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TRANSITION-METAL CATALYZED SILYLZINCATION AND SILYLALUMINATION OF ACETYLENIC COMPOUNDS

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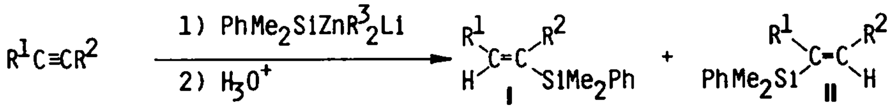
Abstract: Dialkyl(dimethylphenylsilyl)zinclithium and trialkyl(dimethylphenylsilyl)aluminiumlithium add effectively to internal acetylenes as well as terminal ones in the presence of transition-metal catalysts to provide vinylsilanes with high stereo- and regioselectivities.

The previously reported reaction[1] of Si-Mg, Si-Al, or Si-Zn reagents with an acetylenic linkage affords a simple and general method of vinylsilane synthesis. The regio- and stereochemistry of the reaction heavily depend on the nature of transition-metal catalyst employed. The method, however, has two major drawbacks: (1) The terminal acetylenes react with these reagents very easily, whereas the internal acetylenes are reluctant to react. (2) Regioselective preparation of 1-silyl-1-alkenes from 1-alkynes is easily performed with the combination of $PhMe_2SiMgMe$-CuI or $PhMe_2SiMgMe$-$PtCl_2(PBu_3)_2$. In contrast, it is difficult to obtain 2-silyl-1-alkenes with high regioselectivity. The combination of $PhMe_2SiAlEt_2$-$PdCl_2(P(o\text{-}tolyl)_3)_2$ gave the best results so far and provided 2-silyl-1-dodecene as a main product (85%) along with 1-silyl isomer (15%) upon treatment of 1-dodecyne. Here we wish to report the new silylmetalation reactions which solve these problems.[2]

Extensive studies have been devoted with the reactions of cuprates such as conjugate addition or substitution.[3] In contrast, few examples are known for the synthetic utility of organozincate reagents.[4] The ate complexes such as R_4BLi and R_4AlLi are much more reactive than the corresponding organometallic reagents, R_3B and R_3Al.[5] Thus, the ate complexes, $PhMe_2SiZnR_2Li$ and $PhMe_2SiAlR_3Li$, were hoped to react with internal acetylenes as well as terminal ones. This was indeed the case and the representative results are shown in Table 1 and Table 2.[6] The reaction has following characteristics: (1) CuI, CuCN, and $Pd(PPh_3)_4$ were effective catalysts for these silylmetalation reaction, while $RhCl(PPh_3)_3$ and $RuCl_2(PPh_3)_3$ were not efficient.[7] The uncatalyzed reaction of silylzinc and silylaluminium compounds with acetylenes proceeded very slowly to provide silylated olefins in low yield after prolonged reaction time. For instance, the CuCN catalyzed reaction of $PhMe_2SiZnEt_2Li$ with 1-dodecyne gave a mixture of 1-dimethylphenylsilyl-1-dodecene and the 2-silyl

Table 1. Silylzincation of Acetylenes[a]

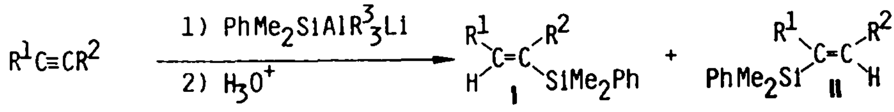


Entry	Substrate R^1	R^2	Reagent[b]	Catalyst	Y(%)	Ratio of I/II I	:	II
1	$^nC_{10}H_{21}$	H	$Ph_3SiZnEt_2Li$	CuI	90[c]	100	:	0
2			$PhMe_2SiZnEt_2Li$	$Pd(PPh_3)_4$	80	75	:	25
3			$PhMe_2SiZnEt_2Li$	CuCN	81	58	:	42
4			$PhMe_2SiZnEt_2Li$	$CoCl_2(PPh_3)_2$	60	30	:	70
5			$PhMe_2SiZn^tBu_2Li$	CuCN	92	1	:	99
6	$THPOCH_2CH_2$	H	$(PhMe_2Si)_3ZnMgMe$[d]	CuCN	97	100	:	0
7			$PhMe_2SiZnEt_2Li$	CuCN	80	67	:	33
8			$PhMe_2SiZn^iPr_2Li$	CuCN	97	30	:	70
9			$PhMe_2SiZn^tBu_2Li$	CuCN	87	1	:	99
10	$PhCH_2OCH_2CH_2$	H	$Ph_3SiZnEt_2Li$	CuI	87[c]	100	:	0
11			$PhMe_2SiZnEt_2Li$	CuCN	78	67	:	33
12			$PhMe_2SiZn^iPr_2Li$	CuCN	91	33	:	67
13			$PhMe_2SiZn^tBu_2Li$	CuCN	98	5	:	95
14	$HOCH_2$	H	$PhMe_2SiZnEt_2Li$[e]	CuCN	82	100	:	0
15	$HOCH_2CH_2$	H	$PhMe_2SiZnEt_2Li$[e]	CuCN	84	75	:	25
16			$PhMe_2SiZn^tBu_2Li$[e]	CuCN	83	47	:	53
17	$^nC_5H_{11}$	$^nC_5H_{11}$	$PhMe_2SiZnEt_2Li$	CuCN	90		——	
18	$HOCH_2$	CH_3	$PhMe_2SiZnEt_2Li$[e]	CuCN	85	100	:	0
19	$HOCH_2CH_2$	CH_3	$(PhMe_2Si)_3ZnLi$[e]	CuCN	89	100	:	0
20	$THPOCH_2CH_2$	$^nC_3H_7$	$(PhMe_2Si)_3ZnLi$	CuCN	96	50	:	50
21	$PhCH_2OCH_2CH_2$	CH_3	$PhMe_2SiZnEt_2Li$	CuCN	78	80	:	20
22	$^tBuMe_2SiOCH_2CH_2$	CH_3	$PhMe_2SiZnEt_2Li$	CuCN	62	83	:	17

a) The reactions were performed at 25°C in THF. Reagent (2.0 mmol), acetylene (1.0 mmol), and catalyst (2 mol%) were employed. b) Prepared from $PhMe_2SiLi$ and the corresponding dialkylzinc (1:1) at 0°C. c) The corresponding triphenylvinylsilane was obtained. d) Prepared from $PhMe_2SiMgMe$ (3.0 mmol) and $ZnBr_2$ (1.0 mmol). e) Reagent (3.0 mmol) and acetylene (1.0 mmol) were employed.

isomer (5:3) in 13% combined yield after sitrring at 25°C for 20 h. (2) The regioselectivity of the reaction was strongly affected by the nature of the dialkylzinc and trialkylaluminium employed. The use of bulky alkyl group favours the formation of 2-silyl-1-alkenes. Silylzinc reagent, $PhMe_2SiZn^tBu_2Li$[8] gave higher regioselectivity than the silylalanate, $PhMe_2SiAl^tBu_3Li$.[9] In the case of former reagent, high selectivity (>95%) was achieved for all examined substrates except entry 16 in Table 1. The selective preparation of 1-dimethylphenylsilyl-1-alkenes has already been achieved with $PhMe_2SiMgMe$ in the presence of CuI or $PtCl_2(PBu_3)_2$ catalyst.[1a] Thus, we have succeeded to obtain both

Table 2. Silylalumination of Acetylenes[a]

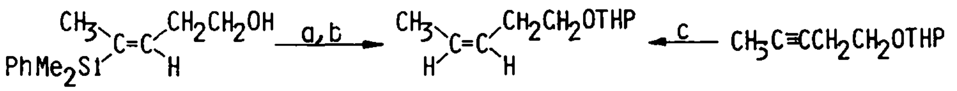


Entry	Substrate R^1	R^2	Reagent[b]	Catlyst	Y(%)	Ratio of I/II I : II
1	$^nC_{10}H_{21}$	H	$PhMe_2SiAlMe_3Li$	CuCN	78	67 : 33
2			$PhMe_2SiAlEt_3Li$	$Pd(PPh_3)_4$	73	64 : 36
3			$PhMe_2SiAl^tBu_3Li$	$Pd(PPh_3)_4$	65	40 : 60
4			$PhMe_2SiAl^tBu_3Li$	CuCN	45	17 : 83
5	$PhCH_2OCH_2CH_2$	H	$PhMe_2SiAlEt_3Li$	CuCN	72	83 : 17
6	$HOCH_2$	H	$PhMe_2SiAlEt_3Li$	CuCN	89	100 : 0
7			$PhMe_2SiAlEt_3Li$	$Pd(PPh_3)_4$	90	100 : 0
8			$PhMe_2SiAl^tBu_3Li$	$Pd(PPh_3)_4$	90	67 : 33
9			$PhMe_2SiAl^tBu_3Li$	CuCN	90	14 : 86
10	$HOCH_2$	CH_3	$PhMe_2SiAlEt_3Li^c$	CuCN	90	100 : 0
11	Bu(HO)CH	$^nC_3H_7$	$PhMe_2SiAlEt_3Li^c$	$Pd(PPh_3)_4$	63	100 : 0
12	$HOCH_2CH_2$	H	$PhMe_2SiAlEt_3Li^c$	$Pd(PPh_3)_4$	90	64 : 36
13			$PhMe_2SiAlEt_3Li^c$	CuCN	40	83 : 17

a) The reactions were performed at 25°C in THF. Reagent (2.0 mmol), acetylene (1.0 mmol), and catalyst (2mol%) were employed. b) Prepared from $PhMe_2SiLi$ and the corresponding trialkylaluminium (1:1). c) Reagent (3.0 mmol) and acetylene (1.0 mmol) were employed.

regioisomers with high selectivity (>95%). (3) Regioselective silylmetalation was performed for propargylic and homopropargylic alcohols. As shown in Table 1 (entry 18 and 19) and Table 2 (entry 10), 2-butyn-1-ol or 3-pentyn-1-ol gave (E)-3-dimethylphenylsilyl-2-buten-1-ol or (E)-4-dimethylphenylsilyl-3-penten-1-ol as a single product. The silylanion attacks the remote acetylenic carbon from hydroxyl group exclusively.

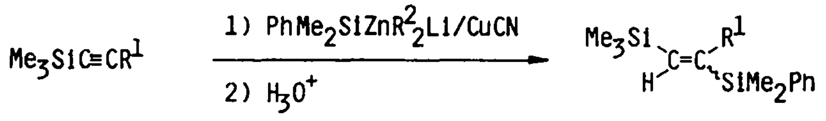
The cis mode of the addition was confirmed by the comparison of the tetrahydropyranyl ether of (Z)-3-penten-1-ol derived from the silylzincation product of 3-pentyn-1-ol (entry 19 in Table 1) with an authentic sample.



a: dihydropyran, $TsOH/CH_2Cl_2$ b: $^nBu_4NF/HMPA$[10]
c: $H_2/Pd-C$, 5% $BaSO_4$, quinoline

In further extension of this technique, we have examined the reaction of silylated acetylenes with the silylzinc reagents. The results are summarized in Table 3. 1,2-Disilylated alkenes were obtained exclusively regardless of the nature of the other substituent on acetylenic carbon. However, the stereochemistry of the reaction depends on the structure of the substrates. 1-Tri-

Table 3. Silylzincation of Trimethylsilylacetylenes in the Presence of CuCN catalyst[a]

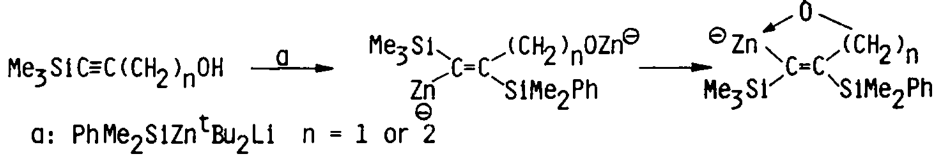


Entry	Substrate R^1	Reagent	Y(%)	Ratio of E/Z E : Z
1	H	$PhMe_2SiZnEt_2Li$	38	100 : 0
2		$PhMe_2SiZn^tBu_2Li$	78	100 : 0
3	$^nC_6H_{13}$	$(PhMe_2Si)_3ZnLi$	42	100 : 0
4		$PhMe_2SiZn^tBu_2Li$	53	100 : 0
5	CH_2OH	$PhMe_2SiZn^tBu_2Li^b$	75	0 : 100
6	CH_2CH_2OH	$PhMe_2SiZn^tBu_2Li^b$	44	0 : 100
7	CH_2CH_2OTHP	$PhMe_2SiZn^tBu_2Li$	72	100 : 0
8	$CH_2CH_2CH_2OH$	$PhMe_2SiZn^tBu_2Li^b$	74	100 : 0

a) Reagent (2.0 mmol), acetylene (1.0 mmol), and catalyst (2 mol%) were employed. b) Three mmol of reagent was used per 1.0 mmol of substrate.

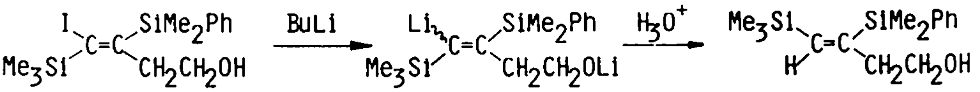
methylsilyl-1-octyne and 4-(2-tetrahydropyranyloxy)-1-trimethylsilyl-1-butyne gave the corresponding cis addition products, (E)-1,2-disilylated alkenes. Meanwhile, silylacetylenes having free hydroxyl group such as 3-trimethylsilyl-2-propyn-1-ol and 4-trimethylsilyl-3-butyn-1-ol provided (Z)-2-dimethylphenylsilyl-3-trimethylsilyl-2-propen-1-ol and (Z)-3-dimethylphenylsilyl-4-trimethylsilyl-3-buten-1-ol, respectively (Table 3, entry 5 and 6).[11,12] Apparently, the reaction proceeded in trans fashion in contrast to other substrates. These exceptional results could be explained by assuming the isomerizatin of primary cis adducts into (Z)-isomers which are stabilized by the chelation of neighbouring oxygen atom forming five, or six-membered ring depicted below (Scheme 1). Alternatively, trans addition of silyl group and zinc might occur by the intramolecular assistance of zincalkoxy group. However, no trans adducts were observed in the reaction mixture of 2-butyn-1-ol or 3-pentyn-1-ol with $PhMe_2SiZnEt_2Li$. The coexistence of silyl group and free hydroxyl group is essential for the trans addition. Thus, we prefer the former isomerization process to the direct trans addition mechanism for the formation of (Z)-disilylated alkenes. This was confirmed by the fact that (Z)-3-dimethylphenyl-

Scheme 1



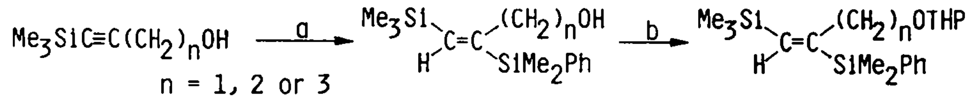
silyl-4-iodo-4-trimethylsilyl-3-buten-1-ol gave (Z)-3-dimethylphenylsilyl-4-trimethylsilyl-3-buten-1-ol exclusively on treatment with BuLi followed by aqueous workup (Scheme 2).[13]

Scheme 2



The authentic samples of tetrahydropyranyl ethers were prepared by hydrosilylation followed by treatment with PhMgBr (Scheme 3).[17]

Scheme 3



a: $HSiMe_2Cl/H_2PtCl_6$, PhMgBr b: dihydropyran, TsOH

EXPERIMENTAL

Melting points and boilng points are uncorrected. Bulb-to-bulb distillation was carried out by use of Kugelrohr (BÜchi) and bp was determined by measuring the bath temperature. ^{1}H-NMR spectra (tetramethylsilane as an internal standard unless otherwise noted) were obtaind on a Varian EM-390 or XL-200 spectrometer, chemical shifts being given in ppm units. IR data of neat liquid film samples (unless otherwise noted) were recorded on a JASCO IR-810 spectrometer, MS on a Hitachi M-80 spectrometer. Thin-layer chromatograph (TLC) analyses were performed on commercial glass plates bearing 0.25 mm layer of Merck silica-gel 60 F_{254}. Preparative TLC plates were prepared with Merck Kiesel-gel PF_{254}. Column chromatography was carried out with silica-gel (Wakogel C-200) at atmospheric pressure. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. Tetrahydrofuran was distilled from sodium benzophenone ketyl.

General Procedure for the Preparation of Vinylsilanes. The reaction of 1-dodecyne with $PhMe_2SiZnEt_2Li$ in the presence of CuCN catalyst is representative. A THF solution of $PhMe_2SiLi$ (0.71 M, 2.8 ml, 2.0 mmol) was added to a hexane solution of Et_2Zn (1.0 M, 2.0 ml, 2.0 mmol) at 0°C under an argon atmosphere and the whole was stirred for 15 min. Then a catalytic amount of CuCN (4 mg, 0.04 mmol) and a solution of 1-dodecyne (0.17 g, 1.0 mmol) in THF (3.0 ml) were added. After being stirred for 30 min at room temperature, the reaction mixture was poured into saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organic layers were dried over anhydrous sodium sulfate and concentrated. The crude product was purified by preparative thin-layer chromatography on silica-gel to give a mixture of (E)-1-dimethylphenylsilyl-1-dodecene and 2-dimethylphenylsilyl-1-dodecene in 81% combined yield (0.25 g, 58/42). The isomeric ratio was determined by glpc (PEG 20 M 5%, 1.5 m, 180°C, R_t = 9 min (2-silyl isomer) R_t = 11 min (1-silyl isomer)).

(E)-1-Triphenylsilyl-1-dodecene: Bp 195°C (bath temp, 2 Torr); IR (neat) 3070, 2930, 2850, 1615, 1430, 1110, 1070, 1000, 740, 700 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz) δ0.85 (bt, 3H), 1.05-1.55 (m, 16H), 2.08-2.30 (m, 2H), 6.08-6.22 (m, 2H), 7.23-7.65 (m, 15H); MS m/z (rel intensity) 426 (M, 18), 285 (100), 259 (90), 183 (44). Found: C, 84.36; H, 9.01%. Calcd for $C_{30}H_{38}Si$: C, 84.44; H, 8.98%.

(E)-1-Dimethylphenylsilyl-1-dodecene. The analytical pure sample was obtained by preparative glpc (PEG 20 M, 5% 1.5 m, 180°C). Bp 125°C (bath temp, 2 Torr); IR (neat) 3050, 2930, 2860, 1620, 1472, 1425, 1252, 1112, 990, 815 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz) δ0.30 (s, 6H), 0.87 (bt, 3H), 1.05-1.50 (m, 16H), 1.89-2.24 (m, 2H), 5.63 (d, *J* = 18.9 Hz, 1H), 6.01 (dt, *J* = 18.9 and 5.4 Hz, 1H), 7.10-7.46 (m, 5H); MS m/z (rel intensity) 302 (M, 12), 287 (71), 162 (100), 148 (26), 135 (60), 127 (54). Found: 302.2306. Calcd for $C_{20}H_{34}Si$: M$^+$, 302.2431.

2-Dimethylphenylsilyl-1-dodecene. The pure sample was prepared by the reaction of 1-dodecyne with $PhMe_2SiZn^tBu_2Li$ (Table 1, entry 5). Bp 125°C (bath temp, 2 Torr); IR (neat) 3050, 2940, 2850, 1475, 1434, 1254, 1114, 925, 832, 815 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz) δ0.35 (s, 6H), 0.87 (bt, 3H), 1.06-1.49 (m, 16H), 1.86-2.20 (m, 2H), 5.32 (m, 1H), 5.60 (m, 1H), 7.12-7.48 (m, 5H); MS m/z (rel intensity) 302 (M, 8), 287 (14), 224 (14), 176 (34), 161 (47), 135 (100), 121 (16). Found: C, 79.25; H, 11.41%. Calcd for $C_{20}H_{34}Si$: C, 79.39; H, 11.33%.

(E)-1-Dimethylphenylsilyl-4-(2-tetrahydropyranyloxy)-1-butene: Bp 123°C (bath temp, 2 Torr); IR (neat) 3070, 2950, 2870, 1620, 1430, 1250, 1140, 1120, 1040, 990, 820, 730, 700 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz) δ0.30 (s, 6H), 1.33-1.73 (m, 6H), 2.38 (dt, *J* = 6 and 6 Hz, 2H), 3.23-3.92 (m, 4H), 4.47-4.63 (m, 1H), 5.80 (d, *J* = 18 Hz, 1H), 6.15 (dt, *J* = 18 and 6 Hz, 1H), 7.20-7.60 (m, 5H); MS m/z (rel intensity) 290 (M, 0.3), 235 (26), 135 (14), 85 (100). Found: C, 70.42; H, 9.27%. Calcd for $C_{17}H_{26}O_2Si$: C, 70.29; H, 9.02%.

2-Dimethylphenylsilyl-4-(2-tetrahydropyranyloxy)-1-butene: Bp 123°C (bath temp, 2 Torr); IR (neat) 3050, 2950, 1430, 1350, 1250, 1120, 1030, 990, 930, 820, 780, 730, 700 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz) δ0.37 (s, 6H), 1.33-1.63 (m, 6H), 2.35 (t, *J* = 7.5 Hz, 2H), 3.10-3.83 (m, 4H), 4.37-4.47 (m, 1H), 5.40-5.50 (m, 1H), 5.70-5.80 (m, 1H), 7.20-7.57 (m, 5H); MS m/z (rel intensity) 290 (M, 0.2), 235 (21), 205 (29), 191 (38), 135 (33), 129 (28), 85 (100). Found: C, 70.45; H, 9.23%. Calcd for $C_{17}H_{26}O_2Si$: C, 70.29; H, 9.02%.

(E)-4-Benzyloxy-1-triphenylsilyl-1-butene: Bp 210°C (bath temp, 2 Torr); IR (neat) 3070, 2850, 1620, 1430, 1110, 1000, 780, 730, 700 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz) δ2.40-2.70 (m, 2H), 3.53 (t, *J* = 6.8 Hz, 2H), 4.47 (s, 2H), 6.22-6.33 (m, 2H), 7.23-7.77 (m, 20H); MS m/z (rel intensity) 420 (M, 0.3), 329 (58), 259 (40), 199 (43), 144 (100), 91 (28). Found: C, 82.96; H, 6.68%. Calcd for $C_{29}H_{28}OSi$: C, 82.81; H, 6.71%.

(E)-4-Benzyloxy-1-dimethylphenylsilyl-1-butene: Bp 145°C (bath temp, 2 Torr); IR (neat) 3080, 2970, 2870, 1623, 1434, 1250, 1115, 992, 820, 730, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ0.30 (s, 6H), 2.49 (dt, *J* = 6.5 and 6.5 Hz, 2H), 3.58 (t, *J* = 6.5 Hz, 2H), 4.55 (s, 2H), 5.88 (d, *J* = 19 Hz, 1H), 6.15 (dt, *J* = 19 and 6.5 Hz, 1H), 7.27-7.60 (m, 10H); MS m/z (rel intensity) 296 (M, 0.5), 281 (2), 205 (10), 144 (24), 135 (42), 91 (100). Found: C, 77.13; H, 8.37%. Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16%.

4-Benzyloxy-2-dimethylphenylsilyl-1-butene: Bp 145°C (bath temp, 2 Torr); IR (neat) 3050, 2960, 2860, 1460, 1430, 1360, 1250, 1115, 930, 820, 780, 735, 700 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz) δ0.33 (s, 6H), 2.37 (t, *J* = 6.8 Hz, 2H), 3.35 (t, *J* = 6.8 Hz, 2H), 4.30 (s, 2H), 5.43 (d, *J* = 3 Hz, 1H), 5.70-5.80 (m, 1H), 7.20-7.57 (m, 10H); MS m/z (rel intensity) 296 (M, 2), 281 (4), 241 (14), 219 (28), 190 (19), 135 (36), 127 (43), 113 (100), 91 (49). Found: C, 76.95; H, 8.31%. Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16%.

(E)-3-Dimethylphenylsilyl-2-propen-1-ol: Bp 75°C (bath temp, 2 Torr); IR (neat) 3320, 3070, 2950, 1620, 1430, 1250, 1120, 1080, 990, 840, 730, 700 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz) δ0.33 (s, 6H), 1.83-2.00 (bs, 1H), 2.96 (d, *J* = 3 Hz, 2H), 4.33 (d, *J* = 18 Hz, 1H), 4.53 (dt, *J* = 18 and 3 Hz, 1H), 5.26-5.53 (m, 5H); MS m/z (rel intensity) 192 (M, 1), 191 (M-1, 2), 177 (34), 135 (13), 75 (100). Found: C, 68.81; H, 8.67%. Calcd for $C_{11}H_{16}OSi$: C, 68.69; H, 8.38%.

A mixture of (E)-4-Dimethylphenylsilyl-3-buten-1-ol and 3-Dimethylphenylsilyl-3-buten-1-ol: Bp 85°C (bath temp, 2 Torr); IR (neat) 3350, 3070, 2950, 1620, 1430, 1250, 1115, 995, 820, 730, 700 cm^{-1}; ^{1}H-NMR (CCl$_4$, 90 MHz) δ0.32 (s, 6H), 1.43 (bs, 1H), 2.30 (t, *J* = 6 Hz, 0.5H), 2.33 (dt, *J* = 6 and 6 Hz, 1.5H), 3.45 (t, *J* = 6 Hz, 0.5H), 3.58 (t, *J* = 6 Hz, 1.5H), 5.47-5.57 (m, 0.25H), 5.70-5.80 (m, 0.25H), 5.80 (d, *J* = 19.5 Hz, 0.75H), 6.10 (dt, *J* = 19.5 and 6 Hz, 0.75H), 7.23-7.60 (m, 5H); MS m/z (rel intensity) 206 (M, 0.3), 205 (M-1, 0.5), 191 (100), 178 (67), 163 (100), 137 (64), 130 (100), 104 (72), 75 (100). Found: C, 69.90; H, 9.04%. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79%.

(E)-6-Dimethylphenylsilyl-6-dodecene: Bp 110°C (bath temp, 2 Torr); IR (neat) 2960, 2930, 2860, 1610, 1470, 1430, 1250, 1110, 830, 820, 770, 730, 700 cm^{-1}; ^{1}H-NMR (CCl$_4$, 90 MHz) δ0.30 (s, 6H), 0.67-1.00 (m, 6H), 1.00-1.50 (m, 12H), 1.90-2.23 (m, 4H), 5.75 (t, *J* = 6.8 Hz, 1H), 7.20-7.57 (m, 5H); MS m/z (rel intensity) 302 (M, 3), 287 (9), 224 (16), 166 (29), 135 (100), 82 (10). Found: C, 79.12; H, 11.58%. Calcd for $C_{20}H_{34}Si$: C, 79.39; H, 11.33%.

(E)-3-Dimethylphenylsilyl-2-buten-1-ol: Bp 90°C (bath temp, 2 Torr); IR (neat) 3325, 3175, 2960, 1430, 1250, 1110, 1070, 1010, 835, 820, 700 cm^{-1}; ^{1}H-NMR (CCl$_4$, 90 MHz) δ0.35 (s, 6H), 1.03 (bs, 1H), 1.67 (s, 3H), 4.18 (d, *J* = 6 Hz, 2H), 5.93 (t, *J* = 6 Hz, 1H), 7.23-7.56 (m, 5H); MS m/z (rel intensity) 206 (M, 0.8), 205 (M-1, 0.8), 191 (18), 135 (47), 75 (100). Found: C, 69.97; H, 9.03%. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79%.

(E)-4-Dimethylphenylsilyl-3-penten-1-ol: Bp 85°C (bath temp, 2 Torr); IR (neat) 3350, 3075, 2960, 1430, 1250, 1115, 1050, 830, 820, 700 cm^{-1}; ^{1}H-NMR (CCl$_4$, 90 MHz) δ0.32 (s, 6H), 1.47 (bs, 1H), 1.67 (s, 3H), 2.33 (dt, *J* = 6 and 6 Hz, 2H), 3.58 (t, *J* = 6 Hz, 2H), 5.80 (t, *J* = 6 Hz, 1H), 7.23-7.57 (m, 5H); MS m/z (rel intensity) 220 (M, 0.3), 205 (100), 177 (100), 143 (100), 137 (78), 135 (45), 127 (100), 75 (100). Found: C, 70.86; H, 9.37%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%.

A mixture of (E)-4-Dimethylphenylsilyl-1-(2-tetrahydropyranyloxy)-3-heptene and (E)-3-Dimethylphenylsilyl-1-(2-tetrahydropyranyloxy)-3-heptene: Bp 115-120°C (bath temp, 2 Torr); IR (neat) 3070, 2950, 2870, 1615, 1430, 1250, 1120, 1035, 820, 700 cm^{-1}; ^{1}H-NMR (CCl$_4$, 90 MHz) δ0.32 (s, 3H), 0.33 (s, 3H), 0.92 (t, *J* = 7.5 Hz, 3H), 1.35-1.68 (m, 8H), 1.90-2.55 (m, 4H), 3.20-3.83 (m, 4H), 4.35-4.50 (m, 0.5H), 4.50-4.63 (m, 0.5H), 5.87 (t, *J* = 6 Hz, 1H), 7.17-7.60 (m, 5H); MS m/z (rel intensity) 332 (M, 0.3), 235 (38), 135 (31), 85 (100). Found: C, 72.11; H, 9.81%. Calcd for $C_{20}H_{32}O_2Si$: C, 72.23; H, 9.70%.

A mixture of (E)-5-Benzyloxy-2-dimethylphenylsilyl-2-pentene and (E)-5-Benzyloxy-3-dimethylphenylsilyl-2-pentene: Bp 125°C (bath temp, 2 Torr); IR (neat) 3060, 2950, 2850, 1720, 1620, 1450, 1430, 1360, 1250, 1110, 1030, 830, 815, 770, 730, 700 cm^{-1}; ^{1}H-NMR (CDCl$_3$, 200 MHz) δ0.33 (s, 6H), 1.68 (s, 2.4H), 1.73 (d, *J* = 7 Hz, 0.6H), 2.40-2.58 (m, 2H), 3.27 (t, *J* = 6.8 Hz, 0.4H), 3.53 (t, *J* = 6.8 Hz, 1.6H), 4.40 (s, 0.4H), 4.53 (s, 1.6H), 5.86 (t, *J* = 7 Hz, 0.8H), 6.04 (q, *J* = 7 Hz, 0.2H), 7.30-7.63 (m, 10H); MS m/z (rel intensity) 310 (M, 0.5), 295 (3), 241 (54), 204 (18), 158 (70), 143 (100), 135 (88), 127 (54), 91 (76). Found: C, 77.20; H, 8.62%. Calcd for $C_{20}H_{26}OSi$: C, 77.36; H, 8.44%.

A mixture of (E)-5-(t-Butyldimethylsilyloxy)-2-dimethylphenylsilyl-2-pentene and (E)-5-(t-Butyldimethylphenylsilyloxy)-3-dimethylphenylsilyl-2-pentene: Bp 113°C (bath temp, 2 Torr); IR (neat) 3370, 2950, 2850, 1620, 1470, 1430, 1250, 1100, 940, 830, 770, 700 cm^{-1}; ^{1}H-NMR (CDCl$_3$, 200 MHz) δ-0.03 (s, 1H), 0.04 (s, 5H), 0.31 (s, 6H), 0.85 (s, 1.5H), 0.89 (s, 7.5H), 1.68 (s, 2.5H), 1.75 (q, *J* = 6 Hz, 0.5H), 2.30-2.48 (m, 2H), 3.40 (t, *J* = 7.5 Hz, 0.3H), 3.68 (t, *J* = 7.5 Hz, 1.7H), 5.85 (t, *J* = 5.5 Hz, 0.17H), 6.03 (q, *J* = 6 Hz, 0.83H), 7.33-7.45 (m, 3H), 7.45-7.60 (m, 2H); MS m/z (rel intensity) 334 (M, 0.3), 319 (1), 277 (100), 209 (100), 135 (100), 89 (100). Found: C, 68.09; H, 10.54%. Calcd for

$C_{19}H_{34}OSi_2$: C, 68.19; H, 10.24%.

(E)-7-Dimethylphenylsilyl-6-decen-5-ol: Bp 110°C (bath temp, 2 Torr); IR (neat) 3350, 2950, 2870, 1465, 1430, 1250, 1110, 1000, 830, 820, 770, 730, 700 cm^{-1}; ^{1}H-NMR (CDCl$_3$, 200 MHz) δ0.38 (s, 6H), 0.84 (t, J = 7.5 Hz, 3H), 0.94 (t, J = 7 Hz, 3H), 1.15-1.73 (m, 9H), 2.15 (t, J = 8 Hz, 2H), 4.45-4.60 (m, 1H), 5.80 (d, J = 8 Hz, 1H), 7.35-7.63 (m, 5H); MS m/z (rel intensity) 290 (M, 2), 289 (M-1, 2), 272 (6), 169 (42), 135 (50), 75 (100). Found: C, 74.38; H, 10.53%. Calcd for $C_{18}H_{30}OSi$: C, 74.42; H, 10.41%.

Desilylation of (E)-5-(2-Tetrahydropyranyloxy)-2-dimethylphenylsilyl-2-pentene. A solution of the silylzincation product of 3-pentyn-1-ol (0.22 g, 1.0 mmol) in CH_2CH_2 ((3 ml) was treated with dihydropyran in the resence of a catalytic amount of TsOH. A THF solution of ^{n}Bu$_4$NF (3.0 mmol) was added to a solution of the crude tetrahydropyranyl ether in HMPA (3 ml). The mixture was stirred at 25°C for 2 h. Workup and purification by preparative tlc on silica gel gave (Z)-5-(2-tetrahydropyranyloxy)-2-pentene (0.14 g, 80% yield). The physical data was identified with the sample obtained from hydrogenation of 5-(2-tetrahydropyranyloxy)-2-pentyne.

(E)-1-Dimethylphenylsilyl-2-trimethylsilylethene: Bp 80°C (bath temp, 2 Torr); IR (neat) 3070, 2950, 1430, 1250, 1170, 1120, 1010, 840, 720, 700 cm^{-1}; ^{1}H-NMR (CDCl$_3$, 200 MHz) δ0.08 (s, 9H), 0.35 (s, 6H), 6.73 (s, 2H), 7.35-7.63 (m, 5H); MS m/z (rel intensity) 234 (M, 100), 219 (100), 161 (100), 146 (97), 135 (100), 73 (100). Found: C, 66.74; H, 9.69%. Calcd for $C_{13}H_{22}Si_2$: C, 66.59; H, 9.46%.

(E)-2-Dimethylphenylsilyl-1-trimethylsilyl-1-octene: Bp 105°C (bath temp, 2 Torr); IR (neat) 3070, 2950, 2930, 2850, 1470, 1430, 1250, 1115, 835, 770, 700 cm^{-1}; ^{1}H-NMR (CDCl$_3$, 200 MHz) δ0.13 (s, 9H), 0.35 (s, 6H), 0.85 (t, J = 5 Hz, 3H), 1.13-1.33 (m, 8H), 2.18-2.30 (m, 2H), 6.15 (s, 1H), 7.35-7.63 (m, 5H); MS m/z (rel intensity) 318 (M, 3), 248 (19), 168 (15), 135 (100), 73 (14). Found: C, 71.58; H, 10.84%. Calcd for $C_{19}H_{34}Si_2$: C, 71.62; H, 10.75%.

(Z)-2-Dimethylphenylsilyl-3-trimethylsilyl-2-propen-1-ol: Bp 105°C (bath temp, 2 Torr); IR (neat) 3300, 2950, 2900, 1430, 1250, 1110, 1070, 1020, 850, 730, 700 cm^{-1}; ^{1}NMR (CDCl$_3$, 200 MHz) δ-0.003 (s, 9H), 0.44 (s, 6H), 1.5 (bs, 1H), 4.21 (d, J = 1.72 Hz, 2H), 6.72 (t, J = 1.72 Hz, 1H), 7.32-7.64 (m, 5H); MS m/z (rel intensity) 249 (M-15, 2), 248 (7), 208 (30), 135 (73), 112 (86), 73 (100). Found: C, 63.79; H, 9.32%. Calcd for $C_{14}H_{24}OSi_2$: C, 63.57; H, 9.15%.

Desilylation of (Z)-2-Dimethylphenylsilyl-3-trimethylsilyl-2-propen-1-ol with ^{n}Bu$_4$NF in THF: Selective desilylation was performed according to the literature[10]. A THF solution of ^{n}Bu$_4$NF (2.0 mmol) was added to a solution of disilylated alcohol (66 mg, 1.25 mmol) in THF (5 ml) and the mixture was stilled at 25°C for 2h. Work up (AcOEt, H_2O) and purification by preparative tlc on silica gel gave (E)-3-Trimethylsilyl-2-propen-1-ol (10 mg, 31%). The physical data of the compound was identical with the reported ones.[14]

(Z)-3-Dimethylphenylsilyl-4-trimethylsilyl-3-buten-1-ol: Bp 105°C (bath temp, 2 Torr); IR (neat) 3300, 3070, 2960, 1430, 1250, 1120, 1070, 830, 780, 730, 700 cm^{-1}; ^{1}NMR (CDCl$_3$, 200 MHz) δ-0.03 (S, 9H), 0.43 (s, 6H), 1.63 (bs, 1H), 2.56 (dt, J = 1.1 and 6.5 Hz, 2H), 3.63 (t, J = 6.5 Hz, 2H), 6.60 (t, J = 1.1 Hz, 1H), 7.38-7.63 (m, 5H); MS m/z (rel intensity) 263 (M-15, 7), 262 (43), 208 (100), 165 (53), 147 (53), 135 (62), 103 (36), 73 (64). Found: 279.1481. Calcd for $C_{15}H_{27}OSi_2$: M^++1, 279.1601.

(E)-4-Trimethylsilyl-3-buten-1-ol. Following the procedure described for the desilylation of (Z)-2-dimethylphenylsilyl-3-trimethylsilyl-2-propene-1-ol, (Z)-3-dimethylphenylsilyl-4-trimethylsilyl-3-buten-1-ol was converted into the title compound (69% yield) which was spectrometrically identical with an authentic sample.[15]

(E)-2-Dimethylphenylsilyl-4-(2-tetrahydropyranyloxy)-1-trimethylsilyl-1-butene: Bp 120°C (bath temp, 2 Torr); IR (neat) 3070, 2950, 1430, 1250, 1120, 1035, 840, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ0.15 (s, 9H), 0.37 (s, 6H), 1.43-1.74 (m, 6H), 2.65 (t, *J* = 7.5 Hz, 2H), 3.18-3.90 (m, 4H), 4.40-4.48 (m, 1H), 6.31 (s, 1H), 7.35-7.63 (m, 5H); MS m/z (rel intensity) 347 (M-15, 0.08), 346 (0.15), 345 (0.5), 262 (38), 234 (78), 173 (100), 147 (47), 135 (100), 102 (57), 85 (100), 73 (60). Found: C, 66.20; H, 9.62%. Calcd for $C_{20}H_{34}O_2Si_2$: C, 66.24; H, 9.45%.

(E)-4-Dimethylphenylsilyl-5-trimethylsilyl-4-penten-1-ol: Bp 105°C (bath temp, 2 Torr); IR (neat) 3350, 2950, 1430, 1250, 1110, 1060, 830, 770, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ0.14 (s, 9H), 0.38 (s, 6H), 1.43-1.59 (m, 2H), 1.88-2.08 (bs, 1H), 2.28-2.40 (m, 2H), 3.53 (t, *J* = 6.5 Hz, 2H), 6.21 (s, 1H), 7.35-7.60 (m, 5H); MS m/z (rel intensity) 277 (M-15, 1), 276 (4), 247 (22), 174 (16), 135 (100), 73 (27). Found: C, 65.68; H, 9.81%. Calcd for $C_{16}H_{28}OSi_2$: C, 65.69; H, 9.65%.

Transformation of (Z)-3-Dimethylphenylsilyl-4-iodo-4-trimethylsilyl-3-buten-1-ol into (Z)-3-Dimethylphenylsilyl-4-trimethylsilyl-3-buten-1-ol. Butyllithium (1.4 M, 0.1 ml, 0.14 mmol) was added to a solution of vinyl iodide (15 mg, 0.037 mmol) in THF (3.0 ml) at 25°C. After stirring for 1 h, the resulting mixture was poured into water and extracted with ethyl acetate (5 ml x 3). Concentration of the dried (Na_2SO_4) organic layer gave an oil which was identical with the sample generated from the reaction of 4-trimethylsilyl-3-butyn-1-ol with $PhMe_2SiZn^tBu_2Li$.

Preparation of (E)-3-Dimethylphenylsilyl-4-trimethylsilyl-3-buten-1-ol and its Tetrahydropyranyl Ether by Hydrosilylation. Hydrosilylation of trimethylsilylacetylene was performed following the reported procedure.[16] A mixture of Me_2SiClH (0.5 ml, 4.5 mmol) and a trace of chloroplatinic acid (2 mg) was stirred in an ice bath for 10 min. 4-Trimethylsilyl-3-butyn-1-ol (0.20 g, 1.4 mmol) was added and the mixture was stirred at 0°C for 15 min then at 25°C for 2 h. The resulting mixture was cooled (ice bath) and diluted with ether (5 ml) and PhMgBr (1.8 M ether solution, 3.0 ml, 5.4 mmol) was added. The mixture was stirred for another 1 h at 25°C and then added to aqueous NH_4Cl and extracted with ether. Purification by preparative tlc on silica gel gave (E)-3-dimethylphenylsilyl-4-trimethylsilyl-3-buten-1-ol (0.32 g, 80% yield): IR (neat) 3330, 3070, 2950, 1430, 1250, 1110, 1040, 830, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ0.16 (s, 9H), 0.38 (s, 6H), 2.58 (t, *J* = 7.5 Hz, 2H), 3.46 (t, *J* = 7.5 Hz, 2H), 6.38 (s, 1H), 7.35-7.63 (m, 5H). Upon treatment with dihydropyran and a catalytic amount of TsOH, the alcohol was transformed into tetrahydropyranyl ether which was identical with the sample prepared by the reaction of 4-(2-tetrahydropyranyloxy)-1-trimethylsilyl-1-butyne with $PhMe_2SiZnEt_2Li$.

Preparation of (E)-Dimethylphenylsilyl-5-trimethylsilyl-4-penten-1-ol by Hydrosilylation Method. In similar fashion, the title compound was obtained by hydrosilylation of 5-trimethylsilyl-4-pentyn-1-ol with Me_2SiClH followed by treatment with PhMgBr. The alcohol was spectrometrically identical with the sample derived from the silylzincation reaction of 5-trimethylsilyl-4-pentyn-1-ol (Table 3 entry 8).

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6. The reagents are also effective for 1,4-addition to α,β-unsaturated carbonyl compounds. For instance, the addition of $PhMe_2SiZnEt_2Li$ to 2-cyclohexenone gave the 1,4-adduct, 3-dimethylphenylsilylcyclohexanone in 80% yield, while $PhMe_2SiLi$ provided 1-dimethylphenylsilyl-2-cyclohexen-1-ol (60% yield) as the main product. See ref. 4d.
7. $CoCl_2(PPh_3)_2$ was also effective catalyst for silylzinc reagent, but not for silylaluminium reagent.
8. Dialkyl zincs were prepared according to the following references. $^tBu_2Zn$: M. H. Abraham, *J. Chem. Soc.*, **1960**, 4130. $^iPr_2Zn$: M. W. Rathke and H. Yu, *J. Org. Chem.*, **37**, 1732 (1972). We thank Toyo Stauffer Chemical Company for the gift of Et_2Zn.
9. $^tBu_3Al$ was prepared from ^tBuMgCl and $AlCl_3$ in situ and used directly without further purification.
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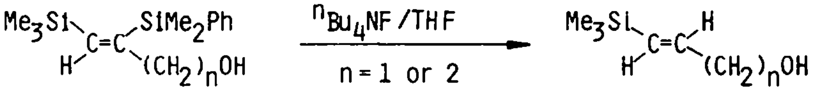
11. Selective desilylation ($PhMe_2Si$) of these products in the presence of Me_3Si group by $^nBu_4NF$ in THF[10] provided (E)-3-trimethylsilyl-2-propen-1-ol and (E)-4-trimethylsilyl-3-buten-1-ol, respectively.



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