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SELECTIVITY IN THE REACTIONS OF ALKYLLITHIUM REAGENTS WITH α,ω-DICHLOROPERMETHYLSILOXANES

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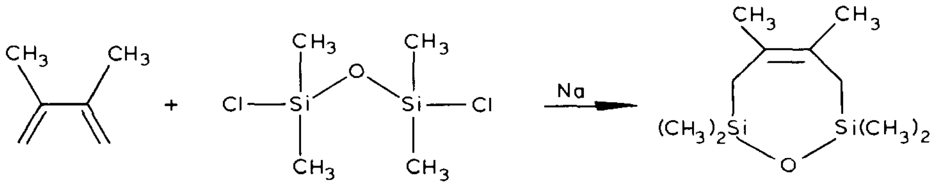
Summary

The reactions of 1,3-dichlorotetramethyldisiloxane and 1,5-dichlorohexamethyltrisiloxane with alkyllithium reagents have been studied. At low temperature (−78°C) only one of the two silicon–chlorine bonds of 1,3-dichlorotetramethyldisiloxane reacts readily with alkyllithium reagents. This permits the selective preparation of 1-alkyl-3-chlorotetramethyldisiloxanes or by hydrolysis 1-alkyl-3-hydroxytetramethyldisiloxanes. The silicon–chlorine bond of 1-alkyl-3-chlorotetramethyldisiloxanes reacts with alkyllithium reagents at higher temperatures (0°C). Both the silicon–chlorine bonds of 1,5-dichlorohexamethyltrisiloxane react competitively with alkyllithium reagents at −78°C. No cleavage of siloxane bonds by alkyllithium reagents is observed under these conditions. Spectral properties of a number of 1-alkyl-3-hydroxytetramethyldisiloxanes and 1-alkyl-5-hydroxyhexamethyltrisiloxanes are reported.

Introduction

We have been interested recently in developing new methods to modify siloxanes [1]. The reaction of organolithium or Grignard reagents with chlorosilanes is one of the standard methods to prepare substituted organosilanes [2,3]. On the other hand, there are only a few examples of the corresponding reactions of organometallic reagents with chloro-substituted siloxanes to yield organosubstituted siloxanes. Among these are several examples of reaction of 1,3-dichlorotetramethyldisiloxane with bis-organometallic reagents to yield heterocycles which possess a disiloxane unit [4–7].



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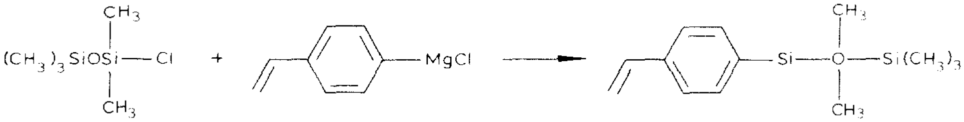
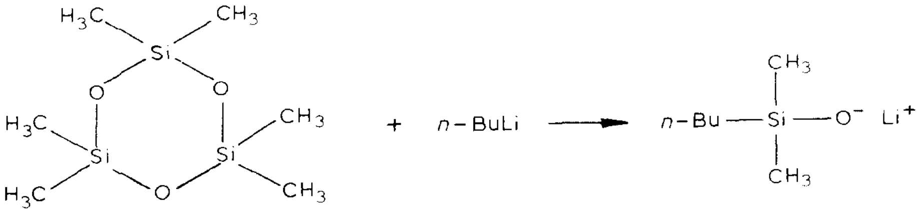
A few examples of reaction of aryl Grignard as well as vinyl-substituted aryl- or vinyl-lithium reagents with chloro-substituted siloxanes to yield aryl-substituted siloxanes have also been reported [8–14].



The infrequent utilization of such reactions may be due to the fact that alkyllithium reagents have been reported to cleave siloxane substrates at ambient temperature to yield lithium siloxanoates [15–18].



Results

We would like to report our results on the low temperature reaction of primary, secondary, and tertiary alkyllithium reagents with 1,3-dichlorotetramethyldisiloxane and 1,5-dichlorohexamethyltrisiloxane. Such α,ω-dichloropermethylpolysiloxanes are commercially available [19,20] or may be readily prepared by hydrolysis of dimethyldichlorosilane with a limited amount of water [21]. Reactions of primary alkyllithium reagents with α,ω-dichloropermethylpolysiloxanes have been previously studied [12]. The fact that secondary and tertiary alkyllithium reagents are often significantly more reactive than primary alkyllithium reagents partially motivated our study [1,22].

We find that primary, secondary, and tertiary alkyllithium reagents react nonselectively at low temperature in ether with both the silicon–chlorine bonds of 1,5-dichlorohexamethyltrisiloxane to yield after low temperature hydrolysis hexamethylcyclotrisiloxane (D_3), octamethylcyclotetrasiloxane (D_4), 1-alkyl-5-hydroxyhexamethyltrisiloxane, and 1,5-dialkylhexamethyltrisiloxane. In independent experiments, low temperature hydrolysis of 1,5-dichlorohexamethyltrisiloxane gave both D_3 and D_4. The ratio of these products is dependent on the ratio of 1,5-dichlorohexamethyltrisiloxane to alkyllithium reagent. Apparently the two silicon–chlorine bonds of 1,5-dichlorohexamethyltrisiloxane and the silicon–chlorine bond of 1-alkyl-5-chlorohexamethyltrisiloxane have approximately equal reactivity. This lack of selectivity is consistent with previously obtained results with primary alkyllithium reagents [12].

On the other hand, reaction of 1,3-dichlorotetramethyldisiloxane with alkyllithium reagents is quite different. Thus reaction of 1,3-dichlorotetramethyldisiloxane with primary, secondary, or tertiary alkyllithium reagents in ether at −78°C results in selective reaction of only one of the silicon–chlorine bonds. Low temperature hydrolysis thus results in selective formation of 1-alkyl-3-hydroxytetramethyldisiloxane as well as D_3 and D_4. With sufficient alkyllithium reagents neither D_3 nor D_4 are found. Apparently, the silicon–chlorine bonds of 1,3-dichlorotetramethyldisiloxane are significantly more reactive toward alkyllithium reagents than the silicon–chlorine bond of 1-alkyl-3-chlorotetramethyldisiloxanes. We assume the origin of this difference in reactivity is electronic rather than steric.

The silicon–chlorine bond of 1-alkyl-3-chlorotetramethyldisiloxanes can be substituted by alkyllithium reagents by warming the solution to 0°C. By carrying out the reaction of 1,3-dichlorotetramethyldisiloxane with one equivalent of isopropyllithium at −78°C followed addition of an equivalent of n-butyllithium and gradual warming to 0°C, 1-n-butyl-3-isopropyl-tetramethyldisiloxane was selectively prepared. This difference in reactivity permits the selective preparation of unsymmetrical 1-alkyl′-3-alkyl″-tetramethyldisiloxanes.

Under these reaction conditions no appreciable cleavage of the siloxane bonds by alkyllithium reagents has been observed. Alkyllithium reagents have previously been reported to cleave siloxane substrates at ambient temperature to yield lithium alkyldimethylsiloxanoates [15–18]. We believe this basic difference if probably due to different solvent, ether rather than toluene, hexane or THF, and to the significantly lower temperature utilized in our experiments. In the absence of ether solvents, the less basic siloxane oxygens probably coordinate to the electron deficient alkyllithium aggregate which may favor siloxane cleavage. Under our reaction conditions silicon–chlorine bonds are significantly more reactive than siloxane bonds towards alkyllithium reagents. As far as we are aware, the selectivity observed with 1,3-dichlorotetramethyldisiloxane is novel.

Experimental

All reactions were carried out under an atmosphere of purified nitrogen. ^1H NMR spectra were obtained on a Varian XL-100 spectrometer operating in the CW or FT modes using respectively 20 or 5% solutions in deuterochloroform. Chloroform was utilized as the internal standard. The integration of the NMR spectra sometimes gave too small intensities for the Si-CH_3 signals because of saturation problems. However, in all cases the integration was within 10% of the calculated value [1,23]. ^{13}C NMR spectra were obtained on a Varian XL-200 using 10–15% solutions in deuterochloroform. ^{13}C NMR spectra were run with broad band proton decoupling (A) or with off resonance decoupling (B) to determine the multiplicity. IR spectra were obtained on a Perkin–Elmer 281 spectrometer. IR bands were calibrated against known bands of a polystyrene film. Mass spectra were obtained on a Hewlett–Packard 5985 GC-MS at an ionizing voltage of 70 eV. A 6′ × 1/2″ 5% OV-101 column was used in the gas chromatograph inlet of the mass spectrometer. GLPC analysis was performed on a Hewlett–Packard F&M 700 using a 28′ × 1/4″ 20% SE-30 on 60/80 mesh Chromosorb W column. Yields were calculated using n-decane as an internal standard. Starting materials are known compounds and had spectra in complete agreement with literature values. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, TN.

1,3-Dichlorotetramethyldisiloxane (I) and 1,5-dichlorohexamethyltrisiloxane (II) were purchased from Silar. n-Butyllithium and sec-butyllithium were obtained from Aldrich. t-Butyllithium was obtained from Alfa. Isopropyllithium [24] was prepared by reaction of isopropyl chloride [25] and lithium shot in olefin free petroleum ether. Alkyllithium solutions were standardized by double titration [26,27]. Diethyl ether was distilled from the sodium/benzophenone ketyl immediately prior to use.

Reaction of I with t-butyllithium in 1 / 1 molar ratio

In a 100 ml two-necked round bottom flask equipped with a pressure equalizing addition funnel and a rubber septum were placed 20 ml of ether, I (1 g, 4.9 mmol) and a Teflon covered magnetic stirring bar. The solution was cooled to −78°C. t-Butyllithium (2.0 *M* in pentane) (2.5 ml, 5 mmol) was added slowly from an additional funnel. A sample was withdrawn from the reaction mixture after 50 min and hydrolyzed. GLPC analysis showed only 1-t-butyl-3-hydroxytetramethyldisiloxane. It is presumed that this product arises from hydrolysis of 1-t-butyl-3-chlorotetramethyldisiloxane. Apparently I is totally converted to 1-t-butyl-3-chlorotetramethyldisiloxane prior to any further reaction with t-butyllithium. The reaction mixture was quenched by addition of a mixture of H_2O/THF in 1/20 ratio at −78°C. The mixture was kept at −78°C for another 20 min and then allowed to warm to room temperature. More water was added. The organic layer was separated, washed till neutral, dried over Na_2SO_4 and filtered. The ether layer was evaporated under reduced pressure. GLPC analysis of the residue indicated the formation of 1-t-butyl-3-hydroxytetramethyldisiloxane in quantitative yield. Neither D_3, D_4 nor 1,3-di-t-butyltetramethyldisiloxane was found under these reaction conditions. In independent experiments, hydrolysis of I under these conditions yields hexamethylcyclotrisiloxane (D_3) and octamethylcyclotetrasiloxane (D_4). 1-t-Butyl-3-hydroxytetramethyldisiloxane had the following spectral properties: ^1H NMR: δ 0.11 (s, 6H), 0.2 (s, 6H), 0.94 (s, 9H), 2.02 (s, 1H) ppm. Addition of D_2O to the NMR tube caused the disappearance of the peak at δ 2.02 ppm. IR: $\bar{\nu}$ 1080 (Si–O–Si) [28], 3320 (Si–OH; neat) 3680 cm^{-1} (Si–OH in CCl_4) [1]. Anal. Found: C, 46.35, H, 10.98. $C_8H_{22}O_2Si_2$ calcd.: C, 46.55, H, 11.14%.

Reaction of I with t-butyllithium in 1 / 4.5 molar ratio

t-Butyllithium (11 ml, 22 mmol) and I (1 g, 4.9 mmol) in 20 ml of ether were reacted as above at −78°C for 3 h. The reaction mixture was then warmed up to 0°C. Stirring was continued until GLPC analysis of samples withdrawn from the reaction mixture indicated the total consumption of 1-t-butyl-3-chlorotetramethyldisiloxane and the quantitative formation of 1,3-di-t-butyl-tetramethyldisiloxane. The reaction mixture was worked-up as above. 1,3-Di-t-butyltetramethyldisiloxane had the following spectral properties: ^1H NMR: δ 0.05 (s, 12H), 0.84 (s, 18H) ppm. ^{13}C NMR: δ −2.916 (q), 18.160 (s), 25.732 (q). IR: $\bar{\nu}$ 1065 cm^{-1} (Si–O–Si). MS: *m/e* 246 (0.8%) $M^{+\cdot}$, 231 (1.6%) $M^+ - 15$, 189 (22.2%), 147 (100%), 133 (6.7%), 115 (10.7%), 84 (52.2%), 73 (19.2%). Anal. Found: C, 58.31; H, 12.10%. $C_{12}H_{30}OSi_2$ calcd.: C, 58.46; H, 12.26%.

Reaction of I with sec-butyllithium in 1 / 1.4 molar ratio

sec-Butyllithium (1.4 *M* in hexane) (5 ml, 7 mmol) and I (1 g, 4.9 mmol) in 20 ml of ether were reacted as above at −78°C for 1 h. 1-sec-Butyl-3-hydroxytetramethyldisiloxane was formed. Neither 1,3-di-sec-butyltetramethyldisiloxane, D_3 nor D_4 were obtained. 1-sec-Butyl-3-hydroxytetramethyldisiloxane had the following properties: ^1H NMR: δ 0.14 (s, 6H), 0.19 (s, 6H), 0.4–0.8 (br. m, 1H), 0.95–1.36 (m, 6H), 1.36–1.4 (m, 6H), 2.0 (s, 1H) ppm. Addition of D_2O to the NMR tube caused the disappearance of the peak at δ 2.0 ppm. IR: $\bar{\nu}$ 1060 (Si–O–Si), 3400 (Si–OH, neat), 3660 cm^{-1} (Si–OH in CCl_4). MS: m/e 132 (12.5%), 75 (100%). Anal. Found: C, 46.63; H, 10.99% $C_8H_{22}O_2Si_2$ calcd.: C, 46.55; H, 11.14%.

Reaction of I with sec-butyllithium in 1 / 3.6 molar ratio

sec-Butyllithium (12.5 ml, 17.5 mmol) and I (1 g, 4.9 mmol) in 20 ml of ether were treated at −78°C for 2.5 h, then the reaction mixture was warmed up to 0°C. Stirring was continued (2 h) until GLPC analysis of samples withdrawn from the reaction mixture indicated the formation of only 1,3-di-sec-butyltetramethyldisiloxane. It had the following spectral properties: ^1H NMR: δ 0.09 (s, 12H), 0.21–0.71 (m, 2H), 0.85–1.05 (m, 12H), 1.05–1.67 (m, 4H) ppm. ^{13}C NMR: δ −1.327 (q) [*meso*], −1.238 (q) [*d*, *l*], 13.100 (q), 13.412 (q), 23.502 (d), 24.158 (t) ppm. IR: $\bar{\nu}$ 1075 cm^{-1} (Si–O–Si). MS: $m/e = 246$ (0.5%) $M^{+\cdot}$, 231 (0.7%) $M^+ - 15$, 189 (25.8%), 147 (15.9%), 133 (100%), 117 (12%), 73 (8.6%). Anal. Found: C, 58.40; H, 12.12%. $C_{12}H_{30}OSi_2$ calcd.: C, 58.46; H, 12.26%.

Reaction of I with n-butyllithium in 1 / 1 molar ratio

n-Butyllithium (1.6 M in hexane) (3 ml, 4.8 mmol) and (1 g, 4.9 mmol) in 20 ml of ether were treated at −78°C for 1.5 h. 1-n-Butyl-3-hydroxytetramethyldisiloxane was formed. Neither 1,3-di-n-butyltetramethyldisiloxane, D_3 nor D_4 were formed. 1-n-Butyl-3-hydroxytetramethyldisiloxane had the following spectral properties: ^1H NMR: δ 0.14 (s, 6H), 0.17 (s, 6H), 0.46–0.7 (m, 2H), 0.92 (t, 3H, J 7 Hz), 1.2–1.46 (m, 4H), 2.07 (s, 1H) ppm. Addition of D_2O to the NMR tube caused the disappearance of the peak at δ 2.07 ppm. IR: $\bar{\nu}$ 1060 cm^{-1} (Si–O–Si), 3680 cm^{-1} (Si–OH in CCl_4). MS: 132 (5.7%), 117 (68.5%), 75 (100%). Anal. Found: C, 46.77; H, 10.95%. $C_8H_{22}O_2Si_2$ calcd.: C, 46.55; H, 11.14%.

Reaction of I with n-butyllithium in 1 / 2.7 molar ratio

n-Butyllithium (8.5 ml, 13.6 mmol) and I (1 g, 4.9 mmol) in 20 ml of ether were treated at −78°C for 1.5 h. The reaction mixture was then warmed up to 0°C. Stirring was continued until GLPC analysis of samples withdrawn from the reaction mixture indicated the formation of only 1,3-di-n-butyltetramethyldisiloxane (2.5 h) [29,30]. It had the following spectral properties: ^1H NMR: δ 0.08 (s, 12H), 0.40–0.68 (m, 4H), 0.92 (t, 6H, J 6 Hz), 1.14–1.48 (m, 8H) ppm. ^{13}C NMR δ 0.051 (q), 13.541 (q), 17.812 (t), 25.285 (t), 26.073 (t) ppm. IR: $\bar{\nu}$ 1075 cm^{-1} (Si–O–Si). MS: $m/e = 231$ (2.7%) $M^+ - 15$, 189 (35.7%), 133 (100%), 119 (19.3%), 73 (5.7%).

Reaction of I with isopropyllithium in 1 / 2 molar ratio

Isopropyllithium (0.65 M in petroleum ether) (15 ml, 9.75 mmol) and I (1 g, 4.9 mmol) in 20 ml of ether were treated at −78°C for 3 h as above. After low temperature hydrolysis, a mixture of 1-isopropyl-3-hydroxytetramethyldisiloxane, D_3 and D_4 were formed. On the other hand, no 1,3-diisopropyltetramethyldisiloxane was obtained. 1-Isopropyl-3-hydroxytetramethyldisiloxane had the following spectral properties: ^1H NMR: δ 0.01 (s, 6H), 0.08 (s, 6H), 0.76–1.06 (m, 7H), 2.08 (s, 1H) ppm. Addition of D_2O to the NMR tube caused the disappearance of the peak at δ 2.08 ppm. IR: $\bar{\nu}$ 1090 (Si–O–Si), 3380 cm^{-1} (Si–OH, neat). MS: 177 (7.8%) $M^+ - 15$, 149 (100%), 133 (46.8%), 119 (6.7%), 75 (4.7%). Anal. Found: C, 43.61; H, 10.69%. $C_7H_{20}Si_2O_2$ calcd.: C, 43.69; H, 10.47%.

Reaction of I with isopropyllithium in 1/3.3 molar ratio

Isopropyllithium (25 ml, 16.25 mmol) and I (1 g, 4.9 mmol) in 20 ml of ether were treated at −78°C for 3 h. Then the reaction mixture was warmed up to 0°C. Stirring was continued until GLPC analysis of samples withdrawn from the reaction mixture indicated the formation of only 1,3-diisopropyltetramethyldisiloxane (1.5 h). It had the following spectral properties: ^{1}H NMR: δ 0.01 (s, 12H), 0.72–1.08 (m, 14H) ppm. ^{13}C NMR: −1.904 (q), 15.793 (d), 16.871 (q) ppm. IR: $\bar{\nu}$ 1060 cm^{-1} (Si–O–Si). MS: 218 (65%) $M^{+\cdot}$, 203 (5.5%) $M^+ - 15$, 191 (100%), 149 (97.9%), 133 (94.7%), 117 (13.9%), 73 (13.7%). Anal. Found: C, 55.14; H, 12.21%. $C_{10}H_{26}Si_2O$ calcd.: C, 54.97; H, 11.99%.

Sequential reaction of I with isopropyllithium followed by n-butyllithium

n-Butyllithium (1.55 *M* in hexane) (8 ml, 12.5 mmol) was added at −78°C to the reaction mixture containing 1-chloro-3-isopropyltetramethyldisiloxane which was generated by reaction of I with isopropyllithium as above. The reaction mixture was then warmed up to 0°C. Stirring was continued until GLPC analysis indicated to total consumption of 1-chloro-3-isopropyltetramethyldisiloxane (2 h). The following products were formed, 1,3-Diisopropyltetramethyldisiloxane (6%), 1,3-Di-n-butyltetramethyldisiloxane (24%), and 1-n-butyl-3-isopropyltetramethyldisiloxane (70%). 1-n-Butyl-3-isopropyltetramethyldisiloxane had the following spectral properties: ^{1}H NMR: δ 0.01 (s, 6H), 0.04 (s, 6H), 0.40–0.64 (m, 2H), 0.72–1.08 (m, 10H), 1.2–1.5 (m, 4H) ppm. ^{13}C NMR: δ −1.904 (q), 0.361 (q), 13.828 (q), 15.778 (d), 16.867 (q), 18.128 (t), 25.554 (d), 26.410 (d) ppm. IR: $\bar{\nu}$ 1080 cm^{-1}. MS: $m/e = 232$ (2.2%) $M^{+\cdot}$, 217 (4.6%) $M^+ - 15$, 189 (100%), 175 (25%), 161 (7.6%), 73 (12%), 59 (9.3%). Anal. Found: C, 57.04; H, 12.32% $C_{11}H_{28}Si_2O$ calcd.: C, 56.82; H, 12.15%.

Reaction of II with t-butyllithium in 1/1 Molar ratio

t-Butyllithium (2 ml, 4 mmol) and II (1 g, 3.6 mmol) in 20 ml of ether were treated at −78°C for 1 h. GLPC analysis of samples withdrawn from the reaction mixture indicated that formation of 1-t-butyl-5-hydroxyhexamethyltrisiloxane (38.3%), D_3 (19.7%), D_4 (35.4%), and 1,5-di-t-butylhexamethyltrisiloxane (6.3%). The ratio of these products depends on the exact time of quenching the reaction and the molar ratio of reactants. 1-t-Butyl-5-hydroxyhexamethyltrisiloxane had the following spectral properties: NMR: δ 0.12 (s, 6H), 0.15 (s, 6H), 0.21 (s, 6H), 0.94 (s, 9H), 2.08 (s, 1H) ppm. Addition of D_2O to the NMR tube caused the disappearance of the peak at δ 2.08 ppm. IR: $\bar{\nu}$ 1060 (Si–O–Si), 3300 (Si–OH neat) 3690 cm^{-1} (Si–OH in CCl_4). Anal. Found: C, 42.81, H, 10.05%. $C_{10}H_{28}O_3Si_3$ calcd.: C, 42.80; H, 10.05%.

Reaction of II with t-butyllithium in 1/3.2 molar ratio

t-Butyllithium (5.8 ml, 11.6 mmol) and II (1 g, 3.6 mmol) in 20 ml ether were treated at −78°C for 3 h. 1,5-Di-t-butylhexamethyltrisiloxane was formed in quantitative yield. It had the following spectral properties: ^{1}H NMR: δ 0.09 (s, 12H), 0.16 (s, 6H), 0.91 (s, 18H) ppm. ^{13}C NMR: −2.991 (q), 1.248 (q), 18.073 (s), 25.692 (q) ppm. IR: $\bar{\nu}$ 1070 cm^{-1} (Si–O–Si). Anal. Found: C, 52.36, H: 11.12%. $C_{14}H_{36}O_2Si_3$ calcd.: C, 52.43; H, 11.31%.

Reaction of II with sec-butyllithium in 1/1 molar ratio

sec-Butyllithium (2.5 ml, 4.9 mmol) and II (1 g, 3.6 mmol) in 20 ml of ether were treated at −78°C for 1 h. GLPC analysis of samples withdrawn from the reaction mixture indicated the formation of 1-sec-butyl-5-hydroxyhexamethyltrisiloxane (22%), D_3 (27%), D_4 (12%), and 1,5-di-sec-butylhexamethyldisiloxane (39%). 1-sec-Butyl-5-hydroxyhexamethyltrisiloxane had the following spectral properties: ^{1}H NMR: δ 0.11 (s, 6H), 0.12 (s, 6H), 0.18 (s, 6H), 0.28–0.76 (m, 1H), 0.93 (d, 3H, J 2 Hz), 1.0 (t, 3H, J 3 Hz), 1.08–1.64 (m, 2H), 2.02 (s, 1H) ppm. Addition of D_2O to the NMR tube caused the disappearance of the peak at δ 2.02 ppm. IR: $\bar{\nu}$ 1070 (Si–O–Si), 3300 (Si–OH, neat), 3600 (Si–OH in CCl_4) cm^{-1}. Anal. Found: C, 42.67; H, 9.93%. $C_{10}H_{28}O_3Si_3$ calcd.: C, 42.80; H, 10.05%.

Reaction of II with sec-butyllithium in 1 / 4.2 molar ratio

sec-Butyllithium (11 ml, 15.4 mmol) and II (1 g, 3.6 mmol) in 20 ml of ether were treated at −78°C for 2.5 h. 1,5-Di-sec-butylhexamethyltrisiloxane was formed in quantitative yield. It had the following spectral properties: ^{1}H NMR; δ 0.08 (s, 6H), 0.1 (s, 12H), 0.38–1.74 (m, 2H), 0.84–1.08 (m, 12H), 1.08–1.68 (m, 4H) ppm. ^{13}C NMR: δ −1.59 (q) [*meso*], −1.492 (q) [d,1], 1.221 (q), 12.964 (q), 13.307 (q), 23.277 (d), 24.005 (t). IR: $\bar{\nu}$ 1050 cm^{-1} (Si–O–Si). Anal. Found: C, 52.69; H, 11.19% $C_{14}H_{36}O_2Si_3$ calcd.: C, 52.43; H, 11.31%.

Reaction of II with n-butyllithium in 1 / 1 molar ratio

n-Butyllithium (2.5 ml, 4 mmol) and II (1 g, 3.6 mmol) in 20 ml in ether were treated at −78°C for 1 h. GLPC analysis of samples withdrawn from the reaction mixture indicated the formation of 1-n-butyl-5-hydroxyhexamethyltrisiloxane (5.4%), D_3 (21.6%), D_4 (5.9%), and 1,5-di-n-butylhexamethyltrisiloxane (67%). 1-n-Butyl-5-hydroxyhexamethyltrisiloxane had the following spectral properties. ^{1}H NMR: δ 0.12 (s, 12H), 0.18 (s, 6H), 0.41–0.73 (m, 2H), 0.83–1.03 (m, 3H), 1.23–1.47 (m, 4H), 1.99 (s, 1H). Addition of D_2O to the NMR tube caused the disappearance of the peak at δ 1.99 ppm. IR: $\bar{\nu}$ 1050 (Si–O–Si), 3340 (Si–OH, neat), 3680 cm^{-1} (Si–OH in CCl_4). Anal. Found: C, 43.64; H, 10.30% $C_{10}H_{28}O_3Si_3$ calcd.: C, 42.80%; H, 10.05%.

Reaction of II with n-butyllithium in 1 / 4 molar ratio

n-Butyllithium (9 ml, 14.4 mmol) and II (1 g, 3.6 mmol) in 20 ml of ether were treated at −78°C for 2.5 h. 1,5-Di-n-butylhexamethyltrisiloxane was formed in quantitative yield [29,30]. It had the following spectral properties: ^{1}H NMR: δ 0.08 (s, 6H), 0.12 (s, 12H), 0.48–0.7 (m, 4H), 0.94 (t, 6H, J 6 Hz), 1.16–1.64 (m, 8H) ppm. ^{13}C NMR: δ 0.207 (q), 1.301 (q), 13.846 (q), 18.017 (t), 25.496 (t), 26.420 (t) ppm. IR: $\bar{\nu}$ 1050 cm^{-1} (Si–O–Si). Anal. Found: C, 52.11; H, 11.18%. $C_{14}H_{36}O_2Si_3$ calcd.: C, 52.43; H, 11.31%.

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