Mechanism and stereochemistry of domino reaction of 2,3-dichloroprop-1-ene with diphenyl dichalcogenides in the system hydrazine hydrate—KOH

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A new scheme of the domino reactions of diphenyl dichalcogenides with 2,3-dichloroprop-1-ene in the system hydrazine hydrate—KOH was suggested, which included nucleophilic substitution of the allylic chlorine atom in dichloropropene, dehydrochlorination of the product obtained with the formation of an allene derivative, addition of a nucleophile to the allene system, allene-acetylene rearrangement, addition of a nucleophile to the triple bond with the formation of a Z-adduct, isomerization of a 2,3-dichalcogenide product to Z-1,2-dichalcogenylprop-1-enes, and isomerization of Z-adducts to E-isomers. The most plausible mechanisms of individual steps, involving carbanions stabilized by the α -chalcogen atom, were considered.

Key words: domino reactions, 2,3-dichloroprop-1-ene, chalcogen-containing nucleophiles, stable carbanions, hydrazine hydrate, stabilization, stereochemistry, mechanism.

A growing sphere of application of organosulfur¹ and -selenium² compounds continuously stimulates development of synthetic methods of organochalcogen chemistry. An important role in the synthesis of sulfur and selenium organic derivatives is played by the chalcogen-containing nucleophilic agents, which are easily obtained by reductive activation of available elementary chalcogens and organic dichalcogenides.³ Among a large number of basic reductive systems for the generation of chalcogen-containing nucleophiles, an important place is taken by the systems based on hydrazine used as commercially available hydrazine hydrate.³ Using such systems, preparatively simple methods for the synthesis of organic chalcogenides and dichalcogenides were developed,³ as well as oligomeric products containing chalcogen atoms in the chain.⁴ This type of reactions use organic halides and dihalides as electrophiles in which halogen is attached to the carbon atom in the sp³-hybridization state.

2,3-Dichloroprop-1-ene (1) is an dielectrophile, in which two chlorine atoms are attached to the different sp^3 - and sp^2 -hybridized carbon atoms. A well known "inertness" of halogens at the double bond to nucleophilic reactions⁵ considerably affects direction of the reaction of dichloropropene 1 with the chalcogen-containing nucleophiles.

Earlier,⁶ we have shown that elementary sulfur activated in the system hydrazine hydrate—KOH to anions S_2^{2-} reacts with dichloropropene 1 with the formation of bis(2-chloroprop-2-en-1-yl) sulfide (only the chlorine

atom attached to the sp³-hybridized carbon atom is involved in the reaction). Bis(2-chloroprop-2-en-1-yl) disulfide was obtained using the system hydrazine hydrate—monoethanolamine from sulfur and dichloropropene 1.⁷ Selenium in both basic reductive systems formed only bis(2-chloroprop-2-en-1-yl) selenide.⁸

The reaction of Ph_2S_2 (see Ref. 9) and Ph_2Se_2 (see Ref. 10) with dichloropropene **1** proceeds through sequential transformations, including nucleophilic substitution of the chlorine atom at the sp³-hybridized carbon atom, dehydrochlorination of the product obtained with the formation of an allene derivative, allene-acetylene rearrangement, and addition of the PhS⁻ and PhSe⁻ anions to the triple bond (domino reaction). In the last step, the addition product has the Z-configuration. The studies showed^{9,10} that the nature of the chalcogen atom in the PhY⁻ anion (Y = S, Se) has a considerable influence on the course of individual steps of the domino reaction.

These reactions allow one to obtain unsaturated organochalcogen compounds possessing a wide synthetic scope for design of new, sometimes unique, chalcogen-containing structures.¹¹

In the present work, we consider individual steps of domino reactions from the point of view of their possible mechanism. To obtain additional information on the influence of the nature of the chalcogen atom in nucleophile PhY⁻, we also studied the phenoxide anion obtained by dissolution of phenol in the system hydrazine hydrate—KOH (Scheme 1).

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Scheme 1

PhOH + KOH
$$\rightarrow$$
 PhOK **2a**

Reagent **2a** was synthesized at the ratio phenol : KOH = = 1 : 2.5. Excess of KOH corresponds to the amount of the alkali used for the reductive cleavage of Ph₂Y₂ (Y = S, Se).³ For obtaining reagents **2b,c**, we used the ratio Ph₂Y₂ : KOH = 1 : 5 (Scheme 2).^{9,10} Benzenechalcogenolates **2a**-**c** were used in the reaction without isolation from the solutions in hydrazine hydrate.

Scheme 2

$$2 \operatorname{Ph}_{2}\operatorname{Y}_{2} + 4 \operatorname{KOH} + \operatorname{N}_{2}\operatorname{H}_{4} \cdot \operatorname{H}_{2}\operatorname{O} \longrightarrow$$

$$4 \operatorname{Ph}\operatorname{Y}\operatorname{K} + \operatorname{N}_{2} + 5 \operatorname{H}_{2}\operatorname{O}$$

$$2 \operatorname{Ph}_{2} \operatorname{C}$$

Y = S(b), Se(c)

According to the literature data,^{9,10} the domino reaction under consideration (Scheme 3) includes the formation of 2-chloro-3-phenylchalcogenylpropenes **3b**,**c** (step *a*), allene derivatives **4b**,**c** (step *b*), 1-phenylchalcogenylprop-1-ynes **5b**,**c** (step *c*), and Z-1,2-bis(phenylchalcogenyl)prop-1-enes Z-**6b**,**c** (step *d*). By more detailed studies of the influence of the ratio Ph₂Y₂ : KOH and the reaction time, two more types of compounds were additionally identified in the products: *E*-1,2-bis(phenylchalcogenyl)prop-1-enes (*E*-**6b**,**c**) (the highest yields were 6 and 5% for Y = S and Se, respectively) and 2,3-bis(phenylchalcogenyl)prop-1-enes (**7b**,**c**) (the highest yields were 2 and 8% for Y = S and Se, respectively).

The yields of the domino reaction products involving three types of nucleophiles $2\mathbf{a}-\mathbf{c}$ under different conditions (taking into account the data in the works^{9,10}) are given in Table 1. It can be suggested that compounds $7\mathbf{b},\mathbf{c}$ are kinetically controlled products and transform to

Z-isomers of compounds **6b**, c upon prolongation of the contact, which, in turn, slowly isomerize to the corresponding *E*-isomers. Based on this, we suggested a new sequence for the steps of the process, as it is shown in Scheme 3.

Step *a* of the domino reaction (see Scheme 3) virtually is the only possible when reaction is carried out at the temperatures from -25 to -35 °C for PhS⁻ anions (see Ref. 9) and from -5 to -10 °C for PhSe⁻ anions.¹⁰ At temperatures within 30–35 °C, only first three steps *a*–*c* proceed, in which case the ratio of products **3**–**5** considerably depends on the nature of the chalcogen atom.^{9,10} Step *d* and steps *e*–*f* are possible only at higher temperatures (60 °C).

Potassium phenoxide (2a) obtained in the system hydrazine hydrate—KOH (see Scheme 1) virtually does not react with 2,3-dichloroprop-1-ene (1). Carrying out the reaction at 0 °C for 14 h gives the product of the first step of the domino reaction (see Scheme 3), *viz.*, 2-chloro-3phenoxyprop-1-ene (3a), in only ~2% yield.

When the temperature of the process is raised to 30-35 °C (4 h), compound **3a** is formed only in trace amounts, whereas at 60 °C (19 h) the product **3a** is absent. These reactions lead to the products of alkylation of hydrazine in 25-40% yield, mainly to (2-chloroprop-1-en-3-yl)hydrazine (**8**) (Scheme 4).

A possibility of alkylation of hydrazine with dichloropropene **1** presents itself when the reactivity of nucleophiles present in the reaction mixture is low, which was discussed by us earlier.⁶ A low reactivity of the PhO⁻ anions (as compared to the PhS⁻ and PhSe⁻ anions) in the nucleophilic substitution reactions is a well known fact.¹²

Step *e* is a nucleophilic addition of the PhY⁻ anions to allene chalcogenide **4b**,**c** (Scheme 5). In this case, the nucleophilic attack is directed on the central atom of the allene fragment of molecule **4b**,**c** with the formation of the intermediate carbanion **A**, in which the negative charge is concentrated on the carbon atom at α -position to the sulfur (or selenium) atom (anti-Markovnikov addition).



Scheme 3

Y = O(a), S(b), Se(c)

| PhY ⁻ | Ratio (mol.) | | <i>T</i> /°C | τ/h | Product yields (%) | | | | | | Ref. |
|--------------------------------|-----------------|---------------|--------------|-----|--------------------|------------------|-----------------|-------------|--------|---|------|
| | $KOH : Ph_2Y_2$ | Ph_2Y_2 : 1 | | | 3 | 4 | 5 | <i>Z</i> -6 | E-6 | 7 | |
| PhS ⁻ (2 b) | 5:1 | 1:2 | -(25-35) | 7.5 | 70 | Traces | _ | _ | _ | _ | 9 |
| | 5:1 | 1:2 | -(5-10) | 7 | 56 | 15 | _ | _ | _ | _ | 9 |
| | 2:1 | 1:2 | -(12-20) | 12 | 66 ^a | — | _ | _ | _ | _ | 9 |
| | 5:1 | 1:2 | 30-35 | 4 | 5 | 23 | 23 | _ | _ | _ | 9 |
| | 5:1 | 1:2 | 60 | 19 | _ | Traces | 22 | 40 | _ | _ | 9 |
| | 10:1 | 1:1 | 60 | 18 | _ | — | _ | 47 | 6 | _ | b |
| | 5:1 | 1:1 | 60 | 2 | _ | 1 | 38 | 24 | 1 | 2 | b |
| PhSe ⁻ (2c) | 5:1 | 1:2 | -(5-10) | 7.5 | 85 | Traces | _ | _ | _ | _ | 10 |
| | 5:1 | 1:2 | 5-10 | 7.5 | 81 | 12 | _ | _ | _ | _ | 10 |
| | 10:1 | 1:2 | 25 | 15 | _ | 19 | 58 | _ | _ | _ | 10 |
| | 10:1 | 1:2 | 25 | 33 | _ | 13 | 59 ^c | _ | _ | _ | 10 |
| | 5:1 | 1:1 | 30-35 | 7 | 36 | 43 | 8 | _ | _ | _ | 10 |
| | 5:1 | 1:1 | 60 | 19 | _ | _ | _ | 60 | Traces | 5 | b |
| | 5:1 | 1:1 | 60 | 5 | _ | _ | _ | 54 | 1 | 8 | b |
| | 10:1 | 1:1 | 60 | 18 | _ | _ | _ | 50 | 5 | 5 | b |
| PhO ⁻ (2a) | $2.5:1^{d}$ | $1:1^{e}$ | 0 | 14 | 2^{f} | _ | _ | _ | _ | _ | b |
| | $2.5:1^{d}$ | $1:1^{e}$ | 30-35 | 4 | Traces | See ^g | _ | — | — | — | b |

Table 1. The yields of products of domino reactions of nucleophiles PhY^- from compounds 2a-c with dichloropropene 1

^{*a*} Conversion of Ph₂S₂ 95%.⁹

^b The data obtained in this work.

^c 1-Phenylselanylpropene (2–3%) was also identified in the reaction mixture.¹⁰

^{*d*} The ratio KOH : PhOH.

^{*e*} The ratio PhOH : 1.

^f Chloropropenylhydrazine **8** was identified in 39% yield.

^g Compound 8 was identified in 28% yield.¹⁰

Scheme 4







Step f of the domino reaction (see Scheme 3) is a well known in chemistry of organosulfur compounds allyl-propenyl rearrangement.¹³ A possibility of isomerization of allyl phenyl chalcogenides in the system hydrazine hydrate—alkali was studied and it was shown that under the same conditions, a sulfide isomerizes by 95%, whereas a corresponding selenide by 53%. The isomerization degree of allyl phenyl telluride was only 3%.¹⁴ The propenyl derivatives in the cases of sulfide and selenide are formed predominantly as Z-isomers. In our systems, we observe a similar pattern, namely, sulfide 7b undergoes isomerization to compound Z-6b faster than the selenium derivative. Compound 7b was detected (2% yield) only when reagents contacted at 60 °C for 2 h. In this case, allene derivative **4b** (~1% yield) and acetylene sulfide **5b** (38% yield) remain unreacted in the reaction mixture (see Table 1).

When a pre-synthesized sulfide **3b** reacted with the PhS⁻ anions of compound **2b** (60 °C, 5 h), the yield of compound **7b** was 5%, the yield of the Z-isomer of compound **6b** was 40%. However, acetylene derivative **5b** was obtained in this case in 33% yield. Thus, under these conditions, a considerable amount of compound **5b** remains, but the yield of compound **7b** is only several percent because of its rapid enough isomerization to Z-**6b**.

In the reaction of selenium derivative 3c with the PhSe⁻ anions of compound 2c (60 °C, 18 h), as it was expected, the formation of Z-isomer 6c was observed (63% yield). The stereochemical direction of the process in this case is determined by the same regularities as in the direct domino reaction of dichloropropene 1 with the PhSe⁻ anions of compound 2c (*E*-isomer is virtually absent). This reaction results also in the formation of 2,3-bis(phenylselanyl)prop-1-ene 7c in 26% yield, which isomerizes to the corresponding Z-isomer slower than compound 7b.

A possibility of the isomerization processes $7c \rightarrow Z-6c$ and $Z-6 \rightarrow E-6$ was confirmed by independent experiments. Heating a mixture of compounds Z-6c and 7c (3 : 1) in the system hydrazine hydrate—KOH at 60 °C for 19 h led to a mixture of Z-6c-E-6c-7c (18 : 3 : 1). This means that a 82% isomerization $7\mathbf{c} \rightarrow Z-6\mathbf{c}$ took place under these conditions, whereas isomerization $Z-6\mathbf{c} \rightarrow E-6\mathbf{c}$ occurs only by 14%. Under similar conditions, isomerization $Z-6\mathbf{b} \rightarrow E-6\mathbf{b}$ took place by only 4.5%. An increased stability of Z-isomers of compounds 6 can be interpreted in the framework of the hypothesis,

which takes into account the presence of the p-d-intramolecular interaction between the sulfur atoms in the Z-position and the multiple bond with the forma-



tion of the 6π -electron structure.¹⁵ Apparently, such an interaction in the case of selenium atoms is less efficient.

From the data in Tables 1, it is also seen that under conditions of only first three steps (a-c) in the case of selenium derivatives the processes of dehydrochlorination with the formation of allene derivative **4c** (step *b*) and isomerization of the latter to acetylene selenide **5c** (step *c*) are considerably slower. The effects of the replacement of sulfur atom with selenium one in these transformation we interpreted taking into account the mechanisms of proceeding reactions.

Two mechanism can be considered for dehydrochlorination of compounds **3b**,**c**: a synchronous *E*2 and a *E*1*cB* mechanism, which are hardly distinguishable in kinetic studies.¹² In the early period of development of concepts of organic reaction mechanisms, there was a suggestion that the E1cB mechanism was applicable only in limited cases,¹⁶ when a carbonyl or other electron-withdrawing group existed near the anionic center in the conjugate base. In the examples studied,¹⁶ the leaving atoms and groups were attached to the sp³-hybridized carbon atoms. In dehydrochlorination of monochalcogenide derivatives 3, the hydrogen atom leaves the sp^3 -hybridized C atom, whereas the Cl⁻ anion leaves the sp²-hybridized one. Therefore, the most plausible mechanism of dehydrochlorination of compounds **3b**,**c** is the *E*1*cB* mechanism, which involves the conjugate base, 12 the carbanion **B** (Scheme 6). A possibility to effect the process in this case is determined by stability of carbanion **B**.

Scheme 6



A major factor, which defines stability of anion **B**, is the nature of the chalcogen atom Y neighboring to the anionic center. Since the electronegativities of sulfur and selenium are close enough (according to Pauling scale: for S 2.58, for Se 2.55; according to Allred—Rochow scale: for S 2.44, for Se 2.48),¹⁷ the delocalization of the negative charge should be determined by the involvement of d-orbitals of the hetero atom. The smaller d-orbitals of

sulfur atom correspond better to p-orbitals of carbon atom than selenium d-orbitals. This allows us to suggest that carbanion **B** for Y = S is more stable than for Y = Se, and the dehydrochlorination process in the case of sulfide is easier to take place.

It is obvious that the vacant 5d-orbitals of tellurium and 2p-orbitals of carbon differ even greater. Therefore, in the case of Y = Te (see Scheme 6), there is virtually no stabilization of anion **B** by the neighboring heteroatom. It is possible that this is the reason that the reaction of diphenyl ditelluride with dichloropropene 1 even at 45-50 °C included only the first step of the domino reaction.¹⁸ Neither allene, nor acetylene derivative were detected in these studies.

Earlier, ¹⁹ based on the quantitative data on deprotonation of different sulfides and selenides, a suggestion has been made that anions, in which the negative charge is concentrated on the orbital with a higher percentage of p-character (sp³-hybridized orbital), are more efficiently stabilized by sulfur atom than by selenium. But if the negative charge is concentrated on the orbital with higher s-character (for example, sp²-hybridized orbital), the corresponding anion is better stabilized by selenium. Dehydrochlorination according to Scheme 6 involves anion **B**, in which the negative charge is concentrated on the sp³-hybridized orbital, therefore this process should be more efficient for the case Y = S.

The allene-acetylene isomerization $4 \rightarrow 5$ (step *c*, see Scheme 3) with the formation of acetylene chalcogenide with the internal triple bond is a thermodynamically favorable process,²⁰ which also follows a carbanionic mechanism (Scheme 7).





The formation and stability of anion **C** are determined by the same factors as those of anion **B**. However, in anion **C** the negative charge is concentrated on the sp²-hybridized orbital, therefore, according to the work,¹⁹ in the case of Y = Se it should be more stable than for Y = S. It is obvious that the rate of isomerization is determined by the contribution of the resonance structure **C**', which for Y = Sshould be larger because of the reasons mentioned above. In this connection, in the case of Y = Se the conversion $4 \rightarrow 5$ proceeds slower and allene derivative **4c** has proved more stable than in the case of the corresponding sulfurcontaining compound.

In conclusion, the schemes of possible mechanisms suggested for the individual steps of domino reactions of

phenylchalcogenolate anions with dichloropropene 1 allow us to explain the influence of the nature of the chalcogen atom on the ratio of products formed and predict their stereochemistry.

The structures of compounds synthesized were confirmed by a combination of IR spectroscopy, NMR spectroscopy (¹H, ¹³C, ⁷⁷Se), and chromato-mass spectrometry. The structures of Z- and E-isomers of compounds **6b**,**c** were established using a 2D NOESY procedure.²¹ The spectra of Z-isomers exhibited the cross-peaks between the protons of the Me groups and the vinyl proton of the =C-H group. The mass spectra of isomers Z-, E-**6** and **7** did not differ much. This can be due to the fact that molecular ions of three isomers under study have similar structure, which is rapidly formed upon ionization of the molecules.

Experimental

Monitoring of purity of the starting dichloropropene **1** and analysis of products formed were carried out on a a LKhM 80-MD-2 chromatograph (2000×3-mm column, liquid phase Silicon XE-60 (5%) on Chromaton N-AW-HMDS, the column temperature was programmed linearly from 30 to 230 °C at 12 °C min⁻¹, carrier gas helium). ¹H, ¹³C, and ⁷⁷Se NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.13 (¹H), 100.61 (¹³C), and 76.31 MHz (⁷⁷Se)) in solutions in CDCl₃, internal standard Me₄Si (Me₂Se for ⁷⁷Se).

Mass spectra were obtained on a Shimadzu GCMS-QP5050A chromato-mass spectrometer (a SPB-5 column, 60000×0.25 mm), the stationary phase film was 0.25 µm thick; the injector temperature was 250 °C, carrier gas helium, the flow rate 0.7 mL min⁻¹, the temperature was programmed to increase from 60 to 260 °C at 15 °C min⁻¹, the detector temperature was 250 °C, a quadrupole mass analyzer, electron ionization, energy of electrons 70 eV, the source of ions temperature 200 °C, the range of detecting masses 34–650 Da.

Reaction of phenol with dichloropropene 1. 2-Chloro-3-phenoxyprop-1-ene (3a). Phenol (9.42 g, 0.1 mol) was added to a solution of KOH (14.0 g, 0.25 mol) in hydrazine hydrate (60 mL) at 45 °C. After the phenol was dissolved, the reaction mixture was cooled to 0 °C, followed by a dropwise addition of dichloropropene 1 (11.1 g, 0.1 mol) with stirring. The reaction mixture was stirred for 14 h at 0 °C and extracted with dichloromethane (3×50 mL). The extract was dried with MgSO₄, the solvent was evaporated. The residual light yellow liquid (4.36 g) contained (¹H NMR data) 0.3 g (~2% yield) of compound 3a and 4.06 g (38% yield) chloropropenylhydrazine 8. Spectral characteristics of compound 8 are identical to those described in the literature.⁶ Compound 3a was identified in the mixture according to the ¹H NMR data, δ : 4.55 (s, 2 H, OCH₂); 5.43 (s, 2 H, =CH₂); 5.53 (s, 2 H, =CH₂); 6.88 (m, 2 H, H_a); 6.95 (m, 1 H, H_n); 7.26 (m, 2 H, H_m). ¹³C NMR, δ: 69.89 (OCH₂); 113.54 $(=CH_2)$; 115.10 (C_o); 120.61 (C_p); 129.45 (C_m); 136.24 (=CCl-). MS, m/z (I_{rel} (%)): 170 [M⁺ · for ³⁷Cl] (1), 168 [M⁺ · for ³⁵Cl] (4), 133 $[M - Cl]^+$ (40), 105 $[PhCO]^+$ (9), 94 $[PhOH]^+$ (5), 79 (3), 77 [Ph]⁺ (6), 75 (3), 66 (3), 65 (10), 63 (5), 58 (4), 51 (7). $C_{9}H_{9}OCl.$ Calculated: M = 168.6225.

Reactions of dichalcogenides Ph_2S_2 and Ph_2Se_2 with dichloropropene 1 were carried out as described in the works.^{9,10} The reaction conditions and the ratios of reagents are given in Table 1. The mixtures of products were analyzed by GLC, IR spectroscopy, NMR spectroscopy, and chromato-mass spectrometry. Spectral characteristics of compounds **4b,c**, **5b,c** and **Z-6b,c** agree with the literature data.^{9,10} Compounds *E*-**6b,c** and **7b,c** are newly characterized.

E-1,2-Bis(phenylsulfanyl)prop-1-ene (*E*-(6b)) was obtained in 6% yield by the reaction of Ph_2S_2 with dichloropropene 1 at 60 °C (18 h) and characterized in a mixture with *Z*-isomer. ¹H NMR, δ : 2.03 (d, 3 H, Me); 6.38 (q, 1 H, =CH, ⁴J_{HH} = 1.0 Hz); 7.17–7.38 (m, 10 H, Ph). ¹³C NMR, δ : 29.67 (Me); 125.0–136.0 (C=C, Ph).

Isomerization of Z-6b to E-6b. A mixture of KOH (2.26 g, 0.04 mol), hydrazine hydrate (7 mL), and a 11 : 1 mixture of isomers Z-6b and E-6b (1.04 g, 0.004 mol) was stirred for 19 h at 60 °C. A work-up gave a colorless liquid (0.93 g), which was a mixture of compounds Z-6b and E-6b in the ratio 7.5 : 1. The isomerization degree was 4.5%.

E-1,2-Bis(phenylselanyl)prop-1-ene (*E*-6c) was synthesized in 5% yield by the reaction of Ph₂Se₂ with dichloropropene 1 at 60 °C (18 h), the ratio Ph₂Se₂ : KOH = 10 : 1. ¹H NMR, δ : 2.08 (d, 3 H, Me); 6.71 (q, 1 H, =CH, ⁴J_{HH} = 1.0 Hz); 7.18–7.48 (m, 10 H, Ph). ¹³C NMR, δ : 29.58 (Me); 121.90 (=CH), 125.0–136.0 (MeC=, Ph). ⁷⁷Se NMR, δ : 369.1 (PhSeCH=); 491.6 (PhSeC(Me)=); for *Z*-isomer: 385.1 (PhSeCH=); 427.3 (PhSeC(Me)=, ³J_{SeC=CSe} = 91.4 Hz).

Isomerization compounds Z-6c and 7c. A mixture of KOH (1.6 g, 0.03 mol), hydrazine hydrate (7 mL), and a 3 : 1 mixture of isomers *Z*-6c and 7c (1.0 g) was stirred for 19 h at 60 °C. A work-up gave the product (0.83 g) containing (the ¹H NMR data) isomer *Z*-6c (0.68 g), isomer *E*-6c (0.11 g), and compound 7c (0.04 g). The $Z \rightarrow E$ isomerization degree was 14%. The isomerization degree of compound 7c \rightarrow *Z*-6c was 82%.

2,3-Bis(phenylsulfanyl)prop-1-ene (7b). *A*. A mixture of KOH (3.21 g, 0.057 mol), hydrazine hydrate (14 mL), Ph_2S_2 (2.5 g, 11.4 mmol), and dichloropropene **1** (1.27 g, 11.4 mmol) was heated for 2 h (60 °C). The yield of the product was 2%. A work-up gave 1.48 g of the residue (a light brown liquid) containing (¹H NMR data) a mixture of compounds **4b**, **5b**, *Z*-**6b**, *E*-**6b**, and **7b** in the ratio 1.0 : 41.0 : 25.5 : 1.4 : 2.35. ¹H NMR of compound **7b**, 8: 3.61 (d, 2 H, CH₂S, ⁴J_{HH} = 1.2 Hz); 5.04 (s, 1 H, *cis*-CH=); 5.34 (t, 1 H, *trans*-CH=, ⁴J_{HH} = 1.2 Hz); 7.10–7.40 (m, 10 H, Ph).

B. The compound Ph_2S_2 (1.0 g, 4.6 mmol) was added to a solution of KOH (1.3 g, 0.023 mol) in hydrazine hydrate (6 mL). The reaction mixture was stirred for 2.5 h at 85–90 °C and cooled to 60 °C, followed by a dropwise addition of compound **3b** (1.69 g, 9.2 mmol) and stirring for 5 h at this temperature. A work-up gave a light yellow liquid (1.55 g), which was a mixture of compounds **4b**, **5b**, Z-**6b**, E-**6b**, and **7b** in the ratio 1.0 : 47.2 : 57.5 : 3.0 : 7.0. The mixture contained compound **7b** (0.115 g, 5%).

2,3-Bis(phenylselanyl)prop-1-ene (7c). *A.* Diphenyl diselenide (2.0 g, 6.4 mmol) was added in portions to a solution of KOH (1.8 g, 0.032 mol) in hydrazine hydrate (8 mL) at 40-50 °C. The reaction mixture was heated for 3 h at 85-90 °C and cooled to 60 °C. Dichloropropene **1** (0.71 g, 6.4 mmol) was then added dropwise at this temperature with stirring, and the stirring was continued for 5 h. Then, the mixture was cooled and treated as described in the work¹⁰ to obtain the product as a yellow liquid

(1.42 g), which contained compound **7c** (0.18 g). ¹H NMR, δ : 3.66 (d, 2 H, CH₂Se, ⁴*J*_{HH} = 0.7 Hz, ²*J*_{SeCH} = 12.3 Hz); 5.09 (s, 1 H, *cis*-CH=); 5.46 (t, 1 H, *trans*-CH=, ⁴*J*_{HH} = 0.7 Hz, ³*J*_{SeC=CH} = 16.3 Hz); 7.18–7.48 (m, 10 H, Ph). ¹³C NMR, δ : 35.66 (SeCH₂, ¹*J*_{CSe} = 64.7); 119.43 (=CH₂, ¹*J*_{CSe} = 9.3), for aromatic protons, first are reported signals for the Ph-protons of the PhSeCH₂ group, then those of the ring of the PhSe group 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 (<u>C</u>=CH₂, ¹*J*_{CSe} = 105.2 Hz). ⁷⁷Se NMR, δ : 336.2 (CH₂Se); 430.6 (SeC=).

B. Diphenyl diselenide (1.0 g, 3.2 mmol) was added in portions to a solution of KOH (0.9 g, 0.016 mol) in hydrazine hydrate (4.5 mL) (40–50 °C). The reaction mixture was stirred and heated for 3 h at 85–90 °C, then cooled to 60 °C. 2-Chloro-3-phenylselanylprop-1-ene (**3c**) (1.47 g, 6.4 mmol) was added dropwise at this temperature, the mixture was stirred for 18 h at 60 °C, cooled, and treated as described in the work¹⁰ to obtain the product as a yellow liquid (2.0 g), which contained *Z*-isomer of compound **6c** (1.4 g, 63%) and compound **7c** (0.6 g, 26%).

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