

However, small amounts of $\text{Mn}_2(\text{CO})_{10}$ and some phosphorus-containing species were present. After filtration, the volatiles were removed and the residue was washed with hexane and dried to yield impure $(\text{cyclenPH}_2)[\text{Mn}(\text{CO})_5]$ as a yellow solid (0.18 g).

Reaction of cyclenPH and $\text{HWCP}(\text{CO})_3$. cyclenPH (0.112 g, 0.559 mmol) and $\text{HWCP}(\text{CO})_3$ (0.214 g, 0.641 mmol) were added to a flask, the flask was immersed in a -78°C bath, and 5 mL of cold THF was added. The mixture was stirred and allowed to warm to ambient temperature over 1 h, yielding a pink solution and white precipitate. The mixture was filtered and the solid washed thoroughly with hexane. The solid was further washed twice with 1-mL portions of THF (a minimum of THF should be used since the product is reasonably soluble in THF). The solid was pumped dry yielding pure $(\text{cyclenPH}_2)[\text{WCp}(\text{CO})_3]$ as an off-white powder (0.210 g, 70%). Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{N}_4\text{O}_3\text{PW}$: C, 35.97; H, 4.35; N, 10.49; P, 5.80. Found: C, 36.05; H, 4.39; N, 10.35; P, 6.17.

Reaction of CH_3I and $(\text{cyclenPH}_2)[\text{WCp}(\text{CO})_3]$ (9). A reaction mixture (in THF) prepared as above using cyclenPH (0.15 g, 0.75 mmol) and $\text{HWCP}(\text{CO})_3$ (0.25 g, 0.75 mmol) was treated with CH_3I (0.047 mL, 0.75 mmol) and stirred for 1 h at ambient temperature. The solid which precipitated was filtered, washed with THF, and dried to yield pure $(\text{cyclenPH}_2)\text{I}$ as an off-white solid (0.18 g, 73%); mp $174\text{--}175^\circ\text{C}$. Anal. Calcd for $\text{C}_8\text{H}_{18}\text{IN}_4\text{P}$: C, 29.28; H, 5.54; N, 17.08; P, 9.44. Found: C, 29.06; H, 5.65; N, 16.61; P, 9.16. Removal of the volatiles from the original THF supernatant left spectroscopically pure $\text{CH}_3\text{WCp}(\text{CO})_3$ (0.22 g, 84%).

X-ray Structure Determination. 6 was recrystallized from THF yielding transparent yellow crystals. A suitable single crystal was mounted on an Enraf-Nonius CAD-4F diffractometer. A total of 3080 independent reflections were collected in the $\theta/2\theta$ scan mode. Of these, 2448 were considered observed with $I > 3\sigma(I)$ and used in the solution and refinement of the structure.

(30) For IR, ^{13}C , and ^1H spectra of $\text{CH}_3\text{WCp}(\text{CO})_3$ see: (a) Todd, L. J.; Wilkinson, J. R.; Hickey, J. P.; Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* 1978, 154, 151. (b) Patil, H. R. H.; Graham, W. A. G. *Inorg. Chem.* 1966, 5, 1401.

Data were corrected for Lorentz and polarization effects. (An empirical absorption correction was also applied.) The structure was solved by standard Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions 0.95 Å from their respective carbon atoms and included in the subsequent refinement. Unit weights were used in the weighting scheme. Final refinement yielded $R = 0.0228$ and $R_w = 0.0254$ with no chemically significant peaks present in the final difference Fourier map. Complex neutral atom scattering factors were used throughout.³¹ All calculations were performed on a DEC PDP 11/44 computer using Enraf-Nonius SDP Plus structure solution programs.³²

Pertinent crystallographic data are summarized in Table IV and atomic positional parameters listed in Table V.

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Registry No. 4, 100349-94-8; 5, 100334-12-1; 6, 100349-95-9; 7, 100334-14-3; 8, 100334-16-5; 9, 100334-18-7; 10, 100349-96-0; cyclenPH, 64317-97-1; tetratosylcyclen, 52667-88-6; cyclen, 294-90-6; $\text{P}(\text{NMe}_2)_3$, 1608-26-0; $\text{Co}_2(\text{CO})_8$, 15226-74-1; $[\text{MoCp}(\text{CO})_3]_2$, 12091-64-4; $\text{Mn}_2(\text{CO})_{10}$, 10170-69-1; $\text{HWCP}(\text{CO})_3$, 12128-26-6; $\text{CH}_3\text{WCp}(\text{CO})_3$, 12082-27-8.

Supplementary Material Available: Tables of complete bond distances and angles, thermal parameters, and observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Preparation of Oligomeric and Polymeric α,ω -Bis(trimethylsiloxy)polymethylchlorosiloxanes and Their Reactions with Alkylolithium Reagents

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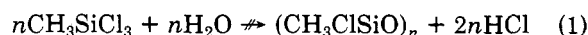
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A series of α,ω -bis(trimethylsiloxy)polymethylchlorosiloxanes ($\text{MD}^{\text{Cl}}_n\text{M}$) ($n = 1\text{--}5$ and ~ 35) as well as $\text{MD}^{\text{Cl}}\text{D}^{\text{H}}\text{M}$ have been prepared by the palladium on carbon-catalyzed exchange reaction of $\text{MD}^{\text{H}}_n\text{M}$ with allyl or benzyl chloride. The reaction of these with alkylolithium reagents in ether at -78°C has been studied. Alkylation without cleavage of the siloxane backbone is observed with the oligomers $\text{MD}^{\text{Cl}}_n\text{M}$. On the other hand, $\text{MD}^{\text{H}}\text{M}$ and $\text{MD}^{\text{Cl}}\text{D}^{\text{H}}\text{M}$ undergo facile siloxane cleavage. Some cleavage is also observed with the polymer $\text{MD}^{\text{Cl}}_{\sim 35}\text{M}$. The spectral properties, in particular ^1H , ^{13}C , and ^{29}Si NMR, of both $\text{MD}^{\text{H}}_n\text{M}$ and $\text{MD}^{\text{Cl}}_n\text{M}$ are reported. The interpretation of the ^{13}C and ^{29}Si NMR spectra of siloxane oligomers which are chiral at both Si and C is discussed.

We have been interested in the development of methods to modify siloxane oligomers and polymers without breaking Si-O bonds.¹⁻³ The following abbreviations will be used: $\text{M} = (\text{CH}_3)_3\text{SiO}_{0.5}$, $\text{D} = (\text{CH}_3)_2\text{Si}(\text{O}_{0.5})_2$, $\text{D}^{\text{H}} =$

$\text{CH}_3\text{Si}(\text{O}_{0.5})_2\text{H}$, and $\text{D}^{\text{Cl}} = \text{CH}_3\text{Si}(\text{O}_{0.5})_2\text{Cl}$. While it is possible to prepare α,ω -dichloropermethoxysiloxane oligomers and polymers ($\text{Cl-D}_n\text{-Cl}$) by reaction of dimethyldichlorosilane with a limited amount of water (eq 1),⁴ it is



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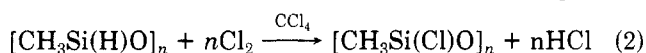
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not feasible to prepare α,ω -bis(trimethylsiloxy)polymethylchlorosiloxanes ($\text{MD}^{\text{Cl}}_n\text{M}$) by cohydrolysis of trimethylchlorosilane and methyltrichlorosilane since this reaction yields silsesquioxanes.⁵⁻⁷ Likewise, *sym*-polymethylchlorocyclosiloxanes (D^{Cl}_n) cannot be generated by hydrolysis of methyltrichlorosilane.

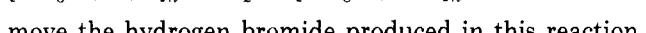
On the other hand, it is possible to prepare α,ω -bis(trimethylsiloxy)polymethylhydrosiloxanes ($\text{MD}^{\text{H}}_n\text{M}$) by cohydrolysis of trimethylchlorosilane and methyltrichlorosilane.⁸ Likewise, *sym*-methylhydrochlorosiloxanes (D^{H}_n) result from the hydrolysis of methyltrichlorosilane.⁹ Hence D^{Cl}_n and $\text{MD}^{\text{Cl}}_n\text{M}$ could be prepared by converting the Si-H bonds of D^{H}_n and $\text{MD}^{\text{H}}_n\text{M}$, respectively, into reactive Si-Cl bonds.

The conversion of Si-H bonds of both D^{H}_n and $\text{MD}^{\text{H}}_n\text{M}$ into Si-Cl bonds has been achieved by low-temperature reaction with chlorine in carbon tetrachloride (eq 2).¹⁰⁻¹⁴



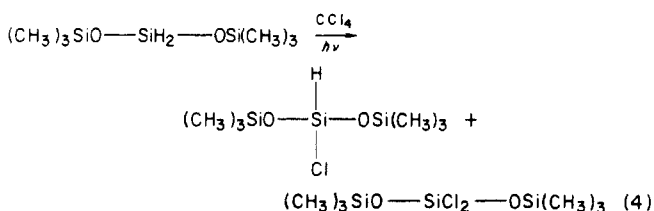
This reaction involves the simultaneous formation of hydrogen chloride, which can cleave siloxane bonds under the reaction conditions.¹² The use of nitrogen to sweep the hydrogen chloride from the reaction as it is formed has been recommended.¹³

In a similar manner, the Si-H bonds of both $\text{MD}^{\text{H}}_n\text{M}$ and D^{H}_n have been converted to Si-Br bonds by reaction with bromine (eq 3).¹² Pyridine has been utilized to re-



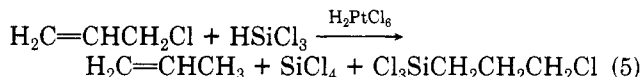
move the hydrogen bromide produced in this reaction. This serves to protect the siloxane bonds from acid cleavage. *sym*-Methylbromocyclotrisiloxane and -tetrasiloxane have also been prepared by electrophilic cleavage of silicon-phenyl bonds of the corresponding *sym*-phenylmethylcyclosiloxanes at low temperature.¹⁵

The Si-H bonds of alkylsilanes have been converted into Si-Cl bonds by a free radical chain reaction in which carbon tetrachloride is used as the chlorinating agent.^{16,17} This reaction has recently been applied to the chlorination of Si-H bonds in siloxanes (eq 4).¹⁸



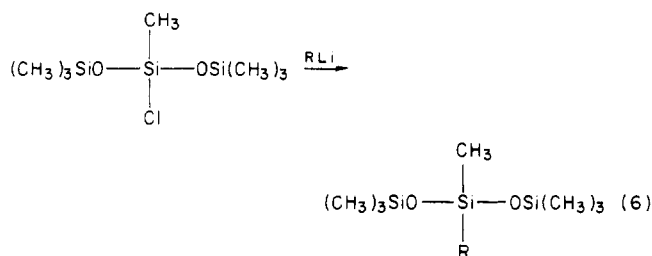
An alternative approach to convert Si-H bonds into Si-Cl bonds is a chloroplatinic acid catalyzed exchange of

Si-H compounds with allyl chloride.^{19,20} An attractive feature of this reaction is that a neutral by product, propene, is formed. This exchange occurs in competition with the normal hydrosilation reaction as outlined in eq 5.



A related palladium on carbon (Pd/C) catalyzed exchange has been used to chlorinate the Si-H bonds of pentamethyldisiloxane and 1,1,1,3,5,5,5-heptamethyltrisiloxane ($\text{MD}^{\text{H}}\text{M}$).²¹

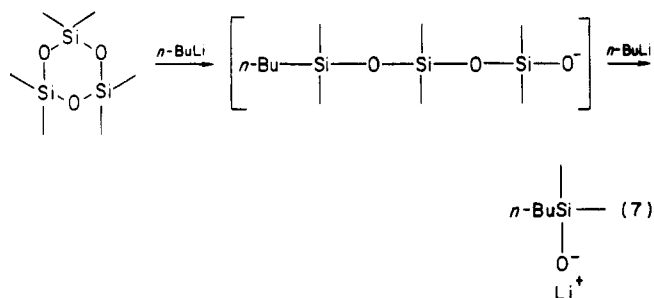
$\text{MD}^{\text{Cl}}_n\text{M}$ oligomers are potential precursors to various unsymmetrically substituted siloxanes by nucleophilic substitution reactions with alkyllithium reagents (eq 6).^{1,12,22,23} The Si-Cl bond in organosilicon compounds is



usually more reactive toward nucleophilic reagents than comparable Si-H or Si-OR bonds.²⁴ Since chlorosilanes are prepared industrially, their reactions with organolithium or Grignard reagents is a standard method for Si-C bond formation.²⁵⁻³⁰ This reaction has not been widely explored with chloro-substituted siloxanes. While Si-Cl bonds are usually more reactive than Si-O bonds, reaction of organometallic reagents with Si-O bonds have been reported. Thus alkyllithium reagents have been reported to cleave siloxane substrates at ambient temperature to yield lithium silanates.³¹⁻³⁴ For example, hexamethylcyclotrisiloxane (D_3) reacts with *n*-butyllithium in hexane/toluene to give lithium *n*-butyldimethylsilanolate (eq 7).^{34,35} Cleavage of hexamethyldisiloxane by methyl-lithium in ether/THF has been reported to yield lithium

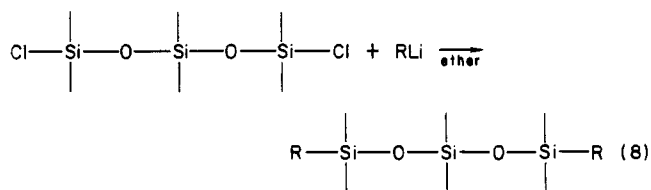
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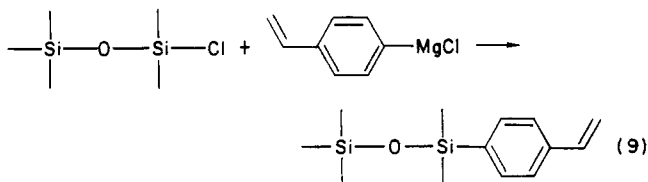


trimethylsilylanolate and tetramethylsilane.³³ Triorgano-silanolate anions are good leaving groups because silanols are more acidic than alcohols and in fact more acidic than H_2O .³⁶

There are only a few examples of reaction of organo-metallic reagents with Si-Cl bonds of chlorosiloxanes. Among these are the reactions of 1,3-dichlorotetra-methylsiloxane or 1,5-dichlorohexamethyltrisiloxane with alkyl lithium reagents at low temperature to yield 1,3-di-alkyltetramethylsiloxanes or 1,5-dialkylhexamethyl-trisiloxanes (eq 8).^{1,13,37,38} Aryl Grignard reagents also react



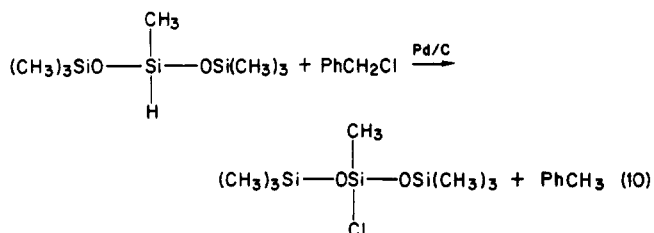
preferentially with the Si-Cl bond of chloro-substituted siloxanes to yield aryl-substituted siloxanes (eq 9).³⁹⁻⁴⁴



We wanted to determine if $\text{MD}^{\text{Cl}}_n\text{M}$ ($n = 1-5, \sim 35$) would undergo exclusive nucleophilic substitution of the internal Si-Cl bonds by primary, secondary, and tertiary alkyl lithium reagents.

Results and Discussion

Preparation of $\text{MD}^{\text{Cl}}_n\text{M}$ Oligomers. We have explored the generality of the Pd/C catalyzed exchange reaction of allyl or benzyl chloride with $\text{MD}^{\text{H}}_n\text{M}$ oligomers and polymers (eq 10). Palladium on carbon catalyzes the



exchange reaction between allyl chloride and $\text{MD}^{\text{H}}_n\text{M}$ to yield 3-chloro-1,1,1,3,5,5,5-heptamethyltrisiloxane

($\text{MD}^{\text{Cl}}_1\text{M}$) and propene.²¹ Similar Pd/C catalyzed chlorination reactions of 1,1,1,3,5,7,7,7-octamethyltetrasiloxane ($\text{MD}^{\text{H}}_2\text{M}$), 1,1,1,3,5,7,9,9,9-nonamethylpentasiloxane ($\text{MD}^{\text{H}}_3\text{M}$), 1,1,1,3,5,7,9,11,11,11-decamethylhexasiloxane (MD^{H}_4), and 1,1,1,3,5,7,9,11,13,13,13-undecamethylheptasiloxane ($\text{MD}^{\text{H}}_5\text{M}$) as well as $\text{MD}^{\text{H}}_{\sim 35}\text{M}$ with allyl chloride were carried out. $\text{MD}^{\text{H}}_2\text{M}$ which has two Si-H bonds can be converted to a mixture of 3-chloro-1,1,1,3,5,7,7,7-octamethyltetrasiloxane ($\text{MD}^{\text{ClD}}_2\text{M}$) and 3,5-dichloro-1,1,1,3,5,7,7,7-octamethyltetrasiloxane ($\text{MD}^{\text{Cl}}_2\text{M}$). The ratio of these products depends on the ratio of allyl chloride to $\text{MD}^{\text{H}}_2\text{M}$ (see Experimental Section). Similarly, $\text{MD}^{\text{H}}_3\text{M}$, $\text{MD}^{\text{H}}_4\text{M}$, and $\text{MD}^{\text{H}}_5\text{M}$ were converted to 3,5,7-trichloro-1,1,1,3,5,7,9,9,9-nonamethylpentasiloxane ($\text{MD}^{\text{Cl}}_3\text{M}$), 3,5,7,9-tetrachloro-1,1,1,3,5,7,9,11,11,11-decamethylhexasiloxane ($\text{MD}^{\text{Cl}}_4\text{M}$), and 3,5,7,9,11-pentachloro-1,1,1,3,5,7,9,11,13,13,13-undecamethylheptasiloxane ($\text{MD}^{\text{Cl}}_5\text{M}$), respectively. Benzyl chloride was also useful for the conversion of $\text{MD}^{\text{H}}_n\text{M}$ into $\text{MD}^{\text{Cl}}_n\text{M}$. Benzyl chloride was reduced to toluene in these reactions.

The structures of $\text{MD}^{\text{Cl}}_1\text{M}$, $\text{MD}^{\text{ClD}}_2\text{M}$, $\text{MD}^{\text{Cl}}_2\text{M}$, $\text{MD}^{\text{Cl}}_3\text{M}$, $\text{MD}^{\text{Cl}}_4\text{M}$, and $\text{MD}^{\text{Cl}}_5\text{M}$ are based on their IR, ^1H , ^{13}C , and ^{29}Si NMR, and mass spectra and elemental analyses. The mass spectra of $\text{MD}^{\text{Cl}}_1\text{M}$, $\text{MD}^{\text{ClD}}_2\text{M}$, $\text{MD}^{\text{Cl}}_2\text{M}$, and $\text{MD}^{\text{Cl}}_3\text{M}$ had significant $\text{M}^+ - 15$ peaks characteristic of methyl-substituted organosilicon compounds.⁴⁵ The mass spectra of $\text{MD}^{\text{Cl}}_4\text{M}$ and $\text{MD}^{\text{Cl}}_5\text{M}$ were more complicated. The ^1H , ^{13}C , and ^{29}Si NMR spectra were very characteristic permitting differentiation of each D^{Cl} unit in these compounds (See Table I). Infrared spectra of these compounds had no bands at 2200 cm^{-1} characteristic of Si-H stretching,⁴⁶ with the exception of $\text{MD}^{\text{ClD}}_2\text{M}$.

The disappearance of the starting materials: $\text{MD}^{\text{H}}_n\text{M}$, $\text{MD}^{\text{H}}_2\text{M}$, $\text{MD}^{\text{H}}_3\text{M}$, $\text{MD}^{\text{H}}_4\text{M}$, and $\text{MD}^{\text{H}}_5\text{M}$ was monitored by GLPC during the chlorination reaction. The conversion of $\text{MD}^{\text{H}}_{\sim 35}\text{M}$ to $\text{MD}^{\text{Cl}}_{\sim 35}\text{M}$ was monitored by both ^1H NMR and IR spectroscopy. The characteristic Si-H IR absorption band at 2200 cm^{-1} and ^1H NMR resonances at 4.5 ppm disappeared as the reaction proceeded. In both the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, the terminal M unit was clearly resolved from the D^{Cl} units in the polymer and appeared as a single peak. The methyl group signals of the D unit in ^1H NMR of $\text{MD}^{\text{Cl}}_{\sim 35}\text{M}$ shift downfield significantly from those of $\text{MD}^{\text{H}}_{\sim 35}\text{M}$ as expected.⁴⁷

Reaction of Alkyl lithium Reagents with $\text{MD}^{\text{Cl}}_n\text{M}$ Oligomers. Reaction of primary, secondary, and tertiary butyllithium reagents as well as methyllithium with $\text{MD}^{\text{Cl}}_n\text{M}$ at $-78\text{ }^\circ\text{C}$ in ether gave 3-alkyl-1,1,1,3,5,5,5-heptamethyltrisiloxanes in high yield. The reaction of $\text{MD}^{\text{Cl}}_2\text{M}$ and $\text{MD}^{\text{Cl}}_3\text{M}$ with *sec*-butyllithium gave 3,5-di-*sec*-butyl-1,1,1,3,5,7,7,7-octamethyltetrasiloxane and 3,5,7-tri-*sec*-butyl-1,1,1,3,5,7,9,9,9-nonamethylpentasiloxane in 90% and 89% yields, respectively. The reaction of $\text{MD}^{\text{Cl}}_4\text{M}$ and $\text{MD}^{\text{Cl}}_5\text{M}$ with methyllithium at low temperature gave tetradecamethylhexasiloxane (MD_6M) and hexadecamethylheptasiloxane (MD_7M) in 76% and 74% yields.

The reaction of $\text{MD}^{\text{Cl}}_{\sim 35}\text{M}$ with both excess and equivalent amounts of *sec*-butyllithium were carried out. Analysis of these reaction mixtures by gel permeation chromatography (GPC) showed two components: di-*sec*-

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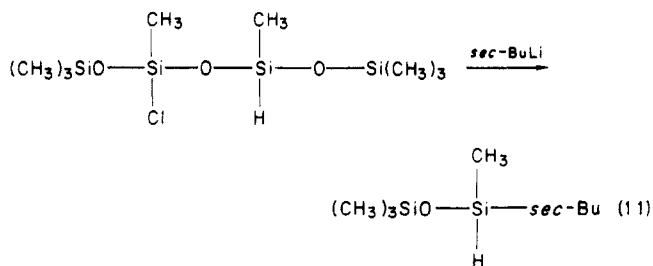
Table I. Spectral Properties of MD^{H_n}M (n = 1-5)^a

| | ¹ H | ¹³ C | ²⁹ Si | mass, m/e (rel intensity) |
|-------------------------------|-----------------------------|-----------------|------------------|--|
| MD ^H M | 0.101 (18 H, s) | 1.658 (6 C) | 9.28 (2 Si) | M ⁺ , 222 (1.1) |
| | 0.081 (3 H, d, J = 1.95 Hz) | 1.546 (1 C) | -36.47 (1 Si) | M ⁺ - 15, 207 (100) |
| | 4.639 (1 H, q, J = 1.95 Hz) | | | M ⁺ - 89, 133 (9.6) |
| MD ^{H₂} M | 0.112 (18 H, s) | 1.878 (6 C) | 9.90 (2 Si) | 73 (37) |
| | 0.132 (6 H, d, J = 1.46 Hz) | 1.553 (2 C) | -36.01 (2 Si) | M ⁺ , 283 (0.3) |
| | 4.665 (2 H, q, J = 1.46 Hz) | | | M ⁺ - 15, 267 (19.5) |
| | | | | M ⁺ - 89, 193 (100) |
| MD ^{H₃} M | 0.104 (18 H, s) | | | 133 (7.0), 73 (48.9) |
| | 0.135 (6 H, d, J = 1.47 Hz) | 1.821 (6 C) | 10.00 (2 Si) | M ⁺ , 342 (0.2) |
| | 0.175 (3 H, d, J = 1.47 Hz) | 1.548 (2 C) | -35.86 (2 Si) | M ⁺ - 15, 327 (6.4) |
| | 4.620 (2 H, q, J = 1.47 Hz) | 1.330 (1 C) | -35.70 (1 Si) | M ⁺ - 89, 253 (100) |
| | 4.660 (1 H, q, J = 1.47 Hz) | | | 193 (7.6), 133 (13.8), 73 (30) |
| MD ^{H₄} M | 0.106 (18 H, s) | | | M ⁺ , 402 (0.2) |
| | 1.137 (6 H, d, J = 1.46 Hz) | 1.590 (6 C) | 10.22 (2 Si) | M ⁺ - 15, 387 (3.4) |
| | 0.183 (6 H, d, J = 1.46 Hz) | 1.210 (2 C) | -35.63 (2 Si) | M ⁺ - 89, 313 (67) |
| | 4.656 (2 H, q, J = 1.46 Hz) | 0.994 (2 C) | -35.15 (2 Si) | 253 (100), 193 (35.4), 133 (20.1), 73 (85) |
| | 4.703 (2 H, q, J = 1.46 Hz) | | | |
| MD ^{H₅} M | 0.102 (18 H, s) | | | M ⁺ - 15, 447 (0.6) |
| | 0.134 (6 H, d, J = 1.63 Hz) | 1.590 (6 C) | 10.21 (2 Si) | M ⁺ - 89, 373 (6.0) |
| | 0.158 (9 H, m) | 1.210 (2 C) | -35.10 (2 Si) | 313 (75.4), 253 (60.1), 193 (71.5), 133 (20.8), 73 (100) |
| | 4.640 (2 H, q, J = 1.6 Hz) | 0.939 (2 C) | -35.10 (2 Si) | |
| | 4.690 (3 H, m) | 0.938 (1 C) | -34.76 (1 Si) | |

^a¹H, ¹³C, and ²⁹Si chemical shifts are in ppm relative to tetramethylsilane (0.00 ppm).

butylmethylsilanol (13%) and a nonvolatile high molecular weight residue which appeared by GPC as a single Gaussian peak whose spectral properties are consistent with those expected for α,ω -bis(trimethylsiloxy)poly-*sec*-butylmethylsiloxane (MD^{*sec*-Bu}_{~35}M). It should be noted that the MD^H_{~35}M, which was used to prepare MD^{Cl}_{~35}M, was a single Gaussian peak by GPC.

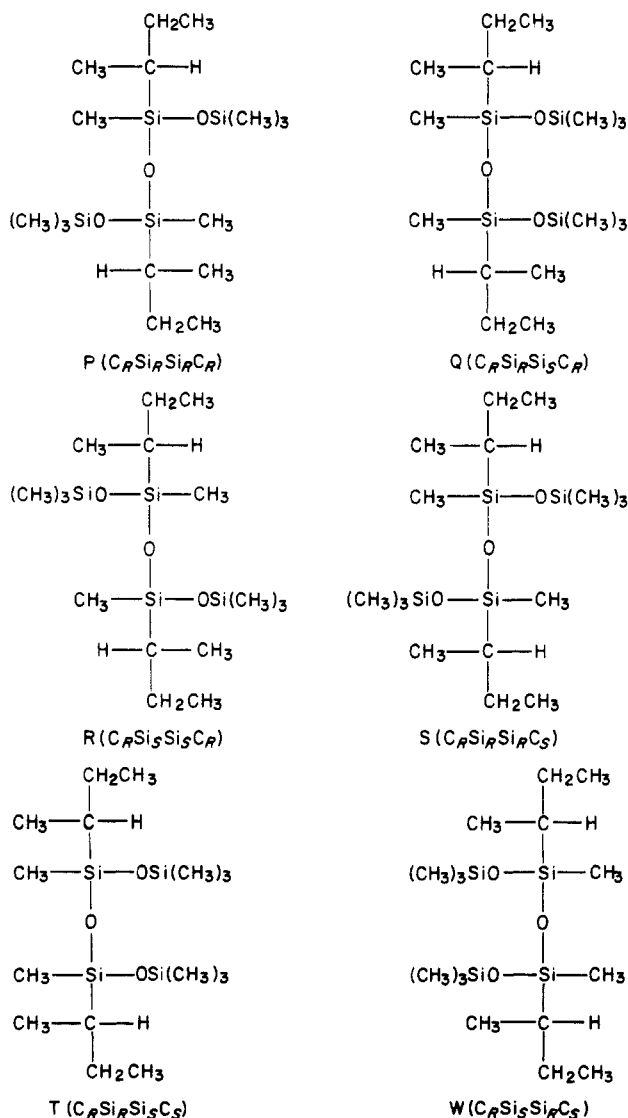
It occurred to us that this difference in behavior of MD^{Cl}_nM oligomers which showed no cleavage and MD^{Cl}_{~35}M polymer which was partially cleaved might result from the presence of a few Si-H bonds in the MD^{Cl}_{~35}M which had escaped chlorination. D^H units have been previously shown to be very susceptible to nucleophilic attack.⁴⁸ To test this possibility, the reaction of MD^{Cl}D^HM with either an excess or an equivalent amount of *sec*-butyllithium was examined (eq 11). Both reactions



gave 1-*sec*-butyl-1,3,3,3-tetramethyldisiloxane as the major product. Similarly, reaction of MD^HM with *sec*-butyllithium gave 1-*sec*-butyl-1,3,3,3-tetramethyldisiloxane. Apparently, a hydrogen attached to silicon facilitates nucleophilic attack which results in cleavage of adjacent siloxane bonds. Hence any residual Si-H bonds in the MD^{Cl}_{~35}M would be expected to promote cleavage of the oligomer chain. Once cleavage has begun apparently it continues resulting in monomeric products as previously observed in the reaction of D₃ and *n*-butyllithium.³⁴

NMR Spectra. The ¹³C and ²⁹Si NMR spectra of MD^{*sec*-Bu}₂M, MD^{*sec*-Bu}₃M, and di-*sec*-butylmethylsilanol are of interest because of the effect of chirality in these systems. For example, 3,5-di-*sec*-butyl-1,1,1,3,5,7,7,7-octamethyltetrasiloxane contains two chiral silicon as well as

Chart I



two chiral carbon centers. Chirality affects both the ¹³C and ²⁹Si NMR spectra. These four chiral centers result in four pairs of enantiomeric (P, Q, R, S) and two meso

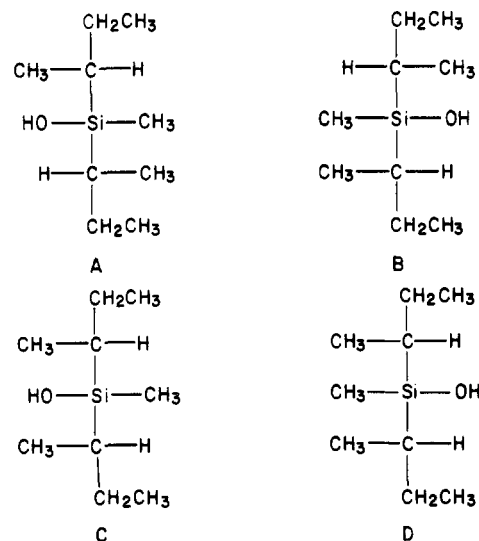
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(T and W) stereoisomers (Chart I). The two $\text{OSi}(\text{CH}_3)_3$ groups of P, R, T, and W are enantiotopic one with the other, while those in Q and S are diastereotopic one with the other. The $\text{OSi}(\text{CH}_3)_3$ groups in P therefore have the same chemical shift while the two in R have a different chemical shift. One of the $\text{OSi}(\text{CH}_3)_3$ groups in Q has an identical local environment (ILE)⁴⁹ to those in P, while the other has an ILE to those in R. The $\text{OSi}(\text{CH}_3)_3$ chemical shifts are independent of the stereochemistry of the chiral silicon and carbon centers which are four or five bonds removed, respectively. Therefore, the two $\text{OSi}(\text{CH}_3)_3$ groups in Q have different chemical shifts one of which is identical with the shift of the $\text{OSi}(\text{CH}_3)_3$ group in P while the other is coincident with the $\text{OSi}(\text{CH}_3)_3$ group in R. A similar analysis applies to the two diastereotopic $\text{OSi}(\text{CH}_3)_3$ groups of S. Both $\text{OSi}(\text{CH}_3)_3$ groups of T have ILE with those of P, while the $\text{OSi}(\text{CH}_3)_3$ groups of W have ILE to those of R. This analysis predicts two $\text{OSi}(\text{CH}_3)_3$ resonances of equal intensity as observed.

The ^{29}Si resonances of the $\text{CH}_3\text{Si}(\text{sec-Bu})$ are dependent on the stereochemistry of the adjacent chiral carbon but appear to be independent of the chirality of the silicon and carbon centers which are two and three bonds removed, respectively. This predicts that both enantiotopic silicons of CH_3Si groups in P are identical while those of R are identical one with the other but different from those of P. One silicon in Q has a ILE with those in P while the other is identical with those of R. Similar analysis of stereoisomers S, T, and W leads to a prediction of two nonequivalent CH_3Si resonances of equal intensity as observed.

The ^{13}C resonances of the $\text{CH}_3\text{Si}(\text{sec-Bu})$ groups can not be accounted for by the previously employed local environment model which considered only adjacent chiral centers. To account for the spectra, both adjacent carbon and silicon chiralities must be considered. In stereoisomer P both the methyl groups in $\text{CH}_3\text{Si}(\text{sec-Bu})$ are in enantiotopic environments and hence identical. Similarly, both methyl groups of each stereoisomer R, T, and W are identical but different from each other as well as from those of P. One of the methyl groups of S is identical with those of P, while the other is identical with those of R. Finally, one methyl group of Q is identical with those of W, while the other is identical with those of T. This leads to the prediction of four methyl resonances of equal intensity. The fact that only three resonances in a 1:2:1 ratio are observed near -2 ppm results from the accidental degeneracy of two signals. Similarly, the ^{13}C NMR of the *sec*-butyl groups can be explained by analysis of the chirality of the adjacent silicon. This predicts two resonances of equal intensity for the CH_3 groups bonded to the chiral carbon. Similarly, the other methyl group " CH_3 " CH_2 is also sensitive to the chirality of the adjacent silicon center. Surprisingly, the methine and methylene ^{13}C resonances of the *sec*-butyl groups appear to be influenced by the chirality of both silicon centers. This leads to the prediction of four resonances for each. In fact, three resonances in a 2:1:1 ratio are observed. This results from a fortuitous degeneracy of two of each set of resonances. The reason for these differences in sensitivity to local environments of different carbons is not understood.

Di-*sec*-butylmethylsilanol also has unique ^{13}C and ^{29}Si NMR spectra. Two chiral carbon centers result in four stereoisomers: A and B are enantiomers, while C and D are meso compounds. The ^{29}Si NMR is affected by both adjacent chiral carbon centers. Thus, A and B have a



unique ^{29}Si resonance as do each of the meso isomers C and D. This results in three ^{29}Si resonances near 12.1 ppm in a ratio of 2:1:1. Similarly, there are three unique signals in the ^{13}C spectrum for the CH_3Si group again in a 2:1:1 ratio.

In the ^{13}C spectra of the *sec*-butyl groups each carbon is affected by both adjacent silicon and carbon stereochemistries. Each carbon of the *sec*-butyl groups in A and B are diastereotopic, while those in C and D are each enantiotopic. This predicts eight resonances for the two methyl groups, four resonances for the methine and four for the methylene carbons. In fact six resonances are observed for the methyl carbons near 21 ppm in an intensity ratio of 1:2:1:1:1:2, three for the methine at ~ 29 ppm in a ratio of 2:1:1, and two for the methylene carbons at ~ 32 ppm in a 1:3 ratio. We believe these intensity patterns result from accidental coincidence of some resonances.

Conclusion

Highly selective alkylation of $\text{MD}^{\text{Cl}}_n\text{M}$ by reaction with allyllithium reagents was achieved. Cleavage of siloxane bonds is important for siloxanes which possess Si-H bonds and for the polymer system.

Experimental Section

All reactions were carried out under an atmosphere of purified nitrogen in flame-dried glassware unless otherwise indicated. ^1H and ^{13}C NMR spectra were obtained on an IBM-Bruker WP-270-SY spectrometer or Varian XL-200-15 spectrometer in the FT mode. Five percent solutions in either chloroform-*d* or acetone-*d*₆ were needed for ^1H , while 10–15% solutions were used for ^{13}C spectra. ^{13}C NMR spectra were run with broad-band proton decoupling or with gated decoupling to determine the multiplicity. Both chloroform and acetone were utilized as internal standards. ^{29}Si NMR spectra were obtained on IBM-Bruker WP-270SY spectrometer using 30–40% solution in chloroform-*d*. Tetramethylsilane was utilized as an external standard. ^{29}Si NMR spectra were run with gated broad-band proton decoupling with a 100-s delay in order to suppress the NOE effect.⁵⁰

Infrared spectra were obtained on a Perkin-Elmer 281 spectrometer. Samples were run as 5% solutions in carbon tetrachloride in KBr cells. Absorption bands were calibrated against known absorption bands of a polystyrene film. Low-resolution mass spectra were obtained on a Hewlett-Packard 5985 GC-MS at an ionizing voltage of 70 eV. Volatile samples were introduced by a GC inlet equipped with an 100/120 mesh Chromosorb W column. Less volatile samples were introduced by use of the direct inlet. GLPC analyses were performed on a Hewlett-Packard F&M

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Table II. Spectral Properties of MD^{Cl}_nM (n = 1-5)^a

| | ¹ H | ¹³ C | ²⁹ Si | mass, m/e (rel intensity) |
|---------------------------------|-----------------|-----------------|------------------|---|
| MD ^{Cl} M | 0.135 (18 H, s) | 1.446 (6 C) | 6.71 (2 Si) | M ⁺ - 15, 241 (100) |
| | 0.354 (3 H, s) | 1.634 (1 C) | -49.544 (1 Si) | M ⁺ - Cl, 221 (4.2) |
| MD ^{Cl} ₂ M | 0.149 (18 H, s) | 1.400 (6 C) | 8.35 (2 Si) | 133 (11.6%), 73 (58.2) |
| | 0.438 (6 H, s) | 1.730 (2 C) | -49.16 (2 Si) | M ⁺ - 15, 335 (10.8) |
| | | | -49.20 (2 Si) | 227 (100), 207 (20.1), 73 (46.8) |
| MD ^{Cl} ₃ M | 0.157 (18 H, s) | 1.39 (6 C) | 8.31 (2 Si) | M ⁺ - 15, 431 (1.4) |
| | 0.457 (6 H, s) | 1.50 (2 C) | -49.18 (1 Si) | 321 (100), 227 (11.7), 167 (67), 73 (54.5) |
| | 0.526 (3 H, s) | 1.66 (1 C) | -49.35 (1 Si) | |
| MD ^{Cl} ₄ M | 0.335 (18 H, s) | 1.39 (6 C) | 8.40 (2 Si) | M ⁺ - 2Cl, 415 (5.0) |
| | 0.635 (6 H, s) | 1.45 (2 C) | -48.90 (2 Si) | 287 (11.2), 167 (10.5), 73 (100) |
| | 0.722 (6 H, s) | 1.67 (2 C) | -49.08 (2 Si) | |
| MD ^{Cl} ₅ M | 0.160 (18 H, s) | | 8.43 (2 Si) | M ⁺ - 123, 509 (0.4) |
| | 0.461 (6 H, s) | 1.374 (6 C) | -48.442 (1 Si) | 415 (3.3), 287 (8.8), 167 (10.8), 93 (34.2), 73 (100) |
| | 0.549 (6 H, s) | 1.427 (2 C) | -48.8059 (2 Si) | |
| | 0.566 (3 H, s) | 1.655 (3 C) | -49.0447 (2 Si) | |

^a¹H, ¹³C, and ²⁹Si chemical shifts are in ppm relative to tetramethylsilane (0.00 ppm).

700 gas chromatograph using 12 ft × 1/4 in. 20% SE-30 on 60/80 mesh Chromsorb W column. It is critical that the GLPC column be deactivated by silylation with hexamethyldisilazane immediately prior to the analysis of MD^{Cl}_nM oligomers. Product yields were calculated by using *n*-decane as an internal standard. Gel permeation chromatograms (GPC) were obtained on a Perkin-Elmer Series 10 liquid chromatograph equipped with a 30 cm × 7.8 mm Ultrastaygel 100-Å gel permeation column, LC-25 Refractory Index detector, 3600 Data Station, and 660 printer. THF was used as carrier solvent at a flow rate of 0.5 mL/min. The retention times were calibrated against a known polystyrene standard of $M_p = 1900, 4800, \text{ and } 7600$ where M_w/M_n was less than 1.09. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, TN.

Methylolithium (ether), *n*-butyllithium (hexane), and *sec*-butyllithium (cyclohexane) were obtained from Aldrich Chemical Inc. *tert*-Butyllithium (pentane) was obtained from Alfa. All alkylolithium solutions were standardized by double titration.^{51,52} THF and ether were distilled from sodium/benzophenone ketyl immediately prior to utilization.

Allyl chloride was obtained from Aldrich Chemical Co. Benzyl chloride was obtained from Mallinckrodt Inc. Both were redistilled before use. Pd/C 10% catalyst was obtained from Matheson Coleman & Bell Inc. and was used as received. Trimethylchlorosilane, methyldichlorosilane, and bis(trimethylsilyl)acetamide were obtained from Petrarch System Inc. and distilled before use.

Trimethylsilylation of MD^H_{~35}M. The MD^H_{~35}M (Alfa) as received had bands in its IR spectra at 3200 cm⁻¹ characteristic of Si-OH groups.⁴⁶ These were silylated by reaction with bis(trimethylsilyl)acetamide.⁵³

To 10 g of MD^H_{~35}M in a 100-mL round-bottom flask equipped with a Teflon covered magnetic stirring bar was added 50 mL of bis(trimethylsilyl)acetamide. The mixture was stirred at room temperature for 24 h. The extent of silylation was monitored by IR spectroscopy by following the disappearance of the Si-OH absorption at 3200 cm⁻¹.⁴⁶ Excess bis(trimethylsilyl)acetamide and (trimethylsilyl)acetamide were removed by evaporation under vacuum (0.5 mm). MD^H_{~35}M was a single Gaussian peak by GPC analysis whose retention time was between that of two polystyrene standards $M_p = 4800$ and 1900.

Preparation of MD^H_nM Oligomers.⁷ MD^H₂M, MD^H₃M, MD^H₄M, and MD^H₅M were prepared by cohydrolysis of trimethylchlorosilane and methyldichlorosilane as below. A mixture of trimethylchlorosilane (440 g) and methyldichlorosilane (60 g) was put in a 2-L three-necked round-bottom flask equipped with a dry ice-acetone cold finger condenser, Tru-bore stirrer equipped with a Teflon propeller-type blade, and a pressure equalizing addition funnel. A mixture of H₂O (27 g) and 200 mL

of pyridine was put into the addition funnel and was added dropwise to the chlorosilane mixture with vigorous agitation. When the addition was complete, the reaction mixture was stirred for an additional 0.5 h until the reaction had subsided. The mixture was poured into a slurry of ice and was stirred vigorously until an oily layer separated from the aqueous layer. The oily layer was washed twice with water, dried over CaCl₂, and filtered. Careful distillation through a Stedman column of about 30 theoretical plates yielded the following: hexamethyldisiloxane, 35 g (100 °C (760 mm)); MD^H₂M, 10 g (141.5 °C (760 mm)); MD^H₃M, 11.3 g (92 °C (50 mm)); MD^H₄M, 13.5 g (85 °C (10 mm)); MD^H₅M, 9.5 g (107 °C (10 mm)); MD^H₆M, 7.5 g (95 °C (2 mm)). In addition there was 27.4 g of higher boiling residue.^{54,55} For ¹H, ¹³C, and ²⁹Si NMR and GC-MS data see Table I.

General Chlorination Procedure. Ten percent Pd/C and allyl chloride were placed in a 50-mL two-necked round-bottom flask equipped with a rubber septum and a dry ice-acetone cold finger condenser. The mixture was heated at reflux for 20 min prior to addition of the particular MD^H_nM oligomer by syringe. The reaction mixture was refluxed until none of the starting MD^H_nM was left (GLPC). Gas produced in this reaction was passed through a solution of bromine in carbon tetrachloride. In this way, propene was converted to 1,2-dibromopropane identical with an authentic sample. The reaction was cooled, excess allyl chloride was distilled out, and then the residue was bulb-to-bulb distilled under reduced pressure. Each pure MD^H_nM oligomer gave only a single MD^{Cl}_nM as expected. The amount of MD^{Cl}_nM obtained depended upon the scale on which the reaction is run. This is due to unavoidable adventitious moisture on the surface of the glass equipment which lowers the yield of MD^{Cl}_nM when the reaction is carried out on a small scale. Analytical samples of MD^{Cl}_nM use for the determination of spectral properties were obtained by preparative GLPC.

Reaction of MD^H₂M with Allyl Chloride Catalyzed by Pd/C. Allyl chloride (75 mol) and 10% Pd/C (53 mg, 0.5 mmol) were heated at reflux for 20 min at which time MD^H₂M (25 mmol) was added. After removal of excess allyl chloride, MD^{Cl}₂M was obtained in 95% yield.²¹ For ¹H, ¹³C, and ²⁹Si NMR and GC-MS data of MD^{Cl}₂M see Table II.

Reaction of MD^H₂M and Allyl Chloride Catalyzed by Pd/C in a 1:6 Ratio. MD^H₂M (10 mmol), allyl chloride (60 mmol), and 10% Pd/C (1.2 mmol) were reacted as above. The reaction mixture was refluxed for 4 h. MD^{Cl}₂D^HM and MD^{Cl}₂M were obtained in 1:4 ratio based on GLPC analysis.

Reaction of Allyl Chloride with MD^H₂M in 2:1 Ratio. MD^H₂M (30 mmol), allyl chloride (60 mmol), and 10% Pd/C (1.2 mmol) were reacted as above. A substantial amount of MD^H₂M was recovered (56%). MD^{Cl}₂D^HM and MD^{Cl}₂M were obtained in a 5:1 ratio.

MD^{Cl}₂D^HM had the following spectral properties. ¹H NMR: δ 0.12 (s, 9 H), 0.147 (s, 9 H), 0.170 (d, *J* = 1.5 Hz, 1 H), 0.3907

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(s, 3 H), 4.658 (q, $J = 1.5$ Hz, 1 H). ^{13}C NMR: δ -0.656 (1 C), -0.900 (3 C), -1.060 (3 C), -1.408 (1 C). ^{29}Si NMR: δ 7.33 (s, M next to D^{Cl}), 5.56 (s, M next to D^{H}), -40.44 (D^{H}), -40.52 (D^{H}), -49.53 (s, D^{Cl}). The two ^{29}Si signals, which were observed for the D^{H} units, are due to the different diastereomers. A similar doubling was not observed in the ^{29}Si signals for the D^{Cl} unit. We were unable to separate these diastereomers. IR: ν 2940 (s), 2150 (s), 1250 (s), 1050 (s) cm^{-1} . MS: m/e (relative intensity) 301 (9.0, $\text{M}^+ - 15$), 301 (9.0), 227 (15.7), 207 (44.3), 193 (100), 73 (23). Anal. Calcd for $\text{Si}_4\text{C}_8\text{H}_{25}\text{O}_3\text{Cl}$: C, 30.66; H, 8.04. Found: C, 30.59; H, 8.09.

For ^1H , ^{13}C , and ^{29}Si NMR and GC-MS data for $\text{MD}^{\text{Cl}}_2\text{M}$ see Table II. Two signals were observed for the ^{29}Si nuclei. One for the d,l and the other for meso D^{Cl} units. We were unable to separate these isomers. IR: ν 2950 (s), 1420 (w), 1250 (s), 1050 (s) cm^{-1} . Anal. Calcd for $\text{Si}_4\text{C}_8\text{H}_{24}\text{O}_3\text{Cl}_2$: C, 27.33; H, 6.88. Found: C, 27.36; H, 6.88.

Reaction of Allyl Chloride with $\text{MD}^{\text{H}}_2\text{M}$ in 10:1 Ratio. $\text{MD}^{\text{H}}_2\text{M}$ (10 mmol), allyl chloride (100 mmol), and 10% Pd/C (2.0 mmol) were reacted as above. $\text{MD}^{\text{Cl}}_2\text{M}$ was obtained as the only product.

Reaction of $\text{MD}^{\text{H}}_3\text{M}$ with Allyl Chloride Catalyzed by Pd/C. Allyl chloride (100 mmol), 10% Pd/C (2.0 mmol, 210 mg), and $\text{MD}^{\text{H}}_3\text{M}$ (10 mmol) were reacted as above. $\text{MD}^{\text{Cl}}_3\text{M}$ was obtained in 90% yield.

Reaction of $\text{MD}^{\text{H}}_3\text{M}$ with Benzyl Chloride Catalyzed by Pd/C. Benzyl chloride (100 mmol) and 10% Pd/C (2.0 mmol) were heated at 110 $^\circ\text{C}$ for 30 min at which time $\text{MD}^{\text{H}}_3\text{M}$ (10 mmol) was added. After 6 h, toluene and unreacted benzyl chloride were removed by distillation at reduced pressure. $\text{MD}^{\text{Cl}}_3\text{M}$ was obtained in 80% yield by bulb to bulb distillation.

For ^1H , ^{13}C , and ^{29}Si NMR and GC-MS data for $\text{MD}^{\text{Cl}}_3\text{M}$ see Table II. IR: ν 2950 (s), 1430 (w), 1250 (s), 1050 (s) cm^{-1} . Anal. Calcd for $\text{Si}_5\text{C}_9\text{H}_{27}\text{O}_4\text{Cl}_3$: C, 24.23; H, 6.10. Found: C, 24.24; H, 6.16.

Reaction of $\text{MD}^{\text{H}}_4\text{M}$ with Allyl Chloride Catalyzed by Pd/C. $\text{MD}^{\text{H}}_4\text{M}$ (5 mmol), allyl chloride (100 mmol), and 10% Pd/C (2.0 mmol) 210 mg were reacted as above. $\text{MD}^{\text{Cl}}_4\text{M}$ was obtained in 80% yield.

Reaction of $\text{MD}^{\text{H}}_4\text{M}$ with Benzyl Chloride Catalyzed by Pd/C. Benzyl chloride (100 mmol), 10% Pd/C (2.0 mmol, 210 mg), and $\text{MD}^{\text{H}}_4\text{M}$ (5 mmol) were reacted as above. $\text{MD}^{\text{Cl}}_4\text{M}$ was obtained in 70% yield.

For ^1H , ^{13}C , and ^{29}Si NMR and GC-MS data for $\text{MD}^{\text{Cl}}_4\text{M}$ see Table II. Anal. Calcd for $\text{Si}_6\text{C}_{10}\text{H}_{30}\text{O}_5\text{Cl}_4$: C, 22.21; H, 5.59. Found: C, 22.22; H, 5.67.

Reaction of $\text{MD}^{\text{H}}_5\text{M}$ with Allyl Chloride Catalyzed by Pd/C. $\text{MD}^{\text{H}}_5\text{M}$ (5 mmol), allyl chloride (100 mmol), and 10% Pd/C (2.0 mmol, 210 mg) were reacted as above. $\text{MD}^{\text{Cl}}_5\text{M}$ was obtained in 75% yield.

Reaction of $\text{MD}^{\text{H}}_5\text{M}$ with Benzyl Chloride Catalyzed by Pd/C. Benzyl chloride (100 mmol), 10% Pd/C (2.0 mmol, 210 mg), and $\text{MD}^{\text{H}}_5\text{M}$ (5 mmol) were reacted as above. $\text{MD}^{\text{Cl}}_5\text{M}$ was obtained in 64% yield.

For ^1H , ^{13}C , and ^{29}Si NMR and GC-MS data for $\text{MD}^{\text{Cl}}_5\text{M}$ see Table II. IR: ν 2960 (s), 1405 (m), 1250 (s), 1050 (s), 800 (s) cm^{-1} . Anal. Calcd for $\text{Si}_7\text{C}_{11}\text{H}_{35}\text{O}_6\text{Cl}_5$: C, 20.80; H, 5.24. Found: C, 21.58; H, 5.50.

Reaction of $\text{MD}^{\text{H}}_{\sim 35}\text{M}$ with Allyl Chloride Catalyzed by Pd/C. Allyl chloride (15 mL) and 10% Pd/C (400 mg) were heated at reflux for half hour at which time $\text{MD}^{\text{H}}_{\sim 35}\text{M}$ (1.5 g) was added. The reaction mixture was refluxed until no unreacted $\text{MD}^{\text{H}}_{\sim 35}\text{M}$ was left in the reaction mixture. This was determined by the disappearance of the Si-H band at 2200 cm^{-1} in the IR. The formation of $\text{MD}^{\text{Cl}}_{\sim 35}\text{M}$ was monitored by ^1H NMR and IR spectroscopy.

Reaction of $\text{MD}^{\text{H}}_{\sim 35}\text{M}$ with Benzyl Chloride Catalyzed by Pd/C. Benzyl chloride (8 mL) and 10% Pd/C (200 mg) were heated at 120 $^\circ\text{C}$ for 1 h at which time $\text{MD}^{\text{H}}_{\sim 35}\text{M}$ (1 g) was added. The reaction mixture was continuously heated for 24 h until no unreacted $\text{MD}^{\text{H}}_{\sim 35}\text{M}$ is present in the reaction mixture as determined by ^1H NMR and IR spectroscopy. Excess benzyl chloride was removed from the reaction mixture by evaporation under the high vacuum (0.1 mm). The residue was identified as $\text{MD}^{\text{Cl}}_{\sim 35}\text{M}$. $\text{MD}^{\text{Cl}}_{\sim 35}\text{M}$ has the following properties. ^1H NMR: δ 0.155 (s, M), 0.455-0.564 (m, D^{Cl}). ^{13}C NMR: δ 0.560 (s, M),

1.373 (m, D^{Cl}). IR: ν 2960 (m), 1400 (w), 1260 (s), 1050 (s), 800 (s) cm^{-1} . Chlorine analysis of $\text{MD}^{\text{Cl}}_{\sim 35}\text{M}$ was carried out by hydrolysis of a freshly prepared sample of $\text{MD}^{\text{Cl}}_{\sim 35}\text{M}$ (0.180 g) in THF. The HCl generated was titrated against standardized 0.0995 N NaOH solution to a phenolphthalein end point. Anal. Calcd: Cl, 35.73. Found: C, 35.45.

Reactions of $\text{MD}^{\text{Cl}}\text{M}$ with Alkylolithium Reagents. Methylolithium. In a 50-mL two-necked round-bottom flask equipped with a pressure equalizing addition funnel and a rubber septum were placed 10 mL of ether, $\text{MD}^{\text{Cl}}\text{M}$ (1.28 g, 5 mmol), and a Teflon covered magnetic stirring bar. The solution was cooled to -78 $^\circ\text{C}$. Methylolithium (1.25 M) (10 mL, 12.5 mmol) was added slowly from an addition funnel. After the addition was complete, the reaction mixture was stirred at -78 $^\circ\text{C}$ for 1 h. A sample withdrawn from the reaction mixture was hydrolyzed. GLPC analysis showed formation of octamethyltrisiloxane (MDM). The reaction mixture was quenched by addition of a mixture of $\text{H}_2\text{O}/\text{THF}$ in 1:20 ratio at -78 $^\circ\text{C}$. The mixture was kept at -78 $^\circ\text{C}$ for another half hour and then allowed to warm to room temperature. Water was added and the organic layer separated, washed till neutral, dried over anhydrous MgSO_4 , and filtered. The ether and THF were removed from the filtrate by evaporation under reduced pressure. GLPC analysis of the residue indicated the formation of MDM in 80% yield, whose spectral properties in agreement with literature data.⁵⁶⁻⁵⁸

tert-Butyllithium (2.0 M) (10 mL, 20 mmol) and $\text{MD}^{\text{Cl}}\text{M}$ (1.28 g, 5 mmol) in 10 mL of ether were reacted at -78 $^\circ\text{C}$ for 4 h. The reaction mixture was worked up as above. 3-*tert*-Butyl-1,1,1,3,5,5,5-heptamethyltrisiloxane was obtained in 89% yield. It had the following spectral properties. ^1H NMR: δ 0.048 (s, 3 H), 0.170 (s, 18 H), 0.910 (s, 9 H). ^{13}C NMR: δ -0.3863 (1 C), 1.897 (5 C), 18.170 (1 C), 25.4637 (3 C). IR: ν 2980 (s), 1460 (m), 1250 (s), 1100 (s), 850 (s) cm^{-1} . MS: m/e (relative intensity) 278 (0.2, $\text{M}^+ - 263$), 263 (5.9, $\text{M}^+ - 15$), 221 (100, $\text{M}^+ - \text{C}_4\text{H}_9$), 73 (18.7). Anal. Calcd for $\text{Si}_3\text{C}_{11}\text{H}_{30}\text{O}_2$: C, 47.42; H, 10.85. Found: C, 47.60; H, 11.10.

n-Butyllithium (1.6 M) (9 mL, 14.4 mmol) and $\text{MD}^{\text{Cl}}\text{M}$ (1.28 g, 5 mmol) in 10 mL of ether were treated at -78 $^\circ\text{C}$ for 2.5 h. The reaction mixture was worked up as above. 3-*n*-Butyl-1,1,1,3,5,5,5-heptamethyltrisiloxane was obtained in 87% yield. Although this compound is known,⁵⁹ no spectral data has been previously reported. ^1H NMR: δ 0.075 (s, 3 H), 0.165 (s, 18 H), 0.508-1.436 (m, 9 H). ^{13}C NMR: δ -0.280 (1 C), 1.308 (6 C), 12.823 (1 C), 17.477 (1 C), 25.462 (1 C), 26.178 (1 C). IR: ν 2980 (s), 1450 (m), 1260 (s), 1050 (s), 850 (s) cm^{-1} .

sec-Butyllithium (1.4 M) (10 mL, 14 mmol) and $\text{MD}^{\text{Cl}}\text{M}$ (1.28 g, 5 mmol) in 10 mL of ether were treated at -78 $^\circ\text{C}$ for 1.5 h. The reaction mixture was worked up as above. 3-*sec*-Butyl-1,1,1,3,5,5,5-heptamethyltrisiloxane was obtained in 94% yield. It had the following spectral properties. ^1H NMR: δ 0.402 (s, 3 H), 0.064 (s, 18 H), 0.844-0.951 (m, 9 H). ^{13}C NMR: δ -2.024 (1 C), 1.877 (6 C), 13.137 (1 C), 13.310 (1 C), 23.004 (1 C), 24.088 (1 C). ^{29}Si NMR: δ -21.6474 (1 Si); 6.672, 6.6608 (2 Si). IR: ν 2975 (s), 1460 (m), 1260 (s), 1050 (s), 850 (s) cm^{-1} . MS: m/e (relative intensity) 278 (0.1, $\text{M}^+ - 263$), 263 (6.5, $\text{M}^+ - 15$), 221 (98, $\text{M}^+ - \text{C}_4\text{H}_9$), 207 (22.4), 133 (16.9); 73 (100). Anal. Calcd for $\text{Si}_3\text{C}_{11}\text{H}_{30}\text{O}_2$: C, 47.42; H, 10.85. Found: C, 47.27; H, 11.04.

Reaction of $\text{MD}^{\text{Cl}}\text{D}^{\text{H}}\text{M}$ with *sec*-Butyllithium in a 1:2 Molar Ratio. *sec*-Butyllithium (1.4 M) (9 mL, 10 mmol) and $\text{MD}^{\text{Cl}}\text{D}^{\text{H}}\text{M}$ (1.58 g, 5 mmol) in 10 mL of ether were reacted at -78 $^\circ\text{C}$ for 2.5 h. After workup, 1-*sec*-butyl-1,3,3,3-tetramethyl-disiloxane was obtained in 87% yield.

Reaction of $\text{MD}^{\text{Cl}}\text{D}^{\text{H}}\text{H}$ with *sec*-Butyllithium in 1:4 Molar Ratio. *sec*-Butyllithium (1.4 M) (15 mL, 21 mmol) and $\text{MD}^{\text{Cl}}\text{D}^{\text{H}}\text{H}$ (1.58 g, 5 mmol) in 10 mL of ether were reacted at -78 $^\circ\text{C}$ for 2.5 h. After workup, 1-*sec*-butyl-1,3,3,3-tetramethyl-disiloxane was obtained in 92% yield. Although this compound has been reported,⁶⁰ no spectral data are available. ^1H NMR: δ 0.067 (s, 9

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H), 0.107 (s, 3 H), 0.856–0.995 (m, 9 H), 4.429–4.473 (m, 1 H). ^{13}C NMR: δ -2.7320, -2.6503 (1 C); 1.5876 (1 C); 13.1014 (1 C); 13.1591, 13.1909 (1 C); 22.4972, 22.6357 (1 C); 24.4031, 24.4811 (1 C). ^{29}Si NMR: δ -3.3634, -3.0455 (1 Si); 9.2727, 9.3182 (1 Si). IR: ν 2960 (s), 2120 (s), 1440 (m), 1265 (s), 1060 (s), 850 (s) cm^{-1} . MS: m/e (relative intensity) 190 (2.8, M^+), 175 (5.0, $\text{M}^+ - 15$), 133 (100, $\text{M}^+ - \text{C}_4\text{H}_9$), 119 (27.9), 173 (16). Anal. Calcd for $\text{Si}_2\text{C}_8\text{H}_{22}\text{O}$: C, 50.46; H, 11.66. Found: C, 50.68; H, 11.55.

Reaction of $\text{MD}^{\text{H}}\text{M}$ with *sec*-Butyllithium. *sec*-Butyllithium (1.35 M) (12 mL, 16 mmol) and $\text{MD}^{\text{H}}\text{M}$ (1.66 g, 7.5 mmol) in 10 mL of ether were reacted at -78°C for 2 h. After workup, 1-*sec*-butyl-1,3,3,3-tetramethyldisiloxane was obtained in 90% yield.

Reaction of $\text{MD}^{\text{Cl}_2}\text{M}$ with *sec*-Butyllithium. *sec*-Butyllithium (1.4 M) (30 mL, 42 mmol) and $\text{MD}^{\text{Cl}_2}\text{M}$ (1.75 g, 58 mmol) in 10 mL of ether were reacted at -78°C for 2.5 h. After workup, 3,5-di-*sec*-butyl-1,1,1,3,5,7,7,7-octamethyltetrasiloxane was obtained in 90% yield. ^1H NMR: δ 0.00 (s, 6 H), 0.0826 (s, 18 H), 0.400–1.600 (m, 18 H). ^{13}C NMR: δ -1.9443, -1.9215, -1.8960 (2 C); 1.8821 (6 C); 13.0875, 13.1015 (2 C); 13.2507, 13.2844 (2 C); 23.2258, 23.2385, 23.2556 (2 C); 24.0850, 24.1288, 24.1357 (2 C). ^{29}Si NMR: δ -27.8218, -27.7874 (2 Si), 1.3398, -1.3063 (2 Si). IR: ν 2980 (s), 1430 (w), 1250 (s), 1050 (s), 830 (s) cm^{-1} . MS: m/e (relative intensity) 379 (10, $\text{M}^+ - 15$), 337 (100, $\text{M}^+ - \text{C}_4\text{H}_9$), 249 (15.2), 207 (76.3), 193 (67.7), 73 (32). Anal. Calcd for $\text{Si}_4\text{C}_{16}\text{H}_{42}\text{O}_3$: C, 48.73; H, 10.66. Found: C, 48.67; H, 10.71.

Reaction of $\text{MD}^{\text{Cl}_3}\text{M}$ with *sec*-Butyllithium. *sec*-Butyllithium (1.4 M) (40 mL, 56 mmol) and $\text{MD}^{\text{Cl}_3}\text{M}$ (2.22 g, 0.5 mmol) in 10 mL of ether were reacted at -78°C for 3 h. After workup, 3,5,7-tri-*sec*-butyl-1,1,1,3,5,7,9,9,9-nonamethylpentasiloxane was found in 84% yield. ^1H NMR: δ -0.007 (s, 6 H), 0.018 (s, 3 H), 0.068 (s, 18 H), 0.300–1.200 (m, 27 H). ^{13}C NMR: δ -1.936 (3 C); 1.900 (6 C); 12.916, 13.010 (3 C); 13.283, 13.304, 13.326 (3 C); 22.986, 23.010, 23.037 (3 C); 23.789, 23.878, 23.954 (3 C). IR: ν 2940 (s), 1430 (m), 1250 (s), 1050 (s), 830 (s), 770 (m) cm^{-1} . MS: m/e (relative intensity) 495 (1.7, $\text{M}^+ - 15$), 453 (25, $\text{M}^+ - \text{C}_4\text{H}_9$), 323 (56), 267 (35.3), 133 (53.3), 73 (100). Anal. Calcd for $\text{Si}_5\text{C}_{21}\text{H}_{54}\text{O}_4$: C, 49.35; H, 10.65. Found: C, 49.69; H, 10.49.

Reaction of $\text{MD}^{\text{Cl}_4}\text{M}$ with Methylolithium. Methylolithium (1.25 M) (40 mL, 50 mmol) and $\text{MD}^{\text{Cl}_4}\text{M}$ (2.69 g, 5 mmol) in 10 mL of ether were reacted at -78°C for 4 h. MD_4M was formed in 76% yield. $^{54-56}$ ^1H NMR: δ -0.002 (s, 12 H), 0.030 (s, 12 H), 0.079 (s, 18 H). MS: m/e (relative intensity) 443 (9.7, $\text{M}^+ - 15$), 355 (12.4), 281 (21.2), 221 (39.8), 157 (53.9), 73 (100).

Reaction of $\text{MD}^{\text{Cl}_5}\text{M}$ with Methylolithium. Methylolithium (1.25 M) (48 mL, 60 mmol) and $\text{MD}^{\text{Cl}_5}\text{M}$ (2.84 g, 4 mmol) in 10 mL of THF were reacted at -78°C for 4 h. MD_5M was formed

in 72% yield. $^{54-56}$ ^1H NMR: δ 0.003 (s, 6 H), 0.025 (s, 12 H), 0.036 (s, 12 H), 0.074 (s, 18 H). MS: m/e (relative intensity) 517 (1.5, $\text{M}^+ - 15$), 429 (1.2), 355 (5.5), 281 (4.2), 221 (29.1), 157 (32.8), 73 (100).

Reaction of $\text{MD}^{\text{Cl}}_{\sim 35}\text{M}$ with *sec*-Butyllithium in 4:1 Ratio. *sec*-Butyllithium (1.4 M) (100 mL, 140 mmol) and $\text{MD}^{\text{Cl}}_{\sim 35}\text{M}$ (3.47 g, 1 mmol) in 30 mL of THF were reacted at -78°C for 6 h. After workup, a colorless oily residue was obtained in quantitative yield. A volatile product, di-*sec*-butylmethylsilanol, was obtained by bulb to bulb distillation (0.01 mm, 50°C) in 13% yield. It had the following properties. ^1H NMR: δ 0.017, 0.006, 0.005, -0.012 (3 H), 0.650–1.70 (18 H). ^{13}C NMR: δ 2.0875, 2.2432, 2.4156 (1 C); 20.7894, 20.9449, 20.9661, 20.9742, 21.0103, 21.0195 (4 C); 28.850, 28.8666, 28.9310 (2 C); 31.9802, 32.0375 (2 C). ^{29}Si NMR: δ 13.9754, 14.1307, 14.2895. IR: ν 3660 (s), 2980 (s), 1450 (m), 1250 (m), 820 (s) cm^{-1} . MS: m/e (relative intensity) 174 (6.4, M^+), 157 (1.1, $\text{M}^+ - 15$), 117 (94.7, $\text{M}^+ - \text{C}_4\text{H}_9$), 75 (100), 61 (88). Anal. Calcd for $\text{SiC}_9\text{H}_{22}\text{O}$: C, 62.06; H, 12.64. Found: C, 62.13; H, 12.37. The nonvolatile residue was a single Gaussian peak by GPC. Its retention time was consistent with that expected for α,ω -bis(trimethylsiloxy)poly-*sec*-butylmethylsiloxane ($\bar{M}_p = 4200$) on the basis of comparison with the retention time of polystyrene standards of known $\bar{M}_p = 4800$. It was purified by column chromatography on a silica gel column. A 1:1 ratio of *n*-hexane/methylene chloride was used as eluting solvent. It had the following properties. ^1H NMR: δ -0.004 to 0.079 (SiCH_3), 0.500–1.400 (*Si-sec-butyl*). ^{13}C NMR: δ 13.021–13.346, 21.036, 24.015–24.178. ^{29}Si NMR: δ 13.1773, 13.3111, 13.4365. IR: ν 2980 (s), 1450 (m), 1250 (s), 1050 (s), 850 (m), 780 (s) cm^{-1} . Anal. Calcd for $\text{Si}_{37}\text{C}_{181}\text{H}_{438}\text{O}_{36}$ ($\text{MD}^{\text{sec-Bu}}_{\sim 35}\text{M}$): C, 51.44; H, 10.37. Found: C, 52.01; H, 10.38.

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Registry No. $\text{MD}^{\text{H}}\text{M}$, 1873-88-7; $\text{MD}^{\text{H}_2}\text{M}$, 16066-09-4; $\text{MD}^{\text{H}_3}\text{M}$, 17478-13-6; $\text{MD}^{\text{H}_4}\text{M}$, 17998-54-8; $\text{MD}^{\text{H}_5}\text{M}$, 16096-81-4; $\text{MD}^{\text{Cl}}\text{M}$, 22407-46-1; $\text{MD}^{\text{Cl}_2}\text{M}$, 100045-14-5; $\text{MD}^{\text{Cl}_3}\text{M}$, 100045-15-6; $\text{MD}^{\text{Cl}_4}\text{M}$, 100045-16-7; $\text{MD}^{\text{Cl}_5}\text{M}$, 100045-17-8; $\text{MD}^{\text{Cl}_6}\text{M}$, 100045-18-9; MDM, 107-51-7; MD_2M , 107-52-8; MD_3M , 541-01-5; $(\text{CH}_3)_3\text{SiCl}$, 75-77-4; $\text{CH}_3\text{Si}(\text{H})\text{Cl}_2$, 75-54-7; $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$, 107-46-0; $\text{H}_2\text{C}=\text{CHCH}_2\text{Cl}$, 107-05-1; PhCH_2Cl , 100-44-7; CH_3Li , 917-54-4; *t*-BuLi, 594-19-4; *n*-BuLi, 109-72-8; *sec*-BuLi, 598-30-1; 3-*tert*-butyl-1,1,1,3,5,5,5-heptamethyltrisiloxane, 100045-19-0; 3-*n*-butyl-1,1,1,3,5,5,5-heptamethyltrisiloxane, 18138-63-1; 3-*sec*-butyl-1,1,1,3,5,5,5-heptamethyltrisiloxane, 100045-20-3; 1-*sec*-butyl-1,3,3,3-tetramethyldisiloxane, 100045-21-4; 3,5-di-*sec*-butyl-1,1,1,3,5,7,7,7-octamethyltetrasiloxane, 100045-22-5; 3,5,7-tri-*sec*-butyl-1,1,1,3,5,7,9,9,9-nonamethylpentasiloxane, 100045-23-6; di-*sec*-butylmethylsilanol, 100045-24-7.

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