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REACTIONS OF BIS(TRIMETHYLSILYL)BROMOMETHYLLITHIUM AND TRIS(TRIMETHYLSILYL)METHYLLITHIUM. THE SYNTHESIS OF α-BROMOVINYLSILANES

DIETMAR SEYFERTH *, JAMES L. LEFFERTS and ROBERT L. LAMBERT, Jr.
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

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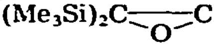
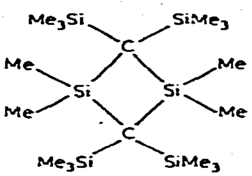
Summary

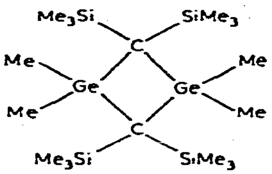
Bis(trimethylsilyl)bromomethyllithium, $(Me_3Si)_2CBrLi$, reacts with aldehydes to give α-bromovinyltrimethylsilanes, $Me_3SiCBr{=}CHR$ (both isomers), but with alkyl ketones only proton abstraction from the enolic form of the ketone occurs. The reaction of this lithium reagent with benzophenone gives the oxirane,  $(Me_3Si)_2C\underset{O}{\frown}CPh_2$. α-Bromovinylsilanes of type $Me_3SiCBr{=}CR_2$ can be prepared by reaction of $R_2C{=}CBrLi$ (prepared by the action of n-butyllithium, or better, t-butyllithium, on $R_2C{=}CBr_2$) with trimethylchlorosilane. The preparation of $(Me_3Si)_3CLi$ by reaction of $(Me_3Si)_3CBr$ and n-butyllithium or lithium sand, as well as various reactions of this reagent, are described.

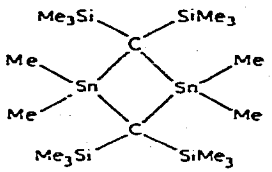
Introduction

In previous studies we have prepared the novel organolithium reagent bis(trimethylsilyl)bromomethyllithium, $(Me_3Si)_2CBrLi$, by the low temperature reaction of bis(trimethylsilyl)dibromomethane with n-butyllithium. From its reactions with trimethylchlorosilane, methyl iodide, n-butyl bromide and water we obtained good yields of $(Me_3Si)_3CBr$, $(Me_3Si)_2CBrMe$, $(Me_3Si)_2CBrBu$-n, and $(Me_3Si)_2CHBr$, respectively [1]. In later work, we investigated the reactions of this reagent with Me_2SiCl_2, Me_2GeBr_2 and Me_2SnCl_2 [2]. The products of these reactions were the novel 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-dimetallacyclobutanes (Ia—Ic).

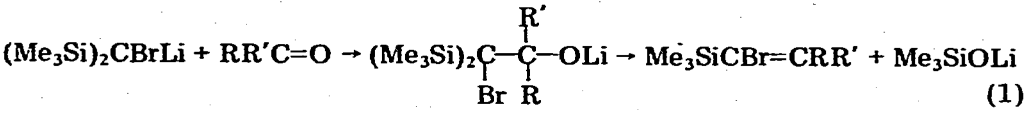
The tris(trimethylsilyl)bromomethane prepared in the $(Me_3Si)_2CBrLi/Me_3SiCl$ reaction itself was found to react with n-butyllithium or lithium sand to give $(Me_3Si)_3CLi$ in good yield, and we report here concerning some of its reactions. Of interest also were the reactions of $(Me_3Si)_2CBrLi$ with aldehydes and ketones. In principle, these should provide a general route to α-bromovinylsilanes by the

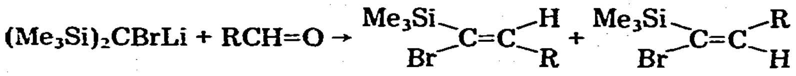

(Ia)


(Ib)

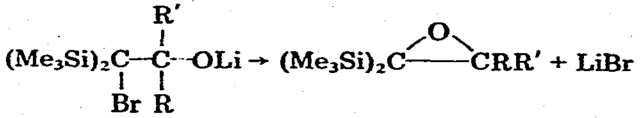

(Ic)

Peterson reaction [3] (eq. 1). Such reactions might be expected to be accompanied by some complications. First, the presence of two trimethylsilyl groups allows the formation of two isomeric products by attack at either silicon when R and R' are different, as shown for the reaction with an aldehyde in eq. 2. Thus, unless some other factors are operative, the reaction cannot be stereospecific.


$$(Me_3Si)_2CBrLi + RR'C{=}O \rightarrow (Me_3Si)_2\underset{Br}{C}{-}\overset{R'}{\underset{R}{C}}{-}OLi \rightarrow Me_3SiCBr{=}CRR' + Me_3SiOLi \qquad (1)$$


$$(Me_3Si)_2CBrLi + RCH{=}O \rightarrow \underset{(Z\text{ isomer})}{(Me_3Si)(Br)C{=}C(H)(R)} + \underset{(E\text{ isomer})}{(Me_3Si)(Br)C{=}C(R)(H)} \qquad (2)$$

Second, this lithium reagent has an α-bromo substituent, and this not only affects the stability of the reagent, but it also provides an alternate site of reactivity. Since bromide ion is a good leaving group, the α-carbon atom would be susceptible to nucleophilic attack by the alkoxide oxygen of the intermediate in an intramolecular process which would lead to formation of an oxirane (eq. 3) *.


$$(Me_3Si)_2\underset{Br}{C}{-}\overset{R'}{\underset{R}{C}}{-}OLi \rightarrow (Me_3Si)_2\overset{O}{\widehat{C{-}C}}RR' + LiBr \qquad (3)$$

Depending on the relative rates of reaction at these positions (α carbon and β silicon), three products are possible for any given substrate.

Results and discussion

Reactions of $(Me_3Si)_2CBrLi$ with aldehydes and ketones

In our studies we have found that $(Me_3Si)_2CBrLi$ reacts with aldehydes to form α-bromovinylsilanes either as the exclusive or the major products. As expected, the reactions are not stereospecific, giving a mixture in which the *Z* isomer, as defined in eq. 2, predominates when the R group is larger than methyl. Except in the case of the crotonaldehyde-derived products, the *Z* and *E* isomers were readily separable by gas—liquid chromatography (GLC). The assignment of configuration to the isomers was based on the position of the resonance due to the vinyl proton in the NMR spectra. In the *Z* isomer, the proton is *trans* to the

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[*] The preparation of trimethylsilyl-substituted oxiranes by the reaction of $Me_3SiCHClLi$ with aldehydes and ketones was reported very recently by Burford et al. [4].

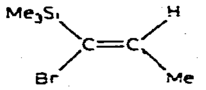
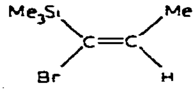
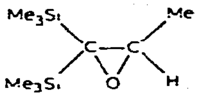
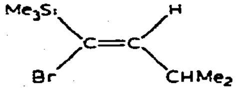
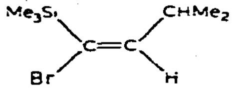
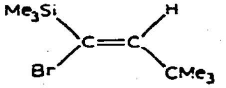
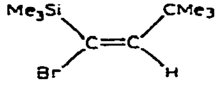
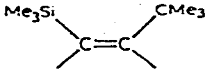
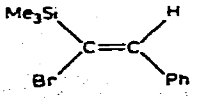
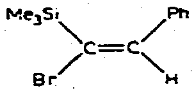
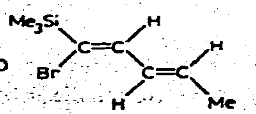
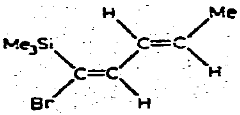
bromine; in the *E* isomer it is *trans* to the trimethylsilyl group and *cis* to the bromine. Bromine has an inductively deshielding effect which tends to move the resonance to lower field. As the effect is strongest for groups in the *trans* position, the proton in the *Z* isomer should be observed at lower field than that in the *E* isomer. For example, the *Z* isomer of $Me_3SiCBr{=}CHMe$ showed its vinyl proton signal 6.76 ppm, while the vinyl proton resonance of the *E* isomer was observed at 6.30 ppm.

The reaction of $(Me_3Si)_2CBrLi$ with acetaldehyde gave, in addition to the α-bromovinylsilane isomers, a low yield of the oxirane I. The reaction of this lithium reagent with pivaldehyde also gave a low yield of a product tentatively identified as $(Me_3Si)_2C{=}CHCMe_3$ whose provenence remains unknown, in addition to the *Z* and *E* isomers of $Me_3SiCBr{=}CHCMe_3$. Table 1 presents the results of the reactions of $(Me_3Si)_2CBrLi$ with aldehydes.

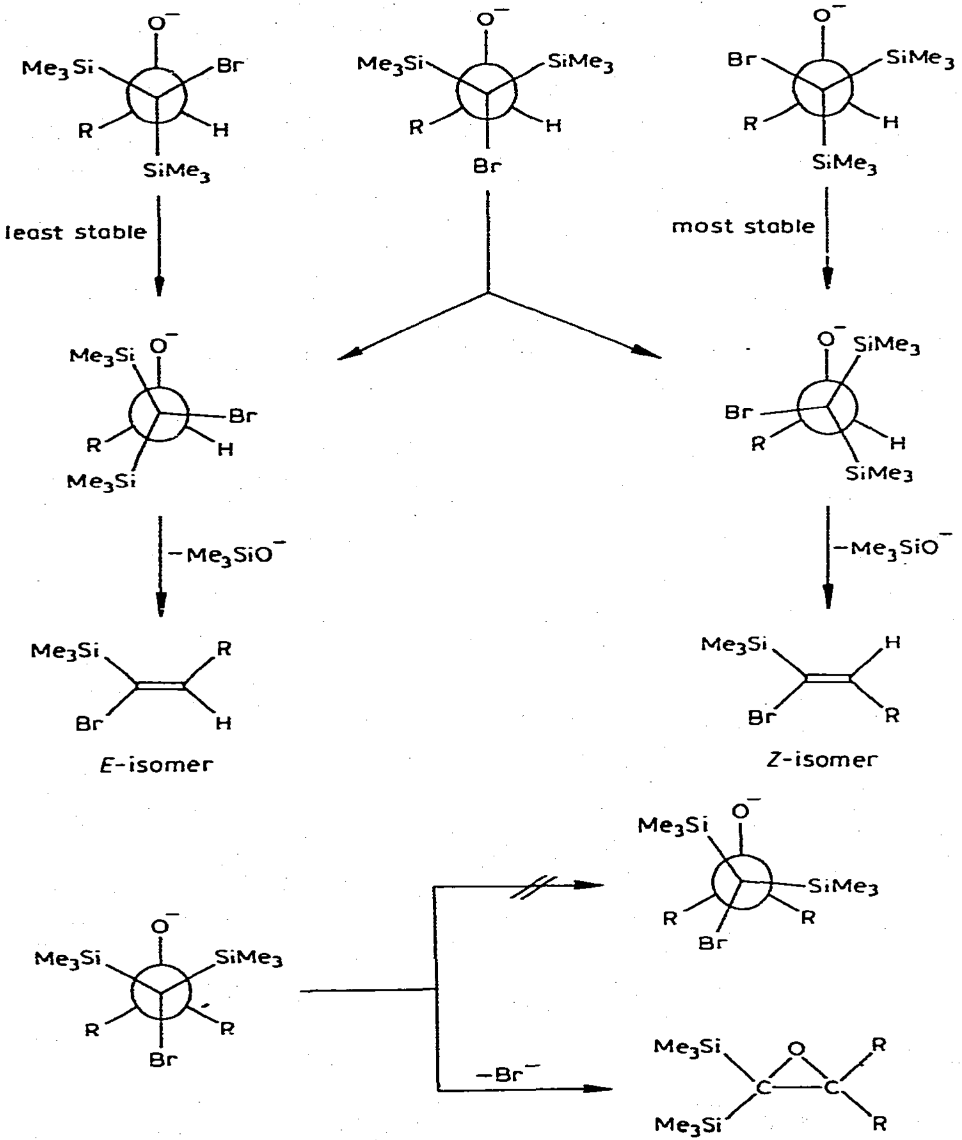
The favored formation of the *Z* isomer in the $(Me_3Si)_2CBrLi/RCH{=}O$ reactions can be understood upon inspection of the Newman projections of the intermediate alkoxides (Scheme 1). Obviously, the more stable conformers are those in which either Me_3Si group is *anti* to the alkyl group R. The optimum geometry for production of the olefin is the eclipsed conformer in which the silyl group is

TABLE 1

REACTIONS OF $(Me_3Si)_2CBrLi$ WITH ALDEHYDES

Aldehyde	Yields *Z*-isomer	 *E*-isomer	Ratio (*Z*/*E*)	Other products
MeCHO	 (39%)	 (39%)	1.0	 (8%)
Me_2CHCHO	 (36%)	 (16%)	2.29	
Me_3CCHO	 (41%)	 (23%)	1.80	 (9%)
PhCHO	 (51%)	 (17%)	3.03	
$MeCH{=}CHCHO$	 (73%)		2.1	

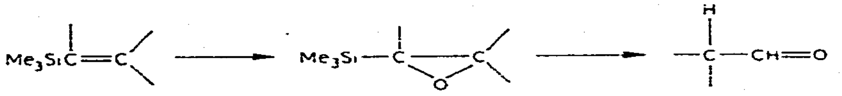
SCHEME 1



brought closest to the alkoxide oxygen. Eclipsing of the silyl group by R, however, is quite unfavorable, but it is just this conformer which leads to the *E* isomer. Thus, as the size of R is increased, one would expect the *Z*/*E* ratio to increase: this is the pattern followed by the reactions in Table 1.

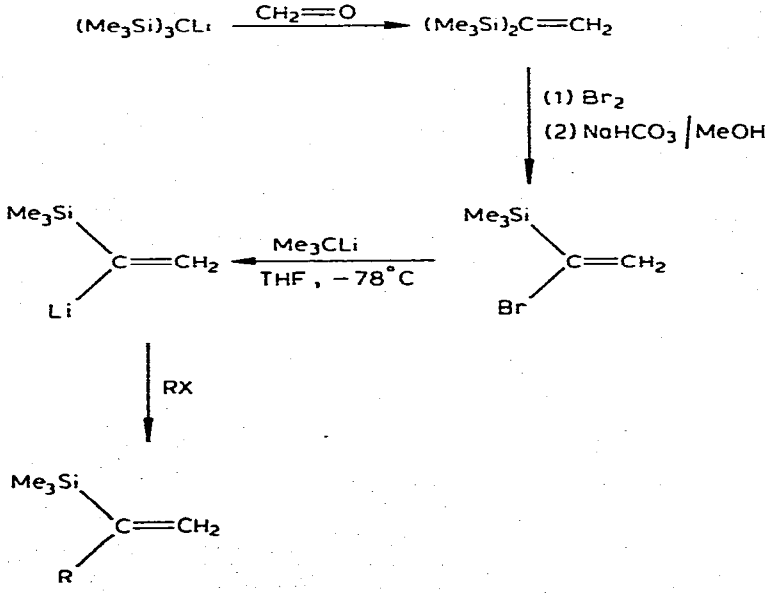
The reactions of $(Me_3Si)_2CBrLi$ with ketones proceeded differently. The lithium reagent behaved as a strong base toward ketones having enolizable protons. When the lithium reagent reacted with acetone, methyl ethyl ketone and acetophenone, only the reduction product of the starting dibromide, $(Me_3Si)_2CHBr$, was isolated. Presumably, the addition of the sterically quite hindered lithium reagent to a ketone is unfavorable and does not occur when another reaction possibility exists. The reaction of $(Me_3Si)_2CBrLi$ with benzophenone, a ketone which does not have an enolizable proton, also did not give the α-bromovinylsilane, $Me_3SiCBr{=}CPh_2$. Instead, the oxirane (R = R' = Ph, eq. 3) was produced. This may be explained by reference to the Newman projections in Scheme 1. In the benzophenone-derived intermediate alkoxide, the substituents on the alkoxide carbon atom are both large phenyl groups. Eclipsing of either silyl group with the oxygen results in an unfavorable eclipse of one phenyl group by the other silyl group. Therefore, the most stable conformer of the intermediate is the one with both silyl groups *anti* to phenyl groups. This places the oxygen and bromine in favorable position to effect an intramolecular S_N2 displacement to give the oxirane.

Vinylsilanes of diverse types, $Me_3SiCH{=}CHR$, $Me_3SiCH{=}CRR'$, $Me_3SiCr{=}CH_2$ and $Me_3SiCR{=}CR'R''$, have become of interest as reagents in organic synthesis since they are readily converted to oxiranes, which in turn may be converted to carbonyl compounds (eq. 4) [5]. It has been shown that vinylsilanes of type $Me_3SiCR{=}CH_2$ may be prepared by the sequence shown in Scheme 2 and



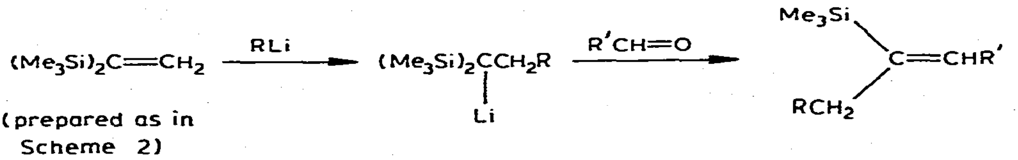
(4)

SCHEME 2

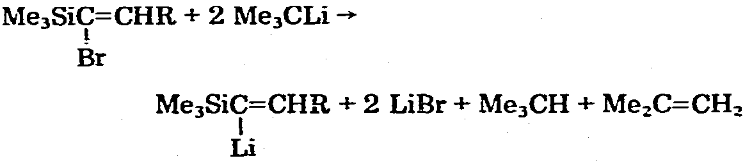


some vinylsilanes of type $Me_3SiCR{=}CHR'$ have been prepared as shown in Scheme 3 [6]. The chemistry shown in Scheme 3, however, has somewhat limited application since the intermediate lithium reagents of type $(Me_3Si)_2CLiCH_2R$, be-

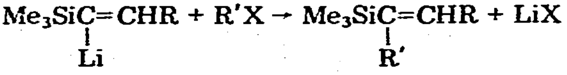
SCHEME 3



cause of their steric bulk, do not add to the C=O bonds of dialkyl ketones, and proton abstraction from enolizable aliphatic aldehydes even is a serious complicating side reaction. Thus a route to such vinylsilanes based on an extension of the chemistry reported here (eq. 5, 6) may provide syntheses of useful reagents of type $\mathrm{Me_3SiCR'{=}CHR}$.



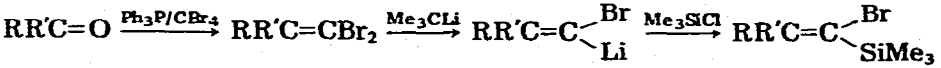
$$\mathrm{Me_3Si\underset{\displaystyle Br}{C}{=}CHR + 2\,Me_3CLi \rightarrow Me_3Si\underset{\displaystyle Li}{C}{=}CHR + 2\,LiBr + Me_3CH + Me_2C{=}CH_2} \tag{5}$$



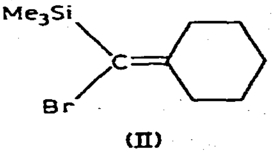
$$\mathrm{Me_3Si\underset{\displaystyle Li}{C}{=}CHR + R'X \rightarrow Me_3Si\underset{\displaystyle R'}{C}{=}CHR + LiX} \tag{6}$$

Also developed during the course of our studies was a route to α-bromovinylsilanes of type $\mathrm{Me_3SiCBr{=}CR_2}$, in particular for R = Me. Application of the chemistry illustrated in eq. 5 and 6 to these would give vinylsilanes of type $\mathrm{Me_3SiCR'{=}CR_2}$. In a previous report, we described the preparation of the novel lithium reagent $\mathrm{Me_2C{=}CBrLi}$, which was used in the synthesis of $\mathrm{(Me_2C{=}CBr)_2Hg}$ [7]. This reagent reacted readily with trimethylchlorosilane to give $\mathrm{Me_3SiCBr{=}CMe_2}$. When $\mathrm{Me_2C{=}CBrLi}$ was prepared by the low temperature reaction of $\mathrm{Me_2C{=}CBr_2}$ with n-butyllithium in THF/hexane, the yield of this silane was only 56%. However, t-butyllithium was found to be much more effective in the preparation of $\mathrm{Me_2C{=}CBrLi}$, and essentially quantitative yields of $\mathrm{Me_3SiCBr{=}CMe_2}$ could be realized. Also prepared were $\mathrm{Me_2ClSiCBr{=}CMe_2}$ and $\mathrm{Me_2Si(CBr{=}CMe_2)_2}$ by this organolithium route. The general availability of dibromides of type $\mathrm{RR'C{=}CBr_2}$ by reactions of aldehydes and ketones with $\mathrm{Ph_3P/CBr_4}$ [8] should make this approach to α-bromovinylsilanes of general applicability (Scheme 4). To provide one additional example, we have prepared α-bromo- α-trimethylsilylmethylenecyclohexane (II) by this procedure.

SCHEME 4



$$\mathrm{RR'C{=}O \xrightarrow{Ph_3P/CBr_4} RR'C{=}CBr_2 \xrightarrow{Me_3CLi} RR'C{=}C\genfrac{}{}{0pt}{}{Br}{Li} \xrightarrow{Me_3SiCl} RR'C{=}C\genfrac{}{}{0pt}{}{Br}{SiMe_3}}$$



(II)

Preparation of $(Me_3Si)_3CLi$ *from* $(Me_3Si)_3Br$

At the time our work on the $(Me_3Si)_3CBr$-to-$(Me_3Si)_3Li$ conversion was begun, this lithium reagent was as yet unknown. However, during the course of this work, Cook et al. [9] reported that $(Me_3Si)_3CLi$ can be prepared by the lithiation of tris(trimethylsilyl)methane with methyllithium in THF/Et_2O medium or by reaction of tris(trimethylsilyl)chloromethane with lithium or methyllithium in THF/Et_2O, or with n-butyllithium/tetramethylethylenediamine in diethyl ether/hexane medium. Reactions of $(Me_3Si)_3CLi$ with Me_3SiCl, Me_2HSiCl, Me_3SnCl, MeI and CO_2 were described.

We found that tris(trimethylsilyl)bromomethane reacts readily with n-butyllithium in diethyl ether/hexane at low temperature (−75 to −80°C) to give tris(trimethylsilyl)methyllithium (eq. 7). (At room temperature, the reaction of the

$$(Me_3Si)_3CBr + n\text{-}BuLi \rightarrow (Me_3Si)_3CLi + n\text{-}BuBr \qquad (7)$$

reagent formed with the other product, n-butyl bromide, complicates matters, making the synthesis under those conditions impractical). An alternate route to $(Me_3Si)_3CLi$ uses the reaction of $(Me_3Si)_3CBr$ with lithium sand in diethyl ether at room temperature. Reactions of the reagent prepared by these routes with Me_3SiCl, Me_3SnCl, Ph_3PbCl, MeI, EtI and D_2O were carried out, giving the expected products, $(Me_3Si)_4C$, $(Me_3Si)_3CSnMe_3$, $(Me_3Si)_3CPbPh_3$, $(Me_3Si)_3CMe$, $(Me_3Si)_3CEt$ and $(Me_3Si)_3CD$, respectively, in yields ranging from 53—79%. However, the route to $(Me_3Si)_3CLi$ which used the more readily available $(Me_3Si)_3CH$ [10] as starting material is the preferred one.

Experimental

General comments

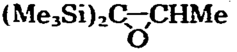
All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen. The standard apparatus used consisted of a three-necked, round-bottomed flask of appropriate size which was equipped with a stirring assembly (magnetic or mechanical), a pressure-equalizing dropping funnel and a Claisen adapter. The addition funnel was topped with a nitrogen inlet tube and the two necks of the Claisen adapter were fitted with a rubber septum and a low-temperature (pentane) thermometer. The latter was of the total immersion type, but it was immersed only to a depth of about 3 cm in the reaction mixture. The actual solution temperatures thus were about 8—10° lower than the reported thermometer readings. Gas—liquid chromatography was employed for collection of samples for analysis, spectroscopic measurements and refractive index determination and for yield determinations using internal standards and empirically determined response factors.

Melting points were determined with a Mel-temp apparatus in capillary tubes which were sealed about 0.75 in. above the sample and are uncorrected. Infrared spectra were obtained using a Perkin—Elmer 457A grating infrared spectrophotometer. Proton NMR spectra were recorded using a Varian T60 spectrometer, and proton chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane.

n-Butyllithium and methyllithium, as well as the lithium sand, were purchased from Alfa/Ventron. Trimethylchlorosilane was kindly donated by Union Carbide Corp. Ether solvents were distilled from sodium benzophenone prior to use.

Characterizing data for compounds prepared in this study are collected in Table 2.

Reactions of bis(trimethylsilyl)bromomethyllithium with aldehydes and ketones

(1) Acetaldehyde. To the standard low temperature apparatus were added at −115°C simultaneously solutions of $(Me_3Si)_2CBr_2$ [1] (26.00 g, 81.6 mmol) in 65 ml of THF and 95 mmol of n-BuLi in 38 ml of hexane. The bright yellow-orange solution was stirred for 20 min at −115°C, and then 8.5 g (193 mmol) of acetaldehyde in 20 ml of THF was added. The solution became completely colorless within 2 min. After a further 30 min at −115 to −110°C, the solution was allowed to warm to room temperature. As the temperature rose, the solution gradually became red in color. The reaction mixture was transferred to a 500 ml separatory funnel and was washed with two 250 ml portions of 0.1 *M* HCl to give a yellow organic layer which was dried over $MgSO_4$. Concentration on the rotary evaporator was followed by GLC examination (F & M 5754, 4′UCW98, 100°C). Four major products were identified by their NMR spectra as (in order of elution) *E*-$Me_3SiCBr{=}CHCH_3$ (31.6 mmol, 39%), *Z*-$Me_3SiCBr{=}CHCH_3$ (31.6 mmol, 39%), $(Me_3Si)_2CHBr$ (5.4 mmol, 6.7%), and  $(Me_3Si)_2\underset{O}{C{-}CHMe}$ (6.7 mmol, 8.2%).

(2) Isobutyraldehyde. The lithium reagent, prepared from 12.46 g (39.2 mmol) of $(Me_3Si)_2CBr_2$ and 44 mmol of n-BuLi, was treated with 7.8 g (108 mmol) of isobutyraldehyde at −115°C. The standard workup yielded a colorless oil shown to be a mixture of *E*-$Me_3SiCBr{=}CH$-i-Pr (6.14 mmol, 15.7%), *Z*-$Me_3SiCBr{=}CH$-i-Pr (14.1 mmol, 35.9%), and $(Me_3Si)_2CHBr$ (trace).

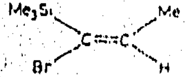
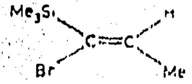
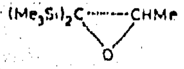
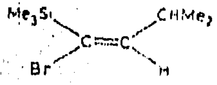
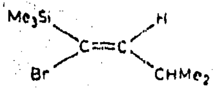
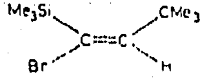
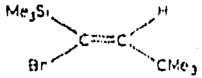
(3) Pivaldehyde. The lithium reagent, prepared from 10.405 g (32.7 mmol) of $(Me_3Si)_2CBr_2$ and 39 mmol of n-BuLi, was treated with 6.55 g (76 mmol) of pivaldehyde at −115°C. Standard workup followed by GLC examination (F & M 5754, 4′UCW98, 100°C) showed three major components. The second peak was further resolved into two compounds which could not be completely separated. The NMR spectrum of the mixed compounds showed that $(Me_3Si)_2CHBr$ was the major component. The minor component was tentatively identified as $(Me_3Si)_2C{=}CH$-t-Bu. The first and third peaks were identified by their NMR spectra as the *E*- and *Z*-isomers, respectively, of $Me_3SiCBr{=}CH$-t-Bu. The yields were determined by comparison of the integrated MeSi resonances of the compounds after having determined the absolute yield of the *Z*-olefin by GLC. The yields were: *E*-isomer (7.4 mmol, 22.5%), $(Me_3Si)_2CHBr$ (7.4 mmol, 22.5%), $(Me_3Si)_2C{=}CH$-t-Bu (2.8 mmol, 8.7%) and *Z*-isomer (13.3 mmol, 40.8%).

(4) Benzaldehyde. The lithium reagent was prepared in the standard way from 15.26 g (48.0 mmol) of $(Me_3Si)_2CBr_2$ and 55 mmol of n-BuLi. The orange solution was then treated at −115°C with 7.23 g (68.1 mmol) of benzaldehyde. Workup as before followed by GLC examination (F & M 5754, 4′UCW98, 130°C) showed the following compounds in order of elution: $(Me_3Si)_2CHBr$ [1] (4.3 mmol, 8.9%), $(Me_3Si)_2CBr_2$ (4.1 mmol, 8.6%), PhCHOHBu (trace), *Z*-$Me_3SiCBr{=}CHPh$ (24.5 mmol, 51.2%) and *E*-$Me_3SiCBr{=}CHPh$ (8.1 mmol, 16.9%).

(continued on p. 50)

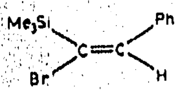
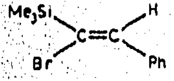
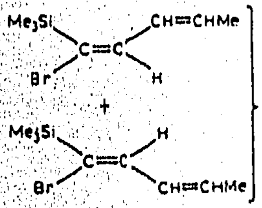
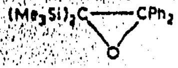
TABLE 2

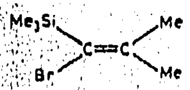
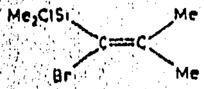
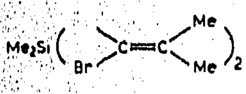
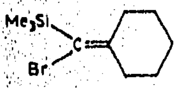
CHARACTERIZATION OF PRODUCTS

Compound	M.p. (°C)	n_D^t	Analysis (Found (calcd.) (%))			NMR (δ(ppm) (in CCl_4))	IR, ν(C=C) (cm^{-1} (film))
			C	H	Br		
		1.4666(24.5)	37.53 [a] (37.31)	6.81 (6.78)		0.19 (s, 9H, Me_3Si); 1.84 (d, *J* 6.5 Hz, Me) 6.30 (q, *J* 6.5 Hz, 1H, =CH)	1618, 1605(sh)
		1.4742(24.5)				0.29 (s, 9H, Me_3Si); 1.76 (d, *J* 7.5 Hz, Me); 6.76 (q, *J* 7.5 Hz, 1H, =CH)	1605
		1.4511(27)	52.93 (53.40)	10.78 (10.95)		0.04 (s, 9H, Me_3Si; 0.15 (s, 9H, Me_3Si); 1.39 (d, *J* 6 Hz, 3H, Me); 3.02 (q, *J* 6 Hz, 1H, CHMe)	
		1.4620(24.5)	43.84 [a] (43.44)	7.81 (7.75)	35.63 (36.12)	0.19 (s, 9H, Me_3Si), 1.06 (d, *J* 7 Hz, 6H, Me_2C); 2.92 (double heptet, 1H, $CHMe_2$); 6.01 (d, *J* 8 Hz, 1H, =CH)	1611
		1.4636(24.5)				0.26 (s, 9H, Me_3Si); 1.04 (d, *J* 6.5 Hz, 6H, Me_2C); 2.56 (double heptet, 1H, Me_2CH); 6.56 (d, *J* 11 Hz, 1H, =CH)	1608
$(Me_3Si)_2C{=}CHCMe_3$						0.17 (s, 9H, Me_3Si); 0.30 (s, 9H, Me_3Si); 1.15 (s, 9H, Me_3C); 6.63 (s, 1H, =CH)	
		1.4610(25.5)	46.06 [a] (45.95)	8.25 (8.14)	33.98 (33.97)	0.18 (s, 9H, Me_3Si); 1.25 (s, 9H, Me_3C); 6.27 (s, 1H, =CH)	1595
		1.4802(25.5)				0.35 (s, 9H, Me_3Si); 1.17 (s, 9H, Me_3C); 7.03 (s, 1H, =CH)	1587

continued

TABLE 2. (Continued)

Compound	M.p. (°C)	n_D^t	Analysis (Found (calcd.) (%))			NMR (δ (ppm) (in CCl$_4$))	IR, ν(C=C) (cm^{-1} (film))
			C	H	Br		
		1.5568(25)	51.79 [a] (51.70)	6.17 (5.92)	30.96 (31.31)	0.27 (s, 9H, Me$_3$Si); 7.10–7.25 (m, 6H, Ph and =CH)	1572
		1.5510(25)				0.007 (s, 9H, Me$_3$Si), 7.00–7.43 (m, 5H, Ph); 7.92 (s, 1H, =CH)	1583
		1.5133(25) [a]	43.93 [a] (43.84)	6.87 (6.90)	35.74 (36.45)	0.17 (s, minor isomer); 0.28 (s, major isomer); 1.66–1.89 (overlapping m, allyl CH); 5.48–7.24 (m, =CH)	
	97.5–98.5		70.57 (70.53)	8.22 (8.20)		–0.13 (s, 18H, Me$_3$Si); 7.12–7.62 (m, 10H, Ph)	

	b.p. 57–58 (7.0 Torr)	1.4828(25)	40.74 (40.57)	7.20 (7.30)	38.36 (38.56)	0.26 (s, 9H, Me_3Si); 1.85 (s, 3H, Me); 1.95 (s, 3H, Me)	1609
	b.p. 33–37 (0.12 Torr)		(not analyzed)			0.77 (s, 6H, Me_2ClSi); 2.12 (s, 3H, Me); 2.17 (s, 3H, Me)	1605
	b.p. 83–85 (0.06 Torr)	1.5382(25)	36.83 (36.83)	5.63 (5.50)	49.11 (49.00)	0.46 (s, 6H, Me_2Si); 1.89 (s, 6H, Me); 2.00 (s, 6H Me)	1605
	b.p. 60–61 (0.2 Torr)	1.5130(25)	48.86 (48.57)	7.62 (7.74)	32.58 (32.32)	0.26 (s, 9H, Me_3Si); 1.4–1.8 (m, 6H); 2.1–2.7 (m, 4H)	1594
$(Me_3Si)_3CCH_2CH_3$	208–211		55.06 (55.30)	12.14 (12.37)		0.18 (s, 27H, Me_3Si); 1.15 (t, 3H, *J* 7.0 Hz, Me); 1.81 (q, 2H, *J* 7.0 Hz, CH_2)	
$(Me_3Si)_3CI$	246–247(dec)		33.86 (33.49)	7.65 (7.49)		0.10 (s, Me_3Si)	
$(Me_3Si)_3CPb(C_6H_5)_3$	195–197		50.37 (50.19)	6.32 (6.32)		0.32 (s, 27H, Me_3Si); 6.9–7.9 (m, 15H, Ph)	

[a] Analysis of isomer mixture.

(5) Crotonaldehyde. The lithium reagent, prepared from 12.035 g (37.8 mmol) of $(Me_3Si)_2CBr_2$ and 50 mmol of n-BuLi, was treated with 5.76 g (82.2 mmol) of *trans*-crotonaldehyde. The standard workup showed only a single major peak on GLC (F & M 5754, 4'UCW98, 120°C). The NMR spectrum of a GLC-collected sample indicated that both olefin isomers had been formed, but that they were not separable. The combined yield was 27.4 mmol, 72.5%.

(6) Acetone, 2-butanone and acetophenone. The lithium reagent prepared from 14.545 g (45.7 mmol) of $(Me_3Si)_2CBr_2$ and 53.1 mmol of n-BuLi was treated with 5.88 g (100 mmol) of acetone at −120°C. After the standard workup, GLC examination showed that a single product was present. This was identified by comparison with authentic material as $(Me_3Si)_2CHBr$ [1]. The yield was 32.0 mmol, 70%.

Similar reactions of $(Me_3Si)_2CBrLi$ with 2-butanone and with acetophenone gave $(Me_3Si)_2CHBr$ in yields of 84 and 89%, respectively.

(7) Benzophenone. The lithium reagent was prepared as above from 19.06 g (59.9 mmol) of $(Me_3Si)_2CBr_2$ and 70 mmol of n-BuLi at −120°C. When a solution of 16.04 g (88 mmol) of benzophenone in 50 ml of THF was added at this temperature, the reaction mixture rapidly turned dark orange-brown in color. This color faded to pale yellow as the solution warmed to room temperature. Aqueous workup as above gave a pale-yellow solution which deposited colorless crystals on removal of most of the solvent at reduced pressure. The NMR spectrum of the filtered solid showed only phenyl and silylmethyl resonances in a 10/18 intensity ratio which indicated that it was the oxirane rather than one of the possible olefinic products, which would have 10/9 ratio. The yield, after recrystallization from pentane, was 13.08 g (38.6 mmol, 64%).

Examination of the filtrate (GLC) showed the presence of at least seven high boiling components in low yields among which could be identified the following (by comparison of retention times with authentic materials): $(Me_3Si)_2CHBr$ [1], $(Me_3Si)_2CBrBu$ [1] and benzophenone.

Preparation of $Me_3SiCBr{=}CMe_2$, $Me_2ClSiCBr{=}CMe_2$ and $Me_2Si(CBr{=}CMe_2)_2$

The standard low temperature reaction apparatus was charged with 43.0 g (0.2 mol) of $Me_2C{=}CBr_2$ (prepared by the Ph_3P/CBr_4 procedure [8] or by dehydrohalogenation [11] of 1,1,2-tribromo-2-methylpropane with potassium hydroxide in ethylene glycol) and 300 ml of dry THF and was cooled to −95°C. n-Butyllithium (130 ml of 1.6 *M* in hexane, 0.21 mol) was added, with stirring under nitrogen, and the resulting solution was stirred at −95°C for 35 min. Subsequently, 28 ml (0.215 mol) of trimethylchlorosilane was added slowly over a period of 90 min. The reaction mixture was stirred at −95°C for 90 min, allowed to warm slowly to room temperature and then hydrolyzed with saturated aqueous ammonium chloride solution. The organic layer was distilled to give 23.0 g (56%) of $Me_3SiCBr{=}CMe_2$, b.p. 57—58°C at 7.0 Torr.

A reaction carried out in the same manner, but in which the lithium reagent used was t-butyllithium in pentane (Alfa/Ventron), gave $Me_3SiCBr{=}CMe_2$ in essentially quantitative yield when carried out on a 27.8 mmol scale.

When 180 mmol of Me_2SiCl_2 was added at −100°C to a $Me_2C{=}CBrLi$ solution prepared from 0.348 mol of $Me_2C{=}CBr_2$ in 500 ml of THF and 0.36 mol of t-butyllithium in 320 ml of pentane at −95°C, a non-hydrolytic work-up gave

21.3 g (60%) of $Me_2ClSiCBr{=}CMe_2$, b.p. 33—37°C at 0.12 Torr, and 12.3 g (21%) of $Me_2Si(CBr{=}CMe_2)_2$, b.p. 83—85°C at 0.06 Torr. The former was characterized by proton NMR and IR spectroscopy only. It was used (93 mmol) directly in another reaction with $Me_2C{=}CBrLi$ (about 102 mmol) at —95°C by the usual procedure, giving $Me_2Si(CBr{=}CMe_2)_2$ in 64% yield.

Preparation of α-bromo- α-trimethylsilylmethylenecyclohexane

The required α,α-dibromomethylenecyclohexane was prepared in 62% yield by the reaction of $PhHgCBr_3$, triphenylphosphine and cyclohexanone (0.28/0.28/0.41 mol ratio) in benzene at reflux (3 h reaction time) by a procedure developed in these Laboratories [12]. The compound was isolated as a colorless liquid, b.p. 56—57°C at 0.7 Torr, n_D^{25} 1.5604, in 98% purity.

The standard low temperature reaction apparatus was charged with 12.70 g (50 mmol) of α,α-dibromomethylenecyclohexane, 100 ml of dry THF and 25 ml of diethyl ether. The contents were cooled to —105°C and 35 ml of 1.6 *M* n-butyllithium (56 mmol) in hexane was added slowly. The resulting mixture was stirred at —105°C for 20 min, and then 8.0 ml (63 mmol) of trimethylchlorosilane was added. The reaction mixture was stirred at —105°C for 15 min, then was allowed to warm to room temperature and was hydrolyzed with saturated aqueous ammonium chloride. Distillation of the dried organic layer gave 6.68 g (54%) of the title product, b.p. 60—61°C at 0.2 Torr.

A better yield of this product should be realizable when the t-butyllithium procedure is used.

Preparation of tris(trimethylsilyl)methyllithium from tris(trimethylsilyl)bromomethane

(a) By reaction of tris(trimethylsilyl)bromomethane with n-butyllithium. The standard low temperature reaction apparatus was charged with 5.42 g (17.4 mmol) of tris(trimethylsilyl)bromomethane [*] and 50 ml of freshly distilled diethyl ether. After the solution had been cooled to —75°C, 11.7 ml of 1.6 *M* n-butyllithium (18.7 mmol) in hexane was added over a 1 min period. The mixture was stirred at —75°C for 25 min and then 2.4 g (19.0 mmol) of dimethyl sulfate was added by syringe. The reaction mixture was stirred for 90 min at —80°C and subsequently was allowed to warm to room temperature and hydrolyzed with 30 ml of water. The dried (Na_2SO_4) organic layer was evaporated at reduced pressure and the residue was recrystallized from methanol to 2.35 g (77%) of $(Me_3Si)_3SiCMe$. An analytical sample, m.p. 158—159°C, was obtained by two further recrystallizations from methanol; lit. [9] m.p. 155—157°C).

Tris(trimethylsilyl)methyllithium prepared in this manner also was allowed to react with trimethylchlorosilane and trimethyltin chloride. Tetrakis(trimethylsilyl)methane and tris(trimethylsilyl)(trimethylstannyl)methane, both known compounds [1], were obtained in yields of 57 and 58%, respectively. Treatment of tris(trimethylsilyl)lithium thus prepared with D_2O gave $(Me_3Si)_3CD$

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[*] Prepared by reaction of $(Me_3Si)_2CBrLi$ with trimethylchlorosilane [1] or by the bromination of $(Me_3Si)_3CH$, using a slight excess of bromine in CCl_4 at reflux in the presence of incandescent lighting. A long reaction time (~180 h in one experiment which was carried out on a 0.07 mol scale) is required. The product is isolated by sublimation after volatiles have been removed to give $(Me_3Si)_3CBr$ in over 70% yield, m.p. 194—195°C.

whose NMR spectrum did not show a resonance due to the CH proton found in the spectrum of $(Me_3Si)_3CH$.

(b) By reaction of tris(trimethylsilyl)bromomethane with lithium sand. A flamed-out 200 ml, three-necked, round-bottomed flask equipped with a glass blade stirrer, a pressure-equalizing addition funnel and a reflux condenser topped with a gas inlet tube was charged with 0.40 g (57 mmol) of lithium sand (Foote Mineral Co.), which had been washed free of hydrocarbon by several ether rinses and dried under argon, and 5 ml of freshly distilled diethyl ether. To this mixture was added over a period of 90 min a solution of 6.47 g (20.8 mmol) of $(Me_3Si)_3CBr$ in 25 ml of ether, resulting in a mildly exothermic reaction. The mixture was stirred overnight under nitrogen, and after 22 h, the precipitated lithium salts were allowed to settle. The clear ether solution of the reagent was transferred by syringe to a constant-rate addition funnel fitted to a 300 ml, three-necked, round-bottomed flask which was equipped with a stirring unit, a reflux condenser and nitrogen inlet, and which was charged with 8.85 g (18.7 mmol) of triphenyllead chloride in 35 ml of THF. The lithium reagent solution was added to the Ph_3PbCl over a 3 h period and the reaction mixture subsequently was stirred at room temperature for 2 h. The volatiles then were removed at reduced pressure and the residue was extracted with 15 ml of water and 100 ml of chloroform. The dried organic layer was evaporated, leaving a solid residue which was recrystallized from 1/1 chloroform/hexane to give 8.2 g of crude product, m.p. 165—187°C. Recrystallization from hexane gave pure material in 59% yield.

Reactions of $(Me_3Si)_3CLi$ prepared by this route with trimethylchlorosilane, trimethyltin chloride, methyl iodide, ethyl iodide and D_2O gave $(Me_3Si)_4Si$ (62%), $(Me_3Si)_3CSnMe_3$ (79%), $(Me_3Si)_3CMe$ (62%), $(Me_3Si)_3CEt$, a new compound (53%) and $(Me_3Si)_3CD$ (66%). A reaction with iodine to give $(Me_3Si)_3CI$ also was carried out as follows.

The reagent prepared from 8.9 mmol of $(Me_3Si)_3CBr$ and lithium sand in diethyl ether was added by syringe to a solution of 2.12 g (8.3 mmol) of iodine in 15 ml of ether at 0°C (nitrogen atmosphere). After an initially exothermic reaction, the reaction mixture was stirred at room temperature for 30 min. After it had been treated with 1 *M* sodium thiosulfate solution, the deeply colored reaction mixture became pale yellow. The organic phase was dried and evaporated and the residue was recrystallized from methanol, giving 2.29 g (72%) of $(Me_3Si)_3CI$.

Acknowledgments

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References

1 D. Seyferth, R.L. Lambert, Jr. and E.M. Hanson, J. Organometal. Chem., 24 (1970) 647.
2 D. Seyferth and J.L. Lefferts, J. Amer. Chem. Soc., 96 (1974) 6237; J. Organometal. Chem., 116 (1976) 257.
3 D.J. Peterson, J. Org. Chem., 33 (1968) 780.
4 C. Burford, F. Cooke, E. Ehlinger and P. Magnus, J. Amer. Chem. Soc., 99 (1977) 4536.

5 P.F. Hudrlik, J. Organometal. Chem. Library, 1 (1976) 127.
6 B.-T. Gröbel and D. Seebach, Angew. Chem., 86 (1974) 102; Chem. Ber., 110 (1977) 852, 867.
7 D. Seyferth and D. Dagani, J. Organometal. Chem., 104 (1976) 145.
8 E.J. Corey and P.L. Fuchs, Tetrahedron Lett., (1972) 3769.
9 M.A. Cook, C. Eaborn, A.E. Jukes and D.R.M. Walton, J. Organometal. Chem., 24 (1970) 529.
10 R.L. Merker and M.J. Scott, J. Amer. Chem. Soc., 85 (1963) 2243.
11 E.A. Braude and E.A. Evans, J. Chem. Soc., (1955) 3324.
12 D. Seyferth, J.K. Heeren, G. Singh, S.O. Grim and W.B. Hughes, J. Organometal. Chem., 5 (1966) 267.