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

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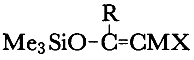
Synopsis. Various vinyl halides including enol silyl ethers of α-halo ketones and esters give the corresponding (1-halo-1-alkenyl)trimethylsilanes in fair to good yields on treatment with lithium diisopropylamide at Dry Ice temperature in the presence of chlorotrimethylsilane.

(1-Bromovinyl)trimethylsilane and its homolog are versatile synthetic reagents[1)] 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 reported[4)] 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.

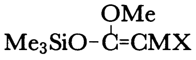
$R^1R^2C{=}CMX$

1, 2a—e



$Me_3SiO\text{-}\overset{R}{C}{=}CMX$

1, 2f—h



$Me_3SiO\text{-}\overset{OMe}{C}{=}CMX$

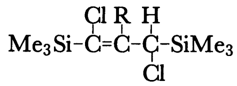
1, 2i—j

1; M=H, **2**; M=$SiMe_3$
a; $R^1=R^2=H$, X=Br **b**; $R^1=R^2=Me$, X=Br
c; $R^1=H$, $R^2=Ph$, X=Br **d**; $R^1=H$, $R^2=Me$, X=Cl
e; $R^1=H$, $R^2=CH_2Cl$, X=Cl **f**; R=Me, X=Cl
g; R=Ph, X=Br **h**; R=CH_2Cl, 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.

$R\text{-}C{\equiv}C\text{-}SiMe_3$

3a; R=$SiMe_3$
3b; R=Ph



$Me_3Si\text{-}\overset{Cl}{C}{=}\overset{R}{C}\text{-}\underset{Cl}{\overset{H}{C}}\text{-}SiMe_3$

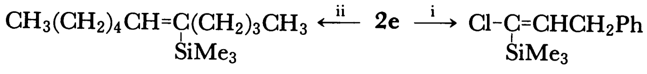
4a; R=H
4b; R=$OSiMe_3$

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.

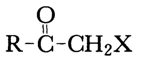
The addition of 1,3-dichloropropene **1e** to a LDA/TMS-Cl mixture led to the predominant formation of a doubly silylated product **4a**. Monosilylation at the vinylic site, however, could be effected by inverse addition of a LDA solution to a mixture of **1e** and TMS-Cl. This procedure provides a convenient route to a versatile compound **2e**[5)] which otherwise is not readily accessible. **2e** underwent a direct displacement reaction with Ph_2CuLi yielding [1-chloro-3-phenyl-1-propenyl)trimethylsilane (**5**, 73%), whereas it reacted with n-BuMgBr in the presence of a catalytic amount of cupper (I) iodide to give (1-butyl-1-heptenyl)trimethylsilane (**6**) in 78% yield via a double rearrangement of the allylic double bond.



$$\underset{\mathbf{6}}{CH_3(CH_2)_4CH{=}\underset{SiMe_3}{C}(CH_2)_3CH_3} \xleftarrow{ii} \mathbf{2e} \xrightarrow{i} \underset{\mathbf{5}}{Cl\text{-}\underset{SiMe_3}{C}{=}CHCH_2Ph}$$

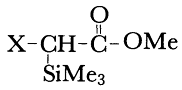
i; Ph_2CuLi, ii; n-BuMgBr/10%CuI

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.



$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2X$

7a; R=Me, X=Cl
7b; R=Ph, X=Br
7c; R=OMe, X=Cl
7d; R=OMe, X=Br



$X\text{-}\underset{SiMe_3}{CH}\text{-}\overset{\overset{O}{\|}}{C}\text{-}OMe$

8a; X=Cl
8b; X=Br

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 cm^3) 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 cm^3) over a period of 20 min and the resulting mixture was stirred for 2h 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}; ^{1}H NMR δ=0.26 (9H, s), 1.89 (3H, s), 1.97 (3H, s). Found: C, 40.62; H, 7.35%. Calcd for $C_7H_{15}BrSi$: C, 40.58; H, 7.30%.

(1,3-Dichloro-1-propenyl)trimethylsilane (2e). An ethereal solution (50 cm^3) 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 cm^3) 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-trimethylsiloxy-1-trimethylsilylpropene (2f). To a mixture of LDA (18 mmol) and TMS-Cl (18 mmol) in THF (20 cm^3) 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 4h. 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}; ^{1}H NMR δ=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 cm^3) 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 cm^3), 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}; ^{1}H NMR δ=0.18 (9H, s), 3.70 (3H, s), 3.72 (1H, s). Found: C, 39.55; H, 7.28%. Calcd for $C_6H_{13}ClO_2Si$: 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}; ^{1}H NMR δ=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}; ^{1}H NMR (Signals of the less abundant isomer were shown in italics.) δ=*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**: ^{1}H NMR δ=0.15 (9H, s), 0.24 (9H, s), 2.03 (3H, s).

2g: Bp 98—100 °C (2 Torr); IR 1605, 1585 cm^{-1}; ^{1}H NMR δ=−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}; ^{1}H NMR δ=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}; ^{1}H NMR δ=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}; ^{1}H NMR δ=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}; ^{1}H NMR δ=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}; ^{1}H NMR δ=0.12 (9H, s), 0.24 (9H, s), 3.95 (1H, s).

8b: Bp 49—50 °C (3 Torr); IR 1745, 1720 cm^{-1}; ^{1}H NMR δ=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 cm^3) 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}; ^{1}H NMR (Signals of the less abundant isomer were shown in italics.) δ=*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 cm^3) was added to a mixture of **2e** (930 mg, *E*/*Z*=1.5) and cupper(I) iodide (0.5 g) in THF (15 cm^3) and HMPA (2 cm^3) 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}; ^{1}H NMR (Signals of the less abundant isomer were shown in italics.) δ=*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%).

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5) Alternatively **2e** can be prepared from 3,3-dichloroallyltriphenyllead 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.