A Short and Efficient Preparation of 2-Trimethylsilylmethyl-2-propen-1-ol

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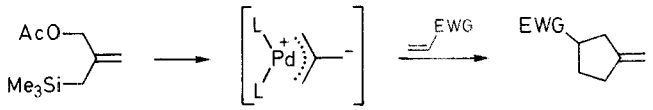
2-Trimethylsilylmethyl-2-propen-1-ol[2-(hydroxymethyl)allyltrimethylsilane] is efficiently prepared in 64% overall yield starting from the cheap propargyl alcohol.

3-Acetoxy-2-(trimethylsilylmethyl)-1-propene **(2)** is a useful precursor of trimethylenemethane (TMM) in [3+2]cycloaddition reactions using the methodology of Trost.[1]

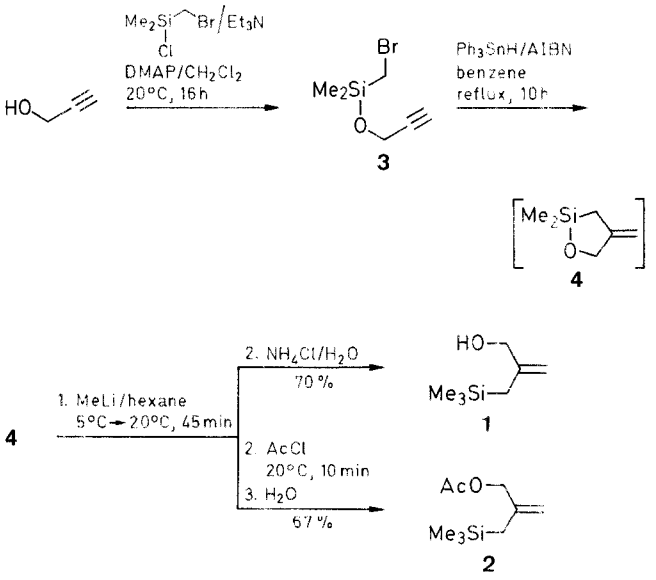


EWG = electron-withdrawing group

The direct precursor of **2**, i.e., 2-trimethylsilylmethyl-2-propen-1-ol[2-(hydroxymethyl)allyltrimethylsilane, **1**], is usually prepared according to Ref. 2 in two steps starting from 2-methyl-2-propen-1-ol: **(1)** formation of the dilithio derivative using butyllithium and subsequent trapping by chlorotrimethylsilane, **(2)** monodesilylation using 1 N aqueous sulfuric acid.

Free-radical chain reactions have gained considerable interest in organic synthesis since they may in many cases be performed under conditions which are mild and are compatible with the presence of a variety of functionalities.

We here report a straightforward route to 2-trimethylsilylmethyl-2-propen-1-ol **(1)** starting from propargyl alcohol. The key step of this short preparation is the radical cyclization of 3-[(bromomethyl)dimethylsiloxy]-1-propyne **(3)**. Compound **3** is readily obtained in 91% yield by treatment of propargyl alcohol with commercially available (bromomethyl)chlorodimethylsilane and triethylamine in dichloromethane in the presence of a catalytic amount of 4-dimethylaminopyridine (DMAP) at room temperature. The radical cyclization of **3** is carried out in boiling benzene by the slow addition of tri-



phenylstannane in the presence of a catalytic amount of azabis-isobutyronitrile (AIBN). After 10 hours, the reaction mixture is vacuum-distilled without fractionation remove the tin derivatives. The clean benzene solution of the very sensitive 1-oxa-2-silacyclopentane **4** is then treated with methyllithium to afford **1** in 70% yield.

Although this method requires the use of benzene as solvent for large scale-preparations it has several advantages: the starting (bromomethyl)dimethylsilyl ether **3** is easily accessible, the radical cyclization is general and can provide a useful access to variously substituted TMM precursors,[3] and 3-acetoxy-2-(trimethylsilylmethyl)propene (**2**) is directly accessible by adding acetyl chloride to the reaction mixture after the treatment with methyllithium.

3-[(Bromomethyl)dimethylsiloxy]-1-propyne (3):
In a dried, N_2-filled, three-neck round-bottomed flask fitted with addition funnel, condenser, and magnetic stirrer are placed propargyl alcohol (1.74 g, 31.1 mmol), Et_3N (3 g, 29.7 mmol), and DMAP (0.743 g, 6 mmol) in CH_2Cl_2 (100 mL). (Bromomethyl)chlorodimethylsilane (5.54 g, 29.7 mmol) is slowly added at 0°C; the mixture is allowed to warm at room temperature and stirred for 16 h, and finally quenched with H_2O (10 mL). The organic phase is separated, washed with H_2O (2 × 10 mL), dried ($MgSO_4$), and evaporated. The residue is distilled under reduced pressure to give pure **3**; yield: 5.6 g (91%); bp 81–82°C/60 Torr; n_D^{20} 1.467.

$C_6H_{11}BrOSi$	calc.	C 34.79	H 5.30
(207.15)	found	34.91	5.14

MS (70 eV): m/z = 206, 208 (1%); 113 (100).

IR (neat): ν = 3300, 2980, 2920, 2120, 1260, 1090, 840 cm^{-1}.

^1H-NMR (80 MHz, $CDCl_3$/TMS): δ = 0.27 (s, 6H, $2CH_3$); 2.48 (s, 2H, CH_2Br); 2.38 (t, 1H, J = 2.4 Hz); 4.31 (d, 2H, J = 2.4 Hz, CH_2O).

2-Trimethylsilylmethyl-2-propen-1-ol [(2-Hydroxymethyl)allyltrimethylsilane, 1]:
In a dried, N_2-filled, 100 mL round-bottomed flask are placed 3-[(bromomethyl)dimethylsiloxy]-1-propyne (**3**; 1.31 g, 6.3 mmol) and AIBN (0.052 g, 0.31 mmol) in benzene (50 mL). The mixture is heated to reflux, a solution of triphenylstannane (3.11 g, 8.8 mmol) in benzene (30 mL) is added slowly over 5 h using a syringe pump, and reflux is maintained for a further 5 h. The mixture is then distilled under reduced pressure without fractionation. To the solution thus obtained is then added, at 5°C MeLi solution (1.1 M in hexane; 6.3 mL, 6.93 mmol). After 45 min at 20°C, the mixture is quenched by adding a 5% solution (5 mL) of NH_4Cl in H_2O. The organic phase is separated, washed with brine (2 × 5 mL), dried ($MgSO_4$), and evaporated. The residue is purified by flash chromatography on silica gel using petroleum ether/Et_2O (1:1) as eluent to afford pure **1**; yield: 0.64 g (70%); bp 59–60°C/4 Torr; n_D^{20} 1.452.

All physical data are in agreement with Ref. 2.

3-Acetoxy-2-(trimethylsilylmethyl)-1-propene (2):
The procedure for the preparation of alcohol **1** is followed till treatment of the mixture with methyllithium inclusive. Then, AcCl (0.55 g, 7 mmol) is added at 20°C, stirring is continued for 10 min, and H_2O (5 mL) is added. The organic phase is separated, washed with brine (2 × 50 mL), dried ($MgSO_4$), and evaporated. The residue is purified by flash chromatography on silica gel using petroleum ether/Et_2O (9:1) as eluent to afford pure **2**; yield: 0.79 g (67%); bp 60–61°C/2.5 Torr; n_D^{20} 1.440.

All physical data are in agreement with Ref. 4.

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