New Route from Si−O to Si−C Bonds: Alkylalkoxysilanes from Alkoxysilanes and Metal Hydrides

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The typical pathway from silicon−oxygen to silicon−carbon bonds involves nucleophilic attack of an organometallic reagent on the silicon center. A new transformation from silicon−oxygen to silicon−carbon bonds is reported that proceeds without nucleophilic attack of a carbanion. The reaction of $Si(OMe)_4$ with NaH yields $MeSi(OMe)_3$ at temperatures above 300 °C. Mechanistic studies indicate that an intact methyl group is transferred from a methoxy group to the silicon center in the Si−C bond-forming step.

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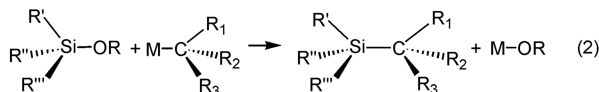
Introduction

Silicone polymers of the general structure $(RR'SiO)_n$ are widely used in numerous applications.[1] The ultimate source of silicon atoms for silicone materials is silicon dioxide. Considering that about 60% of Earth's crust is composed of silica and silicates, the relatively high cost of silicones is not a function of raw material cost, but the result of enormous energy consumption during the manufacturing process. The major contributor to the high cost of silicones is an energy-intensive, carbothermal reduction step from SiO_2 to elemental silicon. An alternative route to silicones is depicted in eq 1, where the reduction and reoxidation of silicon is avoided.

$$SiO_2 \rightarrow Si(OR)_4 \rightarrow R_2Si(OR)_2 \rightarrow (R_2SiO)_n \quad (1)$$

Significant advances have been made in the activation and depolymerization of SiO_2 to produce monomeric Si compounds.[2] The direct conversion of silicon−oxygen to silicon−carbon bonds is currently based on stoichiometric nucleophilic substitution reactions[3] at the silicon center (eq 2) involving costly organometallic reagents, almost exclusively of the alkyllithium and Grignard type.[2b,c,f,4] In this context we decided to explore new routes from Si−O to Si−C bonds.



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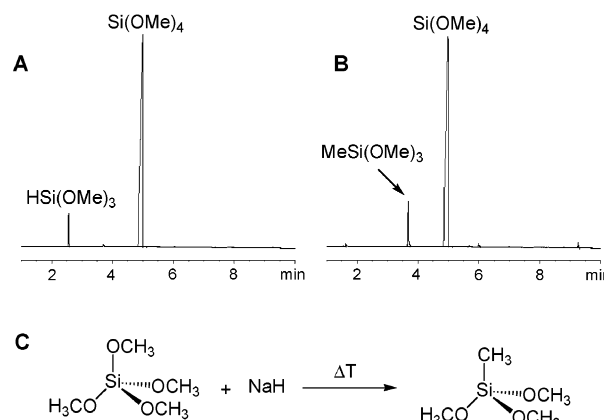

Figure 1. GC traces of the reactor downstream for the reaction of $Si(OMe)_4$ with NaH at 275 °C (A) and at 350 °C (B). $MeSi(OMe)_3$ is the dominant product at 350 °C (C).

Tetramethoxysilane was chosen as starting material since substitution of two methoxy groups by methyl groups results in $Me_2Si(OMe)_2$, a direct precursor to silicones. Additionally, $Si(OMe)_4$ is a low-boiling fluid that can easily be used in various reactor types. In an attempt to react $Si(OMe)_4$ under strongly reducing conditions, we studied the reaction of $Si(OMe)_4$ with NaH in a fixed-bed reactor.

Results and Discussion

When $Si(OMe)_4$ was passed through a bed of NaH at temperatures above 200 °C, a new peak besides unreacted $Si(OMe)_4$ was observed in the GC trace (retention time: 2.6 min; Figure 1A). The peak represented $HSi(OMe)_3$ as confirmed by GC/MS and ^{29}Si NMR.[5] At temperatures above 275 °C, an additional peak (retention time: 3.7 min) was found in the GC trace. The peak increased in intensity as the reactor temperature was raised and represented the only significant product at

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325 °C and above (Figure 1B). Surprisingly, this compound was identified by GC/MS and ^{29}Si NMR to be $MeSi(OMe)_3$. By comparison, Kuznetsov reported that no reaction occurred between $Si(OEt)_4$ and NaH in solution at temperatures up to 168 °C.[6] Other hydrides such as LiH and $NaBH_4$ similarly reacted with $Si(OMe)_4$ to form $MeSi(OMe)_3$, but were found to be less reactive and required higher reaction temperatures. The formation of $MeSi(OMe)_3$ from $Si(OMe)_4$ and NaH (Figure 1C) represents a new and unexpected transformation from Si−O to Si−C bonds.

The low byproduct production combined with the high symmetry of the starting material, $Si(OMe)_4$, allowed us to study the mechanism of this unusual reaction in more detail. The question, if $HSi(OMe)_3$ and $MeSi(OMe)_3$ were formed independently from each other or if $HSi(OMe)_3$ was an intermediate in the formation of $MeSi(OMe)_3$, was addressed by reacting $HSi(OMe)_3$ with NaH. $MeSi(OMe)_3$ was observed as a product at temperatures as low as 200 °C, when $HSi(OMe)_3$ was passed through a bed of NaH. The relative amount of $MeSi(OMe)_3$ formed increased as the reactor temperature was raised. At 325 °C, 37% of the reactor downstream mixture was composed of $MeSi(OMe)_3$. Additionally, the formation of $Me_2Si(OMe)_2$ was observed. In the absence of NaH, $HSi(OMe)_3$ was found to be thermally stable beyond 350 °C. This result suggests that $MeSi(OMe)_3$ is formed from intermediately formed $HSi(OMe)_3$. Significant redistribution of $HSi(OMe)_3$ into SiH_4 and $Si(OMe)_4$ was observed, a reaction with precedence in the literature.[7]

Deprotonation of $HSi(OMe)_3$ by NaH to form a sodium silyl species is a conceivable first step in the formation of $MeSi(OMe)_3$ from intermediately formed $HSi(OMe)_3$. The related formation of $KSiEt_3$ from KH and $HSiEt_3$ was reported by Corriu et al.[8] If in fact NaH reacted as a base with $HSi(OMe)_3$ to form $MeSi(OMe)_3$, then the reaction of $HSi(OMe)_3$ with a different, sufficiently strong base should also lead to formation of $MeSi(OMe)_3$. Indeed, $MeSi(OMe)_3$ was generated in the reaction of $HSi(OMe)_3$ with potassium *tert*-butoxide (K-O-*t*-Bu) at 175 °C. Again, redistribution of $HSi(OMe)_3$ into $Si(OMe)_4$ and SiH_4 was observed. Neat $Si(OMe)_4$ did not react with K-O-*t*-Bu, confirming that only $HSi(OMe)_3$, but not the concurrently formed $Si(OMe)_4$, reacted with base. These results are further evidence that $HSi(OMe)_3$ was an intermediate in the formation of $MeSi(OMe)_3$.

GC/MS analysis of the carrier gas exiting the reactor during the reaction of $Si(OMe)_4$ and NaH at 325 °C revealed the formation of H_2 and methane. When $Si(OMe)_4$ was reacted with LiD at 375 °C, HD and CH_3D were observed as the dominant products. The observed methane formation suggested nucleophilic attack of the hydride or deuteride at a CH_3 group of $Si(OMe)_4$. The generation of H_2 is further indication for the deprotonation of $HSi(OMe)_3$ by NaH.

An important question was whether an intact methyl group was transferred in the Si−C bond-forming step. Reaction of $Si(OMe)_4$ with LiD at 400 °C yielded a mixture that contained 22% $MeSi(OMe)_3$ as determined by GC (Figure 2A). The ^{13}C NMR spectrum (^{1}H decoupled) of the reaction mixture revealed one dominant peak (>90%) in the region expected for $\mathit{C}H_3$−Si (Figure 2B). A singlet at −8.9 ppm suggested that no scrambling of deuterium into $C\mathit{H}_3$−Si had occurred. Similarly, the ^{1}H NMR spectrum exhibited a singlet at 0.11 ppm as the dominant peak in the Si−Me region (Figure 2C). In the ^{2}H NMR, a small signal was detected at −0.05 ppm, only a trace amount based on intensity estimates using the ^{13}C satellites of the solvent signal. Consistent with the ^{1}H and ^{13}C NMR data, the ^{29}Si NMR spectrum exhibited a singlet at −39.3 ppm as expected for $C\mathit{H}_3$−$Si(OMe)_3$. Also, MS (chemical ionization) did not show significant enrichment of deuterium in $MeSi(OMe)_3$. The NMR and MS studies indicated that more than 90% of the formed $MeSi(OMe)_3$ did not contain deuterium and suggested transfer of an intact methyl group to the silicon center in the Si−C bond-forming step.

On the basis of the presented data we propose a mechanism for the formation of $MeSi(OMe)_3$ from $Si(OMe)_4$ and NaH (Figure 3). Initially $HSi(OMe)_3$ is generated from $Si(OMe)_4$ by nucleophilic attack of H^- at the silicon center (Figure 3A). In the second step (Figure 3B), the NaH acts as a base and reacts with $HSi(OMe)_3$ to form a sodium silyl species, presumably $NaSi(OMe)_3$. The sodium silyl derivative presumably reacts by nucleophilic attack on a methoxy group of,

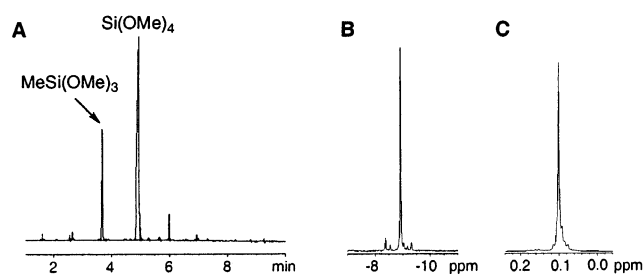

Figure 2. GC trace (A) and NMR data of the reactor downstream for the reaction of $Si(OMe)_4$ with LiD at 400 °C. The ^{13}C NMR (B) and ^{1}H NMR (C) spectra each show the region typical for methyl groups directly bound to silicon.

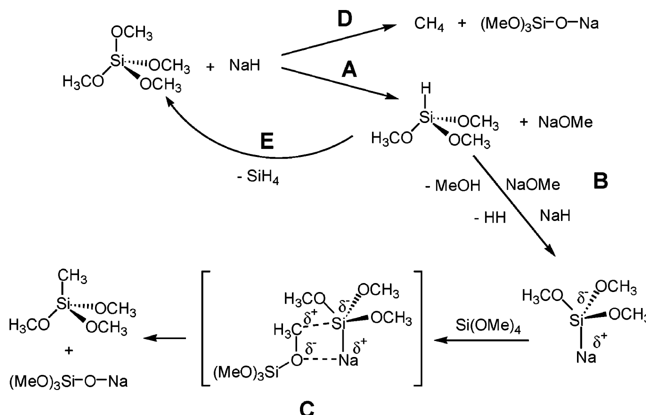

Figure 3. Proposed mechanism of the direct formation of $MeSi(OMe)_3$ from $Si(OMe)_4$ and NaH: (A) Nucleophilic attack of H^- at $Si(OMe)_4$; (B) H-abstraction to form a sodium silyl derivative; (C) Si−C bond formation by nucleophilic attack of the silyl group. Methane formation (D) and redistribution of $HSi(OMe)_3$ (E) are undesired side reactions.

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most likely, another $Si(OMe)_4$ to form $MeSi(OMe)_3$ (Figure 3C).[9] The formation of methane by nucleophilic attack of H^- on a methyl group of $Si(OMe)_4$ (Figure 3D) and the redistribution of $HSi(OMe)_3$ into $Si(OMe)_4$ and SiH_4 (Figure 3E) represent unproductive side reactions negatively affecting the yield of $MeSi(OMe)_3$. Cumulative yields of 35−40% $MeSi(OMe)_3$ based on $Si(OMe)_4$ were found, when a slight excess of NaH was used assuming consumption of two $Si(OMe)_4$ per $MeSi(OMe)_3$ formed. Although pentacoordinate silicon species are likely intermediates during the various reaction steps, no signals were found in the region typical for higher coordinated silicon species in the solid state ^{29}Si NMR spectrum of the bed after partial reaction.

Analogous silicon−carbon bond formation was observed with higher substituted alkoxysilanes such as $Si(OEt)_4$ and $Si(O\text{-}n\text{-}Pr)_4$ in the reaction with NaH to form the corresponding alkyltrialkoxysilanes. Transfer of an intact alkyl group further supports the proposed mechanism.

Conclusions

We report a new reaction pathway from Si−O to Si−C bonds starting from tetraalkoxysilanes and metal hydrides. Mechanistic studies indicate that the formation of $MeSi(OMe)_3$ from $Si(OMe)_4$ proceeds via formation of $HSi(OMe)_3$. The Si−C bond-forming step involves methyl transfer from a methoxy group onto the silicon center. Surprisingly, an electrophilic alkyl fragment is transferred in the Si−C bond-forming step, in contrast to the typical nucleophilic substitution.

Experimental Section

General Considerations. All reactions were performed in a fixed-bed reactor setup installed inside of a fume hood. The reactor outlet stream was vented into the back of the hood to ensure effective ventilation of the outgasses, particularly the highly flammable SiH_4, a product of the significant $HSi(OMe)_3$ disproportion reaction. Sodium hydride (95% purity) was purchased from Aldrich and handled under an inert gas atmosphere. $Si(OMe)_4$ (99.5% purity) was purchased from Aldrich and used as is. The fractions collected at the reactor outlet were analyzed using a Hewlett-Packard 6890 gas chromatograph and frequently reanalyzed using GC/MS (JEOL model HX110 mass spectrometer) equipped with a J&W Scientific DB-5 MS column. All NMR data were obtained on GE NMR Instruments Omega nuclear magnetic resonance spectrometers operating at 500 MHz (11.75T) for ^{13}C, ^{29}Si, and ^{2}H and at 300 MHz (7.06T) for ^{1}H. A JEOL SX-102 mass spectrometer was used for MS gas phase analysis. Elemental analysis of the reactor bed samples was performed using a Varian Liberty II ICP-AES instrument. Digestion methods were used for sample preparation.

Typical Procedure for Reaction of $Si(OMe)_4$ with NaH as a Function of Temperature (Example 1). Sodium hydride (0.97 g; 40 mmol) was charged into a fixed-bed flow reactor with vertical furnace and flushed with argon carrier gas at a rate of 20 mL/min. The initial reactor temperature was 200 °C. The reaction was performed using argon as carrier gas (14 mL/min). Tetramethoxysilane [$Si(OMe)_4$] (2.13 mL/h; 14.4 mmol/h) was fed into the carrier gas stream using a motor-driven syringe. The reactor effluent downstream was collected in fractions using a water-chilled condenser and analyzed by gas chromatography. The reaction was carried out with a temperature ramp starting at 200 °C. After collecting a fraction, typically in a range between 0.5 and 2 g, the reactor temperature was increased by 25 or 50 °C for screening purposes. Methyltrimethoxysilane [$MeSi(OMe)_3$] and trimethoxysilane [$HSi(OMe)_3$] formation was confirmed by gas chromatography, GC/MS, and multinuclear NMR techniques. $HSi(OMe)_3$ formation was first detected at 225 °C, and $MeSi(OMe)_3$ formation was first detected at 325 °C. Total amount of $Si(OMe)_4$ reacted (= $Si(OMe)_{4\ added}$ − $Si(OMe)_{4\ recovered}$): 2.81 g (18.5 mmol); total amount $MeSi(OMe)_3$ formed: 87 mg (0.6 mmol); total amount $HSi(OMe)_3$ formed: 115 mg (0.9 mmol); amount of Si detected in the reactor bed after reaction: 18.2% (344 mg; 12.3 mmol).

Reaction of $Si(OMe)_4$ with NaH at Fixed Temperature. The procedure of example 1 was followed with the following modifications: sodium hydride (1.00 g; 41.7 mmol). Reaction was carried out at a fixed temperature of 325 °C. Total amount of $Si(OMe)_4$ reacted (= $Si(OMe)_{4\ added}$ − $Si(OMe)_{4\ recovered}$): 2.28 g (15.0 mmol); total amount $MeSi(OMe)_3$ formed: 253 mg (1.9 mmol); total amount $HSi(OMe)_3$ formed: 102 mg (0.7 mmol).

Reaction of $HSi(OMe)_4$ with NaH. The procedure of example 1 was followed with the following modifications: sodium hydride (1.01 g; 42.1 mmol); $HSi(OMe)_3$ (2.13 mL; 16.7 mmol/h) was added instead of $Si(OMe)_4$. $MeSi(OMe)_3$ formation was already detected at the initial temperature of 200 °C (0.5% of the reactor downstream). The concentration of $MeSi(OMe)_3$ in the reactor downstream steadily increased with increasing temperature, and at 325 °C, 37.3% of the reactor downstream was found to be $MeSi(OMe)_3$.

Reaction of $Si(OMe)_4$ with LiD. The procedure of example 1 was followed with the following modification: lithium deuteride (1.82 g; 228 mmol) was used instead of sodium hydride. A larger excess of LiD was used to ensure comparable reactor bed height. $MeSi(OMe)_3$ formation was first detected at 350 °C (0.7% of the reactor downstream) and increased with increasing temperature (3.6% $MeSi(OMe)_3$ at 375 °C and 21.5% $MeSi(OMe)_3$ at 400 °C).

Reaction of $Si(OMe)_4$ with $NaBH_4$. The procedure of example 1 was followed with the following modification: sodium borohydride (1.04 g; 27.5 mmol) was used instead of sodium hydride. $MeSi(OMe)_3$ formation was first detected at 375 °C (0.5% of the reactor downstream) and increased with increasing temperature (2.9% $MeSi(OMe)_3$ at 400 °C and 6.3% $MeSi(OMe)_3$ at 425 °C).

Reaction of $HSi(OMe)_3$ with K-O-*t*-Bu. The procedure in example 1 was used with the following modifications: potassium-*tert*-butoxide (0.98 g; 8.7 mmol) was used instead of sodium hydride; trimethoxysilane (2.13 mL/h; 16.7 mmol/h) was used instead of tetramethoxysilane. $MeSi(OMe)_3$ formation was first detected at 175 °C (1.8% of the reactor downstream; 3.5% at 200 °C).

Reaction of $Si(OEt)_4$ with NaH. The procedure in example 1 was used with the following modifications: sodium hydride (95% purity, 1.00 g; 39.6 mmol); tetraethoxysilane (0.5 mL/h; 2.2 mmol/h); nitrogen (1 mL/min) was used as carrier gas. $EtSi(OEt)_3$ formation was first detected at 250 °C (2.1% of the reactor downstream).

Reaction of $Si(O\text{-}n\text{-}Pr)_4$ with NaH. The procedure in example 1 was used with the following modifications: sodium hydride (95% purity, 1.00 g; 39.6 mmol); tetra-*n*-propoxysilane (1.5 mL/h; 5.2 mmol/h); argon (5 mL/min) was used as carrier gas. $n\text{-}PrSi(O\text{-}n\text{-}Pr)_3$ formation was detected at 250 °C (0.2% of the reactor downstream) and at 300 °C (1.1%).

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Supporting Information Available: Detailed description of analytical methods and a diagram of the reactor setup. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Intramolecular rearrangement followed by redistribution is also a viable alternative for the Si−C bond-forming step as one reviewer noted.

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