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Anionic Intermediates in the Reductive Coupling of 1-Chloro-2-phenyltetramethyldisilane with Lithium and Subsequent Redistribution Processes

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Oligosilyl anions have been found to participate in the reaction of 1-chloro-2-phenyltetramethyldisilane with excess lithium in THF at room temperature. The overall reaction was monitored by ^{1}H NMR, HPLC, and UV spectroscopy. The reaction proceeds in four steps. In the first slow stage, the disilyl chloride reacts with lithium to form a disilyllithium anion, which immediately reacts with the remaining disilyl chloride to yield 1,4-diphenyloctamethyltetrasilane. In a second faster stage, the tetrasilane accepts an electron from lithium to form a radical anion and subsequently mono-, di-, and trisilyl anions, which react with the disilyl chloride to form α,ω-diphenyltrisilanes, -tetrasilanes, and -pentasilanes. The third stage begins when all of the silyl chloride has been consumed and the cleavage of Si–Si bonds in α,ω-diphenyloligosilanes by silyl anions produces dodecamethylcyclohexasilane. A thermodynamic product distribution is formed in this scrambling process. During the final stage more electrons are being added to the system from lithium and an equilibrium mixture of (2-phenyltetramethyldisilyl)lithium, (phenyldimethylsilyl)lithium, and dodecamethylcyclohexasilane is established. The silyl anions formed in the process are characterized by various methods (^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, UV, and EPR spectroscopy).

Introduction

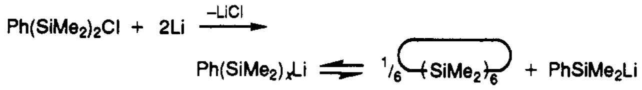
The electronic, optical, and chemical properties of compounds with Si–Si linkages in the main chain have been studied.[1-3] These properties depend upon chain length, substituents at the Si atoms, chain microstructure, and chain conformation. This strongly resembles other delocalized systems such as polyenes. The most important preparative method leading to Si–Si polymers and oligomers is the reductive coupling of chlorosilanes with alkali metals.[1-5] Reaction of disubstituted dichlorosilanes provides oligo- and polysilanes, whereas reaction of monochlorosilanes should only provide products of direct coupling. Therefore, coupling of 1-chloro-2-phenyltetramethyldisilane should yield 1,4-diphenyloctamethyltetrasilane. However, it has been found that, in the reaction of 1-chloro-2-phenyltetramethyldisilane with lithium in THF at room temperature, a series of α,ω-diphenyl permethylated oligosilanes with the formula $Ph(Me_2Si)_nPh$, where n = 2–6, initially forms. In the presence of excess lithium, these oligosilanes are converted to a mixture of cyclic and linear oligosilanes and eventually into a mixture of monosilyl and disilyl anions and cyclohexasilane (Scheme I).

Previously, a thermodynamic distribution of oligosilanes in a similar reaction was studied;[6] however, no kinetic aspects were revealed. In this paper, we discuss the mechanism of the coupling and the redistribution processes.

Results

1. Kinetics of the Reaction of 1-Chloro-2-phenyltetramethyldisilane with Lithium. The reaction of 1-chloro-2-phenyltetramethyldisilane with lithium in THF was studied at room temperature using several techniques: HPLC, ^{1}H NMR, and UV–vis. The dependence of substrate and product concentrations at different reaction times is shown in Figure 1. Four stages can be distinguished.

Scheme I



(1) An induction period (time <5 min) depends on the surface property of lithium, which is difficult to control. No color change is observed.

(2) During the second stage (time 5–125 min), 1-chloro-2-phenyltetramethyldisilane is converted into a mixture of 1,4-diphenyloctamethyltetrasilane (~50%), 1,3-diphenylhexamethyltrisilane (~25%), and 1,5-diphenyldecamethylpentasilane (~25%). A small amount of 1,2-diphenyltetramethyldisilane and longer oligosilanes can also be detected. The reaction mixture is colorless; however, dark green spots on the surface of lithium can be observed.

(3) A strong decrease in the concentration of tetrasilane, as well as penta- and trisilanes, is noted during the third stage (time 125–250 min) of the reaction. The disilane becomes the dominating product, and dodecamethylcyclohexasilane appears. During this stage, green streams which originate at the lithium surface turn red at some distance and decrease in intensity at a further distance, eventually becoming colorless. Soon, the reaction mixture becomes pink and ultimately deep red (UV maximum at 450 nm). One of us has described this process as the "bleeding" of lithium. Somewhere during this stage, a nearly thermodynamic product distribution is formed[6] due to the relatively small concentration of anions present in the reaction mixture.

(4) During the fourth stage (time >250 min), the continuous donation of electrons from lithium to the oligosilanes leads to the formation of an equilibrium mixture of (phenyldimethylsilyl)lithium, (2-phenyltetramethyldisilyl)lithium, and dodecamethylcyclohexasilane. The color of the reaction mixture changes from dark red to dark green (maxima at 350, 450, and 650 nm). The NMR spectrum shows a mixture of anions, and the EPR spectrum shows the presence of radicals. If the lithium is removed from the reaction mixture, the color eventually

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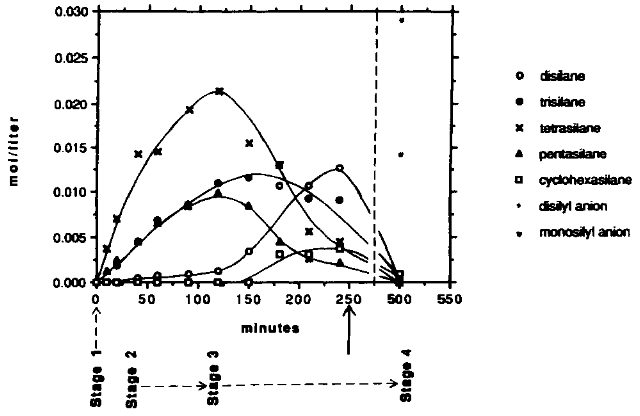

Figure 1. Dependence of substrate and product concentrations as a function of reaction time, as determined by HPLC. The large arrow at 250 min represents the equilibrium distribution obtained by Kumada.[6]

changes back to red and slowly disappears.

2. Characterization of (2-Phenyltetramethyldisilyl)lithium. A variety of monosilyl anions with alkyl and aryl groups have previously been prepared and characterized by spectroscopic methods.[7] The charge in the silyl anions with aryl groups is less delocalized than in analogous carbanions.[8] Disilyl and polysilyl anions have been proposed as intermediates in many reactions but have never been isolated and characterized spectroscopically. One of the reasons is the high reactivity of the Si–Si bonds toward strong nucleophiles and anions, which leads to scrambling and redistribution reactions.[6] Polysilyl anions are important intermediates in the synthesis of polysilanes.[9]

The disilyl anion was prepared either in the reaction of 1-chloro-2-phenyltetramethyldisilane with lithium, (phenyldimethylsilyl)lithium with dodecamethylcyclohexasilane, or 1-chloro-3-phenyl-hexamethyltrisilane with lithium or by reduction of α,ω-diphenyloligosilanes with lithium (Experimental Section; Figure 6). An equilibrium between the disilyl and monosilyl anions is established in all cases. The disilyl anion is always present simultaneously with the monosilyl anion in approximately a 2:1 ratio, in addition to dodecamethylcyclohexasilane. The products of the reaction have been characterized by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, and UV–vis spectroscopy.

The aromatic region in the ^{1}H NMR spectrum of (2-phenyltetramethyldisilyl)lithium anion resembles that of (phenyldimethylsilyl)lithium[8] (Figure 2). A doublet, due to the ortho protons, and two triplets, due to the meta and para protons, are seen for both anions. The downfield shift of the aromatic region for the (2-phenyltetramethyldisilyl)lithium anion relative to the resonances for the phenyldimethylsilyl anion indicates a decrease in the overall electron density in the ring due to the increased distance between the ring and the anion center. Compared with the spectrum for the monosilyl anion, downfield shifts for para (0.29 ppm), meta (0.16 ppm), and ortho (0.14 ppm) protons in the disilyl anion indicate a weaker delocalization of the negative charge by π-polarization effects.[8] Small signals downfield from the disilyl anions may be ascribed to a small amount of longer oligosilyl anions in which the charge is still less localized onto the aromatic ring. A singlet representing the methyl groups of the monosilyl anion is at 0.052 ppm, and two singlets of equal intensity for the disilyl anion are at 0.12 and 0.01 ppm.

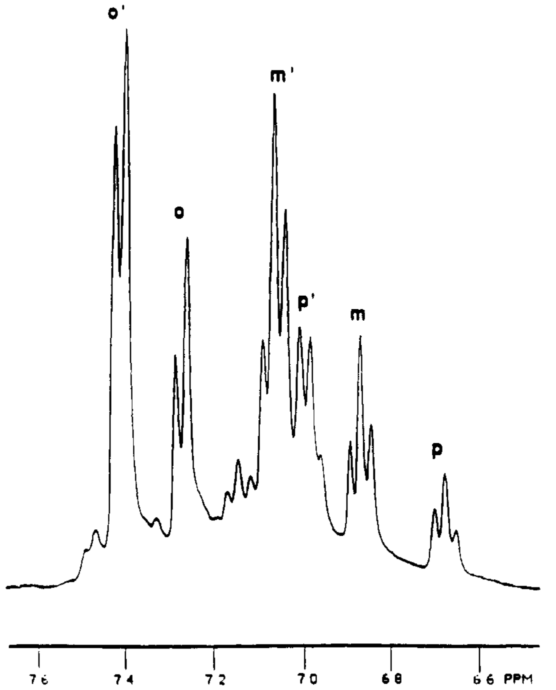

Figure 2. ^{1}H NMR spectrum of the equilibrium mixture showing the ortho (o′), meta (m′), and para (p′) protons of (2-phenyltetramethyldisilyl)lithium as well as the ortho (o), meta (m), and para (p) protons of (phenyldimethylsilyl)lithium.

Table I. ^{13}C NMR Chemical Shifts of Disilanes (ppm)

	PhMe$_2$-SiMe$_2$SiCl	PhMe$_2$-SiMe$_2$SiLi	shift (from Cl to Li)
ipso	137.4	149.0	downfield 11.6
ortho	134.9	134.4	approx same
meta	128.8	128.6	approx same
para	130.0	127.1	upfield 2.9
methyl	2.5, −4.2	1.45, −1.92	upfield >1

Table II. ^{13}C NMR Chemical Shifts of Monosilanes (ppm)

	PhMe$_2$SiCl	PhMe$_2$SiLi	shift (from Cl to Li)
ipso	137.0	166.0	downfield 29
ortho	133.8	133.8	approx same
meta	128.1	126.5	approx same
para	131.0	122.7	upfield 8.7
methyl	2.3	7.5	downfield 5

The ^{13}C NMR spectra confirm a weaker electron delocalization in disilyllithium (Table I) than in monosilyllithium (Table II). A comparison of the ^{13}C NMR chemical shifts for the corresponding chlorides and anions indicates that the ipso carbon is shifted downfield by 29 ppm when going from the phenyldimethylsilyl choride to (phenyldimethylsilyl)lithium, but only by 11.6 ppm for the disilanes.[8] The para carbon atom is shifted upfield by 8.3 ppm for monosilanes, but only 2.9 ppm for disilanes. The chemical shifts of the ortho and meta carbon signals remain essentially the same for both mono- and disilanes.

The ^{29}Si NMR (DEPT) spectrum of the disilyl anion showed two peaks (Figure 3), one at −69.8 ppm (B), which is assigned to the negatively charged silicon atom (42.6 ppm upfield from the monosilyl anion (C)), and the other at −12.6 ppm (A). The coupling constant $^1J_{\text{Si-Si}} = 31$ Hz for the disilyl anion is much less than in phenylpentamethyldisilane (86.1 Hz).[10] This indicates a weaker cou-

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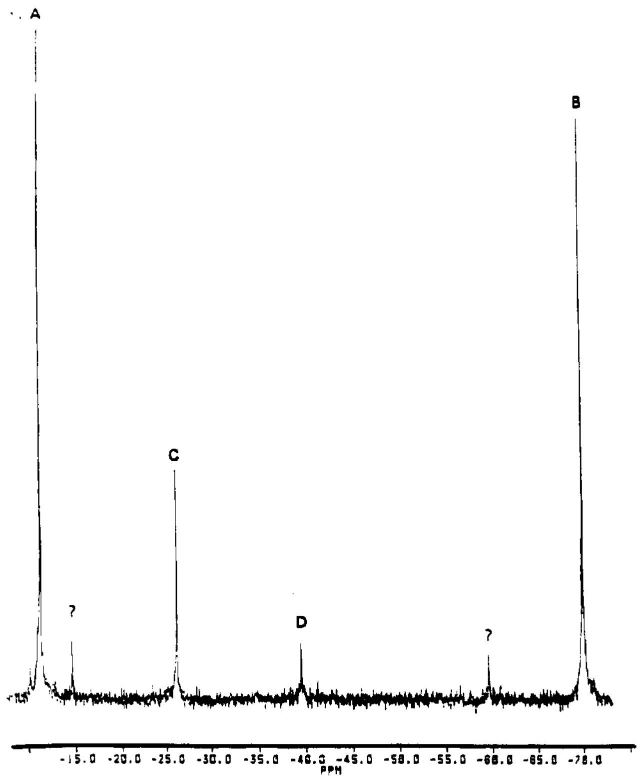

Figure 3. ^{29}Si NMR spectrum of the equilibrium mixture of silyl anions showing the following silicon atoms: (A) $PhMe_2\mathit{Si}Me_2SiLi$, −12.7 ppm; (B) $PhMe_2SiMe_2\mathit{Si}Li$, −69.8 ppm; (C) $PhMe_2\mathit{Si}Li$, −27.2 ppm; (D) $(SiMe_2)_6$, −40.2 ppm.

pling between silicon atoms in the anion than in the neutral species. In comparison with the monosilyl anion, the charge in the disilyl anion was located more on the terminal Si atom than on the aromatic group. The spectrum also shows a signal for dodecamethylcyclohexasilane (D) and perhaps longer oligosilyl anions.

A UV study of the mixture of mono- and disilyl anions reveals two broad maxima of similar intensities centered at 350 and 450 nm. The first maximum is ascribed to the well-known monosilyl anion (340 nm).[7] The second maximum, which is responsible for the deep red color of the anion solution, is ascribed to (2-phenyltetramethyldisilyl)lithium. The disilyl anion absorbs at a longer wavelength due to the delocalization of the charge onto the β-phenyl group. Polysilyl anions with an α-phenyl group which are observed in the formation of poly(phenylmethylsilylene) absorb at 390 nm.[11] Thus, the red shift originates in oligosilyl anions which do not contain α-aromatic groups.

3. UV Studies. Due to the large extinction coefficients of the oligosilanes and the parent anions, UV studies were performed for solutions much more dilute than those used in NMR and HPLC studies. Qualitatively, observations similar to those from high-concentration experiments were made. The appearance of pink and later a red color corresponds to two maxima, 350 and 450 nm. The first peak is the absorption of (phenyldimethylsilyl)lithium (340 nm),[7] and the second maximum corresponds to (2-phenyltetramethyldisilyl)lithium (Figure 4). The small red shift of the monosilyl anion may be due to its overlap with the absorption peak of the disilyl anion or due to a second low-wavelength maximum of the disilyl anion. Unfortunately, the disilyl anion cannot be prepared alone, since it always exists in an equilibrium mixture with the monosilyl anion and dodecamethylcyclohexasilane in a THF solution. The subsequent formation of the green color (650 nm) can be associated with radical anions based on cyclosilanes, probably decamethylcyclopentasilane, radical anions of α,ω-diphenyloligosilanes, or biphenyl radical anion. The green color observed on the surface of lithium, when no cyclosilanes were present, may be ascribed to species formed by electron transfer to oligosilanes with terminal aromatic rings, i.e. the corresponding radical anions.

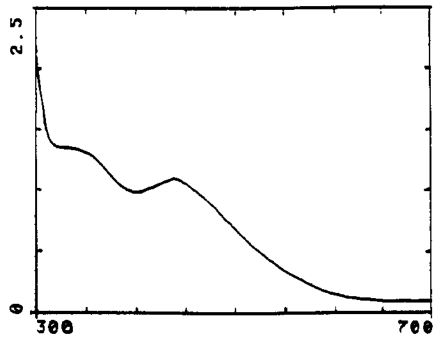

Figure 4. UV spectrum of the reaction mixture at 25 °C in THF.

4. EPR Studies. Attempts to detect unpaired electrons in the reaction mixture prior to the formation of the green color were unsuccessful. However, at the final stages of the reaction a strong EPR signal, containing nine lines with intensities 1:4:8:12:14:12:8:4:1, was found (Figure 5A). The signal was observed at ambient as well as low temperatures. At 136 K a broader spectrum (Figure 5B) was found for the solidified sample. Thermal changes are reversible. In order to associate the coupling to either a polysilane chain or the aromatic rings, a similar reaction with 1-chloro-2-phenyltetramethyldisilane containing a perdeuterated aromatic ring was performed. The reaction behaved in a similar way, but the nine lines collapsed into one signal (Figure 5C). This indicates association of the electron with the aromatic ring. EPR spectra resemble those of biphenyl radical anion[12] but may not be well resolved (no coupling to meta protons observed) due to high spin concentrations (10^{-3} M). Similar spectra are expected for radical anions formed from α,ω-diphenyloligosilanes. It is known that the electron is located on the aromatic ring in (trimethylsilyl)benzene and (pentamethyldisilyl)benzene. The electron can also be associated with the aromatic rings of α,ω-diphenyl permethylated oligosilanes. The electron may rapidly exchange its position between rings either via space or via the oligosilane chain, leading to line broadening. However, the EPR signal appears at the very end of the reaction, when the concentration of α,ω-diphenyloligosilanes is very low. The signal is absent at higher concentrations of oligosilanes. Moreover, it is known that radical anions based on linear oligosilanes decompose easily; for example, the decomposition of diphenyldimethylsilane radical anions is known to form biphenyl radical anions and $[PhSiMe_2PhSiMe_2Ph]^{\bullet -}$ at 20 °C.[13] The green color of the reaction mixture could also be assigned to radical anions from decamethylcyclopentasilane. However, the EPR signal is very different from that reported for these species.[14] Thus, we assume that, at longer

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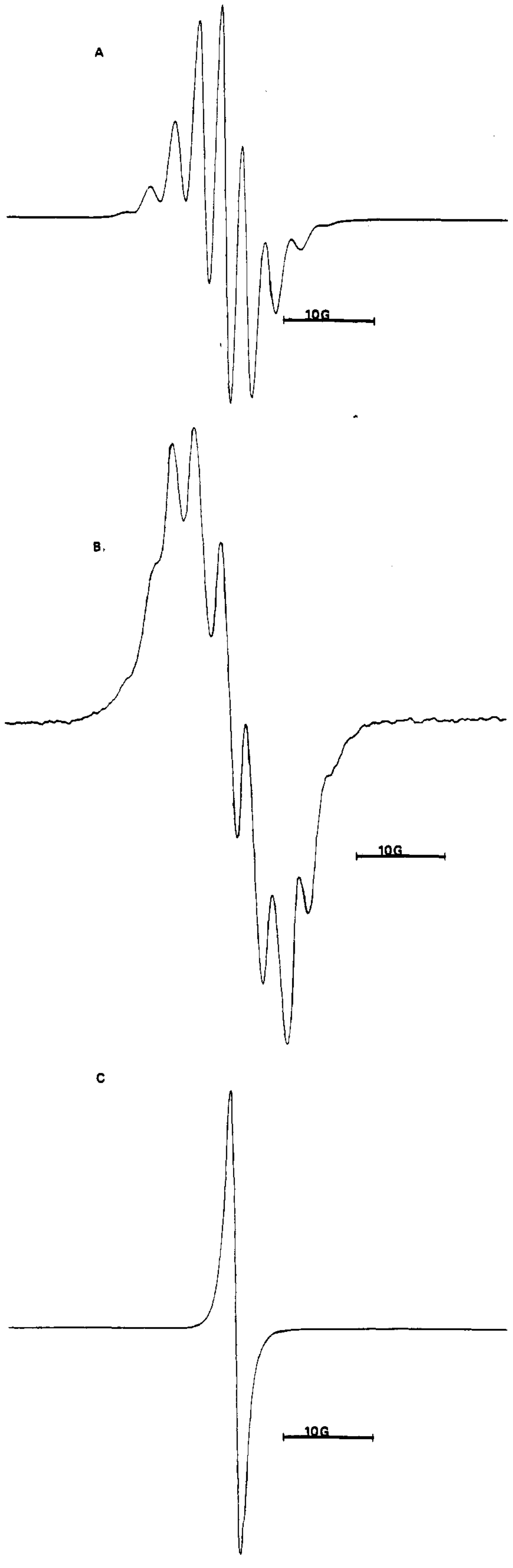
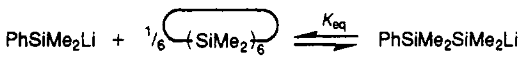


Figure 5. EPR spectra of the equilibrium reaction mixture at (A) 298 K and (B) 136 K and (C) the perdeuterated aromatic ring at 298 K.

Scheme II



reaction times, some side reactions can lead to silicon–phenyl bond cleavage and formation of a small amount of biphenyl. The concentration of biphenyl is too low to be detected by NMR spectroscopy. This reaction is relatively slow and does not compete with the "normal" coupling, scrambling, and redistribution processes.

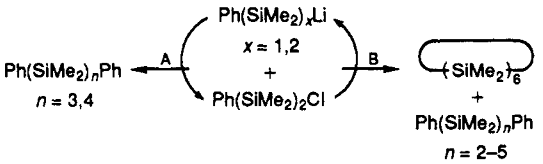
5. Model Reactions. 5.1. Reaction of Dodecamethylcyclohexasilane with (Phenyldimethylsilyl)lithium. (Phenyldimethylsilyl)lithium anion (M$^-$) reacts rapidly with dodecamethylcyclohexasilane (CHS) to form (2-phenyltetramethyldisilyl)lithium anion (D$^-$). No longer chain oligosilyl anions were observed in significant amounts. The equilibrium position in this reaction depends on the concentration of the cyclohexasilane to the $^1/_6$ power (Scheme II). The estimated value of the equilibrium constant is $K_{eq} = 2.7\ (\mathrm{mol/L})^{1/6}$ in THF at 25 °C. This corresponds to approximately a 2:1 ratio of the disilyl anion to the monosilyl anion at concentrations of dodecamethylcyclohexasilane $\sim 10^{-2}$ mol/L. The $^1/_6$ exponent indicates that the equilibrium position is not sensitive to the concentration, and similar ratios are expected in the range of 10^{-4} mol/L.

5.2. Reaction of 1-Chloro-3-phenylhexamethyltrisilane with Lithium: Attempted Synthesis of Trisilyl Anions. The reaction between 1-chloro-3-phenylhexamethyltrisilane and lithium could, in principle, provide (3-phenylhexamethyltrisilyl)lithium anions. The coupling reaction was conducted in a manner identical to the coupling of 1-chloro-2-phenyltetramethyldisilane. Again, the reaction yields a mixture of disilyl anion, monosilyl anion, and cyclohexasilane. The concentration of the trisilyl anions was too low to be clearly detected by NMR spectroscopy, although small signals downfield from the disilyl anions signal may come from the trisilyl anions (Figure 2). Thus, the trisilyl anions with a γ-aromatic group are less stable than those with α- or β-phenyl groups.

5.3. Reaction of α,ω-Diphenyl Permethylated Oligosilanes with Lithium. In a separate reaction 1,4-diphenyloctamethyltetrasilane was reacted in THF with lithium. In this case the reaction started at stage 3 (Scheme III). An induction period due to the activation of the surface was observed, but then stages 3 and 4 were identical to the reaction of 1-chloro-2-phenyltetramethyldisilane and lithium. Also, when 1,3-diphenylhexamethyltrisilane and 1,5-diphenyldecamethylpentasilane were reacted with lithium, a mixture of cyclohexasilane, monosilyl anion, and disilyl anion was afforded.

5.4. Reaction of Silyl Anions with Silyl Chlorides. A mixture of monosilyl and disilyl anions was reacted with an excess of a variety of monochlorooligosilanes and dichlorooligosilanes.

The silyl anions were introduced into the chlorosilane solution in order to avoid the scrambling process. The reaction of the mixture of anions with 1-chloro-2-phenyltetramethyldisilane provides 1,3-diphenylhexamethyltrisilane and 1,4-diphenyloctamethyltetrasilane (eq 1A). If, however, the chlorosilane was added into a mixture of anions the scrambling process was observed and disilane, pentasilane, and dodecamethylcyclohexasilane were also found (eq 1B). Together, these two results indicate that the scrambling process, of Si–Si bond cleavage, is very fast but much slower than the coupling of anions



(1)

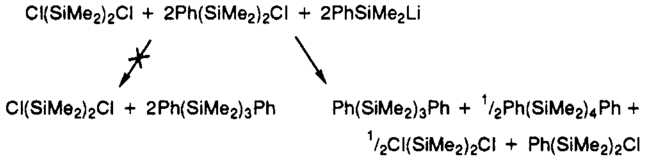
with chlorosilanes. Therefore, no dodecamethylcyclohexasilane was formed during stage 2 (Figure 1).

In the reaction of silyl anions with an excess of dichlorodimethylsilane, 1,2-dichlorotetramethyldisilane, or 1,3-dichlorohexamethyltrisilane, a mixture of doubly reacted silanes and unreacted dichlorosilanes was observed (eq 2). No monochlorosilanes were found. This was an unexpected result, since Allred and Boberski[16] found predominant formation of monoreacted products using methylmagnesium iodide as a nucleophilic reagent.

$$n\mathrm{Ph(SiMe_2)_xLi} + m\mathrm{Cl(SiMe_2)_yCl} \rightarrow \mathrm{Ph(SiMe_2)_zPh} \quad (2)$$

$$n \ll m;\ x = 1, 2;\ y = 1\text{–}3;\ z = y + 2, y + 3, y + 4$$

Since the formation of direacted product suggests a much higher reactivity of the monochlorosilane than the starting dichlorosilane, competitive reactions of monosilyl anion with a mixture of (a) 1,2-dichlorotetramethyldisilane and 1-chloro-2-phenyltetramethyldisilane and (b) 1,2-dichlorotetramethyldisilane and dichlorodimethylsilane (eq 3a,b) were conducted. If the monophenylated products were indeed much more reactive (eq 3a), then the formation of pure 1,3-diphenylhexamethyltrisilane is expected in the presence of an excess of 1,2-dichlorotetramethyldisilane and 1-chloro-2-phenyltetramethyldisilane (a model of the monoreacted product). In the second case (eq 3b), the influence of the chain length on the reactivies of the dichlorosilanes is studied (eq 3b). In both cases the reactivities of the chlorosilanes appear to be similar. This result indicates that the silyl anions react with any chlorosilanes in a diffusion-controlled process in a THF solution and the reactivities are not structurally dependent. Attempts to estimate relative reactivities by improved mixing were not successful. This observation as well as a colorless solution during stage 2 (Figure 1) indicates an extremely fast coupling reaction of silyl anions with chlorosilanes.


$$\mathrm{Cl(SiMe_2)_2Cl + 2Ph(SiMe_2)_2Cl + 2PhSiMe_2Li}$$
$$\not\rightarrow \mathrm{Cl(SiMe_2)_2Cl + 2Ph(SiMe_2)_3Ph}$$
$$\rightarrow \mathrm{Ph(SiMe_2)_3Ph + {}^1\!/_2Ph(SiMe_2)_4Ph + {}^1\!/_2Cl(SiMe_2)_2Cl + Ph(SiMe_2)_2Cl}$$

(3a)

$$\mathrm{Cl(SiMe_2)_2Cl + Cl(SiMe_2)Cl + 2PhSiMe_2Li} \longrightarrow$$
$$\mathrm{{}^1\!/_2Cl(SiMe_2)_2Cl + {}^1\!/_2Cl(SiMe_2)Cl + {}^1\!/_2Ph(SiMe_2)_4Ph + {}^1\!/_2Ph(SiMe_2)_3Ph} \quad (3b)$$

5.5. Coupling of 1-Chloro-2-[*p*-(dimethylamino)phenyl]tetramethyldisilane with Lithium. The kinetic results presented in Figure 1 indicate that, at the very beginning of the reaction, the formation of tetrasilane is accompanied by the formation of trisilane and pentasilane. This is due to the fact that the electron transfer does not occur directly to the chlorodisilane with the formation of disilyl anions which would eventually couple with another chlorodisilane to form 1,4-diphenyloctamethyltetrasilane. Instead, the electron transfer proceeds to linear oligosilanes which randomly generate monosilyl, disilyl, trisilyl, etc. anions which eventually produce oligosilanes by coupling with a chlorodisilane.

Thus, it is impossible to selectively prepare the tetrasilane under the typical reaction conditions (THF, 25 °C). Electron-donating substituents on the aromatic rings decrease the electron affinity of the oligosilanes, and control of the reaction pathway could be obtained. Hence, pure tetrasilane could be prepared (eq 4).

$$\mathrm{2Me_2NPh(SiMe_2)_2Cl + 2Li \rightarrow Me_2NPh(SiMe_2)_4PhNMe_2 + 2LiCl} \quad (4)$$

Indeed, 1-chloro-2-[*p*-(dimethylamino)phenyl]tetramethyldisilane reacts with lithium, forming exclusively a tetrasilane. Moreover, the surface of the lithium metal during the coupling process remains shiny, in contrast to green spots observed in the reaction of 1-chloro-2-phenyltetramethyldisilane. Apparently, oligosilanes with the *p*-(dimethylamino)phenyl groups cannot efficiently form radical anions. Two electrons are transferred to 1-chloro-2-[*p*-(dimethylamino)phenyl]tetramethyldisilane to form the (2-[*p*-(dimethylamino)phenyl]tetramethyldisilyl)lithium anion, which couples with a disilyl chloride to produce the tetrasilane.

Discussion

The overall reaction of 1-chloro-2-phenyltetramethyldisilane with lithium in THF is shown in Scheme III.

Scheme III

stage 1

$$\underset{\text{Cl-2}}{\mathrm{Ph(SiMe_2)_2Cl}} + 2\mathrm{Li} \rightarrow \underset{\text{A-2}}{\mathrm{Ph(SiMe_2)_2Li}} + \mathrm{LiCl}$$

$$\underset{\text{Cl-2}}{\mathrm{Ph(SiMe_2)_2Cl}} + \underset{\text{A-2}}{\mathrm{Ph(SiMe_2)_2Li}} \rightarrow \underset{\text{L-4}}{\mathrm{Ph(SiMe_2)_4Ph}} + \mathrm{LiCl}$$

stage 2

$$\underset{\text{L-4}}{\mathrm{Ph(SiMe_2)_4Ph}} + \mathrm{Li} \rightarrow \underset{\text{RA-4}}{[\mathrm{Ph(SiMe_2)_4Ph}]^{\bullet-}\mathrm{Li}^+}$$

$$\underset{\text{RA-4}}{[\mathrm{Ph(SiMe_2)_4Ph}]^{\bullet-}\mathrm{Li}^+} \rightarrow \underset{\text{A-1, A-2, A-3}}{\mathrm{Ph(SiMe_2)_nLi}} + \underset{\text{R-1, R-2, R-3}}{\mathrm{Ph(SiMe_2)_{4-n}^{\bullet}}}$$

$$\underset{\text{A-1, A-2, A-3}}{\mathrm{Ph(SiMe_2)_nLi}} + \underset{\text{Cl-2}}{\mathrm{Ph(SiMe_2)_2Cl}} \rightarrow \underset{\text{L-3, L-4, L-5}}{\mathrm{Ph(SiMe_2)_nSiMe_2SiMe_2Ph}}$$

$$\underset{\text{R-1, R-2, R-3}}{\mathrm{Ph(SiMe_2)_{4-n}^{\bullet}}} + \mathrm{Li} \rightarrow \underset{\text{A-1, A-2, A-3}}{\mathrm{Ph(SiMe_2)_{4-n}Li}}$$

$$\underset{\text{R-1, R-2, R-3}}{\mathrm{Ph(SiMe_2)_{4-n}^{\bullet}}} \rightarrow \underset{\text{L-2, L-3, L-4, L-5, L-6}}{\mathrm{Ph(SiMe_2)_xPh}}$$

stage 3

$$\underset{\text{A-}n}{\mathrm{Ph(SiMe_2)_nLi}} + \underset{\text{L-}m}{\mathrm{Ph(SiMe_2)_mPh}} \rightarrow \underset{\text{A-}x}{\mathrm{Ph(SiMe_2)_xLi}} + \underset{\text{L-}y}{\mathrm{Ph(SiMe_2)_yPh}}$$

$$y = m + n - x$$

stage 4

$$\underset{\text{A-}z}{\mathrm{Ph(SiMe_2)_zLi}} \rightleftharpoons \underset{\text{A-}(z-6)}{\mathrm{Ph(SiMe_2)_{z-6}Li}} + \underset{\text{C-6}}{\mathrm{(SiMe_2)_6}}$$

Stage 1 is the initiation process in which a slow electron transfer from lithium to the disilyl chloride (Cl-2) produces a transient disilyl anion (A-2), which immediately couples with a remaining disilyl chloride to yield linear 1,4-diphenyloctamethyltetrasilane (L-4).

Stage 2 starts when oligosilanes with terminal phenyl groups are present. Relative to the disilyl chloride, the oligomers are much better electron acceptors and the reaction strongly accelerates. Green spots are observed on the lithium surface due to the corresponding radical anions (RA-4). The radical anions either decompose unimolecularly to radicals (R-*n*) and anions (A-*n*) or directly attack any remaining disilyl chloride to produce linear oligosilanes and radicals. Also, the radicals may take a second electron

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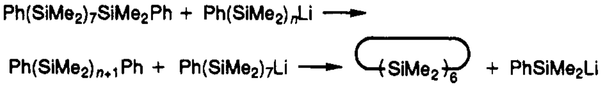
[16] Boberski, W.; Allred, A. L. *J. Am. Chem. Soc.* 1974, *96*, 1244.

from lithium to form anions. They may also recombine, react with solvent, etc. Since no color is observed, the lifetime of the anions appears to be very short when the disilyl chloride is present. No dodecamethylcyclohexasilane was formed at this stage; thus, the scrambling reactions are absent. Therefore, at this stage the disilane could be formed by the coupling of two monosilyl radicals or phenyllithium with the disilyl chloride and not by the scrambling process.

At the end of stage 2 "lithium bleeding" is observed. Green streams which eventually turn red are leaving the lithium surface. The streams initially turn colorless very close to the surface but at longer times remain colored at longer distances. Since the concentration of the disilyl chloride is becoming very low, the lifetime of the anions increases. No scrambling products are found. The rate of the reaction of disilyl chlorides with silyl anions in THF is very fast, probably diffusion controlled. Initially the solution is colorless, which indicates the silyl anion concentration to be below 10^{-6} mol/L.

Stage 3 starts when the disilyl chloride is completely consumed; the linear tetrasilane reaches its maximum concentration and starts to decrease. At the same time the concentration of the linear pentasilane also decreases. The concentration of the disilane increases rapidly, and cyclohexasilane appears. The consumption of lithium continues throughout stage 3. At this stage the reaction mixture is deep red and the color intensifies. The UV study reveals two maxima, 350 and 450 nm, corresponding to the monosilyl and disilyl anions. Since the disilyl chloride has been completely consumed, the silyl anions have a longer lifetime. The anions attack Si–Si bonds, which leads to the scrambling process. For example, a monosilyl anion may attack an α-Si atom and form a disilane. During the scrambling process, longer and longer oligomers may be formed, of course, with a lower and lower probability. The attack of any silyl anion on the α-Si atom in 1,8-diphenylhexadecamethyloctasilane produces a heptasilyl anion, which may by an end-biting process attack its terminal Si atom and form dodecamethylcyclohexasilane and (phenyldimethylsilyl)lithium (eq 5). A similar reaction with an octasilyl anion may generate a disilyl anion and dodecamethylcyclohexasilane. Cyclic compounds are formed only via an extensive scrambling process when longer oligosilyl anions appear. The longer anions are present at very low concentrations. The intermediate anions are continuously generated and provide routes to cyclics which are thermodynamic products.[15]



$$\mathrm{Ph(SiMe_2)_7SiMe_2Ph + Ph(SiMe_2)_{\mathit{n}}Li \longrightarrow Ph(SiMe_2)_{\mathit{n}+1}Ph + Ph(SiMe_2)_7Li \longrightarrow (SiMe_2)_6 + PhSiMe_2Li} \quad (5)$$

Thus, at the end of stage 3, the concentration of the anions is still very low, and the relative concentrations of cyclic and linear oligosilanes are determined by their relative stabilities, i.e., by thermodynamics. These concentrations, indicated by the arrow in Figure 1, correspond quite well to those determined previously by Kumada,[6] who studied the equilibration of 1,4-diphenyloctamethyltetrasilane with a catalytic amount of silyl anions. Stage 3 can be also started from the preformed tetrasilane and lithium. In this case, a random cleavage occurs and a thermodynamic distribution is again formed.

At the end of step 3, cyclosilanes and oligosilanes of various lengths are present simultaneously with an increasing concentration of silyl anions. Electrons are continuously being donated from lithium to oligosilanes to form radical anions, which split into anions and radicals. Upon addition of another electron to a radical anion, a dianion is formed, which rapidly cleaves into two anions. Thus, longer oligomers are continuously converted to anions. Monosilyl and disilyl anions are more stable than their longer counterparts due to the stabilizing effect of α- or β-phenyl groups. Thus, stage 4 is the cleavage of oligosilanes by the continuous donation of electrons from lithium, leading to the formation of radical anions and anions. A thermodynamic mixture of monosilyl anions, disilyl anions, and dodecamethylcyclohexasilane is produced.

The green color at 650 nm and an EPR signal support a structure of a radical anion which is associated with a monosubstituted aromatic ring, probably biphenyl. Thus, coupling constant values similar to those found in the literature[17,18] for *p*-H atoms (5 G) and *o*-H atoms (2.8 G) are observed. Coupling to *m*-H atoms is too weak to be detected in the broad lines.

It is difficult to selectively convert disilyl chlorides into tetrasilanes. First, the electron transfer to oligosilanes generates a statistical mixture of trisilane, tetrasilane, and pentasilane. Then, a scrambling process is responsible for the formation of a thermodynamic mixture of a variety of linear and cyclic oligosilanes. Eventually, the continous donation of electrons from lithium generates a mixture of monosilyl anions, disilyl anions, and cyclosilanes. Similar problems were reported previously when the coupling of pentamethyldisilyl chloride yielded less than 50% of the expected decamethyltetrasilane.[19] Apparently, electron-donating substituents prevent electron transfer and lead to a strong increase in the yield of tetrasilane.

Experimental Section

Equipment. NMR spectra were recorded at room temperature in THF-d_8 solutions with an IBM 300-MHz NR-300 instrument. ^{29}Si NMR chemical shifts were determined using external standards, such as tetramethylsilane (0.0 ppm) or hexamethyldisiloxane (7.2 ppm) in benzene-d_6 solutions.

Absorption spectra were recorded over a range of 190–820 nm on a Hewlett-Packard 8452 UV diode array spectrometer.

EPR spectra were determined using a Bruker ER300 spectrometer at X-band frequencies with 100-kHz field modulation. A chromel–alumel nitrogen-flow cryostat variable-temperature attachment was used.

Materials. 1,2-Dichlorotetramethyldisilane, 1,3-dichlorohexamethyltrisilane, 1-chloro-2-phenyltetramethyldisilane, 1-chloro-3-phenylhexamethyltrisilane, and dodecamethylcyclohexasilane were prepared and purified by literature methods.[20–22] Dichlorodimethylsilane was purchased from Huls and further purified by distillation. Lithium, pyridine, HPLC-grade THF, HPLC-grade methanol, and 1-bromo-4-(dimethylamino)benzene were purchased from Aldrich. THF was dried over and distilled from sodium/benzophenone. THF-d_8 was dried over calcium hydride for at least 12 h.

Determination of Absolute Substrate and Product Concentrations by HPLC (Figure 1). Purified α,ω-diphenyloligosilanes prepared by the literature method[23] were used as standards to determine their retention times under the experimental conditions. A Hewlett-Packard 1090 instrument fit with a Hewlett-Packard Hypresil silica 5-μm analytical column was used for analysis. The flow rate was 0.35 mL/min, and the solvent

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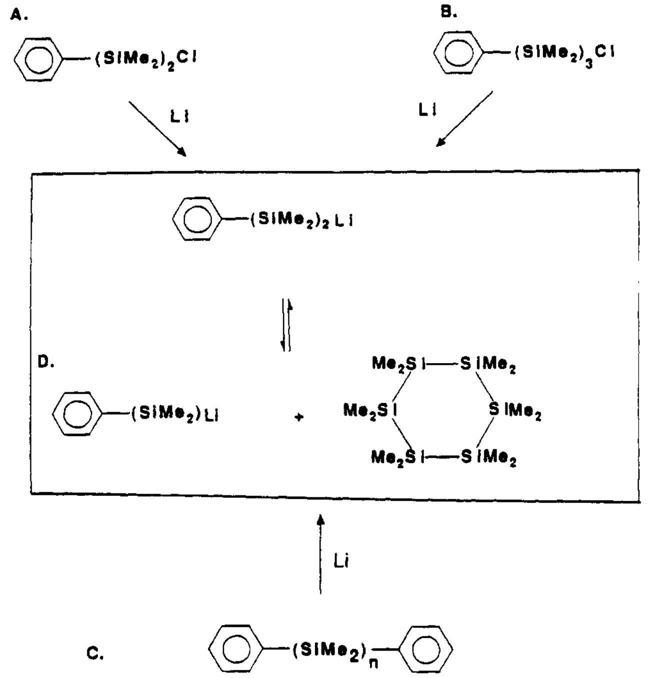

Figure 6. Four experimental routes to the equilibrium mixture of (2-phenyltetramethyldisilyl)lithium, (phenyldimethylsilyl)lithium, and dodecamethylcyclohexasilane.

mixture used was 83:17 methanol/THF. The internal standard was pyridine. A variety of solutions with known concentrations of linear oligosilanes and dodecamethylcyclohexasilane along with pyridine were prepared. Calibration of the response of the HPLC UV detector was determined by plotting the ratio of [pyridine]/[oligosilane] found by the HPLC against the actual [pyridine]/[oligosilane]. The reaction which was analyzed at various time intervals is as follows: An excess of lithium is reacted with $Ph(SiMe_2)_2Cl$ (5 mL, 0.022 mol) in 50 mL of THF at room temperature. In a typical analysis, 250 μL of the reaction solution was withdrawn. The solution was immediately injected into 0.5 mL of methanol, and the solvents were evaporated. The remaining solid was dissolved in 1.5 mL of THF and 1 mL of methanol, and the solution was then filtered. Pyridine (3 μL) was added to 1 mL of the filtered solution and then injected (20 μL). The concentrations given in Figure 1 are therefore 10 times more dilute than in the reaction mixture.

Preparation of $C_6H_5SiMe_2SiMe_2Li$ and $C_6H_5SiMe_2Li$ Solution (Figure 6). (A) An excess amount of lithium was added to an NMR tube. Deuterated THF (0.5 mL) and freshly distilled $PhMe_2SiMe_2SiCl$ (100 μL, 4.4×10^{-4} mol) were then injected into the tube. An equilibrium mixture of (2-phenyltetramethyldisilyl)lithium, (phenyldimethylsilyl)lithium, and dodecamethylcyclohexasilane was obtained within 12 h.

(B) An excess amount of lithium was added to an NMR tube. Deuterated THF (0.5 mL) and freshly distilled $Ph(Me_2Si)_3Cl$ (100 μL, 3.5×10^{-4} mol) were then injected into the tube. ^1H NMR spectroscopy was used to monitor the reaction. In early stages, the only product formed was dodecamethylcyclohexasilane. After 12 h, the reaction mixture was green and the main products formed were (phenyldimethylsilyl)lithium, (2-phenyltetramethyldisilyl)lithium, and dodecamethylcyclohexasilane.

(C) An excess of lithium was added to a solution of α,ω-diphenyl permethylated oligosilanes (0.34 M) in deuterated THF. The reaction was monitored by ^1H NMR spectroscopy. After the lithium addition, the metal surface becomes green and red streams were seen leaving the lithium. ^1H NMR spectra showed the longer oligomers being cleaved, and the product which was formed was dodecamethylcyclohexasilane. After 12 h, the reaction mixture was green and the products were determined by ^1H NMR measurements to be (phenyldimethylsilyl)lithium, (2-phenyltetramethyldisilyl)lithium, and dodecamethylcyclohexasilane.

(D) An excess amount of lithium was added to an NMR tube. Deuterated THF (0.5 mL) and $PhMe_2SiCl$ (100 μL, 5.9×10^{-4} mol) were then injected into the tube. The mixture was allowed to react overnight. The resulting solution was dark brown-yellow. The product was determined to be (phenyldimethylsilyl)lithium by ^1H NMR spectroscopy. The anion solution was reacted with dodecamethylcyclohexasilane (10^{-4} mol). The products were determined by ^1H NMR measurements to be (phenyldimethylsilyl)lithium, (2-phenyltetramethyldisilyl)lithium, and dodecamethylcyclohexasilane.

Preparation of (Phenyldimethylsilyl)lithium. In a drybox an excess amount of lithium was added to an NMR tube. Deuterated THF (0.5 mL) and $PhSiMe_2Cl$ (100 μL, 5.9×10^{-4} mol) were then injected into the tube. The mixture was allowed to react overnight. The resulting solution was dark brown-yellow. The product was determined to be >95% pure by ^1H NMR, ^{13}C NMR, and ^{29}Si NMR spectroscopy. The λ_{max} and ϵ values of the anion correspond to literature values.[8]

Preparation of 1,4-Bis[(*p*-dimethylamino)phenyl]octamethyltetrasilane. An excess amount of lithium was added to an NMR tube. Deuterated THF (0.5 mL) and freshly distilled 1-chloro-2-[(*p*-dimethylamino)phenyl]tetramethyldisilane (100 μL, 3.7×10^{-4} mol) were then injected into the tube. Within 12 h, the product, 1,4-di[(*p*-dimethylamino)phenyl]octamethyltetrasilane, was found to be >90% pure (^1H NMR 7.40, 6.72, 2.95, 0.47 ppm; mp 123–125 °C; λ_{max} 274 nm, ϵ 50 000 mol^{-1} L cm^{-1}).

Competitive Silyl Chloride Reactions. Three competitive reactions were performed. The following two silyl chlorides were competitively reacted: (1) $Ph(SiMe_2)_2Cl$ vs $Cl(SiMe_2)_2Cl$; (2) $Cl(SiMe_2)_2Cl$ vs Cl_2SiMe_2. Both reactions were performed in a glovebox. THF was dried over Na/K alloy. The chlorosilanes were distilled and found to be >95% pure by NMR spectroscopy. In an NMR tube, the silyl chlorides (10^{-4} mol each) were injected into 0.4 mL of deuterated THF. A ^1H NMR spectrum was used to determine the initial integration ratio. A solution of 0.88 M of (phenyldimethylsilyl)lithium in deuterated THF was then sequentially injected into the silyl chloride solution using a microsyringe with a Teflon-tipped plunger. A ^1H NMR spectrum was obtained after each injection, and the ratio of the two silyl chloride integration areas was calculated.

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