Highly Stereoselective Synthesis of Vinylsilanes from Carbonyl Compounds

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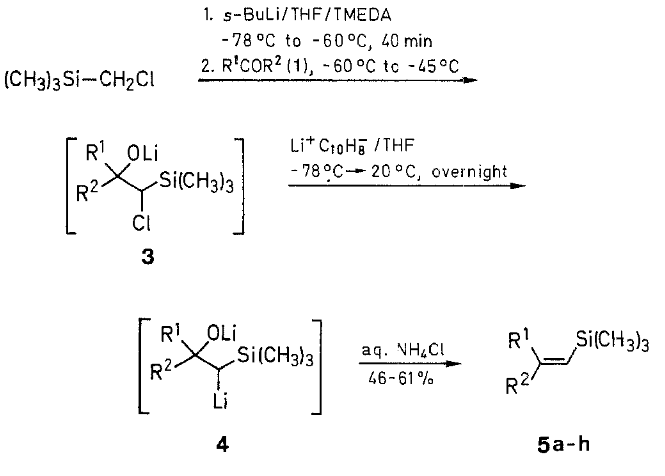
The *in situ* generated (chlorolithiomethyl)trimethylsilane reacts at − 60 °C to − 45 °C with different aldehydes or ketones **1** to afford, after lithiation with lithium naphthalenide at − 78 °C to 20 °C, vinylsilanes **5a–h** in a stereoselective manner.

The great synthetic utility of vinylsilanes[1] is critically dependent on their availability. Most existing methodologies utilize alkynes, carbonyl compounds, or vinyl halides.[2] In the case of starting from carbonyl compounds, the most important procedures involve variants of the Peterson reaction; inconveniences of this route are either by-reactions with enolizable carbonyl compounds or the obtention of (*Z,E*)-mixtures.[2] We report here a new and general method for preparing vinylsilanes from aldehydes and ketones with high stereoselectivity.

When different aldehydes and ketones **1** were allowed to react with (chlorolithiomethyl)trimethylsilane $[CH_3)_3SiCHClLi]$ (**2**) [generated *in situ* by lithiation of (chloromethyl)trimethylsilane[3] with *sec*-butyllithium and tetramethylethylenediamine (TMEDA) at − 78 °C to − 60 °C][4] at temperatures ranging between − 60 °C and − 45 °C, the intermediates **3** were obtained,[5] which by chlorine-lithium interchange using lithium naphthalenide[6] at − 78 °C to 20 °C led to the corresponding *β*-substituted organolithium species **4**;[7] the spontaneous *β*-elimination of this unstable intermediate led to the expected vinylsilanes **5** in a stereoselective manner. Thus, starting from aldehydes **1d–h** the corresponding products **5d–h** were isolated, which had an (*E*)-configuration in > 95 % (determined by GLC) (Table 1).



1, 5	R^1	R^2	1, 5	R^1	R^2
a	C_2H_5	C_2H_5	**e**	H	n-C_4H_9
b	$-(CH_2)_4-$		**f**	H	i-C_4H_9
c	$-(CH_2)_5-$		**g**	H	C_6H_5
d	H	n-C_3H_7	**h**	H	$C_6H_5CH_2CH_2$

Table 1. Vinylsilanes **5** Prepared

Product	Yield[a] (%)	bp (°C)/mbar	Molecular Formula[b] or Lit. bp (°C)/mbar
5a	61	45–47/20	$C_9H_{20}Si$ (156.3)
5b	52	39–41/20	$C_9H_{18}Si$ (154.3)
5c	55	49–52/20	75/39[9]
(*E*)-**5d**[c]	54	53–55/20	135/988[10]
(*E*)-**5e**[c]	51	44–46/20	72–76/39[11]
(*E*)-**5f**[c]	50	37–39/20	–[d]
(*E*)-**5g**[c]	46	90–92/20	90–91/17[13]
(*E*)-**5h**[e]	48	65–67/0.13	–[f]

[a] Overall yield of isolated product based on starting ketone **1**. Purity was confirmed by GLC.
[b] Satisfactory microanalyses obtained: C ±0.1, H ±0.2.
[c] >95% (*E*)-configuration, (GLC).
[d] No data available in ref. 12.
[e] >98% (*E*)-configuration, (GLC).
[f] No data reported in ref. 14.

Vinylsilanes 5; General Procedure:

To a stirred solution of (chloromethyl)trimethylsilane (1.4 mL, 10 mmol) in THF (15 mL) is successively added a 1.4 M solution of *sec*-butyllithium in cyclohexane (7.8 mL, 11 mmol) and TMEDA (1.5 mL, 10 mmol) at −78 °C under argon. Stirring is continued for 40 min allowing the temperature to rise to −60 °C, and then a solution of the carbonyl compound **1** (10 mmol) in THF (3 mL) is added to the resulting mixture, which is stirred 2 h at temperatures ranging between −65 °C and −45 °C. The resulting mixture is then cooled to −78 °C, a solution of lithium naphthalenide in THF (22 mmol) is added and stirring is continued overnight allowing the temperature to rise to 20 °C. The mixture is then hydrolyzed with sat. aq. NH_4Cl, and extracted with ether (3 × 15 mL). The organic layer is dried (Na_2SO_4), and the solvents are distilled. Products are then bulb-to-bulb distilled (0.13 mbar, 40 °C bath temperature) and further purified by distillation (20 mbar).

This paper is dedicated to the memory of Dr. Antonio Ara.

Received: 20 July 1987

Table 2. Spectral Data of Compounds **5**

Product	IR (film)[a] $\nu_{C=C}$ (cm^{-1})	^{1}H-NMR ($CDCl_3$)[b,c] δ, *J* (Hz)	^{13}C-NMR ($CCl_4 + D_2O$ capillary)[b,d] δ	MS[e] *m/z* (%)
5a	3025, 1605 (HC=C)	0.0 (s, 9H, 3 × $SiCH_3$); 0.9 (t, 6H, *J* = 5, 2 × CH_3); 1.9–2.2 (m, 4H, 2 × CH_2); 5.1 (s, 1H, CH=C)	0.5 ($SiCH_3$); 13.0, 14.1 (2 × CH_3); 29.4, 31.2 (2 × CH_2); 121.1 ($\underline{C}$H=C); 162.8 ($\underline{C}$=CSi)	156 (M^+, 17); 142 (15); 141 (M^+ − 15, 100); 113 (17); 99 (30); 87 (29); 73 (51); 59 (56); 45 (12); 43 (10)
5b	3025, 1615 (HC=C)	0.0 (s, 9H, 3 × $SiCH_3$); 1.4–1.7 (m, 4H, 2 × CH_2); 2.1–2.3 (m, 4H, 2 × CH_2C=C); 5.3 (s, 1H, CH=C)	−0.6 ($SiCH_3$); 16.0, 27.2, 32.4, 37.5 (ring CH_2); 118.6 ($\underline{C}$H=C); 163.0 ($\underline{C}$=CSi)	154 (M^+, 18); 140 (11); 139 (M^+ − 15, 100); 111 (10); 79 (26); 73 (23); 59 (49); 45 (6); 43 (7)
5c	3040, 1610 (HC=C)[9]	0.0 (s, 9H, 3 × $SiCH_3$); 1.4–1.6 (m, 6H, 3 × CH_2); 2.0–2.2 (m, 4H, 2 × CH_2C=C); 5.0 (s, 1H, CH=C)[f,9]	−0.5 ($SiCH_3$); 25.9, 28.0, 28.4, 35.1, 40.2 (ring CH_2); 120.4 ($\underline{C}$H=C); 159.3 ($\underline{C}$=CH)	168 (M^+, 20); 154 (15); 153 (M^+ − 15, 100); 125 (31); 93 (16); 85 (10); 73 (19); 59 (44); 45 (7); 43 (5)
(*E*)-**5d**	3030, 1615 (HC=C)	0.0 (s, 9H, 3 × $SiCH_3$); 0.8 (t, 3H, *J* = 5, CH_3); 1.1–1.5 (m, 2H, $C\underline{H}_2CH_3$); 1.8–2.2 (m, 2H, CH_2C=C); 5.6 (d, 1H, *J* = 19, SiCH=C); 6.1 (2t, 1H, *J* = 19 and 5, CH=CSi)	−1.0 ($SiCH_3$); 13.9 (CH_3); 22.0, 39.1 (2 × CH_2); 130.6 (Si$\underline{C}$H=C); 147.8 ($\underline{C}$H=CSi)	142 (M^+, 6); 128 (10); 127 (M^+ − 15, 100); 99 (32); 85 (16); 73 (29); 59 (61); 45 (9); 43 (10)
(*E*)-**5e**	3020, 1610 (HC=C)[g,11]	0.0 (s, 9H, 3 × $SiCH_3$); 0.8–1.0 (m, 3H, CH_3); 1.2–1.5 (m, 4H, $C\underline{H}_2C\underline{H}_2CH_3$); 1.9–2.2 (m, 2H, CH_2C=C); 5.6 (d, 1H, *J* = 19, SiCH=C); 6.1 (2t, 1H, *J* = 19, 5, CH=CSi)[11]	−1.0 ($SiCH_3$); 15.1 (CH_3); 22.8, 31.6, 37.1 (3 × CH_2); 130.7 (Si$\underline{C}$H=C); 149.4 ($\underline{C}$H=CSi)	156 (M^+, 2); 142 (11); 141 (M^+ − 15, 100); 114 (28); 99 (15); 85 (15); 81 (13); 73 (46); 59 (67); 45 (15); 43 (12)
(*E*)-**5f**	3030, 1610 (HC=C)	0.0 (s, 9H, 3 × $SiCH_3$); 0.8 (d, 6H, *J* = 5, 2 × CH_3); 1.4–1.8 (m, 1H, CH); 1.9 (t, 2H, *J* = 5, CH_2C=C); 5.6 (d, 1H, *J* = 19, SiCH=C); 6.0 (2t, 1H, *J* = 19, 5, CH=CSi)	−1.5 ($SiCH_3$); 21.8 (CH_3); 27.6 (CH); 46.5 (CH_2); 131.2 (Si$\underline{C}$H=C); 146.0 ($\underline{C}$H=CSi)	156 (M^+, 3); 142 (14); 141 (M^+ − 15, 100); 114 (17); 113 (15); 99 (22); 85 (16); 73 (58); 59 (62); 45 (10); 43 (12)
(*E*)-**5g**	3040, 3010, 1605, 1570, 1495, 750, 685 (HC=C)	0.0 (s, 9H, 3 × $SiCH_3$); 6.3 (d, 1H, *J* = 19, SiCH=C); 6.8 (d, 1H, *J* = 19, CH=CSi); 7.1–7.4 (m, 5H_{arom})	−0.6 ($SiCH_3$); 127.3, 128.6, 129.4, 130.0, 139.5, 145.6 (7 × $\underline{C}$H=C and C_{ipso})	176 (M^+, 28); 162 (15); 161 (M^+ − 15, 100); 145 (55); 135 (30); 59 (31); 43 (12)
(*E*)-**5h**	3030, 3010, 1610, 1600, 1495, 750, 700 (HC=C)	0.0 (s, 9H, 3 × $SiCH_3$); 2.2–2.8 (m, 4H, 2 × CH_2); 5.6 (d, 1H, *J* = 19, SiCH=C); 6.1 (2t, 1H, *J* = 19, 5, CH=CSi); 7.2–7.4 (m, 5H_{arom})	−0.9 ($SiCH_3$); 35.8, 38.9 (2 × CH_2); 126.7, 129.0, 130.2, 142.5, 147.3 (7 × $\underline{C}$H=C and C_{ipso})	204 (M^+, 2); 189 (M^+ − 15, 37); 131 (10); 130 (100); 129 (61); 91 (86); 73 (71); 59 (88); 45 (11); 43 (10)

[a] Recorded on a Perkin-Elmer 577 IR spectrometer.
[b] Recorded on a Varian FT-80 spectrometer.
[c] Referred to the Si−CH_3 signal (δ = 0.0) in compound **5**.
[d] Referred to the solvent CCl_4.
[e] Recorded on a Hewlett-Packard 5987 A spectrometer.
[f] In $CCl_4 + D_2O$ capillary.
[g] In CCl_4.

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(5) When the reaction mixture is hydrolyzed at this point, the corresponding silylated chlorohydrin is obtained (see Ref. 4).

(6) The metallation with lithium powder needs to be carried out at higher temperature; under these conditions side-reactions occur yielding a mixture of reaction products.

(7) For stabilized dianions of this type see: Barluenga, J., Fernández-Simón, J.L., Concellón, J.M., Yus, M. *J. Chem. Soc. Chem. Commun.*, **1987**, 915, and references cited therein.

(8) For an application of these types of reactions in the synthesis of unsaturated compounds, see: Barluenga, J., Alvarez, F., Concellón, J.M., Bernad, P., Yus, M. *Synthesis* **1987**, 318.

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