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# Synthesis of Unsaturated Organoselenium Compounds via the Reaction of Organic Diselenides with 2,3-Dichloro-1-propene in the Hydrazine Hydrate–KOH System

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**Abstract**—Dimethyldiselenide reacts with 2,3-dichloro-1-propene at 20–25°C in the hydrazine hydrate–KOH medium to form 2-chloro-3-methylselanyl-1-propene with 90% yield. Diphenyldiselenide in the reaction with 2,3-dichloro-1-propene, depending on the conditions, can give quite selectively four products: 2-chloro-3-phenylselanyl-1-propene, phenylselanylpropadiene, 1-phenylselanyl-1-propyne, and *Z*-1,2-bis(phenylselanyl)-1-propene. The effect of the selenium atom on the reaction direction and the products structure is discussed.

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The chemistry of organoselenium compounds has been actively developing over recent decades [1]. This is not only due to expansion of their industrial applications [2] and unique biological activity of some organoselenium compounds [3] but also due to wide use of organoselenium compounds in organic synthesis [4]. Especially large synthetic potential is offered by unsaturated organic structures containing selenium [5].

Reactions of addition of selenols or diselenides to alkynes [5, 6] as well as the substitution reactions with selenium nucleophiles are used for the synthesis of unsaturated selenides. Nucleophilic substitution readily occurs at the allylic carbon [7], although in the presence of transition metal complexes [8, 9] or phase transfer catalysts [10] the substitution of halogen by organoselenium moiety can proceed also at the $sp^2$-hybridized carbon atom.

2,3-Dichloro-1-propene (**I**), containing chlorine atoms both at the $sp^3$- and $sp^2$-hybridized carbon atoms, is one of the key reagents for the synthesis of unsaturated organoselenium compounds. We have shown that the structure of the products formed in the reaction of **I** with the chalcogen-containing nucleophiles depends on the nature of the nucleophile, temperature, and the redox properties of the system used to generate chalcogen-containing anions from elemental chalcogens or organic dichalcogenides [11–13].

The systems based on hydrazine (in the form of commercially available hydrazine hydrate) are convenient and highly efficient reductive systems for activation of elemental chalogens by their conversion into chalcogenide anions ($Y_n^{2-}$, where Y = S, Se, Te; $n$ = 1–3) [14]. Sulfur activated to disulfide anions by the hydrazine hydrate–KOH system reacts with 2,3-dichloro-1-propene (**I**) to form bis(2-chloro-1-propene-3-yl)sulfide via exclusively the chlorine atom at the $sp^3$-hybridized carbon atom of **I** [11]. When the activation of sulfur is carried out in the hydrazine hydrate–monoethanolamine system (which also generates $S_2^{2-}$ anions), the product of the reaction is bis(2-chloro-1-propene-3-yl)disulfide [12]. With selenium, in both reductive systems bis(2-chloro-1-propen-3-yl)-selenide is the only product [13]. The reaction with tellurium, priorly activated to ditelluride anions, with **I** proceeds just the other way: allene is formed and elementary tellurium is regenerated, that is, both chlorine atoms of **I** take part in the reaction [11].

Recently, we have discovered an unexpected sequence of transformations in the reaction of diphenyldisulfide with **I** in the hydrazine hydrate–KOH system [15], namely, the nucleophilic substitution of chlorine at the allyl position with the PhS group followed by dehydrochlorination into the allene derivative, the allene–acetylene rearrangement, and finally the addition of $PhS^-$ anion to the appeared triple bond. Varying the conditions, each of the products of this sequence can be selectively obtained.

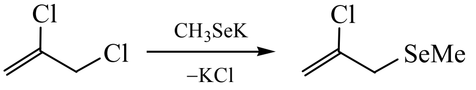
Developing these studies, in this work we examined the possibility of unsaturated organoselenium compounds preparation on the basis of the reaction of **I** with dimethyldiselenide and diphenyldiselenide **II**. The reactions were performed in the hydrazine hydrate–KOH system in which the Se–Se bond of diselenides was reductively split. Reduction of diselenides is not that smooth as of the corresponding disulfides [14], therefore, in all cases the excess of alkali was used ($R_2Se_2$:KOH = 1:5) [scheme (1)].

$$2R_2Se_2 + N_2H_4{\cdot}H_2O + 4KOH \rightarrow 4RSeK + N_2 + 5H_2O, \quad (1)$$

R = Me, Ph.

The so obtained solutions of potassium selenolate were introduced in the reaction with **I** without isolation.

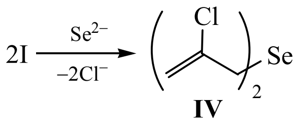
2-Chloro-3-methylselanyl-1-propene (**IIIa**) was obtained with 90% yield via the reaction with dimethyldiselenide reduced to potassium methaneselenolate at 20–25°C [scheme (2)].



(2)

**I** **IIIa**

A somewhat unexpected result of this reaction was the formation of bis(2-chloro-1-propene-3-yl)selenide (**IV**) with 5–7% yield. Taking into account the results of [13], the formation of selenide **IV** occurred due to the presence of $Se^{2-}$ and $Se_2^{2-}$ anions in the reaction mixture [scheme (3)].



(3)

**IV**

In turn, $Se^{2-}$ or $Se_2^{2-}$ anions could be generated from elemental selenium, which was the product of dimethyldiselenide decomposition, caused by thermal instability of aliphatic diselenides [16].

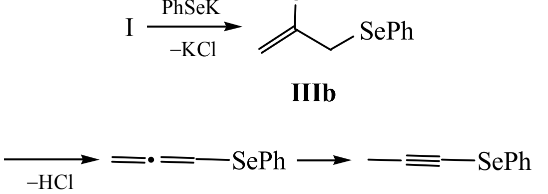
$$Me_2Se_2 \rightarrow Me_2Se + Se,$$

$$2Se + N_2H_4{\cdot}H_2O + 4KOH \rightarrow 2K_2Se + N_2 + 5H_2O,$$

$$\text{or } 4Se + N_2H_4{\cdot}H_2O + 4KOH \rightarrow 2K_2Se_2 + N_2 + 5H_2O.$$

The increase of reaction (2) temperature to 50°C resulted in the formation of a complex mixture of nonidentified products. Noteworthily, dimethyldisulfide formed a complex mixture of products upon reaction with **I** in the hydrazine hydrate–alkali system even at room temperature.

Similarly to diphenyldisulfide (see [15]), diphenyldiselenide **II** gave the mixture of three products (from GC, chromato-mass spectrometry, and NMR) upon reaction with **I** at 30–35°C: 2-chloro-3-phenylselanyl-1-propene (**IIIb**) (36%), 1-phenylselanylpropadiene (**V**) (43%), and 1-phenylselanyl-1-propyne (**VI**) (8%) (yields were calculated from $^1H$ NMR) in the molar ratio **IIIb**:**V**:**VI** = 5:5:1 [scheme (4)].



**IIIb**

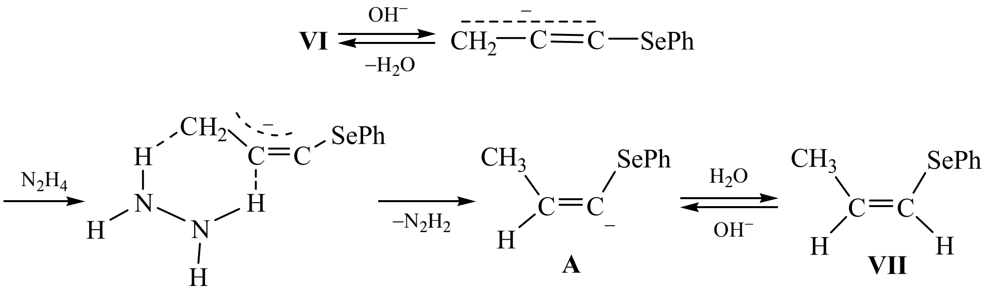
(4)

**V** **VI**

According to [15], the ratio of the respective products of the reaction with diphenyldisulfide was 1.0:3.3:3.3. Thus, in the case of diphenyldiselenide the reactions of dehydrochlorination with the formation of allenylselenide **V** and isomerization of the latter into the acetylenic selenide **VI** were much slower.

Variation of the reaction conditions allowed altering its selectivity. When the reaction of diselenide **II** with **I** was performed at –5 to –10°C, the selenide **IIIb** was obtained with 85% yield, the allenylselenide **V** was found in trace amounts, and selenide **VI** was absent in the products. In the same reaction run at 5 to 10°C, selenide **IIIb** was formed with 81% yield, selenide **V** was obtained with 12% yield, while acetylenic selenide **VI** was not detected. The selectivity of acetylenic selenide formation **VI** could be substantially increased by increasing of the KOH:$Ph_2Se_2$ molar ratio to 10:1 and by increasing the reaction longer. At 25°C with the above-mentioned ratio of the reagents, selenide **VI** was the major product (58%), allenylselenide **V** was formed with 19% yield, selenide **IIIb** was not detected. When increasing the time of the reaction to 33 h, the yield of acetylenic selenide **VI** was of 59%, and that of selenide **V** was of 13%. Thus, with lower concentration of allenylphenylselenide **V** in the reaction mixture, the rate of its isomerization into the corresponding acetylene **VI** was notably decreased.

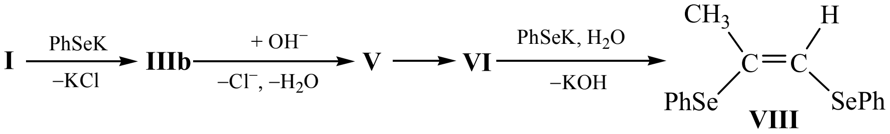
In such a protracted reaction (after 33 h), another product was detected in the products mixture, *Z*-1-phenylselanyl-1-propene (**VII**) (yield of 2–3%), which was apparently formed by hydrogenation of the acetylenic selenide **VI** in the hydrazine hydrate–alkali system. It was previously shown that hydrogenation of multiple bonds in that system was observed only when the unsaturated compound and the reducer (hydrazine) were in the same phase [17]. Transfer of compound **VI** to the water-hydrazine phase was possible only upon its ionization by the alkali [scheme (5)].



(5)

Hydrogenation, apparently, gave rise to anion **A** stabilized by selenium atom. Due to steric effects, exclusively *Z*-isomer of **VII** (from NMR) was formed in the reaction.

At 60°C, behavior of diphenyldisulfide [15] and diphenyldiselenide **II** in the reaction with **I** was practically the same. At reagents molar ratio of 1:5:1 (reaction time 19 h) the only product extracted from the reaction mixture was *Z*-1,2-bis(phenylselanyl)-1-propene **VIII** formed with 65% yield with respect to diselenide **II**. Compound **VIII** was the product of potassium selenophenolate addition to acetylenic selenide **VI**. Thus, at 60°C the following transformations occurred [scheme (6)]:



(6)

Formation of the *Z*-isomer of 1,2-bis(phenylselanyl)-1-propene (**VIII**) was in accordance with the rule of *trans*-addition of nucleophilic reagents to the triple bond [18]. Selenides **V** and **VI** were not detected in the reaction products.

Reaction (6) proceeded with full conversion of dichloropropene **I** but the yield of compound **VIII** was far from quantitative. Therefore, after the extractive separation of bis(phenylselanyl)-1-propene **VIII**, the water-hydrazine layer was treated with methyl iodide, and selenoanisole **IX** was obtained with the yield of 23% with respect to $Ph_2Se_2$ [scheme (7)].

$$PhSeK + CH_3I \xrightarrow[-KI]{} \underset{\textbf{IX}}{PhSeCH_3} \qquad (7)$$

Taking into account the amount of potassium selenophenolate unreacted according to Eq. (6), the yield of compound **VIII** was 84%.

1-Phenylselanyl-1-propyne (**VI**) was earlier prepared in a multistage synthesis via the derivative of 1,2,3-selenadiazole [19]. The method suggested in this work was advantageous due to the availability of the reagents and milder conditions of the process.

The structure of all synthesized compounds was proved by IR, $^1$H, $^{13}$C, $^{77}$Se NMR spectroscopy and by chromato-mass spectrometry. Fragmentation of the allenic and acetylenic selenides **V** and **VI** in the mass spectra was similar to that of the corresponding sulfides [15]. The ratio of the ions peaks intensities $(M - H)^+/M^+$ (estimated from the signal corresponding to $^{80}$Se isotope) equaled 2.0 for compound **V** and 0.4 for compound **VI**, which supported the analogy of transformations of the molecular ions upon electron impact declared in [15].

Thus, the reaction of organic diselenides with 2,3-dichloro-1-propene **I** in the hydrazine hydrate–KOH system could be used as a convenient method for preparation of chlorinated allylselenides, allenylselenides, propynylselenides, and diselanyl-substituted propenes. Those compounds are prospective for organoselenium synthesis applications due to high reactivity of the unsaturated species.

## EXPERIMENTAL

IR spectra were recorded in thin layer using Bruker IFS-25 spectrometer. $^{1}$H, $^{13}$C, $^{77}$Se NMR spectra were registered with Bruker DPX 400 spectrometer at 400.13, 100.62 and 76.31 MHz, respectively, in $CDCl_3$ solutions, internal standards being HMDS ($^{1}$H, $^{13}$C) or $Me_2Se$ ($^{77}$Se). Electron impact mass spectra were obtained with Shimadzu GCMS–QP5050A chromato-mass spectrometer (column SPB-5, 60000×0.25 mm, quadruple mass analyzer, energy of ionization 70 eV, ionic source temperature of 190°C, range of detected masses 34-650 Da). The values of *m/z* of ions containing Se and Cl atoms were given for the signals corresponding to $^{80}$Se and $^{35}$Cl isotopes. Relative intensities $I_{\mathrm{rel}}$ were calculated taking into account the peaks of all isotopes.

The reactions were monitored and the liquid products were analyzed with LKhM 80-MD-2 chromatograph (column 2000×3 mm, liquid phase DC-550, 5% on Chromaton N-AW-HMDS, in the linear temperature programming mode, 12 deg/min, as gas carrier was helium).

**2-Chloro-3-methylselanyl-1-propene (IIIa).** Freshly distilled dimethyldiselenide (2.0 g, 0.0106 mol) was added dropwise upon stirring at 45–50°C to the solution of 2.97 g (0.053 mol) of KOH in 13.5 ml of hydrazine hydrate. The reaction mixture was stirred at this temperature for 2 h, then cooled to 20-25°C, and 2.35 g (0.0212 mol) of 2,3-dichloro-1-propene **I** was added. The mixture was further stirred for 7 h, diluted with water (30 ml), and extracted with $CH_2Cl_2$ (2× 30 ml); the extract was dried over $MgSO_4$ and the solvent was removed to obtain 3.58 g of the residue, which contained (GLC, chromato-mass and $^{1}$H NMR) 3.24 g (90%) of compound **IIIa** and 0.18 g (7%) of bis(2-chloro-1-propen-3-yl)selenide (**IV**). Compound **IIIa** was isolated by vacuum distillation, bp 92–94°C (82 mm Hg). IR spectrum, ν, cm$^{-1}$: 3104, 2998, 2925, 2858, 2820, 1625 ($\nu_{C=C}$), 1527, 1419, 1273, 1194, 1099, 828, 713, 648, 620, 506, 470. $^{1}$H NMR, δ, ppm: 2.0 s (3H, MeSe, $^{2}J_{\mathrm{H–Se}}$ 11 Hz), 3.37 s (2H, $CH_2Se$, $^{2}J_{\mathrm{H–Se}}$ 14 Hz), 5.22 br.s, 5.26 br.s (2H, $CH_2$=). $^{13}$C NMR, $\delta_C$, ppm: 4.64 (MeSe, $^{1}J_{\mathrm{C–Se}}$ 63 Hz), 32.05 ($CH_2Se$, $^{1}J_{\mathrm{C–Se}}$ 66 Hz), 113.49 (=$CH_2$), 139.11 (ClC=). $^{77}$Se NMR, δ, ppm: 122.72. Mass spectrum, *m/z* ($I_{\mathrm{rel}}$, %): 170 [*M*] (15), 153 ($M - CH_3 - H_2$) (3), 135 (*M* – Cl) (5), 119 ($M - CH_3 -$ Cl) (4), 107 ($C_2H_3Se$) (3), 94 ($CH_2Se$) (43), 75 ($C_3H_4Cl$) (16), 53 (11). Found, %: C 28.56; H 4.47; Se 45.72; Cl 20.49. $C_4H_7SeCl$. Calculated, %: C 28.34; H 4.16; Se 46.58; Cl 20.91.

**Bis(2-chloro-1-propen-3-yl)selenide (IV)** was identified by GC, GC–MS, and $^{1}$H, $^{13}$C, $^{77}$Se NMR methods by comparison with the reference specimen [13].

**Reaction of 2,3-dichloro-1-propene (I) with diphenyldiselenide (II).** Diselenide **II** (6.0 g, 0.019 mol) was added in several portions to the solution of 5.38 g (0.096 mol) of KOH in 24 ml of hydrazine hydrate at 45–50°C. The reaction mixture was heated at 85–90°C for 3 h, then cooled to 30–35°C, and 4.26 g (0.038 mol) of 2,3-dichloro-1-propene **I** was added dropwise. The resulting mixture was stirred for 7 h (30–35°C), cooled to room temperature, and extracted with $CH_2Cl_2$ (3× 50 ml); the combined extracts were dried with $MgSO_4$, and the solvent was removed. From the GLC, GC–MS and $^{1}$H NMR data, the residue (7.0 g) contained three products **IIIb, V,** and **VI** in the ratio of 1.7:1.7:0.3 (yields are given in the discussion part).

**2-Chloro-3-phenylselanyl-1-propene (IIIb)** was obtained with the highest yield from 7.0 g (0.022 mol) of diphenyldiselenide **II**, 6.27 g (0.112 mol) of KOH, 28 ml of hydrazine hydrate, and 4.97 g (0.045 mol) of dichloropropene **I**. The splitting of $Ph_2Se_2$ was performed as described above, the reaction of the so prepared PhSeK solution with compound **I** was performed for 7.5 h at –5 to –10°C. The reaction mixture was treated with $CH_2Cl_2$. After removal of the solvent, 8.84 g of the residue was obtained, containing selenide **IIIb** and traces of allenic selenide **V**. Pure selenide **IIIb** was obtained by vacuum distillation, bp 85–86°C (1.5 mm Hg), being a colorless liquid turning yellow upon storage. IR spectrum, ν, cm$^{-1}$: 1624 ($\nu_{C=C}$). $^{1}$H NMR, δ, ppm: 3.64 s (2H, $CH_2Se$, $^{2}J_{\mathrm{H–Se}}$ 14 Hz), 5.02 br.s, 5.08 br.s (2H, $H_2C$=), 7.23 m (3H, $H_m$, $H_p$), 7.47 m (2H, $H_o$). $^{13}$C NMR, $\delta_C$, ppm: 36.12 ($CH_2Se$, $^{1}J_{\mathrm{C–Se}}$ 68 Hz), 114.40 ($H_2C$=), 128.00 ($C_p$), 128.81 ($C_i$), 129.28 ($C_m$), 134.36 ($C_o$), 138.86 (ClC=). $^{77}$Se NMR, δ, ppm: 339.0 t, ($^{2}J_{\mathrm{Se–H}}$ 14 Hz). Mass spectrum, *m/z*: 232 [*M*], 197 (*M* – Cl), 157 (PhSe), 115 ($PhC_3H_2$), 91 ($C_7H_7$), 77 (Ph). Found, %: C 46.71; H 3.78; Se 34.61; Cl 15.30. $C_9H_9SeCl$. Calculated, %: C 46.68; H 3.92; Se 34.10; Cl 15.31.

**1-Phenylselanylpropadiene (V)** was isolated by vacuum distillation, bp 94°C (2.5 mm Hg). Colorless liquid, rapidly turning yellow. IR spectrum, ν, cm$^{-1}$: 1942 ($\nu_{C=C=C}$). $^{1}$H NMR, δ, ppm: 4.74 d (2H, $H_2C$=, $^{4}J_{\mathrm{H–H}}$ 6.2 Hz), 6.02 t (1H, =CH–, $^{4}J_{\mathrm{H–H}}$ 6.2 Hz, $^{2}J_{\mathrm{Se–H}}$ 20.1 Hz), 7.23 m (3H, $H_m$, $H_p$), 7.51 m (2H, $H_o$). $^{13}$C NMR, $\delta_C$, ppm: 77.12 ($CH_2$=), 77.40 (=CH–), 127.28

($C_p$), 129.21 ($C_m$), 132.02 ($C_o$), 134.40 ($C_i$), 207.91 (=C=). $^{77}$Se NMR, δ, ppm: 352.4 ($^2J_{Se–H}$ 20.1 Hz). Mass spectrum, *m/z*: 196 [*M*], 195 (*M* – H), 157 (PhSe), 115 ($PhC_3H_2$), 91 ($C_7H_7$), 77 (Ph). Found, %: C 55.85; H 4.43; Se 40.19. $C_9H_8Se$. Calculated, %: C 55.40; H 4.13; Se 40.47.

**1-Phenylselanyl-1-propyne (VI)** was obtained with the highest yield (68%) via the reaction of 6.0 g (0.019 mol) of diphenyldiselenide, 10.76 g (0.192 mol) of KOH, 48 ml of hydrazine hydrate, and 4.26 g (0.038 mol) of dichloropropene **I** (33 h at 20–25°C). Product **VI** was isolated by vacuum distillation of the residue after removal of solvent from the extract, bp 95–96°C (2.5 mm Hg). Colorless liquid, rapidly turning yellow. IR spectrum, ν, cm$^{-1}$: 2191 (w) ($\nu_{C\equiv C}$). $^1$H NMR, δ, ppm: 2.05 s (3H, $CH_3$), 7.25 m (5H, Ph). $^{13}$C NMR, $\delta_C$, ppm: 5.63 ($CH_3$), 57.00 (≡C–Se, $^1J_{C–Se}$ 174.1 Hz), 99.83 (Me–$\underline{C}$≡, $^2J_{C–Se}$ 32.6 Hz), 126.91 ($C_p$), 128.89 ($C_o$, $^2J_{C–Se}$ 14.6 Hz), 129.49 ($C_m$), 130.61 ($C_i$). $^{77}$Se NMR, δ, ppm: 269.2. Mass spectrum, *m/z*: 196 [*M*], 195 (*M* – H), 115 ($PhC_3H_2$), 77 (Ph). Found, %: C 55.25; H 4.27; Se 40.36. $C_9H_8Se$. Calculated, %: C 55.40; H 4.13; Se 40.47.

**Dehydrochlorination of 2-chloro-3-phenylselanyl-1-propene (IIIb).** At 25°C, 2.09 g (0.009 mol) of **IIIb** was added dropwise to the solution of 0.55 g (0.01 mol) of KOH in 9 ml of hydrazine hydrate. The reaction mixture was stirred at 35–38°C for 7.5 h, cooled and extracted with $CH_2Cl_2$ (3×10 ml). The extract was dried over $MgSO_4$, and the solvent was removed to give 1.36 g of the residue containing (GLC, GC–MS, and $^1$H NMR) 0.51 g of allenylselenide **V** and 0.85 g of phenylselanylpropyne **VI**.

*Z*-**1-Phenylselanyl-1-propene (VII)** was identified in the mixture by using $^1$H, $^{77}$Se NMR and GC–MS. $^1$H NMR, δ, ppm: 1.76 d.d (3H, $CH_3$, $^3J_{H–H}$ 6.7 Hz, $^4J_{H–H}$ 1.2 Hz, 6.08 d.q [1H, Me–CH=, $^3J_{HC=CH}$ 8.7 Hz, $^3J$ ($CH_3$–CH=) 6.7 Hz], 6.43 d.q (1H, SeCH=, $^3J_{HC=CH}$ 8.7 Hz, $^4J_{H–H}$ 1.2 Hz), 7.16–7.27 m (3H, $H_{m,p}$), 7.48 m (2H, $H_o$) (cf. [20]). $^{77}$Se NMR, δ, ppm: 383.8. Mass spectrum, *m/z*: 198 [*M*], 183 (*M* – $CH_3$), 157 (PhSe), 117 ($PhC_3H_4$), 105 ($CH_3Se$), 91 ($C_7H_7$), 78 ($C_6H_6$)$^{\cdot}$, 77 (Ph).

*Z*-**1,2-Bis(phenylselanyl)-1-propene (VIII).** 2,3-Dichloro-1-propene **I** (2.49 g, 0.022 mol) was added dropwise at 60°C to the solution of potassium selenophenolate prepared from 7.0 g (0.022 mol) of diphenyldiselenide **II** and 6.27 g (0.112 mol) of KOH in 28 ml of hydrazine hydrate. The reaction mixture was stirred at this temperature for 19 h, then cooled to 25°C, diluted with water (30 ml), and extracted with $CH_2Cl_2$ (2×50 ml). The extract was dried over $MgSO_4$, the solvent was removed to give 5.1 g (64%) of crude product **VIII**. IR spectrum, ν, cm$^{-1}$: 1639 w ($\nu_{C=C}$). $^1$H NMR, δ, ppm: 2.12 d (3H, $CH_3$, $^4J_{H–H}$ 1.2 Hz), 6.89 d (1H, =CH, $^4J_{H–H}$ 1.2 Hz), 7.34 m, 7.61 m (10 H, $2C_6H_5$). $^{13}$C NMR, $\delta_C$, ppm: 27.00 ($CH_3$), 124.71 (CH=, $^1J_{C–Se}$ 100.8 Hz, $^2J_{C–Se}$ 19.7 Hz, 133.18 [=C(Me)–Se]. Aromatic signals are given first for the PhSe group in the geminal position to the methyl group: $C_p$ (127.31, 127.80), $C_m$ (129.23, 129.32), $C_o$ (132.40, $^2J_{C–Se}$ 11.1 Hz, 134.16, $^2J_{C–Se}$ 10.9 Hz), $C_i$ (119.69, $^1J_{C–Se}$ 70.2 Hz, 131.27, $^1J_{C–Se}$ 99.3 Hz). Mass spectrum, *m/z*: 354 [*M*], 314 ($Ph_2Se_2$), 234 ($Ph_2Se$), 197 (*M* – PhSe), 182 (*M* – PhSe – $CH_3$), 157 (PhSe), 116 ($PhC_3H_3$), 115 ($PhC_3H_2$), 77 (Ph). Found, %: C 51.89; H 4.23; Se 44.15. $C_{15}H_{14}Se_2$. Calculated, %: C 51.15; H 4.01; Se 44.84.

**Methylselanylbenzene (selenoanisole) (IX).** Methyl iodide (2.71 g, 0.019 mol) was added dropwise upon stirring to the water-hydrazine raffinate obtained after extraction of compound **VIII**. The reaction mixture was extracted with $CH_2Cl_2$ (2×30 ml), the extract was dried over $MgSO_4$, and the solvent was removed to give 1.8 g (23%) of selenoanisole **IX**. $^1$H NMR, δ, ppm: 2.28 s (3H, $CH_3$, $^2J_{H–Se}$ 11.0 Hz), 7.13 m (1H, $H_p$), 7.19 m (2H, $H_m$), 7.37 m (2H, $H_o$). $^{13}$C NMR, $\delta_C$, ppm: 7.14 ($CH_3$, $^1J_{C–Se}$ 63.6 Hz), 125.96 ($C_p$), 128.87, 130.32 ($C_o$, $C_m$), 131.78 ($C_i$, $^1J_{C–Se}$ 104.1 Hz) [21]. $^{77}$Se NMR, δ, ppm: 200.9 [22]. Mass spectrum, *m/z*: 172 [*M*].

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