

Synthesis of Unsaturated Organochalcogen Compounds Proceeding from Dichloroethenes and Organyl Dichalcogenides

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Abstract—Reaction of 1,1- and 1,2-dichloroethenes with Ph_2S_2 , Ph_2Se_2 , Bn_2S_2 , and $i\text{-Pr}_2\text{S}_2$ in a system hydrazine hydrate – KOH proceeds as a sequence of successive transformations: dehydrochlorination of initial dichloroethenes to form chloroacetylene, chlorine substitution for the chalcogen-containing nucleophile (ethynylchalcogenides formation), and the addition of the nucleophilic reagent to the triple bond affording 1,2-dichalcogenylethenes. In reactions with PhS^- and PhSe^- nucleophiles due to the high rate of all stages 1,2-bis(phenylchalcogenyl)ethenes are obtained having mainly the *Z*-configuration. In reactions with BnS^- and $i\text{-PrS}^-$ in the IR, NMR and chromato-mass spectra intermediate ethynylchalcogenides were identified, and the final products consisted of a mixture with the prevalence of the *Z*-isomer.

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Unsaturated organochalcogen compounds are important synthons in organic synthesis [1, 2]. Besides the multiple bonds and chalcogen atoms contained in organic molecules may behave as effective π - and n -donors in coordination with transition metal ions thus providing a possibility of designing bifunctional ligands for complex formation [3, 4].

Chalcogen-substituted ethenes belong to the simplest organochalcogen structures, where at the presence of two chalcogen atoms in the 1, 2 positions the *Z*- or *E*-mutual position of the chalcogenyl fragments is strictly fixed. Their *Z*-position with respect to the double bond is favorable for the formation of coordination compounds. Yet the lack of simple and stereoselective methods of the synthesis of this type ligands impedes the development of the corresponding part of the coordination chemistry and as a consequence the preparation of new efficient extractants, homogenic catalysts, and reagents for organic synthesis.

The first specimens of 1,2-dichalcogenylethenes were obtained from 1,2-dichloroethene and organic sulfides [5], yet the yields and configurations of the prepared compounds were not reported. 1,2-Bis(phenylsulfanyl)ethene formed in a yield of only 5–

14% at the UV-irradiation of a mixture $(\text{PhS})_2\text{Hg}$ with *Z*- or *E*-1,2-dichloroethene in DMSO, and regardless of the configuration of the initial dichloroethene the reaction product formed as an isomers mixture (*E/Z* 0.4) [6]. When in the reaction were used preliminary prepared *E*- or *Z*-isomers $\text{ClCH}=\text{CHSPH}$, under the same conditions the yield of 1,2-bis(phenylsulfanyl)ethene reached 81–84% (the ratio of *E*- and *Z*-isomers in the reaction products obtained from both initial isomers was 0.5) [6].

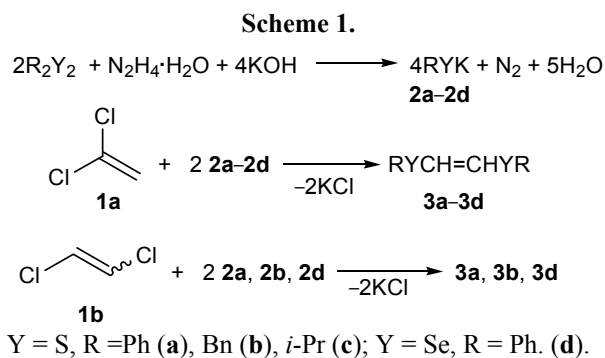
The reaction of 1,2-dibromoethene and PhSCu in quinoline with added 2–10% of pyridine at 200°C provided 1,2-bis(phenylsulfanyl)ethene in a 50% yield (the ratio of *E*- and *Z*-isomers 2.3) [7]. The addition of anions PhSe^- (generated from Ph_2Se_2 and NaBH_4 in polyethylene glycol PEG-400) to ethynylselanylbenzene resulted in a selective formation of *E*-isomer 1,2-bis(phenylselanyl)ethene in a 20% yield [8].

The application of metal complex catalysis which is extensively used in the formation of C–chalcogen bonds [9] only once was utilized in the synthesis of dichalcogenyl-substituted ethenes free of other substituents [10], in the presence of the complex $(\text{bipy})_2\text{NiBr}_2$ from 1,2-dibromoethene and PhSeNa (prepared from Ph_2Se_2 and NaBH_4) 1,2-bis(phenylselanyl)ethene

(the configuration of the product not reported) formed in a 70% yield.

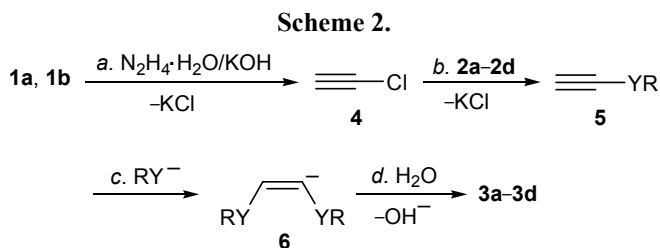
In the synthesis of 1,2-bis(benzylsulfanyl)ethene a difficultly accessible sodium 1,2-ethenedithiolate was utilized [11]. 1,2-Bis(benzylselenanyl)ethene was obtained in a 95% yield by the reaction of dibenzyldiselenide with acetylene in a pressure reactor (12 at) [12]. In the course of structural transformations of dialkylacetals of sulfanyl-substituted acetaldehydes in the presence of sulfuric or polyphosphoric acids or zinc chloride 1,2-bis(phenylsulfanyl)- and 1,2-bis(benzylsulfanyl)-ethenes were formed [13].

We showed that 1,2-dichalcogenylethenes formed in the reactions of diorganyl dichalcogenides R_2Y_2 with 1,1-dichloroethene **1a** or 1,2-dichloroethene (mixture of *E*-, *Z*-isomers, ~1 : 1) **1b** in a system hydrazine hydrate – KOH. In this system dichalcogenides R_2Y_2 suffer a reductive cleavage at the Y–Y bond giving potassium chalcogenolates **2a–2d** [14]. The prepared solutions of potassium chalcogenolates in hydrazine hydrate were used in subsequent syntheses without isolation of compounds **2a–2d**. Vinylidene chloride **1a** and 1,2-dichloroethene **1b** react with chalcogenolates **2a–2d** affording as final products 1,2-dichalcogenylethenes **3a–3d** (Scheme 1).



The formation of one type compounds suggests that presumably in the intermediate stages in the system hydrazine hydrate–KOH first dehydrochlorination of compounds **1a** and **1b** occurs furnishing chloroacetylene **4** (Scheme 2, stage *a*). The cleavage of HCl from dichlorides **1a** and **1b** at the action of bases is well known [15]. Chloroacetylene **4** is a highly reactive compound where the chlorine atom is readily substituted by RY^- anions (Scheme 2, stage *b*). The arising ethynylchalcogenides **5** add chalcogenolate anions to the triple bond leading to the formation of the

final reaction products **3** (Scheme 2, stages *c*, *d*). The addition of RY^- anions to the triple bond occurs to the β -position since the forming carbanion **6** is stabilized with the contiguous chalcogen atom.



Compounds **3a** and **3d** (R = Ph) according to NMR data consist of a single isomer. GC-MS shows that compound **3a** contains traces (<1%) of the second isomer. Dichalcogenylethene **3b** forms as a mixture of isomers in a ratio 10 : 1, and compound **3c** also contains two isomers in a ratio 5 : 1.

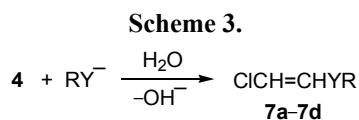
According to the rule of the nucleophilic addition to acetylenes the formed adduct should possess the *Z*-configuration [16]. The analysis of satellite signals ($H-C^{13}$) in the 1H NMR spectra of compounds **3a–3c** (major isomer) shows that the coupling constant in the ethenyl fragment $^3J(HC^{12}-C^{13}H)$ is 8.1–8.5 Hz, corresponding to the *Z*-position of hydrogen atom and chalcogenyl substituent [17]. The mixture of *E*- and *Z*-isomers **3b** was separated by fractional crystallization from ethanol [7], *E*-isomer was obtained as crystals, *Z*-isomer, as oily fluid. Compound **3a** that we isolated both in the reaction with vinylidene chloride **1a** and with 1,2-dichloroethene **1b** was a light red fluid whose boiling point was in agreement with the data of [7]. Therefore it is presumable that compounds **3a** and **3d** form as *Z*-isomers, and in compounds **3b** and **3c** the *Z*-isomer prevails. The formation of a small amount of *E*-isomers in these cases probably is due to the steric hindrances from the groups *i*-Pr and Bn.

As follows from Scheme 3, the transformation **5** → **3** is governed by the reactivity of nucleophiles RY^- and by the stability of the intermediate carbanion **6**; the latter in its turn depends on the stabilizing effect of the chalcogenyl substituent. We showed in [18] that the stabilizing effect of the chalcogene-containing group decreased in the series $PhS^- > PhSe^- > BnS^-$. Therefore it is presumable that the reaction in question **5** → **3** effectively proceeds with $RY^- = PhS^-$ and $PhSe^-$, but with $RY^- = BnS^-$ and *i*-PrS $^-$ the reaction is impeded. Evidently it is the reason of the appearance in the

reaction products of Bn_2S_2 (with compound **1a** and **1b**) and $i\text{-Pr}_2\text{S}_2$ (only reaction with **1a** was performed) of a considerable amount of the corresponding ethynylchalcogenides **5** as proved by IR and ^1H , ^{13}C NMR spectra and the data of GC-MS analysis. The yield of compound **5b** was 15%, of compound **5c**, 18% with respect to the $i\text{-Pr}_2\text{S}_2$ taken interaction and 34% with respect to the reacted substrate.

The identification of compounds **5**, on the one hand, confirms the assumed scheme of the process, and on the other hand, has an independent practical importance since ethynylsulfides **5** are used as key reagents in the synthesis of versatile functionalized organochalcogen compounds [19].

GC-MS method permitted the identification in the reaction products compounds **7a–7d** containing one chlorine atom each (yield ~1–5%). The presence of chlorine in compounds **7** when the reaction mixture contains active nucleophiles RY^- shows that the chlorine atoms are linked to sp^2 -hybridized carbon. It is presumable that compounds **7a–7d** form by the addition of nucleophiles RY^- to chloroacetylene **4** (Scheme 3).



According to GC-MS data compounds **7a–7d** formed as a single isomer whose configuration we failed to establish. Compound **7d** formed in the least yield (<1%) that may be due to the high reactivity of PhSe^- anion in the substitution of the chlorine in chloroacetylene **4**. At the same time PhS^- anion being the most active in addition reactions to the triple bond sufficiently effectively reacted both along Scheme 2 and Scheme 3 (yield of compound **7a** 5%). BnS^- and PrS^- anions possess an intermediate reactivity, and the yields of compounds **7b** and **7c** are ~3%.

Hence, the preparatively simple (25°C, available reagents) reaction of dichloroethenes with organyl dichalcogenides made it possible to prepare 1,2-dichalcogenyl-substituted ethenes, and at optimization of the reaction conditions, ethynylchalcogenides.

EXPERIMENTAL

IR spectra were recorded on a Bruker IFS-25 from thin films, ^1H , ^{13}C , and ^{77}Se NMR spectra were registered on a spectrometer Bruker DPX-400 (operating fre-

quencies 400.13, 100.62, and 76.31 MHz respectively) in CDCl_3 , internal reference TMS (^1H , ^{13}C), Me_2Se (^{77}Se). Mass spectra were taken on a GC-MS instrument Shimadzu GCMS-QP5050A (column SPB-5, 60000×0.25 mm), quadrupole mass analyzer, electron impact, 70 eV, ion source temperature 190°C, range of detected masses 34–650 Da.

Reactions of dichloroethenes (1a and 1b) with diorganyl dichalcogenides R_2Y_2 . General procedure. To a solution of potassium hydroxide in hydrazine hydrate R_2Y_2 was added at stirring by portions or dropwise in a quantity corresponding to the ratio R_2Y_2 – KOH 1 : 5. The mixture was stirred for 2 h at 80–85°C, cooled to 25°C, and at constant stirring dichloroethene **1a** or **1b** was added dropwise. After the addition of the required amount of dichloroethene **1a** (**1b**) the mixture was stirred for 6 h. Reaction products were extracted with ethyl ether (3 \times 30–50 mL), the extract was washed with water and dried with MgSO_4 . Ether was distilled off, the residue was analyzed by NMR, IR spectroscopy and GC-MS method. Then the product was subjected to further treatment.

Compounds **3a** and **3b** (after recrystallization from ethanol) and **3d** were isolated in an individual state as *Z*-isomers. Compounds **3c**, **5b**, and **5c** were identified in the mixture by ^1H , ^{13}C NMR, and mass spectra. Compounds **7a–7d** were identified only by GC-MS method.

{[(Z)-2-(Phenylsulfanyl)ethenyl]sulfanyl}benzene (Z-3a). *a.* It was obtained from 5.46 g (0.025 mol) of Ph_2S_2 , 7.01 g (0.125 mol) of KOH , 30 mL of hydrazine hydrate, and 2.42 g (0.025 mol) of 1,1-dichloroethene **1a**. Yield 76%. Light red fluid, bp 182–186°C (2 mmHg) [*Z*-isomer, bp 170–171°C (1 mmHg) [7]]. IR spectrum, ν , cm^{-1} : 1583 (C=C). ^1H NMR spectrum, δ , ppm: 6.49 s (2H, CH=, $J(\text{HC}^{12}$, C^{13}H 8.1 Hz), 7.20–7.23 m (2H, H^p , C_6H_5), 7.28–7.32 m (4H, H^m , C_6H_5), 7.37–7.39 m (4H, H^o , C_6H_5). ^{13}C NMR spectrum, δ , ppm: 124.95 (CH=), 126.88 (C^p), 129.09 (C^m), 129.46 (C^o), 135.18 (C^j). Mass spectrum: m/z : 244 [M] $^+$. Found, %: C 68.81; H 4.73; S 26.34. $\text{C}_{14}\text{H}_{12}\text{S}_2$. Calculated, %: C 68.81; H 4.95; S 26.24. M 244.369.

b. It was obtained from 5.13 g (0.0235 mol) of Ph_2S_2 , 6.59 g (0.1175 mol) of KOH , 30 mL of hydrazine hydrate, and 2.28 g (0.0235 mol) of 1,2-dichloroethene **1b**. Yield 64%. Spectral characteristics are identical to those reported above.

{[(E)-2-(Phenylsulfanyl)ethenyl]sulfanyl}benzene (E-3a) was present as admixture (<1%) in crude

compound **3a**. ^1H NMR spectrum, δ , ppm: 6.52 s (2H, CH=). Mass spectrum: m/z 244 $[M]^+$.

{{(Z)-2-(Benzylsulfanyl)ethenyl}sulfanyl}methylbenzene (Z-3b). *a*. It was obtained from 3.0 g (0.012 mol) of Bn_2S_2 in a solution of 3.42 g (0.06 mol) of KOH in 15 mL of hydrazine hydrate and 1.18 g (0.012 mol) of 1,1-dichloroethene **1a**. Yield 1.97 g (59%), according to ^1H NMR spectrum it was a mixture of *Z*- and *E*-isomers, 10 : 1. At adding ethanol and cooling (-18°C) yellow crystals precipitated, mp $54\text{--}56^\circ\text{C}$, according to ^1H NMR data the crystals were pure *Z*-isomer **3b**. IR spectrum, ν , cm^{-1} : 1545 (C=C). ^1H NMR spectrum, δ , ppm: 3.88 s (4H, CH_2), 5.99 s (2H, =CH), 7.20–7.29 m (10H, Ph), satellite signals H-C^{13} , $^3J(\text{HC}^{12}, \text{C}^{13}\text{H})$ 8.5 Hz. ^{13}C NMR spectrum, δ , ppm: 38.07 (CH_2), 123.07 (=CH), 127.22 (C^p), 128.55, 128.87 (C^o, m), 137.63 (C^i). Mass spectrum: m/z 272 $[M]^+$. Found, %: C 69.98; H 5.94; S 24.08. $\text{C}_{16}\text{H}_{16}\text{S}_2$. Calculated, %: C 70.54; H 5.92; S 23.54. *M* 272.422.

b. It was obtained from 2.3 g (0.0093 mol) of Bn_2S_2 , 2.62 g (0.047 mol) of KOH, 12 mL of hydrazine hydrate, and 0.9 g (0.0093 mol) of 1,2-dichloroethene **1b**. Yield 56%. Spectral characteristics are identical to those reported above.

{{(E)-2-(Benzylsulfanyl)ethenyl}sulfanyl}methylbenzene (E-3b). ^1H NMR spectrum, δ , ppm: 3.93 s (4H, CH_2), 6.17 s (2H, =CH), 7.20–7.32 m (10H, Ph). ^{13}C NMR spectrum, δ , ppm: 39.70 (CH_2), 121.25 (=CH). The ^{13}C NMR signals of benzene rings coincide with the same signals of the *Z*-isomer.

Ethynylsulfanylmethylbenzene (5b) was identified in the mixture at the isolation of unpurified compound **3b**. Yield 15%. IR spectrum, ν , cm^{-1} : 3285 ($\equiv\text{C-H}$). ^1H NMR spectrum, δ , ppm: 2.79 s (1H, $\equiv\text{C-H}$), 4.01 s (2H, CH_2), 7.21–7.33 m (5H, Ph). ^{13}C NMR spectrum, δ , ppm: 64.0 ($\equiv\text{C-}$), 83.36 ($\equiv\text{C-H}$), the other signals are overlapped with signals of compound **3b**. Mass spectrum: m/z 148 $[M]^+$.

2-{{(Z)-2-(Propan-2-ylsulfanyl)ethenyl}sulfanyl}propane (Z-3c) was obtained from 2.15 g (0.0143 mol) of *i*- Pr_2S_2 , 4.01 g (0.0715 mol) of KOH, 18 mL of hydrazine hydrate, and 2.77 g (0.0286 mol) 1,1-dichloroethene **1a**. According to ^1H NMR spectrum it was a mixture of the initial *i*- Pr_2S_2 , 2-(ethynylsulfanyl)propane **5c**, and compound **3c** (mixture of *Z*- and *E*-isomers, 5 : 1) in a ratio 5.0 : 2.4 : 1. Conversion of *i*- Pr_2S_2 52%. Yield of compound **3c** (isomers mixture) was 8% (with respect to taken *i*- Pr_2S_2) and 16% (with

respect to reacted *i*- Pr_2S_2), yield of isomer **Z-3c** 7 and 13% respectively. IR spectrum, ν , cm^{-1} : 1544 (C=C). ^1H NMR spectrum, δ , ppm: 1.37 d (6H, CH_3), 3.15 septet (2H, >CHS), 6.16 s (2H, =CH). ^{13}C NMR spectrum, δ , ppm: 23.40 (CH_3), 37.65 (>CHS), 122.30 (=CH). Mass spectrum: m/z 176 $[M]^+$.

2-{{(E)-2-(Propan-2-ylsulfanyl)ethenyl}sulfanyl}propane (E-3c). ^1H NMR spectrum, δ , ppm: 6.11 s (2H, =CH).

2-(Ethynylsulfanyl)propane (5c) was identified in a mixture with compound **3c**. Yield 34% with respect to reacted *i*- Pr_2S_2 . IR spectrum, ν , cm^{-1} : 3293 ($\equiv\text{C-H}$), 2039 (C $\equiv\text{C}$). ^1H NMR spectrum, δ , ppm: 2.85 s (1H, $\equiv\text{C-H}$), the rest of the signals are overlapped with the proton signals of compound **3c**. ^{13}C NMR spectrum, δ , ppm: 23.52 (CH_3), 39.23 (CH<), 65.78 ($\equiv\text{C-}$), 83.57 ($\equiv\text{C-H}$). Mass spectrum: m/z 100 $[M]^+$.

{{(Z)-2-Phenylselenylethenyl}selenyl}benzene (Z-3d). *a*. It was obtained from 3.12 g (0.01 mol) of Ph_2Se_2 , 2.81 g (0.05 mol) of KOH, 12 mL of hydrazine hydrate, and 0.97 g (0.01 mol) of 1,1-dichloroethene **1a**. After extraction from the reaction mixture and removal of the solvent we obtained 2.94 g (87%) of yellow fluid, pure biselenide **3d**. IR spectrum, ν , cm^{-1} : 1577 (C=C). ^1H NMR spectrum, δ , ppm: 7.14 s (2H, SeCH= , $^2J_{\text{SeH}}$ 11.6 Hz), 7.24–7.52 m (10H, Ph). ^{13}C NMR spectrum, δ , ppm: 125.97 (CH=, $^1J_{\text{Se-C}}$ 103.9, $^2J_{\text{Se-C-C}}$ 15.9 Hz). ^{77}Se NMR spectrum, δ , ppm: 381.9. Mass spectrum: m/z 340 $[M]^+$.

{{(E)-2-Phenylselenylethenyl}selenyl}benzene (E-3d) was detected only by GC-MS method. Mass spectrum: m/z 340 $[M]^+$.

Compounds **7a–7d** were identified only by GC-MS method. The m/z value of the molecular ion is given only for isotopes ^{35}Cl , ^{37}Cl (their intensity ratio corresponds to the presence of a single chlorine in the molecule).

(2-Chloroethenyl)sulfanylbenzene (7a). Mass spectrum: m/z 172, 170 $[M]^+$.

{{(2-Chloroethenyl)sulfanyl}methylbenzene (7b). Mass spectrum: m/z 186, 184 $[M]^+$.

2-(2-Chloroethenylsulfanyl)propane (7c). Mass spectrum: m/z 138, 136 $[M]^+$.

(2-Chloroethenyl)selenanylbenzene (7d). Mass spectrum: m/z 220, 218 (^{80}Se) $[M]^+$.

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