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

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The reaction of $TeCl_4$ with diorganyl diethynyl silanes $RR^1Si(C{\equiv}CH)_2$ in $CHCl_3$ 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% stereoselectively 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 (^1H, ^{13}C, ^{29}Si, ^{125}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 $^5J_{HH}$ 0.2–0.5 Hz lacking in *E*-isomers. In the mass spectra the heterocycles manifest themselves as the fragment ions $[M-Cl_2]^+$.

1. Introduction

Electrophilic addition of tellurium tetrahalides TeX_4 (X = Br, Cl) to acetylenic compounds is poorly studied and is limited only to the monoacetylenes such as $PhC{\equiv}CH$, $PhC{\equiv}CPh$, $C_5H_{11}C{\equiv}CH$, $CH{\equiv}CCH_2OH$ [1a–1i]. The reactions proceed with the formation of both monoadducts $RCH{=}CHTeCl_3$ as *Z*-isomers [1a,1b,1d,1i,1g] and diadducts $(CRX{=}CH)_2TeX_2$ [1e,1f,1i]. As a rule, *syn*-addition is realized but in the case of $TeBr_4$ 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-dihydrofurane [1d].

The reactions of aryl tellurium trichlorides and tribromides with the terminal acetylenes $RC{\equiv}CH$ (R = C_4H_9, C_5H_{11}, *cyclo*-C_6H_{11}, $HOCH_2$, HO-*cyclo*-C_6H_{10}, Ar) in apolar solvents (CCl_4, $CHCl_3$, C_6H_6) proceed as the Markovnikov-type regio- and stereoselective, mainly *syn*, additions [1e,1f,1i,2a–2e]. The interaction of $ArTeBr_3$ 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 $ArTeBr_3$ 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 SeX_4 (X = Cl, 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 SeX_2 (X = Cl, 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 (^1H, ^{13}C, ^{29}Si, ^{125}Te), 2D NOESY NMR techniques and mass-spectrometry.

2. Results and discussion

2.1. Electrophilic addition-cyclization of $TeCl_4$ with diorganyl diethynyl silanes

We have found that the interaction of diorganyl diethynyl silanes **1a–d** with $TeCl_4$ in chloroform at room temperature presents a new regio- and stereoselective reaction resulting in a new class of

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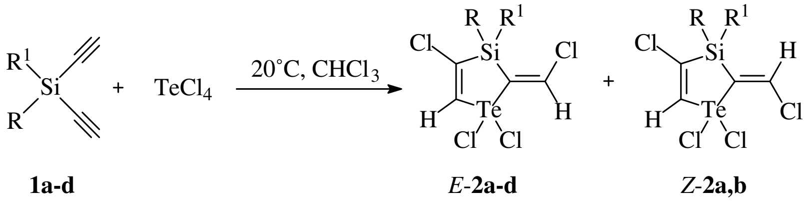


Scheme 1. **1**, **2**: R + R^1 = $(CH_2)_4$ (**a**), $(CH_2)_5$ (**b**), R = R^1 = Me (**c**), R = Me, R^1 = $Me_3Si(CH_2)_2$ (**d**).

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.

Table 1
The yields and the *Z*:*E* ratio of the heterocycles **2**

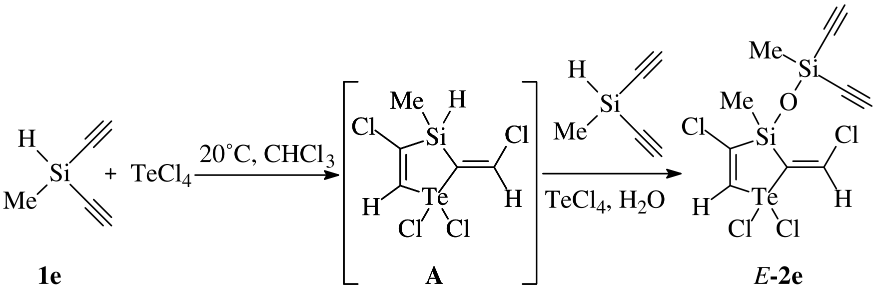
	R	R^1	Yield (%)	*E*:*Z*
2a		$(CH_2)_4$	84	65:35
2b		$(CH_2)_5$	85	75:25
2c	Me	Me	80	100:0
2d	Me	$Me_3Si(CH_2)_2$	72	100:0
2e	Me	$OSiMe(C{\equiv}CH)_2$	28	100:0

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 $TeCl_4$ 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.

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

Compound	R	R^1	Si–CCl=CH–Te, δ, ppm	$^5J_{H-H}$, Hz	$^2J_{Te-H}$, Hz	$^3J_{Si-H}$, Hz	Te(Cl$_2$)C=CHCl, δ, ppm	$^5J_{H-H}$, Hz	$^3J_{Te-H}$, Hz	$^3J_{Si-H}$, Hz	R, R^1, δ, ppm
E-**2a**		$(CH_2)_4$	8.41s	–	123.5	9.1	8.06s	–	15.7	9.9	1.99–1.85m (CH_2CH_2) 1.25–1.04m (CH_2Si)
Z-**2a**		$(CH_2)_4$	8.46d	0.5	122.7	9.0	7.55d	0.5	19.3	–	1.95m 1.70m (CH_2CH_2); 1.19m, 0.87m (CH_2Si);
E-**2b**		$(CH_2)_5$	8.36s	–	124.0	8.8	8.04s		17.9	9.8	1.70–1.46m (CH_2); 2.10–2.02m, 2.00–1.92m (CH_2CH_2Si); 1.37–1.27m, 1.21–1.16m (CH_2Si);
Z-**2b**		$(CH_2)_5$	8.41d	0.24	127.9	8.6	7.61d	0.24	20.0	–	1.73–1.50m (CH_2); 2.21–1.96m (CH_2CH_2Si); 1.31–0.83m (CH_2Si);
E-**2c**	Me	Me	8.45s	–	123.6	8.3	8.14s	–	15.3	8.9	0.60s, 0.41s (CH_3Si);
E-**2d**	Me	$Me_3Si(CH_2)_2$	8.39s	–	124.0	9.0	8.05s	–	16.0	9.0	0.03s (Me_3Si), 0.64s (MeSi), 0.46s (CH_2), 0.31s (CH_2)
E-**2e**[a]	Me	$OSiMe(C{\equiv}CH)_2$	8.12s	–	137.8	10.2	7.68s		19.0	9.4	0.51s (CH_3), 0.79s (CH_3), 2.53s (≡CH), 2.54s (≡CH)

[a] In $CDCl_3$.