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New Methodology of Heterocyclization: the Electrophilic Addition Reactions of Selenium Di- and Tetrahalides and Tellurium Tetrachloride to Diethynyl Silanes and Germanes

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Abstract: The syntheses and structures of new classes of unsaturated five-membered heterocycles containing selenium or tellurium and silicon or germanium in the rings prepared on the basis of new heterocyclization reactions of selenium dihalides and tetrahalides or tellurium tetrachloride with the bridged diacetylenes are described. The mechanism of the heterocyclization is discussed.

Keywords: Selenium dihalides, Selenium tetrahalides, Tellurium tetrachloride, Diorganyl diethynyl silanes, Diorganyl diethynyl germanes, Unsaturated five-membered heterocycles.

1. INTRODUCTION

Unsaturated five-membered 1,3-dichalcogenole heterocycles are currently among the most studied chalcogen-containing systems [1] since they represent the parent compounds affording 2,2'-bis(1,3-dichalcogenolylidenes). The latter, more known as "tetrachalcogenofulvalenes", have been intensively studied for the last three decades owing to their unique electrochemical [2] and synthetic properties [3]. It was found that charge transfer salts of these heterocycles, so called "organic metals", possess conductivity and semiconductivity [4], and the most prospective compounds are molecular superconductors at temperatures below 5 K [5]. In the last decade, a considerable interest has been attracted to thiazole systems as analogs of 1,3-dithioles in which one sulfur atom is substituted with a nitrogen atom, and accordingly to dithiadiazafulvalenes as analogs of tetrathiafulvalenes where two sulfur atoms are replaced by two nitrogen atoms [6].

There are known saturated heterocycles containing in the ring the elements of 14a (Si, Ge) and 16a (S, Se, Te) groups. They have been prepared mainly by the heterocyclization of diallyl systems with sulfur dichloride, and selenium and tellurium tetrahalides. Thus, the preparation of 4,4-dichloro-3,5-bis(2-chloroethyl)-1-element-4-telluracyclohexanes by the reaction of $TeCl_4$ with diallyl ethers and sulfides has been reported in [7]. However, later, Bergman et al. have shown that only in the case of diallyl ethers due to the addition of $TeCl_4$ simultaneously to two ethylenic groups, cis-3,5-di(chloromethyl)-4,4-dichloro-1,4-oxatellurane(IV) is really formed [8]. In the case of diallyl sulfide, the addition of $TeCl_4$ occurs only at one allylic group to form a crystal complex having structure of 1-allyl-2,2,2,4-tetrachloro-1-thia-2-telluracyclopentane [9]. In the reaction of $SeCl_4$ with diallyl sulfide, the elimination of elemental selenium is observed and the product of intramolecular cyclization is not formed [9]. Sulfur dichloride reacts with diallyl sulfide to afford 2,5-dichloromethyl-1,3-dithiacyclohexane [10]. Among chalcogen,germanium-containing heterocycles are known benzodiselenagermoles and spiro-bisbenzodiselenagermoles formed by the interaction of diselenophenylcyrconocenes with different aryldichloro- and -trichlorogermanes and $GeCl_4$ correspondingly [11].

The methods of preparation of four- and five-membered sulfur, silicon-containing saturated heterocycles based on the reactions of divinyl sulfide with diorganyl silanes or chloroethyl vinyl silane with hydrogen sulfide have been described [12].

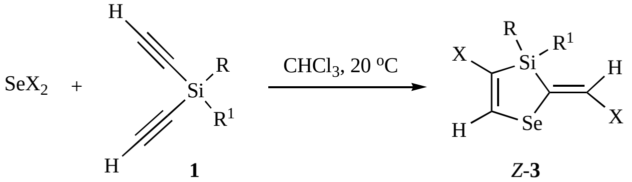
The method is known for preparation of tellurium-containing unsaturated heterocycles – 2,6-diorganyltellurapyran-4-ones [1h,13] and 1-thia-4-telluracyclohexan-2,5-dienes [13a,14] – by nucleophilic addition of Na_2Te to diethynyl ketones and diethynyl sulfide correspondingly.

In the present review, we report the results of our research on the synthesis of new classes of unsaturated five-membered heterocycles containing in a cycle the elements of 14a (Si, Ge) and 16a (Se, Te). These heterocycles are the products of new regio- and stereoselective electrophilic addition reactions of chalcogen di- and tetrahalides ($SeCl_2$, $SeBr_2$ $SeCl_4$, $SeBr_4$, $TeCl_4$) with the bridged diacetylenes – diorganyl diethynyl silanes (**1**) and diorganyl diethynyl germanes (**2**). New reagents of organic synthesis, generated *in situ* selenium dichloride and dibromide, for the first time have been involved in organic synthesis by Potapov et al. in novel regio- and stereoselective heterocyclization reaction with dimethyl diethynyl silane leading to first representatives of new class of heterocycles, 1,4-selenasilafulvenes [15a,b]. The reactions of these reagents with diethynyl silanes bearing various substituents have been systematically studied [15]. It should be pointed out that the reactions of $SeCl_2$ and $SeBr_2$ with diorganyl silanes [15] and diorganyl germanes [16] are the first examples of the convenient and easy Se-C bond formation using selenium dihalides. In continuation of these investigations the reactions of selenium dihalides with divinyl chalcogenides have been studied [17].

2. PRERARATION

2.1. 3,6-Dihalogen-4,4-diorganyl-1,4-selenasila(germa)fulvenes

The syntheses of selenium,silicon(germanium)-containing five-membered unsaturated heterocycles of fulvene structure – 3,6-dihalogen-4,4-diorganyl-1,4-selenasila(germa)fulvenes (**3**) and (**4**) – on a basis of earlier unknown heterocyclization reaction of diorganyl diethynyl silanes (**1**) [15] and germanes (**2**) [16] with $SeCl_2$ and $SeBr_2$ generated *in situ* from Se and SO_2Cl_2 or Br_2 accordingly are presented in Schemes **1** and **2**.



3: X = Br, R+R^1 = $(CH_2)_4$ (**a**), $(CH_2)_5$ (**b**); R = R^1 = Me (**c**);
R = Me, R^1 = $(CH_2)_2SiMe_3$ (**d**); R = Me, R^1 = H (**e**);
X = Cl, R+R^1 = $(CH_2)_4$ (**f**), $(CH_2)_5$ (**g**); R = R^1 = Me (**h**); R = Me, R^1 = H (**k**)

Scheme 1.

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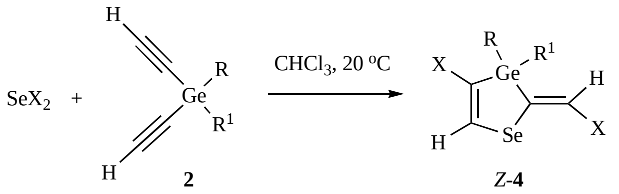


4: X = Br, R + R^1 = $(CH_2)_5$ (**a**), R = R^1 = i-Pr (**b**), R = Et, R^1 = t-Bu (**c**);
X = Cl, R = R^1 = i-Pr (**d**)

Scheme 2.

It has been shown that the initial $SeBr_2$ exists in acetonitrile and aprotic solvents in equilibrium with Se_2Br_2 and Br_2, while $SeCl_2$ is in equilibrium with Se_2Cl_2 and $SeCl_4$ [18]. In THF, both selenium dihalides are known to disproportionate to Se_2X_2 and SeX_4 [19] (Scheme **3**).

$$2\ SeBr_2 \xrightleftharpoons{CH_3CN} Se_2Br_2 + Br_2$$

$$3\ SeX_2 \xrightleftharpoons{THF} Se_2X_2 + SeX_4$$

X = Cl, Br

Scheme 3.

Nevertheless, the application of these reagents in the reactions with diethynyl silanes and germanes leads to regio- and stereoselective formation of 3,6-dihalogen-4,4-diorganyl-1,4-selenasilafulvenes (**3**) [15] and 3,6-dihalogen-4,4-diorganyl-1,4-selenagermafulvenes (**4**) [16] as *Z*-isomers in preparative yields (Schemes **1,2**, Table **1**). *E*-Isomers, formed in the reactions, are apparently the products of post-isomerization of the *Z*-isomers. 1,4-Silaselenafulvenes (**3a,b,f,g**) prepared from the cyclic 1,1-diethynyl-1-silacyclopentane (**1a**) and -1-silacyclohexane (**1b**) as well as 1,4-selenagermafulvene (**4a**) generated from the cyclic 1,1-diethynyl-1-germacyclopentane (**2a**) are of spirocyclic structure.

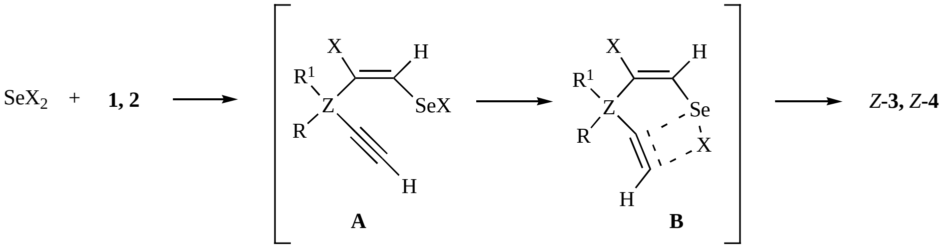
We assume that the heterofulvenes (**3**) and (**4**) are formed as a result of the successive regio- and stereoselective electrophilic addition of selenium dihalides to the triple bonds of diethynyl silanes and germanes. At the first stage of Markovnikov-type anti-addition, 2-halogenovinyl selenenyl halides (**A**) are formed. At the second stage, intramolecular anti-Markovnikov syn-addition of selenenyl halide moiety of the intermediate (**A**) to the second ethynyl group is realized through probably four-centered transient state (**B**) (Scheme **4**) [15c,16].

The formation of *Z*-3,6-dichloromethyl-4,4-dimethyl-1,4-selenasilafulvene (**3h**) in high yield is possible also by the reaction of dimethyl diethynyl silane (**1c**) with 1,2-dichlorodiselane Se_2Cl_2

Table 1. Reaction of SeX_2 with Diethynyl Silanes (1) and Germanes (2)

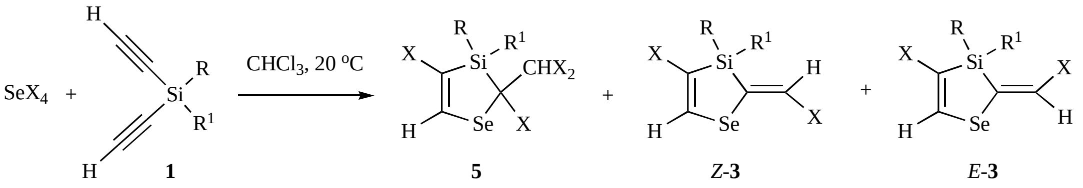
1,2	**R**	**R^1**	**SeX_2**	**Reaction Time, h**	**3,4**	**Yield, %**	***Z* : *E*[a]**
1a	$(CH_2)_4$		$SeBr_2$	5.5	**3a**	92.5	84 : 16
1a	$(CH_2)_4$		$SeCl_2$	7	**3f**	40	73 : 27
1b	$(CH_2)_5$		$SeBr_2$	6	**3b**	91	97.5 : 2.5
1b	$(CH_2)_5$		$SeCl_2$	6	**3g**	71	85 : 15
1c	Me	Me	$SeBr_2$	3	**3c**	70	85.5 : 14.5
1c	Me	Me	$SeCl_2$	3	**3h**	72	83 : 17
1d	$Me_3Si(CH_2)_2$	Me	$SeBr_2$	2	**3d**	86.5	89.5 :10.5
1e	Me	H	$SeBr_2$	24	**3e**	75	88 : 12
1e	Me	H	$SeCl_2$	24	**3k**	43	83 : 17
2a	$(CH_2)_5$		$SeBr_2$	2	**4a**	99[a]	96 : 4
2b	*i*-Pr	*i*-Pr	$SeBr_2$	1	**4b**	84.5[b]	94 : 6
2c	Et	*t*-Bu	$SeBr_2$	4	**4c**	66.5[b]	82: 18
2b	*i*-Pr	*i*-Pr	$SeCl_2$	3	**4d**	45.5[b]	100 : 0

[a] NMR ^{1}H data. [b] GC-MS data



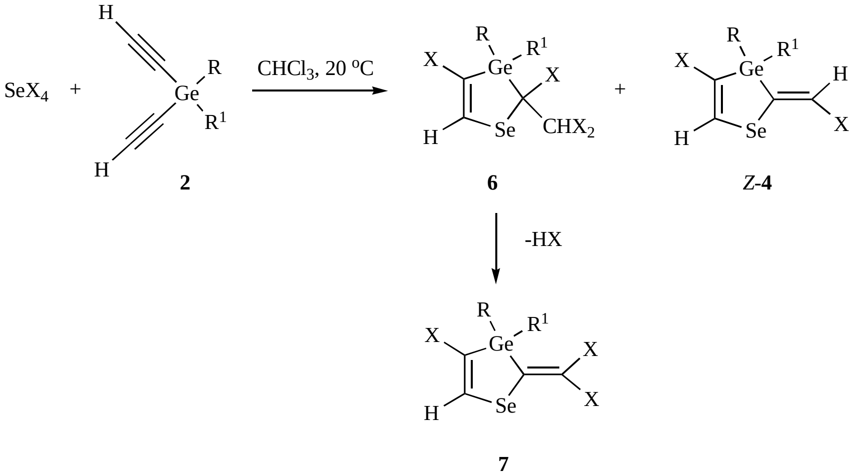
Z = Si, Ge; X = Cl, Br

Scheme 4.



5: X = Br, R+R^1 = $(CH_2)_4$ (**a**), $(CH_2)_5$ (**b**); R = R^1 = Me (**c**); R = Me, R^1 = $(CH_2)_2SiMe_3$ (**d**);
X = Cl; R+R^1 = $(CH_2)_4$ (**e**), $(CH_2)_5$ (**f**); R = R^1 = Me (**g**)

Scheme 5.



4: X = Br, R + R^1 = $(CH_2)_5$ (**a**); X = Cl, R = R^1 = i-Pr (**d**)

6: X = Br, R + R$_1$ = $(CH_2)_5$ (**a**)**;** X = Cl, R = R$_1$ = i-Pr (**b**)

7: X = Br, R + R^1 = $(CH_2)_5$ (**a**), R = R^1 = i-Pr (**b**), R = Et, R^1 = i-Pr (**c**); X = Cl, R = R^1 = i-Pr (**d**)

Scheme 6.

proceeding in chloroform with elimination of the elemental selenium both at 20 °C and -40 °C [20].

2.2. 2,4-Dihalogen-2-dihalogenomethyl-3,3-diorganyl-1-selena-3-sila(germa)cyclopentenes-4

Selenium,silicon(germanium)-containing unsaturated five-membered heterocycles of cyclopentene structure – 2,4-dihalogen-2-dihalogenomethyl-3,3-diorganyl-1-selena-3-silacyclopentenes-4 (**5**) [15c,21] and 2,4-dihalogen-2-dihalogenomethyl-3,3-diorganyl-1-selena-3-germacyclopentenes-4 (**6**) [16] – have been prepared by the earlier unknown regioselective addition reaction of selenium tetrahalides with diorganyl diethynyl silanes (**1**) and germanes (**2**) (Schemes **5**,**6**, Tables **2**,**3**). The reactions proceed in chloroform at the ambient temperature, and in both cases they are accompanied by the formation of the corresponding heterofulvenes (**3**) and (**4**). Presumably, this fact is connected with halogenating properties of $SeBr_4$ and $SeCl_4$ resulting in generation of $SeBr_2$ and $SeCl_2$ in the reaction mixtures due to halogenation of diethynyl silanes (**1**) and germanes (**2**).

1-Selena-3-silacyclopentenes-4 (**5a,b,e,f**) and 1-selena-3-germacyclopentene-4 (**6a**) prepared in the reactions of selenium tetrahalides with the cyclic diethynyl silanes and germanes – 1,1-diethynyl-1-silacyclopentane (**1a**), -1-silacyclohexane (**1b**) and 1,1-diethynyl-1-germacyclohexane (**2a**) – have spirocyclic structures. 1-Selena-3-silacyclopentene-4 (**5d**) prepared from diethynyl silane (**1d**) with different substituents at silicon atom is formed as two diastereomers.

1-Selena-3-germacyclopentenes-4 (**6**) are unstable and under the reaction conditions they are dehydrohalogenated to deliver 3,6,6-trihalogen-4,4-dialkyl-1,4-selenagermafulvenes (**7**) in the mixture with the parent compounds (**6**) [16]. In the case of bromo-derivatives and alkyl substituents at the germanium atom, 3,6,6-tribromo-1,4-selenagermafulvenes (**7**) are the only products of the reaction of $SeBr_4$ with dialkyl diethynyl germanes (**2**). Dehydrohalogenation of 1-selena-3-silacyclopentens-4 (**5**) proceeds much more slower, so the formation of 3,6,6-trihalogen-4,4-dialkyl-1,4-selenasilafulvenes has been registered in the reaction mixtures only after storage at 20 °C for several months.

To elucidate a mechanism of the reaction of $SeBr_4$ with dimethyl diethynyl silane (**1c**) and to explain the formation of only five-membered heterocycles 1-selena-3-silacyclopentenes-4 (**5**), quantum chemical computations of possible routes of the $SeBr_4$ interaction with diethynyl silane (**1c**) have been performed out using DFT/B3LYP method with LANL2DZ basis of the program complex GAUSSIAN-98W [22]. It has been found that the first stage of the reaction involves the conversion of $SeBr_4$ into a complex containing molecular bromine and $SeBr_2$. This process is catalyzed by diethynyl silane, and in the pre-reaction trimolecular complex ($SeBr_2$…Br_2…**1c**), the bromination of ethynyl moiety of the silane (**1c**) turns to be more favorable. Consequent regio- and stereoselective addition of $SeBr_2$ to a second ethynyl moiety of the silane (**1c**) leads to the formation of the intermediate 2-(1,2-dibromoethenyldimethylsilyl)-2-bromo-1-ethenelselenenyl bromide $Me_2Si(CHBr{=}CBr)CBr{=}CHSeBr$. Cyclization of this intermediate to five-membered but not isomeric six-membered heterocycles is due to much lower activation barrier (141.2 kJ/mol) of the four-centered transition state leading to 1-selena-3-silacyclopentenes-4 as compared to the activation barrier of the formation of cyclic

Table 2. Reaction of SeX_4 with Diethynyl Silanes (1)

1	**R**	**R^1**	**SeX_4**	**Reaction Time, h**	**3**	**Yield, %**	***Z : E*[a]**	**5**	**Yield,[b] %**
1a	$(CH_2)_4$		$SeBr_4$	2	**3a**	27	74 : 26	**5a**	73
1a	$(CH_2)_4$		$SeCl_4$	7	**3h**	73	68 : 32	**5e**	21
1b	$(CH_2)_5$		$SeBr_4$	6	**3b**	35.5	70.5 : 29.5	**5b**	58.5
1b	$(CH_2)_5$		$SeCl_4$	5	**3f**	18	60 : 40	**5f**	75.5
1c	Me	Me	$SeBr_4$	6				**5c**	60
1c	Me	Me	$SeCl_4$	6	**3e**	40	75 : 25	**5g**	32
1d	$Me_3Si(CH)_2$	Me	$SeBr_4$	1				**5d**	62[c]

[a] NMR ^{1}H data. [b] GC-MS data. [c] Ratio of diastereomers 62 : 38, according to the NMR ^{1}H data.

Table 3. Reaction of SeX_4 with Diethynyl Germanes (2)

2	**R**	**R^1**	**SeX_4**	**Reaction Time, h**	**4**	**Yield, %**	***Z : E*[a]**	**6**	**Yield, %**	**7**	**Yield, %**
2a	$(CH_2)_5$		$SeBr_4$	5.5	**4a**	13[a]	100 : 0	**6a**	67[a]	**7a**	19[a]
2b	i-Pr	i-Pr	$SeBr_4$	1		-	-		-	**7b**	86[b]
2c	Et	t-Bu	$SeBr_4$	4		-	-		-	**7c**	83.5[b]
2b	i-Pr	i-Pr	$SeCl_4$	6	**4d**	26.5[a]	100 : 0	**6б**	21.5[a]	**7d**	41[a]

[a] NMR ^{1}H data. [b] GC-MS data.

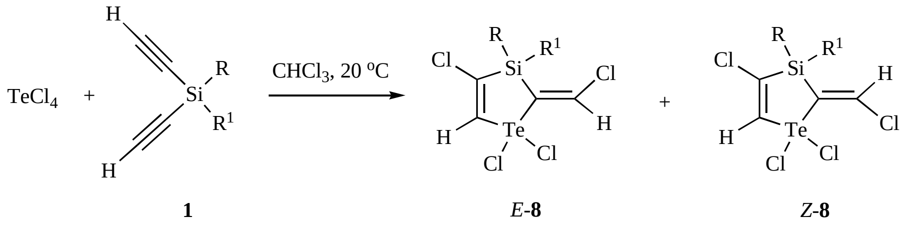
seleniranium cation (257.9 kJ/mol) giving six-membered heterocycles.

2.3. 1,1,3,6-Tetrachloro-4,4-diorganyl-1,4-tellura(IV)silafulvenes

The first representatives of a new class of tellurium,silicon-containing unsaturated five-membered heterocycles – 1,1,3,6-tetrachloro-4,4-diorganyl-1,4-tellura(IV)silafulvenes (**8**) – have been prepared in good yields predominantly or exclusively as *E*-isomers by regio- and stereoselective reaction of tellurium tetrachloride with diorganyl diethynyl silanes (**1**) (Scheme **7**, Table **4**) [23]. The heterocycles (**8a,b**) formed from the cyclic diethynyl silanes (**1a,b**) have spirocyclic structure. *E*-Isomers of the heterocycles (**8**) are easily isolated from the chloroform solutions as white fine-grained powder.

In the case of methyl diethynyl silane (**1e**), the intermediate *E*-1,1-dichloro-1,4-tellura(IV)silafulvene (**A**) reacts with the starting silane (**1e**) to form *E*-1,1,3,6-tetrachloro-1-methyl-1-methyldiethynyloxy-1,4-tellura(IV)silafulvene (**8e**) due to acidic hydrolysis in the presence of traces of water (Scheme **8**) [24].

To explain the formation of *E*-isomers of the heterocycles (**8**) we have suggested two-stage mechanism. The first stage is anti-Markovnikov anti-addition of $TeCl_4$ to ethynyl moiety of diethynyl silane, while the second one involves the electrophilic intramolecular addition of $TeCl_3$-fragment of the intermediate vinyl tellurium

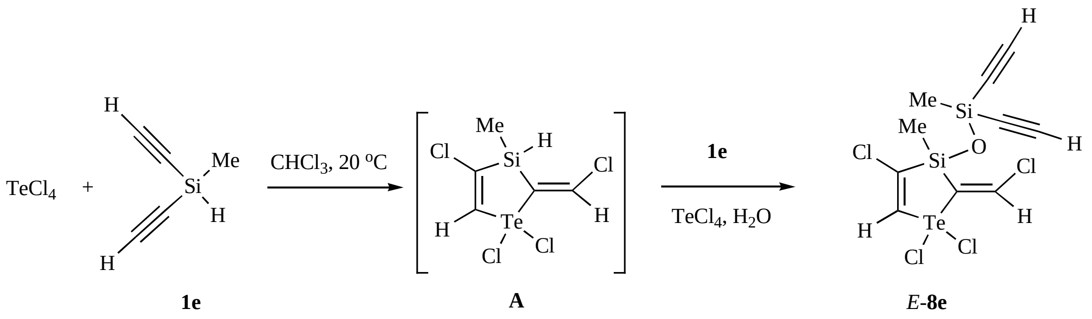


8: R+R^1 = $(CH_2)_4$ (**a**), $(CH_2)_5$ (**b**), R = R^1 = Me (**c**), R = Me, R^1 = $Me_3Si(CH_2)$ (**d**)

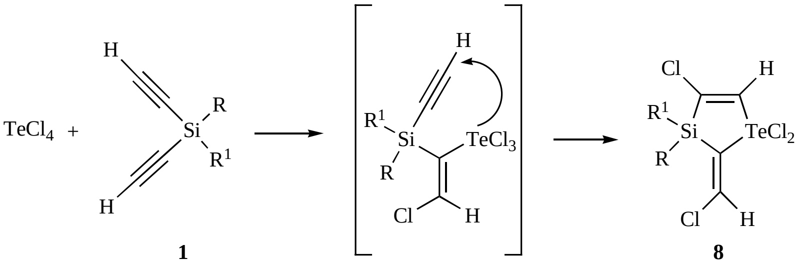
Scheme 7.

Table 4. Yields and *E:Z* Ratio of 1,1,3,6-tetrachloro-4,4-diorganyl-1,4-tellura(IV)silafulvenes (8)

	R	R^1	Yield, %	*E* : *Z*
8a	$(CH_2)_4$		84	65 : 35
8b	$(CH_2)_5$		85	75 : 25
8c	Me	Me	80	100 : 0
8d	Me	$Me_3Si(CH_2)_2$	72	100 : 0
8e	Me	OSiMe(C≡CH)$_2$	28	100 : 0



Scheme 8.

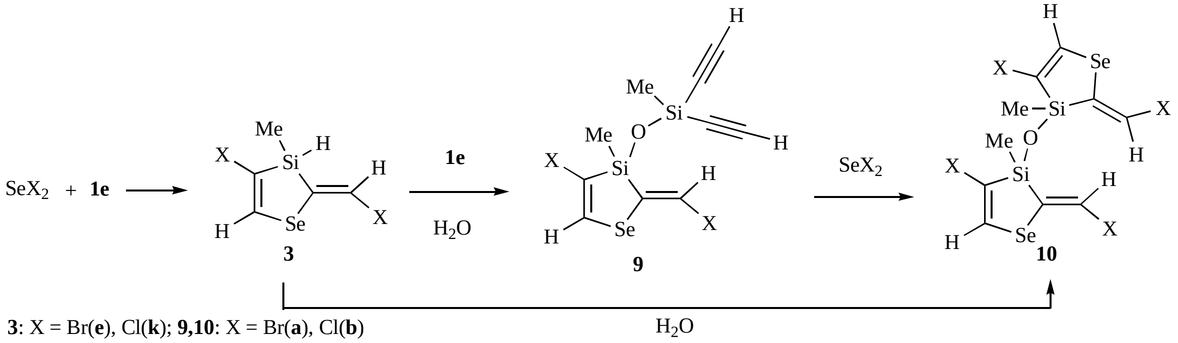


Scheme 9.

trichloride to the second ethynyl group (Scheme **9**). Anti-Markovikov addition of $TeCl_4$ to ethynyl silane has been shown in the model reaction of $TeCl_4$ with trimethyl ethynyl silane $Me_3SiC{\equiv}CH$ [25].

2.4. Peculiarities of the Interaction of Selenium Di- and Tetrahalides with Methyl Diethynyl Silane

Regio- and stereoselective electrophilic addition reactions of $SeCl_2$, $SeBr_2$, $SeCl_4$, $SeBr_4$ with methyl diethynyl silane (**1e**) containing Si-H group easily hydrolyzed in acidic media lead along with the formation in high yields of *Z*- and *E*-isomers of 3,6-dihalogen-4-methyl-1,4-selenafulvenes (**3**) (Table **1**) to disiloxanes (**9**) and (**10**) – products of the further conversions of the compounds (**3**) [24]. The reaction selectivity depends on the reaction conditions and the nature of selenium dihalides. In the reaction of selenium dihalides in chloroform in the presence of even traces of moisture, *Z*-isomers of 3,6-dihalogen-4-methyl-4-(methyldiethynyl)siloxy-1,4-selenasilafulvenes (**9**) are formed due to acidic hydrolysis of the Si-H bond and subsequent condensation with diethynyl silane (**1e**). Further reaction of products (**9**) with SeX_2 affords 3,6-dihalogen-4-(3',6'-dihalogen-4'-methyl-4'-oxa-1,4-selenasilafulveno)-4-methyl-1,4-selenasilafulvenes (**10**) (Scheme **10**). The formation of the heterocycle (**9a**) along with the 1,4-selenasilafulvene (**3e**) is realized when less reactive $SeBr_2$ is used at ambient temperature. But at -5 °C intermediate heterocycle (**9a**) is fully consumed in the reaction with $SeBr_2$ and only compound (**10a**) along with 1,4-selenasilafulvene (**3e**) are present in the reaction mixture. With more reactive $SeCl_2$ intermediate heterocycle (**9**) is not registered, only heterocycle (**10b**) is present in the reaction mixture, which could be explained by immediate reaction of the intermediate (**9**) with $SeCl_2$. It is not unlikely though that product (**10**) could be formed primarily from heterocycle (**3**) at the expense of its acidic hydrolysis and condensation.



3: X = Br(**e**), Cl(**k**); **9**,**10**: X = Br(**a**), Cl(**b**)
9: X = Br(**a**)
10: X = Br(**a**), Cl(**b**);

Scheme 10.

Table 5. ^{1}H and ^{77}Se NMR Spectra of Fulvene-Type Heterocyles (3,4,9,10)

Heterocycle	14a Element	R	R^1	X	Isomer	^{1}H NMR, δ, ppm (from HMDS)					^{77}Se NMR, δ, ppm
						SiCX=CHSe	SeC=CHX	$^5J_{HH}$, Hz	$^2J_{SeH}$, Hz	$^3J_{SeH}$, Hz	
3a	Si	$(CH_2)_4$		Br	*Z*	7.54d	6.97d	0.9	54.6	13.6	558.9dd
					E	7.46s	6.92s	–			573.9dd
3b	Si	$(CH_2)_5$		Br	*Z*	7.49d	7.05d	0.8	54.5	14.4	554.7dd
3f	Si	$(CH_2)_4$		Cl	*Z*	7.24d	6.66d	1.1	54.1	11.5	496.8dd
					E	7.19s	6.68s	–	54.9	8.6	509.1dd
3g	Si	$(CH_2)_5$		Cl	*Z*	7.19d	6.75s	0.5	54.4	11.5	492.7dd
					E	7.14s	6.64s	–	50.2	7.3	504.6dd
3d	Si	Me	$(CH_2)_2SiMe_3$	Br	*Z*	7.46d	6.90d	1.1	54.6	14.1	560.3dd
					E	7.40s	6.81s		53.8	10.3	523.2dd
3c	Si	Me	Me	Br	*Z*	7.42d	6.92d	1.1	54.0	14.0	653.0dd
					E	7.34s	6.79s	–	54.0	11.2	568.0dd
3h	Si	Me	Me	Cl	*Z*	7.15d	6.64d	1.1	54.0	12.1	491.5dd
					E	7.09s	6.61s	–	54.0	9.3	503.5dd
3e	Si	Me	H	Br	*Z*	7.53d	7.03dd*	1.1	54.5	13.4	571.4dd
					E	7.50s	7.16d*	–	55.3	13.5	534.9dd
4a	Ge	$(CH_2)_5$		Br	*Z*	7.40d	6.83d	1.1	57.0	14.0	556.6dd
					E	7.34s	6.81s	–			–
4b	Ge	i-Pr	i-Pr	Br	*Z*	7.49d	6.62d	1.0	58.4	13.6	578.1dd
					E	7.45s	6.84s	–			
4c	Ge	Et	t-Bu	Br	*Z*	7.50d	6.65d	0.8	56.3	14.6	575.2dd
					E	7.46s	6.89s	–	58.1	7.7	
4d	Ge	i-Pr	i-Pr	Cl	*Z*	7.17d	6.37d	1.0	52.0	12.0	516.3dd
9a	Si	Me	O-SiMe(C≡CH)$_2$	Br	*Z*	7.58d	7.21d	1.1	53.3	9.4	576.8dd
10a**	Si			Br	*Z,Z*	7.62d	7.28d		53.7	12.4	555.7dd
10b**	Si			Cl	*Z,Z*	7.37d	6.96d	0.7	52.9	9.2	488.6dd
				Cl	*E,E*	7.33s	6.79s	–	54.2	8.7	503.4dd

* $^4J_{(Si)HH}$ 1.2 Hz, ** 3,6-Dihalogen-4-(3',6'-dihalogen-4'-methyl-4'-oxa-1,4-selenasilafulveno)-4-methyl-1,4-selenasilafulvenes

In contrast to the reaction with diorganyl diethynyl silanes (**1**), the reactions of $SeBr_4$ and $SeCl_4$ with methyl diethynyl silane do not give cyclopentene heterocycl1es (**5**). In this reaction, disiloxanes (**9**) are formed as *Z,Z*-isomers predominantly, in the case of $SeBr_4$, or exclusively, in the case of $SeCl_4$.

Table 6. ^{1}H and ^{77}Se NMR Spectra of Selenium-Containing Cyclopentene-Type Heterocycles (5, 6, 7)

Heterocycle	14a Element	R	R^{1}	X	^{1}H NMR, δ, ppm. (from HMDS)			^{77}Se NMR, δ, ppm
					SiCX=CHSe	SeCXCHX$_2$	$^{2}J_{SeH}$, Hz	
5a	Si	(CH$_2$)$_4$		Br	7.51s	6.52s	56.4	607.3d
5b	Si	(CH$_2$)$_5$		Br	7.48s	6.42s	52.3	604.0d
5e	Si	(CH$_2$)$_4$		Cl	7.22s	6.44s	50.7	649.4d
5f	Si	(CH$_2$)$_5$		Cl	7.20s	6.35s	51.2	634.2d
5d	Si	Me	Me$_3$Si(CH$_2$)$_2$	Br	7.51s*	6.47s*	55.7	608.7d
					7.42s	6.44s	55.7	608.7d
5c	Si	Me	Me	Br	7.74s	7.06s	52.0	707.5d
5g	Si	Me	Me	Cl	7.16s	6.40s	54.0	638.0d
6a	Ge	(CH$_2$)$_5$		Br	7.43s	6.48s	57.0	594.7d
6b	Ge	Me	Me	Cl	7.19s	6.41s	57.5	538.7d
7a	Ge	(CH$_2$)$_5$		Br	7.34s		57.5	594.7d
7b	Ge	i-Pr	i-Pr	Br	7.46		59.7	609.3d
7c	Ge	Et	t-Bu	Br	7.45s		58.1	613.4d
7d	Ge	i-Pr	i-Pr	Cl	7.11s		57.2	538.7d

*major of two diastereomers (ratio 68: 32)

3. INVESTIGATIONS OF SELENIUM,SILICON (GERMANIUM)- AND TELLURIUM,SILICON-CONTAINING UNSATURATED FIVE-MEMBERED HETEROCYCLES BY THE MULTINUCLEAR (^{1}H, ^{13}C, ^{29}SI,^{77}SE, ^{125}TE) NMR SPECTROSCOPY, MASS-SPECTROMETRY AND XRD ANALYSIS

The ^{77}Se NMR spectra of selenium,silicon- (**3**) and selenium,germanium-containing (**4**) heterocycles are characterized by doublets of doublets of the selenium-77 signals with $^{2}J_{SeH}$ 50-60 Hz specific of cyclic unsaturated selenides [26] and $^{3}J_{SeH}$ 11-14 Hz for the major *Z*-isomers of the heterocycles (**3**) and (**4**), 7-13 Hz for the minor *E*-isomers of the heterocycles (**3**) (Table **5**). The similar fine structure is observed in the ^{1}H NMR spectra of the above heterocycles where spin-spin coupling of protons with selenium atom manifests itself as the doublet satellite signals to the signals of the corresponding exocyclic and endocyclic olefinic protons.

The distinctive feature of the ^{1}H NMR spectra of *Z*-isomers of the heterofulvenes (**3**) and (**4**) is a presence of a characteristic long-range splitting between exo- and endocyclic olefinic protons ($^{5}J_{HH}$ 0.5-1.2 Hz) which allows easy identification of these isomers since the splitting is absent in *E*-isomers (Table **5**). Predominant formation of *Z*-isomers has been confirmed by the 2D NOESY ^{1}H NMR spectrum of 3,6-dibromo-4,4-tetramethylene-1,3-selenasilafulvene (**3a**). The value of $^{3}J_{SiH}$ 3.9 Hz for spin-spin coupling of silicon atom with proton of the exocyclic double bond complying with the cis-arrangement of Si and H atoms [27] also points to the *Z*-structure of the main isomers of the heterocycles (**3**).

It should be noted that in [26,28] the values of $^{3}J_{SeH}$ 11-14 Hz have been associated with the cis-arrangement of Se and H atoms in vinyl selenides. But the results [15] found by us show that in the case of selenium,silicon-containing heterofulvenes (**3**), these values correspond to the trans-arrangement of Se and H atoms. In the recent conformational and NMR study of divinyl selenide [29], it has been shown that both geminal and vicinal ^{1}H-^{77}Se spin-spin coupling constants are subject to conformational effects originating in the internal rotation around C$_{sp2}$-Se bond which reasonably explains this discrepancy.

The ^{1}H NMR spectra of 3,6-dihalogen-4-methyl-1,4-selenasilafulvenes (**3e,k**) are characterized by additional splitting of the olefinic protons of the exocyclic double bond with the protons of the Si-H group [24] (Table **5**). The ^{1}H and ^{77}Se NMR spectra of 3,6-dibromo-4-methyl-4-(methyldiethynyl)siloxy-1,4-selenasilafulvenes (**9a**) and 3,6-dihalogen-4-(3'6'-dihalogen-4-methyl-4'-oxa-1,4-selenasilafulveno)-4-methyl-1,4-selenasilafulvenes (**10a,b**) generated from 3,6-dihalogen-4-methyl-1,4-selenasilafulvenes (**3e,k**) are by and large identical to the spectra of the parent compounds (**3e,k**) (Table **5**).

In the ^{77}Se NMR spectra, 1-selena-3-silacyclopentenes-4 (**5**) and 1-selena-3-germacyclopentenes-4 (**6**) are presented as the doublets with the splitting constants $^{2}J_{SeH}$ 52-56 Hz for the former and 57-60 Hz for the latter (Table **6**). The formation of five-membered heterocycle (**5**) rather than isomeric six-membered 1-selena-4-silacyclohexene-2 has been confirmed by the 2D NOESY ^{1}H NMR spectrum of 2,4-dichloro-2-dichloromethyl-3,3-pentamethylene-1-selena-3-silacyclopentene-4 (**5f**). In the ^{1}H NMR spectra of the heterocycles (**5**) and (**6**), the signals of the olefinic protons of endocyclic double bond are observed as singlets (Table **6**).

In the ^{1}H NMR spectra of 3,6,6-trichalogen-4,4-dialkyl-1,4-selenagermafulvenes (**7**) there are registered only singlet signals of the olefinic protons of the endocyclic double bond, while in the ^{77}Se NMR spectra – the doublet signals of the selenium-77 with the geminal constant $^{2}J_{SeH}$ 57-60 Hz [16] (Table **6**).

In the ^{1}H NMR spectra of 1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvenes (**8**), as in the case of heterofulvenes (**3**) and (**4**), the *Z*-isomers of the compounds (**8**) are easily identified by the doublet signals of the olefinic protons with the characteristic long-range constant $^{5}J_{HH}$ 0.2-0.5 Hz [23] (Table **7**). At the same time, the *E*-isomers are characterized by the values of $^{3}J_{SiH}$ 9-10 Hz complying with the trans-arrangement of Si and H atoms [27]. The *Z*-isomer of 1,1,3,6-tetrachloro-4,4-tetramethylene-1,4-tellura(IV)silafulvene (**8c**) has been identified by the 2D NOESY ^{1}H NMR spec-

Table 7. ^{1}H and ^{125}Te NMR Spectra of 1,1,3,6-tetrachloro-1,4-tellura(IV)silafulvenes (8) (in d$_6$-acetone)

Heterocycle	R	R^1	Isomer	Si-CCl=CH-Te, δ, ppm.	Te(Cl$_2$)C=CHCl, δ, ppm	$^5J_{HH}$, Hz	$^2J_{TeH}$, Hz	$^3J_{TeH}$, Hz	$^3J_{SiH}$, Hz	^{125}Te NMR, δ, ppm
8a	(CH$_2$)$_4$		*E*	8.41s	8.06s	–	123.5	15.7	9.9	920.1
			Z	8.46d	7.55d	0.5	122.7	19.3	–	870.8
8b	(CH$_2$)$_5$		*E*	8.36s	8.04s	–	124.0	17.9	9.8	926.9
			Z	8.41d	7.61d	0.2	127.9	20.0	–	875.5
8c	Me	Me	*E*	8.45s	8.14s	–	123.6	15.3	8.9	921.3
8d	Me	Me$_3$Si(CH$_2$)$_2$	*E*	8.39s	8.05s	–	124.0	16.0	9.0	925.0
8e*	Me	OSiMe(C≡CH)$_2$	*E*	8.12s	7.68s	–	137.8	19.0	9.4	854.8

* in CDCl$_3$

trum. In the ^{125}Te spectra, *Z*- and *E*-isomers of 1,1-dichloro-1,4-tellura(IV)silafulvenes (**8**) manifest themselves by the doublet signals of tellurium-125 in the range 870-875 and 920-930 ppm, correspondingly. This range is known to be specific for tetracoordinated tellurium atom [30].

Mass-spectra of the heterofulvenes (**3**) and (**4**) as well as trihalogen-1,3-selenagermafulvenes (**7**) are characterized by the stable polyisotopic molecular ions. We have studied the chemical behavior of 3,6-dihalogen-4,4-dimethyl-1,4-selenasilafulvenes (**3**) under the electron impact ionization and in the thermodestruction and have found that on their fragmentation the skeletal rearrangements take place with the positive charge localized mainly on ions containing silicon atom [31]. In the mass-spectra of the heterocycles (**5**) and (**6**), the molecular ions are absent since on electron impact their dehydrohalogenation or dehalogenation take place and as a result these heterocycles are identified only by the fragment ions [M - X$_2$]$^+$ и [M - HX]$^+$ [31]. Similar picture is observed in the mass-spectra of 1,1-dichloro-1,4-tellura(IV)silafulvenes (**8**) that are characterized only by the fragment ions [M - Cl$_2$]$^+$ [23].

The XRD analysis of 2,4-dibromo-2-dibromomethyl-3,3-dimethyl-1-selena-3-silacyclopentene-4 (**5c**) [22] has shown that five-membered ring of the heterocycle is characterized by the envelope conformation and that the molecules in the crystal are combined in centrosymmetrical dimers at the expense of secondary interactions between bromine atoms in different positions probably due to charge transfer from the lone electron pair of Br to the antibonding orbital (σ*) of the C(1)-Br(1) bond (Fig. **1**).

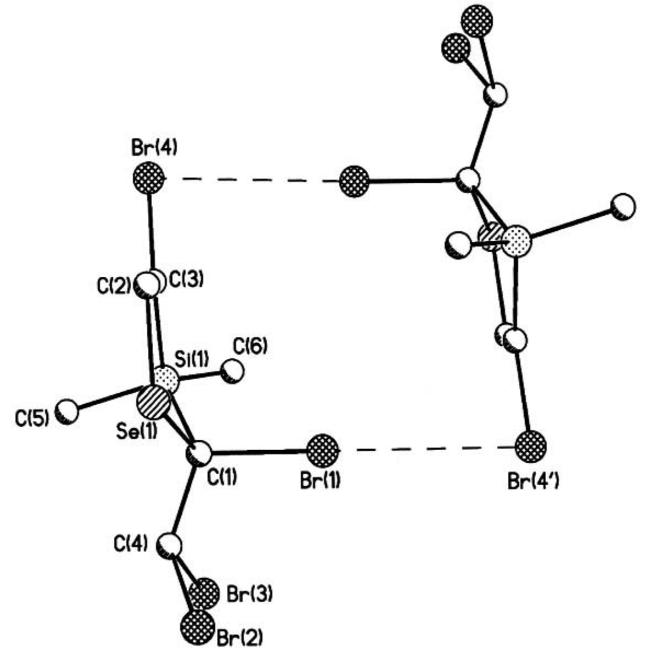


Fig. (1).

CONCLUSION

A series of earlier unknown regio- and stereoselective reactions of chalcogen di- and tetrahalides, SeCl$_2$, SeBr$_2$, Se$_2$Cl$_2$, SeCl$_4$, SeBr$_4$, TeCl$_4$, with diethynylsilanes RR^{1}Si(C≡CH)$_2$ and germanes RR^{1}Ge(C≡CH)$_2$ has been found. They proceed as electrophilic addition-cyclization involving both ethynyl groups of the bridged diacetylenes and lead to formation in high yields of new classes of unsaturated five-membered heterocycles of fulvene or cyclopentene structure. These reactions represent a new approach to heterocyclization allowing easy and convenient formation of selenium- or tellurium-containing heterocycles. In the reaction with dimethyl diethynyl silane selenium dihalides for the first time have been involved in organic synthesis with the formation of the C-Se bond. It should be mentioned that intensively developing chemistry of 1,4-dichalcogenafulvenes – precursors of tetrachalcogenafulvalenes, electroconducting heterocycles, has aroused interest to their derivatives in which one chalcogen atom is substituted with another element. New classes of chalcogen,element(14a)-containing five-membered unsaturated heterocycle which are basically analogs of 1,4-dichalcogenofulvenes with one chalcogen atom being substituted with element of 14a group (silicon or germanium) represent further modifications of 1,4-dichalcogenofulvenes. These new heterocycles, possessing such reaction centers as double bonds and halogen atoms, are able to functionalization by addition and nucleophilic substitution reactions with various reagents and could be interesting as new building blocks for construction of the complex molecular structures such as macrocycles, dendrimers, polymers (cyclophanes, cage molecules, catenanes, rotaxanes).

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