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Electrophilic Addition of Selenium and Telluriom Halides to Methyldiethynylsilane

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Abstract—Regio- and stereoselective electrophilic addition reactions of $SeCl_2$, $SeBr_2$, $SeCl_4$, $SeBr_4$ to methyldiethynylsilane lead to predominant formation of the *Z*-isomers of 3,6-dihalo-4-methyl-1,4-selenasilafulvenes, disiloxanes on their bases, as well as disiloxanes formed upon the reaction with methyldiethynylsilane. $TeCl_4$ reacts with methyldiethynylsilane with predominant formation of the *E*-isomer of 1,1,3,6-tetrachloro-1-methyl-1-(methyldiethynylsiloxy)-1,4-tellura(IV)silafulvene as a result of the reaction of the intermediate *E*-isomer of 4-methyl-1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvene with methyldiethynylsilane. The structure of the products was proved by the methods of ^1H, ^{77}Se NMR, IR spectroscopy and chromatomass spectrometry.

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Addition of Se_2Cl_2, SCl_2 to terminal and internal alkynes is known to lead to the corresponding bis(2-chloroalkenyl)diselenides and sulfides by the mechanism of *anti*-addition [1–4]. The reaction of Se_2Cl_2 with acetylene affords *E*-2-chloro-1-ethenéselenenylchloride due to expulsion of the selenium atom [5]. Until now, electrophilic reactions of alkynes with selenium dihalides have not been studied.

Prior to our investigations, the electrophilic addition of selenium tetrahalides SeX_4 (X = Br, Cl) to the triple bond has been described only on the example of alkynes. Addition of $SeCl_4$ and $SeBr_4$ to acetylene at low temperatures (from –45 to –78ºC) leads to the *Z,Z*- and *E,E*-bis(2-haloethenyl)selenodihalides [3, 6–9] and at 20ºC to *E,E*-bis(2-haloethenyl)selenide [10].

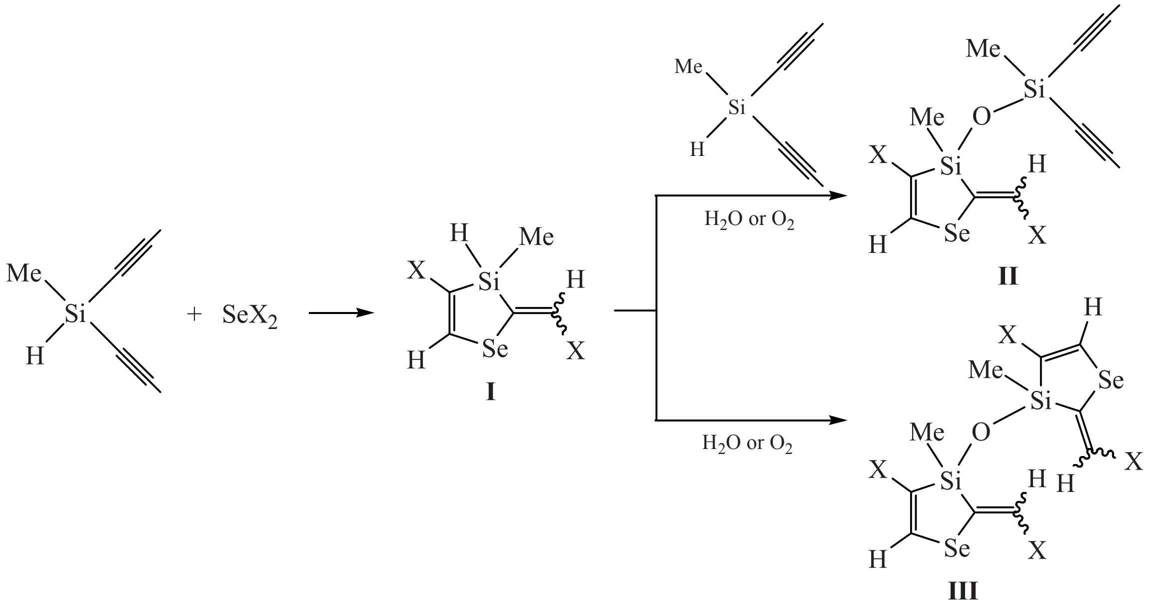
Electrophilic addition of TeX_4 (X = Br, Cl) to acetylene compounds was studied on the example of only substituted acetylenes: PhC≡CH, PhC≡CPh, $C_5H_{11}C{\equiv}CH$, $CH{\equiv}CCH_2OH$ [11–19]. The reactions proceed with the formation of either monoadducts *Z*-$RCH{=}CHTeCl_3$ [11–13, 18, 19] or diadducts $(RXC{=}CH)_2TeX_2$ [11, 14, 15]. Normally, the *syn*-addition takes place although in the case of $TeBr_4$ in benzene the *anti*-addition occurs along with the *syn*-addition resulting in the mixtures of the *Z*- and *E*-isomers of the corresponding adducts [14, 15].

Symmetrical 1,4-substituted derivatives of butynediol upon the reaction with $TeCl_4$ give the products of propargyl rearrangement. Adduct of 1:1 composition formed in the reaction of TeX_4 with 1,4-butynediols is dehydrated to give disubstituted 2,5-dihydrofurane [19].

Earlier we have reported on the synthesis of selenasilicon-containing [20–25] and tellurasilicon-containing unsaturated five-membered heterocycles [26]. They have been obtained by the discovered by us reactions of electrophilic addition of $SeCl_2$, $SeBr_2$, $SeBr_4$, $SeCl_4$, and $TeCl_4$ to diorganyldiethynylsilanes. Before our studies the reactions of selenium dihalides to alkynes were unknown, and electrophilic addition of SCl_2, $SeCl_4$, and $TeCl_4$ was studied only on the example of 4-heterosubstituted hepta-1,6-dienes [27–32].

In continuation of our systematic studies of the reactions of electrophilic addition of selenium and tellurium halides to diorganyldiethynylsilanes [20–26] we have studied electrophilic reactions of $SeCl_2$, $SeBr_2$, $SeCl_4$, $SeBr_4$, and $TeCl_4$ with methyldiethynylsilane (MDES). It was established that the reaction of $SeBr_2$ with MDES, from the data of ^1H NMR, leads mainly to the mixture of the *Z*- and *E*-isomers of 4-methyl-3,6-dibromo-1,4-selenasilafulvene (**Ia**) in the ratio of 5:1 in total yield of 84% (Scheme 1). The *Z*-isomer is manifested in the ^1H NMR spectrum as the

Scheme 1.



I, **II**, **III**: X = Br (**a**), Cl (**b**).

signals of the vinyl protons with characteristic for this isomer long-range coupling constant $^5J_{HH}$ 1.1 Hz. The presence of the Si–H bond results in splitting of the doublet signal of the exocyclic olefinic proton at 7.03 ppm to a doublet of doublets with coupling constant $^4J_{(Si)HH}$ 1.2 Hz. In the spectrum of the *E*-isomer the endocyclic olefinic proton is displayed as a singlet at 7.50 ppm), whereas the exocyclic one as a doublet at 7.21 ppm with the same coupling constant $^4J_{(Si)HH}$ 1.2 Hz. The SiH proton in the spectra of both isomers shows a characteristic doublet of quartets (4.86 and 4.94 ppm for the *Z*- and *E*-isomers, respectively). GC–MS of the isomers of heterofulvene **Ia** show polyisotopic molecular ions $[M]^+$ 334.

A specific feature of the prepared heterofulvenes **I** is the presence on their molecules the fragment which under the conditions of isolation suffers bimolecular oxidation or co-hydrolysis with MDES to the SiOSi group, that is, 4-methyl-4-(methyldiethynyl)siloxy-3,6-dibromo-1,4-selenasila-fulvene (**IIa**). A similar bimolecular reaction of heterofulvene **Ia** affords disiloxane framed with two 1,4-selenasilafulvene groups **IIIa** (Scheme 1). Compound **IIa** is formed as the *Z*-isomer as witnessed by the presence in its ^{1}H NMR spectrum a long-range coupling $^5J_{HH}$ 1.1 Hz between the signals of the exo- and endocyclic olefinic protons (7.16 and 6.85 ppm). GC–MS of compound **IIa** shows a polyisotope molecular ion $[M]^+$ 442, the content of **IIa** in the reaction mixture amounts to 10%. The presence of diethynylsilyl group in molecule **IIa** is also confirmed by the IR spectrum which contains the absorption bands of ethynyl groups.

From the ^{1}H NMR data, disiloxane **IIIa** is formed in 16.5% yield along with 38% of heterofulvene **Ia**. GC-MS of disiloxane **IIIa** shows the corresponding molecular ion $[M]^+$ 680. The presence of a long-range coupling $^5J_{HH}$ 1.1 Hz in the ^{1}H NMR spectrum between the exo and endocyclic olefinic protons is indicative of the *Z,Z*-configuration of disiloxane **IVa** [22].

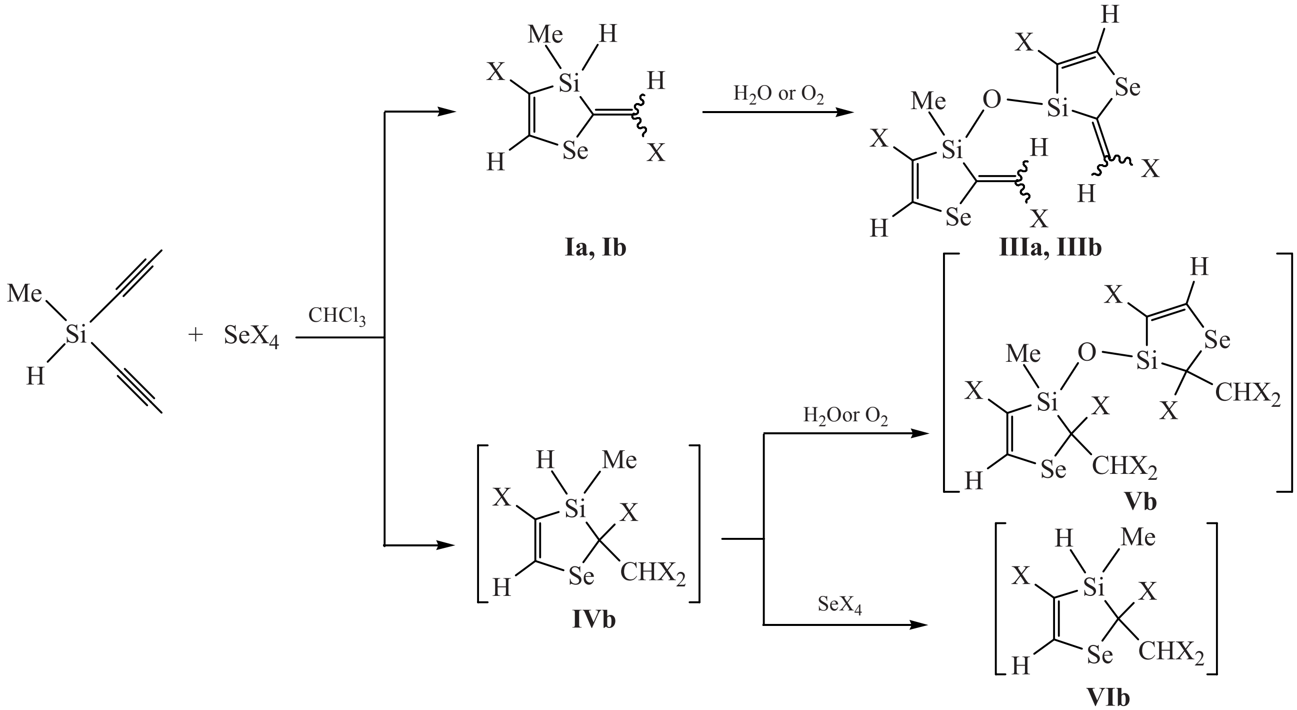
In the reaction of MDES with $SeCl_2$, from the data of GC-MS and ^{1}H NMR, a mixture of the *Z*- and *E*-isomers of 4-methyl-3,6-dichloro-1,4-selenasilafulvene **Ib** (2:1 from ^{1}H NMR) and *Z,Z*- and *E,E*-isomers of disiloxane **IIIb** (3:2 from ^{1}H NMR) is formed (Scheme 1). 1,4-Selenasilafulvene **Ib** and disiloxane **IIIb** in GC–MS show the corresponding molecular ions $[M]^+$ 244 and 502, respectively. The formation of the *Z*- and *E*-isomers of 1,4-selenasilafulvene **Ib** and *Z,Z*- and *E,E*-isomers of disiloxane **IIIb** is confirmed by the ^{1}H NMR spectrum of the reaction mixture, in which the *Z*-isomers are displayed by a long-range coupling $^5J_{HH}$ 1.0–1.2 Hz between the exo and endocyclic olefinic protons [22]. In the ^{77}Se NMR spectra, these compounds are characterized by the signals of ^{77}Se in the range of 488–510 ppm with the doublet of doublets spin–spin coupling pattern of the ^{77}Se signal and exo and endocyclic hydrogen atoms, which typical for the 1,4-selenafulvene ring.

The reaction of $SeBr_4$ with MDES is nonselective and from the data of ^1H and ^{77}Se NMR leads to the mixture of products containing 6% of the *Z*-isomer of heterofulvene **Ia** and 30% of the *Z,Z*-isomer of disiloxane **IIIa** (Scheme 2). ^1H and ^{77}Se NMR spectra of compounds **Ia** and **IIIa** are identical to those of the products formed in the reaction with $SeBr_2$.

The reaction of $SeCl_4$ with DMES practically quantitatively affords disiloxane **IIIb** as the *Z,Z-* and *E,E-*isomers in the ratio of 5 : 1 from the data of ^1H NMR (Scheme 2). The ^1H NMR spectrum of the *Z,Z-*isomer of disiloxane **IIIb** shows characteristic doublet signals of olefinic protons with long-range coupling $^5J_{HH}$ 0.7 Hz, whereas its *E,E*-isomer shows only singlet signals of the exo- and endocyclic protons (7.34 and 6.78 ppm). The GC-MS of disiloxane **IIIb** shows polyisotopic molecular ion $[M]^+$ 502. From the data of ^1H and ^{77}Se NMR, the reaction mixture contains 10% of unidentified compound, probably, chloroderivative **VIb** of 3-methyl-2,6-dichloro-2-dichloromethyl-1,3-selenasilacyclopentene-4 (**IVb**). This is indicated by the presence of a doublet signal at δ 652 ppm with the geminal coupling constant $^2J_{SeH}$ 50 Hz in the ^{77}Se NMR spectrum, typical for unsaturated selenasila-containing cyclopentene heterocycles [22, 33], and the absence in the ^1H NMR spectrum of the protons of groups ≡CH and SiH suggesting either the formation of the disiloxane group Si–O–Si binding the two 1,3-selenasilacyclopentene fragments in the structure of 3-methyl-3-(2',4'-dichloro-2'-dichloromethyl-3'-methyl-3'-oxa-1',3'-selenasilacyclopentene-4)-2,4-dichloro-2-dichloromethyl-1,3-selenasilacyclopentene-4 (**Vb**), or chlorination of the Si–H bond with selenium tetrachloride with the formation of 2,3,4-trichloro-2-dichloromethyl-1,3-selenasilacyclopentene-4 (**VIb**) (Scheme 2).

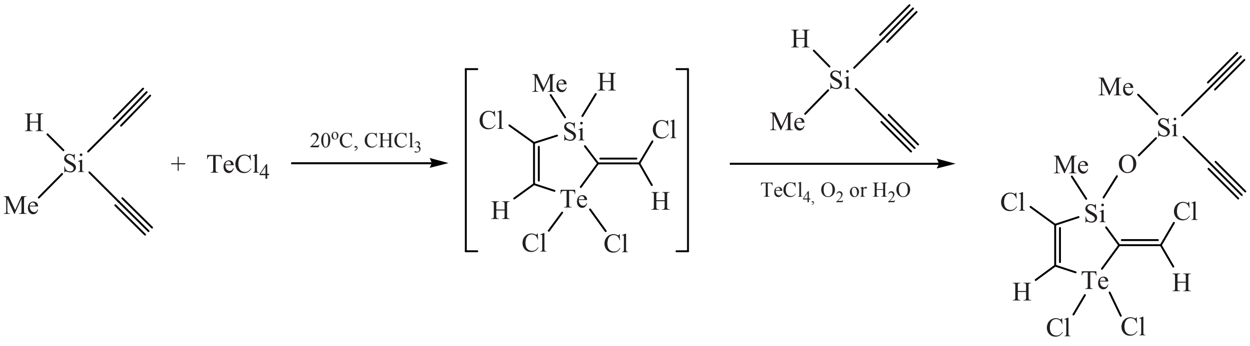
Unlike the reactions of selenium tetrahalides with MDES, $TeCl_4$ reacts with the latter without reduction of Te(IV) to Te(II), similar to the reaction of $TeCl_4$ with diorganyldiethynylsilanes [26], and gives rise to the formation of the *Z*- and *E*-isomers of the five-membered tellurium(IV)silicon-containing heterocycle, 4-methyl-1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvene **VII**. However, intermediate **VII** immediately reacts with MDES leading, from the data of ^1H NMR, to the formation of the *Z*- and *E*-isomers of 1,1,3,6-tetrachloro-1-methyl-1-(methyldiethynylsiloxy)-1,4-tellura(IV)sila-fulvene **VIII** in 36% yield and with the ratio *Z* : *E* = 1 : 5 (Scheme 3).

Scheme 2.



I, III, IV, V, VI: X = Br (**a**), Cl (**b**).

Scheme 3.



VII **VIII**

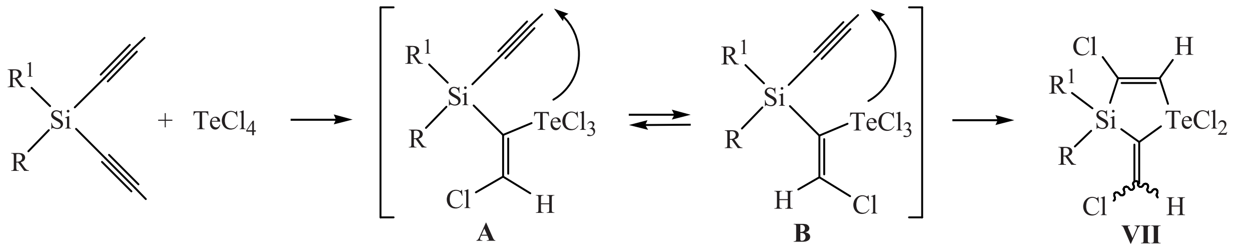
Tetracoordination of tellurium atom in heterocycle **VIII** was proved by the method of ^{125}Te NMR showing the signal at δ 855 ppm which is indicative of a tetracoordinated tellurium atom [34–36]). The doublet signal of tellurium is characterized by geminal coupling constant $^2J_{\text{Te–H}}$ 118 Hz, and a similar coupling of the satellite signals of the olefinic protons is observed in the ^{1}H NMR spectrum. Since, according to calculations, the coupling constants between tellurium-125 and proton are approximately twice as large as the corresponding constants for selenium-77 [37], the experimentally obtained geminal constants $^2J_{\text{Te–H}}$ are in good agreement with the values of the geminal constants $^2J_{\text{Se–H}}$ of 50–60 Hz found by us earlier [20–23], as well as with those for compounds **I–VI** described above. The *Z*- and *E*-isomers of heterocycle **VIII** were identified by the presence of a long-range coupling constant $^5J_{\text{HH}}$ 0.7 Hz between the exo- and endocyclic olefinic protons in the *Z*-isomer, lacking in the predominant *E*-isomer. As was shown by us earlier [20–26] and demonstrated above, the presence of such a coupling is a clear evidence of the formation of the *Z*-isomers of the five-membered unsaturated chalcogenosilicon-containing heterocycles of fulvene structure.

In the mass spectrum of heterocycle **VIII** only the ions of fragmentation appear $[M - \text{Cl}_2]^+$, that is typical for the five-membered unsaturated chalcogenosilicon-containing heterocycles [20–22, 24–26, 38]. From the data of elemental analysis, the ratio Te : Cl = 1 : 4, that proves the composition of heterocycle **VIII**.

Formation of heterofulvenes **Ia** and **Ib** and their derivatives **IIa, IIIa,** and **IIIb** in the reaction of MDES with selenium tetrahalides is, apparently, due to concurrent reduction of selenium tetrahalides by methyldiethynylsilane to selenium dihalides which enter further reactions. Since in the starting MDES the Si–H bond is rather stable as proved by its stability upon storage at 0ºC, the formation of the disiloxane bond in heterofulvenes **Ia** and **Ib** is, probably, due to enhanced accessibility of the hydrogen atom at the silicon atom in the heterocycle.

Formation of heterocycle **VII** and its further transformation into product **VIII** can be explained by successive electrophilic addition of TeCl_4 to two acetylenic fragments of MDES (Scheme 4). Since the reaction results mainly in the *E*-isomer **VII** it can be assumed that on the first stage the anti-Markovnikov anti-addition occurs with subsequent cycloaddition of the intermediate telluriumtrichloride **A** to the second ethynyl fragment of MDES. Appearance of the *Z*-isomer of **VII** leading to the *Z*-isomer of **VIII** is, apparently, due to post-isomerization of the intermediate monoadduct of the *anti*-addition **A** into the monoadduct of the formal *syn*-addition **B** which can be

Scheme 4.



A **B** **VII**

stabilized by intramolecular interaction of the chlorine atom at the double bond with the tellurium atom of the $TeCl_3$ group.

EXPERIMENTAL

^{1}H (400.1 MHz), ^{77}Se (76.30 MHz), and ^{125}Te (126.4 MHz) NMR spectra were registered on a Bruker DPX-400 spectrometer in 5–10% solutions in $CDCl_3$ of acetone-d_6 with HMDS as an internal standard; ^{125}Te NMR spectra were obtained with respect to Me_4Te. Chromatomass spectra were taken on a Shimadzu QP5050A spectrometer, electron impact, 70 eV, capillar column SPB-5ms, 60 m, injector temperature 260°C, column temperature 70–260°C. IR spectra were taken on a Bruker IPS 25 spectrometer in thin layer and vaseline oil. Methyldiethynylsilane **I** was prepared by the known procedure [39].

Reaction with selenium dibromide. To the solution of 1.10 g of $SeBr_2$ in 10 ml of $CHCl_3$, prepared from 0.36 g of powdered selenium and 0.74 g of bromine, in argon atmosphere at –5°C was slowly added 0.43 g of MDES (containing 15% of hardly separable admixture of Et_2O) in 15 ml of $CHCl_3$. The reaction mixture was allowed to reach room temperature and stirred for 24 h. The precipitate was filtered off, the solvent removed in vacuum to obtain 1.52 g of the mixture containing, from the data of GC–MS and multinuclear NMR spectroscopy, the *Z*- and *E*-4-methyl-3,6-dibromo-1,4-selenasilafulvenes **Ia** and *Z*-4-methyl-4-methyldiethynylsiloxy-3,6-dibromo-1,4-selenasilafulvene **IIa**. From the data of ^{1}H NMR, the ratio *Z*-**Ia** : *E*-**Ia** : *Z*-**IIa** is 67 : 9 : 15. The calculated yield of heterofulvene **Ia** is 75%.

Compound Ia. ^{1}H NMR, δ, ppm, for ***Z*-isomer**: 0.46 d (3H, CH_3–Si, $^{3}J_{HH}$ 3.7 Hz), 4.86 d q (1H, Si–H, $^{3}J_{HH}$ 3.7, $^{4}J_{(Si)H-H}$ 1.3 Hz), 7.03 d d (1H, =CHBr, $^{5}J_{HH}$ 1.1, $^{3}J_{(Si)H-H}$ 6.7, $^{4}J_{(Si)H-H}$ 1.2, $^{3}J_{SeH}$ 13.4 Hz), 7.53 d (1H, SeCH=, $^{5}J_{HH}$ 1.1, $^{2}J_{Se-H}$ 54.5 Hz); for ***E*-isomer**: 0.55 d (3H, CH_3–Si, $^{3}J_{(Si)H-H}$ 3.7 Hz), 4.94 d.q (1H, Si–H, $^{3}J_{(Si)H-H}$ 3.6 Hz, $^{4}J_{(Si)H-H}$ 1.6 Hz), 7.16 d (1H, =CHBr, $^{4}J_{(Si)H-H}$ 1.1 Hz), 7.50 c (1H, SeCH=, $^{2}J_{Se-H}$ 55.3 Hz). ^{77}Se NMR, δ, ppm, for ***Z*-isomer**: 571.4 d.d ($^{2}J_{Se-H}$ 54.3, $^{3}J_{Se-H}$ 13.6 Hz); for ***E*-isomer**: 534.9 d.d ($^{2}J_{Se-H}$ 53.3, $^{3}J_{Se-H}$ 13.5 Hz). GC–MS, *m/z* ($I_{rel.}$, %) (^{80}Se, ^{28}Si, ^{79}Br): 2 peaks, 334 (24.5) [M^+]; 319 (5.6) $[M - CH_3]^+$; 293 (3.4), 253 (10.4) $[M - Br]^+$; 229 (26.3) $[M - C_2Br]^+$; 203 (59.6), 147 (28.2), 123 (17.0), 109 (17.1), 93 (6.7), 77 (11.6), 69 (38), 67 (12.1), 53 (100), 43 (58.2).

Compound *Z*-IIa. IR spectrum, ν, cm^{-1}: 1068 (Si–O–Si), 2042, 2154 (C≡C), 3276 (≡CH). ^{1}H NMR, δ, ppm: 0.44 s, 0.47 s (CH_3–Si, CH_3–Si–O–), 2.53 s, 2.54 s (≡CH), 7.21 d (1H, =CHBr, $^{5}J_{HH}$ 1.1 Hz), 7.58 d (1H, SeCH=, $^{5}J_{HH}$ 1.1 Hz). ^{77}Se NMR, δ, ppm: 576.8 d.d ($^{2}J_{Se-H}$ 53.3 $^{3}J_{Se-H}$ 9.4 Hz). Mass spectrum, *m/z* ($I_{rel.}$, %) (^{80}Se, ^{28}Si, ^{79}Br): 442 (16.4) [M^+]; 361 (6.2), 347 (5.2), 335 (8.16), 311 (26), 297 (4.4), 261 (15.4), 233 (70.8), 231 (66.2), 207 (10.1), 193 (7.3), 177 (18.2), 147 (13), 115 (8.6), 93 (74), 83 (44), 67 (15.5), 53 (100), 43 (24).

Similarly, to 1.10 g of $SeBr_2$ prepared as above, in 10 ml of $CHCl_3$ in the atmosphere of dry oxygen-free argon 0.40 g of MDES in 15 ml of $CHCl_3$ was added dropwise at –5ºC, after 14 h of stirring 0.84 g of the mixture was obtained containing, from the data of ^{1}H NMR, 65% of heterofulvene **Ia** as the *Z*-isomer (yield 39%), and 35% of *Z,Z*-4-methyl-4-(3',6'-dibromo-4'-methyl-4'-oxa-1,4-selena-silafulvene)-3,6-dibromo-1,4-selenasilafulvene **IIIa** (yield 10%).

Compound *Z,Z*-IIIa. ^{1}H NMR, δ, ppm: 0.57 s (3H, CH_3–Si), 0.88 s (3H, CH_3–Si), 7.28 d]1H, =CHBr, $^{5}J_{HH}$ 1.1, $^{3}J_{Se-H}$ 12.4, $^{3}J_{Si-H(cis)}$ 5.4 Hz], 7.62 d [1H, =CHSe, $^{5}J_{HH}$ 1.1, $^{2}J_{Se-H}$ 53.7, $^{3}J_{Si-H(trans)}$ 12.6 Hz]. ^{77}Se NMR, δ, ppm: 555.7 d.d ($^{2}J_{Se-H}$ 53.3, $^{3}J_{Se-H}$ 12.5 Hz). IR spectrum, ν, cm^{-1}: 1091 (Si–O–Si), 1555 s (C=C), 2850-3041 (CH_3). Mass spectrum, *m/z* (I_{rel}, %) (^{80}Se, ^{28}Si, ^{79}Br): 680 (11.5) [M^+]; 601 (31.3) [M – Br]; 520 (13.3), 441 (11.5), 417 (6.5), 363 (19.5), 341 (32.7), 287 (95.6), 261 (24.5), 231 (37.7), 207 (23.2), 183 (20.2), 147 (32.3), 137 (15.8), 107 (26.5), 93 (86), 83 (78.5), 53 (100), 43 (53).

Reaction with selenium dichloride. To the solution of 0.62 g of selenium dichloride prepared in 24 h from 0.33 g of fine-powdered selenium and 0.56 g of SO_2Cl_2 in 10 ml of $CHCl_3$ 40 g of MDES, containing Et_2O as an admixture, in 15 ml of $CHCl_3$ was slowly added at –5ºC in argon atmosphere, the obtained reaction mixture stirred for 24 h, then kept in the solution for 5 days. The precipitate was filtered off, solvent removed in vacuum to afford 0.77 g of the mixture containing, from the data of GC-MS, 57% of 4-methyl-3,6-dichloro-1,4-selenasilafulvene **Ib** (yield 43%) and 33.5% of *Z,Z*- and *E,E*-3,6-dichloro-4-methyl-4-(3',6'-dichloro-4'-methyl-4'-oxa-1',4'-selena-silafulvene)-1,4-selenasila-fulvene **IIIb** in the ratio of 2 : 1 from the data of ^{1}H NMR.

Compound *Z*- and *E*-Ib. ^{1}H NMR, δ, ppm: 4.99 q (1H, Si–H, $^{3}J_{HH}$ 3.6 Hz) 4.90 q (1H, Si–H, $^{3}J_{HH}$ 3.3 Hz), in the range δ 7.5–6.6 ppm a groups of signals of similar intensity is observed from which it is impossible to separate the signals belonging to compound **Ib**. GC–MS, *m/z* (I_{rel}, %) (^{80}Se, ^{28}Si, ^{35}Cl): 2 peaks, 244 (24.9) [M^+]; 229 (7.9) $[M - CH_3]^+$; 158 (12.2) , 141 (16), 139 (29), 113 (93), 105 (19), 97 (20), 79 (19.5), 63 (50.4), 53 (49.5), 44 (100).

Compound IIIb. IR spectrum, ν, cm^{-1}: 1070 (Si–O–Si), 2042, 2162 (C≡C), 3281 (≡CH). ^{1}H NMR, δ, ppm, for ***Z,Z*-isomer:** 0.76 s (3H, CH_3–Si), 6.96 d (1H, $^5J_{HH}$ 0.7, $^3J_{Se-H}$ 9.2 Hz), 7.37 d (1H, $^5J_{HH}$ 0.7, $^2J_{Se-H}$ 52.9 Hz); for ***E,E*-isomer:** 0.90 s (3H, CH_3–Si), 6.79 s (1H, $^3J_{Se-H}$ 8.7 Hz), 7.33 s (1H, $^2J_{Se-H}$ 54.2 Hz). ^{77}Se NMR, δ, ppm, for ***Z,Z*-isomer:** 488.6 d.d ($^2J_{Se-H}$ 53.3, $^3J_{Se-H}$ 10.4 Hz); for ***E,E*-isomer:** 503.4 d.d ($^2J_{Se-H}$ 54.3, $^3J_{Se-H}$ 8.2 Hz). GC-MS, *m/z* (I_{rel}, %) (^{80}Se, ^{28}Si, ^{35}Cl): 2 peaks, 502 (9.6) [M^+]; 243 (6.3), 219 (8.2), 207 (37.6), 197 (33.2), 187 (9), 157 (7.7), 115 (15.8), 93 (19.4), 83 (11.6), 65 (9.1), 53 (17.1), 44 (100), 36 (27).

Reaction with selenium tetrabromide. Mixture of 1.39 g $SeBr_4$ prepared in situ from 0.27 g of fine dispersed selenium and 1.12 g Br_2, and 0.33 g MDES in 45 ml of chloroform were stirred in argon atmosphere at room temperature for 24 h. After removing of solvent in vacuum 1.52 g of the mixture of products was obtained as black viscous liquid containing, from the data of ^{1}H NMR, *Z*-4-methyl-3,6-dibromo-1,4-selenasilafulvene **Ia** (6% from the data of ^{1}H NMR) and *Z,Z*-4-methyl-4-(3',6'-dibromo-4'-methyl-4'-oxa-1,4-selenasilafulvene)-3,6-dibromo-1,4-selenasilafulvene **IIIa** (30% from the data of ^{1}H NMR). ^{1}H, ^{77}Se NMR and mass spectra of compounds *Z*-**Ia** and *Z,Z*-**IIIa** see above.

Reaction with selenium tetrachloride. 1.17 g $SeCl_4$ (Aldrich) and 0.50 g MDES containing Et_2O as an admixture was stirred in 30 ml of chloroform in argon atmosphere at room temperature for 4 h and allowed to stay overnight. The precipitate was filtered off and after removal of the solvent in vacuum 1.54 g (100% yield) of the mixture of the *Z,Z*- and *E,E*-isomers of 4-methyl-4-(3',6'-dichloro-4'-methyl-4'-oxa-1',4'-selenasilafulvene)-3,6-dichloro-1,4-selenasilafulvene **IIIb** in the ratio of 5 : 1 was obtained, containing 10% of unidentified product, possibly, 3-methyl-3-(2',4'-dichloro-2'-dichloromethyl-3'-methyl-3'-oxa-1',3'-selenasilacyclopentene-4)-2,4-dichloro-2-dichloromethyl-1,3-selenasilacyclopentene-4 **Vb** or 3-methyl-2-dichloromethyl-2,3,4-trichloro-1,3-selenasilacyclopentene-4 **VIb**. ^{1}H NMR, δ, ppm: 0.94 s (3H, CH_3–Si), 6.54 s (1H, $CHCl_2$), 7.41 s (1H, =CH). ^{77}Se NMR, δ, ppm: 651.5 d ($^2J_{SeH}$ 50.2 Hz). ^{1}H, ^{77}Se NMR and GC–MS of compounds *Z,Z*- and *E,E*-**IIIb** see above.

Reaction with tellurium tetrachloride. 1.42 g $TeCl_4$ and 0.50 g MDES were stirred in argon atmosphere in 35 ml $CHCl_3$ for 8 h at room temperature. The precipitate of dark tarry substance formed (Te and unreacted $TeCl_4$) was filtered off. After removal of solvent in vacuum 0.45 g (36%) of the mixture of the *Z*- and *E*-isomers of 4-methyl-4-methyldiethynylsiloxy-1,1,3,6-tetrachloro-1,4-tellura(IV)-silafulvene **VIII** was obtained (the ratio *Z* : *E* = 1 : 5, from the data of ^{1}H NMR) as a yellow-brown powder, mp 80–85°C.

Compound VIII. ^{1}H NMR, δ, ppm (acetone-d_6) for the ***E*-isomer**: 0.64 s (6H, CH_3), 2.07 s (2H, ≡CH, coincides with the signal of acetone-d_6), 8.07 s (1H, $^3J_{Te-H}$ 14.4 Hz), 8.30 s (1H, $^2J_{Te-H}$ 123, $^3J_{Te-H}$ 10 Hz); for the ***Z*-isomer**: 0.58 s (6H, CH_3), 2.07 s (2H, ≡CH, coincides with the signal of acetone-d_6), 7.69 d (1H, $^5J_{HH}$ 0.7 Hz), 8.34 d (1H, $^5J_{HH}$ 0.7, $^2J_{Te-H}$ 133 Hz). ^{125}Te NMR, δ, ppm (acetone-d_6, from Me_4Te) for the ***E*-isomer**: 854.7 d ($^2J_{Te-H}$ 139.9 Hz). GC–MS, *m/z* (I_{rel}, %) (^{130}Te, ^{35}Cl, ^{28}Si): 2 peaks, 402 (20.4) $[M - Cl_2]^+$; 335 (3.1), 290 (3.5), 247 (19.7), 237 (6.0), 221 (11.7), 207 (15.0), 197 (57.1), 187 (100), 157 (10.4), 137 (16.0), 115 (14.6), 93 (67.9), 83 (40.5), 63 (27.4), 53 (77.6), 43 (26.7), 36 (66.9). Found, %: C 25.43, H 2.45, Cl 29.55, Si 11.68, Te 26.88. $C_{10}H_{10}Cl_4Si_2TeO$. Calculated, %: C 25.46, H 2.14, Cl 30.06, Si 11.91, Te 27.05.

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