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METALATION OF VINYLTRIMETHYLSILANES

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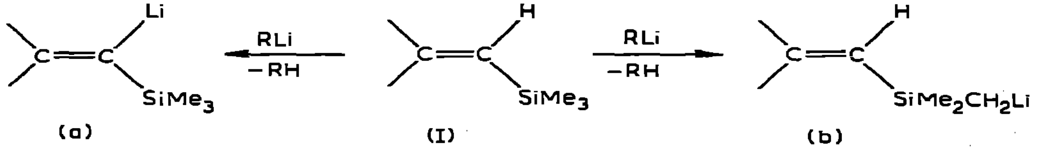
SUMMARY

Metalation of vinyltrimethylsilane and both *trans*-(VIII) and *cis*-(IX) 1-(trimethylsilyl)-3,3-dimethyl-1-butene with organolithium/TMEDA complexes was explored. Vinyltrimethylsilane underwent exclusive addition of tert-butyllithium to the double bond. Metalation of (VIII) occurred only at the trimethylsilyl function, while (IX) afforded both α-silylvinyl and trimethylsilyl position metalation.

INTRODUCTION

The possibility that silicon, by way of *d*-orbital participation, can act as an electronic conduit between two formally silicon-isolated π-systems ("through-conjugation") is a topic of some current interest[1,2]. We are unaware, however, of any instance in which chemical, rather than physical, evidence has been advanced either for or against this hypothesis. In this respect, it appeared that metalation of a substrate incorporating the structural unit (I) shown in Scheme 1 might afford information concerning this type of phenomenon.

SCHEME 1
POSSIBLE METALATION MODES FOR A VINYLTRIMETHYLSILANE

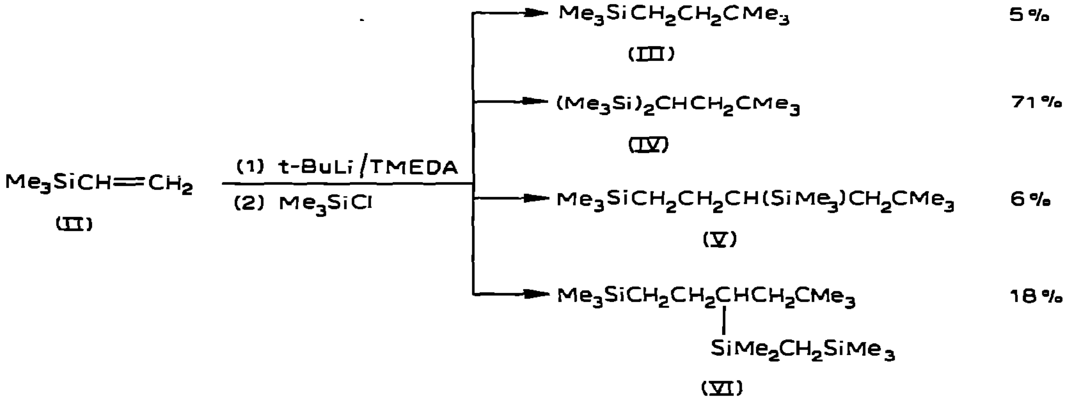


It is well known that protons α to silicon undergo ready metalation with organolithium reagents activated with *N,N,N′,N′*-tetramethylethylenediamine (TMEDA)[3]. Although past reports have been concerned only with metalation at saturated sites, it seemed reasonable to expect that factors which stabilize an sp^3-hybridized α-silyl carbanion would also stabilize an sp^2-hybridized α-silyl carbanion. Since the thermodynamic acidity of a vinyl proton in ethylene is 3–7 pK_a units greater than that of methyl protons in saturated compounds[4], (a) would be expected to be the more thermodynamically stable carbanion derivable from (I) if other effects did not intervene. Conversely, the principle behind through-conjugation seems to provide a mechanism whereby carbanion (b) could be stabilized relative to (a) by interaction, through silicon, with the π-system*. Also lending impetus to this investigation was a report which rationalized the appearance of certain products in the reductive trimethylsilylation of bis(trimethylsilyl)acetylene in terms of a vinyl to methyl carbanionic rearrangement[6]:

$$(Me_3Si)_2C{=}CLiSiMe_3 \rightarrow (Me_3Si)_2C{=}CHSiMe_2CH_2Li$$

RESULTS AND DISCUSSION

Although treatment of vinylsilanes with organolithium reagents is known to result in addition to the double bond[7-10], the behavior of vinyltrimethylsilane (II) with the tert-butyllithium/TMEDA complex was investigated on the possibility that metalation with this potent reagent would be competitive with addition**. When this reaction was carried out with a 1/1/1 molar ratio of tert-butyllithium/TMEDA/(II), followed by addition of trimethylchlorosilane, total consumption of (II) occurred to give only the compounds (III)-(VI) in significant amounts, No higher molecular weight material was present. Since under these conditions, trimethylchlorosilane can act as a proton donor, as well as couple with an organolithium reagent, the reactions shown in Scheme 2 would account for the observed products.



The initial step is visualized as the addition of tert-butyllithium to the double bond of (II) to give (c) as a stable intermediate. Products derived from this species upon trimethylchlorosilane derivatization (III and IV) account for 76% of all products obtained. There appears to be no significant rearrangement of (c) to (d), as no bis(silyl)-methylene compound corresponding to the product expected upon coupling of (d) with trimethylchlorosilane was detected. Although primary carbanions are generally

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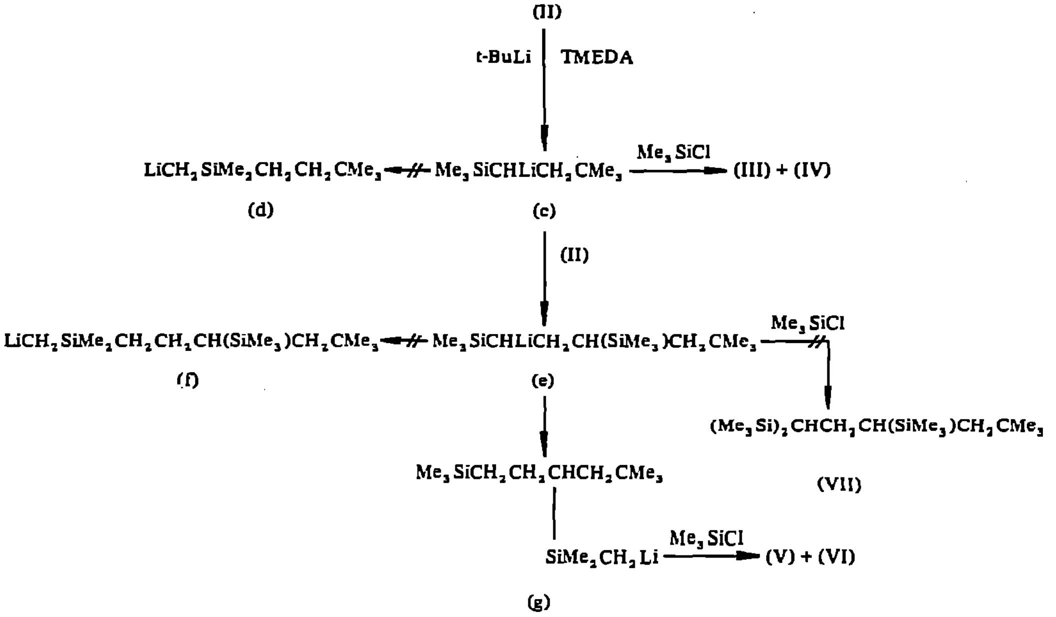
* Metalation of $(Me_3Si)_2C{=}C{=}CHSiMe_3$ occurs with n-butyllithium alone, and appears to result in exclusive metalation at the vinyl position[5]. This is undoubtedly due to resonance stabilization of the resulting carbanion: $[(Me_3Si)C{=}C{\equiv}CSiMe_3]^-$.

** Metalation of the methyl groups of trimethylsilyl halides, also quite reactive towards nucleophilic substitution at silicon, has been reported[3].

SCHEME 2

SUGGESTED REACTION SCHEME FOR THE REACTION BETWEEN VINYLTRIMETHYLSILANE AND TERT-BUTYLLITHIUM/TMEDA



considered to be more thermodynamically stable than secondary species, no facile intramolecular mechanism seems available to (c) under these conditions to effect isomerization. The product (III) is thus presumed to arise directly from (c) by way of proton abstraction from trimethylchlorosilane.

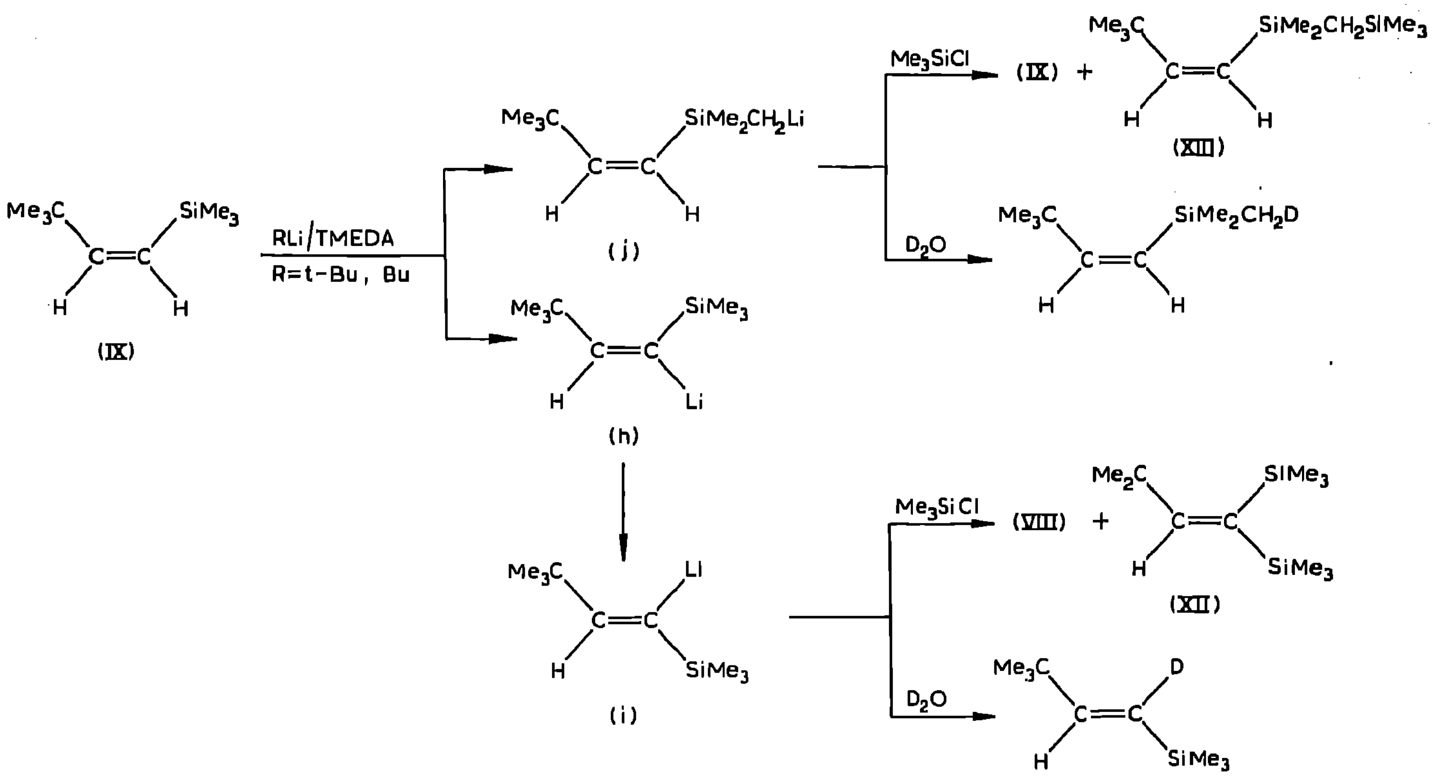
Upon further reaction with additional (II), (c) leads to the intermediate (e), which is postulated to undergo intramolecular isomerization to (g). Models show that the molecular geometry in (e) is ideal for proton transfer from the pendant trimethylsilyl group *via* a six-membered transition state. Although available spectral evidence does not allow a distinction between (VI) and the possible coupling product from (f) and trimethylchlorosilane, (VI) is favored as the structure by analogy to the behavior of (c) (absence of 1,3-proton migration). Supportive of complete rearrangement of (e) is the fact that (VII) was not obtained as a reaction product, even though its analogue, (IV), was produced in high yield from (c). These observations suggest that primary α-silyl carbanions are indeed more stable than their secondary counterparts, but that 1,3-migration is not an energetically allowable mode for their facil interconversion.

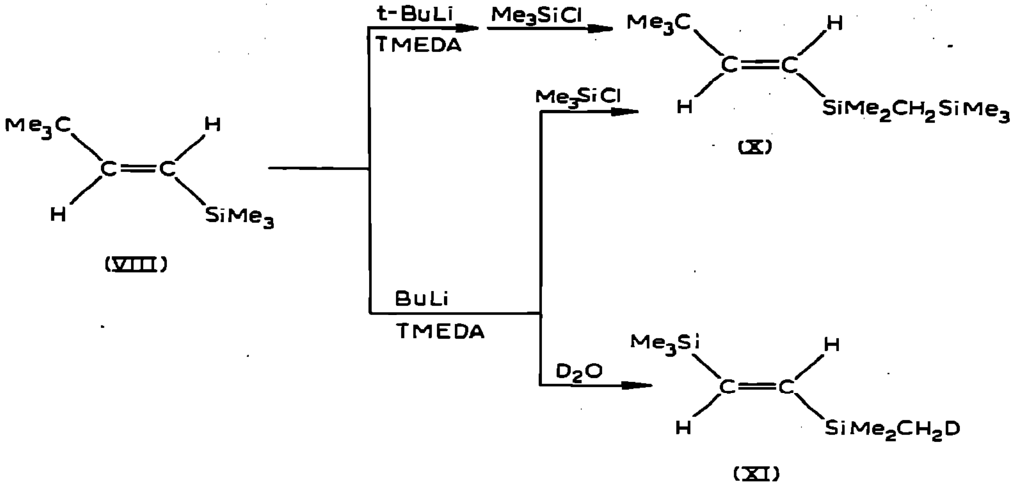
Since metalation of neither sp^3- nor sp^2-hybridized positions in (II) was detectably competitive with addition, a model substrate was sought containing a double bond inert towards addition. For this purpose, the sterically hindered *trans*-(VIII) and *cis*-(IX) isomers of 1-(trimethylsilyl)-3,3-dimethyl-1-butene were utilized.

Treatment of (VIII) with tert-butyllithium/TMEDA in pentane followed by derivatization with trimethylchlorosilane afforded, besides recovered (VIII), only the *trans* methyl-silylated product (X). Since the vinyl proton α to silicon is quite hindered

SCHEME 3

REACTION SCHEME FOR THE METALATION OF *cis*-1-TRIMETHYLSILYL-3,3-DIMETHYL-1-BUTENE (IX)





by the adjacent tert-butyl group, the size of both the metalating and derivatizing agent was reduced. Thus, (VIII) was treated with the n-butyllithium/TMEDA complex followed by derivatization with both trimethylchlorosilane and deuterium oxide. The former again led only to (X) as the silylated product. Analysis of the deuterated product (XI) by NMR indicated that no vinyl deuteration had occurred; instead, the trimethylsilyl group absorption had decreased by the expected factor of one-ninth.

Although these results provided convincing evidence that methyl-metalation was greatly favored over vinyl metalation for (VIII), significantly different results were obtained from metalation studies on the *cis* isomer (IX) (Scheme 3).

When pure (IX) was metalated by tert-butyllithium/TMEDA, followed by reaction with trimethylchlorosilane, the recovered olefins were a 1/8 mixture of (VIII) and (IX)*, respectively, and the trimethylsilylated products consisted of (XII) and (XIII) in a ratio of 2/14. Thus, in contrast to the *trans* isomer (VIII), metalation of (IX) does afford a vinyllithium species (h). The structure of (XII), however, does not allow a choice between (h) and the isomerized (i) as the immediate precursor to (XII). An indication that such isomerization might occur was afforded by hydrolysis of a portion of the reaction mixture prior to derivatization with trimethylchlorosilane. If (i) is the immediate precursor to (XII), hydrolysis will yield a ratio of (VIII) to (IX) which is equal to $(1+2)/(8+14)=3/22$. If (h) is this precursor, this ratio should be $1/(8+2+14)=1/24$. The observed ratio was 3/20, supportive of extensive rearrangement of (h) to (i). Further proof of this point is given below.

The use of n-butyllithium/TMEDA for the metalation of (IX) led to the same products as afforded by tert-butyllithium, but (XII) and (XIII) were now obtained in a 3/1 ratio. To gain further information concerning the nature of the lithiated intermediate directly leading to (XII), metalation of (IX) was carried out with n-butyllithium/TMEDA followed by quenching with deuterium oxide. GLC collected samples of the deuterated (VIII) and (IX) were then examined by NMR. The *trans* isomer (VIII) was found to be 95% deuterated at the vinyl position α to silicon, while the *cis* isomer (IX)

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* Olefins (VIII) and (IX) can arise from either proton abstraction from trimethylchlorosilane by the intermediate organolithium species, or by reaction with traces of moisture.

showed no detectable amount of vinyl deuteration. This confirms that (i) is the species that undergoes derivatization. Although some vinyllithium compounds have moderate configurational stability[11], relief of strain would provide a strong driving force for the isomerization of (h) to (i)*.

Unfortunately, this isomerization precluded equilibration studies of the species (h) and (j) necessary to determine their relative thermodynamic stabilities. Moreover, the methyl-lithiated species obtained from (VIII) was found not to equilibrate with (i) when allowed to stand in contact with excess (VIII) for 15 days [trimethylchlorosilane derivatization of this mixture afforded only (X)]. Although this information is consistent with the premise of enhanced stability for methyl-lithiated over vinyl-lithiated (VIII), it does not require this interpretation. Intermolecular proton exchange may be rendered impossible by the steric inaccessibility of the α-silylvinyl hydrogen in (VIII), while no facile mechanism may exist for intramolecular migration.

Available evidence thus does not allow a resolution of the original question. Although resonance stabilization of these silylmethyl carbanions may be present, the exclusive methyl-metalation of (VIII) could be solely the result of kinetic factors resulting from steric effects. A similar conclusion may be arrived at for the behavior of (IX) with the organolithium reagents employed. The larger (h) to (j) ratio afforded by n-butyllithium (*vs.* the bulkier tert-butyllithium) may be taken as another indication of the importance of steric considerations in this regard.

EXPERIMENTAL

All experiments were carried out under dry nitrogen or helium atmospheres. Apparatus was flame-dried before use and reagents charged to flasks by syringe through septum-stoppered side arms. n-Butyllithium in hexane and tert-butyllithium in pentane were obtained from Foote Mineral Co., Exton, Pennsylvania.

Metalations were carried out by mixing components at −78° and then allowing solutions to warm to 25°. Hydrolysis and trimethylsilylation were conducted at −40° to −78°. All experiments involving alkyllithium reagents and TMEDA were worked up by adding water, acidifying with 2 *N* hydrochloric acid, extracting with pentane or ether and drying over anhydrous magnesium sulfate.

Both *trans*-(VIII) and *cis*-(IX) 1-(trimethylsilyl)-3,5-dimethyl-1-butene were prepared from 1-(trimethylsilyl)-3,5-dimethylbutyne (XIV) by the method of Eisch[12] to give material containing only a trace of the opposite stereoisomer in each case. Small amounts of (XIV) which remained were removed by silver nitrate/potassium cyanide treatment[13]. Olefins were vacuum distilled from calcium hydride before use.

Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, and by Mr. Gary Martinie of this Department. Infrared spectra (recorded to the nearest 0.05 μm) were taken on neat films using a Beckmann IR 8 spectrophotometer. NMR spectra were obtained in capillary tubes in CCl_4 solutions containing benzene as internal standard (taken as δ 7.27) using a Varian A-60A spectrometer. In all cases, integration agreed with the proton assignments made. Gas–liquid chromatographic (GLC) analyses and separations were made using either column A (8 ft. stainless steel

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* It is just barely possible to construct a Fisher/Hirschfelder/Taylor model of (IX); the tert-butyl-trimethylsilyl group interaction is severe.

20% SE-30 on 60/80 mesh Chromosorb W) or column B (10 ft. stainless steel 15% FFAP on 60/80 mesh Chromosorb W) with a Varian-Aerograph Model 1720 gas chromatograph.

Reaction of tert-butyllithium with vinyltrimethylsilane

Vinyltrimethylsilane (4.0 g, 40 mmol) was added dropwise to a mixture of TMEDA (4.7 g, 40 mmol) and 33.3 ml of 1.2 *N* tert-butyllithium in pentane at −20°. After 1$\frac{1}{2}$ h at 25°, 4.4 g (48 mmol) of trimethylchlorosilane was added at −30° and the reaction worked up after 18 h more at 25°. Distillation afforded 5.6 g of material which consisted of the compounds (III)–(VI) in the percentages indicated in the text (as shown by column A, 140°). The amount of distillation residue was negligible.

1-(Trimethylsilyl)-3,3-dimethylbutane (III) afforded the following spectral data: NMR, δ 1.0–1.4 (m, CH_2), δ 0.90 (s, CMe_3), δ 0.2–0.6 (m, $SiCH_2$), δ 0.0 (s, $SiMe_3$); IR: 3.35 s, 3.40 s, 6.80 w, 7.20 vw, 7.30 m, 8.00 s, 8.20 w, 8.60 w, 9.60 vw, 11.25 m, 11.65 s, 12.10 s, 13.25 w, 13.70 vw, 14.55 m μm. (Found: C, 68.05; H, 14.07. $C_9H_{22}Si$ calcd.: C, 68.27; H, 14.01%.)

1,1-Bis(trimethylsilyl)-3,3-dimethylbutane (IV), b.p. 107–110°/20 mm showed NMR absorption at δ 1.44 (d, *J* 4, CH_2), δ 0.90 (s, CMe_3), δ 0.09 (s, $SiMe_3$), δ −0.20 (t, *J* 4, CH); IR: 3.35 s, 3.40 m, 6.80 m, 7.15 w, 7.30 m, 8·00 s, 9.95 m, 11.20 m, 11.55 s, 12.05 vs, 13.15 m, 14.75 m μm. (Found: C, 62.31; H, 12.87. $C_{12}H_{30}Si_2$ calcd.: C, 62.53; H, 13.12%.)

1,3-Bis(trimethylsilyl)-5,5-dimethylhexane (V), b.p. 107–110°/20 mm showed NMR absorption at δ 1.14–1.74 (c, CH_2, CH_2), δ 0.92 (s, CMe_2), δ 0.34–0.76 (m, SiCH, $SiCH_2$), δ 0.03 (s, $SiMe_3$); IR: 3.35 s, 3.40 m, 6.80 w, 7.15 vw, 7.30 w, 8.00 s, 10.95 w, 11.75 s, 12.10 s, 13.40 w, 14.60 m μm. GLC traces of (V) indicated the presence of small but inseparable quantities of impurities. The best analysis obtained was: (Found: C, 64.24; H, 13.28. $C_{14}H_{34}Si_2$ calcd.: C, 65.04; H, 13.26%.)

2,2,4,4,8,8-Hexamethyl-5-(2,2-dimethylpropyl)-2,4,8-trisilanonane (VI), b.p. 100–106°/1 mm showed NMR absorption at δ 1.2–1.8 (m, CH_2, CH_2), δ 0.95 (s, CMe_3), δ 0.4–0.8 (m, SiCH, $SiCH_2$), δ 0.08 (s, $SiMe_3$), δ 0.05 (s, $SiMe_2$), δ 0.02 (s, $SiMe_3$), δ −0.26 (s, $SiCH_2Si$); IR: 3.35 s, 3.40 m, 6.80 m, 7.15 vw, 7.30 w, 8.00 s, 9.55 m, 11.70 s, 12.05 vs, 13.25 m, 14.60 m μm. (Found: C, 62.12; H, 12.80. $C_{17}H_{42}Si_3$ calcd.: C, 61.74; H, 12.80%.)

Metalation of trans-*1-(trimethylsilyl)-3,3-dimethyl-1-butene (VIII)*

A mixture of 0.10 g (0.64 mmol) (VIII), 0.075 g (0.65 mmol) of TMEDA and 0.66 ml (0.79 mmol) of a 1.2 *N* tert-butyllithium in pentane solution was stirred at 25° for 6 h and then derivatized with trimethylchlorosilane. GLC analysis (column B, 90°) showed the presence of only (VIII) and (X); no (XII) or (XIII) was present.

A similar experiment containing (VIII) and tert-butyllithium/TMEDA in a 2/1 molar ratio was carried out in a sealed ampoule for 15 days. Trimethylchlorosilane derivatization again afforded only (X).

In a larger run using 4.0 g of (VIII), distillation after trimethylchlorosilane derivatization afforded 60% of 1,1-bis(trimethylsilyl)-3,3-dimethyl-1-butene (X), b.p. 118–124°/45 mm; distillation residue was negligible. (Found: C, 63.29; H, 12.41. $C_{12}H_{28}Si_2$ calcd.: C, 63.08; H, 12.35%.) Spectral data for (X) was as follows. NMR: δ 5.54 (SiCH=) and 5.99 (=CH) (AB pattern, *J* 19 Hz), δ 1.06 (s, CMe_3), δ 0.12 (s, $SiMe_2$),

δ 0.17 (s, $SiMe_3$), δ −0.19 (s, $SiCH_2Si$); IR: 3.35 s, 3.40 m, 3.45 m, 6.20 m, 6.85 w, 7.15 w, 7.35 m, 8.00 s, 9.55 s, 10.10 m, 12.10 vs, 13.75 m, 14.6 m μm.

Metalation of 2.4 g (15 mmol) (VIII) with 1.7 g (15 mmol) TMEDA and 10.5 ml (16 mmol) of a 1.5 *N* n-butyllithium solution in hexane for 24 h was followed by partitioning of the reaction mixture. One part was treated with trimethylchlorosilane to afford only (X) as the silylated product. The other part was treated with D_2O and the (XI) collected by GLC. NMR analysis showed no evidence for deuterium incorporation at either vinylic position. The peak due to the trimethylsilyl group protons had diminished by a factor of one-ninth relative to the vinyl proton absorptions.

Metalation of cis-1-(trimethylsilyl)-3,3-dimethyl-1-butene (IX)

A mixture of 1.8 g (12 mmol) (IX), 1.4 g (12 mmol) of TMEDA and 10 ml (12 mmol) of a 1.2 *N* tert-butyllithium solution in pentane was stirred at 25° for 2 h and separated into two portions. One portion was treated with trimethylchlorosilane to give the compounds (VIII), (IX), (XII) and (XIII) (order of elution, column B, 110°) in a respective ratio of 1/8/2/14. The other portion was hydrolyzed to give (VIII) and (IX) in a ratio of 3/20. Distillation of the trimethylchlorosilane-treated aliquot afforded 67% [based on recovered (VIII) and (IX)] of the (XII)–(XIII) mixture, b.p. 120–124°/45 mm. Separation of these components was carried out using column B, 100°.

1,1-Bis(trimethylsilyl)-3,3-dimethyl-1-butene, (XII) showed NMR absorption at δ 6.79 (s, CH=), δ 1.16 (s, CMe_3), δ 0.29 (s, $SiMe_3$), δ 0.16 (s, $SiMe_3$); IR: 3.35 s, 3.40 m, 6.45 m, 7.10 vw, 7.35 w, 8.00 s, 8.35 w, 10.55 m, 10.95 w, 11.40 s, 12.00 vs, 13.10 m, 13.55 w, 14.80 m, 15.35 m μm. (Found: C, 63.14; H, 12.46. $C_{12}H_{28}Si_2$ calcd.: C, 63.08; H, 12.35%.)

cis-2,2,5,5,7,7-Hexamethyl-5,7-disila-3-octene, (XIII) showed NMR absorption at δ 5.32 (SiCH=) and 6.28 (=CH) (AB pattern, *J* 15.5 Hz), δ 1.11 (s, CMe_3), δ 0.22 (s, $SiMe_2$), δ 0.08 (s, $SiMe_3$), δ −0.09 (s, $SiCH_2Si$); IR: 3.35 s, 3.40 m, 3.45 w, 6.25 m, 7.10 vw, 7.35 w, 8.00 s, 9.55 s, 12.00 vs, 12.70 s, 13.15 m, 14.70 m μm. (Found: C, 63.44; H, 12.22. $C_{12}H_{28}Si_2$ calcd.: C, 63.08; H, 12.35%.)

A mixture of (IX) (0.5 g, 3.2 mmol), 0.37 g (3.2 mmol) TMEDA and 2.2 ml (3.3 mmol) of 1,5 *N* n-butyllithium was partitioned in two after 6 h at 25°. Trimethylsilylation of one part of the reaction mixture then afforded a 3/1 mixture of (XII) to (XIII). The rest of the reaction mixture was treated with D_2O, and the deuterated (VIII) and (IX) recovered by GLC (column B, 70°). NMR analysis of this d_1-(VIII) showed it to be 95% deuterated at the vinyl position *alpha* to silicon [1/1/1 three-line pattern centered at δ 6.0 (lit.[12] δ 6.07), *J* 3 Hz]*. The usual absorption at δ 5.6 had virtually disappeared. The vinyl portion of (IX) was found to be wholly undeuterated.

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* $J_{H,H}$ = 6.55 $J_{H,D}$[14]. On this basis, the predicted *J* is 19/6.55 = 2.9 Hz.

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