

# Unsaturated five-membered selenium–germanium containing heterocycles based on the reactions of selenium di- and tetrahalides with diorganyl diethynyl germanes

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## ABSTRACT

Regio- and stereoselective reactions of selenium dihalides with diorganyl diethynyl germanes in  $\text{CHCl}_3$  afford in yields from preparative to quantitative the first representatives of a new class of selenium–germanium containing heterocycles – 3,6-dihalogen-4,4-diorganyl-1,4-selenagermafulvenes. The reaction of selenium tetrachloride under the same conditions leads to the first representatives of a new class of selenium–germanium containing cyclopentene heterocycles – 2-dichloromethyl-2,4-dichloro-3,3-diorganyl-1-selena-3-germacyclopentenes-4 as well as to the unknown 3,6,6-trichloro-4,4-dialkyl-1,4-selenagermafulvenes formed as a result of a spontaneous dehydrochlorination of the cyclopentene heterocycles. In a case of  $\text{SeBr}_4$  the process of dehydrobromination is dominating. The structures of the heterocycles were proved by multinuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{77}\text{Se}$ ) spectroscopy and mass-spectrometry. In the  $^1\text{H}$  NMR spectra of *Z*-isomers of 1,4-selenagermafulvenes a long-range spin–spin interaction between *exo*- and *endocyclic* olefinic protons through five bonds is revealed lacking in the *E*-isomers.

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## 1. Introduction

Addition of selenium and tellurium tetrahalides to alkynes is known to afford at low temperatures ( $-45$  to  $-78$  °C) *Z,Z*- and *E,E*-(bis(2-halogenalkenyl)chalcogen dihalides [1a–e] while the reaction of  $\text{SeCl}_4$  with acetylene at room temperature gives *E,E*-bis(2-chloroethenyl)selenide [2]. Earlier we have found that the reaction of selenium tetrahalides with diorganyl diethynyl silanes  $\text{RR}^1\text{Si}(\text{C}\equiv\text{CH})_2$  leads to the unknown class of selenium–silicon containing heterocycles of the cyclopentene structure – 2-dihalogenomethyl-2,4-dihalogen-3,3-diorganyl-1-selena-3-silacyclopentenes-4 – in preparative yields [3a–f] while the reaction of selenium dihalides with the same diethynyl silanes results in the unknown heterofulvenes – 3,6-dihalogen-4,4-diorganyl-1,4-selenasilfulvenes – in yields up to 75% [3a,c–e,4].

Among chalcogen–germanium containing heterocycles were known only benzodiselenagermoles and spiro-bisbenzodiselenagermoles formed by the interaction of diselenophenylcyclocones and different aryldichloro- and trichloro-germanes or  $\text{GeCl}_4$ , correspondingly [5a,b]. But no data are available in the literature on unsaturated selenium–germanium containing heterocycles.

In this work, as a continuation of our investigation of electrophilic cycloaddition of selenium di- and tetrahalides to bridged diacetylenes [3a–d,f,4], we have studied the interaction of selenium di- and tetrahalides with cyclic diethynyl germane – 1,1-diethynyl-1-germacyclohexane **1a** – and dialkyl diethynyl germanes  $\text{RR}^1\text{Ge}(\text{C}\equiv\text{CH})_2$  [ $\text{R} = \text{R}^1 = i\text{-Pr}$  (**1b**),  $\text{R} = \text{Et}$ ,  $\text{R}^1 = t\text{-Bu}$  (**1c**)].

Earlier unknown 1,1-diethynyl-1-germacyclohexane **1a** was synthesized according to the method [6a,b] by treatment of 1,1-dichloro-1-germacyclohexane **8**, prepared from  $\text{GeCl}_4$  and 1,5-dibromopentane, with ethynyl magnesium bromide.

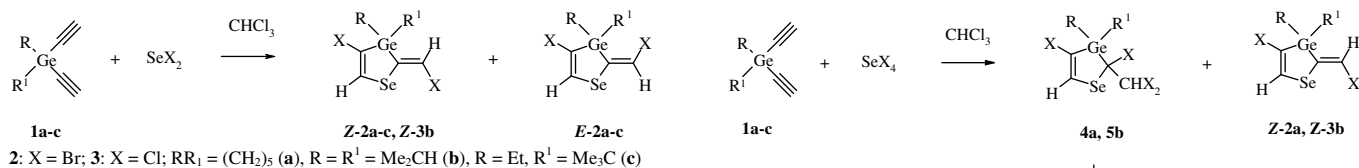
## 2. Results and discussion

We have found that the reactions of  $\text{SeBr}_2$  and  $\text{SeCl}_2$  with diorganyl diethynyl germanes lead to first representatives of a new class of five-membered selenium–germanium containing heterocycles of the fulvene structure – 3,6-dibromo(dichloro)-4,4-diorganyl-1,4-selenagermafulvenes **2a–c**, **3b** – as *Z*-isomers or a mixture of *Z*- and *E*-isomers with the former largely predominating, in yields from preparative to quantitative (Scheme 1, Table 1).

Formation of the heterocycles **2a–c**, **3b** has been demonstrated by the GC–MS and  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{77}\text{Se}$  NMR spectroscopy. In the mass-spectra the intensive peaks of the molecular ions were detected. The heterofulvene structure of these heterocycles was evidenced in the  $^1\text{H}$  and  $^{77}\text{Se}$  NMR spectra by the geminal coupling constants  $^2J_{\text{Se–H}}$

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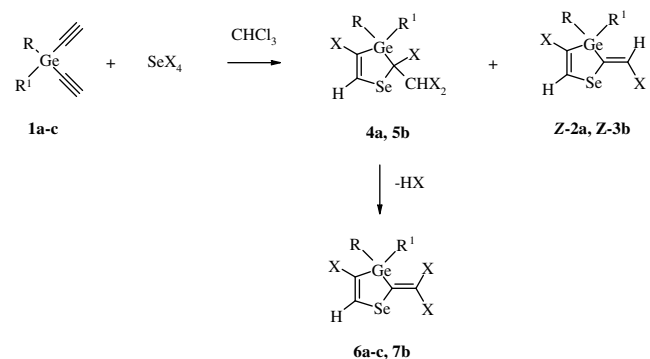
E-mail address: [amosova@irioch.irk.ru](mailto:amosova@irioch.irk.ru) (S.V. Amosova).



57 Hz common to the cyclic unsaturated selenides [7] and by the vicinal coupling constants between selenium atom and exocyclic olefinic protons  $^3J_{\text{Se-H}}$  10–12 Hz. *Z*-Configuration of the major isomer of the heterocycles **2a–c**, **3b** was confirmed by the presence in the  $^1\text{H}$  NMR spectra of the long-range coupling constant between *exo*- and *endocyclic* olefinic protons  $^5J_{\text{HH}}$  1.2 Hz characteristic of the fixed *W*-shaped *trans*-arrangement of the hydrogen atoms in the unsaturated systems [8]. In the *E*-isomers of the heterocycles **2a–c** olefinic protons manifest themselves as singlets. We have found a similar dependence of the NMR spectra fine structure on the isomerism in the case of the silicon analogs – 3,6-dichloro(bromo)-4,4-*R,R*<sup>1</sup>-1,4-selenasilafulvenes [3d,4]. The coupling through five bonds in the  $^1\text{H}$  NMR spectra has been noted also for 2,5-diacyl-1,4-dithiafulvenes [9] and 2,6-bis(organylsulfonyl)-1,4-dithiafulvenes [10]. The  $^{13}\text{C}$  NMR spectra of the *Z*-isomers of the heterocycles **2a–c**, **3b** were characterized by the presence of four signals of the  $\text{sp}^2$ -hybridized carbon atoms and three signals of the  $\text{sp}^3$ -hybridized carbon atoms.

The reaction of  $\text{SeBr}_4$  and  $\text{SeCl}_4$  with diethynyl germanes **1a–c** depends on the nature of halogen and the structure of the substituents at the germanium atom (Scheme 2, Table 1). With  $\text{SeBr}_4$  and 1,1-diethynylgermacyclohexane **1a** as well as with  $\text{SeCl}_4$  and di-*iso*-propyl diethynyl germane **1b** five-membered selenium–germanium containing heterocycles of a new type, namely, 2-dihalogenomethyl-2,4-dihalogen-3,3-diorganyl-1-selena-3-germacyclopentenes-4 **4a** and **5b** are formed in the yields of 67 and 21.5%, respectively, along with *Z*-isomers of heterofulvenes **2a** and **3b**. Besides, in these reactions the formation of trihalogeno-derivatives of five-membered selenium–germanium heterofulvenes **6a** and **7b** has been detected (Scheme 2). In the reaction of  $\text{SeCl}_4$  with di-*iso*-propyl diethynyl germane **1b** the heterocycle **7b** is a main product. As the only products the tribromo-derivatives of selenium–germanium containing heterofulvenes – 3,6,6-tribromo-4,4-dialkyl-1,4-selenagermafulvenes **6b,c** – are formed in the similar reaction of  $\text{SeBr}_4$  with dialkyl diethynyl germanes **1b,c** (Table 1).

Conclusion about the structure of the heterocycle **4a** has been made on the basis of the GC–MS and  $^1\text{H}$  and  $^{77}\text{Se}$  NMR spectroscopy data. In its mass spectrum the molecular ion does not appear because under electron impact dehydrobromination occurs and as a result compound **4a** is identified only by its fragment ion  $[\text{M}-\text{HBr}]^+$ . Earlier we have found instability under electron impact of the tetrabromo-derivatives of the heterofulvenes of the similar structure in the case of 2-dibromomethyl-2,4-dibromo-3,3-diorga-



**2, 4, 6:** X = Br; **3, 5, 7:** X = Cl;  $\text{RR}_1 = (\text{CH}_2)_5$ (a), R = R<sup>1</sup> = Me<sub>2</sub>CH (b), R = Et, R<sup>1</sup> = Me<sub>3</sub>C (c)

nyl-1-selena-3-silacyclopentenes-4 being decomposed during analysis by the GC–MS. As a result only fragment ions  $[\text{M}-\text{Br}_2]^+$  и  $[\text{M}-\text{HBr}]^+$  have been observed in the mass spectra of these heterocycles [3c,e]. Practically complete coincidence of the decomposition schemes for the heterocycles **2a** and **4a** under electron impact, in particular, formation of the fragment ions  $[\text{CH}=\text{CSeC}=\text{CH}]^+$ ,  $m/z$  130, in the case of the compound **2a** and  $[\text{CH}=\text{CSeC}]^+$ ,  $m/z$  129, in the case of the compound **4a**, points clearly to the identity of these compounds, i.e. to the realization for the compound **4a** of the five-membered heterocycle structure but not that of the isomeric six-membered 3,5,5,6-tetrabromo-4,4-pentamethylene-1-selena-4-germacyclohexene-2 **8** (Scheme 3). In favor of the structure **4a** speaks the  $^{77}\text{Se}$  NMR spectrum in which doublet signal of the selenium-77 due to coupling with the geminal hydrogen atom is registered while for the heterocycle **8** a doublet of doublets due to additional coupling through two bonds with the hydrogen atom in the Se–CHBr system should be expected. In the isomeric cyclopentene heterocycle **4a** manifestation of the coupling of the selenium-77 with the hydrogen atoms through three bonds in the Se–CCHBr<sub>2</sub> system is unlikely since it is absent in the similar selenium–silicon containing cyclopentene heterocycles [3e]. The  $^{13}\text{C}$  NMR spectroscopy data satisfy the structure **4a**.

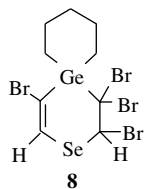
The structure of the tribromofulvene heterocycles **6a–c** is confirmed by the  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{77}\text{Se}$  NMR spectroscopy and GC–MS data. In the mass-spectra these heterocycles manifest themselves by the corresponding molecular ions. In the  $^1\text{H}$  NMR spectra there is only one singlet signal of olefinic proton, while in the  $^{77}\text{Se}$  NMR spectra the selenium atom shows itself as a doublet with the coupling constant  $^2J_{\text{SeH}}$  55–58 Hz found for the heterocycles **4, 5** and characteristic in general of unsaturated selenium containing heterocycles [7].

**Table 1**  
Reactions of  $\text{SeX}_2$  and  $\text{SeX}_4$  with diethynyl germanes (1)

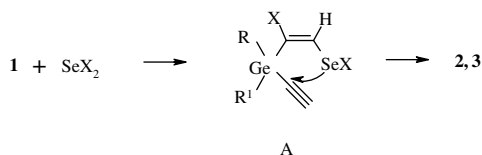
1	R	R <sup>1</sup>	SeX <sub>n</sub>	Reaction time (h)	2, 3	Yield (%)	Z:E <sup>a</sup>	4, 5	Yield (%)	6, 7	Yield (%)
<b>1a</b>	(CH <sub>2</sub> ) <sub>5</sub>		SeBr <sub>2</sub>	2	<b>2a</b>	99 <sup>a</sup>	96:4		–		–
<b>1b</b>	Me <sub>2</sub> CH	Me <sub>2</sub> CH	SeBr <sub>2</sub>	1	<b>2b</b>	84.5 <sup>b</sup>	94:6		–		–
<b>1c</b>	Et	Me <sub>3</sub> C	SeBr <sub>2</sub>	4	<b>2c</b>	66.5 <sup>b</sup>	82:18		–		–
<b>1b</b>	Me <sub>2</sub> CH	Me <sub>2</sub> CH	SeCl <sub>2</sub>	3	<b>3b</b>	45.5 <sup>b</sup>	100:0		–		–
<b>1a</b>	(CH <sub>2</sub> ) <sub>5</sub>		SeBr <sub>4</sub>	5.5	<b>2a</b>	13 <sup>a</sup>	100:0	<b>4a</b>	67 <sup>a</sup>	<b>6a</b>	19 <sup>a</sup>
<b>1b</b>	Me <sub>2</sub> CH	Me <sub>2</sub> CH	SeBr <sub>4</sub>	1		–	–		–	<b>6b</b>	86 <sup>b</sup>
<b>1c</b>	Et	Me <sub>3</sub> C	SeBr <sub>4</sub>	4		–	–		–	<b>6c</b>	83.5 <sup>b</sup>
<b>1b</b>	Me <sub>2</sub> CH	Me <sub>2</sub> CH	SeCl <sub>4</sub>	6	<b>3b</b>	26.5 <sup>a</sup>	100:0	<b>5b</b>	21.5 <sup>a</sup>	<b>7b</b>	41 <sup>a</sup>

<sup>a</sup> According to the  $^1\text{H}$  NMR data.

<sup>b</sup> According to the GC–MS data.



Scheme 3.



Scheme 4.

The formation of the heterocycles **6a–c** and **7b** can be explained by the spontaneous dehydrohalogenation of the intermediate tetrahalogen-derivatives of cyclopentenes **4**, **5**. This is evidenced, in particular, by the complete transformation of the heterocycle **4a** into tribromofulvene **6a** on storage at room temperature for 8 months.

The formation of the heterocycles **2** and **3** is most likely explained by two successive steps of electrophilic regio- and stereo-selective additions of selenium dihalides to triple bonds of diethynyl germanes **1** (Scheme 4). On the first step, proceeding according to the Markovnikov rule due to influence of the diorganylgermyl group, the 2-halogenoethenyl selenenyl halide **A** is formed. On the second step the intramolecular addition of the selenenyl halide **A** to the second ethynyl group of the diethynyl germane **1** goes against Markovnikov rule, apparently, owing to the steric difficulties in the selenirenium cation formed, which promotes addition of the bulky halogen atom to the  $\beta$ -position of the ethynyl group.

Taking into account chemical similarity of the IV period elements it can be suggested that the reaction of selenium tetrabromide with diethynyl germanes proceeds similar to the reaction with diethynyl silanes [3f]. Hence, according to the mechanistic scheme considered for diethynyl silanes [3f], in the pre-reaction bimolecular complex of diethynyl germane with  $\text{SeBr}_4$  the bromination of an ethynyl group of diethynyl germane with the subsequent selenenylbromination of the second one obviously takes place. The formed intermediate adduct **B** undergoes intramolecular cyclization via four-centered transition state **C**, which leads to five-membered cyclopentene heterocycle **4** (Scheme 5).

The formation of the fulvenes **2** and **3** in the reaction of diethynyl germanes **1** with selenium tetrahalides can be plausibly

explained by the competitive reaction of these diethynyl germanes with  $\text{SeX}_2$  generated in the reaction mixtures.

### 3. Experimental

#### 3.1. General procedure

All reactions were carried out under atmosphere of dry argon. The  $^1\text{H}$  (400.1 MHz),  $^{13}\text{C}$  (100.6 MHz) and  $^{77}\text{Se}$  (76.3 MHz) NMR spectra were recorded on a Bruker DPX-400 spectrometer in 5–10% solution in  $\text{CDCl}_3$ , internal reference – HMDS. GC–MS spectra of the heterocycles **2–7** and their mixtures were recorded on the spectrometer Shimadzu QP5050A at electron energy 70 eV, 60 m capillary column SPB-5ms, injection temperature 260 °C, column temperature 70–260 °C.

#### 3.2. Materials

Di-*iso*-propyl diethynyl germane **1b** and ethyl *tert*-butyl diethynyl germane **1c** were prepared according to the method [6b].

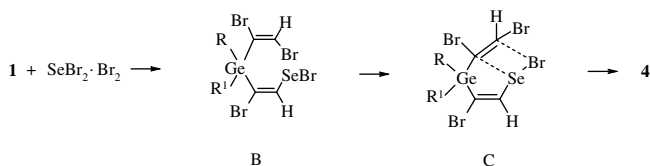
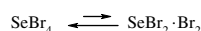
##### 3.2.1. Synthesis of 1,1-diethynyl-1-germacyclohexane **1a**

To Mg (5.0 g, 200 mg a) in  $\text{Et}_2\text{O}$  was added drop-wise a mixture of  $\text{Br}(\text{CH}_2)_5\text{Br}$  (23.0 g, 100 mmol) and  $\text{GeCl}_4$  (21.46 g, 100 mmol). The reaction was activated by addition of several drops of  $\text{Br}(\text{CH}_2)_3\text{Br}$  and the resulting mixture was heated for 0.5 h. Then the reaction mixture was quenched with  $\text{H}_2\text{O}$  and 5% HCl and extracted with  $\text{Et}_2\text{O}$ . The ether extract was dried over  $\text{CaCl}_2$ . After removal of  $\text{Et}_2\text{O}$  a distillation in vacuum afforded 1,1-dichloro-1-germacyclohexane **9** (5.10 g, 24 mmol, 24%), b.p. 85 °C (10 mm Hg),  $n_D^{20}$  1.5105,  $d_4^{20}$  1.5149. To thus prepared compound **9** in  $\text{Et}_2\text{O}$  (50 ml) was added drop-by-drop a solution of ethynyl magnesium bromide prepared from Mg (2.0 g, 80 mg a), EtBr (8.72 g, 80 mmol) and acetylene in THF (100 ml). The resulting mixture was stirred for 1 h, quenched with  $\text{H}_2\text{O}$  and 5% HCl, extracted with  $\text{Et}_2\text{O}$ . The organic layer was dried over  $\text{CaCl}_2$ . After removal of the solvents at the reduced pressure the residue was distilled in vacuum to afford 1,1-diethynyl-1-germacyclohexane **1a** (3.70 g, 19.2 mmol, 80.0%), b.p. 71–72 °C (5 mm Hg),  $n_D^{20}$  1.4995,  $d_4^{20}$  1.2121.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 2.37 (s, 2H,  $\equiv\text{CH}$ ), 1.79 (m, 4H,  $\text{CH}_2$ -2,4), 1.44 (m, 2H,  $\text{CH}_2$ -3), 1.21 (t, 4H,  $^3J_{\text{HH}} = 6.6$  Hz,  $\text{CH}_2\text{Ge}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 93.56 ( $\equiv\text{CH}$ ), 84.01 ( $\equiv\text{C}$ ), 28.98 (C-3), 24.64 (C-2,4), 15.88 ( $\text{CH}_2\text{Ge}$ ).

#### 3.3. Reactions of selenium dihalides with diethynyl germanes (**1**)

##### 3.3.1. Synthesis of 3,6-dibromo-4,4-pentamethylene-1,4-selenagermafulvene (**2a**)

To  $\text{SeBr}_2$  prepared by stirring a Se powder (0.20 g, 2.5 mg a) and  $\text{Br}_2$  (0.40 g, 2.5 mmol) in  $\text{CHCl}_3$  (20 ml) for 1 h at 20 °C was added a solution of 1,1-diethynyl-1-germacyclohexane **1a** (0.48 g, 2.5 mmol) in  $\text{CHCl}_3$  (10 ml) and stirring was continued for 2 h. Removal of the solvent under reduced pressure afforded *Z*- and *E*-isomers (*Z*:*E* = 96:4, according to the  $^1\text{H}$  NMR) of the heterocycle **2a** (1.05 g, 99%) as a brown oil. Anal. Calc. for  $\text{C}_9\text{H}_{12}\text{Br}_2\text{GeSe}$ : C, 25.05; H, 2.80; Se, 18.30. Found: C, 25.17; H, 2.49; Se, 18.31%. GC–MS (EI, *m/z*, %) ( $^{80}\text{Se}$ ,  $^{79}\text{Br}$ ,  $^{74}\text{Ge}$ ): 2 compounds, 432(35) ( $\text{M}^+$ ), 362(5) ( $\text{M}^+ - (\text{CH}_2)_5$ ), 283(5) ( $\text{M} - (\text{CH}_2)_5 - \text{Br}$ ), 258(4), 223(27), 195(9), 177(7), 153(40), 143(9), 130(20), 119(7), 67(27), 55(11), 41(100).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) *Z*: 7.40 (d, 1H,  $^5J_{\text{HH}} = 1.10$  Hz,  $^2J_{\text{SeH}} = 57$  Hz,  $\equiv\text{CHSe}$ ), 6.83 (d, 1H,  $^5J_{\text{HH}} = 1.10$  Hz,  $^3J_{\text{SeH}} = 14$  Hz,  $\text{SeC}=\text{CHBr}$ ), 2.03–1.19 (m, 10H,  $(\text{CH}_2)_5$ ); *E*: 7.34 (s, 1H,  $\equiv\text{CHSe}$ ), 6.81 (s, 1H,  $\text{SeC}=\text{CHBr}$ ), 2.03–1.19 (m, 10H,  $(\text{CH}_2)_5$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 140.4 ( $\text{SeC}=\text{CHBr}$ ), 130.8 ( $\text{GeCBr}=\text{CHSe}$ ), 113.2 ( $\text{GeCBr}=\text{CHSe}$ ), 107.9 ( $\text{SeC}=\text{CHBr}$ ), 29.1, 25.3, 15.6 [ $(\text{CH}_2)_5$ ].  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 556.6 (dd,  $^2J_{\text{SeH}} = 57$  Hz,  $^3J_{\text{SeH}} = 14$  Hz).



Scheme 5.

### 3.3.2. Reaction of $\text{SeBr}_2$ with di-iso-propyl diethynyl germane (**1b**)

Similarly, reaction of  $\text{SeBr}_2$  (2.4 mmol), prepared from Se (0.19 g, 2.4 mg a) and  $\text{Br}_2$  (0.38 g, 2.4 mmol), with diethynyl germane **1b** (0.49 g, 2.4 mmol) in  $\text{CHCl}_3$  (20 ml), 1 h, 20 °C, afforded the mixture (0.98 g) containing, according to the GC–MS, 92% of Z- and E-isomers of 3,6-dibromo-4,4-di-iso-propyl-1,4-selenagermafulvene **2b** (Z:E = 50:3, according to the  $^1\text{H}$  NMR). GC–MS (EI,  $m/z$ , %) ( $^{80}\text{Se}$ ,  $^{79}\text{Br}$ ,  $^{74}\text{Ge}$ ): 2 compounds, 448(5) ( $\text{M}^+$ ), 405(11) ( $\text{M}^+ - \text{C}_3\text{H}_7$ ), 363(2) ( $\text{M}^+ - \text{C}_3\text{H}_7 - \text{C}_3\text{H}_6$ ), 275(1), 221(5), 197(1), 177(1), 153(6), 131(2), 115(1), 99(5), 91(2), 67(2), 51(1), 43(100) ( $\text{C}_3\text{H}_7$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): Z: 7.49 (d, 1H,  $^2J_{\text{HH}} = 1.0$  Hz,  $^2J_{\text{Se-H}} = 58.4$  Hz,  $\text{CBr}=\text{CHSe}$ ), 6.62 (d, 1H,  $^3J_{\text{HH}} = 1.3$  Hz,  $^3J_{\text{Se-H}} = 13.6$  Hz,  $\text{CHBr}=\text{C}$ ), 1.67 (m, 2H,  $^3J_{\text{HH}} = 7.4$  Hz,  $(\text{CH}_3)_2\text{CH}$ ), 1.22 (d, 6H,  $^3J_{\text{HH}} = 7.4$  Hz,  $(\text{CH}_3)_2\text{CH}$ ), 1.23 (d, 6H,  $^3J_{\text{HH}} = 7.4$  Hz,  $(\text{CH}_3)_2\text{CH}$ ); E: 7.45 (s, 1H,  $\text{CBr}=\text{CHSe}$ ), 6.84 (s, 1H,  $\text{CHBr}=\text{C}$ ), 1.98 (m, 2H,  $^3J_{\text{HH}} = 7.6$  Hz,  $(\text{CH}_3)_2\text{CH}$ ), 1.27 (d, 6H,  $^3J_{\text{HH}} = 7.1$  Hz,  $(\text{CH}_3)_2\text{CH}$ ), 1.26 (d, 6H,  $^3J_{\text{HH}} = 7.7$  Hz,  $(\text{CH}_3)_2\text{CH}$ ).  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 578.1 (dd,  $^2J_{\text{SeH}} = 57.5$  Hz,  $^3J_{\text{SeH}} = 14.6$  Hz). An attempt to purify compound **2b** by a column chromatography (silica gel, hexane– $\text{CHCl}_3$ , 95:5) failed.

### 3.3.3. Reaction of $\text{SeBr}_2$ with ethyl tert-butyl diethynyl germane (**1c**)

Similarly, reaction of  $\text{SeBr}_2$  (3.0 mmol), prepared *in situ* from Se (0.23 g, 3.0 mg a) and  $\text{Br}_2$  (0.50 g, 3.0 mmol), with diethynyl germane **1c** (0.63 g, 3.0 mmol) in  $\text{CHCl}_3$  (45 ml) afforded after 4 h of stirring at room temperature the mixture (1.26 g) containing, according to the GC–MS, 71% of 3,6-dibromo-4-ethyl-4-tert-butyl-1,4-selenagermafulvene **2c** (Z:E = 4.5:1, according to the  $^1\text{H}$  NMR). GC–MS (EI,  $m/z$ , %) ( $^{80}\text{Se}$ ,  $^{79}\text{Br}$ ,  $^{74}\text{Ge}$ ): 2 compounds, 448(4) ( $\text{M}^+$ ), 392(8) ( $\text{M}^+ - \text{C}_4\text{H}_9$ ), 363(2) ( $\text{M}^+ - \text{C}_4\text{H}_9 - \text{C}_2\text{H}_5$ ), 287(1) ( $\text{M}^+ - 2\text{Br}$ ), 261(3), 207(6), 179(2), 153(5), 149(2), 130(1), 115(1), 99(6), 57(100) ( $\text{C}_4\text{H}_9$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): Z: 7.50 (d, 1H,  $^2J_{\text{HH}} = 0.8$  Hz,  $^2J_{\text{Se-H}} = 56.3$  Hz,  $\text{SeCH}=\text{C}$ ), 6.65 (d, 1H,  $^2J_{\text{HH}} = 0.8$  Hz,  $^3J_{\text{Se-H}} = 14.6$  Hz,  $\text{CHBr}=\text{C}$ ), 1.21–1.13 (m, 3H,  $\text{CH}_3\text{CH}_2$ ), 1.15 (s, 9H,  $(\text{CH}_3)_3\text{C}$ ), 1.13–1.06 (m, 2H,  $\text{CH}_3\text{CH}_2$ ); E: 7.46 (s, 1H,  $^2J_{\text{Se-H}} = 58.1$  Hz,  $\text{SeCH}=\text{C}$ ), 6.89 (s, 1H,  $^3J_{\text{Se-H}} = 7.7$  Hz,  $\text{CHBr}=\text{C}$ ), 1.24 (s, 9H,  $(\text{CH}_3)_3\text{C}$ ), 1.21–1.13 (m, 3H,  $\text{CH}_3\text{CH}_2$ ), 1.15 (s, 9H,  $(\text{CH}_3)_3\text{C}$ ), 1.13–1.06 (m, 2H,  $\text{CH}_3\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 132.7, 107.3, 29.1, 27.5, 9.4, 8.8, 8.5, 5.6, 5.1, 2.3.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 575.2 (dd,  $^2J_{\text{SeH}} = 57.5$  Hz,  $^3J_{\text{SeH}} = 14.6$  Hz). An attempted column chromatography on silica gel (hexane– $\text{CHCl}_3$ , 95:5) failed to purify this compound.

### 3.3.4. Reaction of $\text{SeCl}_2$ with di-iso-propyl diethynyl germane (**1b**)

To  $\text{SeCl}_2$  prepared by slow addition of  $\text{SO}_2\text{Cl}_2$  (0.96 g, 6.7 mmol) in  $\text{CHCl}_3$  (15 ml) to Se powder (0.53 g, 6.7 mg a) in  $\text{CHCl}_3$  (15 ml) and stirring for 5 h at room temperature, was added diethynyl germane **1b** (1.39 g, 6.7 mmol) and stirring was continued for 3 h at room temperature. Removal of the solvent under reduced pressure afforded the mixture (1.51 g) of products containing, according to the GC–MS, 86.5% of Z-3,6-dichloro-4,4-di-iso-propyl-1,4-selenagermafulvene **3b** and unidentified products. MS (EI,  $m/z$ , %) ( $^{35}\text{Cl}$ ,  $^{74}\text{Ge}$ ,  $^{80}\text{Se}$ ): 360(4) ( $\text{M}^+$ ), 315(12) ( $\text{M}^+ - \text{C}_3\text{H}_7$ ), 273(5) ( $\text{M}^+ - 2\text{C}_3\text{H}_7$ ), 177(1), 131(2), 109(9), 91(4), 67(3), 43(100) ( $\text{C}_3\text{H}_7$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 7.17 (d,  $^2J_{\text{HH}} = 1.0$  Hz,  $^2J_{\text{Se-H}} = 52.0$  Hz,  $\text{C}=\text{CHCl}$ ), 6.37 (d, 1H,  $^2J_{\text{HH}} = 1.0$  Hz,  $^3J_{\text{Se-H}} = 12.0$  Hz,  $\text{SeCH}=\text{C}$ ), 1.65 (m, 2H,  $^3J_{\text{HH}} = 7.5$  Hz,  $(\text{CH}_3)_2\text{CH}$ ), 1.19 (d, 12H,  $^3J_{\text{HH}} = 7.5$  Hz,  $(\text{CH}_3)_2\text{CH}$ ).  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 516.3 (dd,  $^2J_{\text{SeH}} = 56$  Hz,  $^3J_{\text{SeH}} = 11$  Hz). An attempt to purify this compound by column chromatography (silica gel, hexane– $\text{CHCl}_3$ , 95:5) failed.

## 3.4. Reaction of selenium tetrahalides with diorganyl germanes (**1**)

### 3.4.1. Reaction of $\text{SeBr}_4$ with 1,1-diethynyl-1-germacyclohexane (**1a**)

To  $\text{SeBr}_4$  prepared by stirring a Se powder (0.40 g, 5.1 mg a) and  $\text{Br}_2$  (1.62 g, 10.1 mmol) in  $\text{CHCl}_3$  (30 ml) for 2.5 h at 20 °C was

added 1,1-diethynyl-1-germacyclohexane **1a** (0.98 g, 5.1 mmol) in  $\text{CHCl}_3$  (20 ml) and stirring was continued for 5.5 h. Removal of the solvent under reduced pressure afforded the mixture (2.98 g) of Z-isomer of heterofulvene **2a**, 2-dibromomethyl-2,4-dibromo-3,3-pentamethylene-1-selena-3-germacyclopentene-4 **4a** and 3,6,6-tribromo-4,4-pentamethylene-1,4-selenagermafulvene **6a** (**2a**:**4a**:**6a** = 13:67:19, according to the  $^1\text{H}$  NMR data). After five days of storage at room temperature ratio **2a**:**4a**:**6a** = 10:38:52. In 8 months heterocycle **4a** has been completely dehydrobrominated to tribromofulvene **6a**. An attempt to separate this mixture by column chromatography (silica gel, hexane– $\text{CHCl}_3$ , 95:5) failed.

2-Dibromomethyl-2,4-dibromo-3,3-pentamethylene-1-selena-3-germacyclopentene-4 (**4a**). MS (EI,  $m/z$ , %) ( $^{80}\text{Se}$ ,  $^{79}\text{Br}$ ,  $^{74}\text{Ge}$ ): 510(25) ( $\text{M}^+ - \text{HBr}$ ), 442(4), 403(2), 363(2), 223(21) ( $(\text{CH}_2)_5\text{GeBr}$ ), 208(12), 195(8), 177(9), 153(37), 143(9), 129(8), 117(15), 93(19), 67(18), 55(6), 41(100) ( $\text{C}_3\text{H}_5$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 7.42 (s, 1H,  $\text{SeCH}=\text{C}$ ), 6.47 (s, 1H,  $\text{SeCBrCHBr}_2$ ), 2.12–1.44 (m, 10H,  $(\text{CH}_2)_5$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 130.7 ( $\text{GeCBr}=\text{CHSe}$ ), 114.2 ( $\text{GeCBr}=\text{CHSe}$ ), 49.2, 44.3 ( $\text{SeCBrCHBr}_2$ ), 28.8, 25.7, 25.4, 15.7, 14.4 ( $(\text{CH}_2)_5$ ).  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 594.7 (d,  $^2J_{\text{SeH}} = 57.0$  Hz).

3,6,6-Tribromo-4,4-pentamethylene-1,4-selenagermafulvene (**6a**). MS (EI,  $m/z$ , %) ( $^{80}\text{Se}$ ,  $^{79}\text{Br}$ ,  $^{74}\text{Ge}$ ): 510(28) ( $\text{M}^+$ ), 440(4), 403(3), 363(3), 336(3), 299(1), 273(2), 259(3), 223(21) ( $(\text{CH}_2)_5\text{GeBr}$ ), 208(15), 195(10), 177(10), 153(39), 143(9), 129(8), 117(18), 93(21), 67(19), 55(8), 41(100) ( $\text{C}_3\text{H}_5$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 7.34 (s,  $\text{SeCH}=\text{C}$ ), 2.12–1.44 (m, 10H,  $(\text{CH}_2)_5$ ).  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 594.7 (d,  $^2J_{\text{SeH}} = 57.5$  Hz).

### 3.4.2. Reaction of $\text{SeBr}_4$ with di-iso-propyl diethynyl germane (**1b**)

Similarly, reaction of  $\text{SeBr}_4$ , prepared *in situ* from Se (0.24 g, 3.0 mg a) and  $\text{Br}_2$  (0.96 g, 3.0 mmol), with diethynyl germane **1b** (0.63 g, 3.0 mmol) in  $\text{CHCl}_3$  (20 ml), 1 h, afforded the mixture (1.60 g) containing, according to the GC–MS, 84% of 3,6,6-tribromo-4,4-di-iso-propyl-1,4-selenagermafulvene **6b**. MS (EI,  $m/z$ , %) ( $^{80}\text{Se}$ ,  $^{79}\text{Br}$ ,  $^{74}\text{Ge}$ ): 526(49) ( $\text{M}^+$ ), 485(52) ( $\text{M}^+ - \text{C}_3\text{H}_7$ ), 443(100) ( $\text{M}^+ - 2\text{C}_3\text{H}_7$ ), 392(15), 355(30), 313(7), 277(94), 239(18), 197(22), 177(34), 153(90), 129(34), 99(30), 67(7), 43(100) ( $\text{C}_3\text{H}_7$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 7.46 (s,  $^2J_{\text{Se-H}} = 59.7$  Hz,  $\text{SeCH}=\text{C}$ ), 1.97 (m, H  $^3J_{\text{HH}} = 7.2$  Hz,  $(\text{CH}_3)_2\text{CH}$ ), 1.33 (d, 3H,  $^3J_{\text{HH}} = 7.4$  Hz,  $(\text{CH}_3)_2\text{CH}$ ), 1.29 (d, 3H,  $^3J_{\text{HH}} = 7.4$  Hz,  $(\text{CH}_3)_2\text{CH}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 133.0, 111.8, 19.8, 19.6, 19.5, 19.4, 19.2, 18.9, 18.8, 18.6, 18.2.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 609.3 (d,  $^2J_{\text{SeH}} = 58.5$  Hz). An attempt to purify the product by column chromatography (silica gel, hexane– $\text{CHCl}_3$ , 95:5) failed.

### 3.4.3. Reaction of $\text{SeBr}_4$ with ethyl tert-butyl diethynyl germane (**1c**)

Similarly, reaction of  $\text{SeBr}_4$ , prepared from Se (0.22 g, 2.75 mg a) and  $\text{Br}_2$  (0.88 g, 5.5 mmol), with diethynyl germane **1c** (0.57 g, 2.75 mmol) in  $\text{CHCl}_3$  (45 ml), 4 h, afforded the product mixture (1.62 g) containing, according to the GC–MS, 75% of 3,6,6-tribromo-4-ethyl-4-tert-butyl-1,4-selenagermafulvene **6c**. MS (EI,  $m/z$ , %) ( $^{80}\text{Se}$ ,  $^{79}\text{Br}$ ,  $^{74}\text{Ge}$ ): 526(2) ( $\text{M}^+$ ), 470(5) ( $\text{M}^+ - \text{C}_4\text{H}_9$ ), 441(2) ( $\text{M}^+ - \text{C}_4\text{H}_9 - \text{C}_2\text{H}_5$ ), 341(1), 261(6), 207(1), 177(2), 153(5), 129(3), 99(3), 71(1), 57(100) ( $\text{C}_4\text{H}_9$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 7.45 (s, 1H,  $^2J_{\text{Se-H}} = 58.1$  Hz,  $\text{SeCH}=\text{C}$ ), 1.25 (s, 9H,  $(\text{CH}_3)_3\text{C}$ ), 1.30–1.17 (m, 5H,  $\text{CH}_3\text{CH}_2$ ).  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 613.4 (d,  $^2J_{\text{SeH}} = 57.5$  Hz). An attempt to purify the product by column chromatography (silica gel, hexane– $\text{CHCl}_3$ , 95:5) failed.

### 3.4.4. Reaction of $\text{SeCl}_4$ with di-iso-propyl diethynyl germane (**1b**)

To  $\text{SeCl}_4$  prepared from Se (0.19 g, 2.4 mg a) and  $\text{SO}_2\text{Cl}_2$  (0.65 g, 4.8 mmol) in  $\text{CHCl}_3$  (40 ml) by stirring for 5 h at 20 °C was added diethynyl germane **1b** (0.50 g, 2.4 mmol) and stirring was contin-

ued for 6 h at room temperature. Removal of the solvent gave the product mixture (0.98 g) containing *Z*-3,6-dichloro-4,4-di-*iso*-propyl-1,4-selenagermafulvene **3b**, 2-dichloromethyl-2,4-dichloro-3,3-di-*iso*-propyl-1-selena-3-germacyclopentene-4 **5b**, 3,6,6-trichloro-4,4-di-*iso*-propyl-1,4-selenagermafulvene **7b** and unidentified product (**3b**:**5b**:**7b** = 26.5:22:42, according to the  $^1\text{H}$  NMR). The  $^1\text{H}$  and  $^{77}\text{Se}$  NMR and GC–MS data for the compounds **3b** are given above.

2-Dichloromethyl-2,4-dichloro-3,3-di-*iso*-propyl-1-selena-3-germacyclopentene-4 (**5b**). MS (EI,  $m/z$ , %) ( $^{35}\text{Cl}$ ,  $^{74}\text{Ge}$ ,  $^{80}\text{Se}$ ): 430(0.5) ( $\text{M}^+$ ), 387(2) ( $\text{M}^+ - \text{C}_3\text{H}_7$ ), 343(0.5) ( $\text{M}^+ - \text{C}_3\text{H}_7 - \text{C}_3\text{H}_6$ ), 187(2), 165(9), 140(2), 109(3), 73(2), 43(100) ( $\text{C}_3\text{H}_7$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 7.19 (s, 1H,  $^2J_{\text{Se-H}} = 56.7$  Hz,  $\text{SeCH}=\text{C}$ ), 6.41 (s, 1H,  $=\text{CClCHCl}_2$ ), 1.90 (m, 1H,  $^3J_{\text{HH}} = 7.5$  Hz,  $(\text{CH}_3)_2\text{CH}$ ), 1.82 (m, 1H,  $^3J_{\text{HH}} = 7.3$  Hz,  $(\text{CH}_3)_2\text{CH}$ ), 1.65 (m, 1H,  $^3J_{\text{HH}} = 7.5$  Hz,  $(\text{CH}_3)_2\text{CH}$ ), 1.21–1.25 (m, 3H,  $(\text{CH}_3)_2\text{CH}$ ).  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 538.7 (d,  $^2J_{\text{Se-H}} = 57.5$  Hz).

3,6,6-Trichloro-4,4-di-*iso*-propyl-1,4-selenagermafulvene (**7b**). MS (EI,  $m/z$ , %) ( $^{35}\text{Cl}$ ,  $^{74}\text{Ge}$ ,  $^{80}\text{Se}$ ): 394(2) ( $\text{M}^+$ ), 351(9) ( $\text{M}^+ - \text{C}_3\text{H}_7$ ), 307(4) ( $\text{M}^+ - 2\text{C}_3\text{H}_7$ ), 187(2), 165(1), 153(1), 129(3), 109(5), 91(2), 67(2), 43(100) ( $\text{C}_3\text{H}_7$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 7.11 (s, 1H,  $^2J_{\text{Se-H}} = 57.2$  Hz,  $\text{SeCH}=\text{C}$ ), 1.90 (m, 1H,  $^3J_{\text{HH}} = 7.5$  Hz,  $(\text{CH}_3)_2\text{CH}$ ), 1.82 (m, 1H,  $^3J_{\text{HH}} = 7.3$  Hz,  $(\text{CH}_3)_2\text{CH}$ ), 1.65 (m, 1H,  $^3J_{\text{HH}} = 7.5$  Hz,  $(\text{CH}_3)_2\text{CH}$ ), 1.21–1.25 (m, 3H,  $(\text{CH}_3)_2\text{CH}$ ).  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 538.7 (d,  $^2J_{\text{Se-H}} = 57.5$  Hz).

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