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NEW ANIONIC REARRANGEMENTS
XIII*. REACTIONS OF tert-BUTYLLITHIUM WITH ORGANOSILANES**

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SUMMARY

tert-Butyllithium/*N,N,N',N'*-tetramethylethylenediamine (TMEDA) complex reacts with trimethylchloro- and trimethylbromosilanes to give mixtures of the coupling product tert-butyltrimethylsilane (I) and metalation products 1-chloro-1,1,3,3,3-pentamethyldisilmethylene (II) and 1-bromo-1,1,3,3,3-pentamethyldisilmethylene, respectively. Trimethylfluorosilane and tert-butyllithium/TMEDA give only (I). Compound (I) is also the major product when methoxytrimethylsilane is treated with tert-butyllithium/TMEDA, but ethoxytrimethylsilane gives predominantly the metalation product 1-ethoxy-1,1,3,3,3-pentamethyldisilmethylene (IV). Acetoxytrimethylsilane and tert-butyllithium/TMEDA give, ultimately, 2-(trimethylsiloxy)-3,3-dimethyl-1-butene (VII). Hexamethyldisiloxane is metalated by tert-butyllithium in pentane to give $LiCH_2SiMe_2OSiMe_3$, which in the presence of TMEDA rearranges to give $LiOSiMe_2CH_2SiMe_3$. The difunctional silanes, dimethyldichlorosilane and dimethyldiethoxysilane, react with tert-butyllithium/TMEDA complex to give only the coupling products tert-butyldimethylchlorosilane and tert-butyldimethylethoxysilane (VI).

INTRODUCTION

It has been well established that silicon has a strong acidifying effect on α-protons. Many silylmethyl[1-7] and disilmethylene***[,6,8] compounds undergo metalation by n- or tert-butyllithium. In all these examples the substituents on silicon are not readily cleaved by organolithium reagents. Therefore it was very surprising to find that the methyl group of certain methylsilyl compounds can be metalated by tert-butyllithium even when the silicon atom bears substituents that are highly reactive toward nucleophilic displacement by organolithium reagents.

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* For Part XII see ref. 10.

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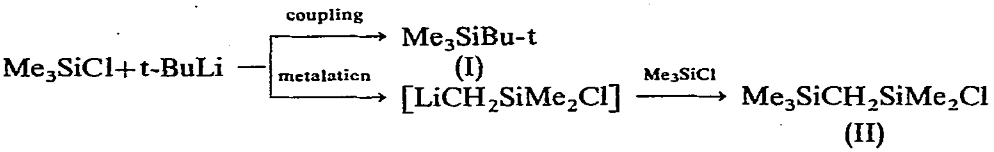
*** Disilmethylene = $\overset{1}{H_3Si}-\overset{2}{CH_2}-\overset{3}{SiH_3}$.

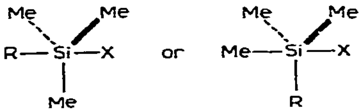
RESULT AND DISCUSSION

Two competing reactions, metalation and coupling, occur when trimethylchlorosilane is treated with tert-butyllithium in the presence of either *N,N,N',N'*-tetramethylethylenediamine (TMEDA) at room temp. or tetrahydrofuran (THF) at −78° :



The intermediate $LiCH_2SiMe_2Cl$, being a primary organolithium compound, readily couples with trimethylchlorosilane to give (II). A substantial amount of 1-tert-butyl-1,1,3,3,3-pentamethyldisilmethylene (III), the coupling product of (II) with tert-butyllithium, is also formed.

Steric hindrance to coupling appears to be necessary for lithiation of trimethylchlorosilane because n-butyllithium under identical conditions gives exclusively the coupling product n-butyltrimethylsilane. Steric hindrance would be expected to decrease the stability of the transition state for the coupling reaction,



but would not be expected to have a large effect on the transition state of the metalation reaction, $LiR\text{-}H\text{-}CH_2SiMe_2Cl$.

Replacing a methyl group with a more bulky alkyl group, or increasing the size of the X substituent, but keeping the nature of the Si–X bond the same, should favor the metalation reaction also. Reactions of alkoxytrimethylsilanes with tert-butyllithium show that increasing the bulk of the alkoxy group does increase the amount of metalation product and decrease the yield of coupling product, *vide infra*. However, replacing a methyl group with a larger alkyl group gives unexpected and unexplained results. Ethyldimethylchlorosilane and tert-butyllithium give a complex mixture of products, some of which may arise from metalation of the methylene protons in the ethyl group.

The highly electronegative chlorine atom greatly increases the acidity of the methyl groups on silicon. Trimethylchlorosilane is lithiated readily by tert-butyllithium in THF at −78° in a few hours, but tetramethylsilane and hexamethyldisiloxane remain unchanged under the same conditions for 24 h. In the presence of TMEDA at room temperature trimethylchlorosilane is lithiated immediately while tetramethylsilane and hexamethyldisiloxane require several days[2].

Other electronegative substituents on silicon lead to variable and often unexpected results upon treatment with tert-butyllithium/TMEDA complex. Trimethylbromosilane, like trimethylchlorosilane, gives both metalation and coupling products:

$$\begin{tikzcd} & \underset{(I)}{Me_3SiBu\text{-}t} & \\ Me_3SiBr+t\text{-}BuLi \arrow[ur, "coupling"] \arrow[dr, "metalation"'] & & \\ & {[LiCH_2SiMe_2Br]} \arrow[r, "Me_3SiBr"] & Me_3SiCH_2SiMe_2Br \end{tikzcd}$$

As with trimethylchlorosilane, (III) also is formed in this reaction.

However, trimethylfluorosilane gives *exclusively* the coupling product tert-butyltrimethylsilane. Either fluorine, even though it is more electronegative than chlorine or bromine, does not increase the acidity of the methyl groups appreciably or the difference in mechanism of the reaction of alkyllithium compounds with fluorosilane favors the coupling reaction*. The smaller size of the fluorine atom may also relieve steric strain in the transition state of the coupling reaction.

The reaction of tert-butyllithium with methoxytrimethylsilane is extremely interesting because three different reaction pathways are possible: (*a*) coupling; (*b*) metalation of a methyl group on silicon; (*c*) metalation of the methyl group on oxygen;

$$\begin{tikzcd} & \underset{(I)}{t\text{-}BuSiMe_3} & & \\ Me_3SiOMe+t\text{-}BuLi \arrow[ur, "(a)"] \arrow[r, "(b)"] \arrow[dr, "(c)"', "/" marking] & {[LiCH_2Si(OMe)Me_2]} \arrow[r, "Me_3SiOMe"] & \underset{(V)}{Me_3SiCH_2Si(OMe)Me_2} & \\ & LiCH_2OSiMe_3 \arrow[r] & LiOCH_2SiMe_3^{**} & \end{tikzcd}$$

Table I shows the major product to be (I) arising from path (*a*), a minor product being 1-methoxy-1,1,3,3,3-pentamethyldisilmethylene (V), from path (*b*). A sample of the reaction mixture was quenched with trimethylchlorosilane to convert any lithium (trimethylsilyl)methoxide, that may have been formed, to (trimethylsilyl)(trimethylsiloxy)methane (XIV):

$$Me_3SiOCH_2Li \rightarrow Me_3SiCH_2OLi \xrightarrow{Me_3SiCl} \underset{(XIV)}{Me_3SiOCH_2SiMe_3}$$

No trace of (XIV) could be detected by gas chromatography. The methyl groups on silicon appear to be more acidic than the methyl group on oxygen† (it is possible that a small amount of $LiCH_2OSiMe_3$ is formed but reacts by another pathway to give unexpected products). With ethoxytrimethylsilane the pathways are completely reversed. The metalation product 1-ethoxy-1,1,3,3,3-pentamethyldisilmethylene (IV) now is the major product and (I) the minor product††. The larger bulk of the ethoxy

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* Chlorosilanes react with alkyllithium compounds with inversion of configuration about silicon while fluorosilanes react with retention of configuration[9].

** Compounds of the type $\mathrm{Li{-}\underset{|}{\overset{|}{C}}{-}O{-}\underset{|}{\overset{|}{Si}}{-}}$ undergo intramolecular rearrangements to give $\mathrm{LiO{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{Si}}{-}}$[10].

† Nometalation of protons α to oxygen was detected when $PhCH_2OSiMe_3$ and $Ph_2CHOSiMe_3$ were reacted with tert-butyllithium/TMEDA[11].

†† Various (aryloxy)trimethylsilanes react with tert-butyllithium to give products arising from metalation and coupling reactions, but relative amounts were not reported[11].

(*continued on p.* 30)

TABLE 1

CHARACTERIZATION OF PRODUCTS

Compound	B.p. [°C (mm)]	n_D^t	Infrared (cm^{-1})	NMR[a]	Analysis (%) Calcd.	Analysis (%) Found
Me_3SiCMe_3 (I)	100–110 lit.[19] 103	m.p. 75° lit.[19] m.p. 75–77°	1250 (MeSi)	9.12 (s, 9, Me_3C) 10.05 (s, 9, Me_3Si)		
$Me_3SiCH_2SiMe_2Cl$ (II)	150–160 lit.[20] 153	n_D^{25} 1.4296 lit.[20] n_D^{20} 1.4322	1250 (MeSi) 1050 (CH_2Si_2)	9.67 (s, 6, Me_2Si) 10.0 (2s, 11, Me_3Si and CH_2Si_2)		
$Me_3SiCH_2SiMe_2CMe_3$ (III)	85 (30)	n_D^{25} 1.4380	1250 (MeSi) 1050 (CH_2Si_2)	9.17 (s, 9, Me_3C) 9.97 (s, 9, Me_3Si) 10.02 (s, 6, Me_2Si) 10.32 (s, 2, CH_2Si_2)	C 59.3 H 12.9 Si 27.8	59.6 13.0 27.5
$Me_3SiCH_2SiMe_2OEt$ (IV)	75–85 (55)	n_D^{23} 1.4155	1250 (MeSi) 1050 (CH_2Si_2)	6.44 (q, 2, CH_2) 8.90 (t, 3, CH_3) 9.97 (s, 6, Me_2Si) 10.0 (s, 9, Me_3Si) 10.22 (s, 2, CH_2Si_2)	C 49.4 H 11.6 Si 29.5	49.5 11.5 29.3
$Me_3SiCH_2SiMe_2OMe$ (V)	145–155 lit.[21] 148–152	n_D^{25} 1.4125 lit.[21] n_D^{25} 1.4120	1250 (MeSi) 1050 (CH_2Si_2)	6.66 (s, 3, MeO) 9.96 (s, 6, Me_2Si) 9.98 (s, 9, Me_3Si) 10.21 (s, 2, CH_2Si_2)		
$Me_3CSi(OEt)Me_2$ (VI)	60–70 (65)	n_D^{25} 1.4025 lit.[22] n_D^{22} 1.4063	1250 (MeSi)	6.35 (q, 2, CH_2) 8.87 (t, 3, CH_3)		

				9.13 (s, 9, Me_3C) 9.98 (s, 6, Me_2Si)		
$Me_3C(Me_3SiO)C{=}CH_2$ (VII)	135–145 lit.[23] 140–142	n_D^{24} 1.4077 lit.[23] n_D^{27} 1.4061	1630 (C=C) 1250 (MeSi)	6.00 (d, 1, =CH) 6.18 (d, 1, =CH) 9.00 (s, 9, Me_3C) 9.82 (s, 9, Me_3Si)		
$Me_3SiCH_2SiMe_2OH$ (VIII)	90–100 (60) lit.[24] 50–52 (5)	n_D^{22} 1.4314 lit.[24] n_D^{20} 1.4318	2300 (OH) 1250 (MeSi)	6 (s, 1, OH) 9.88 (s, 6, Me_2Si) 9.97 (s, 9, Me_3Si) 10.15 (s, 2, CH_2Si_2)		
$Me_3SiOSiMe_2CH_2SiMe_2H$ (IX)	55–60 (15) lit.[5] 85–86 (55)	n_D^{23} 1.4106 lit.[5] n_D^{25} 1.4215	2110 (HSi) 1250 (MeSi)	6.0 (c, 1, HSi) 9.9 (c, 21, MeSi) 10.13 (d, 2, CH_2Si_2)		
$Me_3SiCH_2SiMe_2OSiMe_2H$ (X)	55–60 (15)	n_D^{24} 1.4111	2110 (HSi) 1250 (MeSi)	5.30 (sp, 1, HSi) 9.85 (d, 6, Me_2Si) 9.92 (s, 6, Me_2Si) 10.18 (s, 2, CH_2Si_2)	C 43.5 H 11.0 Si 38.2	43.7 11.0 38.0
$(Me_3Si)_2CH_2$ (XI)	135–140 lit.[25] 132	n_D^{25} 1.4155 lit.[25] n_D^{20} 1.4170	1250 (MeSi) 1050 (CH_2Si_2)			
$Me_3SiCH_2SiMe_2Bu$-n[b] (XII)		n_D^{24} 1.4325	1250 (MeSi) 1050 (CH_2Si_2)	8.3 to 9.7 (c, 9, n-Bu) 9.98 (s, 9, Me_3Si) 10.0 (s, 6, Me_2Si) 10.28 (s, 2, CH_2Si_2)		
$Me_3SiCH_2Si(NEt_2)Me_2$ (XIII)		n_D^{24} 1.4383	1250 (MeSi) 1050 (CH_2Si_2)	7.23 (q, 4, CH_2N) 9.03 (t, 6, CH_3) 9.97 (s, 6, Me_2Si) 10.00 (s, 9, Me_3Si) 10.20 (s, 2, CH_2Si_2)	C 55.2 H 12.5 N 6.4 Si 25.7	55.3 12.3 6.4 25.6

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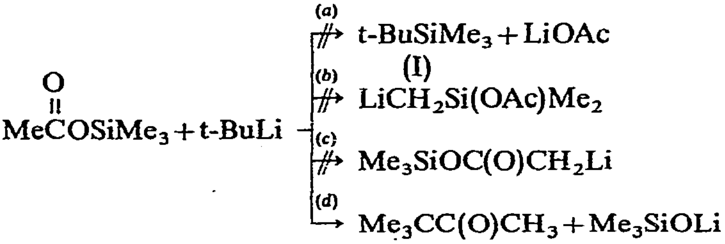
[a] s=singlet, d=doublet, t=triplet, q=quartet, sp=septet and c=complex. Chemical shifts in ppm; TMS=10. [b] NMR identical to that reported in lit.[2].

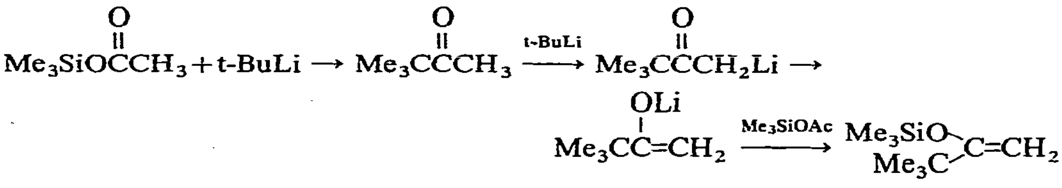
group probably decreases the rate of the coupling reaction more than it decreases the rate of the metalation reaction.

Several pathways are also possible for the reaction of tert-butyllithium with acetoxytrimethylsilane: (*a*) coupling; (*b*) metalation of a methyl group on silicon; (*c*) metalation of the methyl group adjacent to the carbonyl group; (*d*) nucleophillic attack at the carbonyl carbon;



$$\mathrm{Me\overset{O}{\overset{\|}{C}}OSiMe_3+t\text{-}BuLi}\begin{cases}\overset{(a)}{\nrightarrow}\ \mathrm{t\text{-}BuSiMe_3+LiOAc} \\ \qquad\mathrm{(I)} \\ \overset{(b)}{\nrightarrow}\ \mathrm{LiCH_2Si(OAc)Me_2} \\ \overset{(c)}{\nrightarrow}\ \mathrm{Me_3SiOC(O)CH_2Li} \\ \overset{(d)}{\rightarrow}\ \mathrm{Me_3CC(O)CH_3+Me_3SiOLi}\end{cases}$$

The only product isolated is 2-(trimethylsiloxy)-3,3-dimethyl-1-butene (VII) which arises from nucleophilic attack at the carbonyl carbon [pathway (*d*)] followed by metalation of the resulting pinacolone by unreacted tert-butyllithium:



(VII)

$$\mathrm{Me_3SiO\overset{O}{\overset{\|}{C}}CH_3+t\text{-}BuLi} \rightarrow \mathrm{Me_3C\overset{O}{\overset{\|}{C}}CH_3} \xrightarrow{\mathrm{t\text{-}BuLi}} \mathrm{Me_3C\overset{O}{\overset{\|}{C}}CH_2Li} \rightarrow$$

$$\mathrm{Me_3C\overset{OLi}{\overset{|}{C}}{=}CH_2} \xrightarrow{\mathrm{Me_3SiOAc}} \mathrm{\begin{matrix}Me_3SiO\\Me_3C\end{matrix}\!\!>\!C{=}CH_2}\quad\mathrm{(VII)}$$

(VII) is also formed from metallation of pinacolone by tert-butyllithium in the presence of trimethylchlorosilane.

Hexamethyldisiloxane with tert-butyllithium in the presence of TMEDA gives 1-hydroxy-1,1,3,3,3-pentamethyldisilmethylene (VIII), after an aqueous work-up. This product must be formed by metalation of hexamethyldisiloxane followed by rearrangement of the resulting carbanion to a more stable silanolate anion:

$$\mathrm{(Me_3Si)_2O+t\text{-}BuLi} \xrightarrow{\mathrm{TMEDA}} \mathrm{[LiCH_2SiMe_2OSiMe_3]} \rightarrow$$

$$\mathrm{LiOSiMe_2CH_2SiMe_3} \xrightarrow{\mathrm{H_2O}} \mathrm{HOSiMe_2CH_2SiMe_3}$$

$$\mathrm{(VIII)}$$

Recently other workers[5] have metalated hexamethyldisloxane with tert-butyllithium in pentane and found that the product $\mathrm{LiCH_2SiMe_2OSiMe_3}$ is stable, quenching with dimethylchlorosilane gives 1-trimethylsiloxy-1,1,3,3-tetramethyldisilmethylene (IX). We have confirmed their results that $\mathrm{LiCH_2SiMe_2OSiMe_3}$ is stable in pentane. However, when one equivalent of TMEDA is added, $\mathrm{LiCH_2SiMe_2OSiMe_3}$ slowly rearranges to $\mathrm{LiOSiMe_2CH_2SiMe_3}$*:

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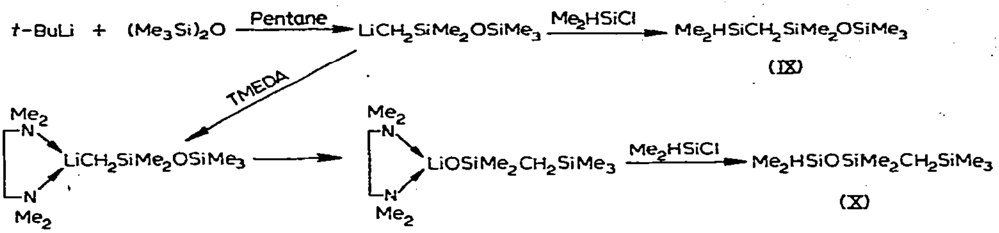
* Brook and his coworkers[12] have studied the rearrangement of silicon from carbon to oxygen. Other rearrangements of silicon from oxygen to carbon will be published soon[10].



(IX) and (X) are readily differentiated by NMR as noted previously[5], the methylene protons of (IX) being a doublet and those of (X) being a singlet. 1-(Trimethylsiloxy)-1,1,3,3,3-pentamethyldisilmethylene, which would be formed from reaction of $LiCH_2SiMe_2OSiMe_3$ with excess hexamethyldisiloxane could not be detected by GLC:

$$LiCH_2SiMe_2OSiMe_3+(Me_3Si)_2O \not\rightarrow Me_3SiCH_2SiMe_2OSiMe_3+LiOSiMe_3$$

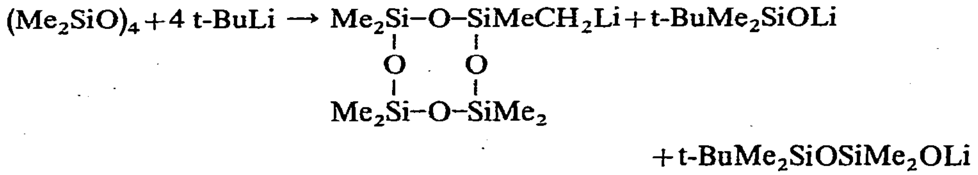
The methyl group of aminotrimethylsilanes can be lithiated without cleaving the amino group from silicon. (Diethylamino)trimethylsilane and n-butyllithium/TMEDA complex give, after quenching with trimethylchlorosilane (XIII).

$$BuLi+Me_3SiNEt_2 \xrightarrow{TMEDA} \xrightarrow{Me_3SiCl} Me_3SiBu+\underset{(XIII)}{Me_3SiCH_2SiMe_2NEt_2}+\underset{(XII)}{Me_3SiCH_2SiMe_2Bu}$$

Compound (XII) may have been formed by cleavage of the silicon–nitrogen bond in (XIII) by n-butyllithium, (XII) could also be formed from the reaction of n-butyllithium with $Me_3SiCH_2SiMe_2Cl$, which would be formed by chlorine–dimethylamino group exchange between (XIII) and trimethylchlorosilane.

Metalation of methyl groups on a silicon that contains more than one substituent susceptible to attack by organolithium reagents has been limited to one example so far. Octamethylcyclotetrasiloxane is readily cleaved by n-butyllithium but with tert-butyllithium metalation of a methyl group on silicon competes with the cleavage reaction[5]:

$$(Me_2SiO)_4+4\ BuLi \rightarrow 4\ BuMe_2SiOLi$$



$$(Me_2SiO)_4+4\ t\text{-}BuLi \rightarrow \begin{array}{c}Me_2Si\text{–}O\text{–}SiMeCH_2Li\\ |\qquad\quad |\\ O\qquad\quad O\\ |\qquad\quad |\\ Me_2Si\text{–}O\text{–}SiMe_2\end{array} + t\text{-}BuMe_2SiOLi + t\text{-}BuMe_2SiOSiMe_2OLi$$

Dimethyldichlorosilane and dimethyldiethoxysilane react with tert-butyllithium to give only the coupling products tert-butyldimethylchlorosilane[13] and tert-butyldimethylethoxysilane (VI), respectively. No significant amounts of products, which could have been formed from metalation of a methyl group on silicon, were found in either reaction.

EXPERIMENTAL

All reactions involving organolithium compounds were run in an atmosphere of anhydrous nitrogen. Analyses were performed by Galbraith Laboratories. Inc., Knoxville, Tenn. ^{1}H NMR spectra were recorded on a Varian A-60 spectrometer. Gas chromatographic (GLC) separations were made on a Varian Aerograph A-700 chromatograph using columns packed with either SE-30 or QF-1 silicone on Chromosorb W. Infrared spectra were recorded on Perkin–Elmer Model 237 and Model 457 spectrometers.

Trimethylchlorosilane, hexamethyldisiloxane, hexamethyldisilazane, ethoxytrimethylsilane, and diethoxydimethylsilane were obtained from Dow Corning Corp. The exthoxysilanes were distilled from sodium prior to use. Tetramethylsilane, THF, and TMEDA were purchased from Aldrich Chemical Co. tert- and n-butyllithium were purchased from Foote Mineral Co. Dimethylchlorosilane was obtained from Peninsular Chemresearch.

Trimethylfluorosilane was prepared from hexamethyldisiloxane, ammonium fluoride and sulfuric acid, b.p. 16–18° (lit.[14] 16°).

Acetoxytrimethylsilane, b.p. 101–102°, n_D^{22} 1.3870 (lit.[15] b.p. 102–103°, n_D^{25} 1.3810), was prepared from trimethylchlorosilane and anhydrous sodium acetate.

(Diethylamino)trimethylsilane, b.p. 124–128° (lit.[16] b.p. 127°), was prepared from diethylamine and trimethylchlorosilane.

Methoxytrimethylsilane was prepared from methanol and hexamethyldisilazane and distilled from sodium, b.p. 55–56° (lit.[16] b.p. 55°).

(Trimethylsilyl)methanol was prepared by the method of Seyferth[17].

(Trimethylsilyl)(trimethylsiloxy)methane, n_D^{25} 1.3975 (lit.[18] n_D^{25} 1.3971), was prepared by treating (trimethylsilyl)methanol with trimethylchlorosilane in the presence of triethylamine.

1-(Trimethylsiloxy)-1,1,3,3,3-pentamethyldisilmethylene was prepared by the procedure of Frye *et al.*[5].

Reactions of tert-butyllithium with organosilanes

A. Trimethylchlorosilane. A solution of 40 ml of 1.2 *M* tert-butyllithium was added dropwise to 25.5 ml (0.2 mole) of trimethylchlorosilane and 1.6 ml (0.012 mole) of TMEDA. Reaction was very vigorous and was cooled with an ice-water bath. A negative Gilman Test was obtained immediately after addition of tert-butyllithium. Lithium chloride was filtered under nitrogen. Distillation of the filtrate gave 1.3 g (20%) of tert-butyltrimethylsilane (I), 1.9 g (20%) of 1-chloro-1,1,3,3,3-pentamethyldisilmethylene (II), and 2.0 g (40%) of 1-tert-butyl-1,1,3,3,3-pentamethyldisilmethylene (III). Compounds (I), (II), and (III) were further purified by preparative GLC and characterized (Table 1).

A solution of 100 ml of 1.2 *M* tert-butyllithium was added to 45 ml (0.36 mole) of trimethylchlorosilane in 100 ml of THF at −78°. Mixture was stirred at −78° for 2 h, warmed to room temperature and worked-up as described above to give 3.8 g

(25%) of (I), 7.3 g (33%) of (II) and 1.5 g (10%) of (III).

B. Trimethylbromosilane. Using the same experimental technique as reported for the first experiment with trimethylchlorosilane, 6.2 ml of 1.2 *M* tert-butyllithium in pentane was added to 2 ml (0.015 mole) of trimethylbromosilane and 0.25 ml (0.002 mole) of TMEDA. GLC analysis showed only three products (area %), (I) (50), 1-bromo-1,1,3,3,3-pentamethyldisilmethylene (25), and (III) (25). (I) and (III) were identified by comparison of GLC retention times with those of authentic samples. The bromodisilmethylene was converted to 1-n-butyl-1,1,3,3,3-pentamethyldisilmethylene (XII) with excess n-butyllithium. (XII) was identified by comparing its GLC retention time with that of an authentic sample.

C. Trimethylfluorosilane. Dropwise addition of a solution of 40 ml of 1.2 *M* tert-butyllithium in pentane to 23 ml (0.2 mole) of trimethylfluorosilane and 1.6 ml (0.012 mole) of TMEDA gave 5.3 g (85%) of (I). Reaction was very vigorous, a Dry Ice condenser being required to keep trimethylfluorosilane in the flask.

D. Methoxytrimethylsilane. A white solid, presumably lithium methoxide, formed immediately when 40 ml of 1.2 *M* tert-butyllithium in pentane was added to 28 ml (0.2 mole) of methoxytrimethylsilane and 1.6 ml (0.012 mole) of TMEDA at about 15°. After 5 h a small sample of the reaction was quenched with excess trimethylchlorosilane and analyzed by GLC. Only (I) and 1-methoxy-1,1,3,3,3-pentamethyldisilmethylene (V) were formed. No trace of (trimethylsilyl)(trimethylsiloxy)methane (XIV) could be detected by GLC. An anhydrous work-up of the rest of the reaction gave 2.7 g (40%) of (I) and 1.2 g (15%) of (V) (Table 1).

E. Ethoxytrimethylsilane. A solution of 19 ml (0.12 mole) of ethoxytrimethylsilane, 1 ml (0.008 mole) of TMEDA, and 25 ml of 1.2 *M* tert-butyllithium in pentane was stirred for 2 days at room temperature. A white solid, presumably lithium ethoxide, formed slowly. An anhydrous work-up gave 0.8 g (20%) of (I) and 2.9 g (50%) of 1-ethoxy-1,1,3,3,3-pentamethyldisilmethylene (IV), characterized in Table 1.

F. Acetoxytrimethylsilane. tert-Butyllithium (40 ml, 0.048 mole in pentane) was added to 30 ml (0.2 mole) of acetoxytrimethylsilane and 1.6 ml (0.012 mole) of TMEDA. Reaction was very vigorous and gave a negative Gilman Test immediately after addition of tert-butyllithium. Anhydrous work-up gave 2.6 g (65%) of 2-(trimethylsiloxy)-3,3-dimethyl-1-butene (VII), properties given in Table 1. No trace of pinacolone or (I) were detected by GLC analysis.

G. Hexamethyldisiloxane. A mixture of 47 ml (0.22 mole) of hexamethyldisiloxane, 3.3 ml (0.025 mole) of TMEDA and 80 ml of 1.2 *M* tert-butyllithium solution in pentane was stirred for 11 days at room temperature. During this time a viscous oil formed. Mixture was added to carbon dioxide/ether slurry. However, no significant amounts of carboxylic acids were obtained. Neutral phase from the carbonation reaction was distilled to give 5.0 g (30%) of 1-hydroxy-1,1,3,3,3-pentamethyldisilmethylene (VIII).

Following the procedure of Frye *et al.*[5], a solution of 25.5 ml (0.12 mol) of hexamethyldisiloxane and 50 ml of 1.2 *M* tert-butyllithium in pentane was stirred for 5 days at room temperature. Reaction was quenched by adding it to 11 ml (0.1 mole) of dimethylchlorosilane in 50 ml of ether. Anhydrous work-up gave 10.3 g (78%) of 1-(trimethylsiloxy)-1,1,3,3-tetramethyldisilmethylene (IX), characterized in Table 1. Hexamethyldisiloxane (25.5 ml, 0.12 mole) was lithiated exactly as above with 50 ml of 1.2 *M* tert-butyllithium in pentane. After stirring the solution for 5 days at room temperature, 10 ml (0.07 mole) of TMEDA was added. Solution was stirred for 3 days at which time a negative Gilman Test was obtained. No oil or solid formed during this time. Solution was added to 11 ml (0.1 mole) of dimethylchlorosilane in 50 ml of ether. After stirring for 24 h at room temperature, mixture was added to 200 ml of water. Organic phase was washed with two-100 ml portions of water, dried with calcium sulfate, and distilled to give 7.7 g (60%) of 1-(dimethylsiloxy)-1,1,3,3,3-pentamethyldisilmethylene (X) (Table 1). No (IX) or 1-(trimethylsiloxy)-1,1,3,3,3-pentamethyldisilmethylene were detected by GLC or NMR analysis of the crude product.

H. Tetramethylsilane. A mixture of 9.5 ml (0.07 mole) of tetramethylsilane, 9.3 ml (0.07 mole) of TMEDA and 50 ml of 1.4 *M* tert-butyllithium in pentane was stirred at room temperature for 24 h. Trimethylchlorosilane (12.7 ml, 0.1 mole) was added. After 1 h, mixture was added to 50 ml of water. Organic phase was washed with 50 ml of dilute hydrochloric acid, dried with sodium sulfate, and distilled to give 3.5 g (40%) of 1,1,1,3,3,3-hexamethyldisilmethylene (XI), characterized in Table 1.

I. Diethoxydimethylsilane. Addition of 16 ml of 1.2 *M* tert-butyllithium in pentane to 14.3 ml (0.08 mole) of diethoxydimethylsilane and 0.7 ml (0.005 mol) of TMEDA gave a white solid, presumably lithium ethoxide. Gilman Test was negative immediately after addition of tert-butyllithium. GLC analysis showed tert-butyl(ethoxy)-dimethylsilane (VI) to be the only product formed. Anhydrous work-up gave 3.0 g (50%) of (VI) further purified by preparative GLC and characterized (Table 1).

Reaction of n-butyllithium with (diethylamino)trimethylsilane

A mixture of 16 ml (0.08 mole) of (diethylamino)trimethylsilane, 2.5 ml (0.019 mole) of TMEDA, and 50 ml of 1.6 *M* n-butyllithium in hexane was stirred at room temperature for 8 days then quenched with 9.5 ml (0.075 mole) of trimethylchlorosilane. Anhydrous work-up gave 3.8 g of liquid b.p. 100–150° at 40 mm. GLC showed this liquid to be a mixture of equal amounts of 1-n-butyl-1,1,3,3,3-pentamethyldisilmethylene (XII) and 1-(diethylamino)-1,1,3,3,3-pentamethyldisilmethylene (XIII). Each compound was isolated by preparative GLC and characterized (Table 1).

Reaction of tert-butyllithium with pinacolone

A solution of 25 ml of 1.2 *M* tert-butyllithium in pentane was added to a solution of 3.8 ml (0.03 mole) of pinacolone and 5 ml (0.04 mole) of trimethylchlorosilane in 25 ml of THF at −78°. Anhydrous work-up gave 4.1 g (80%) of 2-(trimethylsiloxy)-3,3-dimethyl-1-butene (VII) (Table 1).

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