

Preparation of Some Sterically Hindered Organosilicon Compounds

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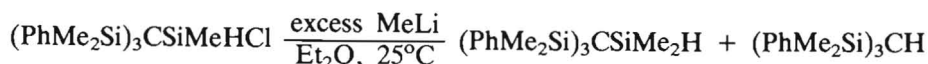
ABSTRACT. Under the conditions where $(\text{PhMe}_2\text{Si})_3\text{CSiMe}_2\text{Cl}$ is inert towards a range of organolithium reagents, the secondary organosilicon chloride $(\text{PhMe}_2\text{Si})_3\text{CSiMeHCl}$ reacts with MeLi , EtLi or LiBu^n to give $(\text{PhMe}_2\text{Si})_3\text{CSiMe}_2\text{H}$, $(\text{PhMe}_2\text{Si})_3\text{CSiMeEtH}$ or $(\text{PhMe}_2\text{Si})_3\text{CSiMeBu}^n\text{H}$, respectively, but not with LiBu^t . Similar results are obtained from reaction of $(\text{Me}_3\text{Si})_3\text{CSiMeHCl}$ with organolithium reagents.

Much chemistry has emerged from studies of highly sterically hindered compounds having tris(trimethylsilyl)methyl ligand (Eaborn *et al.* 1978, Eaborn 1979 and Eaborn and Hopper 1979). Such compounds have been prepared by treating $(\text{Me}_3\text{Si})_3\text{CLi}$ with appropriate silicon halides (Cook *et al.* 1970 and Dua *et al.* 1979). In contrast, the organolithium reagent $(\text{PhMe}_2\text{Si})_3\text{CLi}$ has been reported to react with only Me_2SiHCl and MeSiHCl_2 to give $(\text{PhMe}_2\text{Si})_3\text{CSiMe}_2\text{H}$ and $(\text{PhMe}_2\text{Si})_3\text{CSiMeHCl}$, respectively, but not with a wide range of silicon halides (Eaborn and Mansour 1985). The failure of $(\text{PhMe}_2\text{Si})_3\text{CLi}$ to couple with silicon halides prompted us to investigate the reaction of $(\text{PhMe}_2\text{Si})_3\text{CSiMeHCl}$ with organolithium reagents as possible alternative synthetic route for some sterically hindered organosilicon compounds of the type $(\text{PhMe}_2\text{Si})_3\text{CSiPRR}'\text{H}$.

Results and Discussion

The sterically hindered organosilicon chloride $(\text{PhMe}_2\text{Si})_3\text{CSiMe}_2\text{Cl}$ was recovered unchanged when treated with an excess of MeLi , LiBu^n or LiBu^t in Et_2O at room temperature (25°C) for 24 h. This illustrates the very large steric hindrance

towards nucleophilic substitution at a silicon centre caused by the $(\text{PhMe}_2\text{Si})_3\text{C}$ ligand. In contrast, treatment of the secondary chloride $(\text{PhMe}_2\text{Si})_3\text{CSiMeHCl}$ with an excess of MeLi under similar conditions and subsequent hydrolytic work-up gave a solid, which was shown (^1H nmr spectroscopy and g.l.c.) to contain $(\text{PhMe}_2\text{Si})_3\text{CSiMe}_2\text{H}$ together with less than 10% impurity of $(\text{PhMe}_2\text{Si})_3\text{CH}$ by comparison with an authentic samples (Eaborn and Mansour 1985 and Liu and Ma 1970). We believe that the compound $(\text{PhMe}_2\text{Si})_3\text{CH}$ is formed from direct cleavage of the $\text{C}-\text{SiMeHCl}$ bond.



Although it might seem possible that under the reaction conditions the initially formed hydride $(\text{PhMe}_2\text{Si})_3\text{CSiMe}_2\text{H}$ would react with the excess of MeLi to give $(\text{PhMe}_2\text{Si})_3\text{CH}$, we have independently observed no reaction between MeLi and $(\text{PhMe}_2\text{Si})_3\text{CSiMe}_2\text{H}$. However, subsequent recrystallization of the crude product from methanol gave a pure crystalline solid of $(\text{PhMe}_2\text{Si})_3\text{CSiMe}_2\text{H}$. Successful replacement of chloride by methyl group suggested a useful synthetic route for some sterically hindered organosilicon compounds which could not be made from the reactions between $(\text{PhMe}_2\text{Si})_3\text{CLi}$ and silicon halides. Indeed, treatment of $(\text{PhMe}_2\text{Si})_3\text{CSiMeHCl}$ with an excess of EtLi or LiBu^n under the conditions used for MeLi followed by hydrolytic work-up and subsequent recrystallization from methanol gave exclusively $(\text{PhMe}_2\text{Si})_3\text{CSiMeEtH}$ and $(\text{PhMe}_2\text{Si})_3\text{CSiMeBu}^n\text{H}$, respectively, in satisfactory yields. The relative ease of the reaction of $(\text{PhMe}_2\text{Si})_3\text{CSiMeHCl}$ with organolithium reagents can be attributed to the presence of the sterically undemanding hydrogen atom at the functional centre which seemingly allows the usual direct nucleophilic attack on the substrate. However, $(\text{PhMe}_2\text{Si})_3\text{CSiMeHCl}$ does not react with LiBu^t , possibly because of the large bulk of the nucleophile Bu^{t-} which hinders it from closely approaching the substrate. Correspondingly, the closely related chloride $(\text{Me}_3\text{Si})_3\text{CSiMeHCl}$ reacts with an excess of MeLi, EtLi or LiBu^n to give $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{H}$, $(\text{Me}_3\text{Si})_3\text{CSiMeEtH}$ or $(\text{Me}_3\text{Si})_3\text{CSiMeBu}^n\text{H}$, respectively, in good yield. However, no reaction occurs with LiBu^t . Moreover, no reaction was observed when the tertiary chloride $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{Cl}$ was treated with concerned organolithium reagents.

Experimental

Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. The ^1H nmr spectra were recorded at 60 or 100 MMHz. g.l.c. analysis was carried out on Varian 1800 instrument. Unless otherwise stated, organolithium reagents were supplied by Fluka.

Attempted Reactions of (PhMe₂Si)₃CSiMe₂Cl with Various Organolithium Reagents

A 1.6M solution of MeLi (1.96 mmol) in Et₂O (1.2 cm³) was added to a solution of (PhMe₂Si)₃CSiMe₂Cl (0.5 g, 0.98 mmol) in Et₂O (50 cm³). The mixture was stirred at room temperature under nitrogen for 24 h. Water was then added. The organic layer was separated, washed, dried (MgSO₄), and evaporated to give a solid, which was shown by its ¹H nmr spectrum to be exclusively unchanged starting material.

The same result was obtained when the following organolithium reagents were used:

- a) A 1.2M solution of EtLi (1.96 mmol) in pentane (1.6 cm³)
- b) A 1.4M solution of LiBuⁿ (1.26 mmol) in hexane (1.4 cm³)
- c) A 1.6M solution of LiBu^t (1.96 mmol) in pentane (1.2 cm³)

Preparation of (PhMe₂Si)₃CSiMe₂H

A 1.6M solution of MeLi (4.0 mmol) in Et₂O (2.5 cm³) was added to a solution of (PhMe₂Si)₃CSiMeHCl (1 g, 2 mmol) in Et₂O (100 cm³). The mixture was stirred at room temperature under nitrogen for 24h (a white precipitate of LiCl was observed after 1 h. of reaction time). Water was then added. The organic layer was separated, washed, dried (MgSO₄), and evaporated to give a solid which was shown by g.l.c. analysis and its ¹H nmr spectrum to contain mainly (PhMe₂Si)₃CSiMe₂H together with less than 10% of (PhMe₂Si)₃CH (authentic samples of the products were available for comparison). The crude product was then recrystallized from methanol to give exclusively dimethyl[tris(Phenyl-dimethylsilyl)methyl]silane (0.73 g 76%), showing to be identical with an authentic sample by means of its ¹H nmr spectrum, δ¹H_(CCl₄) 0.58(s, 18H, SiMe₂), 0.30 (d, J=2H, 6H, SiMe₂), 4.48 (m, 1H, SiH), 7-7.8 ppm (m, 5H, SiPh).

Preparation of (PhMe₂Si)₃CSiMeEtH

A 1.2M solution of EtLi (freshly prepared, Bryce-Smith and Turener 1953) (4.0 mmol) in heptane (3.36 cm³) was added to a solution of (PhMe₂Si)₃CSiMeHCl (1.0 g, 2 mmol) in Et₂O (100 cm³). The mixture was stirred at room temperature under nitrogen for 24 h (a precipitate of LiCl was observed after 2 h). Water was then added. The organic layer was separated, washed, dried (MgSO₄), and evaporated to give a solid which was shown by its ¹H nmr spectrum to contain mainly (PhMe₂Si)₃CSiMeEtH together with less than 10% of (PhMe₂Si)₃CH. Recrystallization of the crude product from methanol gave exclusively ethylmethyl[tris(phenyldimethylsilyl)methyl]silane (0.81 g 82%) mp 87°C, δ¹H_(CDCl₃) 0.24 (3H, d 3.6 Hz, SiMeEtH), 0.51 (18H, d, SiMe₂Ph), 0.89 (5H, m, SiMeEtH), 4.33 (1H, m, SiH) and 7.17 ppm (15H, m, Ph) (Found: C,68.6; H,8.6, C₂₈H₄₂Si₄ requires C,68.6; H,8.6%).

Preparation of (PhMe₂Si)₃CSiMe(Buⁿ)H

A 1.4M solution of LiBuⁿ (4.0 mmol) in hexane (2.9 cm³) was added to a solution of (PhMe₂Si)₃CSiMeHCl (1.0 g, 2 mmol) in Et₂O (100 cm³). The mixture was stirred at room temperature under nitrogen for 24 h (a precipitate of LiCl was observed after 5 h). Subsequent work-up and removal of the solvent by rotary evaporation gave a solid which was shown by g.l.c. analysis and its ¹H nmr spectrum to contain mainly (PhMe₂Si)₃CSiMeBuⁿH together with less than 10% of (PhMe₂Si)₃CH. Recrystallization of the crude product from methanol gave exclusively n-butylmethyl[tris(phenyldimethylsilyl)methyl]silane (0.85, 80%) mp 96°C, δ¹H_(CDCl₃) 0.24(3H, d, 3.6Hz, SiMeBuH), 0.51(18H, d, SiMe₂Ph), 0.65-1.5(9H, m, SiMe(Buⁿ)H), 4.37(1H, m, SiH) and 7.18 ppm (15H, m, Ph) (Found C, 69.3; H, 8.7, C₃₀H₄₆Si₄ requires C, 69.5; H, 8.8%).

Attempted Preparation of (PhMe₂Si)₃CSiMe(Bu^t)H

A 1.6M solution of LiBu^t (4.0 mmol) in hexane (2.5 cm³) was added to a solution of (PhMe₂Si)₃CSiMeHCl (1 g, 2 mmol) in Et₂O (100 cm³). The mixture was stirred at room temperature under nitrogen for 24 h. Water was then added. The organic layer was separated, washed, dried (MgSO₄) and evaporated to give a solid which was shown by its ¹H nmr spectrum to be exclusively unchanged starting material.

Attempted Reaction of (Me₃Si)₃CSiMe₂Cl with Various Organolithium Reagents

A 1.6M solution of MeLi (3.1 mmol) in Et₂O (1.93 cm³) was added to a solution of (Me₃Si)₃CSiMe₂Cl (0.5 g, 1.54 mmol) in Et₂O (50 cm³). The mixture was stirred at room temperature under nitrogen for 24 h. Water was then added. The organic layer was separated, washed, dried (MgSO₄) and evaporated to give a solid which was shown by its ¹H nmr spectrum to be exclusively unchanged starting material.

The same result was observed when the following organolithium reagents were used:

- a) A 1.2M solution of EtLi (3.1 mmol) in pentane (2.6 cm³)
- b) A 1.4M solution of LiBuⁿ (3.1 mmol) in hexane (2.2 cm³)
- c) A 1.6M solution of LiBu^t (3.1 mmol) in hexane (1.9 cm³)

Preparation of (Me₃Si)₃CSiMe₂H

A 1.6M solution of MeLi (6.4 mmol) in Et₂O (3 cm³) was added to a solution of (Me₃Si)₃CSiMeHCl (1 g, 3.2 mmol) in Et₂O (100 cm³). The mixture was stirred at room temperature under nitrogen for 24 h. Water was then added. The organic layer was separated, washed, dried (MgSO₄) and evaporated. The residue was washed with methanol followed by filtration to leave a solid which was shown to be

exclusively dimethyl [tris(trimethylsilyl)methyl]silane (0.79 g, 84%) by the identity of its ^1H nmr spectrum with that of an authentic sample. $\delta^1\text{H}_{(\text{CCl}_4)}$ 0.13 (s, 27H, SiMe₃), 0.21 d, 6H, SiMe₂), 4.07 ppm (m, 1H, SiH).

Preparation of (Me₃Si)₃CSiMeEtH

A 1.2M solution of EtLi (6.4 mmol) in pentane (5.4 cm³) was added to a solution of (Me₃Si)₃CSiHCl (1 g, 3.2 mmol) in Et₂O (100 cm³). The mixture was stirred at room temperature under nitrogen for 24 h. Water was then added. The organic layer was separated, washed, dried (MgSO₄) and evaporated. The residue was washed with methanol followed by filtration to leave a solid which was shown to be exclusively ethylmethyl[tris(trimethylsilyl)methyl]silane (0.8 g, 82%) showing to be identical with an authentic sample by means of its ^1H nmr spectrum $\delta^1\text{H}_{(\text{CCl}_4)}$ 0.20 (s, 27H, (SiMe₂); 0.26 (1d, 3H, (SiMe); 0.90 (m, 5H, SiEt); 3.93 ppm (m, 1H, SiH).

Preparation of (Me₃Si)₃CSiMe(Buⁿ)H

A 1.6M solution of LiBuⁿ (6.4 mmol) in hexane (4 cm³) was added to a solution of (Me₃Si)₃CSiMeHCl (1 g, 3.2 mmol) in Et₂O (100 cm³). The mixture was stirred at room temperature under nitrogen for 24 h. Water was then added. The organic layer was separated, washed, dried (MgSO₄) and evaporated to give a solid which was recrystallized from methanol to give n-butylmethyl[tris(trimethylsilyl)methyl]silane (0.68 g, 80%, mp 44.1°C, $\delta^1\text{H}_{(\text{CDCl}_3)}$ 0.21 (s, 27H, SiMe₃); 0.26 (d, 6H, SiMe₂); 0.35-1.54 (m, 9H, SiBuⁿ); 3.96 ppm (m, 1H, SiH) (Found: C, 54.0; H, 12.0, C₁₅H₄₀Si₄ requires C, 54.2; H, 12.1).

Attempted Preparation of (Me₃Si)₃CSiMe(Bu^t)H

A 1.6M solution of LiBu^t (6.4 mmol) in hexane (4 cm³) was added to a solution of (Me₃Si)₃CSiMeHCl (1 g, 3.2 mmol) in Et₂O (100 cm³). The mixture was stirred at room temperature for 24 h. Water was then added. The organic layer was separated, washed, dried (MgSO₄) and evaporated to give a solid which was shown by its ^1H nmr spectrum to be exclusively unchanged starting material.

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تحضير بعض مركبات السلكون العضوية ذات الاعاقة الفراغية

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المملكة العربية السعودية

عند الظروف التي يكون فيها مركب السلكون العضوي ذي الاعاقة الفراغية $(\text{PhMe}_2\text{Si})_3\text{CSiMe}_2\text{Cl}$ حامل، تجاه عدد من كواشف الليثيوم العضوية فإن مركب السلكون العضوي الأقل إعاقة $(\text{PhMe}_2\text{Si})_3\text{CSiMeHC1}$ يتفاعل مع ميثيل الليثيوم وأثيل الليثيوم وبيوتيل الليثيوم النظامي ليعطي المركبات $(\text{PhMe}_2\text{Si})_3\text{CSiMe}_2\text{H}$ و $(\text{PhMe}_2\text{Si})_3\text{CSiMeEtH}$ و $(\text{PhMe}_2\text{Si})_3\text{CSiMe(n-Bu)H}$ على الترتيب لكنه لا يتفاعل مع بيوتيل الليثيوم الثلاثي. تمكن التفاعلات بين المركب $(\text{PhMe}_2\text{Si})_3\text{CSiMeHC1}$ ومركبات الليثيوم العضوية من تحضير بعض مركبات السلكون العضوية ذات الإعاقة الفراغية والتي يتعذر تحضيرها من التفاعل بين المركب $(\text{PhMe}_2\text{Si})_3\text{CLi}$ وهاليدات السلكون العضوية البسيطة بالإضافة إلى ذلك فقد تم الحصول على نتائج مشابهة من تفاعلات مركب السلكون العضوي المشابه $(\text{Me}_3\text{Si})_3\text{CSiMeHC1}$ مع كواشف الليثيوم العضوية.