Tetrahedron Vol 44, No 13, pp 4009 to 4022, 1988
Printed in Great Britain

0040-4020/88 $3.00+.00
© 1988 Pergamon Press plc

NOVEL REARRANGEMENT OF CHLOROMETHYLVINYLSILANES INTO ALLYLSILANES. STEREOSELECTIVE SYNTHESIS OF METALLATED ALLYLSILANES FROM 1-ALKYNES

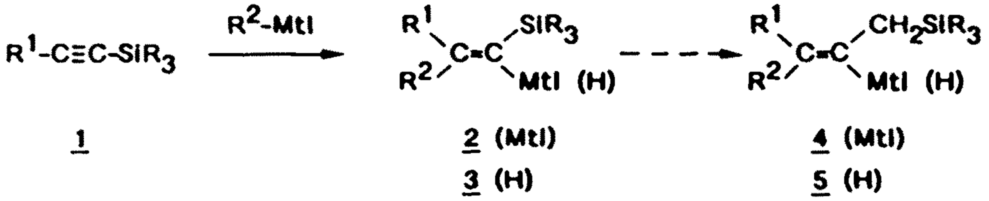
Hiroshi Shiragami, Takuo Kawamoto, Katsuharu Imi, Seijiro Matsubara,
Kiitiro Utimoto*, and Hitosi Nozaki[1]

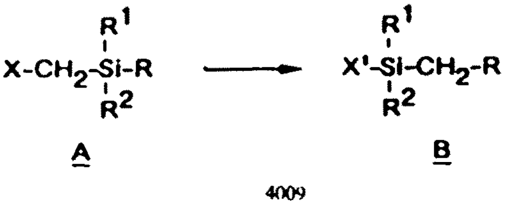
Department of Industrial Chemistry, Faculty of Engineering,
Kyoto University, Yoshida, Kyoto, 606, Japan

(Received in UK 15 November 1987)

Abstract - Regio and stereoselective hydralumination of 1-(chloromethyldimethylsilyl)-1-alkyne with diisobutylaluminium hydride (DIBAH) affords (Z)-1-(chloromethyldimethylsilyl)-1-(diisobutylalumino)-1-alkene. Treatment of the aluminium-substituted vinylsilane with 3 equivalents of methyllithium affords (E)-1-(trimethylsilyl)-2-lithio-2-alkene as a sole product. Reaction of aluminium-substituted vinylsilane with trimethylaluminium in refluxing heptane produces a mixture of (E)-1-trimethyl-silyl-2-alumino-2-alkene and 2-trimethylsilyl-1-alkene. Reaction of 1-(chloromethyldimethylsilyl)-1-alkyne with triisobutylaluminium gives 2-(isobutyldimethylsilyl)-1-alkene exclusively. Reactions of the lithiated allylsilane with several electrophiles give the corresponding carbometallated products, allylsilanes bearing alkyl, allyl, vinyl, or alkoxycarbonyl groups. Protodesilylation of 3-(trimethylsilylmethyl)-1,3-decadiene gives 3-methylene-1-decene selectively. Reaction of trialkylaluminium with trimethylsilylethyne gives bistrimethylsilylated diene by successive addition of silylethyne to the aluminium reagent; in contrast, chloromethyldimethylsilylethyne gives the mono-adduct regio and stereoselectively.

Recent discoveries of regio and stereoselective organic synthetic reactions by means of organosilicon reagents have claimed highly selective preparation of various types of organosilicon compounds including alkynylsilanes, vinylsilanes, and allylsilanes, from easily accessible organic compounds.[2] Along this line, we have disclosed regio and stereoselective syntheses of vinylsilanes; stereoselective syntheses either by carbonyl-olefination of aldehydes with gem-dichromium reagent derived from (dibromomethyl)trimethylsilane,[3] or by hydro- and carbometallation of silylalkynes.[4,5,6] In continuation of these efforts, we engaged in the development of stereoselective transformation of vinylsilanes (2 and 3) into allylsilanes (4 and 5), because vinylsilanes (2 and 3) are selectively prepared from easily accessible 1-trialkylsilyl-1-alkynes (1).



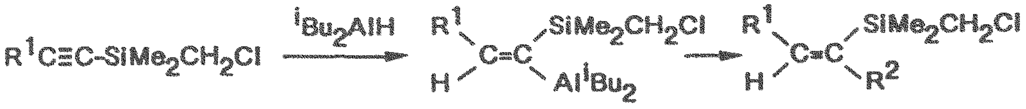


Although Lewis acid-catalyzed rearrangement of a chloromethylsilyl moiety (A) into a silylmethyl group (B) has been reported,[7-11] rearrangement of a 1-(chloromethyldimethylsilyl)-1-alkenes into allylsilanes under Lewis acid-catalysis has not given satisfactory results and does not meet the requirement of organic synthesis.[9,10] Treatment of (chloromethyl)dimethylvinylsilane with sodium methoxide gave allylsilane in low yield, though allyl(chloromethyl)dimethylsilane afforded (3-butenyl)silane in excellent yield.[12] As the reactivities of vinylmetals are increased by the introduction of another metal moiety at the α position,[4,5,13] rearrangement of 1-(chloromethyl)dimethylsilyl-1-metallo-alkenes into metallated allylsilane was attempted from the synthetic point of view.[14] This paper describes a highly stereoselective method for the above-mentioned transformation utilizing a novel methyllithium-mediated rearrangement of chloromethylvinylsilane into an allylsilane as the key reaction.[15] Some selective reactions using silylethynes are added lastly.

RESULTS AND DISCUSSION

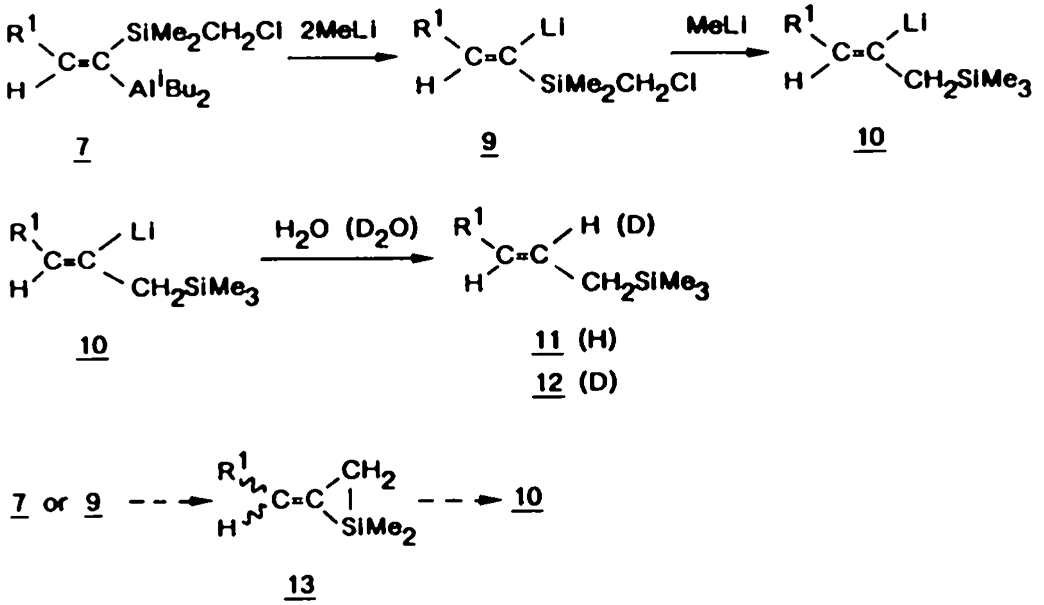
Preparation of Lithiated Allylsilanes from 1-Alkynes

Hydralumination of 1-trimethylsilyl-1-alkynes with DIBAH has been reported to give pure Z-adduct in a mixture of an hydrocarbon and ether. On the other hand, *the reaction in hydrocarbon solvent afforded a mixture of Z- and E-adduct by the* lack of coordination of ether oxygen to aluminium.[5] Hydralumination of 1-(chloromethyldimethylsilyl)-1-alkyne (6) was examined in a hydrocarbon solvent in anticipation of the fixation of product geometry by intramolecular coordination of chlorine to aluminium. The starting material 6 was easily prepared from 1-lithio-1-alkyne by the reaction with chloromethyldimethylsilyl chloride. A heptane solution of 6 was treated with DIBAH at room temperature; then hydrolytic workup of the reaction mixture gave 8 (R^2 = H) almost quantitatively. Formation of 1-deuterated product (8, R^2 = D) by hydrolytic workup with D_2O suggested that hydralumination proceeded regio- and stereoselectively. Hydralumination in heptane-ether also afforded the same 8 exclusively.



6 7 8

When hydraluminated product (7) was treated with an ether solution of MeLi (3 equiv) at room temperature for 2 h, (E)-1-trimethylsilyl-2-alkene (11) was obtained as a sole product after hydrolytic workup. Structure of allylsilane 11 was determined by spectrometric analyses as well as the comparison with the authentic 11.[16,17] Quantitaive generation of deuterated product 12 by the workup with D_2O suggests that the lithiated allylsilane 10 is formed after the rearrangement. Treatment of 7 with one equiv of MeLi gave 8 (R^2 = H) after hydrolysis of the reaction mixture. Reaction of 7 with 2 equiv of MeLi afforded a mixture of 8 (R^2 *= H), (E)-isomer of 8, and 11. In contrast to the treatment with an ethereal* solution of MeLi, treatment of 7 with a hexane solution of BuLi (3 equiv) gave 6 whose formation could be explained by retrohydralumination induced by BuLi. These results suggested that the formation of 11 from 7 by successive treatment with 3 equiv of MeLi and water could be explained: (1) treatment with 2 equiv MeLi gave 9 by transmetallation followed by isomerization to E isomer;[18,19] (2) attack of MeLi on Si of 9 induced the rearrangement of 9 to 10 by elimination of LiCl; analogous nucleophile-mediated rearrangement of allyl-(chloromethyl)silane into homoallylsilane has been reported.[12] Although production of 10 from 9 could be explained by the formation of the intermediary alkylidenesilacyclopropane 13,[20,21] stereospecific transformation of 13 into 10 by MeLi is unprecedented. Results are summarized in Table 1.



In contrast to the reaction of (chloromethyl)dimethylvinylsilane with sodium methoxide affording a complex mixture,[12] reaction of (Z)-1-(chloromethyl)-dimethylsilyl-1-alkene 8 (R^2 = H) with MeLi under the above described conditions did not give any allylsilane and 8 was recovered unchanged. This observation suggests that the migratory aptitude of the olefinic carbon attached to silicon is enhanced by the introduction of lithium at the α position. As 1-(chloromethyl)-dimethylsilyl-1-alkynes 6 are easily prepared from 1-alkynes, the above described procedure opens novel regio and stereoselective synthesis of allylsilanes.

Trialkylaluminium-Induced Rearrangement of (Chloromethyl)vinylsilane

In contrast to the above described MeLi-induced stereoselective rearrangement, trialkylaluminium-induced rearrangement of 7 gave a mixture of allylsilanes (E-isomer 11 and Z-isomer 17) and 2-alkyldimethylsilyl-1-alkene 20; ratio of the products depended upon the employed trialkylaluminium. A heptane solution of 7 (R^1 = n-C$_6$H$_{13}$) was treated with trimethylaluminium (1 equiv) at refluxing temperature for 6 h to give a mixture of 11, 17, and 2-trimethylsilyl-1-nonene 20 in 78% yield (11/17/20 = 67/9/24) after hydrolytic workup. Use of triethylaluminium, in place of trimethylaluminium, afforded a mixture of (E)-allylsilane 18, 17 (R^1 = n-C$_6$H$_{13}$, R^2 = Me), and 20 in 78% yield (11/17/20 = 8/1/91). Treatment of 7 with trimethylaluminium in a mixture of heptane and ether did not give any rearranged product. The structure of the rearranged products (10 and 15) were estimated by regioselective introduction of deuterium to give 12 and the (Z)-isomer 19 (R^1 = n-

C_6H_{13}, R^2 = Me) by the workup with D_2O. The fact that non-deuterated 20 was lated even hydrolytic workup with D_2O indicated that 20 was formed be hydrolytic workup. The structures of 17 and 20 were determined by the parison of ^1H NMR and MS of the products with those of the authentic samples was prepared by the coupling of (Z)-1-bromo-1-octene with trimethylsilylmethyl nesium chloride under nickel catalysis, and 20 was prepared by the coupling o bromo-1-trimethylsilylethene with heptylmagnesium bromide.[16,22]

Table 1. Allylsilanes (11, 12, 17, 18, 19) and Vinylsilane 20 from 1-(Chloromethyl)dimethylsilyl-1-alkynes (6) via Hydralumination Product 7

Entry	R^1	R-Mtl[a)] (equiv)	Solvent[b)]	Temp.[c)]	Time	Workup	Yield[d)] (%)	Product	Rati
1	n-C_6H_{13}	MeLi (3)	Et_2O	r.t.	2 h	H_2O	82	11	
2	n-C_6H_{13}	MeLi (3)	Et_2O	r.t.	2 h	D_2O	80	12	
3	n-C_6H_{13}	MeLi (3)	Et_2O	0°C	2 h	H_2O	90	8 (R^2 = H)	
4	n-C_6H_{13}	BuLi (3)	hexane	r.t.	2 h	---	94	6[f)]	
5	n-C_4H_9	MeLi (3)	Et_2O	r.t.	2 h	H_2O	80	11	
6	Ph	MeLi (3)	Et_2O	r.t.	24 h	H_2O	73	11/17	21/79
7	n-C_6H_{13}	Me_3Al (1.1)	heptane	reflux	6 h	H_2O	78	11/17/20	67/9/
8	n-C_6H_{13}	Me_3Al (1.1)	heptane	reflux	6 h	D_2O	74	12/19/20[h)]	
9	n-C_6H_{13}	Et_3Al (1.1)	heptane	reflux	4 h	H_2O	75	18/17/20	9/4/
10	Ph	Me_3Al (1.1)	heptane	reflux	8 h	H_2O	59	11/17/20	57/0/
11	n-C_6H_{13}	($^iBu_3Al$ (2.0), heptane, reflux for 6 h)[j)]					72	18/17/20	5/3/

a) Silylalkyne 6 was treated with equimolar DIBAH in heptane (or hexane) for 1 at room temperature; then the reaction mixture was treated with R-Mtl (equi

b) Solvent in which R-Mtl was dissolved; therefore hydraluminated product 7 wa treated with R-Mtl in a mixture of heptane (or hexane) and solvent designat here.

c) The reaction mixture of 7 and R-Mtl was treated at designated temperature a time.

d) Overall yield from 6.

e) Determined by GLC as well as 200 MHz ^1H NMR.

f) After the formation of hydraluminated product 7 was confirmed, the reaction mixture was treated with a hexane solution of BuLi.

g) In the case of R^1 = Ph, transmetallation giving 9 from 7 seems slow. Treat of 7 with MeLi at room temperature for 2 h afforded vinylsilane 8 (R^1 = Ph, R^2 = H, containing 23% of E-isomer) as the major product after hydrolytic workup. The above described isomerization from 7 to 14 even at room temper ture would explain the formation of a mixture of 11 and 17.

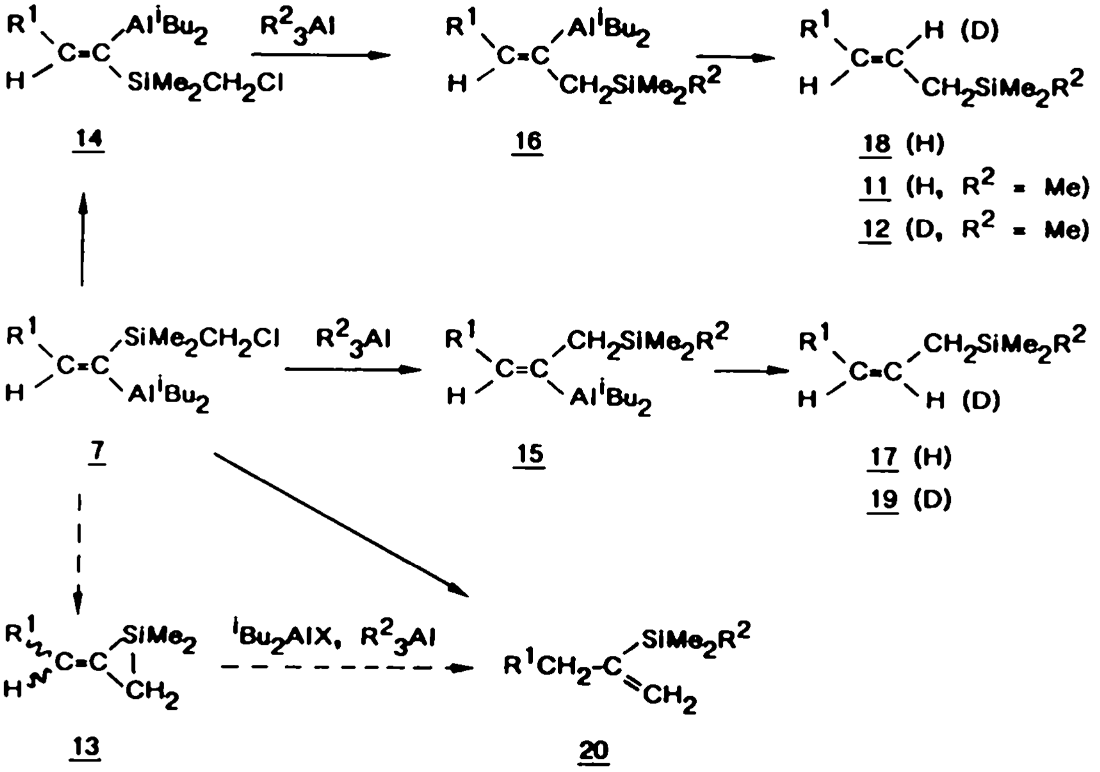
h) Ratio of 12/19/20 was similar to that of 11/17/20.

i) Fast isomerization of 7 into 14 was observed (ref. 24).

j) Direct treatment of 1-(chloromethyl)dimethylsilyl-1-octyne (6, R^1 = n-C_6H_{13} with a heptane solution of $^iBu_3Al$ (2.0 equiv) at reflux for 3 h resulted in formation of 20 (R^2 = ^iBu) selectivity; namely, the initial hydraluminated product 7 rearranged exclusively to 17. Triisobutylaluminium produces DIBA under the reaction temperature.

Direct reaction of a heptane solution of 6 (R^1 = n-C_6H_{13}) with 2 equiv of triisobutylaluminium at refluxing temperature gave 20 predominantly; (1) thermolysis of triisobutylaluminium produced diisobutylaluminium hydride (DIBAH) which added to 6 to give 7 and (2) triisobutylaluminium-mediated rearrangement of 7 to give a mixture of aluminium-substituted allylsilanes (18 and 17) and alkenylsilane 20. Results of trialkylaluminium-mediated formation of (E)-allylsilanes (11 and 18) and vinylsilane 20 are added in Table 1.

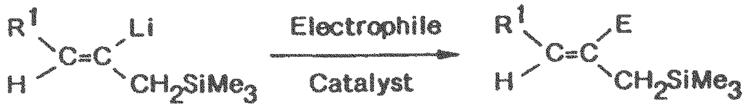
Trialkylaluminium-mediated rearrangement could be explained; (1) Hydralumination in heptane at room temperature gave pure Z-adduct 7 whose isomerization to (E)-isomer 14 would proceed at elevated temperature by the break of intramolecular coordination of chlorine to aluminium;[23] (2) Trimethylaluminium was sufficiently strong Lewis acid in heptane, coordination to chlorine, and transferred methyl to silicon inducing stereospecific rearrangement; (3) As trialkylaluminium-mediated rearrangement of (chloromethyl)dimethylvinylsilane to allylsilane proceeded at refluxing temperature of a heptane solution, E/Z isomerization of 7 to 14 and rearrangement of 7 and 14 to allylsilane 15 and 16, respectively, were competitive processes, therefore the E/Z ratio of the produced allylsilane could be determined by the reactivity of trialkylaluminium used; (4) Geometry of the rearranged products did not change under the applied reaction conditions; (5) Direct formation of 20 from aluminium-containing vinylsilane 7 by the action of trialkylaluminium could be conceivable, (a) either by the successive or simultaneous action of intramolecular diisobutylaluminium group (transfer of hydrogen to olefinic carbon) and intermolecular action of trialkylaluminium (transfer R^2 group to silicon), (b) or by the intermediary formation of alkylidenesilacyclopropane 13 which was attacked by aluminium reagent to give 20.



Compared to the stereoselective formation of (E)-allylsilanes 10 from (chloro-methyl)vinylsilane 7 by MeLi-mediated rearrangement, the above described trialkylaluminium-mediated rearrangement of the same vinylsilane 7 into 2-(alkyl-dimethylsilyl)-1-alkene 20 opens another synthetic utility of 1-alkynes through 1-(chloromethyl)dimethylsilyl-1-alkynes 6.

Reaction of 1-Trimethylsilyl-2-lithio-2-alkenes with Various Electrophiles

Various types of allylsilanes can be prepared by the reaction of 1-trimethylsilyl-2-lithio-alkenes 10 with various carbon electrophiles using transition metal-catalyts.



10

21 E = alkyl, allyl

22 E = vinyl

23 E = COOR'

Table 2. Reaction of 10 (R^1 = n-C_6H_{13}) with Electrophiles.

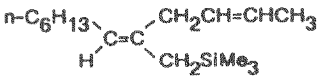
Entry	Electrophile	Catalyst (equiv)	Product (E)	Yield (%)[a)]
1	MeI	CuBr (0.1)	21 (Me)	84
2	MeI	CuI (0.1)	21 (Me)	80
3	MeI	CuCN (0.1)	21 (Me)	79
4	EtI	CuBr (0.1)	21 (Et)	80
5	n-BuI	CuBr (0.1)	21 (n-Bu)	78
6	CH_2=$CHCH_2Br$	CuBr (0.1)	21 (CH_2CH=CH_2)	84
7	CH_2=$CMeCH_2Cl$	CuBr (0.1)	21 (CH_2CMe=CH_2)	65
8	CH_2=CH-CHMeCl	CuBr (0.1)	21a	50[b)]
9	MeCH=$CHCH_2Cl$	CuBr (0.1)	21a/21b[c)]	63 (27/73)[d)]
10	MeCH=$CHCH_2Cl$	CuI (0.1)	21a/21b	58 (25/75)
11	MeCH=$CHCH_2Cl$	CuCN (0.1)	21a/21b	60 (15/85)
12	CH_2=CHBr	$ZnCl_2$ (1.0)/$Pd(PPh_3)_4$ (0.01)	22 (CH=CH_2)	52
13	ClCOOMe	$ZnCl_2$ (1.2)/$Pd(PPh_3)_4$ (0.05)	23 (COOMe)	76
14	ClCOOEt	$ZnCl_2$ (1.2)/$Pd(PPh_3)_4$ (0.05)	23 (COOEt)	78

a) Overall yield from 1-(chloromethyl)dimethylsilyl-1-octyne (6, R^1 = n-C_6H_{13}).

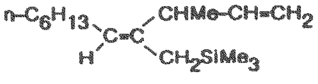
b) Reaction of 3-chloro-2-methyl-1-propene gave 21a selectively.

c) Reaction of crotyl bromide at α-position gave 21a; reaction at γ-position afforded 21b.

d) Ratio of 21a/21b was determined by 200 MHz ^1H NMR as well as GLC.



21a



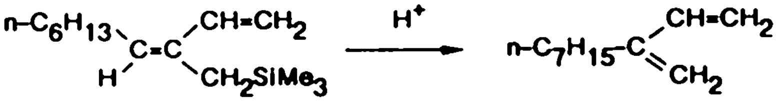
21b

Alkylation is catalyzed by cuprous bromide; successive treatment of the lithiated allylsilane with CuBr (0.1 equiv) and an alkyl iodide gave an alkylated product stereospecifically. Allyl halides reacted at both α and γ positions to give a mixture of allylated products.

In contrast to the above-mentioned alkylation and allylation, reaction of 10 with bromoethene under similar conditions did not produce any vinylated product. Therefore, lithio-intermediate 10 was first transmetallated with $ZnCl_2$ to give vinylzinc intermediate, which reacted with bromoethene under palladium catalysis to give 22 in good yield.

Reaction of 10 with methyl chlorocarbonate also proceeded smoothly via vinylzinc intermediate. Analogous to the above case, palladium-catalyzed reaction of the vinylzinc intermediate with methyl chlorocarbonate produced α,β-unsaturated ester 23 in good yield. As carbodemetallation proceeds without change of olefinic configuration, stereochemistry of each allylsilane, 21, 22, or 23 was reasonably estimated from that of the common precursor 10. Results are summarized in Table 2.

Protodesilylation of the above described (E)-3-(trimethylsilylmethyl)-1,3-decadiene (22) produced 3-methylene-1-decene as shown below.

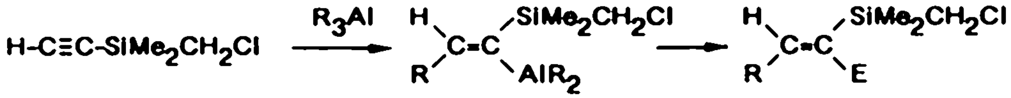


22

Addition of Trialkylaluminium to 1-(Chloromethyldimethylsilyl)-1-alkynes

Although trimethylsilylethyne added to alkylcopper to give (Z)-adduct, (Z)-1-trimethylsilyl-1-alkenylcopper, exclusively,[6] (chloromethyl)dimethylsilylethyne did not give the expected adduct as a main product because of predominant substitution of chlorine with alkyl. After several attempts, carbometallation of (chloro-methyl)dimethylsilylethyne (24) with trialkylaluminium in hydrocarbon solvent afforded satisfactory results.

Reaction of 24 with tripropylaluminium (1.3 equiv) in hexane at 0°C for 3 h gave the (Z)-adduct 25, which upon quenching with H_2O and D_2O afforded 26a and 26b, respectively. Successive treatments of 25 with MeLi and 3-bromo-1-propene gave 26c in excellent yield. Results are summarized in Table 3.



24 25 26a (E = H)

26b (E = D)

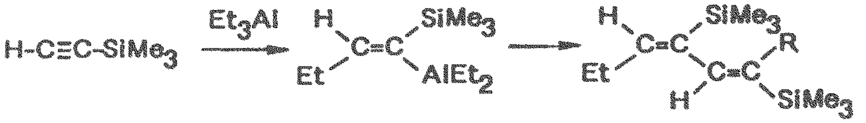
26c (E = $CH_2CH=CH_2$)

Table 3. Formation of 26 from 24.

		Yield (%) of Product		
Entry	R	26a	26b	26c
1	Me	--$^{a)}$	--	--
2	Et	81	78	90
3	n-Pr	87	80	80
4	i-Bu	79	79	83

a) Any adduct could not be detected; starting material was recovered.

In contrast to (chloromethyl)dimethylsilylethyne 24, reaction of trimethylsilylethyne (27, 2 equiv) with triethylaluminium (1 equiv) gave (1E,3E)-2-diethylalumino-1,3-bistrimethyllsilyl-1,3-hexadiene 29a stereoselectively, whose hydrolysis gave 29b in 94% yield. Reaction with D_2O afforded deuterated product 28c. The initial adduct 27 again reacted easily with 26 to yield 28, but the bis adduct 28a did not show any reactivity towards 27 even with large excess of 27 at higher reaction temperature for prolonged reaction time. Although analogous reaction of 1-(chloromethyl)dimethylsilyl-1-propyne with trialkylaluminium was observed to give bis adduct, 1-(chloromethyl)dimethylsilyl-1-octyne did not give any bis adduct by the reaction with trialkylaluminium.



27

28

29a (R = $AlEt_2$)
29b (R = H)
29c (R = D)

In conclusion, a novel stereoselective preparation of allylsilanes from easily accessible 1-(chloromethyldimethylsilyl)-1-alkynes is described making use of a stereospecific rearrangement of the chloromethyldimethylsilyl group to the alkyldimethylsilylmethyl under the intramolecular assistance of the alpha-lithium or aluminium carbanion. Selective formation of 2-trialkylsilyl-1-alkenes from 1-(chloromethyldimethylsilyl)-1-alkynes using trialkylaluminium-mediated rearrangement of aluminated (chloromethyl)dimethylvinylsilane described here opens novel synthetic use of 1-alkynes.

EXPERIMENTAL

All reactions were carried out in argon atmosphere. Solvents used for the reaction were deoxygenated and dried. ^1H NMR spectra were recorded on Varian Associates EM-390 and XL-200 as well as JEOL FX-90Q spectrometers and are reported in parts per million from internal tetramethylsilane on the δ scale. Data are reported as follows: Chemical shift (multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constants.). Infrared spectra were taken with a JASCO IR-810 instrument and are reported in wavenumbers (cm^{-1}). Mass spectra were recorded on a Hitachi M-80 mass spectrometer using PFK as internal standard. Samples on which exact mass were measured exhibited no significant peaks at m/z greater than that of the parent. Combustion analyses were performed by Elemental Analyses Center of Kyoto University.

1-(Chloromethyl)dimethylsilyl-1-octyne (6, R^1 = n-C_6H_{13}) from 1-Octyne. To a THF solution of 1-octyne (6.15 g, 55.9 mmol in 60 mL THF), n-BuLi (55.9 mmol, 37.3 mL of 1.5 M hexane solution) was added at -78°C, and the reaction mixture was stirred for 1 h at 0°C then 15 min at room temperature. To the reaction mixture, a THF solution of (chloromethyl)dimethylsilyl chloride (8.0 g, 55.9 mmol dissolved in 20 mL of THF) was added dropwise during for 1 h at -78°C and the resulting mixture was stirred at the same temperature overnight. The reaction mixture was worked up with sat. NH_4Cl and extracted with ethyl acetate. The organic layer was washed with brine and dried over Na_2SO_4. Distillation of the organic solution afforded 1-(chloromethyl)dimethylsilyl-1-octyne (6, 10.9 g, 99% yield) as a colorless oil (b.p. 54-57°C/3 mmHg); IR (liquid film), 2956, 2930, 2856, 2172, 1252, 817 cm^{-1}; ^1H NMR 0.00 (s, 6H), 0.69 (t, 3H, J = 7.0 Hz), 0.95-1.35 (m, 8H), 1.94 (t, 2H, J = 7.0 Hz), 2.58 (s, 2H). MS Calcd for $C_{11}H_{21}ClSi$: M^+ = 216.110. Found: 216.108.

1-(Chloromethyl)dimethylsilyl-2-phenylethyne (6, R^1 = Ph). IR (liquid film), 3056, 2964, 2156, 1488, 1252, 845 cm^{-1}; ^1H NMR, 0.00 (s, 6H), 2.60 (s, 2H), 6.70-6.95 (m, 5H). MS Calcd for $C_{11}H_{13}ClSi$ M^+ = 208.047. Found: 208.048.

1-(Chloromethyl)dimethylsilyl-1-hexyne (6, R^1 = n-C_4H_9). IR (liquid film), 2960, 2932, 2174, 1252, 843, 817 cm^{-1}; ^1H NMR, 0.00 (s, 6H), 0.69 (t, 3H, J = 7.0 Hz), 1.0-1.3 (m, 4H), 1.94 (t, 2H, J = 7.0 Hz), 2.58 (s, 2H). MS Calcd for $C_9H_{17}ClSi$: M^+ = 202.094. Found: 202.097.

(Z)-1-(Chloromethyl)dimethylsilyl-1-octene (8, R^1 = n-C_6H_{13}). To a heptane solu tion of diisobutylaluminium hydride (DIBAH, 2.3 mmol, 1.8 mL of 1.28 M solution), 1-(chloromethyl)dimethylsilyl-1-octyne (6, R^1 = n-C_6H_{13}, 0.50 g, 2.3 mmol) was added and the resulting mixture was stirred for 1 h at room temperature. The reaction mixture was cooled to 0°C and then poured onto a mixture of ice and dil. hydrochloric acid. The mixture was extracted with ether. Ethereal solution was washed with sat. NaCl, dried over Na_2SO4 and concentrated to give (Z)-1-(chloromethyl)dimethylsiyl-1-octene (8, R^1 = n-C_6H_{13}) quantitatively. ^1H NMR, 0.00 (s, 6H), 0.80 (t, 3H, J = 7 Hz), 1.1-1.5 (m, 8H), 1.95 (m, 2H), 5.30 (dt, 1H, J = 13, 1 Hz), 6.18 (dt, 1H, J = 13, 6 Hz). MS Calcd for $C_{11}H_{23}ClSi$: M^+ = 218.126. Found: 218.125.

(E)-1-Trimethylsilyl-2-nonene (11, R^1 = n-C_6H_{13}) from (Z)-1-(Chloromethyl)dimethylsilyl-1-octyne (6, R^1 = n-C_6H_{13}) by Successive Treatment with DIBAH and MeLi Followed by Hydrolytic Workup. To a heptane solution of DIBAH (2.3 mmol, 1.8 mL of 1.28 M solution), 1-(chloromethyl)dimethylsilyl-1-octyne (6, R^1 = n-C_6H_{13}, 0.50 g, 2.3 mmol) was added and the resulting mixture was stirred for 1 h at room temperature. The reaction mixture was cooled at 0°C and was added with an ethereal solution of MeLi (7.0 mmol, 3.2 mL of 2.2 M solution) at 0°C. The mixture was stirred for 2 h at room temperature, poured onto a mixture of crushed ice and dil. hydrochloric acid, and extracted with ether. The ethereal solution was washed with sat. NaCl, dried over Na_2SO_4, and concentrated to afford 373 mg (1.88 mmol, 82% yield) of (E)-1-trimethylsilyl-2-nonene (11, R^1 = n-C_6H_{13}); Bp 80°C/4 mmHg (Kugelrohr bath temp.); IR (neat) 2954, 2924, 2854, 1248, 838 cm^{-1}; ^1H NMR 0.00 (s, 9H), 0.87 (t, 3H, J = 6.7 Hz), 1.15-1.37 (m, 8H), 1.38 (d, 2H, J = 7.4 Hz) 1.96 (dt, 2H, J = 6.6, 6.2 Hz), 5.22 (dtt, 1H, J = 15.2, 6.2 0.9 Hz), 5.35 (dtt, 1H, J = 15.2, 7.4, 0.9 Hz). Anal. Calcd for $C_{12}H_{26}Si$: C, 72.64; H, 13.21. Found: C, 72.76; H, 13.46.

When the reaction mixture obtained from 1-(chloromethyl)dimethylsilyl-1-octyne (6) by successive treatments with DIBAH and MeLi was treated with D_2O, (E)-1-trimethylsilyl-2-deuterio-2-nonene (12, R^1 = n-C_6H_{13}) was obtained: Bp 60°C/3 mmHg (Kugelrohr bath temp.); IR (neat), 2954, 2924, 2854, 1248, 837 cm^{-1}; ^1H NMR 0.00 (s, 9H), 0.89 (t, 3H, J = 6.7 Hz), 1.15-1.37 (m, 8H), 1.38 (br-s, 2H), 1.97 (dt, 2H, J = 7.0, 5.7 Hz), 5.26 (tt, 1H, J = 1.0, 7.0 Hz). Anal. Calcd for $C_{12}H_{25}DSi$: C, 72.27; H and D, 13.67. Found: C, 71.93; H and D, 13.90.

(E)-1-Trimethylsilyl-2-nonene (11, R^1 = n-C_6H_{13}): Authentic Sample. According to the reported procedure of the coupling of a Grignard reagent with an alkenyl bromide (ref. 16), nickel-catalyzed coupling of bromoalkene with trimethylsilylmethylmagnesium chloride was carried out. An ether solution of trimethylsilylmethylmagnesium chloride (17 mmol, 24 mL of 0.7 M solution) was added to an ether solution of (E)-1-bromo-1-octene (1.53 g, 8 mmol) and $Ni(acac)_2$ (0.13 g, 0.5 mmol) in 10 mL of solution maintained at 0°C. The reaction mixture was stirred for 5 h at room temperature, and then poured onto ice-cooled dil. hydrochloric acid. The mixture was extracted with ether and the ether solution was dried over Na_2SO_4, concentrated, and distilled to give (E)-1-trimethylsilyl-2-nonene (11, R^1 = n-C_6H_{13}, 1.2 g, 75% yield, bp. 120-140°C/20 mmHg (Kugelrohr). IR and ^1H NMR are identical to those of above described 11 obtained by the rearrangement.

(E)-1-Trimethylsilyl-2-heptene (11, R^1 = n-C_4H_9). Analogous treatment of 1-(chloromethyl)dimethylsilyl-1-hexyne (6, R^1 = n-C_4H_9) with DIBAH and MeLi gave (E)-1-trimethylsilyl-2-heptene in 80% yield.

1-Phenyl-3-trimethylsilyl-1-propene (11, R^1 = Ph). When 1-(chloromethyl)dimethylsilyl-2-phenylethyne (6, R^1 = Ph) was successively treated with DIBAH and MeLi as described above, 1-phenyl-3-trimethylsilyl-1-propene (11, R^1 = Ph) was obtained in 73% yield as a mixture of E-isomer 11 and Z-isomer 17 (11/17 = 21/79). Pure samples of each isomer were obtained by GLC.

(E)-1-Phenyl-3-trimethylsilyl-1-propene (11, R^1 = Ph): ^1H NMR 0.00 (s, 9H), 1.60 (m, 2H), 6.30 (m, 2H), 7.25 (m, 5H). MS Calcd for $C_{12}H_{18}Si$: M^+ = 190.118. Found: 190.120.

(Z)-1-Phenyl-3-trimethylsilyl-1-propene (17, R^1 = Ph, R^2 = Me): ^1H NMR 0.00 (s, 9H), 1.80 (dd, 2H, J = 9.0, 1.5 Hz), 5.70 (dt, 1H, J = 12, 9.0 Hz), 6.30 (dt, 1H, J = 12, 1.5 Hz), 7.25 (m, 5H). MS Calcd for $C_{12}H_{18}Si$: m/z = 190.118. Found: 190.119.

Trialkylaluminium-Induced Rearrangement of 1-(Chloromethyl)dimethylsilyl-1-diisobutylalumino-1-alkene (7) into Allylsilane (15 and 16) and Vinylsilane 20. 1-Trimethylsilyl-2-nonene (E-isomer 11 and Z-isomer 17) and 2-trimethylsilyl-1-noncene (20) from 1-(Chloromethyl)dimethylsilyl-1-octyne (6, R^1 = n-C_6H_{13}). A Typical Procedure. To a heptane solution of 1-chloromethyldimethylsilyl-1-octyne (6, R^1 = n-C_6H_{13}, 647 mg, 3.0 mmol in 5 mL solution), DIBAH (neat, 3.0 mmol) was added and the reaction mixture was stirred at room temperature for 30 min. A heptane solution of Me_3Al (3.0 mmol, 1.5 mL of 2 M solution) was added and then the reaction mixture was heated at reflux for 3 h. The reaction mixture was ice-cooled, poured onto ice-cooled dil. hydrochloric acid, and extracted with ether. Organic solution was dried over Na_2SO_4, concentrated, and distilled with Kugelrohr to give a mixture of (E)- and (Z)-1-trimethylsilyl-2-nonene (11 and 17, R^1 = n-C_6H_{13}, R^2 = Me) and 2-trimethylsilyl-1-nonene (20, R^1 = n-C_6H_{13}, R^2 = Me) as a fraction of bath temperature 120-125°C (20 mmHg), 463 mg (78% yield, 11/17/20 = 67/9/24 determined by GLC). Pure samples of each isomer were obtained by GLC.

(Z)-1-Trimethylsilyl-2-nonene (17, R^1 = n-C_6H_{13}, R^2 = Me): ^1H NMR 0.00 (s, 9H), 0.88 (t, 3H, J = 6.7 Hz), 1.12-1.43 (m, 8H), 1.46 (br-d, 2H, 7.7 Hz), 1.98 (dt, 2H, J = 6.8, 6 Hz), 5.26 (dtt, 1H, J = 10.8, 6.8, 1.0 Hz), 5.38 (dtt, 1H, J = 10.8, 7.7, 1.0 Hz). MS Calcd for $C_{12}H_{26}Si$: m/z = 198.180. Found: 198.170.

2-Trimethylsilyl-1-nonene (20, R^1 = n-C_6H_{13}, R^2 = Me): IR (liquid film), 2954, 2924, 2854, 1248, 838 cm^{-1}; ^1H NMR 0.00 (s, 9H), 0.85 (t, 3H, J = 6.0 Hz), 1.10-1.45 (m, 10H), 2.04 (br-t, 2H, J = 6.7 Hz), 5.22 (dt, 1H, J = 3.0, 1.0 Hz), 5.45 (dt, 1H, J = 3.0, 1.6 Hz); MS Calcd for $C_{12}H_{26}Si$: m/z = 198.180. Found: 198.183.

Workup of the above described reaction mixture with D_2O gave a mixture of deuterated allylsilane (12 and 19) and non-deuterated 20. Pure 12 was obtained by GLC; IR and ^1H NMR was identical to those of the above described 12 obtained by MeLi-induced rearrangement.

When the reaction with Me_3Al was carried out at 70°C in the above procedure, E-isomer (11, R^1 = n-C_6H_{13}) was obtained predominantly. Overall yield 80%, 11/20 = 7/3.

(Z)-1-Trimethylsilyl-2-nonene (17, R^1 = n-C_6H_{13}, R^2 = Me): Authentic Sample. Analogous to the above described preparation of authentic 11 (ref. 16), (Z)-1-Trimethylsilyl-2-nonene (17, R^1 = n-C_6H_{13}, R^2 = Me) was obtained by the coupling of (Z)-1-bromo-1-octene with trimethylsilylmethylmagnesium chloride under nickel catalysis.

2-Trimethylsilyl-1-nonene (20, R^1 = n-C_6H_{13}, R^2 = Me): Authentic Sample. According to the procedure described above (ref. 16), a THF solution of 1-bromo-1-trimethylsilylethene (3 mmol, 0.54 g in 3 mL solution) maintained at 0°C was treated successively with a THF solution of heptylmagnesium bromide (7 mmol, 7.8 mL of 0.9 M solution) and $Ni(acac)_2$ (0.13 g, 0.5 mmol) and the reaction mixture was stirred 15 min at 0°C then 1 h at room temperature. The reaction mixture was poured onto ice-cooled dil. hydrochloric acid and extracted with ether. The ether solution was dried over Na_2SO_4, concentrated, and distilled (Kugelrohr) to give an authentic sample of 2-trimethylsilyl-1-nonene (20, R^1 = n-C_6H_{13}, R^2 = Me); Bp. 120-130°C/20 mm Hg; IR, ^1H NMR, and MS as well as the retention time of GLC are identical to those of the above described 20 obtained by trimethylaluminium-mediated rearrangement.

2-(Ethyldimethylsilyl)-1-nonene (20, R^1 = n-C_6H_{13}, R^2 = Et). Use of Et_3Al, in place of Me_3Al, gave a mixture of (E)-1-(ethyldimethylsilyl)-2-nonene (18) and 20 in 75% yield (18/17/20 = 9/4/87).

(E)-1-(Ethyldimethylsilyl)-2-nonene (18, R^1 = n-C_6H_{13}, R^2 = Et): ^1H NMR 0.00 (s, 6H), 0.47 (q, 2H, J = 7.8 Hz), 0.87 (t, 3H, J = 6.3 Hz), 0.91 (t, 3H, J = 7.8 Hz), 1.04-1.35 (m, 8H), 1.39 (d, 2H, J = 7.3 Hz), 1.97 (m, 2H), 5.21 (dtt, 1H, J = 15.2, 6.1, 0.8 Hz), 5.36 (dtt, 1H, J = 15.2, 7.3, 1.0 Hz).

(Z)-1-(Ethyldimethylsilyl)-2-nonene (17, R^1 = n-C_6H_{13}, R^2 = Et): ^1H NMR 0.00

(s, 6H), 0.48 (q, 2H, J = 7.6 Hz), 0.87 (t, 3H, J = 6.9 Hz), 0.92 (t, 3H, J = 7.6 Hz), 1.1-1.4 (m, 8H), 1.45 (d, 2H, J = 8.0 Hz), 1.93-2.10 (m, 2H), 5.24 (dtt, 1H, J = 11.5, 6.4, 1.0 Hz), 5.37 (dtt, 1H, J = 11.5, 8.0, 1.0 Hz).

2-(Ethyldimethylsilyl)-1-nonene (20, R^1 = n-C_6H_{13}, R^2 = Et): ^{1}H NMR 0.00 (s 6H), 0.52 (q, 2H, J = 8.0 Hz), 0.88 (t, 3H, J = 6.5 Hz), 0.90 (t, 3H, J = 8.0 Hz), 1.04-1.48 (m, 8H), 2.05 (br-t, 2H, J = 7.5 Hz), 5.22 (dt, 1H, J = 3.0, 1.0 Hz), 5.45 (dt, 1H, J = 3.0, 1.6 Hz). Ms Calcd for $C_{13}H_{28}Si$: m/z = 212.196. Found: 212.196.

(E)-1-(Isobutyldimethylsilyl)-2-nonene (18, R^1 = n-C_6H_{13}, R^2 = CH_2CHMe_2) and 2-(Isobutyldimethylsilyl)-1-nonene (20, R^1 = n-C_6H_{13}, R^2 = CH_2CHMe_2) from 1-(Chloromethyl)dimethylsilyl-1-octyne (6, R^1 = n-C_6H_{13}) by the Action of Triisobutylaluminium. To a heptane solution of 1-(chloromethyl)dimethylsilyl-1-octyne (6, R^1 = n-C_6H_{13}, 500 mg, 2.3 mmol in 2 mL solution), a heptane solution of triisobutylaluminium (4.6 mmol, 4.6 mL of 1 M solution) was added and the reaction mixture was heated at reflux for 6 h. The reaction mixture was worked up as described above to give a mixture of olefinic silanes in 72% yield. GLC analysis indicated that the ration of (E)-1-(isobutyldimethylsilyl)-2-nonene (18, R^1 = n-C_6H_{13}, R^2 = CH_2CHMe_2)/(Z)-1-(isobutyldimethylsilyl)-2-nonene (17, R^1 = n-C_6H_{13}, R^2 = CH_2CHMe_2)/2-(isobutyldimethylsilyl)-1-nonene (20, R^1 = n-C_6H_{13}, R^2 = CH_2CHMe_2) was 5/3/92. Pure samples were obtained by GLC.

(E)-1-(Isobutyldimethylsilyl)-2-nonene (18, R^1 = n-C_6H_{13}, R^2 = CH_2CHMe_2): ^{1}H NMR 0.00 (s, 6H), 0.50 (d, 2H, J = 6.9 Hz), 0.87 (t, 3H, J = 6.5 Hz), 0.91 (d, 6H, J = 6.5 Hz), 1.10-1.40 (m, 8H), 1.40 (d, 2H, J = 7.3 Hz), 1.75 (m, 1H), 1.9-2.1 m, 2H), 5.19 (dt, 1H, J = 15.0, 7.2 Hz), 5.32 (dt, 1H, J = 15.0, 7.3 Hz).

(Z)-1-(Isobutyldimethylsilyl)-2-nonene (17, R^1 = n-C_6H_{13}, R^2 = CH_2CHMe_2): ^{1}H NMR 0.00 (s, 6H), 0.52 (d, 2H, J = 7.2 Hz), 0.87 (t, 3H, J = 6.2 Hz), 0.92 (d, 6H, J = 6.5 Hz), 1.2-1.4 (m, 8H), 1.45 (d, 2H, J = 7.9 Hz), 1.75 (m, 1H), 1.9-2.1 (m, 2H), 5.24 (dt, 1H, J = 10.5, 7.7 Hz), 5.36 (dt, 1H, J = 10.5, 7.9 Hz).

2-(Isobutyldimethylsilyl)-1-nonene (20, R^1 = n-C_6H_{13}, R^2 = CH_2CHMe_2): ^{1}H NMR 0.00 (s, 6H), 0.58 (d, 2H, J = 6.9 Hz), 0.88 (t, 3H, J = 6.5 Hz), 0.92 (d, 6H, J = 6.6 Hz), 1.10-1.40 (m, 8H), 1.67 (tq, 1H, J = 6.9, 6.6 Hz), 2.02 (br-t, 2H, J = 7.5 Hz), 5.22 (dt, 1H, J = 3.0, 1.0 Hz), 5.45 (dt, 1H, J = 3.0, 1.6 Hz). Ms Calcd for $C_{15}H_{32}Si$: m/z = 240.227. Found: 240.222.

3-Phenyl-2-trimethylsilyl-1-propene (20, R^1 = Ph) and (E)-1-Phenyl-3-trimethylsilyl-1-propene (11, R^1 = Ph). Use of 1-chloromethyldimethylsilyl-2-phenylethyne (6, R^1 = Ph) in the above procedure gave a mixture of (E)-1-phenyl-3-trimethylsilyl-1-propene (11, R^1 = Ph) and 3-phenyl-2-trimethylsilyl-1-propene (20, R^1 = Ph) in 59% yield (11/20 = 57/43). Pure 20 (R^1 = Ph) was obtained by GLC.

3-Phenyl-2-trimethylsilyl-1-propene (20, R^1 = Ph): IR (liquid film), 2950, 1600, 1500, 1250, 915, 840, 760 cm^{-1}; ^{1}H NMR 0.00 (s, 9H), 3.45 (br-s, 2H), 5.41 (dt, 1H, J = 3.0, 1.1 Hz), 5.47 (dt, 1H, J = 3.0, 1.5 Hz), 7.1-7.5 (m, 5H). Ms Calcd for $C_{12}H_{18}Si$: m/z = 190.118. Found: 190.115.

(E)-1-Trimethylsilyl-2-methyl-2-nonene (21) from 1-(Chloromethyl)dimethylsilyl-1-octyne (6) by One-Pot Reaction. General Procedure. To a heptane solution of DIBAH (2.3 mmol, 1.8 mL of 1.28 M solution), 1-(chloromethyl)dimethylsilyl-1-octyne (6, R^1 = n-C_6H_{13}, 500 mg, 2.3 mmol) was added and then the reaction mixture was stirred at room temperature for 1 h. The reaction mixture maintained at 0°C was added with an ethereal solution of MeLi (7.0 mmol, 3.2 mL of 2.2 M solution) and then stirred at room temperature for 2 h. The reaction mixture was cooled to 0°C, treated successively with THF (5 mL), CuBr (33 mg, 0.23 mmol, 0.1 equiv), and MeI (3.5 mmol). The reaction mixture was stirred at 0°C for 3 h, poured onto ice-cooled dil. hydrochloric acid, and extracted with ether. The ethereal solution was washed with brine, dried over Na_2SO_4, and concentrated to afford (E)-1-trimethylsilyl-2-methyl-2-nonene (21, R^1 = n-C_6H_{13}, E = Me, 410 mg, 1.93 mmol, 84 % yield); Bp. 60°C/3 mmHg (Kugelrohr bath temp.); IR (liquid film), 2954, 2924, 2852, 1248, 836 cm^{-1}; ^{1}H NMR 0.00 (s, 9H), 0.86 (t, 3H, J = 6.6 Hz), 1.10-1.40 (m, 8H), 1.48 (br-s, 2H), 1.64 (dt, 3H, J = 2.5, 2.5 Hz), 1.86 (m, 2H), 4.98 (br-t, 1H, J = 6.8 Hz). Anal. Calcd for $C_{13}H_{28}Si$: C, 73.50; H, 13.28. Found: C, 73.33; H, 13.44.

(E)-3-(Trimethylsilylmethyl)-3-decene (21, R^1 = n-C_6H_{13}, E = Et). Obtained by the reaction of iodoethane, in place of MeI. IR (liquid film), 2954, 2922, 2854, 1247, 835 cm^{-1}; ^{1}H NMR 0.00 (s, 9H), 0.86 (t, 3H, J = 6.1 Hz), 1.00 (t, 3H, J = 7.5 Hz), 1.12-1.40 (m, 8H), 1.50 (s, 2H), 1.86 (dt, 2H, J = 6.0, 5.7 Hz), 2.07 (q, 2H, J = 7.5 Hz), 4.98 (t, 1H, J = 6.8 Hz). MS Calcd for $C_{14}H_{30}Si$: M^+ = 226.212. Found: 226.210.

(E)-5-(Trimethylsilylmethyl)-5-dodecene (21, R^1 = n-C_6H_{13}, E = n-C_4H_9). Obtained by the reaction with n-BuI. IR (liquid film), 2954, 2922, 2854, 1247, 835 cm^{-1}; ^{1}H NMR 0.00 (s, 9H), 0.87 (t, 3H, J = 6.5 Hz), 0.88 (t, 3H, J = 6.8 Hz), 1.16-1.45 (m, 12H), 1.48 (s, 2H), 1.90 (t, 4H, J = 7.0 Hz), 4.98 (t, 1H, J = 6.5 Hz). MS Calcd for $C_{16}H_{34}Si$: 254.243. Found: 254.241.

(E)-4-(Trimethylsilylmethyl)-1,4-undecadiene (21, R^1 = n-C_6H_{13}, E = $CH_2CH{=}CH_2$). Prepared by the reaction with 3-bromo-1-propene: ^{1}H NMR 0.00 (s, 9H), 0.86 (t, 3H, J = 6.1 Hz), 1.10-1.40 (m, 8H), 1.48 (s, 2H), 1.86 (dt, 2H, J = 6.0, 5.7 Hz), 2.64 (dt, 2H, J = 6.2, 1.6 Hz), 4.95 (m, 3H), 5.80 (ddt, 1H, J = 9.8, 16.9, 6.2 Hz). MS Calcd for $C_{15}H_{30}Si$: 238.212. Found: 238.215.

(E)-3-(Trimethylsilylmethyl)-1,3-decadiene (22, R^1 = n-C_6H_{13}). After 1-(chloromethyl)dimethylsilyl-1-octyne (6, R^1 = n-C_6H_{13}, 10 mmol) was successively treated with DIBAH and MeLi as described above, the reaction mixture was cooled to 0°C. Tetrahydrofuran (5 mL) and a THF solution of $ZnCl_2$ (10 mL of 1.0M solution) was added to the reaction mixture maintained at 0°C, and then the reaction mixture was stirred for 15 min. To the reaction mixture maintained at 0°C, bromoethene (2.1 g, 20 mmol) and $Pd(PPh_3)_4$ (115.4 mg, 0.1 mmol) were added successively. The reaction mixture was stirred at room temperature for 8 h and worked up in the usual manner to give (E)-3-(trimethylsilylmethyl)-1,3-diene (22, R^1 = n-C_6H_{13}, E = $CH{=}CH_2$) in 65% yield. Bp. 60°C/3 mmHg (Kugelrohr bath temp.); IR (liquid film), 3086, 1630, 1248, 1160, 987, 890 cm^{-1}; ^{1}H NMR, 0.00 (s, 9H), 0.90 (t, 3H, J = 6.5 Hz), 1.10-1.40 (m, 8H), 1.70 (s, 2H), 2.04 (dt, 2H, J = 6.5, 6.5 Hz), 4.90 (d, 1H, J = 11 Hz), 4.98 (d, 1H, 17 Hz), 5.35 (t, 1H, J = 6.5 Hz), 6.31 (dd, 1H, J = 11, 17 Hz). Anal. Calcd for $C_{14}H_{28}Si$: C, 74.91; H, 12.57. Found: C, 74.78; H, 12.72.

Methyl (E)-2-(Trimethylsilylmethyl)-2-nonenoate (23, R^1 = n-C_6H_{13}, R' = Me). After 1-(chloromethyl)dimethylsilyl-1-octyne (6) was successively treated with DIBAH and MeLi as described above, the reaction mixture was maintained at 0°C. To the reaction mixture, THF (5 mL) and $ZnCl_2$ (2.3 mmol, 0.7 ml of 3.5 M ether solution) were added. The reaction mixture was again maintained at room temperature and then treated successively with $Pd(PPh_3)_4$ (2.7 mg, 0.1 mmol) and methyl chlorocarbonate (0.2 mL, 1.1 eq). The reaction mixture was stirred at room temperature for 5 h, and then poured onto ice-cooled dil. hydrochloric acid. Usual extraction, washing, drying, and concentration of the mixture gave methyl (E)-2-(trimethylsilylmethyl)-2-nonenoate (23, R^1 = n-C_6H_{13}, R' = Me, 447 mg, 1.75 mmol, 76% yield): Bp. 120°C/2 mmHg (Kugelrohr bath temp.); IR (liquid film), 2954, 2924, 2854, 1717, 1458, 1249, 838 cm^{-1}; ^{1}H NMR 0.00 (s, 9H), 0.90 (t, 3H, J = 6.9 Hz), 1.18-1.50 (m, 8H), 1.58 (s. 2H), 2.10 (dt, 2H, J = 7.0, 6.0 Hz), 3.73 (s, 3H), 6.63 (t, 1H, J = 7.0 Hz). Anal. Calcd for $C_{14}H_{28}O_2Si$: C, 65.58; H, 11.00. Found: C, 65.54; H, 11.28.

3-Methylidene-1-decene Obtained by Protodesilylation of 22. A dichloromethane solution of (E)-3-(trimethylsilylmethyl)-1,3-decadiene (22, R^1 = n-C_6H_{13}, 224 mg, 1 mmol in 5 mL of solution) was added to a dichloromethane solution of p-toluenesulfonic acid (190 mg, 1mmol, in 5 mL of solution). The reaction mixture was stirred at 50°C (bath temperature) for 8 min. The cooled reaction mixture was poured onto ice-cooled aq. $NaHCO_3$ solution, and extracted with pentane. The pentane solution was dried, concentrated, and distilled to give 3-methylene-1-decene (140 mg, 92% yield). Bp. 100°C/25 mmHg (Kugelrohr bath temp.); IR (liquid film), 3088, 1577, 1250, 991, 892 cm^{-1}; ^{1}H NMR, 0.88 (t, 3H, J = 7.2 Hz), 1.10-1.40 (m, 10H), 2.20 (t, 2H, J = 7.5 Hz), 4.98 (b-s, 2H), 5.04 (d, 1H, J = 10.7 Hz), 5.22 (d, 1H, J = 18.4 Hz), 6.36 (dd, 1H, J = 10.7, 18.4 Hz).

(E)-1-(Chloromethyl)dimethylsilyl-1-butene (26a, R = Et). To an ice-cooled hexane solution of (chloromethyl)dimethylsilylethyne (24, 500 mg, 3.8 mmol, in 4 mL solution), a hexane solution of triethylaluminium (3.8 mmol, 1.9 mL of 2 M solution) was added. The reaction mixture was stirred at 0°C for 2 h, poured onto ice-cooled dil. hydrochloric acid and extracted with ether. Ethereal solution was washed with brine, dried over Na_2SO_4, and concentrated to give 500 mg (3.1 mmol, 81% yield) of (E)-1-(chloromethyl)dimethylsilyl-1-butene (26a, R = Et); IR (liquid film) 2954, 2895, 1248, 838 cm^{-1}; ^{1}H NMR 0.00 (s, 6H), 0.83 (t, 3H, J = 7.5 Hz), 1.98 (dq, 2H, J = 6.0, 7.5 Hz), 2.61 (s, 2H), 5.43 (dt, 1H, J = 18.0, 1.0 Hz), 6.05 (dt, 1H, J = 18.0, 6.0 Hz). MS Calcd for $C_7H_{15}ClSi$: M^+ = 162.065. Found: 162.067.

When the reaction mixture was worked up with 5 mL of D_2O, (E)-1-(chloromethyl)dimethylsilyl-1-deuterio-1-butene (26b, R = Et) was obtained; IR (liquid film), 2954, 2895, 1248, 838 cm^{-1}; ^{1}H NMR 0.00 (s, 6H), 0.83 (t, 3H, J = 7.5 Hz), 1.98 (dq, 2H, J = 6.0, 7.5 Hz), 2.61 (s, 2H), 6.05 (m, 1H). MS Calcd for $C_7H_{14}DClSi$: M^+ = 163.071. Found: 163.066.

(E)-4-(Chloromethyl)dimethylsilyl-1,4-heptadiene (26c). To an ice-cooled hexane solution of (chloromethyl)dimethylsilylethyne (24, 500 mg, 3.8 mmol in 4 mL of solution), a hexane solution of triethylaluminium (3.8 mmol, 1.9 mL of 2 M solution)was added. The reaction mixture was stirred at 0°C for 2 h, and then added with an ethereal solution of MeLi (3.8 mmol, 2.3 mL of 1.65 M solution) at 0°C. The reaction mixture was stirred at 0°C for 15 min, and then 3-bromo-1-propene (460 mg, 3.8 mmol) was added to the mixture. The reaction mixture was stirred overnight at room temperature, poured onto ice-cooled dil. hydrochloric acid, and extracted with ether. The ethereal solution was washed with brine, dried over Na_2SO_4, and concentrated to give (E)-4-(chloromethyl)dimethylsilyl-1,4-heptadiene (26c, R = Et, 693 mg, 90% yield); IR (liquid film), 2955, 2896, 1248, 838 cm^{-1}; ^{1}H NMR 0.00 (s, 6H), 0.83 (t, 3H, J = 7.5 Hz), 1.98 (q, 2H, J = 7.5 Hz), 2.61 (s, 2H), 2.76 (d, 2H, J = 6.0 Hz), 4.76 (m, 1H), 4.85 (m, 1H), 5.40 (m, 1H), 5.72 (t, 1H, J = 6.0 Hz). MS Calcd for $C_{10}H_{19}ClSi$: M^{+} = 202.0944. Found: 202.0940.

(1E,3E)-1,3-Bistrimethylsilyl-1,3-hexadiene (29b). To an ice-cooled hexane solution of trimethylsilylethyne (27, 0.5 g, 5.1 mmol in 5 mL solution), a hexane solution of triethylaluminium (2.6 mmol, 1.3 mL of 2 M solution) was added and the reaction mixture was stirred for 2 h at 0°C. The reaction mixture containing 29a was poured onto ice-cooled dil. hydrochloric acid and the mixture was extracted with hexane (3 times). The organic solution was washed with brine, dried over Na_2SO_4, and concentrated to give (1E,3E)-bistrimethylsilyl-1,3-hexadiene (29b, 542 mg, 94% yield). IR (liquid film), 2954, 2900, 1608, 1247, 835 cm$_{-1}$; ^{1}H NMR, 0.00 (s, 18H), 0.91 (t, 3H, J = 7.5 Hz), 2.01 (q, 2H, J = 7.5 Hz), 5.53 (d, 1H, J = 20 Hz), 5.65 (t, 1H, J = 7.5 Hz), 6.65 (d, 1H, J = 20 Hz). MS Calcd for $C_{12}H_{26}Si_2$: m/z = 226.157. Found: 226.155.

When 5 mL of D_2O was added to the ice-cooled reaction mixture, deuterated bistrimethylsilyl-1,3-hexadiene (29c) was obtained. ^{1}H NMR, 0.00 (s, 18H), 0.91 (t, 3H, J = 7.5 Hz), 2.01 (q, 2H, J = 7.5 Hz), 5.65 (t, 1H, J = 7.5 Hz), 6.65 (br-s, 1H). Ms Calcd for $C_{12}H_{25}DSi_2$: m/z = 227.165. Found: 227.160.

(1E,3E)-4-Methyl-1,3-bistrimethylsilyl-1,3-hexadiene . To a hexane solution of 1-trimethylsilyl-1-propyne (500 mg, 4.5 mmol in 5 mL solution), a hexane solution of Et_3Al (4.6 mmol, 2.3 mL of 2 M solution) was added. The reaction mixture was stirred at room temperature for 24 h, poured onto ice-cooled dil. hydrochloric acid, and extracted with hexane. The hexane solution was dried over Na_2SO_4, and concentrated to give (1E,3E)-4-methyl-1,3-bistrimethylsilyl-1,3-hexadiene (514 mg, 4.05 mmol, 90% yield); IR (liquid film), 2954, 1607, 1591, 1247, 834 cm^{-1}; ^{1}H NMR 0.00 (s, 18H), 0.92 (t, 3H, J = 7.0 Hz), 1.52 (s, 3H), 1.63 (s, 3H), 2.02 (q, 2H, J = 7.0 Hz), 4.68 (s, 1H). MS Calcd for $C_{14}H_{30}Si_2$: m/z = 254.188. Found: 254.187.

Workup with D_2O gave 1-d product: IR no significant difference; ^{1}H NMR 0.00 (s, 18H), 0.92 (t, 3H, J = 7.0 Hz), 1.52 (s, 3H), 1.63 (s, 3H), 2.02 (q, 2H, J = 7.0 Hz).

Acknowledgement. The financial supports by the Grant-in Aid (59470081, 60219015, 61211016) from the the Ministry of Education, Science, and Culture, as well as the Asahi Glass Foundation for Industrial Technology are deeply appreciated.

REFERENCES AND NOTES

1. Present address: Department of Applied Chemistry, Okayama University of Science, Ridai-cho, Okayama 700, Japan.
2. (a) Colvin, E. "Silicon in Organic Synthesis", Butterworths, London, 1981.
   (b) Sakurai, H. Pure Appl. Chem. 1982, 54, 1.
   (c) Weber, W. P. "Silicon Reagents for Organic Synthesis", Springer-Verlag, Berlin, 1983.
3. Takai, K.; Kataoka, Y.; Okazoe, T.; Utimoto, K. Tetrahedron Lett. 1987, 28, 1443.
4. Uchida, K.; Utimoto, K.; Nozaki, H. J. Org. Chem. 1976, 41, 2941.
5. Uchida, k.; Utimoto, K.; Nozaki, H. Tetrahedron 1977, 33, 2987.
6. Obayashi, M.; Utimoto, K.; Nozaki, H. J. Organomet. Chem. 1979, 177, 145.
7. Whitmore, F. C.; Sommer, L. H.; Gold, J. J. Am. Chem. Soc. 1947, 69, 1976.
8. Kumada, M.; Nakajima, J.; Ishikawa, M.; Yamamoto, K. J. Org. Chem. 1958, 23, 292.
9. Tamao, K.; Nakajima, T.; Kumada, M. Organometallics 1984, 3, 1655 and references cited therein.
10. Robinson, L. R.; Burns, G. T.; Barton, T. J. J. Am. Chem. Soc. 1985, 107, 3935.
11. Markl, G.; Horn, M.; Schlosser, W. Tetrahedron Lett. 1986, 27, 4019.
12. Sans, E. A.; Shechter, H. Tetrahedron Lett. 1985, 26, 1119.
13. Reaction of gem-dimetallic reagents: (a) Knochel, P.; Normant, J. F. Tetrahedron Lett. 1986, 27, 1039, 1043.

(b) Takai, K.; Nitta, K.; Utimoto, K. J. Am. Chem. Soc. 1986, 108, 7408.

14. Allylsilane bearing magnesium moiety on β-carbon was first reported: Nishiyama, H.; Yokoyama, H.; Narimatsu, S.; Itoh, K. Tetrahedron Lett. 1982, 23, 1267.
15. Preliminary reported: Shiragami, H.; Kawamoto, T.; Utimoto, K.; Nozaki, H. Tetrahedron Lett. 1986, 27, 589.
16. Authentic sample was prepared by the stereospecific coupling of an alkenyl bromide with a Grignard reagent under nickel catalysis: Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. Bull. Chem. Soc. Jpn. 1976, 49, 1958.
17. Analogous preparation of allylsilanes by the coupling of olefinic carbon and trimethylsilylmethylmagnesium chloride has been reported: (a) Hosomi, A.; Sakurai, H. Tetrahedron Lett. 1976, 1295.
    (b) Hayashi, T.; Fujiwa, T.; Okamoto, Y.; Katsuro, Y.; Kumada, M. Synthesis 1981, 1001.
18. Zweifel, G.; Murray, R. E.; On, H. P. J. Org. Chem. 1981, 46, 1292.
19. Ziegler, F. E.; Mikami, K. Tetrahedron Lett. 1984, 25, 131.
20. Intramolecular alkylation of 9 is conceivable to give alkylidenesilacyclopropane 13; preparation by photochemical reaction and isolation of 13 has been reported (ref. 21).
21. Ando, W.; Saso, H. Tetrahedron Lett. 1986, 27, 5625.
22. Hudrlik, P. F.; Schwartz, R. H.; Hogan, J. C. J. Org. Chem. 1979, 44, 155.
23. Uchida, K.; Utimoto, K.; Nozaki, H. J. Org. Chem. 1976, 41, 2215.
24. Eisch, J. J.; Damasevitz, G. A. J. Org. Chem. 1976, 41, 2214.