APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **13**, 469–474 (1999)

General and Efficient Method for the Synthesis of Alkoxymethylsilanes

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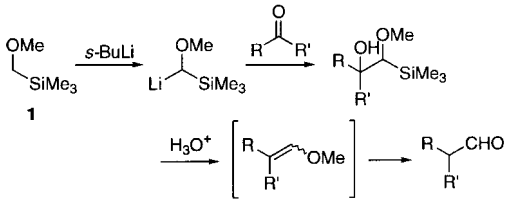
Although alkoxymethylsilanes serve as useful building blocks, various efforts to synthesize them by substitution reaction with an alkoxide ion at the carbon adjacent to the silicon failed. To solve this synthetic problem a new route which is very simple to perform was developed. Bromination of (methoxymethyl)trimethylsilane by using *N*-bromosuccinimide/2,2′-azobisisobutyronitrile (NBS/AIBN) was followed by a substitution by alcohols in the presence of triethylamine to give the corresponding [alkoxy-(methoxy)methyl]trimethylsilanes. These acetals can be used directly for the next reduction with di-isobutylaluminium hydride (DIBAL-H) or $Et_3SiH/BF_3{\cdot}OEt_2$ to give alkoxymethylsilanes in good to moderate yields. The success of the substitution reaction with the alcohols suggests that the mechanism is of somewhat S_N1 by nature and formation of the cationic intermediate seems to release the steric hindrance around the carbon, allowing the attack of alcohols.

Keywords: alkoxymethylsilanes; bromination; acetal; reduction; electro-organic synthesis

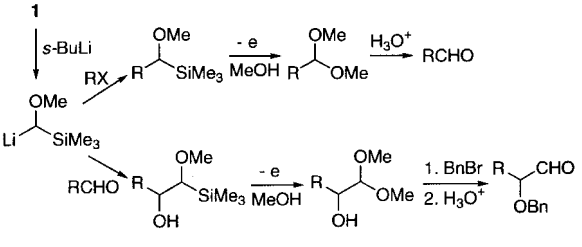
Received 30 September 1998; accepted 10 December 1998

INTRODUCTION

Alkoxymethylsilanes serve as useful building blocks for organic synthesis. Magnus and Roy demonstrated the utility of (methoxymethyl)trimethylsilane (**1**) as a one-carbon homologation reagent.[1] (Methoxymethyl)trimethylsilane is readily deprotonated with *sec*-butyllithium and the resulting anion reacts with aldehydes and ketones (Scheme 1). The β-hydroxy-α-methoxysilanes thus obtained are readily converted to homologated aldehydes. We have demonstrated that alkoxymethylsilanes serve as carbonyl synthons if electrochemical oxidation (Scheme 2) is used.[2] The anion of **1** can be easily alkylated with alkyl halides and anodic oxidation of the resulting (1-methoxy)alkylsilanes in methanol cleaves the carbon–silicon bond to give the corresponding dimethyl acetals, which are readily hydrolyzed to the corresponding aldehydes. The anodic oxidation of β-hydroxy-α-methoxysilanes, which are prepared by the reaction of the anion of **1** with aldehydes, gives the corresponding α-hydroxy acetals. Protection followed by hydrolysis gives the protected α-hydroxy aldehyde. Therefore, the anion of **1** serves as a synthon of the formyl anion. Recently Steckhan and co-workers reported that alkoxymethylsilanes serve as hydroxymethyl anion equivalents in photoinduced radical electron-transfer addition reactions.[3]



Scheme 1



Scheme 2

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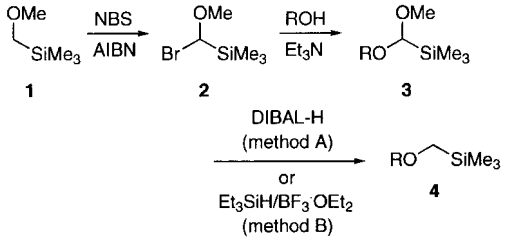
Contract/grant sponsor: Monbusho.

 CCC 0268–2605/99/060469–06 $17.50

Although (methoxymethyl)trimethylsilane (**1**) is readily prepared by treating (chloromethyl)trimethylsilane with methoxide ion,[1,4] the higher homologues cannot be prepared in a similar fashion (Scheme 3). For example, the reaction of (chloromethyl)trimethylsilane with sodium butoxide gives mainly butoxysilane together with a smaller amount of (butoxymethyl)trimethylsilane.[1] Various efforts to synthesize alkoxymethylsilanes by substitution with an alkoxide ion at the carbon adjacent to the silicon failed. For example, Magnus and Roy reported that replacement of the trimethylsilyl group by a dimethylphenylsilyl group led to increasing amounts of alkoxide attack at silicon.[1] They also reported that the treatment of alcohols with (iodomethyl)trimethylsilane in the presence of potassium hydride/18-crown-6 also gave the products derived from alkoxide attack at silicon together with the desired substitution products. We have examined the reaction of the alkoxide with (halomethyl)trimethylsilanes under various conditions but failed. Eisch *et al*., however, reported that the reaction of the halomethylsilane with phenoxide resulted in the facile formation of the corresponding phenoxymethylsilane.[5] The high nucleophilicity of phenoxide seems to be responsible for the success of the substitution reaction in this case.

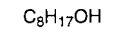
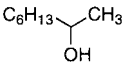
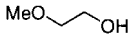
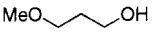
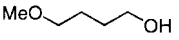
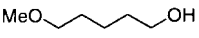
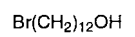
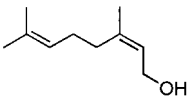
Scheme 3



Scheme 4

The failure of the alkoxymethylsilane syntheses mentioned above is probably due to the strong affinity of silicon for oxygen. In order to avoid this problem we have used transmetalation of alkoxymethylstannanes by treatment with butyl-lithium and trapping of the resulting alkoxymethyl-lithium with chlorosilane for the preparation of various alkoxymethylsilanes (J. Yoshida, Y. Ishichi and S. Isoe, unpublished results) because alkoxymethylstannanes are easily prepared by the direct substitution of (halomethyl)stannane with an alkoxide.[6] This method, however, suffers from several problems, such as the toxicity of tin and the tedium of the procedures. In our program aimed at new synthetic transformations using functionalized alkoxymethylsilanes, we have a strong need for a general and convenient method for the synthesis of alkoxymethylsilanes. We report here a new efficient route to alkoxymethylsilanes via [bromo(methoxy)methyl]trimethylsilane (**2**) (Scheme 4).

Table 1. Synthesis of alkoxymethylsilanes (4) from 1 in three steps

ROH	Method of reduction[a]	Yield of **4** based on **1** (%)
	A	85
	A	68
	B	52
	B	58
	B	68
	B	56
	B	72
	A	71
Cholesterol	B	81

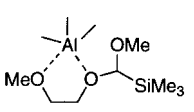
[a] Method A: The reduction of the acetal intermediate **3** was carried out with DIBAL-H. Method B: The reduction of **3** was carried out with $Et_3SiH/BF_3{\cdot}OEt_2$.

Our method is simple to perform. Bromination of (methoxymethyl)trimethylsilane (**1**) with *N*-bromosuccinimide (NBS) in the presence of azobisisobutyronitrile (AIBN) in CCl_4 gives [bromo (methoxy)methyl]trimethylsilane (**2**). Since this compound is quite sensitive to moisture, the crude **2** is directly used for the substitution reaction without purification. The reaction of **2** with an alcohol in the presence of triethylamine takes place smoothly to give the corresponding [alkoxy-(methoxy)methyl]trimethylsilane (**3**). Although it is stable and can be isolated, the crude **3** can be used directly for the next transformation. Reduction of **3** with di-isobutylaluminum hydride (DIBAL-H)[8] (method A) or $Et_3SiH/BF_3{\cdot}OEt_2$ (method B) gives the corresponding (alkoxymethyl)trimethylsilane

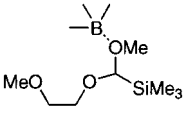
(**4**). (the reduction of acetals is reviewed in Ref. 7, and Ref. 8 discusses the ionic hydrogenation of acetals using $Et_3SiH/BF_3{\cdot}OEt_2$.) Thus, compound **4** is synthesized from **1** quite conveniently without isolation of the intermediates **2** and **3**. Table 1 summarizes the results obtained for several alcohols. The following points warrant comment.

(1) The success of the substitution reaction of **2** with the alcohols suggests the mechanism is somewhat S_N1 by nature, because the adjacent oxygen atom is expected to stabilize the developing cationic center. The formation of the cationic intermediate seems to release the steric hindrance around the carbon, allowing the attack of sterically demanding alcohols with higher alkyl groups.

(2) Although the reduction with DIBAL-H proceeds smoothly for **3** which has simple alkoxy groups, the DIBAL-H reduction of **3**, containing a 2-methoxyethoxy group gave rise to the exclusive formation of **1** instead of **4**. This is probably because the chelation of the oxygen atoms to the aluminum (**A**) facilitates the elimination of the 2-methoxyethoxy group. DIBAL-H (method A) reduced the acetals having 4-methoxybutoxymethyl and 12-bromododecyloxymethyl groups to give the desired products in almost the same yields as method B. In the case of **3** with a 2-methoxyethoxy group, formation of a five-membered ring by chelation of the oxygen atoms to the aluminum might be responsible for the selective cleavage of the methoxyethoxy group. The use of $Et_3SiH/BF_3{\cdot}OEt_2$, however, resulted in the facile elimination of the methoxy group. Presumably, $BF_3{\cdot}OEt_2$, having only one coordination site, interacted with the methoxy group (**B**), facilitating its elimination.



(A)



(B)

In conclusion, the present method provides a new general and efficient route to alkoxymethylsilanes, and opens a new aspect of the chemistry of alkoxymethylsilanes, which can be utilized as convenient building blocks in organic synthesis. The present method also opens up the possibility of the use of the trimethylsilylmethyl group as a protecting group for alcohols, because alkoxymethylsilanes are stable under various conditions but are readily oxidized under electrolytic conditions,[2] providing an efficient method of deprotection.

EXPERIMENTAL

General remarks

(Methoxymethyl)trimethylsilane (**1**) (Aldrich) was used as obtained commercially. $MeO(CH_2)_3OH$,[9a] $MeO(CH_2)_4OH$[9b] and $MeO(CH_2)_5OH$,[9a,c] were synthesized by known methods.

[Bromo(methoxy)methyl]-trimethylsilane (2)

NBS (595.4 mg, 3.35 mmol), AIBN (16.8 mg, 0.10 mmol) and dry CCl_4 (3.0 ml) were placed in a 20-ml Schlenk-type flask fitted with a reflux condenser and a magnetic stirring bar. (Methoxymethyl)trimethylsilane (356.3 mg, 3.01 mmol) was added and the mixture was refluxed for 20 min. After being cooled to room temperature, the reaction mixture was filtered and the solvent was removed under reduced pressure. The residue was purified by bulb-to-bulb distillation (60–70 °C, 28 mmHg) to obtain [bromo(methoxy)methyl]trimethylsilane (**2**) (oil, 316.4 mg, 53%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.18$ (s, 9H), 3.52 (s, 3H), 5.76 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -3.82$, 61.85, 99.35. Since this compound is quite sensitive to moisture, it was usually used for the subsequent transformations without distillation.

[Methoxy(1-octyloxy)methyl]-trimethylsilane (3, R = C_8H_{17})

NBS (997.7 mg, 5.61 mmol), AIBN (25.1 mg, 0.15 mmol) and dry CCl_4 (5 ml) were placed in a 20-ml Schlenk-type flask fitted with a reflux condenser and a magnetic stirring bar. (Methoxymethyl)trimethylsilane (591.4 mg, 5.00 mmol) was added and the mixture was refluxed for 20 min. After being cooled to room temperature, the liquid phase of the reaction mixture containing **2** was transferred into a 20-ml Schlenk-type flask containing 1-octanol (785.4 mg, 6.03 mmol), triethylamine (609.5 mg, 6.02 mmol) and dry Et_2O (5 ml). The resulting mixture was refluxed for 4 h. The reaction

mixture was cooled to room temperature and partitioned between ether and saturated aqueous $NaHCO_3$. The organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by flash chromatography (hexane–Et_2O, 100:1, containing 1% Et_3N) to obtain the title compound (oil, 1.109 g, 90%). TLC: $R_f = 0.43$ (hexane–Et_2O, 20:1). ^1H NMR (300 MHz, $CDCl_3$). $\delta = 0.07$ (s, 9H), 0.87 (t, $J = 6.6$ Hz, 3H), 1.22–1.38 (m, 10H), 1.50–1.62 (m, 2H), 3.40 (s, 3H), 3.41 (dt, $J = 9.6$, 6.6 Hz, 1H), 3.69 (dt, $J = 9.6$, 6.6 Hz, 1H), 4.26 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -3.63$, 13.96, 22.56, 26.12, 29.19, 29.36, 30.10, 31.76, 57.17, 70.29, 106.27. IR (neat) 1248, 1109 cm^{-1}. MS (EI) *m/z* (%) = 231 (17), 133 (100), 73 (77). HRMS (EI): Calcd for $C_{12}H_{27}O_2Si$ (M^+-CH_3): 231.1780: Found: 231.1778.

(1-Octyloxymethyl)trimethylsilane (4, R = C_8H_{17})

[Methoxy(1-octyloxy)methyl]trimethylsilane (**3**, 781.3 mg, 3.17 mmol) and dry toluene (2 ml) were placed in a 20-ml Schlenk-type flask and DIBAL-H (1.5 M toluene solution, 4.23 ml, 6.35 mmol) was added at 0 °C. The reaction mixture was stirred at room temperature for 1 h. After being cooled to 0 °C, aqueous 1 M HCl was added slowly, and the mixture was partitioned between ether and aqueous HCl. The organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by flash chromatography (hexane–EtOAc, 100:1) to obtain the title compound (oil, 645.2 mg, 94%). TLC: $R_f = 0.37$ (hexane–EtOAc, 20:1). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.03$ (s, 9H), 0.87 (t, $J = 6.6$ Hz, 3H), 1.22–1.33 (m, 10H), 1.47–1.58 (m, 2H), 3.07 (s, 2H), 3.36 (t, $J = 6.6$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -3.18$, 13.98, 22.56, 26.00, 29.21, 29.37 (two carbons), 31.76, 64.60, 75.38. IR (neat): 1248, 1105 cm^{-1}. MS (EI) *m/z* (%) = 201 (27), 103 (100), 73 (96). HRMS (EI): Calcd for $C_{11}H_{25}OSi$ (M^+-CH_3): 201.1675. Found: 201.1684. Analysis: Calcd for $C_{12}H_{28}OSi$: C, 66.59; H, 13.04. Found: C, 66.59; H, 13.02%.

(1-Octyloxymethyl)trimethylsilane: a typical procedure for method A

This compound was also synthesized from **1** without isolation of the intermediates **2** and **3**. The reaction mixture containing compound **2** was prepared from NBS (1.977 g, 11.1 mmol), AIBN (53.5 mg, 0.33 mmol) and (methoxymethyl)trimethylsilane (1.201 g, 10.2 mmol) as described above. After being cooled to room temperature, the liquid phase of the reaction mixture was transferred into another 50-ml Schlenk-type flask containing 1-octanol (1.652 g, 12.7 mmol) in the presence of triethylamine (1.196 g, 11.8 mmol) in dry Et_2O (10 ml). The resulting mixture was refluxed for 4 h. After being cooled to room temperature the mixture was partitioned between ether and saturated aqueous $NaHCO_3$. The organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was passed through a short column of silica gel (5 cm; ether–pentane, 1:1, containing 1% Et_3N) to remove Et_3N–HBr, and the solvent was removed under reduced pressure. The crude **3** and dry toluene (5 ml) were placed in a 50-ml Schlenk-type flask and DIBAL-H (1.5 M toluene solution, 14.0 ml, 21.0 mmol) was added at 0 °C. The reaction mixture was stirred at room temperature for 2 h. After being cooled to 0 °C, aqueous 1 M HCl was added slowly, and the mixture was partitioned between ether and aqueous HCl. The organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by flash chromatography (hexane–EtOAc, 100:1) to obtain the title compound (oil, 1.884 g, 85%).

(2-Methoxyethoxymethyl)-trimethylsilane: a typical procedure for method B

The liquid phase of the reaction mixture containing **2**, which was prepared by the reaction of **1** (591.4 mg, 5.00 mmol), NBS (997.7 mg, 5.61 mmol) and AIBN (25.1 mg, 0.15 mmol) in dry CCl_4 (5 ml) as described above, was transferred into a 20-ml Schlenk-type flask containing 2-methoxyethanol (463.2 mg, 6.09 mmol), triethylamine (607.1 mg, 6.00 mmol) and dry Et_2O (5 ml). The mixture was refluxed for 4 h. After being cooled to room temperature the mixture was partitioned between ether and saturated aqueous $NaHCO_3$. The organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was passed through a short column of silica gel (5 cm, ether–pentane, 1:1, containing 1% Et_3N) to remove Et_3N–HBr, and the solvent was removed. The crude **3** and dry CH_2Cl_2 (4 ml) were placed in a 20-ml Schlenk-type flask and cooled at −45 °C. Et_3SiH (701.5 mg, 6.03 mmol) and $BF_3 \cdot OEt_2$ (0.64 ml, 5.05 mmol)

were added, and the reaction mixture was stirred at −45 °C for 1 h, and then warmed to room temperature. Saturated aqueous $NaHCO_3$ was added slowly, and the mixture was partitioned between ether and aqueous $NaHCO_3$. The organic phase was separated, washed with brine and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by flash chromatography (hexane–Et_2O, 10:1) to obtain the title compound (oil, 425.3 mg, 52%). TLC $R_f = 0.36$ (hexane–Et_2O, 5:1). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.04$ (s, 9H), 3.16 (s, 2H), 3.38 (s, 3H), 3.49–3.58 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -3.18$, 59.07, 65.52, 71.84, 74.53. IR (neat): 1248, 1109 cm^{-1}. MS (EI): *m/z* (%) = 147 (2), 103 (43), 73 (100). HRMS (EI): Calcd for $C_6H_{15}O_2Si$ (M^+-CH_3): 147.0841. Found: 147.0845.

(2-Octyloxymethyl)trimethylsilane

This was synthesized by method A and purified by flash chromatography (hexane–EtOAc, 100:1) (oil, 68%). TLC: $R_f = 0.37$ (hexane–EtOAc, 20:1). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.03$ (s, 9H), 0.88 (t, $J = 6.3$ Hz, 3H). 1.07 (d, $J = 6.3$ Hz, 3H), 1.23–1.37 (m, 10H), 2.92 (d, $J = 12.6$ Hz, 1H), 3.16 (d, $J = 12.6$ Hz, 1H), 3.16–3.23 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -3.19$, 13.98, 18.93, 22.53, 25.50, 29.33, 31.82, 36.30, 61.36, 78.79. IR (neat): 1248, 1075 cm^{-1}. MS (EI): m/z (%) = 201 (22), 103 (79), 73 (100). HRMS (EI): Calcd for $C_{11}H_{25}OSi$ (M^+-CH_3): 201.1675. Found: 201.1671.

(3-Methoxypropoxymethyl)-trimethylsilane

This was synthesized by method B and purified by flash chromatography (hexane–Et_2O, 20:1) (oil, 58%). TLC: $R_f = 0.50$ (hexane–Et_2O, 5:1). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.03$ (s, 9H), 1.76–1.86 (m, 2H), 3.08 (s, 2H), 3.33 (s, 3H), 3.44 (t, $J = 6.3$ Hz, 2H), 3.45 (t, $J = 6.3$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -3.22$, 29.74, 58.55, 64.78, 69.83, 71.94. IR (neat): 1248, 1107 cm^{-1}. MS (EI): *m/z* (%) = 161 (2), 103 (55), 73 (100). HRMS (EI): calcd for $C_7H_{17}O_2Si$ (M^+-CH_3): 161.0998. Found: 161.1009.

(4-Methoxybutoxymethyl)-trimethylsilane

This was synthesized by method B and purified by flash chromatography (hexane–Et_2O, 20:1) (oil, 68%). TLC: $R_f = 0.46$ (hexane–Et_2O, 5:1). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.03$ (s, 9H), 1.54–1.68 (m, 4H), 3.07 (s, 2H), 3.33 (s, 3H), 3.38 (t, $J = 6.0$ Hz, 2H), 3.39 (t, $J = 6.0$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -3.21$, 26.02, 26.28, 58.43, 64.64, 72.72, 75.00. IR (neat): 1248, 1103 cm^{-1}. MS (EI): *m/z* (%) = 175 (1), 103 (41), 73 (100). HRMS (EI): Calcd for $C_8H_{19}O_2Si$ (M^+-CH_3): 175.1154. Found: 175.1161.

(5-Methoxypentoxymethyl)-trimethylsilane

This was synthesized by method B and purified by flash chromatography (hexane–Et_2O, 10:1) (oil, 56%). TLC: $R_f = 0.18$ (hexane–Et_2O, 10:1). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.03$ (s, 9H), 1.31–1.43 (m, 2H), 1.51–1.64 (m, 4H), 3.07 (s, 2H), 3.33 (s, 3H), 3.37 (t, $J = 6.6$ Hz, 2H), 3.38 (t, $J = 6.6$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -3.19$, 22.57, 29.21, 29.36, 58.48, 64.69, 72.83, 75.18. IR (neat): 1248, 1105 cm^{-1}. MS (EI): *m/z* (%) = 203 (6), 103 (58), 73 (100). HRMS (EI): Calcd for $C_{10}H_{23}O_2Si$ (M^+-H): 203.1467. Found: 203.1474.

(12-Bromododecyloxymethyl)-trimethylsilane

This was synthesized by method B (reduction temperature = 0 °C) and purified by flash chromatography (hexane–Et_2O, 50:1) (oil, 72%). TLC: $R_f = 0.20$ (hexane–Et_2O, 50:1). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.03$ (s, 9H), 1.23–1.34 (m, 14H), 1.36–1.46 (m, 2H), 1.47–1.57 (m, 2H), 1.79–1.90 (m, 2H); 3.07 (s, 2H), 3.37 (t, $J = 6.6$ Hz, 2H), 3.40 (t, $J = 6.6$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = -3.18$, 26.00, 28.08, 28.66, 29.33, 29.37, 29.42, 29.45, 29.50, 32.76, 33.90, 64.58, 75.36. IR (neat): 1248, 1103 cm^{-1}. MS (EI): m/z (%) = 351 (3), 103 (100), 73 (95). HRMS (EI): Calcd for $C_{16}H_{33}{}^{81}BrOSi$ (M^+-2H): 350.1464. Found: 350.1479. Analysis: Calcd for $C_{16}H_{35}BrOSi$: C, 54.68; H, 10.04. Found: C, 54.72; H, 9.89%.

(Neroloxymethyl)trimethylsilane

This was synthesized by method A and purified by flash chromatography (hexane–Et_2O, 80:1) (oil, 71%). TLC: $R_f = 0.50$ (hexane–Et_2O, 20:1). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.03$ (s, 9H), 1.60 (s, 3H), 1.68 (s, 3H), 1.74 (s, 3H), 2.03–2.08 (m, 4H), 3.07 (s, 2H), 3.92 (d, $J = 6.6$ Hz, 2H), 5.06–5.14 (m, 1H), 5.32 (t, $J = 6.6$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -3.16$, 17.52, 23.39, 25.59, 26.64,

32.21, 64.00, 71.25, 122.70, 124.07, 131.88, 139.95. IR (neat): 1248, 1069 cm^{-1}. MS (EI): *m/z* (%) = 240 (22), 103 (19), 73 (100). HRMS (EI): Calcd for $C_{14}H_{28}OSi$ (M^+): 240.1909. Found: 240.1909. Analysis: Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 69.76; H, 11.66%.

(Cholesteroloxymethyl)-trimethylsilane

This was synthesized by method B, although CH_2Cl_2 was used as solvent instead of Et_2O in the reaction of **2** and cholesterol, the reduction was carried out at room temperature, and the product was purified by flash chromatography (hexane–CH_2Cl_2, 8:1) (crystal, 81%). m.p. 148–149 °C. TLC: R_f = 0.50 (hexane–CH_2Cl_2, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.03 (s, 9H), 0.67 (s, 3H), 0.86 (d, J = 6.6 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H), 0.91 (d, J = 6.6 Hz, 3H), 0.99 (s, 3H), 0.88–1.63 (m, 21H), 1.75–2.17 (m, 6H), 2.32–2.42 (m, 1H), 2.88–3.03 (m, 1H), 3.11 (s, 2H), 5.30–5.37 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = −3.18, 11.75, 18.62, 19.35, 21.01, 22.47, 22.72, 23.74, 24.21, 27.93, 27.98, 28.16, 31.86, 31.91, 35.72, 36.13, 36.90, 37.33, 38.79, 39.45, 39.76, 42.28, 50.19, 56.14, 56.78, 61.27, 82.44, 121.20, 141.62. IR (KBr): 1246, 1092 cm^{-1}. MS (FAB): m/z (%) = 471 (8), 369 (60), 154 (100). HRMS (FAB): Calcd for $C_{31}H_{55}OSi$ (M^+−H): 471.4022. Found: 471.4014. Analysis: Calcd for $C_{31}H_{56}OSi$: C, 78.74; H, 11.94. Found: C, 78.51; H, 12.03%.

Acknowledgements We are pleased to acknowledge the Grant-in-Aid for Scientific Research from Monbusho for financial support. We also thank Shin-etsu Chemical for the gift of some organosilicon compounds.

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