Silylation of silyl- and germylketenes containing bulky substituents at the silicon or germanium atom

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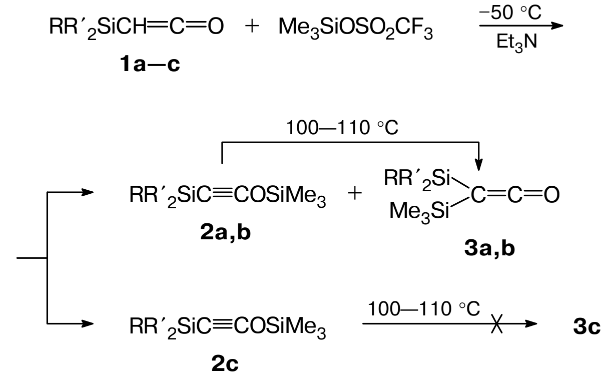
Silylation of silyl- and germylketenes with trialkylsilyl triflates was studied. Either the corresponding bis-organoelement-substituted ketenes or mixtures of these compounds with isomeric (silyloxy)silylacetylenes were formed depending on the size of the substituents at the silicon or germanium atom (both in ketenes and triflates) and on the nature of the heteroelement. The resulting (silyloxy)silylacetylenes were isomerized into the corresponding bis-silylketenes upon prolonged storage.

Key words: silylation, trialkylsilyl(germyl)ketenes, trialkylsilyl triflates, (silyloxy)silylacetylenes, bis-silylketenes, germyl(silyl)ketenes.

In the last decade, the chemistry of bis-heteroelement-substituted ketenes and isomeric bis-heteroelement-substituted ynol ethers attracted considerable attention[1—3] because of their rather high thermodynamic stabilities, the possibility of mutual isomerizations, and the use in the synthesis of organic and organoelement-containing compounds.

Recently, we have demonstrated[4] that the reactions of trimethylsilyl triflate with different triorganosilylketenes (**1**) afforded mixtures of O- and C-isomers, *viz.*, ynol ethers (**2**) and isomeric bis-silylketenes (**3**) (Scheme 1).

Scheme 1



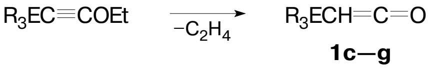
R = R′ = Et (**a**); R = Bu^t, R′ = Me (**b**); R = R′ = Pr^i (**c**)

The isomer ratio **2a,b** : **3a,b** depends on the duration of the reaction. For example, the **2a** : **3a** ratio was changed in the course of distillation from 1.8 : 1 to 1 : 1 (before and after distillation) in one of the experiments.

As part of continuing studies aimed at elucidating the effect of the steric factors on the directed synthesis of bis-heteroelement-containing ynol ethers, in the present work we investigated the reactions of silylated and germylated ketenes with trialkylsilyl triflates, both the reagent and the substrate containing bulky substituents at the silicon or germanium atoms.

The starting silyl- and germylketenes (**1c—g**) containing bulky substituents at the silicon or germanium atom were synthesized by thermal decomposition of the corresponding organosilyl- and organogermyl(ethoxy)acetylenes[5] as reported previously,[4,6] but according to a modified procedure (Scheme 2). The course of pyrolysis was monitored by IR spectroscopy of the reaction mixture by following the appearance of the ν(HC=C=O) absorption band in the region of 2090—2100 cm^{-1} and the disappearance of the ν(C≡C) absorption band in the region of 2180—2190 cm^{-1}.

Scheme 2



$$R_3EC{\equiv}COEt \xrightarrow[-C_2H_4]{} \underset{\textbf{1c—g}}{R_3ECH{=}C{=}O}$$

R$_3$E = Pr$^i_3$Si (**c**), (Me$_3$Si)$_3$Si (**d**), MePh$_2$Si (**e**), Et$_3$Ge (**f**), Pr$^i_3$Ge (**g**)

Ketenes **1** were obtained in 53—93% yields. The compounds synthesized were characterized by the data from elemental analysis and ^{1}H and ^{13}C NMR and IR spectra (Tables 1 and 2).

The ^{13}C NMR spectra of silyl- and germylketenes **1** are characterized by the presence of the high-field resonance signal for the C atom of the Si(Ge)—C(sp^2) group (δ from −12 to −2) and a low-field signal for the carbonyl C atom at δ 178—179, which unambiguously confirm the structures of the ketenes synthesized.[7]

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Table 1. Characteristics of the compounds synthesized

Compound	Yield (%)	B.p. /°C (*p*/Torr)	n_D^{20}	Found/Calculated (%)			Molecular formula
				C	H	Si(Ge)	
1c	93	36—37 (0.5)	1.4658	66.75 66.62	11.18 11.18	—	$C_{11}H_{22}OSi$
1d	56	66—69 (0.01)	1.4952	45.28 45.77	9.72 9.77	—	$C_{11}H_{28}OSi_4$
1e	90	96—98 (0.02)	1.5788	75.78 75.57	5.98 5.92	11.76 11.79	$C_{15}H_{14}OSi$
1f	68	54—58 (8)*	1.4625	—	—	—	—
1g	53	41—45 (0.5)	1.4488	54.31 54.38	9.19 9.15	29.76 29.89	$C_{11}H_{22}GeO$

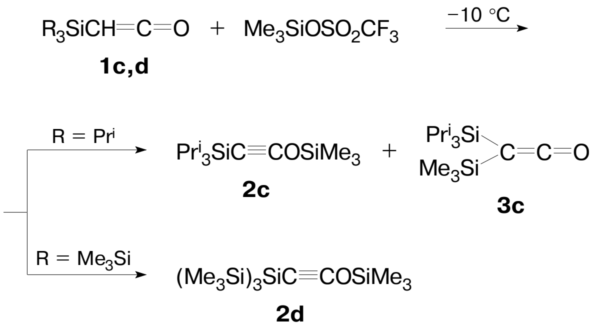
* Lit. data[6]: b.p. 56 °C (8 Torr), n_D^{20} 1.4642.

A change in the conditions of the reaction of triisopropylsilylketene **1c** with trimethylsilyl triflate (see Scheme 1 and the Experimental section) led to a change in the composition of the final products. The IR spectrum of the reaction mixture has an absorption band at 2090 cm^{-1} corresponding to the stretching vibrations of the HC=C=O group, which indicates that the reaction did not proceed to completion. The presence of absorption bands at 2191 (SiC≡COSi) and 2055 cm^{-1} ($Si_2C=C=O$) is consistent with the formation of two isomers **2c** and **3c** (4 : 1) (Scheme 3). The ^{1}H and ^{13}C NMR spectra of the reaction mixture measured before and after fractionation are identical, which is evidence that distillation was not accompanied by isomerization.

At ~20 °C, trimethylsilyloxy(triisopropylsilyl)acetylene (**2c**) slowly isomerized into the corresponding ketene **3c**. After 10 days, the **2c** : **3c** ratio became equal to 1 : 4.

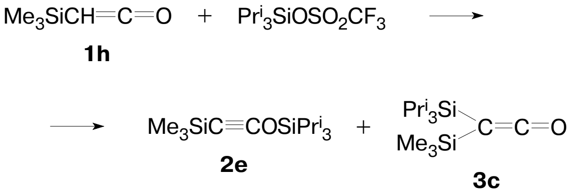
The reaction of [tris(trimethylsilyl)]silylketene (**1d**) with trimethylsilyl triflate proceeded slowly to form the corresponding trimethylsilyloxy(trimethylsilyl)acetylene (**2d**) and was not completed on stirring of the reaction mixture at 20 °C for 8 days. The formation of compound **2d** was confirmed by the ^{13}C NMR spectrum of the reaction mixture, which had signals corresponding to the $OSiMe_3$, $(Me_3Si)_3Si$, SiC≡, and ≡C—O groups (Table 3). However, fractionation afforded a mixture of products which were difficult to identify.

Scheme 3



Next we studied the reaction of trimethylsilylketene (**1h**) with silyl triflate containing the bulky isopropyl group under mild conditions analogous to those used in the reaction of **1c** with Me_3SiOTf. The reaction proceeded more slowly to give initially the corresponding ynol ether **2e**. The ^{1}H and ^{13}C NMR spectra of the reaction mixture measured after 24 h had low-intensity signals corresponding to compound **2e** and intense signals belonging to the initial triflate. After 8 days, the ^{1}H and ^{13}C NMR spectra had signals of Pr^i_3SiOTf and compounds **2e** and **3c** (Scheme 4).

Scheme 4



The reaction mixture contained a substantial amount of unconsumed Pr^i_3SiOTf, which we failed to separate from the reaction products by distillation. Fractionation

Table 2. ^{1}H and ^{13}C NMR and IR spectral data for ketenes $RR'_2ECH=C=O$ (**1c—e,g**)

Compound	RR'_2E	IR, ν/cm^{-1}	NMR, δ	
			^{1}H (*J*/Hz)	^{13}C
1c	Pr^i_3Si	2090	1.08 (d, 18 H, $(C\underline{H}_3)_2CH$, *J* = 4.5); 1.09 (m, 3 H, $Me_2C\underline{H}$); 1.64 (s, 1 H, CH=C=O)	−7.5 ($\underline{C}$=C=O); 12.1 ($Me_2\underline{C}H$); 18.3 ($(\underline{C}H_3)_2CH$); 178.9 (C=$\underline{C}$=O)
1d	$(Me_3Si)_3Si$	2090	1.19 (s, 27 H, $C\underline{H}_3$); 1.46 (s, 1 H, (CH=C=O)	−12.1 ($\underline{C}$=C=O); 0.2 (CH_3); 178.7 (C=$\underline{C}$=O)
1e	$MePh_2Si$	2110	0.75 (s, 3 H, $C\underline{H}_3$); 2.23 (s, 1 H, CH=C=O); 7.40—7.62 (m, 10 H, Ph—H)	−2.0 ($\underline{C}$=C=O); −1.1 (CH_3); 128.0, 129.8, 134.3, 135.8 (C_6H_5); 178.4 (C=$\underline{C}$=O)
1g	Pr^i_3Ge	2095	1.10 (d, 18 H, $(C\underline{H}_3)_2CH$, *J* = 7.2); 1.39 (m, 3 H, $Me_2C\underline{H}$); 1.52 (s, 1 H, CH=C=O)	−8.6 ($\underline{C}$=C=O); 15.7 ($Me_2\underline{C}H$); 19.4 ($(\underline{C}H_3)_2CH$); 178.1 (C=$\underline{C}$=O)

Table 3. ^{1}H and ^{13}C NMR and IR spectral data for ynol ethers **2** and isomeric ketenes **3**

Compound	IR, ν/cm^{-1}	NMR, δ	
		^{1}H (*J*/Hz)	^{13}C
2c + **3c**	2191 (C≡C) 2060 (C=C=O)	0.92—1.15 (m, 21 H, Me_2CH, **2s**, **3c**); 0.33 (s, 9 H, $OSiMe_3$); 0.25 (s, 9 H, $CSiMe_3$)	for **2c** −1.2 ($OSi(\underline{C}H_3)_3$); 11.7 ($Me_2\underline{C}H$); 18.7 ($(\underline{C}H_3)_2CH$); 26.1 (Si—C≡); 107.3 (≡C—O); for **3c** −4.3 ($\underline{C}$=C=O); 1.9 ($CSi(CH_3)_3$); 13.2 ($Me_2\underline{C}H$); 18.6 ($(\underline{C}H_3)_2CH$); 166.5 (C=O)
2d[a]	2182	0.17 (s, 27 H, $(Me_3Si)_3Si$); 0.28 (s, 9 H, $OSiMe_3$)	−1.2 ($OSi(CH_3)_3$); 0.3 ($(Me_3Si)_3Si$); 22.4 (Si—C≡); 107.8 (≡C—O)
2e + **3c**	2175 (C≡C) 2060 (C=C=O)	0.3 (s, 9 H, Me_3Si, **2e**); 0.02 (s, 9 H, Me_3Si, **3c**); 0.94—1.11 (m, 21 H, $(CH_3)_2CH$, **2e**, **3c**)	for **2e** 0.7 ($Si(CH_3)_3$); 12.6 ($Me_2\underline{C}H$); 17.7 ($(\underline{C}H_3)_2CH$); 26.0 (Si—C≡); 107.8 (≡C—O); for **3c** −4.3 ($\underline{C}$=C=O); 1.9 ($Si(CH_3)_3$); 13.2 ($Me_2\underline{C}H$); 18.6 ($(\underline{C}H_3)_2CH$); 166.7 (C=O)
3d	2080[b]	0.18 (s, 9 H, Me_3Si); 0.87 (s, 3 H, MeSi); 7.40—7.70 (m, 10 H, Ph)	−1.1 (CH_3Si); −0.2 ($\underline{C}$=C=O); 1.2 ($Si(CH_3)_3$); 127.9, 129.4, 134.6, 136.1 ($(C_6H_5)_2Si$)
3e	2075[c]	0.19 (s, 9 H, Me_3Si); 0.96 (q, 2 H, $MeC\underline{H}_2Ge$); 1.08 (t, 3 H, $C\underline{H}_3CH_2Ge$)	−4.3 ($\underline{C}$=C=O); 1.4 ($Si(CH_3)_3$); 6.6 ($Me\underline{C}H_2$); 8.4 ($\underline{C}H_3CH_2$); 165.8 (C=O)
3f	2065	0.21 (s, 9 H, Me_3Si); 1.19 (d, 18 H, $(C\underline{H}_3)_2CH$, *J* = 7.6); 1.48 (m, 3 H, $Me_2C\underline{H}$)	−6.0 ($\underline{C}$=C=O); 2.0 ($Si(CH_3)_3$); 17.0 ($Me_2\underline{C}H$); 19.8 ($(\underline{C}H_3)_2CH$); 166.0 (C=O)

[a] Reaction mixture. [b] Lit. data.[5] [c] Lit. data.[6]

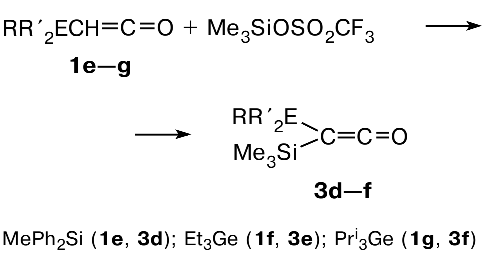
was accompanied by partial isomerization of O-isomer **2e** into C-isomer **3c**.

Therefore, bis-silyl-substituted ynol ether **2e** containing bulky substituents in the silyloxy group isomerized into the corresponding ketene **3c** more rapidly than the ether containing such group at the C atom.

The ratio between products **2** and **3** depends on the experimental conditions. For mixtures of **2** and **3** (**a—c**), the isomer ratio changed after distillation, the content of bis-silylketene **3** being increased.

The reactions of trimethylsilyl triflate with ketenes **1e—g** (Scheme 5) in the presence of triethylamine at −40 °C (the reagent ratio was 1.5 : 1 : 2) gave rise exclusively to ketenes **3d—f**. The IR spectrum of the reaction mixture measured after 0.5 h had the absorption band at 2055 cm^{-1} characteristic of the C=C=O group in bis-heteroelement-substituted ketenes. The absorption band at 2170 cm^{-1} ($GeC{\equiv}COSiMe_3$) was not observed.

Scheme 5



RR'_2E = $MePh_2Si$ (**1e**, **3d**); Et_3Ge (**1f**, **3e**); Pr^i_3Ge (**1g**, **3f**)

The reaction of triethylgermylketene (**1f**)[7] with Me_3SiOTf, unlike that involving triethylsilyl ketene,[4] proceeded less actively and was completed only in 15 h. In this case, the corresponding trimethylsilyloxy(triethylgermyl)acetylene was not detected by spectroscopy, and trimethylsilyl(triethylgermyl)ketene (**3e**) was obtained in 81% yield.

As expected, the reaction of triisopropylgermylketene (**1g**) with Me_3SiOTf proceeded even less actively. After stirring for 90 h, the degree of conversion was ~20% (control by ^{1}H NMR spectroscopy). The reaction afforded trimethylsilyl(triisopropylgermyl)ketene (**3f**) as the only product.

To summarize, silylation of silylketenes containing the phenyl substituents and germylketenes under the action of Me_3SiOTf afforded exclusively C-isomers **3d—f**. The reactions of ketenes and silyl triflate containing rather bulky substituents at the Si atoms gave rise either to ynol ethers or mixtures of the latter with ketenes. Ynol ethers **2c** and **2e** were slowly isomerized into the corresponding ketenes.

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 ^{1}H 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 under an atmosphere of dry argon.

The initial trialkylsilyl(germyl)ethoxyacetylenes,[5,6] Me_3SiOTf,[8] triisopropylsilyl triflate,[9] and trimethylsilylketene (**1h**)[10] were synthesized according to procedures reported previously.

All solvents used in the reactions were dried according to a known procedure.[11]

Methyldiphenylsilylketene (1e). A solution of methyldiphenylsilyl(ethoxy)acetylene (5.68 g, 0.021 mol) in *n*-octane (30 mL) was heated at 120—130 °C until the acetylene was completely converted into ketene (75 min, control by IR spectroscopy: the disappearance of the ν(C≡C) band at 2176 cm^{-1} and the appearance of the ν(C=C=O) band at 2110 cm^{-1}). Ketene **1e** was isolated from the reaction mixture in a yield of 4.8 g (90%) by fractionation.

Ketenes **1c,d,f,g** were synthesized analogously.

Reaction of triisopropylsilylketene (1c) with Me_3SiOTf. A mixture of Me_3SiOTf (3.20 g, 14.4 mmol) and Et_3N (1.94 g, 19.2 mmol) in anhydrous ether (10 mL) was added with stirring to a solution of compound **1c** (1.90 g, 9.6 mmol) in anhydrous ether (5 mL) at −10 °C. The reaction mixture was stirred at 20 °C for 8 days. The ethereal layer was separated from the dark-brown precipitate. Fractionation afforded a mixture of compounds **2c** and **3c** in a yield of 1.51 g (58%), b.p. 66—68 °C (0.002 Torr). The ^{1}H and ^{13}C NMR and IR spectral data are given in Table 3.

The reaction of ketene **1d** with Me_3SiOTf and the reaction of ketene **1h** with Pr^i_3SiOTf were carried out analogously.

The spectral data for compounds **2d**, **2e**, and **3c** are given in Table 3.

Reaction of ketene 1g with Me_3SiOTf. A mixture of Me_3SiOTf (1.25 g, 5.6 mmol) and Et_3N (0.76 g, 7.5 mmol) in anhydrous ether (6 mL) was added with stirring to a solution of compound **1g** (0.9 g, 4 mmol) in anhydrous ether (4 mL) at −40 °C. The reaction mixture was stirred with cooling for 0.5 h and then at 20 °C for 90 h. The ethereal layer was separated from the dark-brown precipitate and the ether was distilled off. Fractionation of the residue afforded the initial ketene in a yield of 0.65 g (72%), b.p. 34—35 °C (0.012 Torr), and trimethylsilyl(triisopropylgermyl)ketene (**3f**) in a yield of 0.27 g (23%), b.p. 70—74 °C (0.012 Torr). Found (%): C, 50.52; H, 9.01. $C_{14}H_{30}GeO_2Si$. Calculated (%): C, 50.83; H, 9.07.

Analogously, the reaction of ketene **1e** (2 g) with Me_3SiOTf (2.8 g) afforded compound **3d** in a yield of 1.6 g (62%), b.p. 120—122 °C (0.01 Torr),[5] n_D^{20} 1.4570 (*cf.* lit. data[5]: b.p. 123—125 °C (0.01 Torr), n_D^{20} 1.4570).

Ketene **3e** was obtained analogously in a yield of 2 g (81%), b.p. 47—48 °C (1 Torr), n_D^{20} 1.4727 (*cf.* lit. data[6]: b.p. 111—112 °C (15 Torr), n_D^{20} 1.4750).

The spectral data for all compounds synthesized are given in Tables 2 and 3.

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