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REACTION OF ORGANOLITHIUM REAGENTS WITH α-CHLOROVINYLTRIMETHYLSILANES

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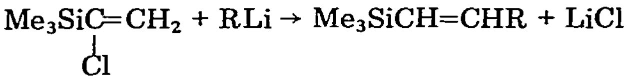
Summary

The reaction of $(CH_3)_3SiC(Cl)=CRR'$ ($R = R' = H$; $R = H$, $R' = CH_3$; $R = R' = CH_3$; $R = R' = C_6H_5$) with organolithium reagents was examined. Alkenylsilanes of structure $(CH_3)_3SiCH=CH$—alkyl were obtained from $(CH_3)_3SiC(Cl)=CH_2$ and alkyllithium reagents. Substrates with R or $R' \neq H$ inhibited addition of the organolithium species to the double bond and led to products derived from chlorine—lithium exchange ($R = R' = C_6H_5$) or proton abstraction from an allylic methyl site ($R = H$, $R' = CH_3$; $R = R' = CH_3$).

Introduction

We have previously described our initial observations concerning the transformation represented by eq. 1, in which treatment of α-chlorovinyltrimethylsilane (I) with n- or t-butyllithium afforded synthetically useful quantities of alkenylsilanes IIa, b [1]. Inasmuch as this method of alkenylsilane preparation was previously unknown, we wished to explore the synthetic scope of the reaction as regards substrates and conditions and to elucidate more fully the pathways by which observed products arose. In particular, the possible extension of the method to include β-substituted analogues of I was of interest, and these findings are reported here.



$$Me_3Si\underset{Cl}{C}=CH_2 + RLi \rightarrow Me_3SiCH=CHR + LiCl \qquad (1)$$

(I) (IV)

(IVa, R = n-Bu)
(IVb, R = t-Bu)
(IVc, R = 3-butenyl)
(IVd, R = allyl)
(IVe, R = phenyl)
(IVf, R = methyl)

TABLE 1

REACTION OF α-CHLOROVINYLTRIMETHYLSILANE (I) WITH ORGANOLITHIUM REAGENTS (RLi) [a]

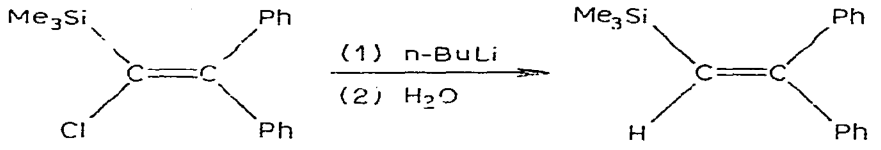
R	Solvent	Temp. (°C)	Reaction Time (h)	Conversion, I (%)	(Products) yield (%) [b]				
					$Me_3SiCH{=}CHR$			$RSiMe_3$	$Me_3SiC{\equiv}CH$
					Total	*trans*	*cis*		
t-Bu	Pentane	−30	1/6	68	(IVb) 73	100	0 [c]		
		25	1	98	(IVb) 84	100	0 [c]	1	6
n-Bu	Hexane	25	48	98	(IVa) 60	84	16	3	3
n-Bu	Hexane	25	72	99	(IVa) 65 [d]	84	16		
3-Butenyl	Hexane	25	36	81	(IVc) 66	82	18	3.5	5
Allyl	Ether/ hexane	25	24	93	(IVd) 58	87 [e]	13 [e]	24	trace
Ph	Ether	25	36	73	(IVe) 1			39	20
Me	Ether	25	70	38	(IVf) 11	82	18	55	11
Me	Ether/ THF	25	43	53	(IVf) 8.5	82	18	67	3
n-Bu	Hexane/ TMEDA	25	24	83	(IVa) 25	84	16	1.5	35
t-Bu	Pentane/ TMEDA	25	24	93	(IVb) 21	100	0 [e]	0.5	30

[a] Equimolar amounts of I and RLi. [b] Yields are based on consumed I and were determined by GLC except as noted. [c] A trace of material which might have been *cis* isomer was also indicated by GLC. [d] Yield based on isolated material. [e] Not separated by GLC; isomer ratio determined from NMR data.

Results

Table 1 summarizes the behaviour of I with a variety of organolithium reagents. Of the combinations tried, good yields of alkenyltrimethylsilanes were only realized from the use of n- and t-butyllithium and from 3-butenyllithium. A somewhat lower yield of expected product was obtained from allyllithium, while in the instances of methyl- and phenyllithium, the main course of reaction was diverted to elimination, rather than addition products. Variation in solvents caused little effect on the yields of products obtained from the reaction of n-butyllithium with I, although strong rate acceleration occurred in ether and THF (Table 2). Addition of tetramethylethylenediamine (TMEDA) to runs employing n- or t-butyllithium led to a severe reduction in the amount of alkenylsilane obtained, and enhanced the formation of ethynyltrimethylsilane by an elimination process (see Discussion).

In order to assess the ability of β-substituted α-chlorovinyltrimethylsilanes to undergo the process described by eq. 1 the behaviour of three mono- and di-substituted olefins with n- and t-butyllithium was examined. Results obtained from the diphenyl substrate XIV were least interesting, as apparent lithium—chlorine exchange led principally to XV after hydrolysis (eq. 2). Treatment of *E*-β-methyl α-chlorovinyltrimethylsilane (VIII) with either n- or t-butyllithium led to some of the expected alkenylsilanes, but trimethylsilylcyclopropanes incorporating the butyl moieties were also obtained (Table 3; Scheme 5). Under similar conditions, β,β-dimethyl-α-chlorovinyltrimethylsilane (XI) gave only cyclopropyl compounds with n-butyllithium. The preparative value of the transformation



(2)

(XIV) (XV)

TABLE 2

REACTION OF n-BUTYLLITHIUM WITH α-CHLOROVINYLTRIMETHYLSILANE (I) IN VARIOUS SOLVENTS

Solvent	Temp. (°C)	Conversion of I (%)/ total time (h)	Yield IVa [a] (%)	$t_{1/2}$
Hexane	25	70/48	72	23 h
Hexane/ cyclohexene	25	69/66	82	18 h
Hexane/ benzene	25	73/46	88	13 h
Hexane/ ether	—10 to 25 [b]	90/4	70	21 min
Hexane/ THF	—25	87/4	73	<2 min

[a] Based on consumed I. [b] I added at —10°C and warmed to 25°C over 15 min.

TABLE 3

REACTION OF β-SUBSTITUTED-α-CHLOROVINYLTRIMETHYLSILANES WITH ALKYLLITHIUM REAGENTS

$Me_3SiC(Cl)$=CR(1)R(2)	RLi, R =	Solvent	Time (h)	Temp. (°C)	(%) Consumed	Products (yield) (%) [a]
XIV	n-Bu	hexane	72	25	0	
XIV	n-Bu	hexane	14	68	100	XV (75)
XIV	n-Bu	hexane/ ether	25	25	76	XV (60)
VIII	t-Bu	pentane	47	25	80	IXB-*t* (20), IXb-*c* (4), Xb (26)
VIII	n-Bu	hexane/ ether	24	25	85	IXa + Xa (45)
XI	n-Bu	hexane	24	25	17	[b]
XI	n-Bu	hexane/ ether	25	25	92	XII + XII′ (54), XIII (33)

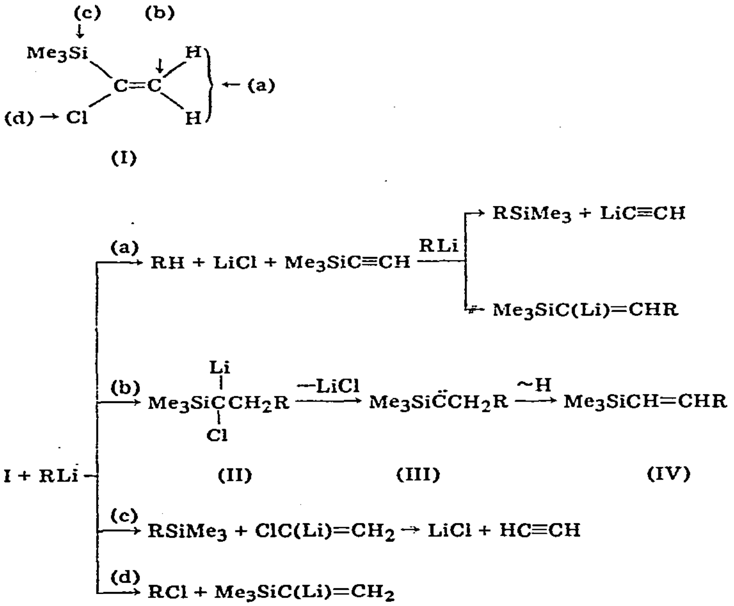
[a] Yields based on consumed chloroolefin. [b] Not determined.

represented by eq. 1 is thus limited to the use of the unsubstituted α-chlorovinyltrimethylsilane (I). n-Butylmagnesium bromide could not be substituted for n-butyllithium in this reaction (see Discussion).

Discussion

The ability of organolithium reagents to add to vinylsilanes so as to form α-lithioalkylsilanes has been demonstrated in a variety of systems [2]. At least part of the driving force for these reactions lies in the ability of silicon to stabilize an adjacent carbanion [3]. In the present system (Scheme 1, path b), addition of an organolithium reagent to I is thought to produce the carbenoid II as an intermediate on the pathway to IV. The preparation of similar intermediates [$Me_3SiCH(Li)Cl$ and $Me_3SiCH(Li)(CH_3)Cl$] has been reported recently, and these have been shown to possess low-temperature stability [4]. Under ambient conditions, II would be expected to suffer geminal elimination and β-hydrogen migration to form the alkenylsilane IV [5]. This process is envisioned as possibly (but not necessarily) proceeding through the intermediary of carbene III (Scheme 1). The stereochemistry of the products (predominantly *trans*-olefin forms) is well explained on the basis that the major product arises from the predominant conformation of the carbenoid (or carbene). Thus, for large R, either IIA or IIB would be the major precursor to IV, as it is the β-hydrogen coplanar with the extant (or developing) carbenic *p* orbital which is predicted to undergo preferential migration [6].

SCHEME 1. POSSIBLE REACTION MODES OF α-CHLOROVINYLTRIMETHYLSILANE WITH ORGANOLITHIUM REAGENTS [a]



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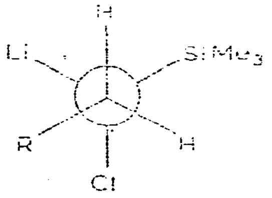
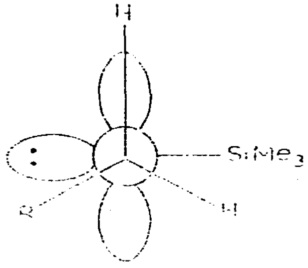
[a] Sites of initial carbanionic attack are lettered.



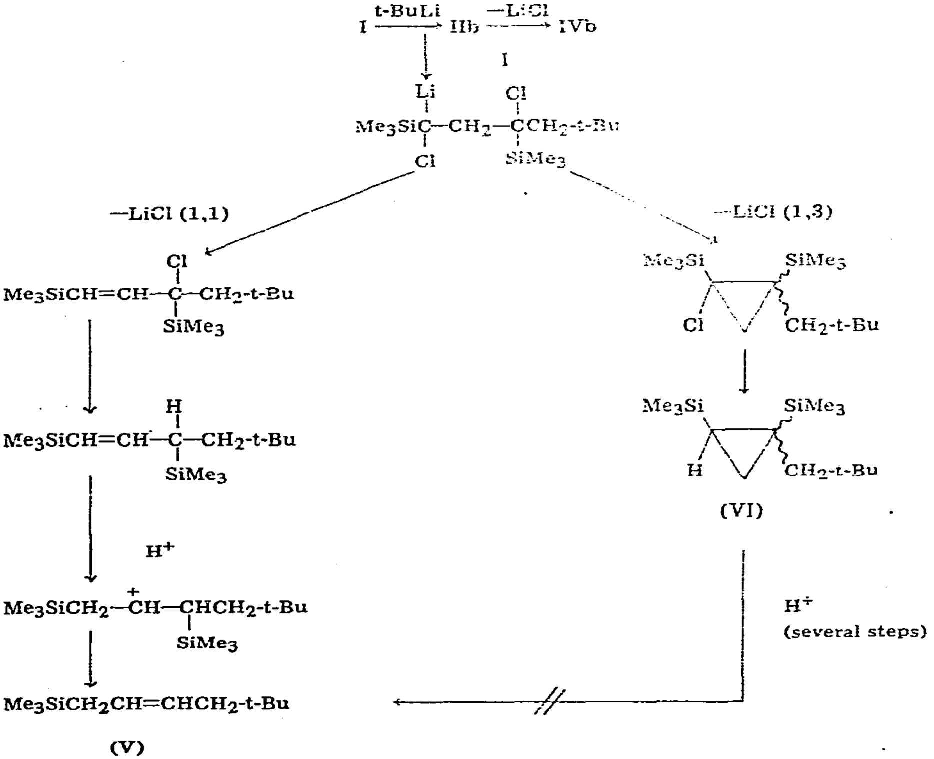
(IIA)



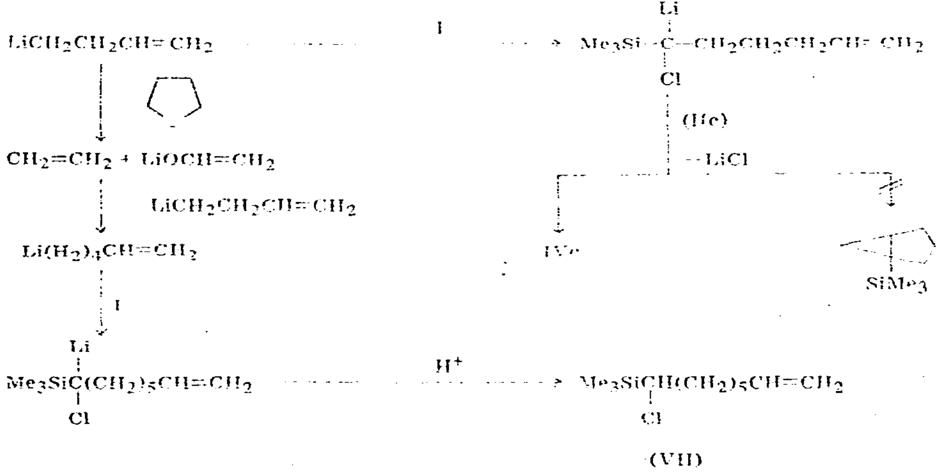
(IIB)

Several attempts were made to confirm the intermediacy of carbenoid species by trapping experiments. The most straightforward of these appeared to be protonation of carbenoid II at low temperatures to afford an α-chloroalkyltrimethylsilane. However, addition of n-butyllithium or t-butyllithium to I did not occur at −100°C. When t-butyllithium was allowed to react with I at −78°C, followed by a methanolic HCl quench, a mixture of products was obtained which included IVb, the *cis* and *trans* isomers of (5,5-dimethyl-2-hexenyl)trimethylsilane (V) and the *cis* and *trans* isomers of 1-neopentyl-1,2-bis(trimethylsilyl)cyclopropane (VI). Scheme 2 suggests a route by which V and

SCHEME 2. POSSIBLE BEHAVIOR OF THE SYSTEM α-CHLOROVINYLTRIMETHYLSILANE/t-BUTYLLITHIUM AT −78°C



SCHEME 3. THE REACTION OF α-CHLOROVINYLTRIMETHYLSILANE WITH 3-BUTENYLLITHIUM



VI may arise. Precedents exist for the cyclization of transient 3-haloalkyllithium species [7], while isomeric acyclic material will result from a geminal elimination of LiCl (followed by hydride migration) identical to that involved in the formation of vinylsilane IV. Reduction of the crowded alkyl chlorides thus produced may have been effected by excess t-butyllithium [8] or could result from a metal—halogen exchange/protonation (upon workup) sequence. Subsequent protonation of the alkene could then effect desilylation of V *. Confirmation of the sequence leading to the olefin V was not attempted, but it was shown that cyclopropane VI does not serve as progenitor to V via acid-catalysed ring opening.

In an attempt to capture the intermediate carbenoid or carbene intramolecularly, I was treated with 3-butenyllithium at —65°C and subsequently quenched with methanolic HCl **. No "internal capture" product of the carbenoid IIc was found (Scheme 3). Instead, the "normal" product IVc was obtained, together with VII. Solutions of organolithium reagents in THF are known to generate ethylene, which could then add the organolithium reagent present [10]. However, it is not clear why VII should be formed under these conditions to the exclusion of the silane derivable from protonation of IIc.

The data of Table I indicate that alkyltrimethylsilanes and ethynyltrimethylsilane accompany the formation of alkenylsilanes IV in the reaction of I with various organolithium reagents. Ethynyltrimethylsilane most likely arises from the vicinal dehydrohalogenation of I by the organolithium species employed (Scheme 1, path a). This interpretation is supported by the higher $Me_3SiC{\equiv}CH$/IV ratio when TMEDA is added to mixtures of I and n- or t-butyllithium, as TMEDA exerts a base-enhancing effect on such reagents [11]. The use of allyl-, phenyl- and methyl-lithium in these reactions also leads to significant amounts of "by-products" at the expense of IV. These results, however, may stem from

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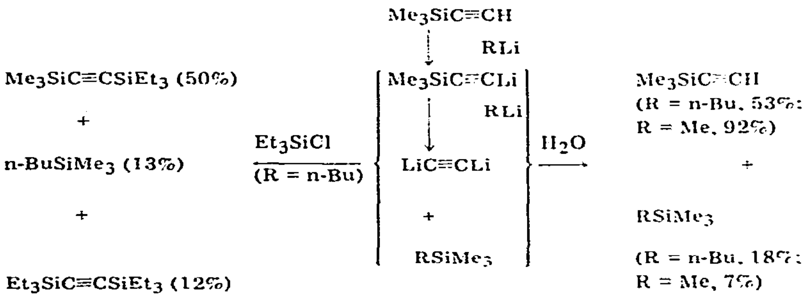
* Loss of that trimethylsilyl group which leads to V is indicated on thermodynamic grounds.

** Kirmse and Grassman have obtained bicyclic intramolecular addition products from unsaturated carbenes (diazo precursors) [9].

SCHEME 4. REACTION OF ETHYNYLTRIMETHYLSILANE WITH ALKYLLITHIUM REAGENTS



a decreased reactivity towards π-bond addition which allows dehydrohalogenation to become more competitive [12]. Several points of interest were established by allowing ethynyltrimethylsilane to react with methyl- and n-butyllithium under conditions similar to those used to generate IV from I. Water quench of these reactions produced no IV, signifying that ethynyltrimethylsilane does not add these organolithium reagents to form α-lithiovinyltrimethylsilane, a possible precursor to IV (Scheme 1, path a). On the other hand, tetramethylsilane and n-butyltrimethylsilane were produced (Scheme 4) suggesting that either ethynyltrimethylsilane itself (Scheme 1) or lithium trimethylsilylacetylide (Scheme 4) can act as a silyl donor to the organolithium reagent present *. Although pathway c of Scheme 1 remains a possible alternative source of alkyltrimethylsilane, its operation seems less likely in view of the behaviour of the diphenyl substrate XIV with n-butyllithium, discussed below. As a final comment on the possible behavior of I with alkyllithium reagents, we note that products expected from Scheme 1, path d (alkyl chloride and vinyltrimethylsilane) were not found when a reaction between n-butyllithium and I was examined for this purpose.

The reaction of n-butyllithium with I in various solvent combinations was examined with a view towards optimizing conditions (Table 2). Although little change in the yields of IVa resulted, a marked increase in rate occurred in proceeding to solvents of greater electron-donating abilities. These results are consistent with previous data detailing the enhancing effect of ethereal solvents on the rate of alkyllithium additions to ethylene [14].

β-Substituted α-chlorovinyltrimethylsilanes were expected to add alkyllithium reagents sluggishly on steric grounds. In fact, several different reaction modes were observed depending on substitution type (eq. 2 and Scheme 5). The major product (XV) obtained from XIV and n-butyllithium most likely is the end result of lithium—chlorine exchange followed by protonation of the intermediate α-silylvinyllithium species. Attack of n-butyllithium at the trimethylsilyl group of XIV would have generated diphenylacetylene via rearrangement

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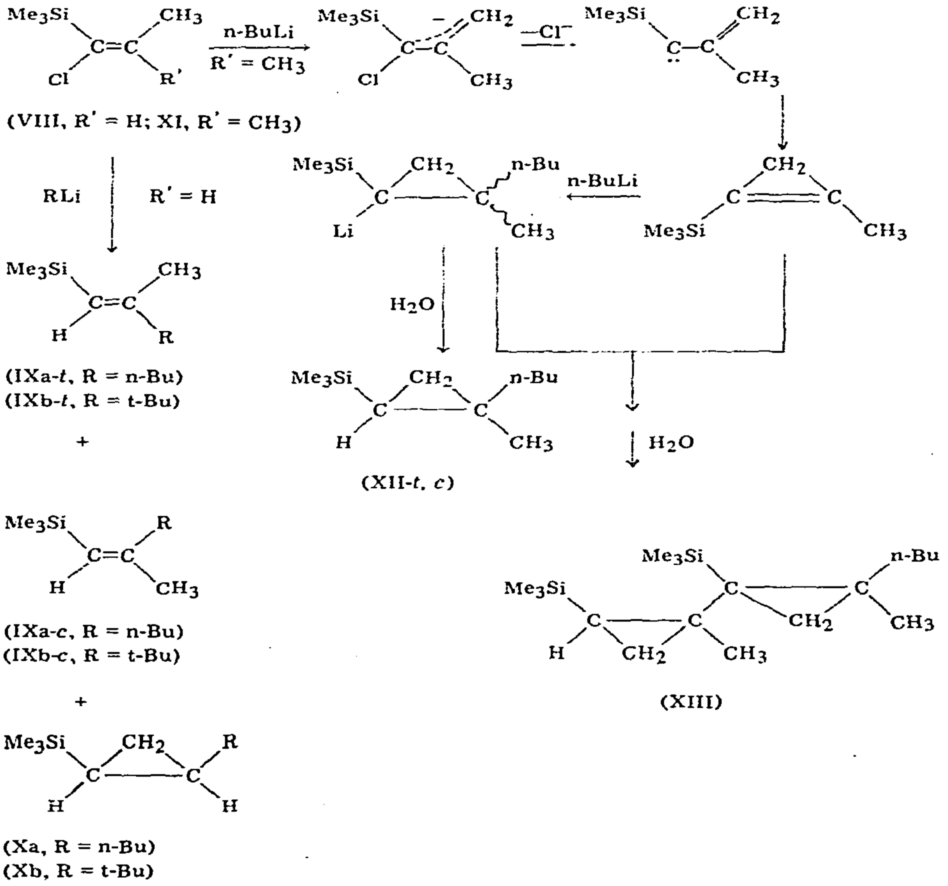
* The known disproportion of lithium acetylide to dilithium acetylide [13] precludes the choice of one of these pathways on the basis of, e.g., the absence of ethynyltriethylsilane among the products of Scheme 4.

SCHEME 5. REACTION MODES OF β-SUBSTITUTED-α-CHLOROVINYLTRIMETHYLSILANES WITH ALKYLLITHIUM REAGENTS



of an α-chlorovinyl carbanion [15]. No trace of this acetylene was found in these runs, which also suggests that the analogue of this process (Scheme 1, path c) is not the source of alkyltrimethylsilanes generated in the reaction of organolithium reagents with I.

Introduction of two methyl groups as β-substituents (in the alkenylsilane XI) again led to complete suppression of π-bond addition. Instead, metalation of the relatively acidic allylic sites led to cyclopropyl compounds XII and XIII by a process interpreted in Scheme 5 *. Vinylcarbenes (or carbenoids) are known to afford cyclopropanes from intramolecular π-bond insertion [17]. The resulting cyclopropene π-bond would be receptive towards n-butyllithium addition due to strain [18], and in the present instance, simultaneous formation of a cyclopropyllithium species additionally stabilized by an adjacent silyl group. The isolation of XIII serves as corroboration of the process proposed for the formation of XII, since the bis-cyclopropane may logically arise from cross-reaction of the immediate precursors to XII. Additional evidence that a

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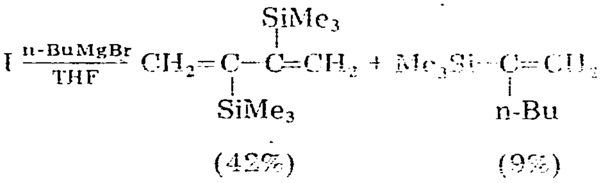
* A similar observation within a non-silicon system has recently come to our attention [16].

cyclopropyllithium species serves as intermediary was obtained by hydrolyzing a separate experiment with D_2O. ^1H NMR analysis of the isolated XII isomeric mixture indicated a 35% deuterium incorporation at the cyclopropyl carbon α to silicon.

Reactions between β-monomethyl substrate VIII and n- or t-butyllithium gave rise to products derived from both π-bond addition and β-methyl proton abstraction (Scheme 5). Thus, the use of t-butyllithium afforded two mixtures of isomers: IXb-*t*/IXb-*c* and Xb-*t*/Xb-*c* (Table 3). In each case, the *trans* isomer was formed in preponderance. The reaction of VIII with n-butyllithium exhibited behavior which appeared to parallel that described above, but experimental difficulties precluded a full characterization of this system. In sum, we believe olefins IXb and IXa arise via path b of Scheme 1, while cyclopropanes Xb and Xa result from the same sequence of events described in Scheme 5 for the formation of biscyclopropane XII.

Vinylsilanes have been shown to add Grignard reagents across the double bond, although in only low yields in the instance of vinyltrimethylsilane [19]. When I was allowed to react with n-butylmagnesium bromide in THF, no IVa was formed. Instead, products were obtained which most likely arose from metal—halogen exchange and coupling processes [20] (eq. 3).



$$\mathrm{I} \xrightarrow[\text{THF}]{\text{n-BuMgBr}} \underset{\text{(42\%)}}{CH_2{=}\underset{\underset{}{SiMe_3}}{C}{-}\overset{SiMe_3}{C}{=}CH_2} + \underset{\text{(9\%)}}{Me_3Si{-}\underset{\text{n-Bu}}{C}{=}CH_2} \qquad (3)$$

Experimental

General

Infrared (IR) data were obtained on neat films using Beckman IR-8 and Perkin—Elmer 237 spectrophotometers. ^1H NMR spectra were recorded on a Varian A60-A spectrometer unless otherwise indicated; a JEOL PFT-100 instrument was used to obtain spectra at 100 MHz. Spectra were obtained on samples in capillary tubes in CCl_4 solvent with benzene (taken as δ 7.24) as internal standard unless otherwise indicated (solvent, internal standard listed sequentially). Analytical and preparative GLC work utilized the following 0.25 in. stainless steel columns prepared on 60/80 Chromosorb W: (A) 10 ft. 20% SE-30; (B) 15 ft. 15% TCEP; (C) 15 ft. 15% Carbowax 20M; (D) 15 ft. 15% FFAP. The following 0.375 in. columns were also used: (E) 20 ft. 25% FFAP; (F) 20 ft. 30% SE-30. GLC yields were obtained using internal standards after determination of relative response ratios. Unless boiling points are stated, product isolation was effected throughout by preparative GLC. Mass spectra were obtained at 70 eV using a Hitachi RMU-6E spectrometer.

Ethereal solvents were distilled from $LiAlH_4$; chlorotrimethylsilane, TMEDA and HMPA were distilled from calcium hydride. Hexane used in the preparation of organolithium reagents was rendered olefin-free by treatment with concentrated H_2SO_4. n-Butyllithium (n-BuLi) in hexane was obtained from both Alfa Division of Ventron Corporation and Foote Mineral Co. t-Butyllithium (t-BuLi) was obtained from Foote Mineral Co. The normality of organolithium reagents was determined by double titration using 1,2-dibromoethane [21]. Except where noted, all reactions were run under nitrogen.

Reaction of α-chlorovinyltrimethylsilane (I) with organolithium reagents

(A) With n-butyllithium. A 15.5 mmole sample of n-BuLi in hexane was treated dropwise at −25°C with 2.0 g (15.0 mmole) of I [22]. After an additional 48 h at 25°C, the reaction mixture was poured into ice water and worked up. GLC analysis (columns A, E) indicated a 60% yield of *cis*- and *trans*-IV [23] as entered in Table 1. The *cis*-IVa isomer showed IR: 6.21m, 8.01s, 12.0s, 13.16m μm and ^{1}H NMR: δ −0.02 (9 H, s), 0.79 (3 H, m), 1.22 (4 H, m), 2.02 (2 H, m), 5.29 (1 H, d of t, J = 14, 1.5 Hz), 6.16 (1 H, d of t, J = 14, 7 Hz). The *trans*-IVa isomer showed IR: 6.18m, 8.01s, 10.13m, 11.62s, 12.00s μm and ^{1}H NMR (CCl_4, ext. $CHCl_3$ taken as δ 7.24): δ −0.15 (9 H, s), 0.73 (3 H, m), 1.14 (4 H, m), 1.91 (2 H, m), 5.31 (1 H, d, J = 19 Hz), 5.82 (1 H, d or t, J = 19.5 Hz).

In a preparative run, 9.8 g (73 mmol) of I afforded 7.3 g (65%) of IVa (84/16 *trans*/*cis* mixture), b.p. 156—158°C/760 mmHg, of 97% purity.

(B) With t-butyllithium. In the same manner as in part A, 2.4 g (18 mmol) of I and 21 mmol t-BuLi in pentane, initially at −30°C and then at 25°C, gave an 84% yield of *trans*-IVb [23,24].

(C) With 3-butenyllithium [25]. Di-3-butenylmercury [25] was prepared in 65% yield (b.p. 103—104°C/14 mmHg, 98% pure) by adding one equivalent $HgCl_2$ (dissolved in THF) to two equivalents of 3-butenylmagnesium bromide in THF. 3-Butenyllithium was then prepared by chopping 1.5 g (0.22 mmol) of lithium wire (1% Na) in 100 ml hexane with a high-speed stirrer (Morton flask with helium atmosphere). After addition of 50 mmol di-3-butenylmercury, the high speed stirrer was replaced by a magnetic stirrer and the reaction flask sealed with wax. Monitoring by GLC indicated total consumption of di-3-butenylmercury after 8 days at 25°C. Filtration afforded a quantitative yield of 3-butenyllithium, as indicated by double titration. Treatment of an aliquot with trimethylchlorosilane afforded 3-butenyltrimethylsilane [26]. Anal.: Found: C, 65.27; H, 12.78. $C_7H_{16}Si$ calcd.: C, 65.54; H, 12.57%. IR: 6.09m, 8.01s, 10.09m, 11.08s, 11.66s, 12.03s, 13.23m, 14.53m μm. ^{1}H NMR: δ −0.17 (9 H, s), 0.28—0.61 (2 H, m), 1.66—2.13 (2 H, m), 4.51—5.01 (2 H, m), 5.34—5.91 (1 H, m).

Following the same procedure as in A, 4.8 g (36 mmol) of I was allowed to react with 35 mmol of 3-butenyllithium. An isomer mixture of *trans*- and *cis*-IVc was obtained (columns A, F) as indicated in Table 1. No intramolecular insertion product was observed by GLC. Anal.: Found (IVc, *trans*): C, 70.13; H, 11.55. $C_9H_{18}Si$ calcd.: C, 70.13; H, 11.69%. ^{1}H NMR: δ −0.17 (9 H, s), 1.96 (4 H, m), 4.57—4.97 (2 H, m), 5.18—5.85 (3 H, m, $J(SiC\underline{H})$ = 19 Hz). Anal.: Found (IVc, *cis*): C, 70.09; H, 11.61. ^{1}H NMR: δ 0.00 (9 H, s), 2.05 (4 H, m), 4.67—5.10 (2 H, m), 5.20—6.37 (3 H, m, $J[SiC\underline{H}{=}CH]$ = 14 Hz.

(D) With allyllithium. Allyllithium was prepared by the addition of 25 mmol n-BuLi in hexane to 8.05 g (25 mmol) allyltri-n-butyltin [27] in ether. GLC indicated that no allyltri-n-butyltin remained after 25 min. Derivatization by trimethylchlorosilane afforded 90.5% allyltrimethylsilane, taken as the

measure of allyllithium concentration; no n-butyltrimethylsilane was observed by GLC. To a solution of allyllithium thus prepared was added 2.80 g (21 mmol) of I at 25°C. After one day, the results shown in Table 1 were obtained. The isomeric products (IVd) could not be separated by GLC on B, C or SE-30 columns, but were inferred to be in a 90/10 *trans*/*cis* ratio by examination of the NMR spectrum of the mixture *. Anal.: Found (IVd, *cis* + *trans*): C, 68.74; H, 11.22. $C_8H_{16}Si$ calcd.: C, 68.49; H, 11.50%. ^{1}H NMR: δ 0.01s (*trans*) and 0.06s (*cis*) (9 H), 2.78 (2 H, m), 4.84 (1 H, m), 5.05 (1 H, m), 5.15—6.32 (3 H, m).

(E) With phenyllithium. A 4.4 g (33 mmol) sample of I was allowed to react with 43 mmol of phenyllithium and the progress of the reaction followed by GLC (column A). Results are shown in Table 1. The presence of β-trimethylsilylstyrene was confirmed by spectral data [29].

(F). With methyllithium. A 1/1 molar ratio of methyllithium and I was used; results (columns A, F) are shown in Table 1. *cis*-1-propenyltrimethylsilane [30] gave an ^{1}H NMR spectrum showing δ 0.09 (9 H, s),as the Me_3Si resonance, while the *trans*-isomer [30] displayed δ 0.02 (9 H, s) for this group.

(G) With alkyllithium reagents and TMEDA. Equimolar amounts of alkyllithium reagent and TMEDA were mixed at —25°C, allowed to warm to 25°C, and an equivalent amount of I then added. Results (columns A, Z) are shown in Table 1.

Attempts at trapping the carbenoid

(A) With n-butyllithium or t-butyllithium. A mixture of 25 mmol of either n-BuLi or t-BuLi, 17 ml hexane (n-BuLi), or 20 ml pentane (t-BuLi), plus 20 ml THF and 5 ml ether [31] was prepared at —78°C. After further cooling to —100°C, 25 mmol of I was added dropwise and the mixture stirred 0.5 h at —100°C. The reaction mixture was then quenched with methanolic HCl; GLC analysis indicated that no reaction had taken place.

When the above reaction was repeated with t-BuLi at —78°C for one hour, 96% of I was consumed to afford (column A) 18% of an isomeric mixture of IV, 25% of a mixture of *cis*- and *trans*-(5,5-dimethyl-2-hexenyl)trimethylsilane (V) [32] and the isomeric cyclopropyl compounds XVI and XVI′ in 3% and 12% yields. MS (*cis*-V): *m*/*e* = 184 (93), 169 (74), 141 (40), 127 (98), 111 (37), 73 (100). IR: 6.07w, 7.18w, 7.33m, 8.02s, 8.67m, 11.8vs μm. ^{1}H NMR: δ —0.03 (9 H, s), 0.86 (9 H, s), 1.38 (2 H, m), 1.82 (2 H, m), 5.31 (2 H, m). MS (*trans*-V): *m*/*e* = 184 (95), 169 (75), 141 (39), 127 (99), 111 (36), 73 (100). IR: 6.05w, 7.19w, 7.33m, 8.02s, 8.65m, 10.36m, 11.8vs μm. ^{1}H NMR: δ —0.04 (9 H, s), 0.82 (9 H, s), 1.35 (2 H, m), 1.81 (2 H, m), 5.24 (2 H, m) **. MS (VI): *m*/*e* = 256 (8), 2.41 (11), 199 (67), 182 (7), 110 (90), 73 (100), 57 (43). IR: 6.81m, 7.18m, 7.33m, 8.02s, 10.18m, 12.0vs, 13.33m, 14.65m, 15.56m μm. ^{1}H NMR (100 MHz): δ —0.21 (SiCH, d of d, *J* = 8, 10 Hz), 0.04 (CH-t-Bu, d, *J* = 15 Hz), 0.06 ($SiMe_3$, s), 0.08 ($SiMe_3$, s), 0.25 (cyclopropyl

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* In a series of α,β-disubstituted vinyltrimethylsilanes, the methyl resonance of a trimethylsilyl group within the *Z* isomer was found to be downfield of that of the corresponding *E* isomer [28].

** Spectral data confirmed by preparation of authentic sample [32]. Literature data quotes *tau* 5.25 for the chemical shift of these olefinic protons [32].

HC<u>H</u>, pattern obscured, $J = 10, 3$ Hz), 0.48 (cyclopropyl <u>H</u>CH, d of d, $J = 8, 3$ Hz), 0.92 (CH-t-Bu, d, $J = 15$ Hz), MS (VI′): $m/e = 256$ (4), 241 (7), 182 (17), 110 (100), 73 (73), 57 (49). IR: Virtually identical to that of VI, except 10.64w replaced by 10.53w and 10.99w by 10.84w μm. ^{1}H NMR (100 MHz): δ −0.48 (SiCH, d of d, $J = 7, 10$ Hz), −0.02 ($SiMe_3$, s), 0.03 ($SiMe_3$, s), 0.15 (CH-t-Bu, d, $J = 14$ Hz), 0.5—1.1 (cyclopropyl HCH, m, pattern obscured), 0.93 (CH-t-Bu, d, $J = 14$ Hz), 0.94 ($SiMe_3$, s). The unusually high-field absorptions assigned to the methylene hydrogens of the neopentyl group may be due to restricted rotation which places at least one of these hydrogens principally within the shielding zone of the cyclopropyl ring [33].

A duplicate run of the above, carried out at −60°C for 5 min before quench, consumed 99% of I and afforded 40% IVb, 8% of *cis*- and *trans*-V, plus 0.5% VI and 3% VI′. Treatment of isolated VI/VI′ with methanolic HCl in THF, with or without added water, did not afford V.

(B) With 3-butenyllithium. A mixture of 2.73 g (20.4 mmol) of I, 30 ml THF and 5 ml ether was cooled to −65°C and treated dropwise with 20.4 mmol of precooled (−65°C) 3-butenyllithium in hexane. After 4.5 h, anhydrous methanolic HCl was added. GLC analysis (column A) showed a 19% consumption of I, and formation of IVc (47%) and 1-chloro-7-octenyltrimethylsilane (32%). Anal.: Found: C, 60.34; H, 10.38; Cl, 16.28. $C_{11}H_{23}ClSi$ calcd.: C, 60.37; H, 10.59; Cl, 16.20%. IR: 6.09m, 6.94m, 8.01s, 8.72m, 10.09m, 11.02s, 11.9vs, 13.39m, 14.45m μm. ^{1}H NMR: δ 0.05 (9 H, s), 1.3—2.3 (10 H, m), 3.12 (1 H, m), 4.72—5.12 (2 H, m), 5.5—5.9 (1 H, m).

Reaction of ethynyltrimethylsilane with organolithium reagents

A 2.0 g (20 mmol) sample of ethynyltrimethylsilane was added dropwise to 25 mmol of n-BuLi in hexane at −25°C. The mixture was allowed to warm to 25°C and stirred for 22.5 h, during which time white solid appeared. A solution of 3.35 g (22.3 mmol) chlorotriethylsilane in 10 ml THF was then added, and the reaction worked up 17.5 h later with water. GLC analysis (columns A, D) indicated a 50% yield of triethylsilyltrimethylsilylacetylene [34], 12% bis(triethylsilyl)acetylene [35], 12% n-butyltrimethylsilane and 8% n-butyltriethylsilane.

A similar run, allowed to stir 68 h at 25°C, was poured into saturated NH_4Cl solution. A product mixture consisting of 53% ethynyltrimethylsilane, 18% n-butyltrimethylsilane and 3% bis(trimethylsilyl)acetylene was obtained. No IV was present in either run, as ascertained by GLC comparison using an authentic sample.

When 2.15 g (21.9 mmol) ethynyltrimethylsilane was allowed to react with 21.9 mmol methyllithium in 17 ml ether for 42 h followed by a hydrolytic workup, 7% tetramethylsilane, a trace of bis(trimethylsilyl)acetylene and 92% ethynyltrimethylsilane was obtained. Again, no IVf was present.

Half-life determinations

Mixtures of n-BuLi in hexane (2.25 *M*) and the appropriate co-solvent were prepared so as to afford 1.125 *M* solutions. These were controlled isothermally at 25 ± 0.5°C, an equivalent amount of I added, and aliquots withdrawn periodically for water quench and analysis (column A). Plots of time vs. % consumption of I were prepared, and $t_{1/2}$ values extracted.

Reaction of α-chloro-β,β-dimethylvinyltrimethylsilane (XI) with n-butyllithium

A mixture of 37 mmol n-BuLi and 50 ml ether was treated with 5.5 g (34 mmol) of XI [36] at 25°C and the mixture poured into saturated NH_4Cl solution after one day. GLC analysis (column A) indicated a 92% consumption of XI, and the formation of two isomeric products in 35% (XII) and 19% (XII′) yields. These were identified as *cis*- and *trans*-1-n-butyl-1-methyl-2-trimethylsilylcyclopropane, but isomeric assignments could not be made. An additional isomeric mixture (33% yield) was disclosed by GLC analysis of the reaction mixture at higher temperatures (column D, 150°C), but these products could not be separated by GLC. Spectral and analytical data obtained on this mixture were most consistent with the gross structure 1-n-butyl-1-methyl-2-(1′-methyl-2′-trimethylsilylcyclopropyl)-2-trimethylsilylcyclopropane (XIII). When XI and n-BuLi were allowed to react in hexane alone at 25°C, only 17% of XI was consumed after one day. Anal.: Found: (XII): C, 71.82; H, 13.09. $C_{11}H_{24}Si$ calcd.: C, 71.65; H, 13.12%. IR: 6.87m, 7.23m, 7.40w, 8.02s, 9.40w, 9.46w, 9.70w, 9.83w, 10.50w, 10.74m, 11.11m, 12.01s, 13.28m. 14.57m, 15.3m μm. ^1H NMR: δ −0.60 (1 H, d, of d, J = 7, 10 Hz), 0.02 (9 H, s), 0.23 (1 H, d of d, J = 3, 7 Hz), 0.49 (1 H, d of d, J 3, 10 Hz), 0.7—1.1(m) plus 1.03(s) (6 H), 1.1—1.6 (m) (6 H). Anal: Found (XII′): C, 71.93; H, 13.14%. IR: identical to that of XII, except additional band at 9.31m μm. ^1H NMR: δ −0.63 (1 H, d of d, J = 7, 10 Hz), −0.01 (9 H, s), 0.21 (1 H, d of d, J = 3 Hz), 0.47 (1 H, d of d, J = 3, 10 Hz), 0.7—1.1 (m) plus 1.02 (s) (6 H), 1.1—1.6 (m) (6 H). Anal.: Found (XIII): C, 69.47; H, 12.28. $C_{18}H_{38}Si_2$ calcd.: C, 69.59; H, 12.33%. The ^1H NMR spectrum displayed multiplets at δ −0.8 to −0.3 (1 H, cyclopropyl Si—C—H), 0.0—0.7 (22 H, Me_3Si and cyclopropyl CH_2) and 0.7—1.7 (15 H, CH_3 and CH_2).

Evidence for the existence of a carbanionic precursor to the observed products was obtained in the following way. Reaction of 2.04 g (12.5 mmol) of XI with 37.5 mmol of n-BuLi in 15 ml hexane and 10 ml ether was carried out for 7.5 h, after which time 3 ml of D_2O was added at 0°C. After workup the XII/XII′ isomer mixture was isolated by GLC. ^1H NMR analysis indicated a 35% deuterium incorporation at the cyclopropyl position α to silicon, as measured vs. the intensity of the methylene cyclopropyl protons.

Reaction of E-1-chloro-1-trimethylsilylpropene (VIII) with organolithium reagents

A mixture of 1.4 g (9.6 mmol) of VIII [36] and 11 mmol of t-BuLi in pentane was allowed to react for 47 h at 25°C. After workup, GLC analysis (column A, 20 ft.) indicated that 80% of VIII was consumed, and that two pairs of products were produced. One pair (IXb-*t*/IXb-*c*) consisted of *trans* and *cis*-2,3,3-trimethyl-1-trimethylsilyl-1-butene in yields of 20 and 4% respectively. Isomeric assignments were made on the basis that a *cis*-methyl (to trimethylsilyl) group in very similar trisubstituted vinylsilanes displays a higher-field chemical shift and a smaller allylic J value than the corresponding *trans*-methyl group [37], although this is not the case for some disubstituted (propenyl) vinylsilanes [30]. Anal.: Found (IXb-*t*): C, 70.76; H, 13.11. $C_{10}H_{22}Si$ calcd.: C, 70.50; H, 13.02%. IR: 6.21m, 6.82m, 7.28m, 7.33m, 8.01s, 11.51s, 11.93s, 13.00w, 13.38m, 13.72m, 14.56m μm. ^1H NMR: δ 0.07 (9 H, s), 1.02 (9 H, s), 1.76 (3 H, s), 5.24 (1 H, s). Anal: Found (IXb-*c*): C, 70.35; H, 13.23%. IR: 6.25m, 6.92m, 7.28m, 7.33m, 8.01s, 8.26m, 9.11m, 11.49s, 11.9s, 13.39m, 14.61m, 15.67m μm. ^{1}H NMR: δ 0.09 (9 H, s), 1.09 (9 H, s), 1.84 (3 H, d, J = 1.5 Hz), 5.20 (1 H, m, J = 1.5 Hz).

The second pair of products consisted of *trans*-1-t-butyl-2-trimethylsilylcyclopropane (Xb-*t*, 22% yield), and a small amount (4%) of what may have been the *cis* isomer. Assignment of *trans* stereochemistry to Xb-*t* is based on the assumption of near equivalency for J_{trans} of H(1)—H(2) and H(2)—H(3), together with the usual $J_c > J_t$ correlation in cyclopropanes [33]. The presumed *cis* isomer showed NMR absorptions attributable to t-butyl and Me_3Si groups, but could not be fully characterized because of separation difficulties. Anal.: Found (Xb-*t*): C, 70.55; H, 12.83. $C_{10}H_{22}Si$ calcd.: C, 70.50; H, 13.02%. IR: 6.8m, 7.15w, 7.33m, 8.01s, 9.65w, 10.20m, 10.48m, 11.09m, 11.03s, 11.8s, 12.0s, 13.4m, 14.5m μm. ^{1}H NMR (100 MHz): δ −0.61 (1 H, apparent AM_2X pattern; intensity ratio 1/2/1/1/2/1, J_c = 10 Hz, J_t = 7 Hz), −0.12 (9 H, s), 0.04—0.60 (3 H, m), 0.76 (9 H, s).

When a similar reaction was carried out employing 18 mmol of VIII and 20 mmol n-BuLi in hexane/ether for one day, a mixture of products was obtained which was not separable on column A. ^{1}H NMR analysis indicated the probable presence of 2-methyl-1-trimethylsilyl-1-hexene (IXa) and 1-n-butyl-2-trimethylsilylcyclopropane (Xa) in a ratio of 4/3 (45% combined yield).

Reaction of α-chloro-β,β-diphenylvinyltrimethylsilane (III) with n-butyllithium

No reaction occurred between XIV [36] and a 10% molar excess of n-BuLi in hexane after 3 days at 25°C. Complete reaction occurred, however, when 2.0 g (7.1 mmol) of XIV and 15 mmol n-BuLi (2.25 *N*) in hexane were refluxed for 14 h. After workup, GLC (column D, 165°C) indicated the formation of 75% β,β-diphenylvinyltrimethylsilane (XV) and 8% of a product (XVI) which spectral data indicated was either α-n-butyl-β,β-diphenyltrimethylsilane or 2,3-diphenyl-1-trimethylsilyl1-hexene.

A parallel experiment, in which 6 ml of ether was added to the initial reaction mixture, and the reaction allowed to proceed at 25°C for 1 day, consumed 76% of XIV and afforded 60% XV and 8% XVI. No diphenylacetylene was produced in either run, as ascertained by GLC comparison with an authentic sample. Anal.: Found (XV) [38]: C, 80.93; H, 8.10. $C_{17}H_{15}Si$ calcd.: C, 80.89; H, 7.99%. IR: 6.31m, 6.38m, 6.72m, 6.93m, 7.48m, 8.02s, 8.24w, 9.34w, 9.71w, 10.78m, 11.13s, 11.7s, 12.0s, 13.16s, 14.28s, 14.46s μm. ^{1}H NMR (CCl_4, external CH_2Cl_2 taken as δ 5.28): δ −0.69 (9 H, s), 6.05 (1 H, s), 6.99 (10 H, m). IR (XVI): 6.35w, 6.72m, 6.92m, 8.01s, 9.34w, 9.74w, 10.95w, 12.0s, 13.13s, 14.30s, μm. ^{1}H NMR (CCl_4, external CH_2Cl_2): δ −0.09 (9 H, s), 0.6—1.5 (7 H, m), 2.26 (2 H, m), 7.21 (10 H, s).

Reaction of α-chlorovinyltrimethylsilane (I) with n-butylmagnesium bromide

A mixture of 42.5 mmol n-butylmagnesium bromide (1.7 *N* in THF), 25 ml THF and 4.6 g (34.3 mmol) of I was held at reflux for 3.5 days. After workup, GLC analysis (column A) showed total consumption of I, and the formation of 42% 2,3-bis(trimethylsilyl)-1,3-butadiene (XVII) [20] and 9% 2-trimethylsilyl-1-hexene (XVIII). A check with authentic samples showed that no IVa was formed. Anal.: Found (XVII): C, 60.34; H, 11.08. $C_{10}H_{22}Si_2$ calcd.: C, 60.52; H, 11.17%. IR: 5.41w, 6.30w, 6.36w, 7.10m, 8.01s, 10.86s, 12.0s, 13.3s, 14.53s, 15.1m, 15.8m μm. ^{1}H NMR: δ 0.07 (9 H, s), 5.37 (4 H, s). Anal;: Found (XVIII): C, 69.00: H, 12.88. $C_9H_{20}Si$ calcd.: C, 69.14; H, 12.89%. IR: 6.2w, 8.01s, 10.85m, 12.0s, 13.23m, 14.53m μm. ^{1}H NMR: δ 0.05 (9 H, s), 0.7—1.6 (7 H, m), 2.12 (2 H, m), 5.28 (1 H, m), 5.51 (1 H, m).

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