

Reactions of Organolithium Reagents with Siloxane Substrates

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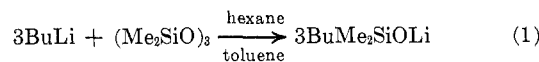
A study of the reactions of organolithium reagents (RLi) with common siloxane substrates has led to the following findings ($M = \text{Me}_2\text{SiO}_{1/2}$ and $D = \text{Me}_2\text{SiO}_{2/2}$). (A) Diorganosiloxanes such as D_2 are cleaved rapidly by RLi at ambient temperatures to yield lithium siloxanates [*i.e.*, $\text{R}(\text{Me}_2\text{SiO})_2\text{Li}$], which are in turn completely consumed by additional RLi in an even faster series of alkylation reactions to yield the simple triorganosilanolate (*i.e.*, RMe_2SiOLi). Even when exceptionally reactive siloxane substrates such as D_3 are employed, the organolithium reagent exhibits exclusive preference for the derived siloxanates; thus the combination of molar equivalents of BuLi and D_3 affords $\text{BuMe}_2\text{SiOLi}$ quantitatively, none of the presumed intermediate siloxanolate species (*e.g.*, $\text{BuMe}_2\text{SiOMe}_2\text{SiOMe}_2\text{SiOLi}$), and unreacted D_3 (*i.e.*, $2/3$ mol). Other cyclic and linear siloxanes react in a similar fashion. (B) Both neutral diorganosiloxanes and derived anionic siloxanates are more reactive than Me_3SiCl toward RLi; hence, although reaction of BuLi with D_3 in the presence of Me_3SiCl did indeed afford the expected siloxanolate derivatives ($\text{BuD}_{1-3}\text{SiMe}_3$), no BuSiMe_3 was detected. (C) RMe_2SiOLi and RLi ($R = \text{Bu}$) are very unreactive with Me_3SiCl in the absence of ether. When ether is added to a hydrocarbon solution of these three reactants, RLi reacts much more rapidly than the silanolate. Siloxanates, on the other hand, are more reactive than either of the above bases toward Me_3SiCl , reacting even in the absence of ethers. (D) Competition of various combinations of reactants for RLi has established the following order of relative reactivities: $D_3 > D_0 \cong \text{MD}_2\text{M} > D_4 \gg \text{MD}_1\text{-M} \gg \text{MM}$. Furthermore, the reactivity (relative to D_3) of MD_2M ($x \cong 10\text{-}1000$) increases with increasing values of x . This is because the relatively infrequent cleavages of MD_2M lead to increasingly larger amounts of RLi consumption by the resulting siloxanolate as the value of x increases. Thus this obviously ionic reaction exhibits certain characteristics of free-radical olefin polymerizations in that the concepts of *kinetic chain length* and *polymer chain length* become intimately related. (E) Displacement of methyl from $\text{BuMe}_2\text{SiOLi}$ by BuLi is rather facile, taking place in refluxing hexane to yield $\text{Bu}_2\text{MeSiOLi}$ and, upon longer treatment, Bu_3SiOLi . A similar displacement on a neutral substrate, MDM, was also observed and rationalized. (F) Although $\text{Me}_3\text{SiOSiMe}_3$ was not cleaved by lengthy reflux with BuLi, the more complicated trimethylsiloxy derivative $\text{Si}(\text{OSiMe}_3)_4$ did react. In this case initial slow attack on the peripheral triorganosilicon produces a siloxanolate which subsequently undergoes several rapid alkylations; thus $\text{Si}(\text{OSiMe}_3)_4$, reacts with BuLi to give BuSiMe_3 and $\text{LiOSi}(\text{OSiMe}_3)_3$, whereupon the latter species undergoes rapid alkylation to yield Bu_2SiOLi and $3\text{Me}_2\text{SiOLi}$. (G) Several interesting metallation reactions were also observed. The most facile of these was the metallation of $\text{Me}_3\text{SiOSiMe}_2\text{CH}_2\text{SiMe}_3$ at the methylene site by *n*-BuLi in the absence of any of the common donor solvents. (H) Lithium triorganosilanolates react cleanly in a selectively stepwise fashion with suitable alkoxysilane substrates. Several examples are provided.

Although organometallic agents have been widely employed for the synthesis of carbon-silicon linkages in organosilicon chemistry,¹ their reactions with siloxane functionality have received relatively little attention.² Kipping and Hackford showed many years ago^{2b} that the reaction of Grignard reagents with silsesquioxanes afforded triorganosilanols upon work-up. Similarly, Sauer^{2c} prepared Me_3SiOH from the reaction of MeMgX with $(\text{Me}_2\text{SiO})_x$. The above reaction generally required rather forcing conditions, *i.e.*, excess Grignard reagent and high temperatures (near 200°). Although organolithium reagents are much more reactive than are Grignard reagents toward siloxane substrates, the literature contains only a few scattered examples of their use. It was determined by Gilman and coworkers^{2d} that the most electrophilic silicon of an unsymmetrical hexaorganodisiloxane underwent preferential alkylation. Seyferth^{2e} demonstrated that, although unreactive in ether, MeLi did react quite readily with $\text{Me}_3\text{SiOSiMe}_3$ in the presence of tetrahydrofuran. Although this constituted a convenient route to Me_3SiOLi , the reaction of ethereal MeLi with dimethylsiloxane substrates was shown^{2f} by Ruidisch and Schmidt to be an even better route, since it made more efficient use of the organolithium reagent (*i.e.*, no loss of Me_4Si).

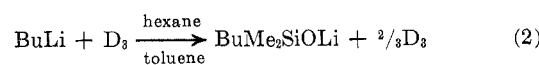
We became interested in elucidating the chemistry

of organolithium reagents with siloxane substrates, motivated at least in part by the knowledge that lithium bases are useful as catalysts for the highly selective polymerization of cyclotrisiloxanes³ leading to novel nonequilibrium polymers.

Reactions of RLi with Dimethylsiloxy Substrates.—The reaction of 3 equiv of BuLi with hexamethylcyclotrisiloxane (*i.e.*, D_3 , where D represents $\text{Me}_2\text{SiO}_{3/2}$) was found to proceed rapidly and exothermally in hydrocarbon media to yield $\text{BuMe}_2\text{SiOLi}$ (*i.e.*, BuD_1Li) (eq 1), paralleling the earlier work^{2f} with ethereal MeLi.



In an attempt to prepare the linear trimeric siloxanolate species BuD_3Li , only 1 equiv of BuLi was added to D_3 ; much to our surprise an essentially quantitative conversion into the simple triorganosilanolate, BuD_1Li , resulted, accompanied by 66% of the unreacted starting trimer (eq 2). Completely analogous results were ob-



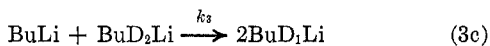
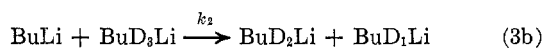
tained in the reaction of BuLi with D_4 . It is apparent that the neutral cyclotrisiloxane substrate undergoes a ring-opening alkylation in a rate-determining step followed by

(1) C. Eaborn, "Organosilicon Compounds," Butterworth and Co. Ltd., London, 1960, pp 10-33.

(2) (a) Reference 1, pp 268-270; (b) F. S. Kipping and J. Hackford, *J. Chem. Soc.*, **99**, 138 (1911); (c) R. O. Sauer, *J. Amer. Chem. Soc.*, **66**, 1707 (1944); (d) H. Gilman, H. N. Benedict, and H. Hartzfeld, *J. Org. Chem.*, **19**, 419 (1954); (e) D. Seyferth and D. L. Alleston, *Inorg. Chem.*, **2**, 418 (1963); (f) I. Ruidisch and M. Schmidt, *Angew. Chem.*, **75**, 575 (1963).

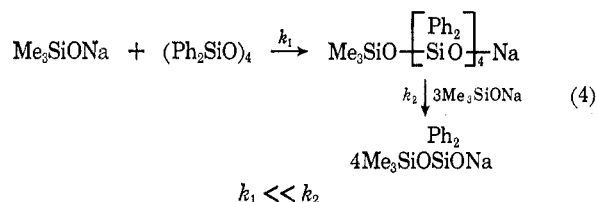
(3) C. L. Lee, C. L. Frye, and O. K. Johannson, *Polymer Preprints*, **10** (2), 1361 (1969). (b) E. E. Bostick, U. S. Patent 3,337,496 (1967).

a very fast series of alkylations on the resulting linear siloxanolate (eq 3a-3c). The above rate relationships



$$k_1 \ll k_2 \text{ or } k_3$$

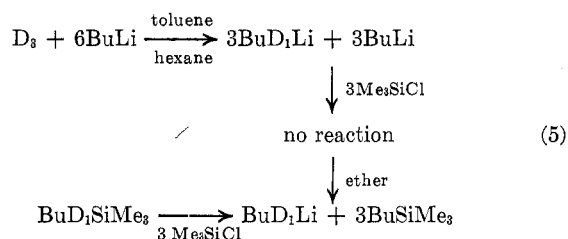
are reminiscent of those observed by Selin⁴ (eq 4). It should be noted, however, that the Selin work in-



involved base-catalyzed siloxane redistribution, whereas in the above lithium systems *no* siloxane redistribution *per se* occurs. Thus the resulting silanolate, BuD_1Li , did not react with the remaining D_3 under the conditions employed (neither at room temperature nor in refluxing hexane). The reaction products in the present work were derivatized for subsequent isolation and analysis by hydrolyzing with dilute acid to give the silanols or by trimethylsilylating with ethereal Me_3SiCl . *Ether is necessary because the lithium triorganosilanolates will not react with Me_3SiCl in hydrocarbon media. Furthermore, even BuLi is very unreactive toward Me_3SiCl in the absence of donor solvents.*

The presumed siloxanolate intermediates, BuD_xLi , were trapped by adding BuLi to a mixture of D_3 with Me_3SiCl . Essentially the same product mixtures were obtained regardless of whether ether was present during or added subsequently to the BuLi addition. In either case, the major product was the simple triorganosilanolate derivative $\text{BuMe}_2\text{SiOSiMe}_3$ (*i.e.*, $\text{BuD}_1\text{SiMe}_3$) accompanied by much smaller amounts of $\text{BuD}_3\text{SiMe}_3$ (the trisiloxanolate derivative) and $\text{BuD}_2\text{SiMe}_3$ (the disiloxanolate derivative), and substantial amounts of unreacted D_3 . Little or no BuSiMe_3 was formed, underscoring the low reactivity of BuLi toward Me_3SiCl (relative to its high reactivity toward D_3 and the resulting siloxanolate). The fact that $\text{BuD}_3\text{SiMe}_3$ and $\text{BuD}_2\text{SiMe}_3$ were formed prior to the addition of the ether shows the lithium siloxanolate to be highly reactive bases toward Me_3SiCl in marked contrast to BuLi or BuD_1Li . The relative reactivity of these last two species was determined. As shown below, the addition of 6BuLi (hexane solution) to a toluene solution of D_3 yields a solution containing 3 BuD_1Li and 3BuLi. This was followed by the addition of 3 Me_3SiCl , which did not react (as evidenced by glpc monitoring) even when the solution was heated at reflux. The addition of a modest amount of ether caused the prompt and exclusive consumption of Me_3SiCl by the BuLi to form 3 BuSiMe_3 . Subsequent addition of another 3 Me_3SiCl produced the expected $\text{BuD}_1\text{SiMe}_3$. Thus, under

these conditions, BuLi was clearly much more reactive than was BuD_1Li (eq 5). It was of some interest to



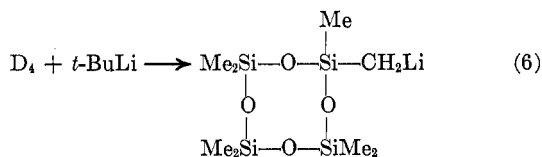
compete the relatively sluggish D_4 with Me_3SiCl for BuLi in the presence of added ether. Under these conditions, D_4 reacted sufficiently rapidly to compete very effectively for the organolithium reagent, the major product being $\text{BuD}_1\text{SiMe}_3$ accompanied by relatively small amounts of BuSiMe_3 and $\text{BuD}_{2-4}\text{SiMe}_3$, and unreacted D_4 . The fact that relatively little BuSiMe_3 was formed indicates that, even in ether, Me_3SiCl is less reactive than D_4 toward BuLi. Ether evidently accelerates the reactivity of D_4 , as well as that of Me_3SiCl , toward BuLi. Increasing the Me_3SiCl to D_4 ratio beyond the above 1:1 value did, of course, produce larger amounts of $\text{BuD}_{2-4}\text{SiMe}_3$ and BuSiMe_3 and correspondingly decreased amounts of $\text{BuD}_1\text{SiMe}_3$.

Competition of various combinations of dimethylsiloxane reactants for BuLi revealed the following qualitative order of relative reactivities (M represents $\text{Me}_3\text{SiO}_{1/2}$): $\text{D}_3 > \text{D}_2 \cong \text{MD}_2\text{M} > \text{D}_4 \gg \text{MD}_1\text{M} \gg \text{MM}$. In this series, D_3 is so much more reactive than D_4 that the addition of 1 equiv of BuLi to a solution containing 1 molar equiv of these two cyclics results in completely selective consumption of the trimer. At the other end of the series, hexamethyldisiloxane is so unreactive that it undergoes no reaction even when heated for several days at reflux with BuLi in hexane solution. The reactivity (relative to D_3) of the linear siloxanes, MD_xM ($x = 10-1000$), appears to become greater with increasing chain length. We will discuss this phenomenon more fully at a later point (*vide infra*).

Other organolithium reagents react in more or less the same fashion with D_3 and related materials. The product distribution was not much affected by the presence of ether in those instances wherein ethereal organolithium reagents were employed (*i.e.*, MeLi and PhLi). Because of its increased steric requirements, it had been anticipated that *t*-BuLi might not be very reactive toward cyclosiloxanes. On the contrary, *t*-BuLi reacted exothermally with D_3 and the use of 3*t*-BuLi per D_3 resulted in essentially quantitative conversion into *t*- $\text{BuMe}_2\text{SiOLi}$. Experiments in which only 1*t*-BuLi per D_3 was added revealed that the siloxanolate alkylation reaction was not as rapid relative to ring opening as in the earlier *n*-BuLi examples. Thus, even in the absence of Me_3SiCl as a trapping agent, the expected product *t*- BuD_1Li (and unreacted D_3) was accompanied by substantial amounts of *t*- BuD_2Li and *t*- BuD_3Li . It is certainly to be expected that steric crowding should decrease the relative rates of siloxanolate alkylations, and especially the one involving *t*-BuLi and the disiloxanolate *t*- BuD_2Li , since in this case juxtaposition of bulky *t*-butyl groups on immediately adjacent silicon sites is necessarily involved. This rationale accords well with the observation that the above reaction

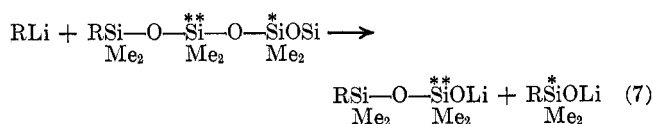
(4) T. G. Selin, Abstracts, Third International Symposium on Organometallic Chemistry, Munich, 1967, p 362.

yielded mostly $t\text{-BuD}_1\text{Li}$ and $t\text{-BuD}_2\text{Li}$ but very little $t\text{-BuD}_3\text{Li}$. Very similar results were obtained from the reaction of $t\text{-BuLi}$ with D_4 ; *i.e.*, in addition to unreacted D_4 , one obtains substantial amounts of $t\text{-BuD}_1\text{Li}$ and $t\text{-BuD}_2\text{Li}$ but almost no $t\text{-BuD}_3\text{Li}$ or $t\text{-BuD}_4\text{Li}$. This reaction was further complicated by a competing D_4 metallation reaction leading to the formation of an unusually unreactive organometallic species (eq 6).

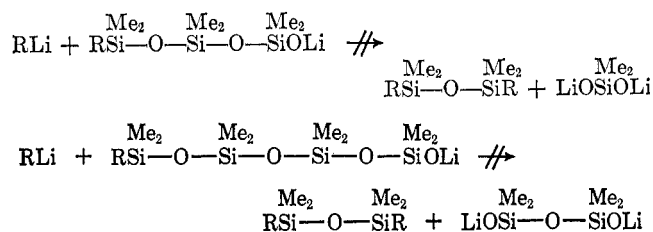


This species was characterized after a 24-hr reaction period as its Me_3SiCl derivative; it is remarkable that this organolithium persisted for so long in the presence of appreciable amounts of dimethylsiloxy material.

No attempt has been made thus far in this paper to rationalize the marked increase of reactivity of siloxanes toward organolithium reagents upon siloxanolate formation. One might have predicted the opposite effect, anticipating that the formal negative charge of the siloxanolate would discourage attack by the nucleophilic organometallic species. Apparently, this is more than offset by other factors. The heightened reactivity of the siloxanolate is presumably related to the tendency of dipolar materials to associate in non-polar media; *i.e.*, the charged siloxanolate species presumably are more able to associate with, or gain entry to, the organolithium micelles, thereby facilitating reaction. It has not yet been unequivocally determined which particular silicon site in a given siloxanolate undergoes preferential alkylation. Our present observations are not inconsistent with a scheme involving preferential attack on the end silicon (eq 7). Cer-

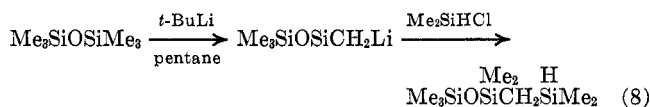


tainly, this is necessarily true in the reaction of RLi with the disiloxanolate, although it should be recognized that in the case of higher siloxanolate, attack at other silicon sites could lead to the same products. One mode of attack singularly absent throughout this work is that involving siloxane cleavage to yield a hexaorganodisiloxane; *i.e.*, processes of the following type do not appear to occur readily on siloxanolate substrates.



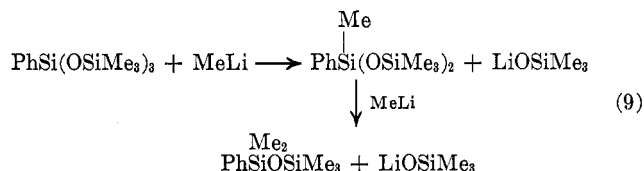
Reactions with Other Siloxanes.—Although attention has been directed mainly at various dimethylsiloxane substrates, several other types have also been examined. Other diorganosiloxanes such as $(\text{PhMe}_2\text{SiO})_x$ and $[\text{F}_3\text{CCH}_2\text{CH}_2(\text{Me})\text{SiO}]_x$ react with organolithium reagents more or less analogously to $(\text{Me}_2\text{SiO})_x$.

As noted previously herein, hexaalkyldisiloxanes are not cleaved by BuLi in hydrocarbon media nor by ethereal MeLi . As anticipated, $t\text{-BuLi}$ also did not cleave $\text{Me}_3\text{SiOSiMe}_3$; however, it did unexpectedly afford the metallated derivative $\text{Me}_3\text{SiOSiMe}_2\text{CH}_2\text{Li}$ in good yield under unprecedentedly mild conditions, *i.e.*, at room temperature and in the absence of a donor solvent.⁵ To establish unequivocally that the above derivative had not undergone rearrangement to the isomeric disilmethylene species, the Me_2SiHCl derivative was prepared (eq 8). The nmr spectrum of this

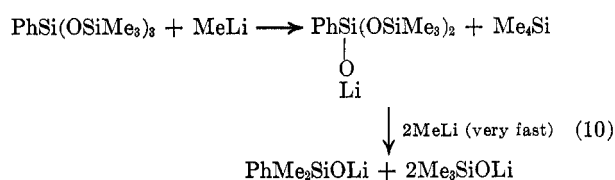


product revealed the expected CH_2 doublet arising from coupling with the immediately adjacent SiH moiety, thus confirming the assignment.

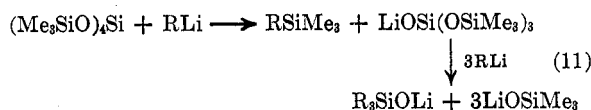
Trimethylsilylated substrates, in addition to those already cited, which have been reacted with organolithium reagents include $\text{PhSi}(\text{OSiMe}_3)_3$ and $\text{Si}(\text{OSiMe}_3)_4$. The first of these two substrates undergoes two types of reaction. One involves alkylation of the most electrophilic silicon center, *i.e.*, the Ph-Si site (eq 9).



$\text{PhMe}_2\text{Si}(\text{OSiMe}_3)_2$ was shown to be *ca.* 5.5 times as reactive as $\text{PhSi}(\text{OSiMe}_3)_3$, presumably as a consequence of decreased steric hindrance about the central silicon site. A competing process involves initial alkylation at one of the peripheral Me_3Si sites, generating a tetraorganosilane and a siloxanolate which then undergoes two very rapid subsequent alkylations to yield the expected silanolate (eq 10). In addition to identifying



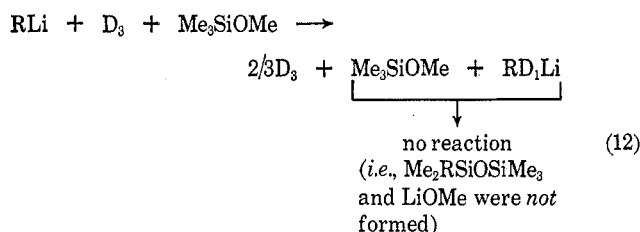
Me_4Si in the ether distillate, treatment of the reaction product with Me_2SiHCl yielded the expected derivative, $\text{PhMe}_2\text{SiOSiHMe}_2$ (as well as $\text{Me}_3\text{SiOSiHMe}_2$). The resulting glpc peak area ratio of $1\text{PhMe}_2\text{SiOSiMe}_2\text{H}/2.8\text{PhMe}_2\text{SiOSiMe}_3$ shows the reaction involving alkylation of a peripheral $\text{Me}_3\text{SiO-}$ group to be an important factor. The compound $\text{Si}(\text{OSiMe}_3)_4$ appears to undergo exclusively this latter mode of reaction, *i.e.*, initial attack on a peripheral $\text{Me}_3\text{SiO-}$ unit followed by successive rapid alkylation of the resulting siloxanolate (eq 11). The species RSiMe_3 was the *only* volatile species



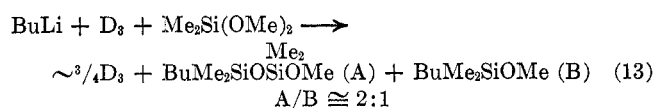
(5) Metallations of this and related substrates in tetramethylethylenediamine were reported: G. A. Gornowicz and R. West, *J. Amer. Chem. Soc.*, **90**, 4478 (1968).

observed as the reaction proceeded. It is interesting to note that these tris- and tetrakis(trimethylsiloxy) compounds do not appear to undergo any detectable alkyl exchange of the type observed with the bistrimethylsiloxy derivative, MDM (*vide infra*). Perhaps the additional steric requirements of the bulky Me_3SiO -substituent preclude the formation of the suggested type of organolithium-siloxane intermediate.

Competition of D_3 vs. Alkoxysilane Substrates for Organolithium Reagents.—The relative reactivity of alkoxysilane substrates toward BuLi has also been briefly examined: D_3 was allowed to compete for BuLi vs. Me_3SiOMe , $\text{Me}_2\text{Si}(\text{OMe})_2$, and $\text{MeSi}(\text{OMe})_3$; Me_3SiOMe was wholly unreactive in hydrocarbon media toward both BuLi and $\text{BuMe}_2\text{SiOLi}$. Very similar results were obtained using ethereal MeLi (eq 12).



However, the more functional alkoxysilanes, $\text{Me}_2\text{Si}(\text{OMe})_2$ and $\text{MeSi}(\text{OMe})_3$, reacted with BuLi at rates comparable with that of D_3 . Thus, while some of the BuLi was intercepted by $\text{Me}_2\text{Si}(\text{OMe})_2$ to give $\text{BuMe}_2\text{SiOMe}$ (B), most of it reacted with D_3 to give $\text{BuMe}_2\text{SiOLi}$, which then attacked $\text{Me}_2\text{Si}(\text{OMe})_2$ to give $\text{BuMe}_2\text{SiOSiMe}_2\text{OMe}$ (A); glpc peak area comparison showed *ca.* a 2:1 ratio of A to B (eq 13). An

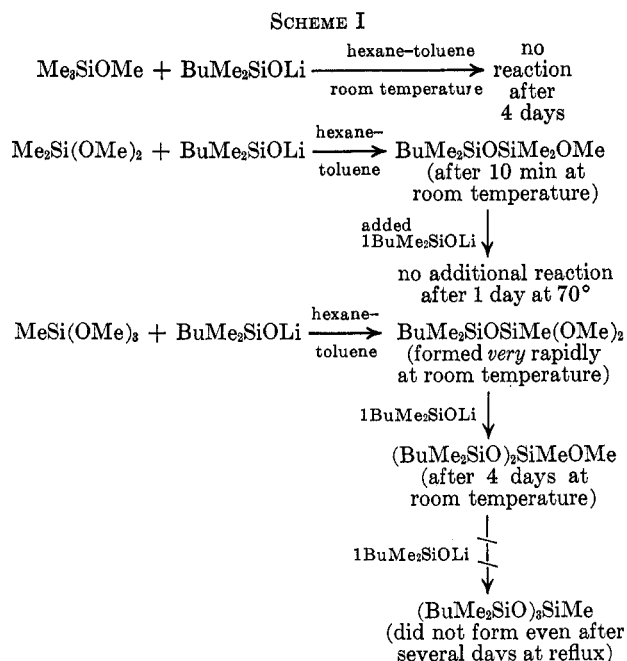


analogous competition reaction employing $\text{MeSi}(\text{OMe})_3$ produced similar results. Part of the BuLi reacted directly with the $\text{MeSi}(\text{OMe})_3$ to give $\text{BuMeSi}(\text{OMe})_2$ (and a little $\text{Bu}_2\text{MeSiOMe}$), but a substantial portion of the BuLi was consumed by the D_3 to yield BuD_1Li , which then coupled with the di- and trimethoxysilanes in the system to give $\text{BuMe}_2\text{SiOSiMe}(\text{OMe})_2$ (a major product) and $\text{BuMe}_2\text{SiOSiBuMeOMe}$.

The implications of the above competition reactions were tested by treating individual alkoxysilanes with $\text{BuMe}_2\text{SiOLi}$ (Scheme I).

It is interesting that lithium silanolates (and presumably the siloxanates) attack alkoxysilanes such as $\text{MeSi}(\text{OMe})_3$ and $\text{Me}_2\text{Si}(\text{OMe})_2$ employing conditions under which siloxanes as reactive as D_3 are unaffected.

Reactivity of D_3 Relative to Longer Chain Polydimethylsiloxanes.—Because of the increased reactivity of lithium siloxanates toward BuLi, it was anticipated that hydroxy end blocked polydimethylsiloxanes (HOD_xH) would be more reactive than the analogous trimethylsiloxy end blocked materials (MD_xM). Our initial attempts to demonstrate this were, however, rather confusing. Thus the hydroxy end blocked polymer (HOD_{270}H) was indeed much more reactive toward BuLi than was D_3 in hydrocarbon solution. However, a comparable MD_xM material was also much more reactive than D_3 when these two substrates were al-



lowed to compete for BuLi in hydrocarbon solution. Suspecting silanol impurities in the MD_xM , we treated it with $(\text{Me}_3\text{Si})_2\text{NH}$ in order to trimethylsiloxyate any such silanolic site. Subsequent competition with D_3 for BuLi did indeed then show a reactivity reversal, but *not because of our endblocking effort*; i.e., this latter competition for BuLi was run in the presence of ether, and we were eventually able to demonstrate a rather profound solvent effect on the relative reactivities of siloxane substrates toward BuLi. In hydrocarbon media, polydimethylsiloxanes of sufficient length react much faster with BuLi than does D_3 , regardless of the nature of the end-blocking moiety. In reaction media containing moderate amounts of donor solvents such as Et_2O , these same long-chain siloxanes react much more slowly with BuLi than does D_3 . One should *not* conclude that linear siloxanes are less reactive in ether media; quite the opposite is true, i.e., *all* of these siloxanes react faster in the presence of ether, but the reactivity of D_3 is increased to a much greater extent. These differences are possibly related to the ability of linear siloxanes to solvate intramolecularly the reactive sites in the absence of donor solvents; i.e., a siloxane moiety, a few units removed from the site of attack, may be able to assume a position in which its oxygen can somehow coordinate with the BuLi as it cleaves a neighboring siloxane bond. Such coordination would be exceedingly unlikely in a rather rigid cyclic structure such as D_3 . This advantage is removed when ether is added, and the greater reactivity inherent in the strained D_3 is then manifested.

One might still wonder why the hydroxy and Me_3SiO end blocked materials were of comparable reactivity. This is just another illustration of the relative unimportance of end group functionality at sufficiently high degree of polymerization (DP). The reaction of BuLi with neutral linear siloxanes, although relatively slow, becomes increasingly competitive with the siloxanolate reaction as the DP of the substrate is increased. When the chain is long enough, the nature of the end group becomes completely irrelevant to the rate of BuLi consumption. Below this limit, it also is to be

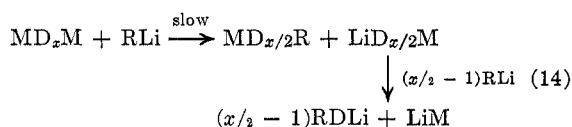
expected that a linear series, MD_xM , should consume BuLi at rates proportional to their molecular weights.

Confirmation is provided by the following tabulation (Table I), which shows the results of treating a series of D_3 - MD_xM solutions (hydrocarbon) with enough BuLi to react with exactly 50% of the available D units (the average DP for these fluids ranges from *ca.* 15 for the 10-cSt fluid to *ca.* 1300 for the 60,000-cSt fluid). It is evident that the relative reactivity of the MD_xM not only is increasing substantially with increasing molecular weight, but that it is also leveling out, as indeed it should when the chain length becomes so long that the ends are again irrelevant.

TABLE I

MD_xM , viscosity at 77° F, cSt	Unreacted D_3 , %
10	24
100	48
1,000	60
12,500	72
60,000	75

These results are consistent with a reaction scheme involving rupture of a siloxane bond in a relatively very slow initial step followed by a series of very fast subsequent alkylations (eq 14).



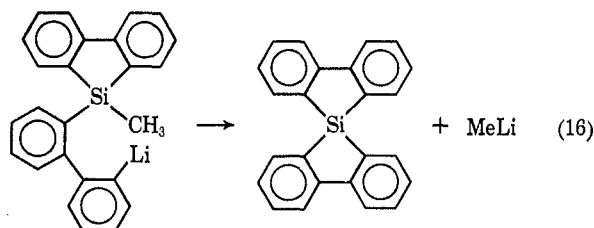
For purposes of illustration, we have arbitrarily ruptured the chain right in the middle. Now it is apparent that as x (the polymer DP) increases, the amount of RLi consumed per initial rupture should also increase. If this picture is correct, then this obviously ionic reaction exhibits kinetics reminiscent of free-radical olefin polymerizations in which the ordinarily independent concepts of *polymer* chain length and *kinetic* chain length become closely related.

Displacement of Methyl from Silicon by Organolithium Reagents.—As noted above, D_4 is much less reactive toward BuLi than is D_3 ; consequently, reflux conditions were generally employed to shorten the reaction time. It was observed that under these conditions the principal product of the BuLi- D_4 reaction (*i.e.*, BuD_1Li) was accompanied by small amounts of an additional product, which was eventually identified as $Bu_2MeSiOLi$ (characterized *via* hydrolysis as the silanol or *via* trapping with Me_3SiCl as $Bu_2MeSiOSiMe_3$). The reaction of D_4 with *n*-BuLi is sufficiently slow that the main product, $BuMe_2SiOLi$, is exposed for a longer time to BuLi, and under these conditions (reflux temperature *ca.* 70°) the following competitive reaction apparently occurs (eq 15).



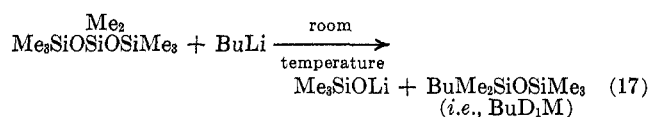
The suggested sequence of events was confirmed by treating D_3 with 6 equiv of BuLi, which rapidly results in a hydrocarbon solution containing $3BuMe_2SiOLi$ and $3BuLi$. Upon heating at reflux for 1 day, most of the silanolate was converted into $Bu_2MeSiOLi$.

The formation of MeLi was established *via* trapping with $PhMe_2SiCl$, which afforded the anticipated $PhMe_3Si$. In a similar run employing 9BuLi, 1-week reflux resulted in almost complete conversion into Bu_2SiOLi . Displacement of the methyl substituent from silicon by organometallic species has been observed previously only in certain cyclization reactions where entropy considerations were presumably very favorable, *e.g.*,⁶ eq 16. The driving force in the present

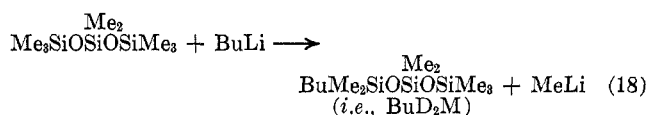


example is possibly the formation of the more stable methyl carbanion.⁷ Since similar results were obtained in ether, the insolubility of MeLi in hydrocarbon media is not a relevant factor.

In addition to the above methyl displacement from the anionic siloxanolate species, we also observed an interesting methyl displacement from a neutral siloxane substrate. Methyl displacement of this type has no precedent and can apparently be observed only under certain favorable conditions, as noted more fully below. Having determined that $Me_3SiOSiMe_3$ did not react to any detectable extent upon refluxing for several days with BuLi in a hydrocarbon solvent, it was of interest to examine the reactivity of $Me_3SiOSi(Me_2)OSiMe_3$ (MDM) toward BuLi. Although this substrate is much less susceptible than D_4 to siloxane cleavage by BuLi in hydrocarbon media, it does slowly undergo the following siloxane cleavage reaction (eq 17).



Under these conditions, however, *most* of the MDM substrate is consumed by the following novel alkyl exchange process (eq 18).

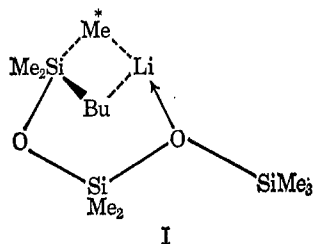


The product, BuD_2M , was unequivocally identified by spectral methods and independent synthesis; the presence of MeLi was confirmed by appropriate derivatization (*i.e.*, $PhMe_2SiCl \rightarrow PhMe_3Si$). Examination of the product mixture by vapor phase chromatography also revealed the gradual formation of a pair of dibutylated linear trimers believed to be $Bu_2MeSiOSiMe_2OSiMe_3$ and $BuMe_2SiOSiMe_2OSiMe_2Bu$; the structure of the latter member of this pair was confirmed by independent synthesis. These unusual exchange reactions are believed to be facilitated by anchimeric assistance

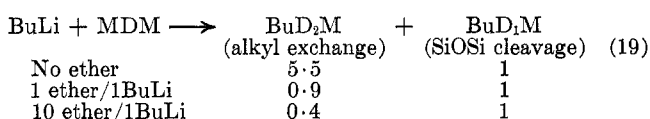
(6) H. Gilman and R. D. Gorsich, *J. Amer. Chem. Soc.*, **80**, 3243 (1958).

(7) R. M. Salinger and R. E. Dessy, *Tetrahedron Lett.*, 729 (1963).

of a strategically situated siloxane oxygen moiety as shown schematically (I). It was anticipated that

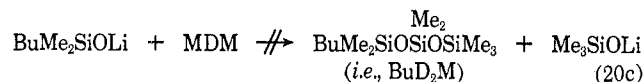


similar exchanges on the next higher homolog, MD₂M, would be precluded by a facile competing siloxane cleavage reaction, since in this case the leaving group (asterisked) in I could be the siloxy moiety, Me₃-SiO-. Although this type of siloxane cleavage did indeed occur, the alkyl exchange reaction *was* competitive, as evidenced by the presence of substantial amounts of BuD₃M in the reaction product. In the presence of increasing amounts of ether, siloxane cleavage of MDM predominated over alkyl exchange, as shown by the indicated relative yields of BuD₂M and BuD₁M (eq 19).



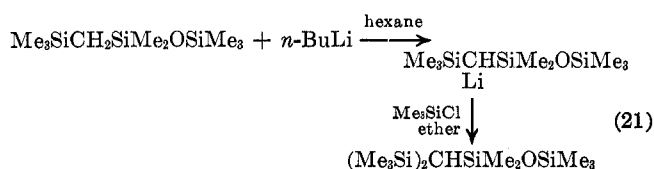
This trend is consistent with the above scheme involving anchimeric assistance; *i.e.*, the organolithium reagent would presumably be coordinated by ether in preference to MDM, and there would then be much less tendency for the organolithium to be held in such a way as to favor alkyl exchange over siloxane cleavage.

The possibility that BuD₂M might have arisen from some combination of siloxane cleavage, butylation of silanolate, and siloxane-silanolate redistribution was also considered; *i.e.*, the following sequence could conceivably have produced BuD₂M (eq 20a-20c).



This possibility was disposed of, however, by demonstrating in a separate experiment that BuMe₂SiOLi underwent no detectable reaction with MDM after 1 week at reflux.

From a consideration of the above schematic (I), it seemed not unreasonable to expect a similar facile alkyl exchange to occur on the closely related substrate Me₃SiCH₂SiMe₂OSiMe₃. However, much to our surprise, this compound underwent extremely facile metalation at the methylene site (eq 21).



Capping the metalated species with Me₃SiCl afforded the expected derivative, which showed the expected nmr proton ratio (SiCH₃, 33; Si₃CH, 1).

Experimental Section

General.—Reactions were performed under dry nitrogen atmosphere and the organometallic reagents were transferred *via* syringe techniques. Organolithium reagents were purchased from commercial sources and used as received; the butyllithium was 1.6 M in hexane, the *t*-BuLi was 1.24 M in pentane, and the MeLi was 1.67 M in ether. The siloxane substrates were commercially available and were shown to be reasonably pure by glpc prior to use.

The organolithium-siloxane reactions were followed by periodic removal of aliquots *via* syringe, which were then subjected to glpc analysis. Although these aliquots were sometimes examined directly, they were usually first treated with water (to convert ≡SiOLi into ≡SiOH) or ethereal R₃SiCl (to convert ≡SiOLi into ≡SiOSiR₃). The glpc analysis generally involved the use of internal standards. In the absence of suitable standards, the fractions in question were isolated by distillation or preparative glpc and characterized by appropriate elemental and spectral analysis. Not every observation described in the above discussion of our results has been detailed in the following examples, which have been selected mainly to illustrate the methods employed.

Reactions of BuLi with D₃. A. 1BuLi/1D₃.—Butyllithium (31 ml, 0.050 mol) in hexane was added to a toluene solution (50% by weight) of D₃ (11.1 g, 0.050 mol), resulting in an exothermic reaction. Analysis by glpc indicated that *ca.* 1/3 of the D₃ had been consumed. The reaction mixture was then heated at reflux for a period of 2 hr, whereupon glpc analysis revealed no additional consumption of D₃. Trimethylchlorosilane (6.3 ml, 0.050 mol) was then added along with a small quantity (15 ml) of ether. Subsequent experience showed that this was not enough ether to cause rapid reaction with Me₃SiCl. After refluxing for several hours, reaction of the Me₃SiCl was substantially complete. The reaction mixture was then filtered and distilled to yield 6.3 g (65% yield) of BuMe₂SiOSiMe₃; bp 80° (45 mm); nmr τ 9.95 (SiMe₃), 9.97 (SiMe₂), 9.3-9.7 (SiCH₂), 9.10 (CCH₃), and 8.45-8.85 (CCH₂). The proper intensity ratio of 9 (H_{Bu}):15 (H_{MeSi}) was observed.

Anal. Calcd for C₉H₂₄Si₂O: C, 52.9; H, 11.83; Si, 27.46. Found: C, 53.1; H, 11.85; Si, 26.51.

B. 3BuLi/1D₃.—Butyllithium (93 ml, 0.15 mol) in hexane was added (exothermic) to a toluene solution (50% by weight) of D₃ (11.1 g, 0.05 mol); immediately subsequent glpc analysis indicated complete consumption of D₃. When the reaction mixture cooled to room temperature, 50 ml of water was added; separation of the resulting organic layer followed by distillation afforded 16.2 g (82% yield) of BuMe₂SiOH, bp 85° (50 mm). The presence of silanol functionality was confirmed by a strong infrared absorption at 3 μ . The nmr spectrum was also consistent with the assigned structure, having absorptions at τ 4.89 (SiOH), 8.6-9.4 (SiBu), and 9.95-9.97 (SiMe), with a proton ratio of 0.9 (H_{OH}):8.9 (H_{Bu}):6 (H_{Me}) (theory 1:9:6). The compound was not obtained analytically pure.

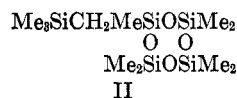
1BuLi/1D₃/1Me₃SiCl.—The addition of butyllithium (0.050 mol) to a solution of D₃ (0.050 mol) and Me₃SiCl (0.050 mol) in toluene (13 ml) produced an exotherm; glpc analysis of a hydrolyzed aliquot showed that *ca.* 50% of the D₃ had been consumed, a large peak attributable to BuMe₃SiOH (*no* BuMe₂SiOSiMe₃, since BuD₁Li does not couple readily with Me₃SiCl in the absence of ether), and a moderate-sized peak attributable to BuD₃SiMe₃. A small amount of ether (25 ml) was then added and the reaction mixture was refluxed for several hours, during which time periodic glpc analysis revealed the appearance and gradual increase of BuMe₂SiOSiMe₃; no further change in the D₃ or BuD₃SiMe₃ peaks was noted. The glpc peak area ratios for the pertinent species in the final reaction mixture were *ca.* 8D₃:7BuD₃SiMe₃:1BuD₂Me₃:4BuD₂SiMe₃. Distillation afforded *ca.* a 20% yield of BuD₃SiMe₃; bp 147° (50 mm); nmr τ 8.65-9.91 (Si-*n*-Bu) and 9.93-9.95 (SiMe), with a proton ratio of 9.3 (H_{Bu}):267 (H_{Me}) (theory 9:27).

Anal. Calcd for C₁₃H₃₆Si₄O₃: C, 44.3; H, 10.31; S, 31.82; mol wt, 352. Found: C, 44.7; H, 10.26; Si, 31.25; mol wt, 337 (vapor phase osmometry).

Very similar results were obtained when ether was present during the addition of the BuLi to the D₃-MeSiCl solution. It was also observed that by increasing the proportion of Me₃SiCl, a larger fraction of the BuD₃Li was converted into BuD₂SiMe₃, as evidenced by glpc analysis. In all cases, the amount of BuD₂SiMe₃ formed was much smaller than that of BuD₃SiMe₃. This suggests that BuD₂Li may be much less reactive than BuD₃Li toward Me₃SiCl. The addition of BuLi to D₄-Me₃SiCl solutions containing ether yielded similar results in that the BuD₁SiMe₃ was the major product. However, the BuD₂₋₄SiMe₃ peaks, while definitely of minor proportions, differed somewhat from the above D₃ reaction in that they were all of approximately the same size; *i.e.*, the BuD₃SiMe to BuD₂SiMe₃ glpc peak area ratio was *ca.* 1 rather than *ca.* 4 as in the above example. This may suggest that BuD₄Li undergoes preferential attack on the penultimate D site. Alternatively, this variation in product ratios may merely be an artifact of variations in reaction procedure; *i.e.*, the effective instantaneous Me₃SiCl to BuLi ratio presumably will determine the extent to which the various intermediate siloxanates are trapped or cleaved.

Reaction of Alkylolithium Compounds with D₄. A. D₄ + *n*-BuLi.—A solution of *n*-BuLi in hexane (31 ml, 0.050 mol) was added dropwise to a solution of D₄ (14.8 g, 0.050 mol) in toluene (10 ml). A mildly exothermic reaction occurred which consumed 25% of the original D₄ within 15 min. After 2 hr the mixture was treated with Me₃SiCl (0.060 mol) in ether (25 ml) to give BuMe₂-SiOSiMe₃, bp 81° (50 mm), yield 8.85 g (87%).

B. D₄ + *t*-BuLi.—A solution of *t*-BuLi (0.050 mol) in pentane was added to a solution of D₄ (14.8 g, 0.050 mol) in toluene. After 24 hr at ambient temperature, the reaction mixture was treated with a solution of Me₃SiCl (0.060 mol) in ether (25 ml). After the vigorous reaction had subsided, the mixture was found (by glpc) to contain three major products, two of which were identified as *t*-BuMe₂SiOSiMe₃ and *t*-Bu(Me₂SiO)₂SiMe₃ by glpc (using internal standards) and by their mass spectra. The mixture was filtered and the filtrate was fractionally distilled to obtain a portion considerably enriched in the unidentified material, which was then isolated by preparative glpc (*n*²⁰D 1.4270) and identified as II on the basis of the following analytical data.



(A) The mass spectrum gave a molecular weight of 368 (theory 368), a loss of a Me group at *m/e* 353, and a loss of Me₂Si from the *m/e* 353 peak at *m/e* 265.

(B) The infrared spectrum showed absorptions at 835 (Me₃Si) and 1355 cm⁻¹ (-SiCH₂-).

(C) The nmr spectrum showed absorptions at τ 9.92-9.97 (SiMe) and 10.19 (SiCH₂) with a proton ratio of 29.8 (H_{SiMe}):2.2 (H_{SiCH₂}) (theory 30:2).

When a similar reaction mixture was treated with deuterium oxide instead of Me₃SiCl, the recovered (Me₂SiO)₄ was shown by mass spectroscopy to contain appreciable amounts of the expected monodeuterio derivative.

Alkyl Exchange Reactions. A. Silanolate Substrate.—Butyllithium (0.200 mol) was added to D₃ (7.4 g, 0.033 mol) dissolved in an equal weight of toluene. The reaction mixture was heated at reflux after the initial exothermic reaction subsided. After 2 hr the formation of a white precipitate (presumably MeLi) was noted. Small samples of the reaction mixture were taken at intervals and hydrolyzed by the addition of a little water; glpc

analysis of these hydrolyzed aliquots showed the presence of a peak assigned to Bu₂MeSiOH which grew at the expense of the BuMe₂SiOH peak. After the mixture had been refluxed overnight, glpc analysis of a hydrolyzed aliquot showed the presence of mainly Bu₂MeSiOH and minor amounts of BuMe₂SiOH and Bu₃SiOH. The assignment of these two new peaks was confirmed by internal standards, employing authentic Bu₂MeSiOH and Bu₃SiOH prepared by the hydrolysis of the monochlorosilanes obtained from the reaction of BuLi with MeSiCl₃ and SiCl₄, respectively. To confirm the presence of MeLi in the above reaction product, PhMe₂SiCl (0.200 mol) and ether (50 ml) were added. The reaction mixture was then stirred for 30 min, washed with water, and distilled to afford PhSiMe₃ (63% yield), which was identified by glpc analysis using an authentic sample as internal standard. The use of larger amounts of BuLi and longer reflux times resulted in the gradual consumption of Bu₂MeSiOLi and the formation of Bu₃SiOLi.

B. A Neutral Siloxane Substrate, MDM.—A mixture of 11.8 g (0.050 mol) of MDM and 31 ml (0.050 mol) of *n*-BuLi in hexane was stirred for 48 hr at ambient temperature. The mixture, which contained some precipitated solids, was treated with a solution of PhMe₂SiCl (9.4 g, 0.055 mol) in ether (15 ml). When the exothermic reaction was complete, the following major components were identified in the reaction mixture by tandem glpc-mass spectroscopic analysis: MDM, *n*-BuMe₂SiOSiMe₃, PhSiMe₃, *n*-Bu(Me₂SiO)₂SiMe₃, PhMe₂SiOSiMe₃, and *n*-Bu(Me₂SiO)₂-*n*-Bu.

Metalation of Me₃SiOSiMe₃ by *t*-BuLi.—A solution of *t*-BuLi in pentane (175 ml, 0.2 mol) was added to Me₃SiOSiMe₃ (100.6 g, 0.6 mol). The solution was stirred for 96 hr and then derivatized with Me₃SiCl (21.7 g, 0.2 mol) in the presence of ether (100 ml), filtered, and distilled to give Me₃SiCH₂Me₂SiOSiMe₃: yield 35 g (85.5%); bp 72-72.5° (15 mm); *n*²⁰D 1.4110; nmr τ 9.93-9.97 (-SiMe) and 10.2 (SiCH₂) with a proton ratio of 24.3 (H_{SiMe}):1.7 (H_{SiCH₂}) (theory 24.0:2.0).

Anal. Calcd for C₉H₂₈Si₃O: C, 46.2; H, 11.1; Si, 35.9; mol wt, 234. Found: C, 46.2; H, 11.04; Si, 36.0; mol wt, 234.

A similar reaction mixture was derivatized with ethereal (100 ml) HMe₂SiCl (189 g, 0.2 mol) to give HMe₂SiCH₂Me₂SiOSiMe₃: yield 29.2 g (66%); bp 85-86° (55 mm); *n*²⁰D 1.4215; nmr τ 6.03 (SiH), 9.90-9.94 (SiMe), and 10.16 (doublet, J_{CH₂-SiH} = 3.5 cps, SiCH₂) with a proton ratio of 0.9 (H_{SiH}):21.3 (H_{SiMe}):1.8 (H_{SiCH₂}) (theory 1:21:2).

Anal. Calcd for C₈H₂₄Si₃O: C, 43.6; H, 10.8; mol wt, 220. Found: C, 44.0; H, 10.8; mol wt, 220 (mass spectrum).

***n*-BuLi Metalation of Me₃SiCH₂Me₂SiOSiMe₃.**—A solution of *n*-BuLi in hexane (32 ml, 0.05 mol) was added to Me₃SiCH₂Me₂SiOSiMe₃ (11.7 g, 0.05 mol). The solution was refluxed for 72 hr before Me₃SiCl (5.4 g, 0.05 mol) and THF (25 ml) were added to give a mixture of products containing one major component (53% by glpc) which was isolated by preparative glpc and identified as (Me₃Si)₂CHMe₂SiOSiMe₃: nmr τ 9.84-9.97 (SiMe) and 10.63 (SiCH) with a proton ratio of 33 (H_{SiMe}):1 (H_{SiCH}) (theory 33:1).

Anal. Calcd for C₁₂H₃₄Si₄O: mol wt, 306. Found: mol wt, 306 (mass spectrum).

Registry No.—BuMe₂SiOSiMe₃, 23667-12-1; BuMe₂SiOH, 23667-13-2; Me₃SiCH₂Me₂SiOSiMe₃Me₂SiOSiMe₃, 23667-14-3; Me₃SiCH₂Me₂SiOSiMe₃, 6231-63-6; HMe₂SiCH₂Me₂SiOSiMe₃, 23667-16-5; (Me₃Si)₂CHMe₂SiOSiMe₃, 23754-35-0.