



## 4,4-Diorganyl-1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvenes – New class of tellurium–silicon containing heterocycles

Svetlana V. Amosova\*, Alexander V. Martynov, Maxim V. Penzik, Natalia A. Makhaeva, Vladimir A. Potapov, Alexander I. Albanov, Larisa V. Zhilitskaya, Mikhail G. Voronkov

A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk, 1, Favorsky Street 664033, Russia

### ARTICLE INFO

#### Article history:

Received 21 March 2008

Received in revised form 14 May 2008

Accepted 26 May 2008

Available online 2 June 2008

#### Keywords:

Tellurium tetrachloride

Diorganyl diethynyl silanes

Tellurium–silicon containing heterocycles

Unsaturated five-membered heterocycles

NMR spectroscopy

### ABSTRACT

The reaction of  $\text{TeCl}_4$  with diorganyl diethynyl silanes  $\text{RR}^1\text{Si}(\text{C}\equiv\text{CH})_2$  in  $\text{CHCl}_3$  at room temperature leads to regio- and stereoselective formation of a new class of unsaturated five-membered heterocycles, 4,4-diorganyl-1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvenes, in high yields. In the case of dialkyl substituents at the silicon atom the reaction proceeds with 100% stereoselectivity to afford only *E*-isomers, while for cyclic diethynyl silanes the spiro-heterocycles formed have *Z*- and *E*-configurations, *E*-isomers being the predominant ones. Structures of the heterocycles have been proved by the multinuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{125}\text{Te}$ ) NMR spectroscopy, 2D NOESY NMR spectroscopy and mass-spectrometry. *Z*-Isomers are characterized by a long-range spin–spin interaction of protons through five bonds with  $^5J_{\text{HH}}$  0.2–0.5 Hz lacking in *E*-isomers. In the mass spectra the heterocycles manifest themselves as the fragment ions  $[\text{M}-\text{Cl}_2]^+$ .

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

Electrophilic addition of tellurium tetrahalides  $\text{TeX}_4$  ( $\text{X} = \text{Br}, \text{Cl}$ ) to acetylenic compounds is poorly studied and is limited only to the monoacetylenes such as  $\text{PhC}\equiv\text{CH}$ ,  $\text{PhC}\equiv\text{CPh}$ ,  $\text{C}_5\text{H}_{11}\text{C}\equiv\text{CH}$ ,  $\text{CH}\equiv\text{CCH}_2\text{OH}$  [1a–1i]. The reactions proceed with the formation of both monoadducts  $\text{RCH}=\text{CHTeCl}_3$  as *Z*-isomers [1a,1b,1d,1i,1g] and diadducts  $(\text{CRX}=\text{CH})_2\text{TeX}_2$  [1e,1f,1i]. As a rule, *syn*-addition is realized but in the case of  $\text{TeBr}_4$  in benzene *anti*-addition occurs along with *syn*-addition, resulting in the mixtures of *Z*- and *E*-isomers of the corresponding adducts [1e,1f].

Symmetrical 1,1,4,4-tetrasubstituted butyndiols afford the products of the propargylic rearrangement. The 1:1-adduct formed in the reaction with butyn-1,4-diol is dehydrated to give disubstituted 2,5-dihydrofuran [1d].

The reactions of aryl tellurium trichlorides and tribromides with the terminal acetylenes  $\text{RC}\equiv\text{CH}$  ( $\text{R} = \text{C}_4\text{H}_9$ ,  $\text{C}_5\text{H}_{11}$ , *cyclo*- $\text{C}_6\text{H}_{11}$ ,  $\text{HOCH}_2$ ,  $\text{HO-cyclo-C}_6\text{H}_{10}$ , *Ar*) in apolar solvents ( $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{C}_6\text{H}_6$ ) proceed as the Markovnikov-type regio- and stereoselective, mainly *syn*, additions [1e,1f,1i,2a–2e]. The interaction of  $\text{ArTeBr}_3$  with alkynes in benzene involves both the *anti*- and *syn*-addition to furnish the mixture of *Z*- and *E*-isomers of the corresponding adducts [1f]. In polar solvent (MeOH) in the case of  $\text{ArTeBr}_3$  only *anti*-addition is realized to afford *E*-monoadducts [2d].

In the literature there are no data on the interaction of tellurium tetrahalides with diacetylenes including the bridged ones.

Earlier, we have found that the reaction of diorganyl diethynyl silanes with  $\text{SeX}_4$  ( $\text{X} = \text{Cl}, \text{Br}$ ) results in two new classes of unsaturated five-membered selenium–silicon containing heterocycles: those with the cyclopentene structure, 2,4-dihalogen-2-dihalogenomethyl-3,3-diorganyl-1-selena-3-silacyclopentenes-4, and those with the fulvene structure, 3,6-dihalogen-4,4-diorganyl-1,4-selenasilafulvenes [3a–3c,3e,3f]. In the reaction of diorganyl diethynyl silanes with  $\text{SeX}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) only *Z*-isomers of the above heterofulvenes are formed with insignificant admixtures of *E*-isomers [3a,3c,3e,3f].

This paper is aimed at the synthesis of new five-membered unsaturated tellurium, silicon-containing heterocycles of fulvene structure on the basis of the electrophilic addition–cyclization reaction of tellurium tetrachloride with diorganyl diethynyl silanes. It continues our systematic investigations of the interaction of the bridged diacetylenes with the selenium and tellurium halides. The structures of the heterocycles prepared were proved by the multinuclear NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{125}\text{Te}$ ), 2D NOESY NMR techniques and mass-spectrometry.

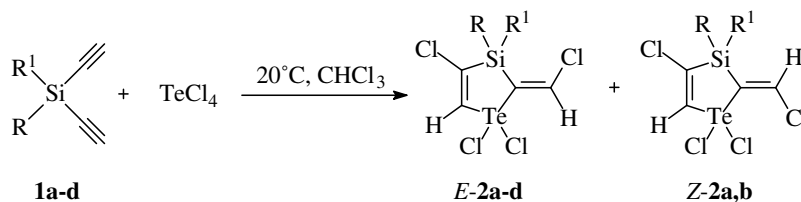
### 2. Results and discussion

#### 2.1. Electrophilic addition–cyclization of $\text{TeCl}_4$ with diorganyl diethynyl silanes

We have found that the interaction of diorganyl diethynyl silanes **1a–d** with  $\text{TeCl}_4$  in chloroform at room temperature presents a new regio- and stereoselective reaction resulting in a new class of

\* Corresponding author.

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



**Scheme 1.** 1, 2: R + R<sup>1</sup> = (CH<sub>2</sub>)<sub>4</sub> (a), (CH<sub>2</sub>)<sub>5</sub> (b), R = R<sup>1</sup> = Me (c), R = Me, R<sup>1</sup> = Me<sub>3</sub>Si(CH<sub>2</sub>)<sub>2</sub> (d).

unsaturated tellurium–silicon containing heterocycles – 4,4-diorganyl-1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvenes **2a–d** in high yields (Scheme 1, Table 1). In the case of dialkyl diethynyl silanes **1c,d** the reaction proceeds with 100% stereoselectivity to afford the heterocycles **2c,d** only as *E*-isomers while with the cyclic diethynyl silanes – 1,1-diethynyl-1-silacyclopentane (**1a**) and -1-silacyclohexane (**1b**) – the spiro-heterocycles **2a,b** formed have *Z*- and *E*-configurations, *E*-isomer being the predominant one.

The reaction with methyl diethynyl silane **1e** also proceeds regio- and stereoselectively to give the expected intermediate *E*-isomer of tellura(IV)silafulvene **A** which in the presence of TeCl<sub>4</sub> and the traces of water undergoes the secondary transformations resulting in the heterocycle **2e** (Scheme 2, Table 1).

*E*-Isomers of the heterocycles **2a–e** are easily separated from the chloroform solution of the reaction mixture as a fine crystalline powder.

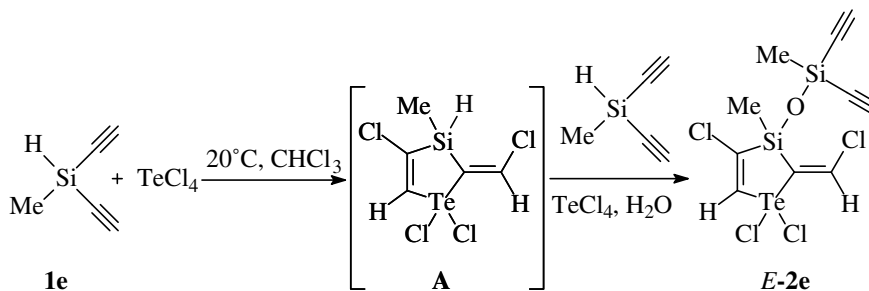
**Table 1**

The yields and the *Z*:*E* ratio of the heterocycles **2**

| Compound  | R  | R <sup>1</sup>                                    | Yield (%) | <i>Z</i> : <i>E</i> |
|-----------|----|---|-----------|---------------------|
| <b>2a</b> |    | (CH <sub>2</sub> ) <sub>4</sub>                   | 84        | 65:35               |
| <b>2b</b> |    | (CH <sub>2</sub> ) <sub>5</sub>                   | 85        | 75:25               |
| <b>2c</b> | Me | Me  | 80        | 100:0               |
| <b>2d</b> | Me | Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>2</sub> | 72        | 100:0               |
| <b>2e</b> | Me | OSiMe(C≡CH) <sub>2</sub>                          | 28        | 100:0               |

## 2.2. Structure definition by the multinuclear NMR spectroscopy and mass-spectrometry

Structure of 4,4-diorganyl-1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvenes (**2**) was proved by the <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si, <sup>125</sup>Te NMR spectroscopy (Tables 2 and 3) as well as GC–MS spectrometry (Experimental). *Z*-Isomer of 4,4-tetramethylene-1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvene (**2a**) was identified in the mixture of *Z*- and *E*-isomers by the presence of the cross-peaks of the



**Scheme 2.**

**Table 2**

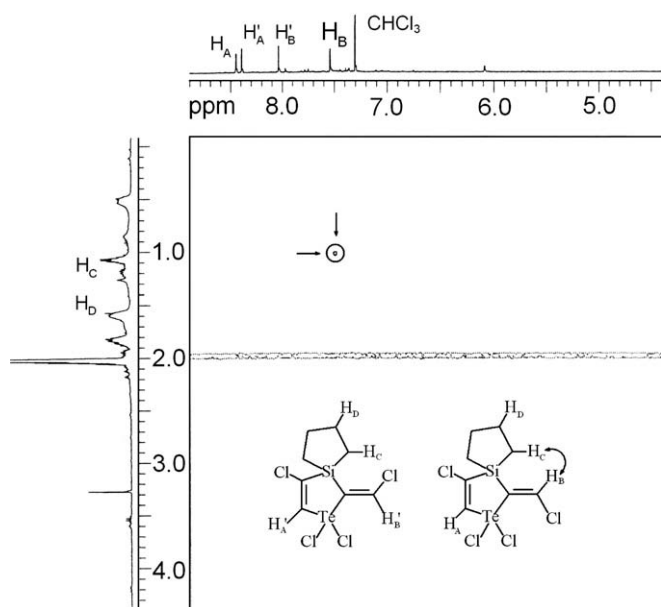
The <sup>1</sup>H NMR spectra of 1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvenes **2a–e** (in d<sub>6</sub>-acetone)

| Compound                          | R  | R <sup>1</sup>                                    | Si–Cl=CH–Te, δ, ppm | <sup>5</sup> J <sub>H–H</sub> , Hz | <sup>2</sup> J <sub>Te–H</sub> , Hz | <sup>3</sup> J <sub>Si–H</sub> , Hz | Te(Cl) <sub>2</sub> C=CHCl, δ, ppm | <sup>5</sup> J <sub>H–H</sub> , Hz | <sup>3</sup> J <sub>Te–H</sub> , Hz | <sup>3</sup> J <sub>Si–H</sub> , Hz | R, R <sup>1</sup> , δ, ppm  |
|-----------------------------------|----|---|---------------------|------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|------------------------------------|-------------------------------------|-------------------------------------|---|
| <i>E</i> - <b>2a</b>              |    | (CH <sub>2</sub> ) <sub>4</sub>                   | 8.41s               | –                                  | 123.5                               | 9.1                                 | 8.06s                              | –                                  | 15.7                                | 9.9                                 | 1.99–1.85m (CH <sub>2</sub> CH <sub>2</sub> );<br>1.25–1.04m (CH <sub>2</sub> Si)   |
| <i>Z</i> - <b>2a</b>              |    | (CH <sub>2</sub> ) <sub>4</sub>                   | 8.46d               | 0.5                                | 122.7                               | 9.0                                 | 7.55d                              | 0.5                                | 19.3                                | –                                   | 1.95m 1.70m (CH <sub>2</sub> CH <sub>2</sub> );<br>1.19m, 0.87m (CH <sub>2</sub> Si);<br>1.70–1.46m (CH <sub>2</sub> );<br>2.10–2.02m, 2.00–1.92m (CH <sub>2</sub> CH <sub>2</sub> Si);<br>1.37–1.27m, 1.21–1.16m (CH <sub>2</sub> Si); |
| <i>E</i> - <b>2b</b>              |    | (CH <sub>2</sub> ) <sub>5</sub>                   | 8.36s               | –                                  | 124.0                               | 8.8                                 | 8.04s                              | –                                  | 17.9                                | 9.8                                 | 1.73–1.50m (CH <sub>2</sub> );<br>2.21–1.96m (CH <sub>2</sub> CH <sub>2</sub> Si);<br>1.31–0.83m (CH <sub>2</sub> Si);  |
| <i>Z</i> - <b>2b</b>              |    | (CH <sub>2</sub> ) <sub>5</sub>                   | 8.41d               | 0.24                               | 127.9                               | 8.6                                 | 7.61d                              | 0.24                               | 20.0                                | –                                   | 0.60s, 0.41s (CH <sub>3</sub> Si);<br>0.03s (Me <sub>3</sub> Si), 0.64s (MeSi), 0.46s (CH <sub>2</sub> ),<br>0.31s (CH <sub>2</sub> )   |
| <i>E</i> - <b>2c</b>              | Me | Me  | 8.45s               | –                                  | 123.6                               | 8.3                                 | 8.14s                              | –                                  | 15.3                                | 8.9                                 | 0.51s (CH <sub>3</sub> ), 0.79s (CH <sub>3</sub> ), 2.53s (≡CH),<br>2.54s (≡CH)   |
| <i>E</i> - <b>2d</b>              | Me | Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>2</sub> | 8.39s               | –                                  | 124.0                               | 9.0                                 | 8.05s                              | –                                  | 16.0                                | 9.0                                 |   |
| <i>E</i> - <b>2e</b> <sup>a</sup> | Me | OSiMe(C≡CH) <sub>2</sub>                          | 8.12s               | –                                  | 137.8                               | 10.2                                | 7.68s                              | –                                  | 19.0                                | 9.4                                 |   |

<sup>a</sup> In CDCl<sub>3</sub>.

**Table 3**  
The  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{125}\text{Te}$  NMR spectra of 1,1,3,6-tetrachloro-1,4-tellura (IV)silafulvenes **2a–e** (in  $d_6$ -acetone)

| Compound             | R                               | R <sup>1</sup>                                    | $^{13}\text{C}$ NMR, $\delta$ , ppm   |   | $^{29}\text{Si}$ NMR, $\delta$ , ppm | $^{125}\text{Te}$ NMR, $\delta$ , ppm ( $^2J_{\text{TeH}}$ ) |
|----------------------|---------------------------------|---|---|---|--------------------------------------|--|
|                      |                                 |   | $\text{SiClCl}=\text{CHTe}(\text{Cl}_2)$ , $\text{Te}(\text{Cl}_2)\text{C}=\text{CHCl}$ | R, R <sup>1</sup>   |                                      |  |
| <i>E</i> - <b>2a</b> | (CH <sub>2</sub> ) <sub>4</sub> |   | 154.6, 144.4, 143.1, 137.8,   | 28.2(CH <sub>2</sub> CH <sub>2</sub> ), 13.1(CH <sub>2</sub> Si)                            | 27.0                                 | 920.1 (123.9)  |
| <i>Z</i> - <b>2a</b> | (CH <sub>2</sub> ) <sub>4</sub> |   | 155.3, 145.8, 143.0, 138.1,   | 28.0(CH <sub>2</sub> CH <sub>2</sub> ), 14.3(CH <sub>2</sub> Si)                            | 29.8                                 | 870.8 (115.9)  |
| <i>E</i> - <b>2b</b> | (CH <sub>2</sub> ) <sub>5</sub> |   | 156.5, 143.4, 137.2, 137.0,   | 29.6(CH <sub>2</sub> ), 24.6(CH <sub>2</sub> CH <sub>2</sub> Si), 12.8(CH <sub>2</sub> Si); | 8.1                                  | 926.9 (134.2)  |
| <i>Z</i> - <b>2b</b> | (CH <sub>2</sub> ) <sub>5</sub> |   | 157.0, 142.3, 138.5, 138.4  | 29.5(CH <sub>2</sub> ), 24.5(CH <sub>2</sub> CH <sub>2</sub> Si), 14.0(CH <sub>2</sub> Si)  | 5.1                                  | 875.5 (128.5)  |
| <i>E</i> - <b>2c</b> | Me                              | Me  | 154.8, 154.2, 141.6, 141.1  | −3.0, −1.17 (CH <sub>3</sub> Si)  | 16.0                                 | 921.3 (134.2)  |
| <i>E</i> - <b>2d</b> | Me                              | Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>2</sub> | 155.0, 142.3, 142.0, 136.8  | 8.2(CH <sub>2</sub> ), 6.0(CH <sub>2</sub> ), −3.1(Me <sub>3</sub> Si), −3.9 (MeSi)         | 3.1(MeSi)–35.2(Me <sub>3</sub> Si)   | 925.0(119.0)   |
| <i>E</i> - <b>2e</b> | Me                              | OSiMe(C≡CH) <sub>2</sub>                          | 151.9, 144.5, 142.4, 137.5,   | 1.2 (CH <sub>3</sub> Si), 3.2 (CH <sub>3</sub> Si), 86.4 (≡C), 97.3 (HC≡)                   | −2.0<br>Si(C≡C)<br>−46.5<br>Si(C=C)  | 854.8 (118.2)  |



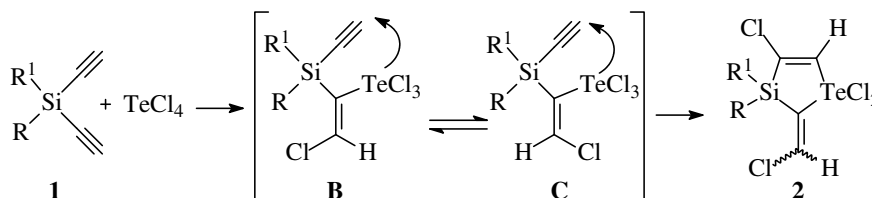
**Fig. 1.** The 2D NOESY NMR spectrum of *Z*- and *E*-isomers of 4,4-tetramethylene-1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvene **2b** (in  $d_6$ -acetone).

exocyclic olefinic proton  $\text{H}_\text{B}$  and methylene protons  $\text{H}_\text{C}$  of the cyclopentane substituent at silicon atom in 2D NOESY NMR spectrum (Fig. 1). In the  $^1\text{H}$  NMR spectra the *Z*-isomers of the heterocycles **2a,b** are characterized by the long-range coupling constants  $^5J_{\text{HH}}$  0.2–0.5 Hz (Table 2) found by us earlier in the spectra of *Z*-isomers of 3,6-dihalogen-4,4-diorganyl-1,4-selenasilafulvenes [3a,3f]. As in the case of 1,4-selenasilafulvenes, the presence of this constant is peculiar only to *Z*-isomers thus allowing easy identification of both isomers of the heterocycles.

The formation of *Z*- and *E*-isomers of the heterocycles **2**, in particular *E*-structure of the only isomer of the compounds **2c–e**, is evidenced also by the analysis of the fine structure of the  $^1\text{H}$  NMR spectra of these heterocycles involving the interaction with the silicon atom. The presence in the spectra of the satellite lines at the resonance lines of the exocyclic olefinic protons, resulting from coupling with *trans*-atom of silicon-29 ( $^3J_{\text{Si-H}}$  8.3–9.9 Hz) (Table 2) [4] speaks in favor of *E*-configuration. In *Z*-isomers of the compounds **2a,b** the satellite lines are not registered since their value at *cis*-arrangement of hydrogen and silicon atoms ( $^3J_{\text{Si-H}}$  3–4 Hz [4]) coincides with the peak width of the olefinic proton signals.

The fact that in the pairs of *Z*- and *E*-isomers **2a,b**, due to the influence of the electron-deficient chlorine atoms at the tellurium atom, the signals of the exocyclic olefinic protons of *Z*-isomers are shifted to the higher field (7.55–7.61 ppm) as compared to the *E*-isomers (8.04–8.06 ppm), can serve as an additional criterion allowing the identification of the isomers of the heterocycles **2**. As a result, in *Z*-isomers the signals are shifted 0.80–0.90 ppm up-field relative to the signals of endocyclic protons (8.41–8.46 ppm), in *E*-isomers – 0.30–0.35 ppm up-field (as compared to 8.36–8.41 ppm). For the only isomers of the heterocycles **2c–e** this value is equal to 0.31–0.44 ppm, which clearly indicates to the *E*-configuration.

1,1-Dichlorotellarane structures of the heterocycles **2** are defined on the basis of the  $^{125}\text{Te}$  NMR data. Both *Z*- and *E*-isomers manifest themselves in the spectra in the range of 870–875 and 920–930 ppm, correspondingly, which specifies tetra-coordinated tellurium atom [5a–5c]. The doublet signals of tellurium-125 are characterized by the geminal coupling constants  $^2J_{\text{Te-H}}$  128–135 Hz (Table 3); they correspond in the  $^1\text{H}$  NMR spectra to the similar splitting of the satellite signals of the olefinic protons (Table 2). Since the values of the coupling constants associated with tellurium-125 are approximately two times higher than those of the corresponding constants associated with selenium-77 [6] the geminal constants  $^2J_{\text{Te-H}}$  obtained are in a good agreement with the values of geminal constants  $^2J_{\text{Se-H}}$  50–60 Hz found by us for 1,1-diorganyl-1,4-selenasilafulvenes [3a,3f].



**Scheme 3.**

The mass spectra of the heterocycles **2a–e** are characterized only by the fragment ions  $[M-Cl_2]^+$ . Earlier we have shown that tetrahalogen-substituted heterocycles – 2-dihalogenomethyl-2,4-dihalogen-3,3-diorganyl-1-selena-3-silacyclopentenes-4 – are registered in the mass spectra only as the fragment ions  $[M-X_2]^+$  and  $[M-HX]^+$  ( $X = Cl, Br$ ) [3d,3f]. But elemental analysis of the heterocycles **2a–e** pointing to the Te:Cl ratio 1:4 proves its compositions.

The presence of the methyl diethynyl siloxy moiety in the structure of heterocycle **2e** was verified also by the IR spectroscopy (3).

Formation of the heterocycles **2** may be conceived as the sequential electrophilic addition of tellurium tetrachloride to both ethynyl moieties of the diethynyl silanes (Scheme 3). Using the model reaction of  $TeCl_4$  with trimethyl ethynyl silane [7a,7b] as an example, it has been shown that the first stage of the reaction turns to be the *anti*-Markovnikov addition. Based on the stereochemistry of the products **2a–e** where the prevalent are the *E*-isomers it could be suggested that the first stage of the reaction involves the *anti*-Markovnikov *anti*-addition followed by cycloaddition of the intermediate tellurium trichloride **B** to the second ethynyl moiety of diethynyl silanes **1a–e**. The formation of *Z*-isomers in the case of cyclic diethynyl silanes **1a,b** can be explained by the post-isomerization of the intermediate *anti*-monoadduct **B** into formal *syn*-addition product **C** that can be stabilized due to the intramolecular interaction of the chlorine atom at the double bond with tellurium atom in  $TeCl_3$  group. We have discovered a similar interaction for the adduct of trimethyl ethynyl silane and  $TeCl_4$  [7b]. Alternatively, *Z*-isomers **1a,b** can be formed by the concurrent *anti*-Markovnikov *syn*-addition of  $TeCl_4$  to diethynyl silane **1a,b**.

### 3. Experimental

#### 3.1. General procedure

The  $^1H$  (400.1 MHz),  $^{13}C$  (100.6 MHz),  $^{29}Si$  (79.5 MHz) and  $^{125}Te$  (126.4 MHz) NMR spectra were recorded on the spectrometer Bruker DPX-400 in 5–10% solution in  $CDCl_3$  or  $d_6$ -acetone, internal reference – HMDS. The IR spectra were recorded on a Bruker IPS 25 spectrometer, the GC–MS spectra were recorded on the spectrometer Shimadzu QP5050A at electron energy 70 eV, 60 m capillary column SPB-5 ms, injection temperature 260 °C, column temperature 70–260 °C.

#### 3.2. Materials

1,1-Diethynyl-1-silacyclopentane (**1a**), -1-silacyclohexane (**1b**), dimethyl diethynyl silane (**1c**), methyl 2-trimethylsilyl ethyl diethynyl silane (**1d**) and methyl diethynyl silane (**1e**) were prepared according to the known procedure [8a–8c].

#### 3.3. Reaction of tellurium tetrachloride with diethynyl silanes (**1**)

##### 3.3.1. Synthesis of 4,4-tetramethylene-1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvene (**2a**)

1,1-Diethynyl-1-silacyclopentane **1a** (0.68 g, 5.1 mmol) and tellurium tetrachloride (1.36 g, 5.1 mmol) were stirred for 25 h in 45 ml of  $CHCl_3$  at room temperature, grey precipitate of Te and unreacted  $TeCl_4$  was filtered off. After evacuation of the solvent and unreacted diethynyl silane 1.71 g (84%) of the mixture of *Z*- and *E*-isomers of the heterocycle **2a** (ratio *Z*:*E* = 35:65 according to the  $^1H$  NMR data) was obtained as a viscous substance. Treatment of the latter with 5 ml of  $CHCl_3$  afforded 0.57 g (28%) of *E*-isomer as a white crystalline powder, m. p. 225–230 °C (decomp.) and 1.00 g of the mixture of *Z*- and *E*-isomers (*Z*:*E* = 56:44 according to

the  $^1H$  NMR data) as a viscous oil. Anal. Calc. for  $C_8H_{10}Cl_4SiTe$ : C, 23.80; H, 2.50; Cl, 36.13; Si, 6.96; Te, 31.61. Found: C, 23.20; H, 2.92; Cl, 36.28; Si, 6.95; Te, 31.82%. GC–MS, (EI, *m/z*, %) ( $^{35}Cl$ ,  $^{130}Te$ ,  $^{28}Si$ ): two compounds, 334(88) ( $M^+ - Cl_2$ ), 278(6), 254(3), 180(5), 155(9), 119(39), 105(17), 91(26), 81(43), 63(81), 53(100). The  $^1H$ ,  $^{13}C$ ,  $^{29}Si$  and  $^{125}Te$  NMR data are given in Tables 2 and 3.

##### 3.3.2. Synthesis of 4,4-pentamethylene-1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvenes (**2b**)

Similarly, from 1,1-diethynyl-1-silacyclohexane (**1b**) (0.55 g, 3.71 mmol) and  $TeCl_4$  (1.00 g, 3.71 mmol) in 30 ml of  $CHCl_3$  after 11 h stirring at room temperature was obtained 1.32 g (85%) of the mixture of *Z*- and *E*-isomers of the heterocycle **2b** (ratio *Z*:*E* = 25:75, according to the  $^1H$  NMR data). Treatment of the latter with 5 ml of  $CHCl_3$  afforded 0.33 g (21.5%) of *E*-isomer as a white crystalline powder, m.p. 262–265 °C (decomp.). Anal. Calc. for  $C_9H_{12}Cl_4SiTe$ : C, 25.88; H, 2.90; Cl, 33.95; Si, 6.72; Te, 30.55. Found: C, 25.85; H, 2.86; Cl, 33.51; Si, 6.80; Te, 30.29%. GC–MS, (EI, *m/z*, %) ( $^{35}Cl$ ,  $^{130}Te$ ,  $^{28}Si$ ): two compounds, 348 (60) ( $M^+ - 2Cl$ ), 278(5), 254(5), 228(9), 180(5), 155(11), 123(28), 105(51), 97(56), 91(39), 79(28), 63(100), 53(95). The  $^1H$ ,  $^{13}C$ ,  $^{29}Si$  and  $^{125}Te$  NMR data are given in Tables 2 and 3.

##### 3.3.3. Synthesis of 4,4-dimethyl-1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvene (**2c**)

Similarly, from dimethyl diethynyl silane **1c** (0.40 g, 3.71 mmol) and  $TeCl_4$  (1.00 g, 3.71 mmol) in 30 ml of  $CHCl_3$  after 9 h stirring at room temperature was obtained after removal of the solvent and unreacted silane **1c** 1.12 g (80%) of *E*-isomer of the heterocycle **2c** as light-yellow crystals, weakly soluble in  $CHCl_3$ , m.p. 90–95 °C (decomp.). Anal. Calc. for  $C_6H_8SiTeCl_4$ : C, 19.08; H, 2.14; Cl, 37.55; Si, 7.44; Te, 33.79. Found: C, 19.65; H, 2.22; Cl, 37.27; Si, 7.27; Te, 34.49%. MS (EI, *m/z*, %) ( $^{35}Cl$ ,  $^{130}Te$ ,  $^{28}Si$ ): 308 (19) ( $M^+ - 2Cl$ ), 293(4), 245(2), 200(3), 180(4), 165(2), 153(17), 128(4), 113(12), 103(18), 93(100), 83(70), 63(36), 53(40), 43(38), 36(14). The  $^1H$ ,  $^{13}C$ ,  $^{29}Si$  and  $^{125}Te$  NMR data are given in Tables 2 and 3.

##### 3.3.4. Synthesis of 4-methyl-4-(2-trimethylsilylethyl)-1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvene (**2d**)

To  $TeCl_4$  (0.54 g, 2.00 mmol) in 20 ml of  $CHCl_3$  in an argon atmosphere at 20 °C on stirring was added diethynyl silane **1d** (0.40 g, 2.00 mmol) in 20 ml of  $CHCl_3$ , the resulting mixture was stirred for 20 h. A grey precipitate was filtered off. After evacuation of the solvent was obtained 0.72 g (73%) of *E*-isomer of the heterocycle **2d** as a yellow glassy substance, m.p. 65–68 °C. Anal. Calc. for  $C_{10}H_{18}Cl_4Si_2Te$ : C, 25.89; H, 3.91; Cl, 30.57; Si, 12.11; Te, 27.51. Found: C, 25.90; H, 4.16; Cl, 30.45; Si, 11.72; Te, 26.94%. The  $^1H$ ,  $^{13}C$ ,  $^{29}Si$  and  $^{125}Te$  NMR data are given in Tables 2 and 3.

##### 3.3.5. Synthesis of 4-methyl-4-(methyl diethynyl siloxy)-1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvene (**2e**)

To  $TeCl_4$  (1.14 g, 4.2 mmol) in 20 ml of dry  $CHCl_3$  in an argon atmosphere was slowly added at –25 °C methyl diethynyl silane **1e** (0.40 g, 4.2 mmol) in 15 ml of  $CHCl_3$ , the temperature was allowed to rise to 20 °C and stirring was continued for 20 h. Precipitated Te and unreacted  $TeCl_4$  (0.50 g) were filtered off. After removal of the solvent in vacuum 0.28 g (28%) of the heterocycle **2e** was obtained as a yellowish-brown powder, m.p. 80–85 °C. Anal. Calc. for  $C_{10}H_{10}Cl_4Si_2TeO$ : C, 25.46; H, 2.14; Cl, 30.06; Si, 11.91; Te, 27.05. Found: C, 25.43; H, 2.45; Cl, 29.55; Si, 11.68; Te, 26.88%. MS (EI, *m/z*, %) ( $^{35}Cl$ ,  $^{130}Te$ ,  $^{28}Si$ ): 402 (23) ( $M^+ - Cl_2$ ), 337(2), 292(3), 257(10), 247(21), 221(9), 207(10), 197(53), 187(100), 161(8), 137(16), 127(9), 115(13), 93(65), 83(36), 67(13), 63(25), 53(70), 43(19). IR (KBr) 3269 ( $\equiv CH$ ), 2042 ( $C\equiv C$ ), 1084 (Si–O–Si)  $cm^{-1}$ . The  $^1H$ ,  $^{13}C$ ,  $^{29}Si$  and  $^{125}Te$  NMR data are given in Tables 2 and 3.

## Acknowledgement

Financial support of this work by the Presidium of Russian Academy of Sciences (Grant No. 8.19) is gratefully acknowledged.

## References

- [1] (a) M. Moura Campos, N.P. Petragani, *Tetrahedron* 18 (1962) 527;  
(b) S. Uemura, H. Miyoshi, M. Okano, *Chem. Lett.* (1979) 1357;  
(c) R.A. Zingaro, N. Petragani, J.V. Comasseto, *Organomet. Synth.* 3 (1986) 649;  
(d) B.I. Pak, I.M. Balog, V.G. Lendel, Yu.V. Migalina, Abstracts of the 16 Ukrainian Conference on Organic Chemistry, Ternopol, 1992, p. 278;  
(e) H.A. Stefani, I.P. Campos de Arruda, L.C. Roque, M.A. Montoro, A.L. Braga, *J. Chem. Res. (S)*, (1996) 54;  
(f) H.A. Stefani, N. Petragani, J. Zukerman-Schpector, L. Dornelles, D.O. Silva, A.L. Braga, *J. Organomet. Chem.* 562 (1998) 127;  
(g) J. Zukerman-Schpector, R.L. Camillo, J.V. Comasseto, R.A. Santos, I. Caracelli, *Acta Crystallogr. C* 55 (1999) 1577;  
(h) J. Zukerman-Schpector, I. Haiduc, M.J. Dabdoub, J.C. Biazotto, A.L. Braga, L. Dornelles, I. Caracelli, *Z. Kristallogr.* 217 (2002) 1;  
(i) I.D. Sadekov, A.V. Zakharov, A.A. Maksimenko, *Sulfur Rep.* 23 (2002) 125.
- [2] (a) I.D. Sadekov, B.B. Rivkin, V.I. Minkin, *Russ. Chem. Rev.* 56 (1987) 343;  
(b) J.V. Comasseto, H.A. Stefani, A. Chieffi, *Organometallics* 10 (1991) 845;  
(c) J. Zukerman-Schpector, E.E. Castellano, G. Oliva, J.V. Comasseto, H.A. Stefani, *Acta Crystallogr. C* 47 (1991) 960;  
(d) X. Huang, Y.P. Wang, *Tetrahedron Lett.* 37 (1996) 7417;  
(e) A. Chieffi, P.H. Menezes, J.V. Comasseto, *Organometallics* 16 (1997) 809.
- [3] (a) V.A. Potapov, S.V. Amosova, O.V. Belozero, A.I. Albanov, O.G. Yarosh, M.G. Voronkov, *Chem. Heterocycl. Comp.* 39 (2003) 549;  
(b) V.A. Potapov, S.V. Amosova, O.V. Belozero, A.I. Albanov, O.G. Yarosh, M.G. Voronkov, *Chem. Heterocycl. Comp.* 39 (2003) 551;  
(c) V.A. Potapov, S.V. Amosova, *J. Org. Chem. (Rus)*. 39 (2003) 1373;  
(d) L.V. Klyba, S.V. Amosova, O.V. Belozero, V.A. Potapov, E.P. Zhanchipova, O.G. Yarosh, M.G. Voronkov, *Rus. Chem. Bull. Int. Ed.* (2005) 650;  
(e) S.V. Amosova, N.A. Makhaeva, A.V. Martynov, O.A. Belozero, M.V. Penzik, A.I. Albanov, O.G. Yarosh, M.G. Voronkov, in: International Conference "Organic chemistry since Butlerov and Beilstein until present", St. Petersburg, Russia, June 26–29, 2006 (Abstract No. 1–123);  
(f) S.V. Amosova, A.V. Martynov, N.A. Makhaeva, O.A. Belozero, M.A. Penzik, A.I. Albanov, O.G. Yarosh, M.G. Voronkov, *J. Organomet. Chem.* 692 (2007) 946.
- [4] J. Schraml, J.M. Bellama, in: F.C. Nachod, J.J. Zuckermann, E.W. Randall (Eds.), *<sup>29</sup>Si Nuclear Magnetic Resonance in Determination of Organic Structure by Physical Methods*, Academic Press, New York, 1976, p. 254.
- [5] (a) N.D. Luthra, J.D. Odom, in: Z. Rappoport, S. Patai (Eds.), *The Chemistry of Organic Selenium and Compounds*, vol. 1, Wiley, New York, 1986, p. 189;  
(b) W. McFarlane, F.J. Berry, B.C. Smith, *J. Organomet. Chem.* 113 (1976) 139;  
(c) H. Schuman, M. Magerstädt, *J. Organomet. Chem.* 232 (1982) 147.
- [6] H.C.E. McFarlane, W. McFarlane, *J. Chem. Soc., Dalton Trans.* 22 (1973) 2416.
- [7] (a) S.V. Amosova, A.V. Martynov, V.A. Shagun, M.V. Musalov, L.I. Larina, L.B. Krivdin, L.V. Zhilitskaya, M.G. Voronkov, *J. Organomet. Chem.* (2008), doi:10.1016/j.jorganchem.2008.04.041;  
(b) A.V. Martynov, S.V. Amosova, *Zh. Obshch. Khim.* (in press).
- [8] (a) N.V. Komarov, O.G. Yarosh, *Zh. Obshch. Khim.* 37 (1967) 264;  
(b) M.G. Voronkov, L.V. Zhilitskaya, O.G. Yarosh, T.D. Burnasheva, A.I. Albanov, L.V. Klyba, *J. Gen. Chem. (Rus)*. 71 (2001) 537;  
(c) L.V. Zhilitskaya, E.E. Istomina, O.G. Yarosh, M.G. Voronkov, *J. Gen. Chem. (Rus)* 76 (2006) 1261.