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Synthesis and reactivity of bis(triethoxysilyl)methane, tris(triethoxysilyl)methane and some derivatives[1]

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Abstract

Syntheses of new poly(trifunctional-silyl)alkanes, which are potent coupling agents of hybrid organic–inorganic materials have been thoroughly examined. Optimization of the Benkeser reaction using chloroform, trichlorosilane and tri-*n*-butylamine (respective ratios 1:4.5:3) afforded bis(trichlorosilyl)methane isolated as bis(triethoxysilyl)methane after ethanolysis (overall yield 60%). With nine equivalents of trichlorosilane, tris(trichlorosilyl)methane is preferentially formed, isolated as tris(triethoxysilyl)methane (30% yield). C-Substituted bis(triethoxysilyl) methanes were obtained after metallation of the α-carbon and trapping experiments with the corresponding alkyl halides. In the case of tris(triethoxysilyl)carbanion, only MeI and Br_2 were able to give the anticipated products. Unexpectedly, CO_2 insertion afforded the stable ketene, $[(EtO)_3Si]_2C{=}C{=}O$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: *Gem*-bis(triethoxysilyl)alkanes; Bis(triethoxysilyl)carbanion; Tris(triethoxysilyl)carbanion; Bis(triethoxysilyl)ketene

1. Introduction

Hybrid organic–inorganic polymers have found recent applications in surface science, ceramic precursors, optics and electronic devices. Either used as coatings or combined in the bulk of the material, their structure allowed to incorporate many organic moieties with specific properties and functionalities in inorganic materials at the nano-size level [1–7].

The recently developed sol–gel process applied to organosilicon species offered a mild approach to the synthesis of hybrid materials with interfacial interactions and domain sizes approaching the molecular level [8]. Among them, silsesquioxanes, with the empirical formula of $R'SiO_{1.5}$, were initially obtained by the carefully controlled hydrolysis/condensation steps of trifunctional-organosilanes [9]. The monomers, with formula $R'SiX_3$ ($X = Cl$, OR, H) with non-labile Si–R′ groups ($R' =$ alkyl, aryl, etc.) and hydrolyzable Si–X bonds have been widely described [10], and many of these molecules are commercially available. Different final forms of the solid, such as gels, colloidal materials or precipitates can be observed [11]. If the R′ group presents a terminal reactive carbon center, organic chemistry can be performed for anchoring to the organic part of the hybrid material [12].

In a somewhat more direct approach, polydentate hybrid organic–inorganic xerogels [13–15] were directly synthesized in mild conditions from molecules such as bis(trialkoxysilanes), $(R'O)_3Si{-}R{-}Si(OR')_3$. These molecules, by hydrolysis of their functions –OR′, give silanols, which condense to give siloxanes of general formula $O_{1.5}Si{-}R{-}SiO_{1.5}$. Successive condensations afford a three dimensional hybrid network, in which the organic part is embedded inside the matrix. It has been observed that the formation of the solid is

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[1] Dedicated to Prof. R. Bruce King, on the occasion of his 60th birthday, in recognition of his outstanding contribution to organometallic chemistry.

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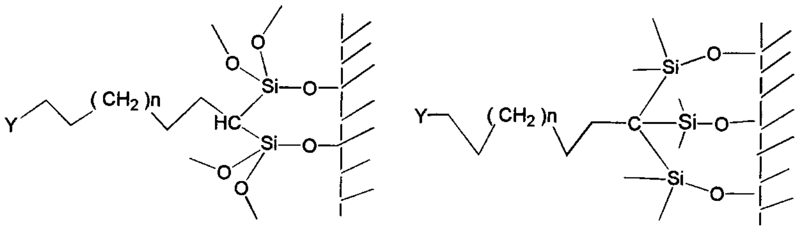


Scheme 1.

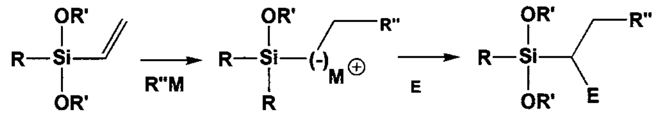
much more easy with these polysilylated precursors than with the monosilylated ones [16,17].

Most of the studies of coupling agents found in the literature for bonding between organic polymer and inorganic counterpart have been performed with mono-organosilanes [18]. Optimization of the silane to substrate interface is a key factor in the control of their properties [19].

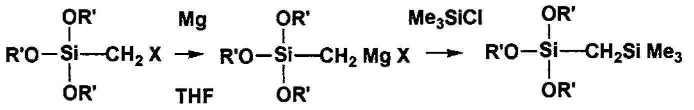
The aim of the present work is the elaboration of new synthons in the series of mono-organosilsesquioxanes with organic chains specifically bis-endcapped or tris-endcapped with tris-alkoxysilyl groups in order to produce efficient coupling agents able to create strong covalent bonds between the different phases (Scheme 1).

Different methods, available for the preparation of carbosilanes, are well documented in the case of $>C(SiR_3)_2$ or $>C(SiR_2X)_2$ derivatives [20]. For example, it has been reported that addition of *n*-BuLi to cold solutions of methylene chloride and trimethylchlorosilane in THF/hexane leads to a complexed product mixture of mono-, di- and tri-silylmethanes [21]. Some more specific results were obtained in the case of Mg/Zn coupling reaction of Me_3SiCl with CH_2Cl_2, in THF [22]. Their extension to the synthesis of $>C(SiRX_2)_2$ or $>C(SiX_3)_2$ seemed difficult, essentially due to further reactions, with for example polyadditions, intramolecular eliminations and rearrangements [23]. Disilylmethanes with functional groups at silicon were obtained from $Me_3SiCH_2SiMe_3$ by selective cleavage of methyl ligand by $AlCl_3/RCOCl$ [24], or Me_3SiCl with $AlCl_3$. Some other methods can be found in the literature, but their absence of selectivity prevents their utilization on a large scale [25]. The chemistry of compounds in which three organosilyl groups are attached to a central carbon atom has been reviewed [26].

We already described three methods in order to access such compounds: addition of Grignard reagents to vinylsilanes [27] (**eq 1**), metallation of chloromethylalkoxysilanes [28] (**eq 2**), or the Heck reaction applied to unsaturated organosilanes [29] (**eq 3**). However, the presence of alkoxy substituents on the silicon atom induced the easy cleavage of the silicon–carbon bonds of $(RO)X_2SiCH_2Y$ derivatives with oxidants [30].

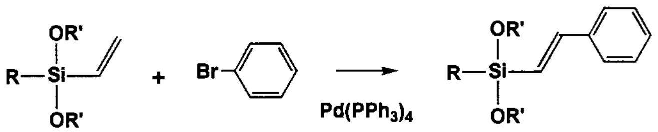


(eq 1)



$$R'O-\underset{OR'}{\overset{OR'}{Si}}-CH_2X \xrightarrow[THF]{Mg} R'O-\underset{OR'}{\overset{OR'}{Si}}-CH_2MgX \xrightarrow{Me_3SiCl} R'O-\underset{OR'}{\overset{OR'}{Si}}-CH_2SiMe_3$$

(eq 2)



(eq 3)

$$CHCl_3 + 3\ nBu_3N + 3\ HSiCl_3 \xrightarrow{CH_3CN} H_2C(SiCl_3)_2 + HC(SiCl_3)_3 \quad (eq\ 4)$$

Table 1
Coupling reactions of $ClSi(OEt)_3^a$ with CH_xX_{4-x}

No.	CH_xX_{4-x}	M	Solvent	Conditions[b]	Si products[c]
1	$CHBr_3$	n-BuLi		A	$ClSi(OEt)_3$ (6) $Si(OEt)_4$ (40) n-$BuSi(OEt)_3$ (5) $(EtO)_3Si{-}O{-}Si(OEt)_3$ (14)
2	CH_2I_2	n-BuLi	Et_2O	A	No reaction
3	CH_2Br_2	n-BuLi	Et_2O	A	$ClSi(OEt)_3$ (18) $Si(OEt)_4$ (40) n-$BuSi(OEt)_3$ (30) $(EtO)_3Si{-}O{-}Si(OEt)_3$ (7)
4				B	No reaction
5				C	No reaction
6		$Mg(\epsilon\ I_2)$	Et_2O	D	No reaction
7		Li	THF	D	$ClSi(OEt)_3$ (71) $Si(OEt)_4$ (18) $(EtO)_3Si{-}O{-}Si(OEt)_3$ (19)
8	CH_2Cl_2	n-BuLi	Et_2O	D	No reaction
9		$Mg(\epsilon\ I_2)$	Et_2O	D	No reaction
10		Li	THF	D	$ClSi(OEt)_3$ (72) $Si(OEt)_4$ (21) $(EtO)_3Si{-}O{-}Si(OEt)_3$ (7)

[a] Initial mixture of 79% $ClSi(OEt)_3$, 18% $Si(OEt)_4$, 1–3% $Cl_2Si(OEt)_2$.

[b] Experimental conditions:

(A) n-BuLi is added dropwise to a cold solution (−80°C) of chlorotriethoxysilane and halogenomethane in the proper solvent. The mixture is warmed up to r.t. and filtered.

(B) The reaction mixture of halogenomethane/n-BuLi/Et_2O maintained at −10°C, is rapidly transferred to a cold solution (−80°C) of chlorotriethoxysilane, dissolved in THF.

(C) The stoichiometric amount of chlorotriethoxysilane dissolved in THF is added immediately to the white precipitate of CH_2X_2/n-BuLi/Et_2O at −80°C

(D) To magnesium/ether or lithium/THF and $ClSi(OEt)_3$, was added dropwise a solution of halogenomethane in the proper solvent. The mixture was then refluxed for 3 h. After work up, the solvent and organics were removed at atmospheric pressure, and fractional distillation at reduced pressure yielded the organosilicon products, the mixture of them being analyzed by GC and ^{29}Si-NMR.

[c] 'No reaction' means that analysis of the mixture after work up by GC and ^{29}Si-NMR afforded only the presence of starting organosilanes, $ClSi(OEt)_3$ and $Si(OEt)_4$.

Another general method of preparation of trifunctional silicon-containing organic molecules involves silylation of polyhalo compounds by the trichlorosilane/amine combination developed by Benkeser et al. **(eq 4)** [31]. The latter reagents also effect the reduction of benzoic acids and some of its derivatives to benzylic trichlorosilanes in good yields [32].

We describe here the different approaches we have developed in order to improve the controlled syntheses of di- or tri-silicon made precursors, affording new synthons which could then be used as coatings in solid materials.

2. Results and discussion

Preliminary experiments of the coupling reaction of *geminal*-dilithiodiphenylmethane [33] with $ClSi(OEt)_3$ afforded only oligomeric materials. From the reaction of CH_nX_{4-n} with $ClSi(OEt)_3$ in the presence of n-BuLi (Table 1), the only product was n-$BuSi(OEt)_3$ which corresponds to the normal substitution of the Si–Cl bond with n-$Bu^{(-)}$ anion. In the case of Li/THF activation, the lithium wires were consumed with formation of a black turbid mixture. However, the only change of the silicon species was a small modification in the ratios of $ClSi(OEt)_3$, $Si(OEt)_4$ and $(EtO)_2SiCl_2$ which moved from the relative ratios 79:18:3 to 72:21:7, with formation of hexaethoxydisiloxane $(EtO)_3Si{-}O{-}Si(OEt)_3$. With Mg/Et_2O, no reaction was observed, despite the fact that a precipitate of magnesium salt was present in the mixture, corresponding to some extent of reaction of CH_nX_{4-n} with Mg. The trimeric 1,3,5-(diethoxysila)-cyclohexane, $[(EtO)_2Si{-}CH_2]_3$, was characterized as the main decomposition product of the metallation of $(EtO)_3$ $Si{-}CH_2Cl$ with Mg/THF at room temperature (r.t.) [34]. The trimer has never been detected in the present case by ^{29}Si-NMR of the crude reaction mixtures, which indicates that $(EtO)_3Si{-}CH_2MgX$ (respectively $(EtO)_3Si{-}CH_2Li$) is not formed in our experimental conditions.

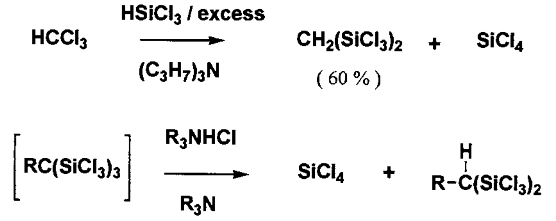
In the absence of efficient synthesis of *gem*-disilylmethanes through the metallation process, we decided to turn our efforts to another approach. The alcoholysis of $H_{n+2}C(SiCl_3)_{3-n}$ has been described [35]. Some results have been reported concerning the synthesis of these chlorosilylalkanes on the laboratory scale with scarce yield [36]. In 1969, Benkeser et al. proposed a different method of forming the silicon–carbon bond (**eq 4**), based on the selective reduction of poly-halo compounds with $HSiCl_3$/*n*-Bu_3N. However, if the method was highly efficient for synthesizing benzylic silanes and analogues, the extension to alkyl halides and polyhalocarbons was unsuccessful, essentially due to the reaction of trichlorosilanes with R_3NHCl in the experimental conditions (Scheme 2) [37].

We therefore decided to prepare the expected compounds in two steps. Initially, we would form the bis(trifunctional-silyl)methanes and tris(trifunctional-silyl)methanes, which could then be metallated on the α-carbon and trapped with the corresponding alkyl halides (Scheme 3).

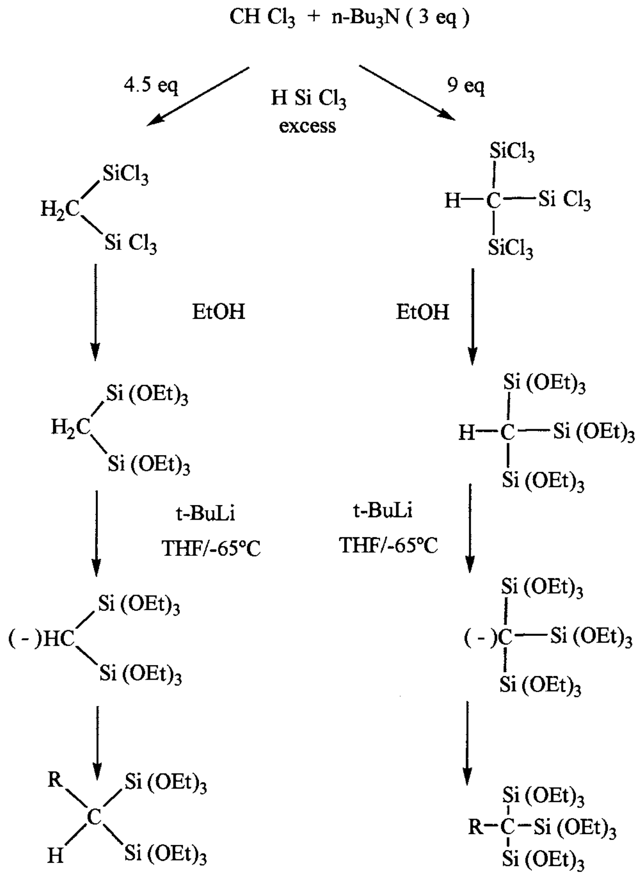
Thus, when chloroform, trichlorosilane and tri-*n*-butylamine are allowed to react in the ratio 1:4.5:3, bis(trichlorosilyl)methane is obtained in 90% yield in the crude mixture, later isolated as bis(triethoxysilyl)methane after ethanolysis (overall yield 60%). On the other hand, if a large excess (nine equivalents) of silicochloroform is introduced in the reaction medium, tris(trichlorosilyl)methane is formed, isolated as tris(triethoxysilyl) methane (30%).

That result deserves some comments. The tris(trichlorosilyl)methane was envisioned by Benkeser et al. [38] in the reactions of trichlorosilane–tertiary amines with organic halides (Scheme 2), but not characterized even as transient species. Conditions used by these authors supposed that cleavage of one of the silicon–carbon bonds in tris(trichlorosilyl) methane to obtain the bis(trichlorosilyl) derivative was a preferred pathway under their conditions of reaction. Our procedure describes the conditions affording both types of compounds with reproducible yields.

As an example of the general protocol we have used, 0.045 mol of $HSiCl_3$, 0.01 mol of $CHCl_3$ and 5 ml of freshly distilled acetonitrile were mixed at −40°C, and tri-*n*-butylamine (0.03 mol) was added dropwise to form a waxy precipitate. Warming up the turbid mixture to r.t., a clean solution was obtained. The mixture was refluxed for 16 h. After concentration in vacuo and addition of 200 ml of pentane, emulsification was observed with two phases. The lower pale white layer contained ammonium/amine species.



Scheme 2.

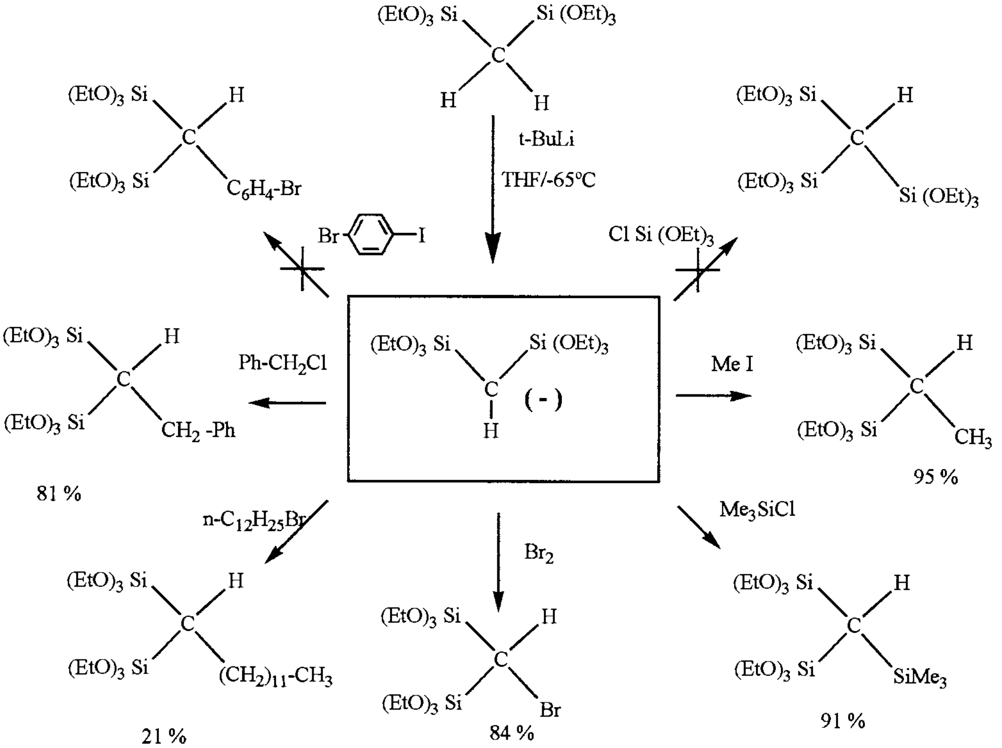


Scheme 3.

At this stage, two different treatments were possible. The upper pentane layer was first concentrated in vacuo and distillation afforded the expected bis(trichlorosilyl) methane in 50% yield (with some thermal decomposition). The second possibility we experienced was to perform the alcoholysis of the pentane extract; formation of a precipitate showed that NR_3 was partially soluble in the upper mixture. After filtration, distillation afforded $(EtO)_3SiCH_2Si(OEt)_3$, with 50% yield.

In a one-pot procedure, ethanolysis of the crude two phases mixture at −40°C afforded the bis(triethoxysilyl)methane with >90% purity, in the upper pentane phase material (GC/MS). Distillation (with some decomposition) afforded analytical sample whose characteristics were comparable with those of authentic compound [34] (overall yield 60%).

A similar procedure was followed to obtain tris(triethoxysilyl)methane from chloroform (2 mmol), $HSiCl_3$ (18 mmol) and tri-*n*-butylamine (6 mmol) in 5 ml of acetonitrile. After work up, ethanolysis with 36 mmol



Scheme 4. Trapping experiments with the bis(triethoxysilyl)carbanion.

of EtOH afforded the expected compound which was isolated by distillation at 100°C (10^{-2} mm Hg), 30% yield. In the first fraction, we isolated the bis(triethoxysilyl)methane (50% yield).

Metallation of bis(triethoxysilyl)methane, with *t*-BuLi, in pentane/THF, was performed at -65°C in 1 h. Various electrophiles were added at that temperature and the mixtures warmed up for an additional 3 h. Work up afforded the products, which were analyzed by GC/MS (Scheme 4).

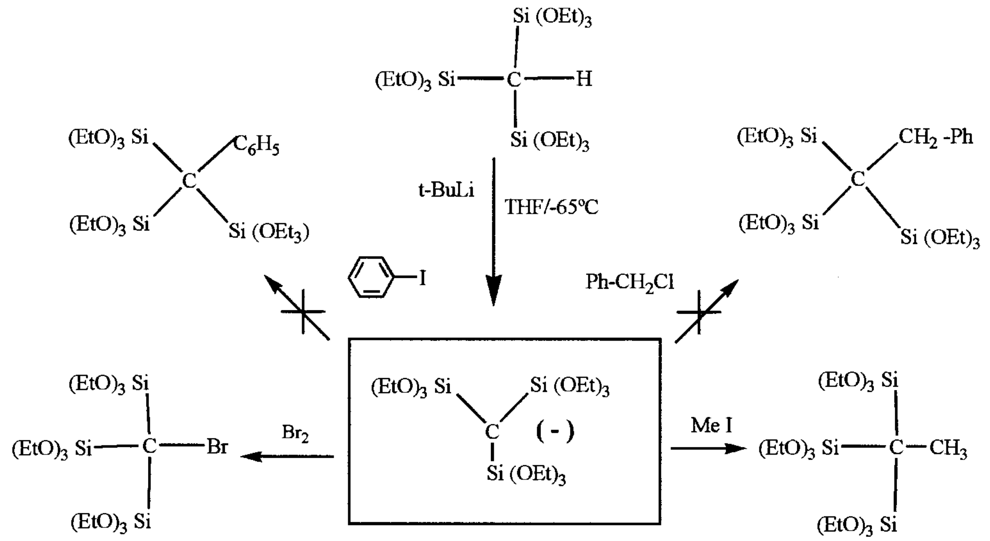
Aromatic halides were unreactive with the disilyl-carbanion, whereas strong electrophiles gave the expected products in fairly good yields. The *gem*-disilylbromomethane afforded the expected bis(triethoxysilyl)ethane by substitution with MeLi, whereas *trans* metallation was observed with PhLi giving PhBr and bis(triethoxysilyl)methane, the carbanion being trapped by reaction with the solvent.

A similar procedure of metallation was used in the case of tris(triethoxysilyl)methane (Scheme 5). In trapping essays with PhI and $PhCH_2Cl$, the starting material is recovered. Only MeI and Br_2 were able to give the expected products. An unexpected reaction occurred with CO_2. Insertion and rearrangement afforded the stable ketene, $[(EtO)_3Si]_2C{=}C{=}O$, which probably is formed by intramolecular elimination of the silanolate (Scheme 6).

That rearrangement emphasizes the particular behavior of the alkoxysilyl groups to induce specific reactivity at the α-carbanion [39]. The comparison with the normal carbonation of [tris(trimethylsilyl)methyl] lithium which affords the carboxylic acid after protonation [40], without decomposition is typical. Interconversion of 1-trimethylsiloxy-2-silylethynes to trimethylsilyl(silyl)ketenes has been recently discussed [41]. IR analysis of the crude mixture showed that siloxyacetylene was not present in our experimental conditions. The spectrum shows characteristic, strong IR absorption band at 2110 cm^{-1} due to the ketene vibrations. Only one signal at δ -56.9 ppm is observed in the ^{29}Si-NMR spectrum and the ^{13}C chemical shift of the sp^2-hybridized carbon at δ 1.35 ppm is characteristic of silylketene [42].

3. Conclusion

The present work describes the different approaches we have tried to optimize the elaboration of reactive synthons in the series of mono-organosilsesquioxanes with organic chains specifically bis-endcapped or tris-endcapped with tris-alkoxysilyl groups. The synthesis of *gem*-disilylmethanes through the metallation process were not successful. An optimization of the Benkeser



Scheme 5. Trapping experiments with tris(triethoxysilyl)carbanion.

reaction, based on the selective reduction of poly-halo compounds with $HSiCl_3$/*n*-Bu_3N allowed to obtain bis(trifunctional-silyl)methanes and tris(trifunctional-silyl)methanes with yield ranging 30–80%. These compounds could then be metallated on the α-carbon and trapped with electrophiles. Aromatic halides were unreactive with the disilyl-carbanion, whereas strong electrophiles gave the expected products in fair yields. Only MeI and Br_2 were able to react with tris(triethoxysilyl)carbanion. With CO_2, insertion and rearrangement afforded the stable ketene, $[(EtO)_3Si]_2$ C=C=O.

4. Experimental

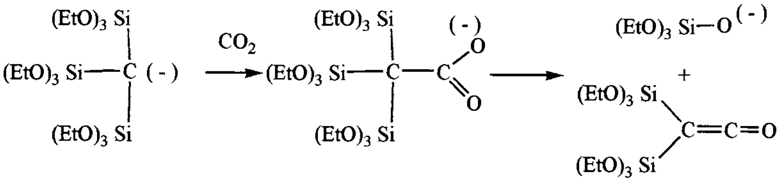
All reactions were carried out under argon or nitrogen with dry solvents. ^{1}H-NMR spectra were recorded on a Bruker DPX 200 spectrometer with TMS as an internal reference. ^{29}Si and ^{13}C-NMR spectra were recorded on a Bruker DPX 200 or a Bruker SP 250 AC instrument. Mass spectra were recorded on a Delsi Nermag gaz chromatograph coupled with an Auto mass spectrometer [diphenyl (5%) dimethylsilicone as stationary phase, electron impact mode, 70 eV] or on a Jeol DX 300 spectrometer (electron impact mode, 70 eV). IR spectra were recorded on a Perkin Elmer 1600 spectrophotometer with polystyrene film used for calibration. Elementary analysis were performed by the 'Service Central d'Analyse du CNRS France'. Carbon and hydrogen contents were established by high temperature combustion and IR spectroscopy. Silicon contents were determined by ICP atomic emission spectroscopy.

4.1. Preparation of bis(triethoxysilyl)methane

Tri-*n*-butylamine (11.1 g, 60 mmol) was added dropwise to a mixture of chloroform (2.4 g, 20 mmol), trichlorosilane (12.2 g, 90 mmol) and acetonitrile (5 ml) at -40°C. The solution was allowed to warm up and stirred overnight at 65°C. After removal of the solvent in vacuo, pentane (50 ml) was added. To this mixture cooled to -40°C was added ethanol (14.1 ml, 240 mmol). After warming up to r.t., extraction with pentane (2×50 ml) and concentration in vacuo, the residue was distilled at 80°C (10^{-2} mm Hg) giving a colorless liquid (yield 60%). ^{1}H-NMR ($CDCl_3$): δ − 0.03 (s, 2H, CH_2Si); 1.21 (t, $J_{HH} = 7.0$ Hz, 18H, CH_3); 3.82 (q, $J_{HH} = 7.0$ Hz, 12H, CH_2O). ^{13}C-NMR: δ − 7.50 (CH_2Si); 18.43 (CH_3); 58.56 (CH_2O). ^{29}Si-NMR: δ -46.12. Mass spectrum (70 eV): *m/e* 295 [$M^+ - 45$ (EtO), 100%]; 267 [$M^+ - 45$ (EtO) $- 28$ (C_2H_4), 64%]; 163 [$(EtO)_3Si^+$, 33%]; 135 [$(EtO)_3Si^+ - 28$ (C2H4), 7.7%]; 45 (EtO^+, 17%). Anal. Calc. for $C_{13}H_{32}O_6Si_2$: C, 45.85; H, 9.47; Si, 16.49; O, 28.19. Found: C, 45.92; H, 9.52; Si, 16.56.

4.2. Preparation of tris(triethoxysilyl)methane

Tri-*n*-butylamine (11.1 g, 60 mmol) was added dropwise to a mixture of chloroform (2.4 g, 20 mmol), trichlorosilane (24.4 g, 180 mmol) and acetonitrile (5 ml) at -40°C. The solution was allowed to warm up, stirred overnight at r.t. for 1 h at 65°C. After removal of the solvent in vacuo, pentane (50 ml) was added. To the mixture cooled at -40°C was added ethanol (21.1 ml, 360 mmol). After warming up to r.t., extraction with pentane (2×50 ml) and concentration in vacuo,



Scheme 6. Carbonation of tris(triethoxysilyl)carbanion.

a colorless liquid (yield 30%). ^1H-NMR ($CDCl_3$): δ -0.09 (s, 1H, CHSi); 1.22 (t, $J_{HH} = 7.0$ Hz, 27H, CH_3); 3.87 (q, $J_{HH} = 7.0$ Hz, 18H, CH_2O). ^{13}C-NMR: δ -4.41 (CHSi); 18.28 (CH_3); 58.58 (CH_2O). ^{29}Si-NMR: δ -49.88. Mass spectrum (70 eV): *m/e* 457 [$M^+ - 45$ (EtO), 100%]; 429 [$M^+ - 45$ (EtO) $- 28$ (C_2H_4), 3.3%]; 163 [$(EtO)_3Si^+$, 22%]; 135 [$(EtO)_3Si^+ - 28$ (C_2H_4), 1.9%]; 45 (EtO^+, 28%). Anal. Calc. for $C_{19}H_{46}O_9Si_3$: C, 45.39; H, 9.22; Si, 16.76. Found: C, 45.46; H, 9.27; Si, 16.65.

4.3. Synthesis of [bis(triethoxysilyl)methyl] lithium salt

To a THF solution (50 ml) of bis(triethoxysilyl)methane (0.68 g, 2 mmol), at -80°C was added dropwise the stoichiometric amount of *t*-BuLi in pentane. After the mixture was stirred for 1 h at -65°C, the lithium salt was ready to use.

4.4. Synthesis of 1,1-bis(triethoxysilyl)ethane

To a solution of [bis(triethoxysilyl)methyl] lithium salt (2 mmol, 30 ml THF) at -80°C was added methyl iodide (6 mmol, 0.85 g). After the solution was warmed up to r.t. and the solvent removed in vacuo, the residue was treated with pentane and filtered. After evaporation of the solvent, the product was obtained as a colorless liquid (0.67 g, 95% yield). ^1H-NMR ($CDCl_3$): δ 0.23 (q, $J_{HH} = 7.6$ Hz, 1H, CH); 1.12 (d, $J_{HH} = 7.6$ Hz, 3H, $C\underline{H}_3$–CH); 1.19 (t, $J_{HH} = 7.0$ Hz, 18H, $C\underline{H}_3$–CH_2O); 3.83 (q, $J_{HH} = 7.0$ Hz, 12H, CH_2O). ^{13}C-NMR: δ 0.34 (CH); 8.22 ($\underline{C}H_3CH$); 18.53 ($\underline{C}H_3$–CH_2); 58.74 (CH_2O). ^{29}Si-NMR: δ -46.02. Mass spectrum (70 eV): *m/e* 309 [$M^+ - 45$ (OEt), 86%]; 281 [$M^+ - 45$ (EtO) $- 28$ (C_2H_4), 62%]; 163 [$(EtO)_3Si^+$, 54%]; 135 [$(EtO)_3Si^+ - 28$ (C_2H_4), 100%]; 45 (EtO^+, 43%).

4.5. Synthesis of [bis(triethoxysilyl)](trimethylsilyl) methane

To a solution of [bis(triethoxysilyl)methyl] lithium salt (2 mmol, 30 ml THF) at -80°C, was added chlorotrimethylsilane (6 mmol, 0.65 g). After the solution was warmed up to r.t. and the solvent removed, the residue was treated with pentane and filtered. After evaporation of the solvent, the compound was isolated by distillation (b.p. 96–98°C, 10^{-2} mm Hg), 91% yield. ^1H-NMR ($CDCl_3$); δ -0.42 (s, 1H, CH); 0.11 (s, 9H, CH_3Si); 1.18 (t, $J_{HH} = 7.0$ Hz, 18H, CH_3–C); 3.81 (q, $J_{HH} = 7.0$ Hz, 12H, CH_2). ^{13}C-NMR: δ -1.67 (CH); 1.94 (CH_3–Si); 18.44 ($\underline{C}H_3$–C); 58.54 (CH_2).^{29}Si-NMR: δ -47.91 [$Si(OEt)_3$]; 0.54 ($SiMe_3$). Mass spectrum (70 eV): *m/e* 397 [$M^+ - 15$ (Me), 100%]; 367 [$M^+ - 45$ (OEt), 15%]; 163 [$(EtO)_3Si^+$, 25%]; 73 (Me_3Si^+, 6.4%); 45 (EtO^+, 8.2%).

4.6. Synthesis of 1,1-bis(triethoxysilyl)-2-phenylethane

To a solution of [bis(triethoxysilyl)methyl] lithium salt (2 mmol, 30 ml THF) at -80°C was added benzyl chloride (6 mmol, 0.76 g). After the solution was warmed up to r.t. and the solvent removed, the residue was treated with pentane and filtered. After evaporation of the solvent, the compound was isolated by distillation (b.p. 121–124°C, 10^{-2} mm Hg), 81% yield. ^1H-NMR ($CDCl_3$): δ 0.64 (t, $J_{HH} = 6.7$ Hz, 1H, CH); 1.22 (t,$J_{HH} = 7.0$Hz, 18H,CH_3); 2.97 (d ,$J_{HH} = 6.7$ Hz, 2H, CH_2Ph); 3.82 (q, $J_{HH} = 7.0$ Hz, 12H, CH_2O); 7.2–7.4 (m, 5H, H_{arom}). ^{13}C-NMR: δ 11.09 (CHSi); 18.56 (CH_3); 30.11 (CH_2Ph); 58.71 (CH_2O); 125.79, 128.26, 129.11, 144.80 (C_{arom}). ^{29}Si-NMR: δ -47.81. Mass spectrum (70 eV): *m/e* 384 [$M^+ - 46$ (EtOH), 100%]; 163 [$(EtO)_3Si^+$, 21%]; 91 ($PhCH_2^+$, 37%]; 45 (EtO^+, 10%).

4.7. Synthesis of bis(triethoxysilyl)bromomethane

To a solution of [bis(triethoxysilyl)methyl] lithium salt (2 mmol, 30 ml THF) at -80°C was added bromine (3 mmol, 0.48 g). After the solution was warmed up to r.t. and the solvent removed, the residue was treated with pentane and filtered. After evaporation of the solvent, the compound was isolated by distillation (b.p. 95–97°C, 10^{-2} mm Hg), 67% yield. ^1H-NMR ($CDCl_3$): δ 1.15 (t, $J_{HH} = 7.0$ Hz, 18H, CH_3); 2.08 (s, 1H, CH); 3.83 (q, $J_{HH} = 7.0$ Hz, 12H, CH_2). ^{13}C-NMR: δ 10.14 (CH); 18.35 (CH_3); 59.60 (CH_2). ^{29}Si-NMR: δ -58.13. Mass spectrum (70 eV): *m/e* 373 ($M^+ - 44$, 3.0%); 375 [$(M^+ + 2) - 44$, 3.1%]; 163 [$(EtO)_3Si^+$, 48%]; 45 (EtO^+, 100%).

4.8. Synthesis of 1,1-bis(triethoxysilyl)tridecane

To a solution of [bis(triethoxysilyl)methyl] lithium salt (2 mmol, 30 ml THF) at −80°C was added 1-bromododecane (4 mmol, 0.98 g). After the solution was warmed up to r.t. and the solvent removed, the residue was treated with pentane and filtered. After evaporation of the solvent, the compound was isolated by distillation (b.p. 150–160°C, 10^{-2} mm Hg), 21% yield. ^{1}H-NMR ($CDCl_3$): δ 0.18 (t, $J_{HH} = 6.6$ Hz, CH, 1H); 0.86 (t, $J_{HH} = 6.5$ Hz, 3H, CH_3); 1.20 (t, $J_{HH} = 7.0$ Hz, 18H, CH_3); 1.24 (m, 18H, CH_2); 1.44 (m, 2H, CH_2); 1.56 (m, 2H, CH_2); 3.83 (q, $J_{HH} = 7.0$ Hz, 12H, CH_2O). ^{13}C-NMR: δ 8.09 (CHSi); 14.37 (CH_3); 18.53 (CH_3); 23.02, 24.29, 29.71, 29.82, 30.01, 30.25, 32.28, 32.56 (CH_2); 58.65 (CH_2O). ^{29}Si-NMR: δ −46.67. Mass spectrum (30 eV): *m*/*e* 463 [$M^+ - 45$ (EtOH), 72%]; 163 [$(EtO)_3Si^+$, 100%]; 57 ($C_4H_9^+$, 16%); 45 (EtO^+, 3.2%).

4.9. Synthesis of [tris(triethoxysilyl)methyl] lithium salt

To a THF solution (50 ml) of tris(triethoxysilyl)methane (1.0 g, 2 mmol) at −80°C was added dropwise the stoichiometric amount of *t*-BuLi in pentane. After the mixture was stirred for 1 h at −65°C, the lithium salt was ready to use.

4.10. Synthesis of 1,1,1-tris(triethoxysilyl)ethane

To a solution of [tris(triethoxysilyl)methyl] lithium salt (2 mmol, 30 ml THF) at −80°C, was added methyl iodide (6 mmol, 0.85 g). After the solution was warmed up to r.t. and the solvent evaporated, the residue was treated with pentane and filtered. The product was then isolated by distillation (b.p. 106–107°C, 10^{-2} mm Hg), 74% yield. ^{1}H-NMR ($CDCl_3$): δ 1.20 (t, $J_{HH} = 7.0$ Hz, 27H, $C\underline{H}_3CH_2$); 1.30 (s, 3H, CH_3–C); 3.90 (q, $J_{HH} =$ 7.0 Hz,, 18H, CH_2–O). ^{13}C-NMR: δ 3.57 (C–Si); 18.50 ($\underline{C}H_3$–CH_2 and $\underline{C}H_3$–C); 59.50 (CH_2O). ^{29}Si-NMR: δ −50.33. Mass spectrum (70 eV): *m*/*e* 471 [$M^+ - 45$ (EtO), 100%]; 163 [$(EtO)_3Si^+$, 15%]; 45 (EtO^+, 100%).

4.11. Synthesis of tris(triethoxysilyl)bromomethane

To a solution of [tris(triethoxysilyl)methyl] lithium salt (2 mmol, 30 ml THF) at −80°C was added bromine (3 mmol, 0.48 g). After the solution was warmed up to r.t. and the solvent was removed, the residue was treated with pentane and filtered. The product was then isolated by distillation (b.p. 109–113°C, 10^{-2} mm Hg), 62% yield. ^{1}H-NMR ($CDCl_3$): δ 1.24 (t, $J_{HH} = 7.0$ Hz, 27H, CH_3); 3.97 (q, $J_{HH} = 7.0$ Hz, 18H, CH_2). ^{13}C-NMR: δ 16.64 (C–Si); 18.36 (CH_3); 60.32 (CH_2). ^{29}Si-NMR: δ −60.16. Mass spectrum (70 eV): *m*/*e* 535 [$M^+ - 45$ (OEt), 5.5%]; 537 [$(M^+ + 2) - 45$ (OEt), 5.7%]; 163 [$(EtO)_3Si^+$, 72%]; 45 (EtO^+, 100%).

4.12. Synthesis of bis(triethoxysilyl)ketene

To a solution of [tris(triethoxysilyl)methyl] lithium salt (2 mmol, 30 ml THF) at −80°C, was added a large excess (~ten equivalents) of CO_2 (dry ice). After the solution was warmed up to r.t. and the solvent removed, the residue was treated with pentane and filtered. After evaporation of the solvent, the product was obtained as a colorless liquid (0.71 g, 97%). ^{1}H-NMR ($CDCl_3$): δ 1.24 (t, $J_{HH} = 7.0$ Hz, 18H, CH_3); 3.88 (q, $J_{HH} = 7.0$ Hz, 12H, CH_2). ^{13}C-NMR: δ 1.35 (Si–C=); 18.35 (CH_3); 59.31 (CH_2); 167.70 (=C=O). ^{29}Si-NMR: δ −56.90. IR ($CDCl_3$): 2110 cm^{-1} (s). Mass spectrum (70 eV): *m*/*e* 366 (M^+, 4.2%); 321 [$M^+ - 45$ (OEt), 22%]; 294 (100%); 45 (EtO^+, 36%).

4.13. Synthesis of chlorotriethoxysilane

To a pentane solution (70 ml) of silicon tetrachloride (17 g, 0.1 mol) at −70°C, was added dropwise ethanol (20 ml, 0.34 mol). After being warmed up to r.t., the solution was stirred overnight. The product was then purified by distillation (b.p. 90–92°C, 71 mm Hg). A mixture (15.3 g) was obtained, containing dichlorodiethoxysilane (1%), chlorotriethoxysilane (80%) and tetraethoxysilane (19%), composition being determined by GC/MS. Characteristic data for chlorotriethoxysilane: ^{1}H-NMR ($CDCl_3$): δ 1.25 (t, $J_{HH} = 7.0$ Hz, 9H, CH_3); 3.89 (q, $J_{HH} = 7.0$ Hz, 6H, CH_2). ^{13}C-NMR: δ 17.92 (CH_3); 60.40 (CH_2). ^{29}Si-NMR: δ −70.26. Mass spectrum (70 eV): *m*/*e* 197 ($M^+ - 1$, 27%); 199 ($M^+ + 1$, 11%); 169 (100%); 163 [$(EtO)_3Si^+$, 15%]; 45 (EtO^+, 27%). Characteristic data for tetraethoxysilane: ^{1}H-NMR ($CDCl_3$): δ 1.23 (t, $J_{HH} = 7.0$ Hz, 12H, CH_3); 3.84 (q, $J_{HH} = 7.0$ Hz, 8H, CH_2). ^{13}C-NMR: δ 18.35 (CH_3); 59.42 (CH_2). ^{29}Si-NMR: δ −81.80. Mass spectrum (70 eV): *m*/*e* 208 (M^+, 9.5%); 193 ($M^+ - 15$, 100%); 163 [$M^+ - 45$ (OEt), 62%]; 45 (EtO^+, 7.1%). Characteristic data for dichlorodiethoxysilane: Mass spectrum (70 eV): *m*/*e* 187 ($M^+ - 1$, 6.2%); 189 ($M^+ + 1$, 4.3%); 173 ($M^+ - 15$, 100%); 175 [$(M^+ + 2) - 15$, 65%]; 45 (EtO^+, 4.2%).

4.14. Reaction of bis(triethoxysilyl)bromomethane with methyllithium

To a THF solution (30 ml) of bis(triethoxysilyl)bromomethane (0.84 g, 2 mmol) at −80°C was added a stoichiometric amount of MeLi in solution in diethylether. After the solution was warmed up to r.t. and the solvent removed, the residue was treated with pentane and filtered. After evaporation of the solvent, 1,1-bis(triethoxysilyl)ethane was obtained as a colorless liquid (0.58 g, 82% yield), identified by GC and NMR spectroscopy by comparison with an authentic sample (see above).

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