) was added to the solution of KOH (6.42 g, 0.114 mol) in 30 mL of hydrazine hydrate. The reaction mixture was heated during 3 h at 85–90ºC. The obtained solutions of PhOK **IIa** and PhSK **IIb** were combined, and dichloropropene **I** (5.1 g, 0.046 mol) was added dropwise at 60ºC to the mixture; the mixture was stirred during 19 h at 60ºC, cooled to 20–25ºC and extracted with CH_2Cl_2 (3 × 50 mL). The extracts were combined, dried over $MgSO_4$; the solvent was removed. From GLC and ^{1}H NMR spectrum, the residue (4.24 g) was practically pure *Z*-1,2-bis(phenylsulfanyl)-1-propene (*Z*-**IIIa**) (yield 72%). Spectral parameters coincided with those in [15].

Reaction of phenol and diphenyldiselenide with 2,3-dichloro-1-propene (I). A solution of PhOK **IIa** was prepared as described above from phenol (2.42 g, 0.026 mol) and KOH (3.61 g, 0.064 mol) in 16 mL of hydrazine hydrate. Diphenyldiselenide (4.0 g, 0.013 mol) was added to the solution of KOH (3.6 g, 0.064 mol) in 16 mL of hydrazine hydrate and stirred during 3 h at 85–90ºC. The obtained solutions of PhOK and PhSeK were combined and dichloropropene **I** (2.85 g, 0.026 mol) was added to the mixture dropwise at 60ºC. The mixture was stirred during 19 h at 60ºC and processed as described above. The residue is a mixture of the products *Z*-**IIIb** (3.34 g, 74%) and 2,3-bis(phenylselanyl)-1-propene **IV** (0.34 g, 8%). Spectral parameters of compound *Z*-**IIIb** coincided with those in [16].

Compound IV. $\nu_{C=C}$ 1601 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 3.66 d (2H, CH_2Se, $^{4}J_{H\text{–}H}$ 0.7 Hz, $^{2}J_{SeCH}$ 12.3 Hz), 5.09 s (1H, $=CH_{cis}$), 5.46 t (1H, $=CH_{trans}$, $^{4}J_{HH}$ 0.7 Hz, $^{3}J_{SeCH=CH}$ 16.3 Hz), 7.18–7.48 m (10H, C_6H_5). ^{13}C NMR, δ_C, ppm: 35.66 ($SeCH_2$, $^{2}J_{CSe}$ 64.7 Hz), 119.43 ($=CH_2$, $^{2}J_{CSe}$ 9.3 Hz); for aromatic carbons the first chemical shifts in pairs are for the Ph group in $PhSeCH_2$, the second ones are for the Ph group in PhSe at the double bond: 127.48, 128.05 (C_p); 128.84, 129.13 (C_m); 133.38 ($^{2}J_{CSe}$ 9.9 Hz); 134.51 ($^{2}J_{CSe}$ 10.3 Hz) (C_o); 138.89 ($\underline{C}=CH_2$, $^{1}J_{CSe}$ 105.2 Hz). ^{77}Se NMR see in Table 2. Mass spectrum, *m/z*: $M^{+\cdot}$ for ^{80}Se 354.

Reaction of diphenyldisulfide and diphenyldiselenide with 2,3-dichloro-1-propene (I). *a*. Diphenyldisulfide (2.8 g 0.013 mol) was dissolved in a mixture of KOH (3.6 g 0.064 mol) and hydrazine hydrate (16 mL) at 85–90ºC (3 h). Diphenyldiselenide (4.0 g 0.013 mol) was dissolved in the same mixture of KOH and hydrazine hydrate. The two solutions were combined, and dichloropropene **I** (2.84 g 0.026 mol) was added at room temperature. The reaction mixture was stirred during 19 h at 60ºC, cooled to room temperature, extracted with CH_2Cl_2 (3 × 50 mL), the extract was dried over $MgSO_4$, and the solvent was removed. According to GLC, chromato-mass spectrometry, and NMR spectroscopy, the residue (4.79 g) contained four products **IIIa, IIIb, Va, Vb** and small amounts of compounds **IV, Xa** (yields are given in the text): *Z*-1,2-bis(phenylsulfanyl)-1-propene **IIIa** and *Z*-1,2-bis(phenylselanyl)-1-propene **IIIb**, their spectral charac-teristics were identical to those in [15, 16].

Z-1-(Phenylselanyl)-2-(phenylsulfanyl)-1-propene (Va) was identified in the mixture with other products. $\nu_{C=C}$ 1579 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 2.05 d (3H, Me, $^{4}J_{H\text{–}H}$ 1.2 Hz), 6.81 q (1H, CH=, $^{2}J_{Se^{-}H}$ 15.9 Hz, $^{4}J_{H\text{–}H}$ 1.2 Hz), 7.20–7.60 m (10H, Ph). ^{77}Se NMR spectrum is given in Table 2. Mass spectrum, *m/z*: $M^{+\cdot}$ for ^{80}Se 306.

***Z*-1-(Phenylsulfanyl)-2-(phenylselanyl)-1-propene (Vb).** $\nu_{C=C}$ 1579 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 1.97 d (3H, Me, $^{4}J_{H\text{–}H}$ 1.1 Hz), 6.69 q (1H, HC=, $^{4}J_{H\text{–}H}$ 1.1 Hz), 7.20–7.60 m (10H, Ph). ^{77}Se NMR is given in Table 2. Mass spectrum, *m/z*: $M^{+\cdot}$ for ^{80}Se 306.

Spectral features of compound **IV** are given above.

2-(Phenylsulfanyl)-3-(phenylselanyl)-1-propene (Xa). ^{1}H NMR spectrum, δ, ppm: 3.57 s (2H, CH_2Se), 4.89 s (1H), 5.11 s (1H) ($=CH_2$), 7.20–7.60 m (10H, Ph). ^{77}Se NMR spectrum is given in Table 2. Mass spectrum: $M^{+\cdot}$ for ^{80}Se 306.

b. 1.75 g (8 mmol) of Ph_2S_2 and 2.5 g (8 mmol) of Ph_2Se_2 were taken for the reaction. Each dichalcogenide was dissolved in a mixture of 20 mL of hydrazine hydrate and 4.49 g (0.08 mol) of KOH (Ph_2Y_2 : KOH = 1 : 10). The solutions were combined, the reaction was performed at 60°C during 18 h, and the mixture was treated as described in method *a*. The residue after removal of the solvent (2.73 g) contained (GLC and NMR) 0.93 g (yield 33%) of compound *Z*-**IIIb**, 0.33 g (16%) of *Z*-**IIIa**, 0.82 g (17%) of *Z*-**Va**, 0.33 g (7%) of *Z*-**Vb**, 0.08 g (1.6%) of *E*-**Va**, and small amounts of compounds **IV, Xa**, and *E*-**Vb**.

***E*-1-(Phenylselanyl)-2-(phenylsulfanyl)-1-propene (*E*-Va).** $\nu_{C=C}$ 1579 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 2.14 d (3H, Me, $^4J_{H-H}$ 1.2 Hz), 6.79 q (1H, CH=, $^4J_{H-H}$ 1.2 Hz), 7.30–7.65 m (10H, Ph). ^{77}Se NMR spectrum is given in Table 2. Mass spectrum, *m/z*: $M^{+\cdot}$ for ^{80}Se 306.

Reaction of 2-chloro-3-organylchalcogenyl-1-propenes (VIIa–VIIc) with diorganyldichalcogenides in hydrazine hydrate–KOH. Dichalcogenide (Ph_2S_2, Ph_2Se_2, Ph_2Te_2, Me_2Se_2) was dissolved in hydrazine hydrate–KOH, and the corresponding 2-chloro-3-organylchalcogenyl-1-propene (**VIIa–VIIc**) was added dropwise to the obtained solution. The reaction mixture was stirred at 60°C during 18 h and treated as described above.

Reaction of the solution of Ph_2S_2 (1.33 g, 6 mmol) and KOH (1.71 g, 0.03 mol) in 8 mL of hydrazine hydrate with compound **VIIb** (2.83 g, 0.012 mol) gave 2.38 g of the residue containing compounds *Z*-**Va** and *E*-**Va** in the ratio of 3.6 : 1. Fraction with bp 180–182°C (1.5 mmHg) contained compounds *Z*-**Va** and *E*-**Va** in the ratio of 4 : 1. Found, %: C 58.83; H 4.47; S 10.61; Se 25.41. $C_{15}H_{14}SSe$. Calculated, %: C 59.01; H 4.62; S 10.50; Se 25.86. IR, ^{1}H, ^{77}Se NMR spectra and chromato-mass spectrometry data for compounds *Z*-**Va** and *E*-**Va** were identical to those described above.

Reaction of Ph_2Se_2 (1.97 g, 6.3 mmol), KOH (1.77 g, 0.032 mol) in 8 mL of hydrazine hydrate with 2-chloro-3-phenylsulfanyl-1-propene **VIIa** (2.33 g, 0.013 mol) gave *Z*-isomer of compound **Vb** in 69% yield. bp 175–176°C (1.5 mmHg). Found, %: C 59.31; H 4.65; S 10.32; Se 25.65. $C_{15}H_{14}SSe$. Calculated, %: C 59.01; H 4.62; S 10.50; Se 25.86. Spectral characteristics were fully identical to those described above.

***Z*-1-(Phenylsulfanyl)-2-(methylselanyl)-1-propene (*Z*-Vc) and *E*-1-(phenylsulfanyl)-2-(methylselanyl)-1-propene (*E*-Vc).** Me_2Se_2 (1.06 g, 6 mmol) was dissolved in 10 mL of hydrazine hydrate containing 1.58 g (0.03 mol) of KOH at 80–85°C in the course of 3 h. The mixture was cooled to 60°C, and 2-chloro-3-phenylsulfanyl-1-propene (**VIIa**) (2.08 g, 0.012 mol) was added dropwise. The mixture was stirred at the same temperature for 18 h, and treated as described above. Light-yellow residue (2.23 g) was a mixture of compounds *Z*-**Vc** and *E*-**Vc** in the ratio 10 : 4 (^{1}H NMR). bp 145–147°C (2 mmHg). Found, %: C 49.20; H 4.82; S 12.78; Se 32.93. $C_{10}H_{12}SSe$. Calculated, %: C 49.38; H 4.97; S 13.18; Se 32.46.

Compound *Z*-Vc. $\nu_{C=C}$ 1582 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 2.181 s (3H, SeMe), 2.21 d (3H, MeC=, $^4J_{H-H}$ 1.3 Hz), 6.28 q (1H, =CH, $^4J_{H-H}$ 1.3 Hz), 7.12–7.22 m (5H, Ph). ^{13}C NMR, δ, ppm: 4.75 (MeSe), 24.51 ($\underline{Me}$C=), 119.76 (=CH), 126.23 (C_p), 128.57 (C_m), 128.99 (C_o), 134.44 (Me$\underline{C}$=), 136.11 (C_i). ^{77}Se NMR is given in Table 2. Mass spectrum, *m/z*: $M^{+\cdot}$ for ^{80}Se 244.

Compound *E*-Vc. $\nu_{C=C}$ 1567 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 2.185 d (3H, MeC=, $^4J_{H-H}$ 1.1 Hz), 2.19 s (3H, SeMe), 6.06 q (1H, =CH, $^4J_{H-H}$ 1.1 Hz), 7.12–7.22 m (5H, Ph). ^{13}C NMR, δ, ppm: 6.08 (MeSe), 20.96 ($\underline{Me}$C=), 116.92 (=CH), 126.10 (C_p), 128.17 (C_m), 129.04 (C_o), 132.47 (Me$\underline{C}$=), 136.67 (C_i). ^{77}Se NMR is given in Table 2. Mass spectrum, *m/z*: $M^{+\cdot}$ for ^{80}Se 244.

***Z*-1-(Phenylsulfanyl)-2-(phenyltellanyl)-1-propene (*Z*-Vd) and 2-(phenyltellanyl)-3-(phenylsulfanyl)-1-propene (Xd).** Compound **VIIa** (1.1 g, 6 mmol) was added dropwise to a solution of Ph_2Te_2 (1.22 g, 3 mmol) in 4 mL of hydrazine hydrate containing 0.84 g (0.015 mol) of KOH; the mixture was stirred for 18 h at 60°C, cooled, and treated as described above to give 1.72 g of the residue (dark-red liquid) containing compounds **Vd**, **Xd**, and Ph_2Te_2 in the ratio of 10 : 1 : 0.2 (^{1}H NMR). The compounds decomposed upon distillation at 1.5–2 mmHg.

Compound *Z*-Vd. $\nu_{C=C}$ 1573 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 2.01 d (3H, Me, $^4J_{H-H}$ 1.0 Hz), 6.59 q (1H, HC=, $^4J_{H-H}$ 1.0 Hz, $^3J_{H-Te}$ 12.9 Hz), 7.12–7.84 m (10H, Ph). ^{13}C NMR, δ_C, ppm: 28.04 (Me), 113.22 (=$\underline{C}$Me), 123.79 (C_p, TePh), 126.26 (C_p, SPh), 128.23 (C_m, TePh), 128.49 (C_m, SPh), 128.96 (C_o, TePh), 129.12 (C_o, SPh), 135.61 (C_i, TePh), 136.70 (C_i, SPh), 141.02 (=CH). ^{125}Te NMR spectrum, δ, ppm: 673.9 ($^3J_{Te-H(Me)}$ 12.9 Hz). Mass spectrum, *m/z*: $M^{+\cdot}$ for ^{130}Te 356.

Compound Xd. $\nu_{C=C}$ 1582 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 3.80 s (2H, CH_2S), 5.35 s (1H of CH_2=, $^3J_{H-Te}$ 12.1 Hz), 6.04 s (1H of CH_2=, $^3J_{H-Te}$ 27.0 Hz), 7.12–7.84 m (10H, Ph). ^{125}Te NMR spectrum, δ, ppm: 689.9. Mass spectrum, *m/z*: $M^{+\cdot}$ for ^{130}Te 356.

Diphenylditelluride. ^{125}Te NMR, δ, ppm: 427.5. Reference data: 420.8 ppm [22].

Reaction of Ph_2Te_2 with 2-chloro-3-phenylselanyl-1-propene (VIIb). Compound **VIIb** (1.43 g, 6 mmol) was added dropwise at 60°C to a solution of Ph_2Te_2 (1.26 g, 3 mmol) in 4 mL of hydrazine hydrate containing KOH (0.87 g, 0.015 mol); the mixture was stirred at the same temperature for 18 h and treated as described above to give 1.6 g of the residue (dark-red liquid). The target product, ***Z*-1-(phenylselanyl)-2-(phenyltellanyl)-1-propene (*Z*-Ve)** was identified in the mixture with other products (the yield calculated using internal standard was of 32%). ^{1}H NMR spectrum, δ, ppm: 2.02 d (3H, Me, $^4J_{H-H}$ 1.0 Hz), 7.01 q (1H, HC=, $^4J_{H-H}$ 1.0 Hz), 7.22–7.88 m (10H, Ph). ^{13}C NMR, δ_C, ppm: 29.97 ($\underline{Me}$C=), 123.68 (=CH), 127.11, 127.95, 128.53, 128.60, 129.35, 129.55, 130.83, 139.03, 140.65. Mass spectrum, *m/z*: $M^{+\cdot}$ (^{80}Se, ^{130}Te) 404.

Reaction of dimethyldiselenide with 2-chloro-3-benzylsulfanyl-1-propene (VIIc). Compound **VIIc** (1.90 g, 0.01 mol) was added dropwise to the solution of Me_2Se_2 (0.9 g, 5 mmol) in 6 mL of hydrazine hydrate containing KOH (1.35 g, 0.025 mol); the mixture was stirred for 18 h at 60°C and treated as described above. The residue (1.96 g, light red liquid) contained *Z*-1-(benzylsulfanyl)-2-(methylselanyl)-1-propene (*Z*-**Vf**), *E*-1-(benzylsulfanyl)-2-(methylselanyl)-1-propene (*E*-**Vf**), and 2-(methylselanyl)-3-(benzylsulfanyl)-1-propene (**Xf**) in the ratio of 13 : 1 : 3.5 (^{1}H NMR). The mixture was distilled at 146–150°C (2 mmHg) practically without change of the ratio of the isomers *Z*-**Vf**, *E*-**Vf**, and **Xf**. Found, %: C 50.84; H 5.37; S 12.34; Se 31.14. $C_{11}H_{14}SSe$. Calculated, %: C 51.36; H 5.49; S 12.46; Se 30.69. Chromato-mass spectroscopy for all three isomers gives $M^{+\cdot}$ (^{80}Se) 258.

Compound *Z*-Vf. $\nu_{C=C}$ 1577 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 2.04 d (3H, $\underline{Me}$C=, $^4J_{H-H}$ 1.3 Hz), 2.09 s (3H, MeSe), 3.85 s (2H, SCH_2), 6.04 q (1H, CH=, $^4J_{H-H}$ 1.3 Hz), 7.20 m (1H, H_p), 7.28 m (4H, H_{o+m}). ^{13}C NMR spectrum, δ_C, ppm: 4.58 (MeSe, $^1J_{C-Se}$ 64.7 Hz), 24.42 ($\underline{Me}$C=), 38.17 (SCH_2), 121.94 (CH=), 127.05 (C_p), 128.44 (C_m), 128.78 (C_o), 126.91 (Me$\underline{C}$=), 137.84 (C_i). ^{77}Se NMR spectrum is given in Table 2.

Compound *E*-Vf. $\nu_{C=C}$ 1577 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 2.00 d (3H, $\underline{Me}$-C=, $^4J_{H-H}$ 1.1 Hz), 2.04 s (3H, MeSe), 3.82 s (2H, SCH_2), 5.91 q (1H, CH=, $^4J_{H-H}$ 1.1 Hz), 7.18–7.31 m (5H, Ph). ^{13}C NMR, δ_C, ppm: 4.26 (MeSe), 20.87 (Me$\underline{C}$=), 38.51 (SCH_2), 120.14 (CH=), 128.35 (C_m), 129.02 (C_o), 127.25 (C_p), C_i and Me$\underline{C}$= signals could not be assigned because of low intensity. ^{77}Se NMR spectrum is given in Table 2.

Compound Xf. $\nu_{C=C}$ 1601 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 2.11 s (3H, MeSe), 3.28 s (2H, SCH_2C=), 3.65 s (2H, SCH_2Ph), 5.02 s, 5.53 narrow m (2H, CH_2=), 7.18–7.31 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 4.91 (MeSe), 35.19 (S$\underline{CH_2}$Ph), 40.03 (SCH_2C=), 112.86 (CH_2=), 128.36 (C_m), 128.87 (C_o), 127.47 (C_p), 136.91 (C_i), 139.80 (CH_2-$\underline{C}$(Se)=). ^{77}Se NMR spectrum is given in Table 2.

Reaction of the mixture of 1-phenylsulfanyl-1-propyne (IXa) and 1-phenylsulfanylpropadiene (VIIIa) with dimethyldiselenide. The mixture of compounds **VIIIa** and **IXa** (1.8 g, 0.012 mol, ratio 1 : 9) was added dropwise to a solution of Me_2Se_2 (1.14 g, 6 mmol) in 8 mL of hydrazine hydrate containing KOH (1.7 g, 0.03 mol), the mixture was stirred for 18 h at 60°C and treated as described above. The residue (2.6 g) was a mixture of compounds *Z*-**VIc** and *E*-**VIc** in the ratio of 5.6 : 1.0. Spectral characteristics of the products *Z*-**VIc** and *E*-**VIc** were fully consistent with those given above.

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