

Preliminary communication
Silylation of silylketenes

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Received 31 October 1996

Abstract

Silylation of silylketenes $\text{RSiCH}=\text{C}=\text{O}$ **1** (**a**, $\text{R} = \text{Et}_3$; **b**, $\text{R} = {}^i\text{BuMe}_2$; **c**, $\text{R} = {}^i\text{Pr}_3$) with trimethylsilyltriflate in the presence of triethylamine was studied. Mixtures of the corresponding 1-trimethylsiloxy-2-silylethyne $\text{RSiC}\equiv\text{COSiMe}_3$ **2** and trimethylsilyl(silyl)ketenes $\text{RSi}(\text{Me}_3\text{Si})\text{C}=\text{C}=\text{O}$ **3** in the case of **1a** and **1b** were obtained. By this reaction only **2c** was prepared from **1c**. Heating of mixtures of **2a**, **3a** and **2b**, **3b** at 100–110 °C affords pure ketenes **3a** and **3b** respectively; heating of **2c** under the same conditions takes place practically without rearrangement. © 1997 Elsevier Science S.A.

Keywords: Silylation; Trimethylsilyl(silyl)ketenes; 1-Trimethylsiloxy-2-silylethyne; Thermal isomerization

1. Introduction

Different siloxyalkynes of the general formula $\text{RC}\equiv\text{COSiR}'_3$ ($\text{R} = \text{Alk}$, Ar ; $\text{R}' = \text{Alk}$) have been described in the literature [1–4]. To our knowledge only two examples of 1-siloxy-2-silylethyne $\text{RSiC}\equiv\text{COSiR}'$ ($\text{R} = \text{Me}_3$, $\text{R}' = {}^i\text{Pr}_3$; $\text{R} = \text{R}' = {}^i\text{BuMe}_2$) are known to date [4,5]. The chemistry of these compounds has not yet been studied, but it is expected that they possess a rich chemistry owing to the presence of several reactive centers in the molecule. They are also of interest due to a possible interconversion of isomeric siloxyacetylenes to silylketenes, widely discussed in the literature [1–3,5], but this is not investigated in detail. The aim of our present work was to prepare previously unknown siloxy(silyl)ethynes and to study the possibility of isomerization between these compounds and their isomeric bis(silyl)ketenes.

Tzschach and Uhlig have synthesized bis(trimethylsilyl)ketene by the reaction of trimethylsilylketene with trimethylsilyltriflate in the presence of triethylamine [6]; we applied this method for the preparation of new siloxy(silyl)ethynes, using monosilylketenes with bulky alkyl substituents at the silicon atom, and describe the thermal isomerization of these compounds to the isomeric bis(silyl)ketenes.

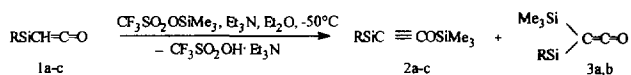
2. Results and discussion

By the reaction of monosilylketenes **1a,b** with trimethylsilyltriflate in the presence of triethylamine in Et_2O , mixtures of the corresponding 1-trimethylsiloxy-2-silylethyne **2a,b** and the isomeric trimethylsilyl(silyl)ketenes **3a,b** were obtained in moderate yield.

Only 1-trimethylsiloxy-2-triisopropylsilylethyne **2c** (69% yield) was prepared as a result of the silylation of **1c**. A mixture of trimethylsilyltriflate (2.76 g, 12.4 mmol) and triethylamine (1.68 g, 16.6 mmol) in 5 ml of Et_2O was added dropwise at -50°C to a solution of **1a** (1.3 g, 8.3 mmol) in 5 ml of Et_2O . Stirring was continued for 30 min after the reaction mixture had reached room temperature. $\text{CF}_3\text{SO}_2\text{OH} \cdot \text{Et}_3\text{N}$ was separated as a brown oil. After evaporation of the volatiles in vacuo the residue was distilled to give 1 g (53%) of a mixture of **2a** and **3a**, b.p. 68–73 °C (0.4 Torr) (Anal. Found: C, 56.99; H, 10.99. $\text{C}_{11}\text{H}_{24}\text{OSi}_2$ Calc.: C, 57.83; H, 10.59%). In a similar way, a mixture of **2b** and **3b** was prepared, yield 53%, b.p. 55–60 °C (0.4 Torr) (Anal. Found: C, 57.58; H, 10.40. $\text{C}_{11}\text{H}_{24}\text{OSi}_2$ Calc.: C, 57.83; H, 10.59%). Acetylene **2c** was also prepared in a similar way, but the time of stirring of the reaction mixture was increased up to 22 h. Yield 69%, b.p. 65–70 °C (0.005 Torr) (Anal. Found: C, 61.94; H, 11.43. $\text{C}_{14}\text{H}_{30}\text{OSi}_2$ Calc.: C, 62.15; H, 11.18%). Mixture of **2a**, **3a**: IR, $\nu(\text{cm}^{-1})$: 2080, 2180. ^1H NMR (300 MHz, CDCl_3): δ 0.98 (t, 9H, $\text{CH}_3\text{CH}_2\text{Si}$, **3a**),

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0.97 (t, 9H, $\text{CH}_3\text{CH}_2\text{Si}$, **2a**), 0.65 (q, 6H, $\text{CH}_3\text{CH}_2\text{Si}$, **3a**), 0.54 (q, 6H, $\text{CH}_3\text{CH}_2\text{Si}$, **2a**), 0.33 (s, 9H, OSiMe_3), 0.2 (s, 9H, CSiMe_3). ^{13}C NMR (75.5 MHz, CDCl_3): δ 166.4 (C=O), 106.5 ($\equiv\text{COSi}$), 27.4 ($\equiv\text{CSi}$), 7.4 ($\text{CH}_3\text{CH}_2\text{Si}$, **2a**), 7.0 ($\text{CH}_3\text{CH}_2\text{Si}$, **3a**), 5.2 ($\text{CH}_3\text{CH}_2\text{Si}$, **3a**), 5.0 ($\text{CH}_3\text{CH}_2\text{Si}$, **2a**), 1.3 (CSiMe_3), -1.4 (OSiMe_3), -3.1 ($\text{sp}^2\text{-C}$). **2b**, **3b**: IR, $\nu(\text{cm}^{-1})$: 2080, 2180. ^1H NMR (300 MHz, CDCl_3): δ 0.89 (s, 9H, ^tBu , **3b**), 0.86 (s, 9H, ^tBu , **2b**), 0.26 (s, 9H, OSiMe_3), 0.17 (s, 9H, CSiMe_3), 0.09 (s, 6H, Me_2Si , **3b**), 0 (s, 6H, Me_2Si , **2b**). ^{13}C NMR (75.5 MHz, CDCl_3): δ 166.7 (C=O), 106.4 ($\equiv\text{COSi}$), 28.5 ($\equiv\text{CSi}$), 26.3 ($(\text{CH}_3)_3\text{C}$, **3b**), 26.1 ($(\text{CH}_3)_3\text{C}$, **2b**), 18.8 ($(\text{CH}_3)_3\text{C}$, **3b**), 16.7 ($(\text{CH}_3)_3\text{C}$, **2b**), 1.6 (CSiMe_3), -1.2 (OSiMe_3), -2 ($\text{sp}^2\text{-C}$), -3.4 (Me_2Si , **3b**), -3.9 (Me_2Si , **2b**). **2c**: IR, $\nu(\text{cm}^{-1})$: 2180. ^1H NMR (300 MHz, CDCl_3): δ 0.94–1.03 (m, 21H, $^i\text{Pr}_3\text{Si}$), 0.27 (s, 9H, OSiMe_3). ^{13}C NMR (75.5 MHz, CDCl_3): δ 107.1 ($\equiv\text{COSi}$), 26.0 ($\equiv\text{CSi}$), 18.5 ($(\text{CH}_3)_2\text{CSi}$), 11.6 ($(\text{CH}_3)_2\text{CSi}$), -1.4 (OSiMe_3).



a $\text{R}=\text{Et}$, b $\text{R}=\text{BuMe}_2$, c $\text{R}=\text{Pr}_2$

(1)

Structures of the synthesized acetylenes **2** and ketenes **3** were confirmed by ^1H , ^{13}C NMR and IR spectroscopy. IR spectra of compounds **2** exhibit the expected intense absorption band at 2180 cm^{-1} due to substituted $\text{C}\equiv\text{C}$ groups [5]. Ketenes **3** show a very strong absorption at 2080 cm^{-1} typical for bis(element)substituted ketenes.

$^1\text{H}/^{13}\text{C}$ NMR spectra are consistent with the proposed structures: particularly noteworthy are the acetylenic carbon signals for acetylenes **2** and the $\text{C}=\text{C}=\text{O}$ signals for ketenes **3** in the ^{13}C NMR spectra. The resonances of the α -carbon atoms for **2a–c** are found at 106.5, 106.4, 107.1 ppm, whereas the signals of β -carbon atoms appear at 27.4, 28.5, 26.0 ppm, analogous to the literature data for siloxyalkynes [2] and 1-tert-butoxy-2-silylethynes [7].

Resonance signals of the carbon atoms of the carbonyl group of compounds **3a,b** appear in the low-field region at 166.4 and 166.7 ppm; signals of the sp^2 -hybridized carbon atoms in ketenes appear at -3.1 and -2 ppm, being characteristic of bis(element)substituted ketenes [8]. Mass spectra of **3a,b** show the proper molecular ion and the appropriate fragmentation pattern. **3a**: MS (EI) m/z : 228 (7.16) (M^+), 199 (100) ($\text{M} - \text{Et}^+$), 171 (67.49) ($\text{M} - \text{Et} - \text{C}_2\text{H}_4^+$), 143 (44.83) ($\text{M} - \text{Et} - 2\text{C}_2\text{H}_4^+$), 115 (1.32) ($\text{M} - \text{Et} - 2\text{C}_2\text{H}_4 - \text{CO}^+$), 73 (24.41) (Me_3Si^+), 70 (2.11) ($\text{M} - \text{Et} - 2\text{C}_2\text{H}_4 -$

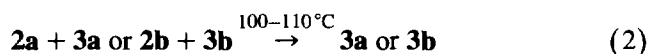
Me_3Si^+), 213 (4.72) ($\text{M} - \text{Me}^+$), 185 (7.82) ($\text{M} - \text{Me} - \text{C}_2\text{H}_4^+$), 157 (7.15) ($\text{M} - \text{Me} - 2\text{C}_2\text{H}_4^+$), 129 (2.95) ($\text{M} - \text{Me} - 3\text{C}_2\text{H}_4^+$), 101 (1.61) ($\text{M} - \text{Me} - 3\text{C}_2\text{H}_4 - \text{CO}^+$). **3b**: MS (EI) m/z : 228 (1.35) (M^+), 171 (100) ($\text{M} - ^t\text{Bu}^+$), 143 (0.13) ($\text{M} - ^t\text{Bu} - \text{CO}^+$), 98 (0.12) ($\text{M} - ^t\text{Bu} - \text{Me}_3\text{Si}^+$), 73 (38.2) (Me_3Si^+), 70 (0.26) ($\text{M} - ^t\text{Bu} - \text{CO} - \text{Me}_3\text{Si}^+$), 213 (0.74) ($\text{M} - \text{Me}^+$), 99 (20.25) ($\text{M} - \text{Me} - \text{C}_4\text{H}_8 - \text{Me}_2\text{Si}^+$), 129 (0.31) ($\text{M} - \text{Me} - \text{C}_4\text{H}_8 - \text{CO}^+$).

We studied the reaction with ketene **2a** in detail: the course of the reaction was monitored by means of IR spectroscopy. The IR spectrum of the reaction mixture (-10°C after 1 h after the reactants were mixed) exhibits $\nu(-\text{CH}=\text{C}=\text{O})$ at 2108 cm^{-1} , characteristic of monosilylketene, and $\nu(\text{C}\equiv\text{C})$ at 2180 cm^{-1} . At room temperature, IR spectra of the reaction mixture exhibit ketene absorptions at 2080 cm^{-1} , characteristic of bis(silyl)ketenes, and for acetylenes at 2180 cm^{-1} .

The ratio of the products **2** and **3** strongly depends on the experimental conditions: the time during which the reaction mixture stands at room temperature, especially after removal of the solvent, and also on the rate of distillation. After distillation and after leaving the reaction mixture at room temperature, the quantity of ketenes **3** increases (controlled by NMR spectroscopy). In fact, in one of the experiments the ratio of **2a:3a** changed from 1.8:1 initially to 1:1 after distillation. When the reaction mixture was allowed to stand at room temperature in the NMR tube without solvent for 1 h, the NMR spectra showed the presence of only pure ketene **3a**. In view of these facts we suggest that isomerization takes place.

In order to study the thermal rearrangement, we heated a mixture of **2a**, **3a** (1:2.5 starting ratio) at $100\text{--}110^\circ\text{C}$ for 5 h; as a result pure ketene **3a** was obtained. Heating of a mixture of **2b**, **3b** (1:1 ratio) at the same temperature for 10 h also afforded pure ketene **3b** in almost quantitative yield. [A mixture of **2a**, **3a** (1:2.5 ratio) (1.2 g, 5.3 mmol) was heated at $100\text{--}110^\circ\text{C}$ (oil bath) for 5 h. The course of the reaction was monitored by IR spectroscopy. Pure ketene **3a** was obtained in a quantitative yield, b.p. $68\text{--}70^\circ\text{C}$ (0.4 Torr), n_{D}^{20} 1.4573 (Anal. Found: C, 57.48; H, 10.75. $\text{C}_{11}\text{H}_{24}\text{OSi}_2$ Calc.: C, 57.83; H, 10.59%). IR, $\nu(\text{cm}^{-1})$: 2080. ^1H NMR (300 MHz, CDCl_3): δ 0.98 (t, 9H, $\text{CH}_3\text{CH}_2\text{Si}$), 0.65 (q, 6H, $\text{CH}_3\text{CH}_2\text{Si}$), 0.2 (s, 9H, SiMe_3). ^{13}C NMR (75.5 MHz, CDCl_3): δ 166.4 (C=O), 7.0 ($\text{CH}_3\text{CH}_2\text{Si}$), 5.2 ($\text{CH}_3\text{CH}_2\text{Si}$), 1.3 (SiMe_3), -3.1 ($\text{sp}^2\text{-C}$). Ketene **3b** was prepared in a similar way, b.p. $57\text{--}60^\circ\text{C}$ (0.4 Torr), n_{D}^{20} 1.4526 (Anal. Found: C, 57.62; H, 10.51. $\text{C}_{11}\text{H}_{24}\text{OSi}_2$ Calc.: C, 57.83; H, 10.59%). IR, $\nu(\text{cm}^{-1})$: 2080. ^1H NMR (300 MHz, CDCl_3): δ 0.89 (s, 9H, ^tBu), 0.17 (s, 9H, SiMe_3), 0.09 (s, 6H, Me_2Si). ^{13}C NMR (75.5 MHz, CDCl_3): δ 166.7 (C=O), 26.3 ($(\text{CH}_3)_3\text{C}$), 18.8 ($(\text{CH}_3)_3\text{C}$), 1.6 (SiMe_3), -2 ($\text{sp}^2\text{-C}$), -3.4 (Me_2Si).] The course of the reaction was moni-

tored by IR spectroscopy, focussing on the disappearance of the acetylenic absorption band at 2180 cm^{-1} :



An attempt to prepare ketene **3c** by heating **2c** under the same conditions was unsuccessful, isomerization practically does not take place: IR spectra show in the beginning the appearance of the $\nu(\text{C}=\text{C}=\text{O})$ band at 2080 cm^{-1} , but this process proceeds very slowly, and decomposition predominates. As a result of heating at $100\text{--}110^\circ\text{C}$ for 4 days we obtained only a complicated mixture of products.

These results of our investigation allow us to suppose that silylation of monosilylketenes **1** with bulky alkyl substituents at the silicon atom with trimethylsilyltriflate occurs via the formation of kinetically controlled products like acetylenes **2** which upon warming of the reaction mixture undergo isomerization to the thermodynamically more stable ketenes **3**. In the case of ketene **1c**, probably steric hindrance caused by the isopropyl group at the silicon atom increases the stability of acetylene **2c** in such a way that the isomerization does not occur.

Acknowledgements

Support from the Government of the County Hessen, Germany (HSP-II-Programme) (for S.N.) and from the Fonds der Deutschen Chemischen Industrie VCI (for J.L.) is gratefully acknowledged.

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