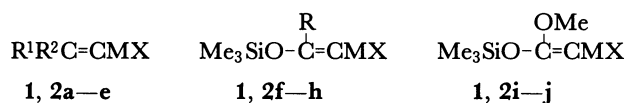


Synthesis of (1-Halo-1-alkenyl)trimethylsilanes via *gem*-Trimethylsilylation of Vinyl Halides

Nobujiro SHIMIZU,* Fumihiko SHIBATA, and Yuho TSUNO
 Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka 812
 (Received July 17, 1986)

Synopsis. Various vinyl halides including enol silyl ethers of α -halo ketones and esters give the corresponding (1-halo-1-alkenyl)trimethylsilanes in fair to good yields on treatment with lithium diisopropylamide at Dry Ice temperature in the presence of chlorotrimethylsilane.

(1-Bromovinyl)trimethylsilane and its homolog are versatile synthetic reagents¹⁾ and obtainable from 1-alkenyl- or 1-alkynyltrimethylsilanes.^{2,3)} An alternative simple route to (1-halo-1-alkenyl)trimethylsilanes may be provided by *gem*-silylation of vinyl halides which are readily available. Cunico and Han have reported that the treatment of 1-chloro-2-methylpropene with butyllithium below -100°C , followed by addition of chlorotrimethylsilane (TMS-Cl), gives (1-chloro-2-methyl-1-propenyl)trimethylsilane in 39% yield.⁴⁾ The scope of this method, however, would be limited due to the anticipated side reactions including a facile rearrangement of *gem*-haloalkenyllithium species to acetylenic compounds, a metal-halogen exchange reaction, and a coupling reaction between butyllithium and TMS-Cl. For example, we found that under similar metalation conditions to those reported⁴⁾ vinyl bromide gave bis(trimethylsilyl)acetylene, while β -bromostyrene afforded β -(trimethylsilyl)styrene as the major product. This paper deals with the *gem*-trimethylsilylation of various vinyl halides **1a**–**j** by a modified procedure using lithium diisopropylamide (LDA) in place of butyllithium.



1; M=H, **2**; M=SiMe₃

a; R¹=R²=H, X=Br **b**; R¹=R²=Me, X=Br

c; R¹=H, R²=Ph, X=Br **d**; R¹=H, R²=Me, X=Cl

e; R¹=H, R²=CH₂Cl, X=Cl **f**; R=Me, X=Cl

g; R=Ph, X=Br **h**; R=CH₂Cl, X=Cl **i**; X=Cl

j; X=Br

Since LDA is inactive toward TMS-Cl below Dry Ice temperature, the metalation of a vinyl halide can be done in the presence of a trapping agent TMS-Cl. Thus, when a vinyl halide **1** was added to an equimolar mixture of LDA and TMS-Cl in THF/ether (2:1) at -75°C or below, there was obtained the corresponding (1-halo-1-alkenyl)trimethylsilane **2** in fair to good yields. The results are shown in Table 1.

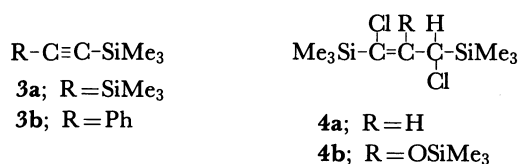


Table 1. *gem*-Trimethylsilylation of Vinyl Halides

Halide	Conditions ^{a)}	Products (Yield/%) ^{b)}
1a	A	2a (60) + 3a (7) ^{c)}
1b	B	2b (54)
1c	B	2c (55) + 3b (30) ^{c)}
1d ^{d)}	A	2d (23) ^{d)}
1e ^{d)}	B	2e (11) ^{d)} + 4a (58) ^{d)}
1e ^{d)}	B ^{e)}	2e (59) ^{d)} + 4a (5) ^{c)}
1e ^{d)}	B ^{f)}	4a (80) ^{d)}
1f ^{g)}	C	2f (84) ^{g)}
7a	C ^{f)}	2f (67) ^{h)}
1g ⁱ⁾	C	2g (80) ⁱ⁾
7b	C ^{f)}	2g (40) ^{j)}
1h	C	4b (74) ^{k)}
1i ^{d)}	C	2i (70) ^{d)}
7c	C ^{f)}	8a (45)
7b	C ^{f)}	8b (45) ^{l)}

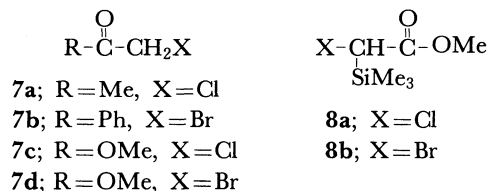
a) The silylation was carried out by adding a halide **1** to an equimolar mixture of LDA and TMS-Cl (1–1.2 equiv.) under following conditions: (A) at -100°C in THF/ether (2:1) for 3 h, (B) at -75°C in THF/ether (2:1) for 2 h, (C) at -75°C in THF for 4 h. b) Isolated yield. c) Determined by GLC. d) A mixture of stereoisomers. e) A LDA solution was added to a mixture of **1** and TMS-Cl. f) An excess amount of a LDA/TMS-Cl mixture was used. g) $E/Z < 0.05$. h) $E/Z = 0.67$. i) $E/Z = 0.15$. j) $E/Z = 20$. k) Corrected for the recovery of **1h** (49%). l) NMR analysis of a crude product before acidic workup indicated the formation of **2j** ($E/Z = 1$) in 58% yield.

The addition of 1,3-dichloropropene **1e** to a LDA/TMS-Cl mixture led to the predominant formation of a doubly silylated product **4a**. Monosilylation at the vinylic site, however, could be effected by inverse addition of a LDA solution to a mixture of **1e** and TMS-Cl. This procedure provides a convenient route to a versatile compound **2e**⁵⁾ which otherwise is not readily accessible. **2e** underwent a direct displacement reaction with $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{C}(\text{CH}_2)_3\text{CH}_3$ to give **6** and **5**.

tion with Ph₂CuLi yielding [1-chloro-3-phenyl-1-propenyl]trimethylsilane (**5**, 73%), whereas it reacted with *n*-BuMgBr in the presence of a catalytic amount of copper (I) iodide to give (1-butyl-1-heptenyl)trimethylsilane (**6**) in 78% yield via a double rearrangement of the allylic double bond.

gem-Silylation was readily accomplished also for vinyl halides bearing an enol ether function. For example, enol silyl ethers (**1f** and **1g**) of α -halo ketones **7a** and **7b** stereoselectively gave **2f** and **2g** in good yields. The use of 2 equiv amounts of a LDA/TMS-Cl

mixture converted these halo ketones directly to **2f** and **2g**, although the concomitant occurrence of the reduction of the carbonyl group with LDA lowered the yield of **2**, especially so in the case of **7b**.⁶ Synthesis of α -trimethylsilyl esters **8a** and **8b** was conveniently accomplished by the treatment of halo esters **7c** and **7d** with excess amounts of a LDA/TMS-Cl mixture followed by acidic workup.



Experimental

NMR spectra were recorded on a Hitachi R-20B spectrometer using carbon tetrachloride as solvent. The following examples are representative.

(1-Bromo-2-methyl-1-propenyl)trimethylsilane (2b). A LDA solution prepared from *n*-BuLi (in hexane, 22 mmol) and diisopropylamine (22 mmol) in THF/ether (2:1, 30 cm³) was cooled to -75°C and TMS-Cl (22 mmol) was added. To this mixture was added 1-bromo-2-methyl-1-propene (2.3 g) in THF (5 cm³) over a period of 20 min and the resulting mixture was stirred for 2 h at -75°C. A crude oil obtained after workup was distilled to give **2b** (1.9 g): Bp 124–125°C (140 Torr: 1 Torr=133.3 Pa); IR 1615 cm⁻¹; ¹H NMR $\delta=0.26$ (9H, s), 1.89 (3H, s), 1.97 (3H, s). Found: C, 40.62; H, 7.35%. Calcd for C₇H₁₅BrSi: C, 40.58; H, 7.30%.

(1,3-Dichloro-1-propenyl)trimethylsilane (2e). An ethereal solution (50 cm³) of LDA (34 mmol) was added to a mixture of 1,3-dichloropropene (3.8 g) and TMS-Cl (3.8 g) in THF (50 cm³) over a period of 1 h at -75°C and the resulting mixture was stirred for 1 h at that temperature. Usual workup gave **2e** (3.4 g) as a mixture of stereoisomers (*E/Z*=0.48): Bp 65–68°C (2 Torr) [lit.⁵ Bp 25°C (0.03 Torr)].

1-Chloro-2-trimethylsilyloxy-1-trimethylsilylpropene (2f). To a mixture of LDA (18 mmol) and TMS-Cl (18 mmol) in THF (20 cm³) was added an enol silyl ether **1f** (*E/Z*<0.05, 2.4 g) over a period of 10 min at -75°C and the mixture was stirred at -75°C for 4 h. A crude oil obtained after workup was distilled to give **2f** (2.98 g, *E/Z*<0.05): Bp 106–108°C (29 Torr); IR 1605 cm⁻¹; ¹H NMR $\delta=0.20$ (18H, s), 1.86 (3H, s).

Methyl Chloro(trimethylsilyl)acetate (8a). To a cold (-75°C) solution of LDA (44 mmol) and TMS-Cl (44 mmol) in THF (25 cm³) was added a THF solution of methyl chloroacetate (2.16 g) and the mixture was stirred at -75°C for 4 h. Solvent was removed on a rotary evaporator and the residue was extracted with petroleum ether. The organic layer was washed first with a cold hydrochloric acid (5 M (1 M=1 mol dm⁻³), 20 cm³), then with a saturated sodium hydrogencarbonate solution, and dried. A crude oil obtained after workup was distilled to give **8a** (1.63 g): Bp 78–79°C (20 Torr); IR 1745, 1720 cm⁻¹; ¹H NMR $\delta=0.18$ (9H, s), 3.70 (3H, s), 3.72 (1H, s). Found: C, 39.55; H, 7.28%. Calcd for C₆H₁₃ClO₂Si: C, 39.88; H, 7.25%.

Physical and spectral data for other new compounds listed in Table 1 are as follows.

2c: Bp 126–128°C (16 Torr); IR 1255, 840 cm⁻¹; ¹H NMR $\delta=0.04$ (9H, s), 7.14 (5H, m), 7.84 (1H, s).

2d: Bp 130–135°C [as a mixture of stereoisomers in the ratio 1:3.3]; IR 1610 cm⁻¹; ¹H NMR (Signals of the less

abundant isomer were shown in italics.) $\delta=0.16$ and 0.24 (together 9H, both s), 1.76 (d, *J*=7 Hz) and 1.82 (d, *J*=7 Hz) (together 3H), 6.02 and 6.41 (together 1H, both q, *J*=7 Hz).

E-2f: ¹H NMR $\delta=0.15$ (9H, s), 0.24 (9H, s), 2.03 (3H, s).

2g: Bp 98–100°C (2 Torr); IR 1605, 1585 cm⁻¹; ¹H NMR $\delta=-0.09$ g (9H, s), 0.06 (9H, s), 7.30 (5H, m); (Found: C, 49.25; H, 6.90%).

2i: Bp 101–103°C (23 Torr); IR 1615, 1250, 840 cm⁻¹; ¹H NMR $\delta=0.13$ (s), 0.23 (s), 0.28 (s) (1.7:1:1.2, together 18H), 3.49 (s) and 3.78 (s) (1.9:1, together 3H).

2j: 105–108°C (7 Torr) (*E/Z*=1): IR 1610 cm⁻¹; ¹H NMR $\delta=0.14$ (s), 0.24 (s), 0.29 (s) (1.8:1:1, 18H altogether), 3.50 (s) and 3.72 (s) (1:1, together 3H)

4a: Bp 95–98°C (2 Torr) (*E/Z*=0.56). *E*-isomer: IR 1580 cm⁻¹; ¹H NMR $\delta=0.14$ (9H, s), 0.27 (9H, s), 3.89 (1H, d, *J*=13 Hz), 6.36 (1H, d, *J*=13 Hz). *Z*-isomer: IR 1600 cm⁻¹; ¹H NMR $\delta=0.12$ (9H, s), 0.18 (9H, s), 4.40 (1H, d, *J*=10.5 Hz), 5.93 (1H, d, *J*=10.5 Hz); (Found (as a mixture of stereoisomers): C, 42.45; H, 7.80%).

4b: Bp 145–146°C (35 Torr); IR 1580 cm⁻¹; ¹H NMR $\delta=0.12$ (9H, s), 0.24 (9H, s), 3.95 (1H, s).

8b: Bp 49–50°C (3 Torr); IR 1745, 1720 cm⁻¹; ¹H NMR $\delta=0.20$ (9H, s), 3.54 (1H, s), 3.70 (3H, s); (Found: C, 31.71; H, 5.60%).

(1-Chloro-3-phenyl-1-propenyl)trimethylsilane (5). **2e** (0.50 g) was added to a solution of lithium diphenylcuprate(I) (12 mmol) in ether (15 cm³) and the mixture was stirred for 1 h at 0°C. Bulb-to-bulb distillation of a crude oil gave **5** 450 mg, as a mixture of stereoisomers in the ratio 1:2.6: IR 1615 cm⁻¹; ¹H NMR (Signals of the less abundant isomer were shown in italics.) $\delta=0.18$ (s) and 0.29 (s) (together 9H), 3.44 (d, *J*=7.8 Hz) and 3.60 (d, *J*=6.6 Hz) (together 2H), 6.08 (t, *J*=6.6 Hz) and 6.51 (t, *J*=7.8 Hz) (together 1H), 7.15 (5H, m); (Found: C, 64.01; H, 7.58%).

(1-Butyl-1-heptenyl)trimethylsilane (6). A solution of butylmagnesium bromide prepared from 2.74 g of butyl bromide in THF (15 cm³) was added to a mixture of **2e** (930 mg, *E/Z*=1.5) and cupper(I) iodide (0.5 g) in THF (15 cm³) and HMPA (2 cm³) and the resulting mixture was stirred for 4 h at 0°C. A crude oil (1.25 g) obtained after workup was distilled to give **6** (880 mg, as a mixture of stereoisomers in the ratio 1:1.9): Bp 108–109°C (12 Torr); IR 1615 cm⁻¹; ¹H NMR (Signals of the less abundant isomer were shown in italics.) $\delta=0.04$ (s) and 0.12 (s) (together 9H), 0.75–1.1 (6H, m), 1.1–1.7 (10H, m), 1.8–2.4 (4H, m), 5.64 (t, *J*=7 Hz) and 5.86 (t, *J*=7 Hz) (together 1H); (Found: C, 74.25; H, 13.28%).

References

- 1) W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, New York (1983), Chap. 7.
- 2) A. Ottolenghi, M. Fridkin, and A. Zilkha, *Can. J. Chem.*, **41**, 2977 (1963); B. T. Gröbel and D. Seebach, *Chem. Ber.*, **110**, 867 (1977); T. H. Chan, W. Mychajlowskij, B. S. Ong, and D.N. Harpp, *J. Org. Chem.*, **43**, 1526 (1978).
- 3) G. Zweifel and W. Lewis, *J. Org. Chem.*, **43**, 2739 (1978); H. Westmijze, J. Meijer, and P. Vermeer, *Tetrahedron Lett.*, **1977**, 1823.
- 4) R. F. Cunico and Y. K. Han, *J. Organomet. Chem.*, **105**, C29 (1978).
- 5) Alternatively **2e** can be prepared from 3,3-dichloroallyl-triphenyllead in two steps: D. Seyferth and R. E. Mammarella, *J. Organomet. Chem.*, **156**, 279 (1978).
- 6) Enol silylation of halo ketones **7a** and **7b** exclusively gave the *Z*-isomer when the reaction was carried out in ether using triethylamine as base, whereas LDA favored the *E*-isomer.