Bis(alkoxyethynyl)-substituted silanes, germanes, and stannanes: synthesis and pyrolysis

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Previously unknown bis(alkoxyethynyl)-substituted silanes, germanes, and stannanes were synthesized. Pyrolysis of bis(ethoxyethynyl)-substituted silanes and germanes was studied. Depending on the reaction conditions (pyrolysis in a solvent or vacuum pyrolysis without a solvent), the process affects either one ethoxyethynyl group to give (ethoxyethynyl)silyl(-germyl)ketenes or both ethoxyethynyl groups, affording silyl- and germylbisketenes. Pyrolysis of bis(alkoxyethynyl)dimethylstannanes follows another route, resulting in 1,1-bis(alkoxy)-2,2-bis[(alkoxyethynyl)dimethylstannyl]ethenes.

Key words: bis(alkoxyethynyl)-substituted silanes, germanes, and stannanes; pyrolysis; silylenebisketenes; (ethoxyethynyl)silylketenes; (ethoxyethynyl)germylketenes; dimethylsilylene-bis(*N,N*-dimethyl)acetamide; dimethylgermylene-bis(*N,N*-dimethyl)acetamide.

Organosilicon, organogermanium, and organotin ethoxyethynes are promising synthons for preparation of organic and organometallic compounds.[1] They can be used for the synthesis of novel types of organoelement compounds, namely, bis- and mono-heteroorganoketenes[2] and heteroorganoaminoacetylenes,[3] owing to the presence of several reactive sites in their molecules.

Among silyl-, germyl-, and stannylalkoxyethynes, compounds of the type $R_3EC{\equiv}COR'$ have been well studied, whereas structurally similar bis(alkoxyethynyl) compounds of silicon, germanium, and tin, $R_2E(C{\equiv}COR')_2$, have not been reported until our studies began. At the same time these compounds are expected to provide a source of even more rich chemistry compared to the well-studied monoalkoxyethynyl derivatives capable of undergoing interesting chemical transformations (reactions with electrophilic and nucleophilic reagents, pyrolysis).

To obtain previously unknown bis(alkoxyethynyl)-substituted silanes and germanes, we employed the known procedures for the synthesis of the corresponding monoalkoxyethynyl derivatives. These were reactions of lithium alkoxyacetylides with the corresponding silicon and germanium dichlorides (Scheme 1) carried out under somewhat optimized conditions.

Lithium alkoxyacetylides necessary for the synthesis of bis(alkoxyethynyl)-substituted silanes **1a—d** and germanes **1e,f** were obtained *in situ* by reactions of butyllithium with alkoxyethynes at temperatures between –20 and –30 °C.

Scheme 1

$$Me(R)ECl_2 + 2\ LiC{\equiv}COR' \xrightarrow[-LiCl]{0\ °C}$$

$$\longrightarrow Me(R)E(C{\equiv}COR')_2$$

1a—f

	a	**b**	**c**	**d**	**e**	**f**
E	Si	Si	Si	Si	Ge	Ge
R	Me	Me	H	H	Me	Me
R´	Me	Et	Me	Et	Me	Et

To prevent side reactions (replacement of OR´ group by Bu group), the alkoxyethynes were taken in 15 to 20% excess with respect to butyllithium. Compounds **1a—f** were obtained in 45 to 75% yields.

Compounds **1a—f** were characterized by elemental analyses (Table 1), by ^1H and ^{13}C NMR spectroscopy data (Table 2), and by IR spectroscopy. The ^{13}C NMR spectra of bis(alkoxyethynyl)-substituted silanes and germanes exhibit resonances of the sp-hybridized α-C atoms at δ 32—36 and of the β-C atoms at δ 108—111, *i.e.*, in the region of the chemical shifts of the corresponding carbon atoms in trialkylsilyl(alkoxy)ethynes.[4] The IR spectra of compounds **1a—f** exhibit a strong ν(C≡C) absorption band in the region 2193—2187 cm^{-1}.

Unlike bis(alkoxyethynyl)-substituted silanes and germanes, bis(alkoxyethynyl)dimethylstannanes **1g,h** were

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Table 1. Characteristics of the compounds synthesized

Compound	Yield (%)	Boiling point/°C (*p*/Torr)	Found/Calculated (%)			Empirical formula
			C	H	Si, Ge	
1a	73	40—41	57.78	7.42	16.58	$C_8H_{12}O_2Si$
		(0.01)	57.10	7.19	16.59	
1b	65	50—51	60.31	8.13	14.20	$C_{10}H_{16}O_2Si$
		(0.01)	61.22	8.16	14.32	
1c	45	51—52	54.55	7.51	18.66	$C_7H_{10}O_2Si$
		(0.02)	54.46	6.90	18.21	
1d	61	56—57	59.28	7.93	16.21	$C_9H_{14}O_2Si$
		(0.02)	59.30	7.74	15.41	
1e	70	50—51	47.92	5.66	34.53	$C_8H_{12}O_2Ge$
		(0.01)	48.16	5.68	34.12	
1f	65	56	49.23	6.52	30.57	$C_{10}H_{16}O_2Ge$
		(0.01)	49.87	6.70	30.14	
3a	69	82	56.48	7.19	16.53	$C_8H_{12}O_2Si$
		(38)	56.43	7.10	16.50	
3b	53	81—82	53.32	6.40	18.19	$C_7H_{10}O_2Si$
		(25)	54.54	6.49	18.18	
3c	64	93—95	44.79	5.62	34.68	$C_8H_{12}O_2Ge$
		(10)	45.16	5.68	34.12	
4a	41	67	50.62	6.09	—	$C_6H_8O_2Si$
		(50)	51.39	5.75		
4b	21	62	46.98	4.65	—	$C_5H_6O_2Si$
		(51)	47.59	4.79		
5a	58	94	51.93	6.60	12.22	$C_{10}H_{22}N_2O_2Si$
		(0.02)	52.14	9.63	12.19	
5b	60	102	44.01	7.63	26.55	$C_{10}H_{22}N_2O_2Ge$
		(0.01)	44.18	7.04	26.70	

synthesized in the reactions of bis(diethylamino)dimethylstannanes and alkoxyethynes at 0 °C.[5] This is a conventional procedure for the synthesis of various ethynylstannanes.[6] Aminostannanes react smoothly with various ethynes to give high yields of products, namely, the target compound and the corresponding secondary amine, which can be removed with ease (Scheme 2).

Scheme 2

$$\mathrm{Me_2Sn(NEt_2)_2 + 2\ HC{\equiv}COR} \xrightarrow[-\mathrm{Et_2NH}]{0\ ^\circ\mathrm{C}}$$

$$\longrightarrow \mathrm{Me_2Sn(C{\equiv}COR)_2}$$

1g,h

R = Me (**g**), Et (**h**)

Reactions carried out at room temperature result in a mixture of products. Monitoring of the reaction mixture by following the ^{119}Sn NMR spectrum showed that the formation of compound **1g** (δ −131) is accompanied by the formation of the product of its thermolysis $(ROC{\equiv}CSnMe_2)_2C{=}C(OR)_2$ (**2a**, R = Me, δ −89, see below). Carrying out this reaction at 0 °C allows one to obtain pure compounds **1g,h** in high yields (70—80%) without distillation (for the spectral data, see Table 2). When stannanes **1g,h** are stored for 240 h at 0 °C, they partially decompose into compounds **2a,b** (R = Me and Et, respectively). However, compounds **1g,h** (their 50% solutions in hexane) can be stored at −30 °C without changes over a period of 2 to 3 months.

We carried out a detailed study on the pyrolysis of bis(ethoxyethynyl)-substituted silanes and germanes **1b,d,f**.

It is known that pyrolysis of mono(ethoxyethynyl)-substituted silanes and germanes is accompanied by ethylene evolution and results in good yields of the corresponding silyl- [7] and germylketenes[8,9] (Scheme 3).

Scheme 3

$$\mathrm{R_3EC{\equiv}COEt} \xrightarrow[-\mathrm{C_2H_4}]{\Delta} \mathrm{R_3ECH{=}C{=}O}$$

E = Si, Ge; R = Alk

Earlier,[10] we have shown that the most convenient way of pyrolyzing triorganosilyl(ethoxy)ethynes is to carry out the reaction in a solvent (*n*-octane); the products thus obtained (silylketenes) were obtained in high yields. In this work, we first pyrolyzed pure compounds **1b,d,f** *in vacuo* (10—38 Torr) at 120—130 °C. Pyrolysis was carried out in a distillation flask. The products with lower boiling points compared to compounds **1b,d,f** were distilled off. This resulted in pure ethoxyethynylsilyl(-germyl)ketenes **3a—c**, *i.e.*, the process affected only one ethoxyethynyl group (the residue in the flask was an undistillable resin) (Scheme 4).

Scheme 4

$$\mathrm{Me(R)E(C{\equiv}COEt)_2} \xrightarrow[-\mathrm{C_2H_4}]{i}$$

1b,d,f

$$\longrightarrow \mathrm{Me(R)E(C{\equiv}COEt)(CH{=}C{=}O)}$$

3a—c

i. 120—130 °C (10—38 Torr).

Compound	E	R	R′
1b, 3a	Si	Me	Et
1d, 3b	Si	H	Et
1f, 3c	Ge	Me	Et

The IR spectra of compounds **3a—c** exhibit two strong absorption bands, one near 2180 cm^{-1} (C≡C bond) and one at 2100 cm^{-1} (CH=C=O group). The ^{1}H NMR spectra exhibit not only signals of the ethoxyethynyl group

Table 2. IR spectra and ^1H and ^{13}C NMR spectra of compounds $RMeE(C{\equiv}COR')_2$ (**1a—h**), $RMeE(C{\equiv}COR')(CH{=}C{=}O)$ (**3a—c**), $RMeSi(CH{=}C{=}O)_2$ (**4a,c**), and $Me_2E(CH_2CONMe_2)_2$ (**5a,b**)

Compound	RE, R′	IR spectrum, ν/cm^{-1}	NMR spectra (δ, *J*/Hz)	
			^1H	^{13}C, $\{^{29}Si\}$, $[^{119}Sn]$
1a	CH_3Si, CH_3	2192	0.45 (s, 6 H, $(C\underline{H}_3)_2Si$); 3.11 (s, 6 H, $OC\underline{H}_3$)	1.8 ($\underline{C}H_3Si$); 34.6 ($Si\underline{C}{\equiv}C$); 64.7 ($O\underline{C}H_3$); 110.8 ($SiC{\equiv}\underline{C}$); {38.7}
1b	CH_3Si, C_2H_5	2187	0.46 (s, 6 H, $(C\underline{H}_3)_2Si$); 0.83 (t, 6 H, $OCH_2C\underline{H}_3$); 3.55 (q, 4 H, $OC\underline{H}_2CH_3$)	2.8 ($\underline{C}H_3Si$); 14.4 ($OCH_2\underline{C}H_3$); 36.6 ($Si\underline{C}{\equiv}C$); 75.1 ($O\underline{C}H_2CH_3$); 110.3 ($SiC{\equiv}\underline{C}$)
1c	HSi, CH_3	2190	0.36 (d, 3 H, $C\underline{H}_3Si$, *J* = 3.6); 3.22 (s, 6 H, $OC\underline{H}_3$); 4.75 (q, 1 H, $Si\underline{H}$, *J* = 3.6)	−0.7 ($\underline{C}H_3Si$); 32.2 ($Si\underline{C}{\equiv}C$); 65.4 ($O\underline{C}H_3$); 111.9 ($SiC{\equiv}\underline{C}$)
1d	HSi, C_2H_5	2190	0.38 (d, 3 H, $C\underline{H}_3Si$, *J* = 3.6); 0.84 (t, 6 H, $OCH_2C\underline{H}_3$, *J* = 7.2); 3.56 (q, 4 H, $OC\underline{H}_2CH_3$, *J* = 7.2); 4.85 (q, 1 H, $Si\underline{H}$, *J* = 3.6)	0.1 ($\underline{C}H_3Si$); 14.4 ($OCH_2\underline{C}H_3$); 33.8 ($Si\underline{C}{\equiv}C$); 75.4 ($O\underline{C}H_2CH_3$); 111.0 ($SiC{\equiv}\underline{C}$)
1e	CH_3Ge, CH_3	2193	0.52 (s, 6 H, $(C\underline{H}_3)_2Ge$); 3.18 (s, 6 H, $OC\underline{H}_3$)	2.4 ($\underline{C}H_3Ge$); 34.6 ($Ge\underline{C}{\equiv}C$); 65.5 ($O\underline{C}H_3$); 110.5 ($GeC{\equiv}\underline{C}$)
1f	CH_3Ge, C_2H_5	2189	0.56 (s, 6 H, $(C\underline{H}_3)_2Ge$); 0.82 (t, 6 H, $OCH_2C\underline{H}_3$); 3.56 (q, 4 H, $OC\underline{H}_2CH_3$)	1.8 ($\underline{C}H_3Ge$); 13.6 ($OCH_2\underline{C}H_3$); 33.8 ($Ge\underline{C}{\equiv}C$); 74.0 ($O\underline{C}H_2CH_3$); 108.4 ($GeC{\equiv}\underline{C}$)
1g [5]	CH_3Sn, CH_3	2167	0.26 (s, 6 H, $(C\underline{H}_3)_2Sn$); 3.18 (s, 6 H, $OC\underline{H}_3$)	−5.4 ($\underline{C}H_3Sn$); 32.1 ($Sn\underline{C}{\equiv}C$); 65.0 ($O\underline{C}H_3$); 113.6 ($SnC{\equiv}\underline{C}$); [−130.9]
1h [5]	CH_3Sn, C_2H_5	2158	0.34 (s, 6 H, $(C\underline{H}_3)_2Sn$); 0.86 (t, 6 H, $OCH_2C\underline{H}_3$); 3.66 (q, 4 H, $OC\underline{H}_2CH_3$)	−5.8 ($\underline{C}H_3Sn$); 14.9 ($OCH_2\underline{C}H_3$); 33.2 ($Sn\underline{C}{\equiv}C$); 74.4 ($O\underline{C}H_2CH_3$); 112.6 ($SnC{\equiv}\underline{C}$); [−130.9]
3a	CH_3Si	2181, 2113	0.27 (s, 6 H, $(C\underline{H}_3)_2Si$); 1.47 (t, 3 H, $OCH_2C\underline{H}_3$); 1.88 (s, 1 H, $C\underline{H}{=}C{=}O$); 4.13 (q, 2 H, $OC\underline{H}_2CH_3$)	0.7 ($Si{-}\underline{C}H{=}C{=}O$); 1.61 ($\underline{C}H_3Si$); 14.2 ($OCH_2\underline{C}H_3$); 34.9 ($Si\underline{C}{\equiv}C$); 75.3 ($O\underline{C}H_2CH_3$); 110.5 ($SiC{\equiv}\underline{C}$); 179.5 ($Si{-}CH{=}\underline{C}{=}O$)
3b	HSi	2180, 2100	0.20 (d, 3 H, $C\underline{H}_3Si$, *J* = 3.6); 0.81 (t, 3 H, $OCH_2C\underline{H}_3$, *J* = 3.6); 1.57 (d, 1 H, $C\underline{H}{=}C{=}O$, *J* = 7.2); 3.52 (q, 2 H, $OC\underline{H}_2CH_3$, *J* = 7.2); 4.73 (m, 1 H, $Si\underline{H}$, *J* = 7.2)	−1.2 ($Si{-}\underline{C}H{=}C{=}O$); −0.5 ($\underline{C}H_3Si$); 14.2 ($OCH_2\underline{C}H_3$); 33.0 ($Si\underline{C}{\equiv}C$); 112.3 ($SiC{\equiv}\underline{C}$); 75.7 ($O\underline{C}H_2CH_3$); 179.8 ($Si{-}CH{=}\underline{C}{=}O$)
3c	CH_3Ge	2181, 2115	0.49 (s, 6 H, $(C\underline{H}_3)_2Ge$); 1.46 (t, 3 H, $OCH_2C\underline{H}_3$); 1.91 (s, 1 H, $C\underline{H}{=}C{=}O$); 4.11 (q, 2 H, $OC\underline{H}_2CH_3$)	0.5 ($Ge{-}\underline{C}H{=}C{=}O$); 1.9 ($\underline{C}H_3Ge$); 14.2 ($OCH_2\underline{C}H_3$); 34.4 ($Ge\underline{C}{\equiv}C$); 75.0 ($O\underline{C}H_2CH_3$); 109.6 ($GeC{\equiv}\underline{C}$); 179.1 ($Ge{-}CH{=}\underline{C}{=}O$)
4a	CH_3Si	2108	0.47 (s, 6 H, $(C\underline{H}_3)_2Si$); 1.95 (s, 2 H, $C\underline{H}{=}C{=}O$)	0.9 ($Si{-}\underline{C}H{=}C{=}O$); 1.2 ($\underline{C}H_3Si$); 179.0 ($Si{-}CH{=}\underline{C}{=}O$)
4c	HSi	2108	0.05 (d, 3 H, $C\underline{H}_3Si$, $^3J_{Si-H-CH_3}$ = 3.44); 1.46 (d, 2 H, $C\underline{H}{=}C{=}O$, $^3J_{Si-H-CH=}$ = 2.95); 4.57 (m, 2 H, $Si\underline{H}$, $^3J_{Si-H-CH_3}$ = 3.44)	−2.1 ($\underline{C}H_3Si$); −1.8 ($Si{-}\underline{C}H{=}C{=}O$); 175.5 ($Si{-}CH{=}\underline{C}{=}O$)
5a	CH_3Si	1655	0.13 (s, 6 H, $Si(C\underline{H}_3)_2$); 2.00 (s, 4 H, $C\underline{H}_2CO$); 2.89 (d, 12 H, $CON(C\underline{H}_3)_2$)	−2.1 ($\underline{C}H_3Si$); 23.0 ($\underline{C}H_2CO$); 35.0, 38.5 ($N(\underline{C}H_3)_2$); 172.0 ($\underline{C}H_2CO$);
5b	CH_3Ge	1629	0.26 (s, 6 H, $Ge(C\underline{H}_3)_2$); 2.12 (s, 4 H, $C\underline{H}_2CO$); 2.94 (d, 12 H, $CON(C\underline{H}_3)_2$)	−2.2 ($\underline{C}H_3Ge$); 23.5 ($\underline{C}H_2CO$); 35.4, 38.6 ($N(\underline{C}H_3)_2$); 172.8 ($\underline{C}H_2CO$)

but also the $CH{=}C{=}O$ proton resonances in the region δ 1.5—1.9. The ^{13}C NMR spectra exhibit signals of the Si(Ge)—CH= carbons in the region δ 0.5—1.0 and a low-field signal of the carbonyl carbon atom in the region δ 179—180, which is in good agreement with the corresponding signals of structurally similar monosilyl- and monogermylketenes.[10] The constants, yields, and elemental analyses data for compounds **3a—c** are listed in Table 1. The IR and NMR spectral data are given in Table 2.

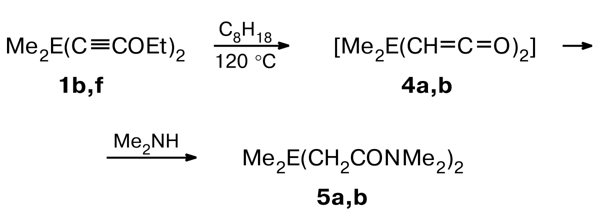
Thus, pyrolysis of pure compounds **1b,d,f** *in vacuo* gave good yields (53—69%) of products of partial pyrolysis.

Then, we studied pyrolysis of bis(ethoxyethynyl)-substituted silanes **1b,d** and germane **1f** in various solvents. The processes were monitored by IR spectroscopy by following a decrease in the intensity and then disappearance of the ν(C≡C) absorption band at 2190 cm^{-1} and the appearance of an absorption band of ketene group at 2100 cm^{-1} in the IR spectra of the reaction mixtures. The results obtained were different depending on the temperature (this is determined by the solvent), concentrations of the acetylenes **1b,d,f**, and the nature of the atom E.

In particular, pyrolysis of compounds **1b,d,f** dissolved in *n*-hexane over a period of 3 h at the temperature equal to the boiling point of the solvent proceeds very slowly (monitored by IR spectroscopy). When **1b** is heated in *n*-octane (a 10% solution) for 1 h, pyrolysis proceeds to completion yielding (dimethylsilylene)bisketene **4a** (monitored by IR spectroscopy). However, we failed to isolate the pure product of pyrolysis by fractionation of the reaction mixture because of the close boiling points of the solvent (*n*-octane) and product **4a**. To confirm the formation of compound **4a**, an excess of dimethylamine was added to the reaction mixture. This allowed isolation of an adduct of dimethylamine with **4a**, dimethylsilylbis(*N,N*-dimethyl)acetamide (**5a**), in 58% yield.

Pyrolysis of germane **1f** in *n*-octane proceeded analogously. However, the formation of (dimethylgermylene)bisketene was detected only when a dilute (3%) solution of compound **1f** was pyrolyzed over a period of 45 min. Similarly to the preceding case, attempts at isolating the product, pure (dimethylgermylene)bisketene, failed (probably, due to instability of this compound). The formation of bisketene **4b** was also confirmed by its reaction with dimethylamine in solution, which results in dimethylgermyl-*bis*(*N,N*-dimethyl)acetamide (**5b**) in 60% yield (Scheme 5).

Scheme 5



$$\underset{\textbf{1b,f}}{Me_2E(C{\equiv}COEt)_2} \xrightarrow[120\ ^\circ C]{C_8H_{18}} \underset{\textbf{4a,b}}{[Me_2E(CH{=}C{=}O)_2]} \longrightarrow \xrightarrow{Me_2NH} \underset{\textbf{5a,b}}{Me_2E(CH_2CONMe_2)_2}$$

1b, 4a, 5a: E = Si; **1f, 4b, 5b:** E = Ge

Compounds **5a,b** were characterized by elemental analyses and by NMR and IR spectroscopy (see Tables 1 and 2).

When silanes **1b,d** were heated in 1,2,3,4-tetrahydronaphthalene (solvent with a higher boiling point) at 120—130 °C, pyrolysis was completed after 60—80 min and pure bisketenes MeRSi(CH=C=O)$_2$ (R = Me (**4a**), H (**4c**)) were isolated by vacuum distillation. The low yields (21—41%) can be explained by relatively low stability of these compounds.

Monitoring the course of pyrolysis of germane **1f** under identical conditions by IR spectroscopy revealed disappearance of the ν(C≡C) band and the appearance of a weak band in the region 2100 cm^{-1} in the IR spectra of the reaction mixture after 1 h. However, product **4b** was not isolated by vacuum distillation due to its instability.

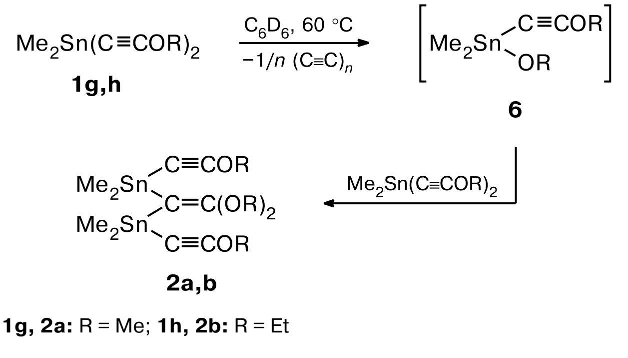
Thus, a complete pyrolysis of compounds **1b,d,f** proceeds only at temperatures at least 120 °C in inert solvents at low concentrations of the starting ethynes (3—10%). The process proceeds stepwise, first affecting one and then the other ethoxyethynyl group (pyrolysis of ketene **3a** in 1,2,3,4-tetrahydronaphthalene also resulted in bisketene **4a**). Compounds **4a—c** are unstable and, probably, can enter in various subsequent reactions, *e.g.*, cycloaddition to the ethoxyethynyl group of compounds **1b,d,f** or **3a—c** in the course of pyrolysis to give polymeric products. No dimerization of bisketenes **4a,c** was observed, which is similar to the behavior of trialkylsilylketenes.[7]

Earlier,[5] we have shown that pyrolysis of structurally similar bis(ethynyl)stannanes **1g,h** follows quite a different route compared to silanes **1b,d** and germane **1f**.

To study the thermal decomposition of bis(ethynyl)stannane **1h**, a solution of this compound in benzene-d$_6$ was heated at 60—70 °C. Monitoring by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy revealed disappearance of the resonance signals of the starting **1h** and the appearance of new resonances assigned to 1,1-bis(ethoxy)-2,2´-bis[(ethoxyethynyl)dimethylstannyl]ethene (**2b**) after heating for 5 h. In this case, the IR and NMR spectra revealed no indications of stannylketene formation. Pyrolysis of stannane **1g** followed an identical pattern and resulted in 1,1-bis(methoxy)-2,2´-bis[(methoxyethynyl)dimethylstannyl]ethene (**2a**).

The formation of compounds **2a,b** can be rationalized as follows: heating of stannanes **1g,h** results in alkoxy(alkoxyethynyl)dimethylstannane **6** as an intermediate, which reacts with the starting compounds **1g,h** to give products **2a,b**, respectively (Scheme 6).

Scheme 6



1g, 2a: R = Me; **1h, 2b:** R = Et

Table 3. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra and spin-spin coupling constants $J_{^{119}\mathrm{Sn},^{13}\mathrm{C}}$, $J_{^{119}\mathrm{Sn},^{1}\mathrm{H}}$, $^2J_{^{119}\mathrm{Sn},^{117}\mathrm{Sn}}$ for compounds **2a,b** [5]

Compound	NMR spectra (δ, *J*/Hz)		
	^{1}H ($J_{^{119}\mathrm{Sn},^{1}\mathrm{H}}$)	^{13}C ($J_{^{119}\mathrm{Sn},^{13}\mathrm{C}}$)	^{119}Sn ($^2J_{^{119}\mathrm{Sn},^{117}\mathrm{Sn}}$)
2a	0.48 (s, 12 H, $\mathrm{(CH_3)Sn}$); 3.20 (s, 6 H, $\mathrm{=C(OCH_3)_2}$); 3.35 (s, 6 H, $\mathrm{\equiv COCH_3}$)	−6.0 ($\mathrm{CH_3Sn}$, *J* = 433.5, *J* = 6.8); 34.8 ($\mathrm{Sn\underline{C}{\equiv}C}$, *J* = 535.2); 56.7 ($\mathrm{=C(O\underline{C}H_3)_2}$); 65.0 ($\mathrm{\equiv CO\underline{C}H_3}$); 81.3 ($\mathrm{\underline{C}{=}C(OCH_3)_2}$, *J* = 432.3); 113.7 ($\mathrm{SnC{\equiv}\underline{C}}$, *J* = 126.2); 166.2 ($\mathrm{C{=}\underline{C}(OCH_3)_2}$, *J* = 2.1)	−89.6 (*J* = 348.0)
2b	0.56 (s, 12 H, $\mathrm{(CH_3)Sn}$, *J* = 62.0); 0.94 (t, 6 H, $\mathrm{=C(OCH_2C\underline{H}_3)_2}$); 1.05 (t, 6 H, $\mathrm{\equiv COCH_2C\underline{H}_3}$); 3.63 (q, 4 H, $\mathrm{=C(OC\underline{H}_2CH_3)_2}$); 3.71 (q, 4 H, $\mathrm{\equiv COC\underline{H}_2CH_3}$)	−5.0 ($\mathrm{CH_3Sn}$, *J* = 430.7, *J* = 7.3); 14.2 ($\mathrm{\equiv COCH_2\underline{C}H_3}$); 14.8 ($\mathrm{=C(OCH_2\underline{C}H_3)_2}$); 36.0 ($\mathrm{Sn\underline{C}{\equiv}C}$, *J* = 537.7); 65.4 ($\mathrm{=C(OC\underline{H}_2CH_3)_2}$); 74.1 ($\mathrm{\equiv CO\underline{C}H_2CH_3}$, *J* = 6.5); 82.6 ($\mathrm{\underline{C}{=}C(OC_2H_5)_2}$, *J* = 437.0); 112.4 ($\mathrm{SnC{=}\underline{C}}$, *J* = 126.8); 164.9 ($\mathrm{C{=}\underline{C}(OC_2H_5)_2}$, *J* = <2]	−89.0 (*J* = 349.0)

The chemical shift patterns in the ^{13}C NMR spectra of compounds **2a,b** are typical of carbon atoms in the C=COR and $\mathrm{C{=}C(OR)_2}$ fragments. The spin-spin coupling constants $J_{^{119}\mathrm{Sn},^{117}\mathrm{Sn}}$ indicate the presence of two tin atoms in the molecules. The $J_{^{119}\mathrm{Sn},^{13}\mathrm{C}}$ constants were obtained from both the ^{13}C and ^{119}Sn NMR spectra. The chemical shifts in the ^{119}Sn NMR spectra of compounds **2a,b** coincide with those for acyclic dimethyltin derivatives containing bis-alkenyl and bis-alkynyl groups.[10] The spin-spin coupling constants $^2J_{\mathrm{Sn,Sn}}$ (**2a:** 348.0 Hz, **2b:** 349.0 Hz) are smaller than for 1,1-bis(trimethylstannyl)alkenes[11] due to the influence of two alkoxyl substituents at the C=C bond. The $^2J_{\mathrm{Sn,Sn}}$ constants for **2a,b** are positive, similarly to 1,1-bis(trimethylstannyl)alkenes.[12] The ^{1}H, ^{13}C, and ^{119}Sn NMR spectral parameters are listed in Table 3.

Thus, bis(alkoxyethynyl)dimethylstannanes are less stable than their silicon- and germanium-containing analogs. Pyrolysis of compounds **1b,d,f** yields silyl- and germylketenes, affecting one or both alkoxyethynyl groups depending on the experimental conditions. Thermal decomposition of the less stable compounds **1g,h** leads to quite different products **2a,b**.

Experimental

IR spectra were recorded on Perkin—Elmer 983G and IKS-22 spectrometers (a cell with *d* = 0.1 mm, $\mathrm{CaF_2}$ plates). ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on Bruker AC-200P (200 MHz), Bruker ARX 250 (250 MHz), Bruker DRX 500 (500 MHz), and Varian VXR-400 (400 MHz) spectrometers using $\mathrm{CDCl_3}$ and $\mathrm{C_6D_6}$ as the solvents. All manipulations were carried out in a dry argon atmosphere. The starting dimethyldichlorogermane, dimethyldichlorostannane, and ethoxyethyne were purchased from Aldrich. Methoxyacetylene was synthesized following the known procedure.[13]

Dimethylbis(methoxyethynyl)silane (1a). To methoxyethyne (4.25 g, 76 mmol) in hexane (100 mL), 1.6 *N* solution of butyllithium in hexane (36 mL, 57 mmol) was added at −25 °C. The mixture was stirred for 40 min at −25 °C and then for an additional 1 h at ~20 °C. A solution of dimethyldichlorosilane (3.6 g, 27 mmol) in hexane (30 mL) was added at 0 °C and the resulting mixture was stirred for 4 h at ~20 °C and filtered. All low-boiling compounds were distilled off at a reduced pressure (water pump). Fractionation of the residue *in vacuo* gave silane **1a** (3.3 g, 73%), b.p. 40—41 °C (0.02 Torr).

Compounds **1b—f** were synthesized analogously.

Dimethylbis(methoxyethynyl)stannane (1g). To a solution of dimethylbis(diethylamino)tin (0.7 g, 2.4 mmol)) in anhydrous ether (3 mL), a 50% solution of methoxyethyne (0.75 g) in hexane (6.6 mmol) was added at 0 °C and the mixture was stirred for 8 h at 0 °C. All low-boiling compounds were removed *in vacuo*, leaving compound **1g** (0.4 g, 70%).*

Compound **1h*** was synthesized analogously in 77% yield.

Dimethyl(ethoxyethynyl)silylketene (3a). Pyrolysis of silane **1b** (8.6 g, 0.043 mol) in a vacuum distillation apparatus at 120—130 °C and a residual pressure of 38 Torr gave a volatile product identified as ketene **3a** (5.1 g, 69%), b.p. 82 °C (38 Torr).

Ketenes **3b** and **3c** were obtained analogously.

Dimethylsilylenebisketene (4a). *A*. Heating of ketene **3a** (7.7 g, 0.046 mol) dissolved in 1,2,3,4-tetrahydronaphthalene (28 mL) in a vacuum distillation apparatus at 120—130 °C and a residual pressure of 50 Torr gave a volatile product identified as bisketene **4a** (colorless liquid), b.p. 65—67 °C (50 Torr). The yield was 3 g (47%).

B. Silane **1b** (4 g, 20 mmol) was heated in 1,2,3,4-tetrahydronaphthalene (12 mL) at 120—130 °C. The course of the reaction was monitored by IR spectroscopy by following a decrease in the intensity and then disappearance of the absorption band at 2178 cm^{-1} and the appearance of an absorption band at 2108 cm^{-1}. Distillation of the reaction mixture gave bisketene **4a** (1 g, 41%), b.p. 67 °C (50 Torr).

Methylsilylenebisketene (**4c**) was obtained analogously.

Reaction of bisketene 4a with dimethylamine. Silane **1b** (1 g, 5 mmol) dissolved in *n*-octane (15 mL) was heated for 1.5 h (until disappearance of the absorption band at 2178 cm^{-1} and appearance of an absorption band at 2100 cm^{-1}). Then, dimethylamine (1.3 g, 29 mmol) was added at 0 °C and the resulting mixture was stirred for 1.5 h. Fractionation *in vacuo* gave dimethylsilylene-bis(*N,N*-dimethyl)acetamide **5a** (0.7 g, 60%), b.p. 94 °C (0.02 Torr).

Pyrolysis of 1b in *n*-hexane. Silane **1b** (0.2 g) dissolved in *n*-hexane (10 mL) was heated for 3 h. No ν(C=C=O) band was detected in the IR spectrum of the reaction mixture.

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* Low stability of compounds **1g,h** precluded obtaining reasonable elemental analyses data (*cf.* Ref. 5).

Pyrolysis of germane 1f. Germane **1f** (1 g, 4 mmol) dissolved in *n*-octane (35 mL) was heated for 1.5 h (until disappearance of the absorption band at 2189 cm^{-1}). Then, dimethylamine (1.2 g, 27 mmol) was added at 0 °C and the resulting mixture was stirred for 1.5 h. Vacuum distillation gave dimethylgermylene-*bis*(*N,N*-dimethyl)acetamide **5b** (0.63 g, 58%), b.p. 102 °C (0.01 Torr).

Pyrolysis of stannane 1g. A solution of **1g** (150 mg) in deuterobenzene (3 mL) was heated in an NMR tube for 5 h at 60—70 °C until disappearance of the absorption band at 2167 cm^{-1}. The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra revealed formation of compound **2a** (see Table 3).

Pyrolysis of stannane **1h** proceeds analogously.

The constants and spectral data for the compounds obtained are listed in Tables 1—3.

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