Organometallic Chemistry

Silylation and germylation of trialkylsilyl(germyl)ethoxyacetylenes containing bulky substituents at the silicon or germanium atom

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Silylation and germylation of trialkylsilyl(germyl)ethoxyacetylenes containing bulky substituents at the silicon or germanium atom were performed. In all cases, the corresponding bis-organoelement-containing ketenes were obtained as the only reaction products. No intermediate isomeric ynol ethers were detected by spectroscopy.

Key words: silylation, germylation, trialkylsilyl(germyl)ethoxyacetylenes, iodotrimethylsilane, bromotrimethylgermane, bis-silicon(germanium)-containing ketenes, ynol ethers.

Si, Ge, Sn-Substituted ketenes belong to a new interesting class of compounds widely used in the synthesis of organic and heteroelement-containing organic compounds.[1] Previously, bis-heteroelement-substituted ketenes have been synthesized by the reactions of heteroelement-containing ynol ethers with trialkylheteroelement-containing halides.[2,3] A possible mechanism of formation of bis-heteroelement-substituted ketenes[3] assumes the formation of the corresponding ynol ethers as intermediates, which are rapidly isomerized into bis-heteroelement-substituted ketenes as the final reaction products. With the aim of elucidating the effects of the nature of the heteroelement and the steric factors on the formation of bis-heteroelement-substituted ketenes or ynol ethers, in the present work we studied the reactions of trialkylsilyl(germyl) halides with organosilyl- and organogermyl-substituted ynol ethers containing bulky substituents at the silicon or germanium atom. The latter belong to a new poorly studied class of reactive organosilicon compounds used in organic and organometallic chemistry.[4—6]

The starting silyl- and germyl(ethoxy)acetylenes (**1**) containing bulky substituents at the silicon or germanium atom were synthesized by the reactions of trialkylsilyl(germyl) halides with ethoxyethynyllithium or ethoxyethynylmagnesium bromide (Scheme 1).

Heteroelement-substituted ethoxyacetylenes containing bulky substituents are rather labile compounds and undergo partial pyrolysis upon heating above 120 °C. Therefore, compounds **1b,d,e** were analyzed and used in subsequent syntheses without fractionation. Acetylenes **1a—f** were obtained in 60—90% yields and were characterized by the data from elemental analysis and the ^{1}H and ^{13}C NMR and IR spectra (Tables 1—3). Acetylene **1d** was synthesized according to another procedure;[9] however, its spectral characteristics were lacking.

Analysis of the ^{13}C NMR spectra of silylethoxyacetylenes **1a—d,g** (see Table 3) demonstrated that the

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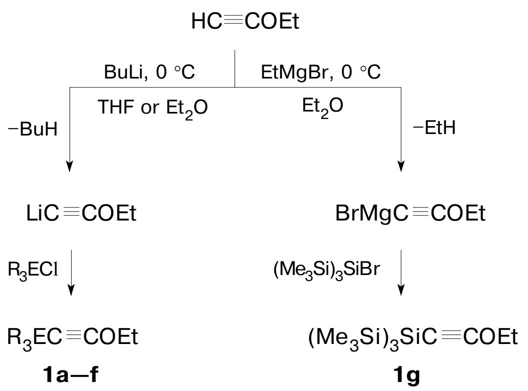
Scheme 1

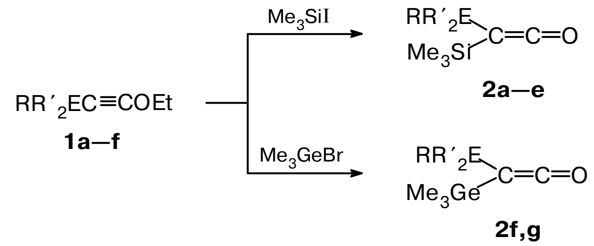


R_3E = Me_2Bu^tSi (**a**), Bu^tPh_2Si (**b**), $Pr^i{}_3Si$ (**c**), $MePh_2Si$ (**d**), Ph_3Si (**e**), $Pr^i{}_3Ge$ (**f**)

introduction of the silicon atom into the acetylene molecule leads to downfield shifts of the resonance signals for the C atoms of the Si—C(sp) and C(sp)—O groups by 6—7 and 18—20 ppm, respectively, compared to those observed in the NMR spectrum of ethoxyacetylene. In the case of the isopropyl derivatives $Pr^i{}_3Si(Ge)C{\equiv}COEt$, an insignificant upfield shift (Δδ 0.5 ppm) of the C atom of the Ge—C(sp) group and a downfield shift (Δδ 0.8 ppm) of the C atom of the C(sp)—O group in the germylated analog are observed.

Trialkylsilyl(germyl)ethoxyacetylenes were silylated or germylated with iodotrimethylsilane or bromotrimethylgermane, respectively, in an atmosphere of argon with dichloromethane or acetonitrile as the solvents (Scheme 2).

Scheme 2



RR'_2E = Bu^tMe_2Si (**a**, **g**); Bu^tPh_2Si (**b**); $Pr^i{}_3Si$ (**c**); $MePh_2Si$ (**d**); Ph_3Si (**e**); $Pr^i{}_3Ge$ (**f**)

The course of the reactions was monitored by IR spectroscopy by following a decrease in the intensity and then complete disappearance of the ν(C≡C) absorption band of the starting alkoxyacetylene in the region of 2175—2190 cm^{-1} and the appearance of an absorp-

Table 1. Characteristics of the compounds synthesized

Compound	Yield (%)	B.p./°C (*p*/Torr)	n_D^{20}	Found/Calculated (%) C	H	Si(Ge)	Molecular formula
1a[a]	74	30—31 (1)	1.4449	—	—	—	—
1b	93	—[b]		—	—	—	—
1c[c]	81	62—63 (0.02)	1.4620	—	—	—	—
1d	80	—[b]	—	—	—	—	—
1e	58	—[b]	—	—	—	8.24 8.55	$C_{17}H_{18}OSi$
1f	85	59—60 (0.02)	1.4685	57.19 57.61	9.77 9.69	26.73 26.79	$C_{13}H_{26}GeO$
1g	65	89—90 (0.02)	1.4994	49.82 49.29	10.17 10.18	34.81 35.47	$C_{13}H_{32}OSi_4$
2a	82	52—54 (0.02)	1.4570	—	—	—	—
2b	47	139—143 (0.02)	1.4445	71.50 71.53	7.93 8.00	—	$C_{21}H_{28}OSi_2$
2c	37	69—70 (0.04)	—	61.90 62.15	11.40 11.18	—	$C_{14}H_{30}OSi_2$
2d	7	123—125 (0.01)	1.4570	69.93 69.62	7.14 7.14	—	$C_{18}H_{22}OSi_2$
2e	26	200—205 (0.01)	—	74.44 74.14	6.75 6.49	14.87 15.08	$C_{23}H_{24}OSi_2$
2f	45	53—57 (0.01)	1.4692	48.01 48.46	8.50 8.80	—	$C_{11}H_{24}GeOSi$
2g	54	69—70 (0.01)	1.4950	46.83 46.75	8.53 8.42	40.20 40.38	$C_{14}H_{30}Ge_2O$

[a] Lit. data[7]: b.p. 66—69 °C (12 Torr).

[b] The compounds were isolated and characterized without distillation.

[c] Lit. data[8]: b.p. 68—73 °C (1 Torr), n_D^{20} 1.4626.

Table 2. ^{1}H NMR and IR spectral data for the compounds $RR'_2EC{\equiv}COEt$ (**1a—g**) and $RR'_2E(Me_3E')C{=}C{=}O$ (**2a—g**)

Compound	RR'_2E	Me_3E'	IR, ν/cm^{-1}	^{1}H NMR (δ, J/Hz)				
				R	R′	$OCH_2C\underline{H}_3$ (t, 3 H)	$OC\underline{H}_2Me$ (q, 2 H)	Me_3E' (s, 9 H)
1a	Bu^tMe_2Si		2190	0.90 (s, 9 H)	0.10 (s, 6 H)	1.40	4.10	
1b	Bu^tPh_2Si		2190	1.14 (s, 9 H)	7.35—7.95 (m, 10 H)	1.63	4.32	
1c	Pr^i_3Si		2185	1.02 (m, 3 H); 1.05 (d, 18 H, J = 5.2)		1.39	4.12	
1d	$MePh_2Si$		2175	0.65 (s, 3 H)	7.33—7.76 (m, 10 H)	1.33	4.12 (J = 7)	
1e	Ph_3Si		2185	7.20—7.70 (m, 15 H)		1.46	4.27	
1f	Pr^i_3Ge		2184	1.22 (m, 3 H); 1.06 (d, 18 H, J = 7.2)			1.30	4.01
1g	$(Me_3Si)_3Si$		2177	0.14 (s, 27 H)		1.30	3.98	
2a	Bu^tMe_2Si	Me_3Si	2085	0.98 (s, 9 H)	0.15 (s, 6 H)			0.22
2b	Bu^tPh_2Si	Me_3Si	2090	1.29 (s, 9 H)	7.30—7.90 (m, 10 H)			0.01
2c	Pr^i_3Si	Me_3Si	2060	1.00 (d, 18 H, J = 3.6)	1.24 (m, 3 H)			0.24
2d	$MePh_2Si$	Me_3Si	2080	0.85 (s, 3 H)	7.40—7.70 (m, 10 H)			0.18
2e	Ph_3Si	Me_3Si	2085	7.30—7.80 (m, 10 H)				1.09
2f	Pr^i_3Ge	Me_3Ge	2060	1.44 (m, 3 H); 1.18 (d, 18 H, J = 7.2)				0.39
2g	Bu^tMe_2Si	Me_3Ge	2070	0.86 (s, 9 H)	0.03 (s, 6 H)			0.32

Table 3. ^{13}C NMR spectral data (δ) for the compounds $RR'_2EC{\equiv}COEt$ (**1a—g**) and $RR'_2E(Me_3E')C{=}C{=}O$ (**2a—g**)

Compound	RR'_2E	E′	R	R′	EC(sp)	C(sp)—O	$OCH_2\underline{C}H_3$	$O\underline{C}H_2Me$	Me_3E'	C(sp^2)	C=O
1a	Bu^tMe_2Si		26.1, 16.6	−4.0	34.8	109.7	14.2	74.8			
1b	Bu^tPh_2Si		27.1, 18.6	127.5, 129.1, 134.6, 135.6	32.5	112.5	14.4	75.2			
1c	Pr^i_3Si		18.6, 11.6		32.4	110.7	14.1	74.7			
1d	$MePh_2Si$		−1.3	127.7, 129.2, 134.3, 135.6	33.7	112.0	14.2	75.2			
1f	Pr^i_3Ge		19.8, 14.8		32.9	110.4	14.1	74.4			
1g	$(Me_3Si)_3Si$		0.3		28.2	110.4	14.1	74.5			
2a	Bu^tMe_2Si	Si	26.3, 18.9	−3.3					1.7	−2.0	166.8
2b	Bu^tPh_2Si	Si	27.6, 20.2	127.8, 129.6, 134.1, 136.2					1.0	−1.0	166.7
2c	Pr^i_3Si	Si	18.6, 13.2						1.9	−4.3	166.6
2d	$MePh_2Si$	Si	−1.0	127.9, 129.4, 134.6, 136.1					1.2	−0.1	166.5
2e	Ph_3Si	Si	127.9, 129.9, 134.2, 135.7						1.1		166.2
2f	Pr^i_3Ge	Ge	19.8, 16.7						1.8	−6.3	165.9
2g	Bu^tMe_2Si	Ge	26.3, 18.7	−3.3					1.6	−5.0	166.2

tion band in the region of 2060—2090 cm^{-1} (ν(C=C=O) in disubstituted ketenes). In addition, the ^{13}C NMR spectra of the reaction mixture were recorded in the course of the reaction and after its completion. The appearance of the C=O resonance signal of ketene at δ 166—167 and the disappearance of a signal at δ 110—112 corresponding to the ≡C—O group of the initial acetylene were observed. For example, the spectrum of the mixture obtained in the reaction **1b** + Me_3SiI (40 °C, 10 h) recorded after removal of the solvent and unconsumed iodotrimethylsilane had signals only of the initial acetylene **1b** and ketene **2b** (δ): 112.5 (C(sp)—O); 75.2, 14.4 (OCH_2Me); 32.5 (SiC(sp)); 27.1, 18.6 (Me_3C); 135.0—129.0 (Ph) for acetylene **1b**; and 166.7 (C=O); 27.6, 20.1 (Me_3C); 1.0 (Me_3Si); −3.9 ($\underline{C}$=C=O) for ketene **2b**.

The IR spectrum of this reaction mixture had two absorption bands corresponding to the stretching vibrations of the C≡C bond (2190 cm^{-1}) of the initial acetylene and to the ketene group (2090 cm^{-1}) of bis-silylketene.

It should be noted that the reactions giving rise to ketenes **2e,c** did not proceed to completion (according to the data from IR spectroscopy of the reaction mixture), which accounts for the low yields of these compounds. The reaction of acetylene **1g** with iodotrimethylsilane proceeded very slowly to yield a mixture of unidentified products. The rate of the reaction depends on the

Table 4. Conditions of the synthesis of bis-organosilyl- and bis-organogermyl-substituted ketenes

Compound	*t* /h	*T* /°C	Solvent
2a	8	20	CH_2Cl_2
2b	30	40	CH_2Cl_2
2c	36	20	MeCN
2d	25	40	CH_2Cl_2
2e	50	40	CH_2Cl_2
2f	150	20	CH_2Cl_2
2g	20	40	MeCN

character of the substituents at the silicon or germanium atom (E) and the nature of the heteroelement (Table 4).

We isolated only bis-organosilyl- and bis-organogermyl-containing ketenes **2** in the reactions studied and even no transient formation of isomeric silyloxy(germyloxy)trialkylsilyl(germyl)acetylenes was observed.

However, the formation of ynol ethers (SiC≡COSi) cannot be excluded based on the results obtained because under the reaction conditions (electrophilic catalysis) the latter could be rapidly isomerized to the corresponding ketenes under the action of the initial organosilyl or organogermyl halide.

Experimental

The IR spectra were recorded on IKS-22 and UR-20 (Carl Zeiss) spectrometers in thin layers and in a cell (d = 0.1 mm, CaF_2 plates). The ^1H and ^{13}C NMR spectra were measured on Bruker AC-200P (200 MHz) and Varian VXR-400 (400 MHz) spectrometers using $CDCl_3$ and C_6D_6 as the solvents. All operations were carried out in an atmosphere of dry argon.

Ethoxyacetylene was synthesized from ethyl vinyl ether according to a standard procedure.[10] A solution of BuLi in hexane (1.31—1.84 *M*) was prepared according to a procedure reported previously.[11] Chlorotriisopropylsilane and -germane were prepared by the reactions of isopropyllithium[12] with tetrachlorosilane(germane).[13,14] For chlorotriisopropylgermane, ^1H NMR (δ): 1.20 (d, 6 H, $(\underline{C}H_3)_2CH$, J = 7.2 Hz); 1.56—1.68 (m, 1 H, $Me_2\underline{C}H$); ^{13}C NMR (δ): 19.1 ($(\underline{C}H_3)_2CH$); 18.8 ($Me_2\underline{C}H$). Bromotris(trimethylsilyl)silane was synthesized according to a known procedure.[15] The purity of intermediate tris(trimethylsilyl)silane obtained in the first stage was confirmed by the data from ^1H and ^{13}C NMR spectroscopy (for the Me_3Si group, δ_H 0.18, δ_C 2.2, δ_H (Si—H) 2.20). Iodotrimethylsilane,[16] bromotrimethylgermane,[17] and bromotriethylgermane[17] were synthesized according to procedures reported previously. *tert*-Butylchlorodimethylsilane, *tert*-butylchlorodiphenylsilane, chlorotriphenylsilane, and chloromethyldiphenylsilane were purchased from Merck and Aldrich.

All solvents used in the reactions were dried according to a known procedure.[18]

(Methyldiphenylsilyl)ethoxyacetylene (1d). A 1.31 *M* BuLi solution (54 mL, 0.07 mol) in hexane was added dropwise to a solution of ethoxyacetylene (5.5 g, 0.079 mol) in anhydrous THF (50 mL) at 0 °C. The reaction mixture was stirred at ~20 °C for 0.5 h. Then a solution of $Ph_2MeSiCl$ (14.5 g, 0.062 mol) in anhydrous THF (30 mL) was added dropwise and the mixture was stirred for 1 h. The precipitate that formed was separated by centrifugation and the solvents were removed *in vacuo* using a water-aspirator pump. Hexane (20 mL), ether (20 mL), and water (20 mL) were successively added with stirring to the residue until the precipitate was completely dissolved. The organic phase was separated and the aqueous phase was extracted with ether (2×15 mL). The combined ethereal extracts were dried with $MgSO_4$. The solvent was distilled off *in vacuo* using a water-aspirator pump and then an oil pump (1 Torr) and the residue was kept for 0.5 h. Compound **1d** was obtained in a yield of 15 g (80%).

Acetylenes **1b,e** were synthesized analogously.

(Triisopropylgermyl)ethoxyacetylene (1f). A 1.84 *M* BuLi solution (14 mL, 0.0258 mol) in hexane was added dropwise with cooling to 0 °C to a solution of ethoxyacetylene (1.99 g, 0.0284 mol) in anhydrous THF (30 mL). The reaction mixture was stirred at ~20 °C for 1 h. Then a solution of $Pr^i{}_3GeCl$ (5.1 g, 0.02215 mol) in anhydrous THF (25 mL) was added dropwise and the mixture was stirred for 8 h. The solvents were distilled off *in vacuo*, hexane (50 mL) was added, and the solution was separated from the residue. Hexane was distilled off *in vacuo* and the residue was fractionated. Acetylene **1f** was obtained in a yield of 5 g (85%), b.p. 59—60 °C (0.02 Torr), n_D^{20} 1.4685.

Acetylenes **1a,c** were synthesized analogously.

[Tris(trimethylsilyl)silyl]ethoxyacetylene (1g). A solution of ethoxyacetylene (2.12 g, 0.03 mol) in a mixture of anhydrous ether (15 mL) and anhydrous THF (5 mL) was added to the Grignard reagent prepared from Mg (0.66 g, 0.0272 g-at.) and EtBr (2.96 g, 0.0272 mol) in ether (20 mL) at 0 °C. The reaction mixture was stirred at 20 °C for 0.5 h. Then a solution of bromotris(trimethylsilyl)silane (6.8 g, 0.0208 mol) in anhydrous THF (20 mL) was added. The reaction mixture was stirred for 4 h, the solvent was distilled off *in vacuo*, hexane (50 mL) was added, and the mixture was washed successively with a saturated aqueous solution of NH_4Cl and water. The aqueous phase was extracted with ether and the combined organic extracts were dried with $MgSO_4$. Fractionation of the residue afforded acetylene **1g** in a yield of 4.3 g (65%), b.p. 89—90 °C (0.02 Torr), n_D^{20} 1.4994.

(*tert*-Butyldimethylsilyl)trimethylsilylketene (2a). Freshly distilled Me_3SiI (2.56 g, 0.013 mol, 1.82 mL) was added to acetylene **1a** (2.15 g, 0.012 mol) in anhydrous CH_2Cl_2 (4.5 mL) and the mixture was stirred for 8 h. Fractionation afforded ketene **2a** in a yield of 2.2 g (82%), b.p. 52—54 °C (0.02 Torr), n_D^{20} 1.4570 (*cf.* lit. data[19]: b.p. 57—60 °C (0.4 Torr), n_D^{20} 1.4526).

Ketenes **2b,d,e,f,g** were synthesized analogously.

(Triisopropylsilyl)trimethylsilylketene (2c). Me_3SiI (3.07 g, 0.015 mol) was added to a solution of acetylene **1c** (2.14 g, 0.0095 mol) in anhydrous MeCN (5 mL) and the mixture was stirred at ~20 °C for 36 h. The solvent and an excess of Me_3SiI were distilled off *in vacuo* and fractionation afforded ketene **2c** as a colored liquid in a yield of 1.64 g (64%), b.p. 69—72 °C (0.04 Torr). After purification from an admixture of iodine by flash chromatography on a dry column with Al_2O_3 (light petroleum—CH_2Cl_2, 4 : 1), ketene was obtained in a yield of 0.94 g (37%), b.p. 69—70 °C (0.04 Torr).

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