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ATTEMPTED PREPARATION OF SILAETHYLENES FROM SILANECARBOXYLATE ESTERS *

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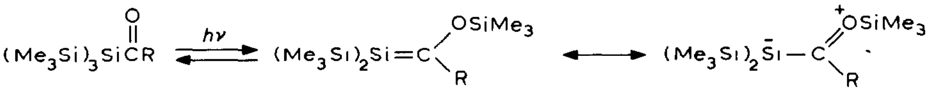
Summary

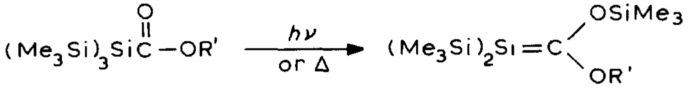
Several esters of tris(trimethylsilyl)silanecarboxylic acid were prepared and characterized. Attempts to isomerize these photochemically or thermally to isomeric silaethylenes failed, and only conventional silanecarboxylate ester behaviour, i.e., loss of CO, was observed.

It has been shown that a variety of tris(trimethylsilyl)acylsilanes are readily isomerized photochemically to the isomeric silaethylenes, some of which are remarkably stable having been isolated as crystalline solids and fully characterized [1,2,3].



(A) (B)

It seems evident that this unusual stability is attributable in part to the presence of the siloxy group on carbon which facilitates resonance stabilization through contributions from structures such as **A** and **B**. If this effect has the importance we believe it has, it seems likely that an additional siloxy or alkoxy group attached to carbon as the group R would further stabilize the silaethylene. This paper reports attempts to synthesize such a silaethylene by photolysis or thermolysis of esters of tris(trimethylsilyl)silanecarboxylic acid.



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* Dedicated with pleasure to my friend and fellow chemist, Prof. Makoto Kumada who has made such an impact on the field of Organosilicon Chemistry.

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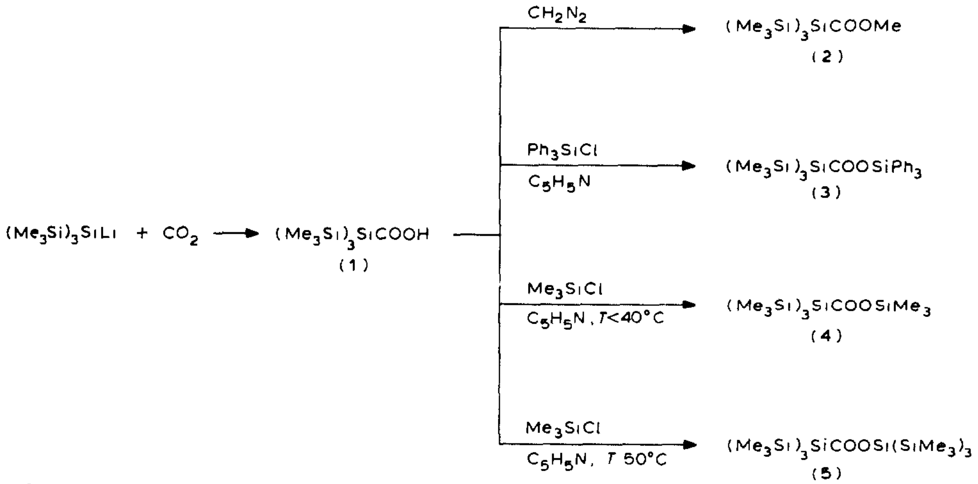
Tris(trimethylsilyl)silanecarboxylic acid (**1**) is readily prepared by carbonation of tris(trimethylsilyl)silyllithium [4]. Like other silanecarboxylic acids [5] it is relatively stable, except to base [5] or to heat [6], where decarbonylation readily occurs. It is easily converted to its methyl ester (**2**) with diazomethane, and to its triphenylsilyl ester (**3**), or trimethylsilyl ester (**4**) using the appropriate silyl chloride with pyridine as a proton trap (Scheme 1) [6].

No problems were encountered in preparing the methyl or triphenylsilyl esters, or the trimethylsilyl ester if the temperature was kept below 40 °C. However, if the coupling of the acid **1** with trimethylchlorosilane was carried out above 40 °C, an interesting decarbonylation-condensation occurred yielding the ester **5**, a type of reaction observed previously but only under much more extreme thermal conditions (Scheme 1) [6].



SCHEME 1

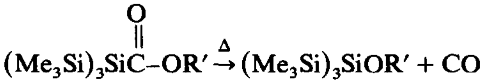
Evidently the tris(trimethylsilyl)silyl ester **5** arose through an alternative reaction pathway during the esterification process, and we have made several attempts to understand what occurred. Formation of **5** does not arise directly from **4** by heating to the higher temperature since **4** can be heated for hours at 50 °C without change, with or without the presence of trimethylchlorosilane. One source of the ester **5** would logically seem to be as a result of the reaction of the silanecarboxylate ion **1**, (or acid), with tris(trimethylsilyl)chlorosilane, (**6**) a reaction which was shown by a separate experiment to proceed readily under the conditions of the original formation (50 °C, pyridine).

$$(Me_3Si)_3SiCOOH \text{ or } (Me_3Si)_3SiCOO^- + \underset{(\mathbf{6})}{(Me_3Si)_3SiCl} \rightarrow \underset{(\mathbf{5})}{(Me_3Si)_3SiCOOSi(SiMe_3)_3}$$

However, despite many experiments we have not found how this sisyl chloride (**6**) is formed (sisyl, by analogy with Eaborn's term trisyl for $(Me_3Si)_3C$). Neither **6** nor **5** were formed from the reaction of the silanecarboxylic acid, or its esters, with trimethylchlorosilane, or with pyridinium hydrochloride at 50–60 °C. Hence a full understanding of how the ester **5** is formed under the experimental conditions is not available at this time.

Attempts to obtain the desired silaethylenes by photolysis, or thermolysis, were completely unsuccessful. Light from a mercury floodlamp (which readily isomerizes acylsilanes) had no detectable effect on the esters over extended time periods, as determined by ^{1}H NMR spectroscopy, and this was also true for moderate time periods using a Hannovia 450 W UV lamp ($\lambda > 2537$ nm) although over very long periods of time the NMR spectra developed a number of silyl signals, suggesting absorption by and fragmentation of the tris(trimethylsilyl)silyl group. We were unable to ascertain where the n–π^* transitions of the esters occur, even in concentrated solution, since from 360 down to about 295 nm there is no detectable UV absorption for the methyl or trimethylsilyl esters. Below 295 nm the absorption becomes appreciable, presumably due to the polysilyl system. Presumably the n–π^* absorption lies under the polysilyl absorption.

It is known that acylsilanes can be thermally isomerized to silaethylenes at moderately high temperatures [3]. In hopes that the esters might isomerize similarly they were heated in solution at various temperatures. Reaction occurred, but not the hoped for silaethylene formation. Instead the well-established thermal decarbonylation of the esters was observed if high enough temperatures were employed [6].



$$(\mathrm{Me_3Si})_3\mathrm{Si}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\!-\!\mathrm{OR'} \xrightarrow{\Delta} (\mathrm{Me_3Si})_3\mathrm{SiOR'} + \mathrm{CO}$$

When the esters were heated for extended periods of time at lower temperatures in the presence of 2,3-dimethyl-1,3-butadiene, known to be an effective diene with silaethylenes in the Diels–Alder reaction [3], only the silyl esters, or their decarbonylation products were obtained.

Hence these approaches to a bis-siloxy- or bis-alkoxysilaethylene have not proven to be successful. In view of the behavior described above, it is clear that some other approach will have to be employed if such silaethylenes, which could be of considerable interest, are to be prepared.

Experimental

Reactions involving organometallic reagents were carried out under argon using sodium-dried solvents. Routine spectroscopic techniques were employed and the more important absorptions are reported. Mass spectral data reports m/e (ion identity, % relative intensity). The mercury flood lamps used were medium pressure 100 W PAR 38 bulbs, $\lambda > 360$ nm.

Preparation of tris(trimethylsilyl)silanecarboxylic acid

The tris(trimethylsilyl)silyllithium obtained by cleavage of 10 g (0.031 mol) of tetrakis(trimethylsilyl)silane in 100 ml THF by 30 ml (0.048 mol) of 1.6 M methyllithium when stirred for 3 d, was poured onto an ethereal slurry of dry ice. After evaporation of the excess CO_2, the residue was poured into a mixture of ether and 2% HCl. Ether extraction, drying over Na_2SO_4, and removal of the solvent gave, after crystallization from acetonitrile, 7.7 g (85%) of the acid, m.p. 134–135 °C: IR (CCl_4) 2500–3300br, 1670 (sh), 1630 (C=O) cm^{-1}; ^1H NMR (CCl_4) δ 0.25; ^{29}Si ($CDCl_3$) $\delta - 6.15$ (Me_3Si), -73.84 (SiCO) ppm: m/e 292 (M^+, 12), 277 ($(M-Me)^+$, 3), 233 ($(M-CO-Me)^+$, 12), 189 ($((Me_3Si)_2SiMe)^+$,15), 73 (Me_3Si^+, 100). Anal. Found: C, 41.12; H, 9.63. $C_{10}H_{28}O_2Si_4$ calcd.: C, 41.04; H, 9.64%.

Preparation of methyl tris(trimethylsilyl)silanecarboxylate

A solution of 1.51 g (5.2 mmol) of tris(trimethylsilyl)silanecarboxylic acid in 10 ml dry ether was treated with diazomethane until a permanent yellow colour persisted. Removal of the solvents gave a glassy liquid which could not be crystallized even after chromatography on silica gel (1.63 g, 100%). The glass melted from 85–105 °C with foaming: IR (CCl_4) 1655 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 0.23 (27H, s), 3.53 (3H, s); ^{29}Si ($CDCl_3$) $\delta - 6.34$ (Me_3Si), -74.45 (SiCO) ppm; m/e 306 (M^+, 12), 291($(M-Me)^+$, 6), 263 ($(M-Me-CO)^+$,19), 247 ($((Me_3Si)_3Si)^+$, 6), 73 (Me_3Si^+, 100); UV (C_6H_{12}); no absorption from 360 to 295 nm, and then increasing absorption to 270 nm. Anal. Found: C, 43.35; H, 9.64. $C_{11}H_{30}Si_4O_2$ calcd.: C, 43.08; H, 9.86%.

Trimethylsilyl tris(trimethylsilyl)silanecarboxylate

A mixture of tris(trimethylsilane)carboxylic acid (1.12 g, 3.8 mmol), trimethylchlorosilane (0.5 g, 4.6 mmol) and pyridine (0.5 g, 6.3 mmol) in 30 ml of dry benzene was stirred first at room temperature, and then at 40 °C for 2 h. After filtration of the pyridinium hydrochloride, evaporation to dryness under reduced pressure gave a viscous oil (1.0 g) which appeared from its ^1H NMR spectrum to be pure. The compound was very soluble in most solvents and could not be crystallized: IR (CCl_4) 1640 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 0.25 (9H, s), 0.27 (27H, s): ^{29}Si ($CDCl_3$) δ 25.10 (Me_3SiO), -6.37 (Me_3Si), -72.86 (SiCO) ppm; m/e, 364 (M^+, 3), 349 ($(M-Me)^+$, 2), 321 ($(M-Me-CO)^+$, 3), 247 ($((Me_3Si)_3Si)^+$, 4), 189 ($(Me_3Si)_2SiMe^+$, 15), 174 ($(Me_3Si)_2Si^+$, 25), 147 ($(Me_5Si_2O)^+$, 30), 73 (Me_3Si^+, 100).

Tris(trimethylsilyl)silyl tris(trimethylsilyl)silanecarboxylate

A mixture of tris(trimethylsilyl)silanecarboxylic acid (1.12 g, 3.8 mmol) trimethylchlorosilane (0.5 g, 4.6 mmol) and pyridine (0.46 g, 5.8 mmol) in 30 ml dry benzene was warmed at 50 °C for 2.5 h. The solution became yellow for a few moments. After filtration and azeotroping with benzene to remove pyridine, the resultant solution on evaporation gave a semi-solid. Chromatography on silica gel using 5% ether in pentane gave 0.4 g of colourless solid, recrystallized from acetonitrile, m.p. 184–186 °C: IR (CCl_4) 1630 cm^{-1} (C=O); ^1H NMR: (CCl_4) δ 0.20 (27H, s), 0.26 (27H, s); ^{29}Si ($CDCl_3$) $\delta - 1.98$ (Si–O), -6.22, -8.96 (each $(Me_3Si)_3Si$), -73.78 (SiCO) ppm; m/e 538 (M^+, 3), 523 ($(M-Me)^+$, 12), 465 ($(M-Me_3Si)^+$, 31), 263 ($((Me_3Si)_3SiO)^+$, 26), 247 ($((Me_3Si)_3Si)^+$, 33), 73 (Me_3Si^+,100). Anal. Found: C, 41.50; H, 9.70. $C_{19}H_{54}Si_8O_2$ calcd.: C, 42.31; H, 10.0%.

Triphenylsilyl tris(trimethylsilyl)silanecarboxylate

To a solution of the carboxylic acid (2.0 g, 6.9 mmol) and triphenylchlorosilane (2.0 g, 6.9 mmol) in 40 ml dry benzene was added 0.71 g (9 mmol) of pyridine at room temperature. A white suspension formed as the material was stirred for 2 h at

40–45 °C. After filtration through Hyflosupercel the clear filtrate was concentrated, azeotroped with benzene, and the residue crystallized from acetonitrile to give 3.2 g (85%) of solid, m.p. 156–158 °C: IR (CCl_4) 1650 cm^{-1} (C=O); ^1H NMR: (CCl_4) δ 0.2 (27H, s, Me_3Si), 7.4 (15H, br m, Ph_3Si); ^{29}Si ($CDCl_3$) δ −5.97 (Me_3Si), −5.36 (Ph_3Si), −71.81 (SiCO) ppm; m/e 550 (M^+, 5), 535 ($(M-Me)^+$,2), 477 ($(M-Me_3Si)^+$,3), 259 ($(Ph_3Si)^+$, 50), 197 ($(Ph_2MeSi)^+$, 60), 135 ($(PhSiMe_2)^+$, 100), 73 ($(Me_3Si^+$, 90). Anal. Found: C, 61.19; H, 7.73. $C_{28}H_{42}Si_5O_2$ calcd.: C, 61.02; H, 7.68%.

Thermolysis of the triphenylsilyl ester

A solid sample of ester was heated in a test tube under nitrogen as the temperature was slowly increased. Melting occurred about 157 °C, and at 187 °C gas evolution began and persisted until the temperature reached 235 °C. The 1,1,1-tris(trimethylsilyl)-3,3,3-triphenyldisiloxane residue was characterized spectroscopically and shown to be uncontaminated with other products: IR (CCl_4) 1230 (Si–Me), 1050 (Si–O) cm^{-1}; ^1H NMR: (CCl_4) δ 0.42 (27H, s), 7.5–7.9 (15H, br); m/e 522 (M^+, 8), 507 ($(M-Me)^+$, 10), 449 ($(M-Me_3Si)^+$, 90), 259 (Ph_3Si^+, 30), 236 ($PhMe_5Si_3{}^+$, 65), 197 (Ph_2SiMe^+, 70), 135 ($PhMe_2Si^+$, 100).

Photolysis of triphenylsilyl tris(trimethylsilyl)silanecarboxylate

Samples of the ester in benzene or cyclohexane were degassed, sealed, and irradiated in an NMR tube either with two mercury flood lamps ($\lambda > 360$ nm) or a 450 W Hannovia mercury lamp (λ 254 nm) for up to 4 h at 10 °C, or for up to 16 h at 70 °C. No change could be detected in the irradiated sample after 4 h, but several silyl signals were present in the NMR spectrum of the sample irradiated for 16 h.

Photolysis of methyl tris(trimethylsilyl)silanecarboxylate

A 1.0 *M* solution of the ester in C_6H_{12}, sealed under vacuum in an NMR tube was irradiated with either two 100 W lamps ($\lambda > 360$ nm) or a 450 W Hannovia lamp (λ254 nm) for 20 h with cooling. The solution remained colourless and the NMR spectrum indicated no change had occurred.

Attempted reaction of trimethylsilyl tris(trimethylsilyl) silanecarboxylate with dimethylbutadiene

A 0.15 g sample of ester in 10 ml of THF and 0.18 g of 2,3-dimethyl-1,3-butadiene was boiled under N_2 for 22 h. No change in colour was noted. Work up led to recovery of the starting material as shown by IR and NMR spectroscopy.

Formation of ester 5

To 0.50 g (1.7 mmol) of tris(trimethylsilyl)silanecarboxylic acid and 0.49 g (1.7 mmol) of tris(trimethylsilyl)chlorosilane **6**, made from $(Me_3Si)_3SiH$ and CCl_4 [7], was added 0.2 g (3 mmol) of pyridine. A precipitate (pyridinium hydrochloride) formed immediately. After 2 h at 50 °C, filtration, evaporation, and crystallization from acetonitrile gave 0.62 g (67%) of tris(trimethylsilyl)silyl tris(trimethylsilyl)silanecarboxylate, m.p. 181–183 °C, m.m.p. not depressed.

Reaction of 1 or 4 with trimethylchlorosilane

Samples of acid **1** or of the trimethylsilyl ester **4** were warmed at 50–60 °C with an excess of trimethylchlorosilane in benzene for 3–4 h. In the case of the acid, some trimethylsilyl ester was detected in the presence of the remaining unchanged acid, but in neither case could any ester **5** be detected by NMR spectroscopy.

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