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The reaction of tris(trimethylsilyl)silyllithium with aliphatic ketones

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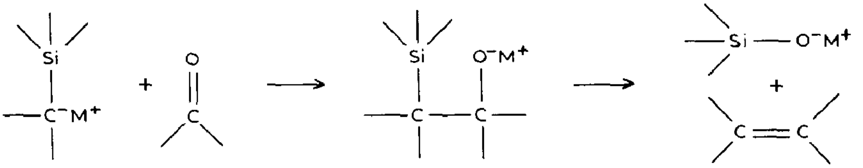
Abstract

Under certain conditions tris(trimethylsilyl)silyllithium (**1**) reacts with aliphatic ketones to give geminal [bis(trimethylsilyl)silyl]-trimethylsiloxyalkanes (**2–6**) or geminal [bis(trimethylsilyl)silyl][tris(trimethylsilyl)silyl]alkanes (**7–10**). The formation of these products is the result of the addition of **1** to the carbonyl group of the ketone (to give intermediate **A**) followed by a 1,3-*Si*,*O*-trimethylsilyl shift to give intermediate **B** ($(Me_3Si)_2Si(Li)CR^1R^2OSiMe_3$; R^1, R^2 = Me, Me; Me, Et; Me, i-Pr; Et, Et; $(CH_2)_5$), which is protonated to yield **2–6**. In presence of excess **1** the siloxy group in **B** is substituted to give **7–10** after hydrolytic work up. Studies of the interaction of **1** with acetone revealed that the negative charge at the silicon atom in **B** is essential for this substitution which leads first to the anionic intermediate **C** [$(Me_3Si)_2Si(Li)CMe_2Si(SiMe_3)_3$] that can be trapped with deuterium oxide to give deuterated **7** or with chlorotrimethylsilane resulting in formation of 2,2-bis[tris(trimethylsilyl)silyl]propane (**11**). The ^{1}H NMR spectra of **7–11** reveal the strong intramolecular interactions that seriously hinder internal rotations around the R^1R^2C–Si bonds. The results of the entire study are discussed with regard to application of the reactions investigated to the synthesis of Si=C double bond systems.

Introduction

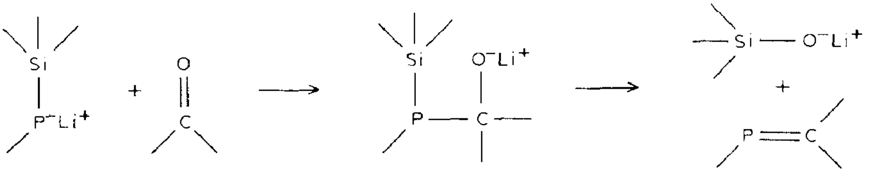
The Peterson reaction is a well established method for preparing olefins and functionalized alkenes [1,2]. The general reaction (eq. 1) involves addition of an α-silylcarbanion to the carbonyl group of an aldehyde or ketone to give a β-silyl alkoxide, which finally eliminates silanolate to yield the alkene. A number of



(1)

excellent studies have been published on the stereochemistry of the reaction and have shown that diastereoisomerically pure β-hydroxyalkylsilanes in presence of base undergo *syn*-elimination, i.e. the second step of the reaction is stereospecific [3,4]. But there is a lack of fine-mechanistic details e.g. the role of a four-centered oxasiletanide anion as a transition state, and particularly the question of an initial 1,3-*C*,*O*-trimethylsilyl shift involving a β-siloxy carbanion transition state [5] still appear to be open.

The Peterson olefination is one version of a general reaction principle, the parent process being the Wittig reaction. In both reactions the carbanion in the starting material as well as the electrophilic phosphonio or silyl group, can be replaced by other suitable functions [1]. The interaction of these related species with aldehydes or ketones leads to phosphine oxides, phosphates, silanolates, sulfurous amides, borinates etc. and to the respective double bond system. An interesting example is the reaction of lithium trimethylsilylphosphides with carbonyl derivatives, which was used for the synthesis of phosphorus carbon double bond systems [6]. The lithium phosphide reacts with the carbonyl group to give an addition product which decomposes spontaneously in a Peterson-type reaction to form lithium silanolate and the respective phosphaalkene (eq. 2). The same mechanism is followed by the NaOH-catalyzed hexamethyldisiloxane elimination from α-trimethylsiloxytrimethylsilylphosphines to form alkylidenephosphines [6a,7] and from α-trimethylsiloxy-*P*-trimethylsilylphosphaalkenes to give alkylidynephosphines [8].



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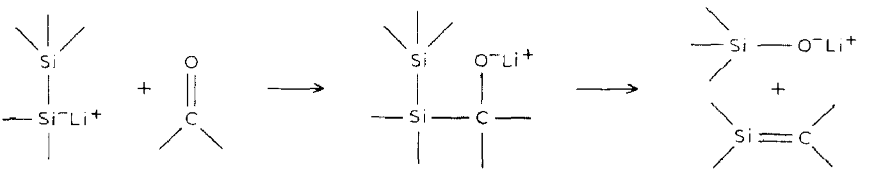
Our efforts to find a new synthetic route to silicon carbon double bond systems entarded attempts to modify the previously discussed reaction paths in a way that α-disilanylalkoxides, made by the interaction of the disilyllithium derivatives with aldehyde or ketone, should eliminate silanolate like the Peterson mechanism, to result in the silene (eq. 3). The substitution pattern determines whether the silenes are isolable, can be detected as dimers or whether they can be trapped.



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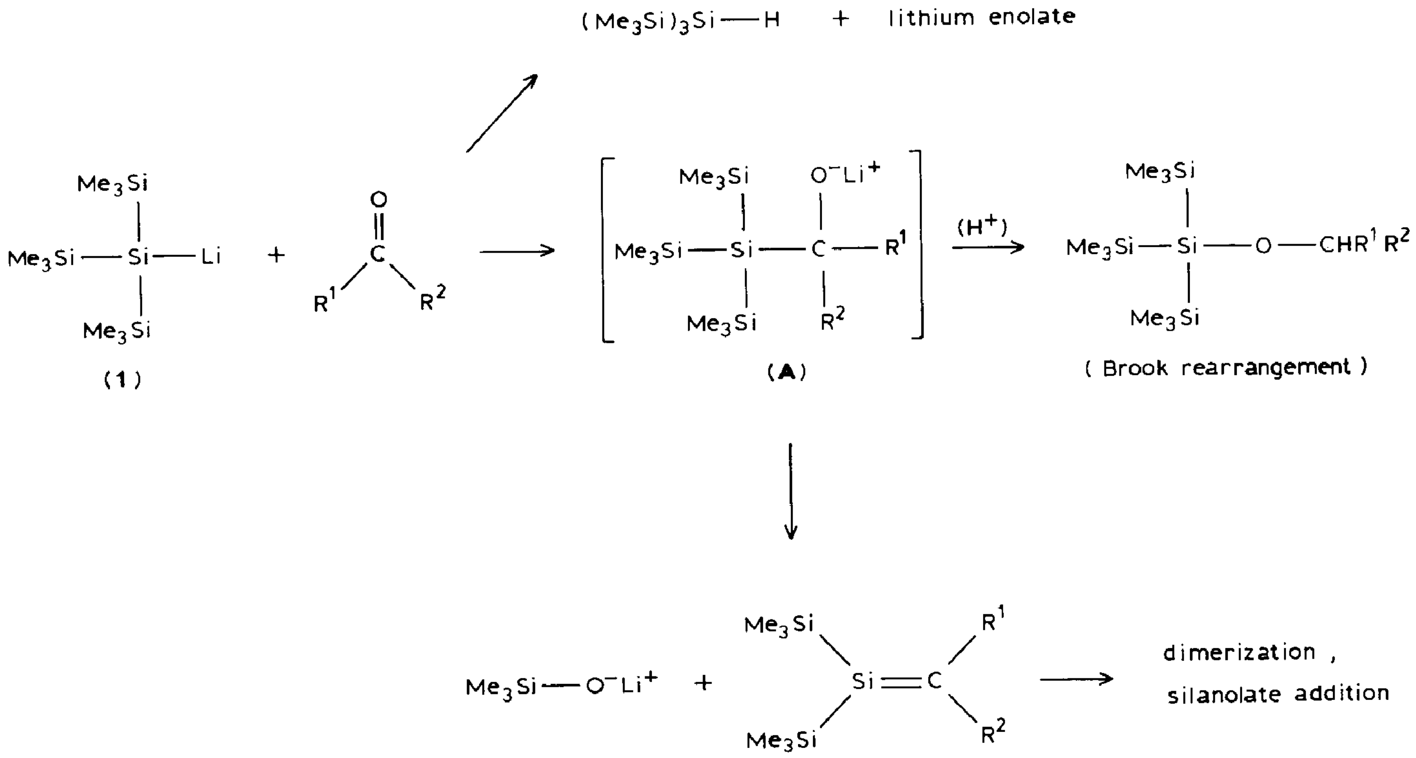
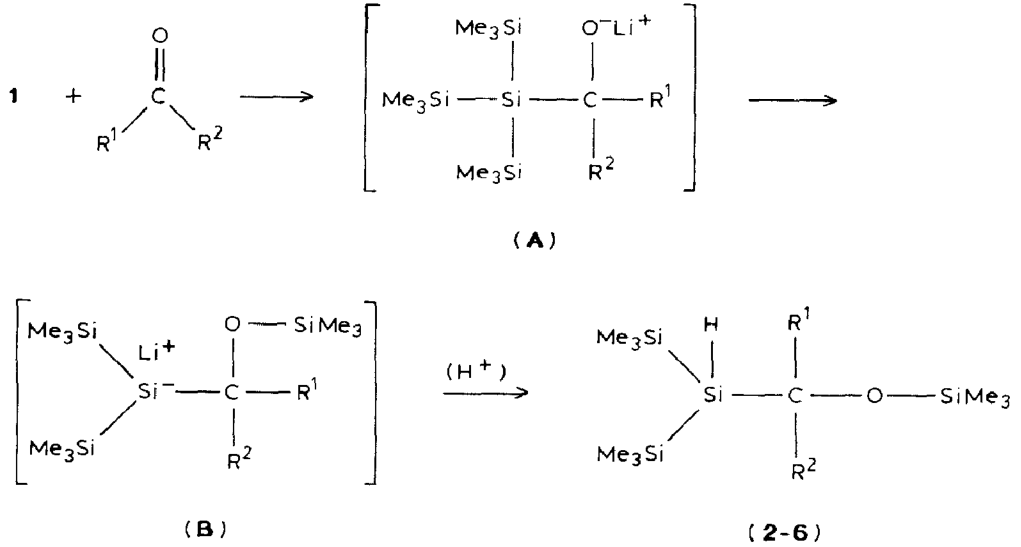
Results and discussion

We have chosen the interaction of tris(trimethylsilyl)silyllithium (**1**) with ketones as the example in these studies. Cleavage of tetrakis(trimethylsilyl)silane by methyllithium readily gives **1** [9]. It was expected that **1** would add to the carbonyl group of the ketone to give intermediate **A** which in turn decomposes to give lithium trimethylsilanolate and the respective silene (Scheme 1). When R^1 and R^2 are small aliphatic groups, the resulting silene is not expected to be stable enough for


(Me3Si)3Si—H + lithium enolate
(1)
(A)
(H+)
(Brook rearrangement)
dimerization ,
silanolate addition

Scheme 1



	R^1	R^2
2	CH_3	CH_3
3	CH_3	C_2H_5
4	CH_3	$i\text{-}C_3H_7$
5	C_2H_5	C_2H_5
6	—$(CH_2)_5$—	

Scheme 2

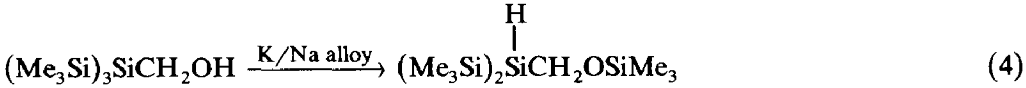
isolation, but should be detectable as the dimer. Furthermore reverse addition of the eliminated lithium trimethylsilanolate to the polarized Si=C bond is possible. With enolizable ketones protonation of the silyl anion **1** may also occur. Furthermore, isomerization of intermediate **A** to give after protonation the alkoxysilane because the Brook rearrangement [10] must be taken into account.

As described previously concerning the interaction of **1** with acetone [11] if a tetrahydrofuran solution of **1** at −30 °C is added to the aliphatic ketone the geminal [bis(trimethylsilyl)silyl]trimethylsiloxyalkanes (**2**–**6**) are formed. The expected protonation of **1** by the enolizable ketones, which predominates at room temperature, can be suppressed by decreasing the reaction temperature so that addition of the Si-nucleophile to the carbonyl group is favoured. Thus only traces of tris(trimethylsilyl)silane were obtained. Products originating from an intermediate silene or from compounds derived from a Brook rearrangement could not be detected.

Compounds **2**–**6** are formed through intermediate **A** which immediately rearranges by an oxoanion silanion interconversion to give intermediate **B** which is gradually protonated by an excess of enolizable ketone (Scheme 2).

Aromatic ketones such as acetophenone or benzophenone cannot be used in this reaction; interaction with **1** leads to deeply coloured solutions indicating electron transfer and formation of radical anions.

The 1,3-*Si*,*O*-trimethylsilyl migration **A** → **B** is one example of a general oxoanion silanion interconversion which was observed for the first time in 1984 by Brook and coworkers, when tris(trimethylsilyl)silylmethanol was treated with K/Na alloy to give bis(trimethylsilyl)trimethylsiloxymethylsilane (eq. 4). Similarly tris-



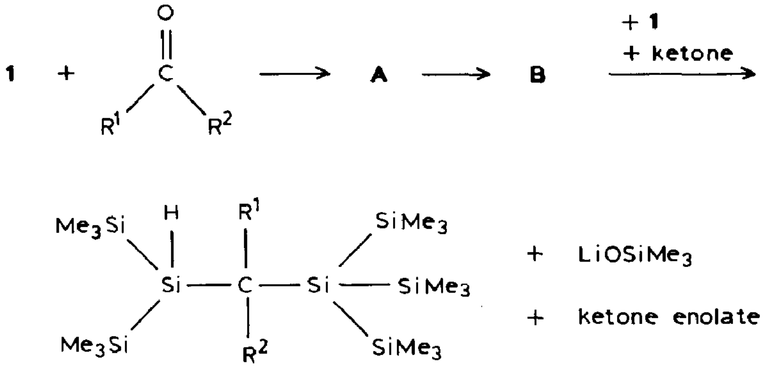
$$(Me_3Si)_3SiCH_2OH \xrightarrow{K/Na\ alloy} (Me_3Si)_2\overset{H}{\overset{|}{Si}}CH_2OSiMe_3 \qquad (4)$$

(trimethylsilyl)silylethanol, in presence of potassium sodium alloy, also rearranges in a 1,4-*Si*,*O*-trimethylsilyl shift to yield the isomeric silyl ether [12].

2–**6** are colourless volatile liquids. Their structures were confirmed on the basis of elemental analysis, IR and ^1H NMR spectra (see experimental).

The reaction procedure was modified in that e.g. acetone was added at −30 °C to a tetrahydrofuran solution of **1**, which after hydrolytic work up led to the isolation of a colourless solid which was identified as 2-[bis(trimethylsily)silyl]-2-[tris(trimethylsilyl)silyl]propane (**7**) [11]. Under these conditions no **2** was obtained. When methyl ethyl ketone, cyclohexanone and methyl isopropyl ketone were used decreased yields of the geminal [bis(trimethylsilyl)silyl][tris(trimethylsilyl)silyl]alkanes (**8**–**10**) along with increased quantities of the alkoxysilanes **2**–**4** and **6** were obtained. Use of diethyl ketone gives **5** exclusively. The formation of **7**–**10** is interpreted as the result of a surprisingly fast substitution of the siloxy group in the intermediate **B** by a second equivalent of **1** (Scheme 3). Hydrolytic work up generates hexamethyldisiloxane which is detected by gas chromatography.

The replacement of the siloxy group at this sterically strained carbon atom by the bulky tris(trimethylsilyl)silyl group even under gentle conditions to give **7**–**10** is



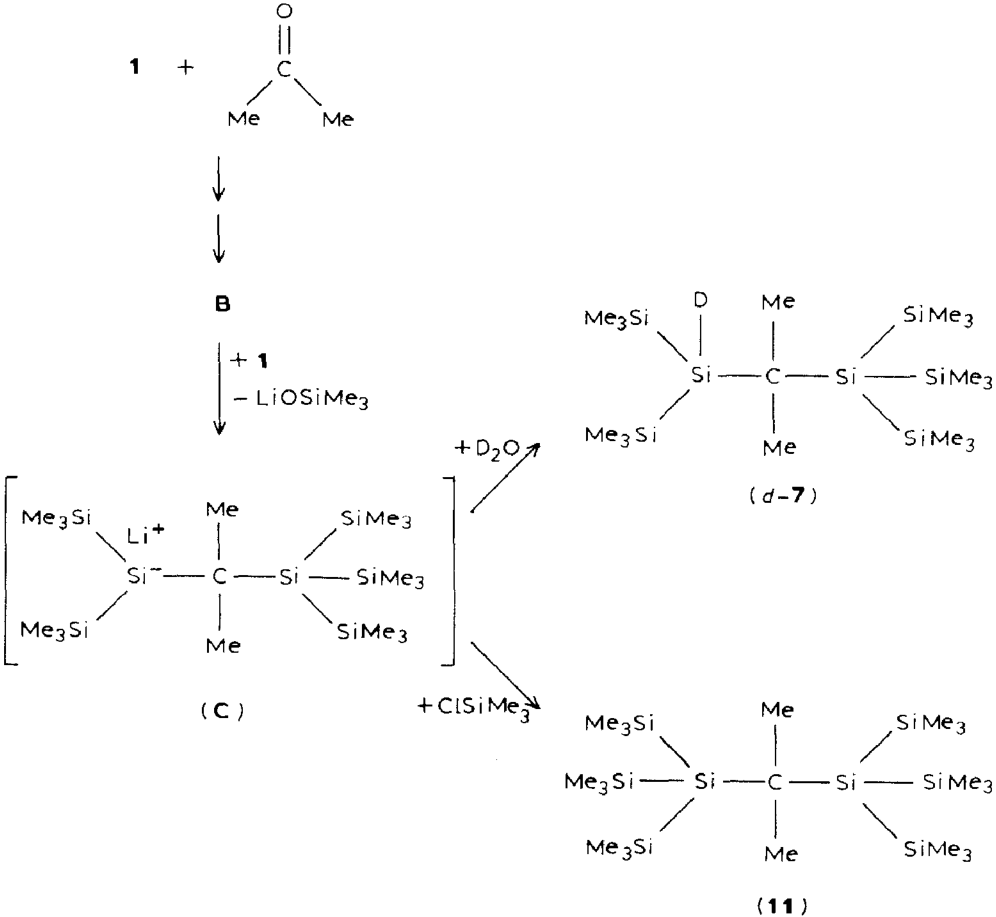
(7-10)

	R^1	R^2
7	CH_3	CH_3
8	CH_3	C_2H_5
9	CH_3	$i\text{-}C_3H_7$
10	—$(CH_2)_5$—	

Scheme 3

surprisingly facile. So for us the detailed mechanism of the substitution reaction is of particular interest. For the conversion of intermediate **B** into the products **7**–**10** two alternative ways can be considered: (i) anion **B** is protonated by an excess of ketone to give the hydrido silanes **2**–**4** and **6** which react with a second equivalent of **1** to yield lithium trimethylsilanolate in addition to **7**–**10**; (ii) the siloxy group in the anionic intermediate, **B** is replaced first by **1** to give lithium trimethylsilanolate and yet another anionic intermediate, **C** which is then protonated by the ketone or by water during the work up to give **7**–**10**.

Detailed studies of the reaction of **1** with acetone have revealed that the negative charge at the silicon atom is preserved (intermediate **C**) after displacement of the trimethylsiloxy group in **B** by a tris-(trimethylsily)-silyl group. Work up of the reaction mixture obtained by addition of equimolar quantities of acetone to a solution of **1** in tetrahydrofuran at −30 °C with deuterium oxide leads to a product identical with **7** in most aspects, but its IR spectrum shows bands at 2065 cm^{-1} (Si–H) (**C** is gradually protonated by acetone also at −30 °C) and in addition an absorption band at 1496 cm^{-1} (Si–D) of approximately equal intensity (Scheme 4).



Scheme 4

If chlorotrimethylsilane is added to the mixture at −30 °C immediately after the reaction of the acetone with **1** the anion **C** is trapped as the symmetrical polysilane 2,2-bis[tris(trimethylsilyl)silyl]propane (**11**) (Scheme 4).

On the other hand, **2** does not react with **1** to give **7**, even at elevated temperatures. ^1H NMR spectroscopy of the reaction in THF revealed that there were no changes at −30 °C; when the mixture was left to stand for several weeks at room temperature tris(trimethylsilyl)silane ($(Me_3Si)_3SiH$) was formed.

The results of our study show that replacement of the silanolate in **B** by the tris(trimethylsilyl)silyl group occurs when the neighbouring silicon atom bears a negative charge. The neutral H-silane **7** behaves indifferently towards **1**. This suggests that the transition state of the substitution reaction is stabilized by the negatively charged silicon atom, which, as far as we are aware, would be the first case of an α-silyl anion supported nucleophilic substitution at a carbon atom and may indicate some $p\pi$-interaction between the silyl anion lone pair and the adjacent carbon atom.

^1H NMR studies

The structures of the H-silanes **7**–**10** and that of the polysilane **11** are characterized by strong intramolecular interactions that prevent internal rotations. Dreiding-model studies have revealed that the structures of **7**–**11** are mainly determined by the steric demands of the bulky trimethylsilyl groups at the two silicon atoms in 1,3-position rather than by the 1,2-interactions of the silicon atoms and their substituents with the central carbon atom. The likely, most stable and, completely frozen conformation of **7**–**10** is given in Fig. 1. The tris(trimethylsilyl)silyl group adopts a staggered conformation with respect to the central carbon atom and its substituents, whereas the $SiH(SiMe_3)_2$ moiety is fixed in the eclipsed form thus placing H in the gap between the two trimethylsilyl groups.

The 200 MHz ^1H NMR data are consistent with this model. In the case of **7** ($R^1 = R^2 = Me$) we found three Si–Me ^1H signals in an intensity ratio of 1/2/2, trimethylsilyl groups in addition to the Si–H and $C-CH_3$ signals. The Si–Me signal at highest field (9H) must be assigned to the group antiperiplanar with respect to $SiH(SiMe_3)_2$. The assignment of the other Si–Me signals is not possible. As expected, **10** ($R^1-R^2 = [CH_2]_5$) gives a similar pattern of Si–Me signals. When R^1 and R^2 are different, such as in **8** and **9**, all trimethylsilyl groups are expected to be magnetically non-equivalent. This was in fact observed. For **8** ($R^1 = Me$, $R^2 = Et$) and **9** ($R^1 = Me$, $R^2 = i\text{-}Pr$) we found five distinct Si–Me signals of equal intensity, in addition to the Si–H and CCH signals. In **9** the methyl signals of the isopropyl

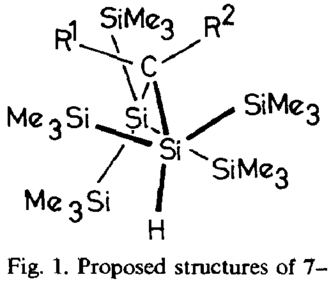


Fig. 1. Proposed structures of **7**–**10**.

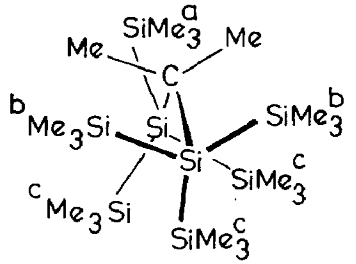


Fig. 2. Proposed structure of **11** and some 200 MHz ^1H NMR data: δ(C–Me) 1. 262 ppm (6H), δ(Si–Me_3 (a)) 0.063 ppm (9H), δ(Si–Me_3 (b)) 0.280 ppm (18H), and δ(Si–Me_3 (c)) 0.305 ppm (27H).

group appear as two doublets which indicates that additionally rotation around the C–$CHMe_2$ bond is also restricted. With exception of the signals appearing at highest field (0.031–0.155 ppm), analogously assigned as in compound **7**, concrete assignment of the other Si–Me signals cannot be given.

The 200 MHz ^1H NMR spectrum of **11** shows four signals, one due to the CCH_3 group and the other three to Si–Me signals in an intensity ratio of 1/2/3. Use of the same model enabled these signals to be assigned as given in Fig. 2.

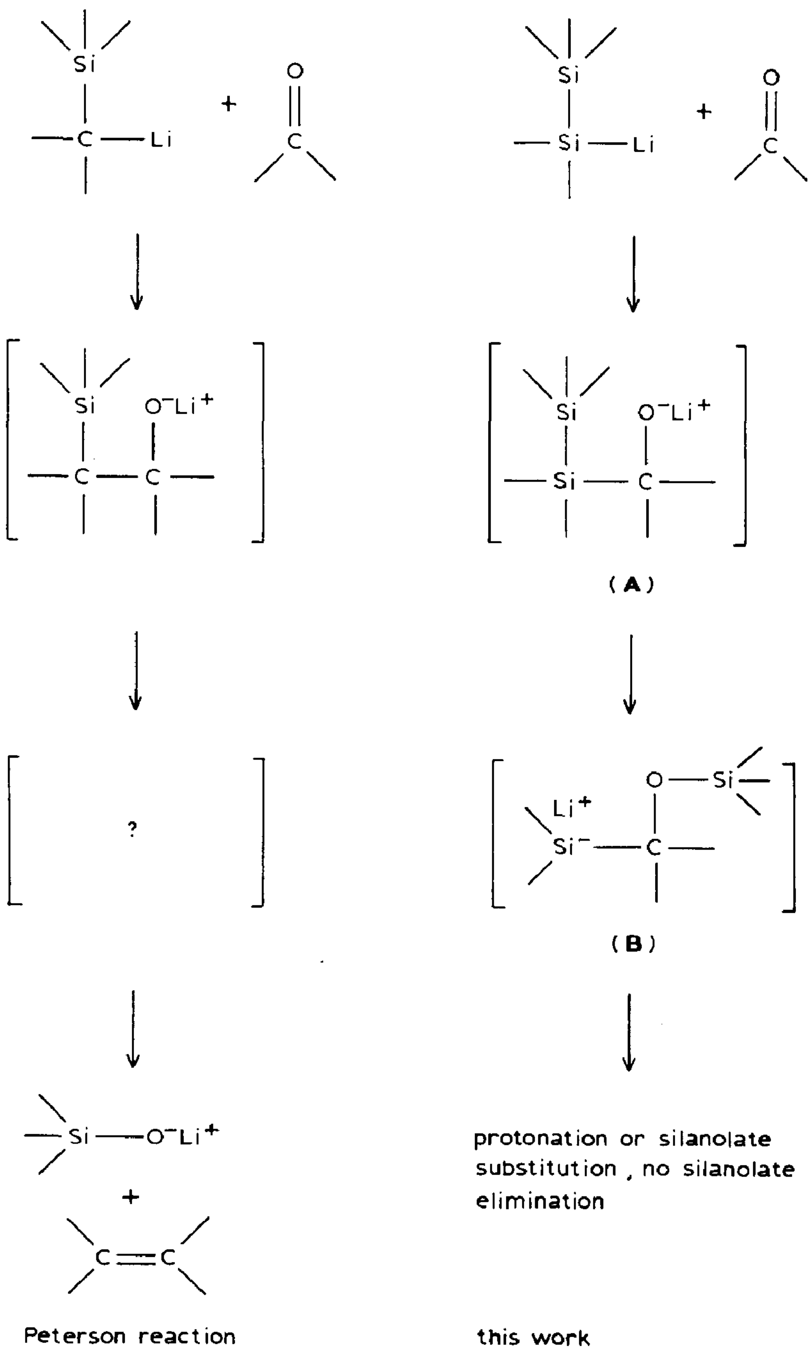
Conclusions

With regard to the initial problem of the applicability of a Peterson type mechanism for establishing Si=C double bond systems it is worthwhile to compare the results of the interaction of **1** with aliphatic ketones, described in this paper, with those of a common Peterson olefination process, e.g. the reaction of tris(trimethylsilyl)methyllithium with aldehydes (with simple aliphatic ketones only α-H-abstraction is observed) [13]. As demonstrated in the very generalized reaction path given in Scheme 5, the first steps of the two reactions are similar. In both cases the nucleophilic lithium derivatives add to the carbonyl groups to give lithium-β-trimethylsilyl alkoxides or intermediate **A**. **A** then undergoes a 1,3-*Si*,*O*-trimethylsilyl shift to give **B**. Unfortunately, the detailed mechanism of the Peterson reaction is not known, so that the role of the β-siloxy carbanion, the analogue of **B**, is not clear. The lithium β-trimethylsilyl alkoxide finally eliminates lithium silanolate to give the olefin. In the case of **B**, lithium trimethylsilanolate elimination and generation of a silene or its decomposition products could not be detected. **B** is either protonated to give **2**–**6** or if an excess of **1** is used the siloxy group is replaced which yields **7**–**10**.

The differences observed in the behaviour of **1** towards aliphatic ketones and the general reaction of α-silyl carbanions with carbonyl compounds following the Peterson reaction mechanism, respectively, are not fully understood at present. Possibly the reluctance of **A** or **B** to eliminate lithium trimethylsilanolate to form a silene is because of thermodynamic reasons, i.e. the differences in the stability of an olefinic C=C double bond and an Si=C double bond system. Studies on the influence of various substituents on the reaction path are in progress.

Experimental

All reactions involving organometallic reagents were carried out under exclusion of air and water under dry argon. ^1H NMR spectra were obtained with either a Bruker WP 200 or a Tesla BS 487C spectrometer. Mass spectra were recorded with a



Scheme 5

LKB 9000 instrument (70 eV, source temp. 290 °C); IR spectra with a UR-20 photometer of VEB Carl Zeiss Jena. Tetrakis(trimethylsilyl)silane was prepared by a published procedure [14].

2-[Bis(trimethylsilyl)silyl]-2-trimethylsiloxy-butane (*3*). The procedure is analogous to that described for **2** [11]. A solution of 5,2 g (0.072 mol) of methyl ethyl ketone in 50 ml tetrahydrofuran was placed in a 500 ml three-necked flask equipped with a stirrer and a dropping funnel. A solution of **1** was prepared by cleavage of 9.6 g (0.030 mol) of tetrakis(trimethylsilyl)silane in 120 ml THF by 0.036 mol methyllithium in ether (30 ml). This cleavage reaction, which is always monitored spectroscopically (^{1}H NMR), takes about two days for completion at room temperature. The solution of **1** is added to the ketone at −30 °C within 2 h. After stirring the mixture for an additional 2 h it is warmed to 0 °C and poured into a saturated solution of NH_4Cl in water. The mixture was extracted with ether, then dried over $MgSO_4$ and then the solvents were removed. Distillation of the residue gave 6.6 g (69%) of **3**; b.p. 62–63 °C/0.1 torr.

Analysis. Found: C, 49.35; H, 11.28. $C_{13}H_{36}OSi_4$ (320.78) calcd.: C, 48.67; H, 11.31%. IR (cap.) 2070 cm^{-1} (SiH); ^{1}H NMR (80 MHz, CCl_4) δ 3.44 (s, 1H, SiH), 1.68 (q, J 7.0 Hz, 2H, CH_2Me), 1.51 (s, 3H, CMe), 1.02 (t, J 7.0 Hz, 3H, CH_2*Me*), 0.28 (s, 18H, $Si(SiMe_3)_2$), 0.19 (s, 9H, $OSiMe_3$) ppm.

2-[Bis(trimethylsilyl)silyl]-2-trimethylsiloxy-3-methylbutane (***4***). Similarly, reaction of 6.2 g (0.072 mol) of methyl isopropyl ketone in THF (50 ml) with **1**, obtained by cleavage of 9.6 g (0.030 mol) of tetrakis(trimethylsilyl)silane, gave 7.3 g (73%) of **4**; b.p. 70–71 °C/0.08 torr.

Analysis. Found: C, 51.00; H, 11.55. $C_{14}H_{38}OSi_4$ (334.80) calcd.: C, 50.22; H, 11.44% IR (cap.) 2072 cm^{-1} (SiH); ^{1}H NMR (80 MHz, CCl_4) δ 3.34 (s, 1H, SiH), 1.76 (sep., J 7.0 Hz, 1H, C*H*Me_2), 1.49 (s, 3H, CMe), 0.98 (d, J 7.0 Hz, 6H, CH*Me*$_2$), 0.25 (s, 9H, $SiSiMe_3$), 0.23 (s, 9H, $SiSiMe_3$), 0.19 (s, 9H, $OSiMe_3$) ppm.

3-[Bis(trimethylsilyl)silyl]-3-trimethylsiloxypentane (*5*). Similarly, reaction of 11.9 g (0.138 mol) of diethyl ketone in THF (100 ml) with **1**, obtained by cleavage of 19.2 g (0.060 mol) tetrakis(trimethylsilyl)silane, gave 15.1 g (75%) of **5**; b.p. 85 °C/0.1 torr.

Analysis. Found: C, 50.35; H, 11.55. $C_{14}H_{38}OSi_4$ (334.80) calcd.: C, 50.22; H, 11.44. IR (cap.) 2062 and 2086 cm^{-1} (SiH); ^{1}H NMR (80 MHz, CCl_4): δ 3.42 (s, 1H, SiH), 1.77 (q, J 7.0 Hz, 4H, CH_2Me), 0.99 (t, J 7.0 Hz, 6H, CH_2*Me*), 0.23 (s, 18H, $Si(SiMe_3)_2$), 0.16 (s, 9H, $OSiMe_3$) ppm.

1-[Bis(trimethylsilyl)silyl]-1-trimethylsiloxycyclohexane (***6***). Similarly, reaction of 9.4 g (0.096 mol) of cyclohexanone in THF (50 ml) with **1**, made from 12.8 g (0.040 mol) of tetrakis(trimethylsilyl)silane, gave 8.8 g (63%) of **6**; b.p. 88–90 °C/0.1 torr.

Analysis. Found: C, 52.85; H, 11.05. $C_{15}H_{38}OSi_4$ (346.81) calcd.: C, 51.94; H, 11.04%. IR (cap.) 2065 cm^{-1} (SiH); ^{1}H NMR (80 MHz, CCl_4) δ 3.71 (s, 1H, SiH), 1.40–2.02 (m, 10H, CH_2), 0.26 (s, 18H, $SiSiMe_3$), 0.19 (s, 9H, $OSiMe_3$) ppm.

2-[Bis(trimethylsilyl)silyl]-2-[tris(trimethylsilyl)silyl]butane (***8***). The procedure used to prepare **8** was similar to that used for **7** [11]; a solution of **1** was prepared by cleavage of 19.2 g (0.060 mol) of tetrakis(trimethylsilyl)silane in THF (250 ml) by 0.072 mol of methyllithium in ether (75 ml). Then a solution of 6.9 g (0.096 mol) of butanone in THF (50 ml) was added and the mixture was stirred for 1 h at −30 °C. After warming to 0 °C the reaction mixture was poured into a saturated solution of NH_4Cl in water. The mixture was extracted with ether, dried over $MgSO_4$, then the solvents were removed and distillation yielded 2.5 g (13%) of **3**, recrystallization of the semi-solid residue gave 6.9 g (48%) of colourless crystalline **8**; m.p. 130–132 °C.

Analysis. Found: C, 48.20; H, 11.15. $C_{19}H_{54}Si_7$ (479.25) calcd.: C, 47.61; H, 11.36%. IR (Nujol) 2065 cm^{-1} (SiH); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.352 (s, 1H, SiH), 1.442 (m, 2H, CH_2Me), 1.197 (s, 3H, CMe), 0.901 (t, *J* 7.45 Hz, 3H, CH_2*Me*), 0.265 (s, 9H, $SiSiMe_3$), 0.262 (s, 9H, $SiSiMe_3$), 0.246 (s, 9H, $SiSiMe_3$), 0.238 (s, 9H, $SiSiMe_3$), 0.084 (s, 9H, $SiSiMe_3$) ppm.

2-[Bis(trimethylsilyl)silyl]-2-[tris(trimethylsilyl)silyl]-3-methylbutane (***9***). Analogous to the preceding procedure, reaction of **1**, made by methyllithium cleavage of 19.2 g of tetrakis(trimethylsilyl)silane, with 11.9 g (0.138 mol) of methyl isopropyl ketone in THF (50 ml) gives 7.9 g (38%) of **4** and 1.5 g (10%) of **9**, m.p. 151–153 °C.

Analysis. Found: C, 48.35; H, 11.40. $C_{20}H_{56}Si_7$ (493.28) calcd.: C, 48.69; H, 11.44%. IR (Nujol) 2065 cm^{-1} (SiH); ^1H NMR (200 MHz, $CDCl_3$) δ 2.449 (s, 1H, SiH), 1.5 (m, 1H, *CH*Me_2), 1.278 (s, 3H, CMe), 1.134 (d, *J* 7.02 Hz, 3H, CH*Me*), 0.964 (d, *J* 6.91 Hz, 3H, CH*Me*), 0.277 (s, 9H, $SiSiMe_3$), 0.272 (s, 9H, $SiSiMe_3$), 0.262 (s, 9H, $SiSiMe_3$), 0.255 (s, 9H, $SiSiMe_3$), 0.144 (s, 9H, $SiSiMe_3$) ppm.

1-[Bis(trimethylsilyl)silyl]-1-[tris(trimethylsilyl)silyl]cyclohexane (***10***). Analogous to preparation of **8**, 7.1 g (0.072 mol) cyclohexanone were added to a solution of **1**, made by cleavage of 9.6 g (0.030 mol) of tetrakis(trimethylsilyl)silane with methyllithium. Usual work up gave 4.2 g (40.5%) of **6** and 1.2 g (16%) of **10**; m.p. 168–170 °C.

Analysis. Found: C, 49.98; H, 11.80. $C_{21}H_{56}Si_7$ (505.29) calcd.: C, 49.91; H, 11.18%. IR (Nujol) 2068 cm^{-1} (SiH); ^1H NMR (200 MHz, $CDCl_3$) δ 2.350 (s, 1H, SiH), 1.3–2.1 (m, 10 H, CH_2), 0.268 (s, 18H, $SiSiMe_3$), 0.246 (s, 18H, $SiSiMe_3$), 0.155 (s, 9H, $SiSiMe_3$) ppm.

2-[Bis(trimethylsilyl)deuterosilyl]-2-[tris(trimethylsilyl)silyl]propane (***d-7***). To a solution of **1** made by cleavage of 9.6 g (0.030) mol) of tetrakis(trimethylsilyl)silane with methyllithium, was added 1.0 g (0.018 mol) acetone in THF (20 ml) at −30 °C during 1 h. After stirring the reaction mixture for 1 h at −30 °C 0.6 g (0.036 mol) deuterium oxide in THF (20 ml) was added. Usual work up as described for **8** gave 3.5 g (50%) of a mixture of **7** and ***d*-7**. IR (KBr) 2059 (SiH) and 1496 cm^{-1} (SiD).

2,2-Bis[tris(trimethylsilyl)silyl]propane (***11***). A solution of **1** was made by cleavage of 9.6 g (0.030 mol) of tetrakis(trimethylsilyl)silane in 120 ml THF with 0.036 mol of methyllithium in 40 ml ether. To this solution was added 1.0 g (0.018 mol) of acetone in THF (20 ml) at −30 °C during 1 h and the mixture was stirred for an additional hour at the same temperature. Then 3.9 g (0.036 mol) chlorotrimethylsilane in THF (20 ml) was added. Usual work up then gave a semi-solid which was recrystallized from ethanol. Removal of traces of tetrakis(trimethylsilyl) silane by fractional vacuum sublimation and repeated recrystallization gave 0.9 g (11%) of pure **11** as colourless crystals; m.p. 234–236 °C.

Analysis. Found: C, 47.50; H, 11.50. $C_{21}H_{60}Si_8$ (537.41) calcd.: C, 46.93; H, 11.25%. ^1H NMR (200 MHz, $CDCl_3$) δ 1.262 (s, 6H, CMe_2), 0.305 (s, 27H, $SiSiMe_3$), 0.273 (s, 18H, $SiSiMe_3$), 0.063 (s, 9H, $SiSiMe_3$) ppm. MS *m/e* (% rel. intensity; ion identity); 421 (0.25; $M-CH_3$), 289 (26.2; $M-Si(SiMe_3)_3$), 247 (7.1; $Si(SiMe_3)_3$), 73 (100, $SiMe_3$).

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