August, 1984] *Bull. Chem. Soc. Jpn.,* *57, 2167—2170 (1984)*

Reactions of 2-Chloroacyltrimethylsilanes with Grignard Reagents. Preparation of 3-(Trimethylsilyl)-2-alkanones and 2-(Trimethylsilyl)-1-alkanols[1)]

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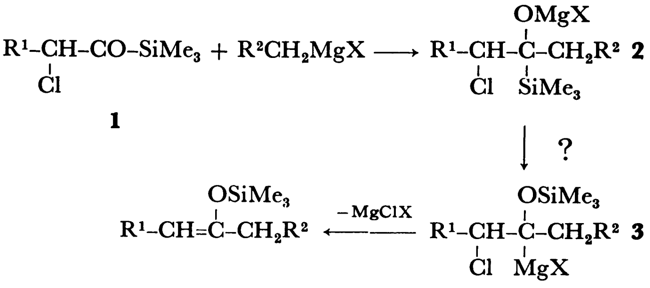
(Received January 11, 1984)

Reactions of 2-chloroacyltrimethylsilanes with Grignard reagents have been examined. Thus, treatment with methylmagnesium iodide affords the corresponding 3-(trimethylsilyl)-2-alkanones through an initial addition followed by removal of chloride anion and 1,2-rearrangement of silyl group. In contrast, the reaction proceeds with 2 equiv of the Grignard reagents bearing β-hydrogen to give 2-(trimethylsilyl)-1-alkanols, where initial reduction of the silylcarbonyl group followed by such rearrangement and addition of the Grignard reagents to the resulting 2-(trimethylsilyl)alkanals have been proposed.

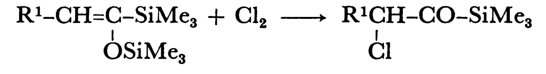
Enol silyl ethers have recently been employed as one of the most promising nucleophiles in organic synthesis.[2)] Use of this class of compounds has allowed regioselective introduction of a variety of functional groups or carbon chain onto α-carbons of the carbonyl compounds. For regioselective preparation of enol silyl ethers from the corresponding ketones, difference of thermodynamically and kinetically favorable enolates has usually been utilized to reflect their geometries to those of enol silyl ethers.[3)] Based on these features, various methods have been developed for regioselective synthesis of enol silyl ethers, but there have been still encountered several difficulties on occasions where such difference is very small or negligible. In order to explore a new methodology for regioselective synthesis of enol silyl ethers,[4)] we have examined the reaction of 2-chloroacyltrimetylsilanes **1** with Grignard reagents, assuming that the initially formed adduct **2** undergoes 1,2-rearrangement[5)] of silyl group from carbon to oxygen to yield **3**. The resulting **3** may be converted to the corresponding enol silyl ethers regiospecifically through removal of magnesium halides as shown in Scheme 1.


$$\underset{\displaystyle\mathbf{1}}{R^1\text{-}\underset{Cl}{CH}\text{-}CO\text{-}SiMe_3} + R^2CH_2MgX \longrightarrow R^1\text{-}\underset{Cl}{CH}\text{-}\overset{OMgX}{\underset{SiMe_3}{C}}\text{-}CH_2R^2\ \mathbf{2}$$
$$\downarrow ?$$
$$R^1\text{-}CH\text{=}\overset{OSiMe_3}{C}\text{-}CH_2R^2 \xleftarrow{-MgClX} R^1\text{-}\underset{Cl}{CH}\text{-}\overset{OSiMe_3}{\underset{MgX}{C}}\text{-}CH_2R^2\ \mathbf{3}$$

Scheme 1.

Results and Discussion

The requisite 2-chloroacyltrimethylsilanes **1** can be prepared in excellent yields by treating the corresponding enol silyl ethers of acyltrimethylsilanes[6)] with an equimolar amount of chlorine in carbon tetrachloride at ambident temperature (see Table 1). Direct chlorination of acyltrimethylsilanes is also employable, but formation of a small amount of dichlorides accompanies as by-products.[7)]

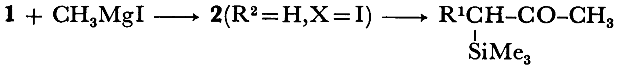

$$R^1\text{-}CH\text{=}\underset{OSiMe_3}{C}\text{-}SiMe_3 + Cl_2 \longrightarrow R^1\underset{Cl}{CH}\text{-}CO\text{-}SiMe_3$$

1

TABLE 1. PREPARATION OF 2-CHLORO- AND 2-BROMOACYLTRIMETHYLSILANES **1**

R^1	Yield/%	
	Chloride	Bromide
a) n-C_4H_9	83	81
b) n-C_6H_{13}	89	92
c) $C_6H_5CH_2$	87	87
d) CH_2=CH-$(CH_2)_7$	82	85

In contrary to our assumption, treatment of 2-chlorohexanoyltrimethylsilane with an equimolar amount of methylmagnesium iodide in tetrahydrofuran (THF) at −78 °C has never afforded the expected enol silyl ether, but its isomer, 3-trimethylsilyl-2-heptanone has been isolated in 91% yield (Eq. 1). Other chlorides also afforded the corresponding 3-(trimethylsilyl)-2-alkanones **4** in excellent yields (Table 2). Similar reactions were also examined with methyllithium, but afforded much less satisfactory results.

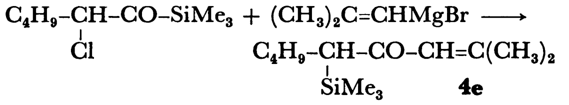

$$\mathbf{1} + CH_3MgI \longrightarrow \mathbf{2}(R^2\text{=}H, X\text{=}I) \longrightarrow R^1\underset{SiMe_3}{CH}\text{-}CO\text{-}CH_3$$

4 (1)

TABLE 2. PREPARATION OF 3-(TRIMETHYLSILYL)-2-ALKANONES **4**

R^1	Yield/%
a) n-C_4H_9	91
b) n-C_6H_{13}	90
c) $C_6H_5CH_2$	98
d) CH_2=CH-$(CH_2)_7$	91

Similarly, 2-methyl-1-propenylmagnesium bromide afforded the corresponding unsaturated silyl ketone **4e** in 72% yield.


$$C_4H_9\text{-}\underset{Cl}{CH}\text{-}CO\text{-}SiMe_3 + (CH_3)_2C\text{=}CHMgBr \longrightarrow C_4H_9\text{-}\underset{SiMe_3}{CH}\text{-}CO\text{-}CH\text{=}C(CH_3)_2\ \ \mathbf{4e}$$

These results have clearly indicated that transfer of silyl group to the neighboring carbon atom takes place preferentially even under such mild reaction conditions. Intermediary formation of α,β-epoxysilane can

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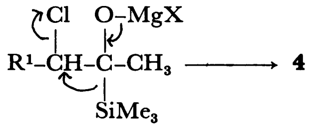
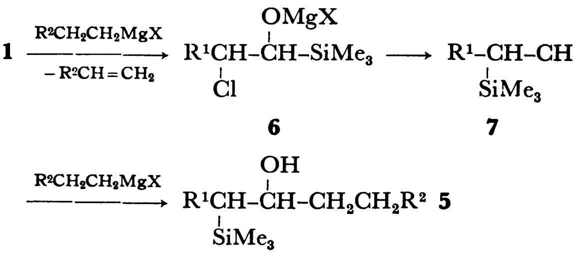
be ruled out because Mg^{2+} cation induced rearrangement of such material should afford the corresponding 2-halo-2-(trimethylsilyl)-3-alkanol as reported.[8] Instead, the reaction is considered to proceed through removal of chloride anion from the initially formed alkoxide **2** followed by rearrangement of trimethylsilyl group to the resulting cationic site to afford **4**. We have found no evidence on the question whether these processes occur successively or in concerted manner, but both of them are expected to be greatly favored. The first stage may be facilitated by σ-π interaction with the neighboring silyl group[9] and the second one may be accelerated by the aid of an anionic character of O–Mg bond. A combination of these three factors is considered to induce this characteristic transformation so efficiently.



In contrast, on using Grignard reagents bearing β-hydrogen in the reaction with **1**, 2 equiv of the Grignard reagent are required to complete a conversion, and 2-(trimethylsilyl)-1-alkanol **5** has been obtained in place of **4**. For example, the reaction of **1** (R^1=$C_6H_5CH_2$) with 1 equiv of hexylmagnesium bromide resulted in formation of a mixture of **5** (R^1=$C_6H_5CH_2$, R^2=C_4H_9, 39%) and 3-phenylpropanal (18%) together with the recovered starting material (17%), whereas use of 2 equiv of the Grignard reagent led to the exclusive formation of the corresponding **5**.

In connection with this transformation, it has been reported by Brook *et al.*[10] that in stead of an addition reaction, acylsilanes undergo reduction preferentially to yield 2-(trimethylsilyl)-1-alkanols on treating with Grignard reagents bearing β-hydrogen. Similarly, it appears to be reasonable to assume that the corresponding alkoxide **6** is formed as an initial product in this case. Then, **6** may undergo the same type of transformation to yield the corresponding 2-(trimethylsilyl)alkanal **7**, which reacts further with the Grignard reagent to give **5** as shown in Eq. 2. Higher reactivity of an aldehyde function to such nucleophiles has made it very difficult to isolate 7. Although several attempts to isolate **7** have failed, formation of 3-phenylpropanal in the above experiment supports **7** as a plausible intermediate.

According to Cram's rule,[11,12] selective formation of erythro isomer **5** has been expected in the reaction of **7** with Grignard reagents because trimethylsilyl group should behave as much more bulky one than most of alkyl groups. Hudrlik *et al.* recently described threo selective reduction of 2-(trimethylsilyl)alkanones with diisobutylaluminium hydride (DIBAL) and stereoselective conversion of the resulting alcohols to (*E*)- and (*Z*)-olefins under the influence of base and Lewis acid, respectively.[12a)]

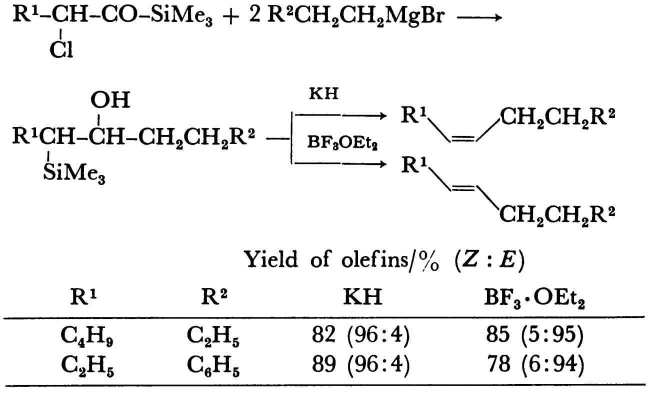


$$\mathbf{1} \xrightarrow[-R^2CH=CH_2]{R^2CH_2CH_2MgX} \underset{\mathbf{6}}{R^1CH(Cl)\text{-}CH(OMgX)\text{-}SiMe_3} \longrightarrow \underset{\mathbf{7}}{R^1\text{-}CH(SiMe_3)\text{-}CH{=}O} \xrightarrow{R^2CH_2CH_2MgX} R^1CH(SiMe_3)\text{-}CH(OH)\text{-}CH_2CH_2R^2 \ \mathbf{5} \quad (2)$$

Table 3. Preparation of 2-(trimethylsilyl)-1-alkanols **5**

R^1	R^2	Yield/%
a) n-C_4H_9	n-C_2H_5	85
b) n-C_4H_9	n-C_4H_9	90
c) n-C_6H_{13}	n-C_4H_9	90
d) $C_6H_5CH_2$	n-C_2H_5	92
e) $C_6H_5CH_2$	n-C_4H_9	96
f) CH_2=CH-$(CH_2)_7$	n-C_4H_9	92

In order to confirm stereochemical outcome of this addition reaction, 2-chlorohexanoyltrimethylsilane was treated with 2.2 equiv of butylmagnesium bromide in THF at −78 °C for 30 min, and the corresponding **5** (R^1=C_4H_9, R^2=C_2H_5) was isolated in 85% yield. As expected, on treating with potassium hydride and boron trifluoride etherate, the resulting alcohol **5** afforded (*E*)- and (*Z*)-5-decene, respectively, in highly stereo-controlled manner as shown in the following equation. These results apparently verified highly selective formation of erythro isomer **5** in the present one-pot procedure.



$$R^1\text{-}CH(Cl)\text{-}CO\text{-}SiMe_3 + 2\,R^2CH_2CH_2MgBr \longrightarrow R^1CH(SiMe_3)\text{-}CH(OH)\text{-}CH_2CH_2R^2$$

Yield of olefins/% (*Z* : *E*)

R^1	R^2	KH	$BF_3\cdot OEt_2$
C_4H_9	C_2H_5	82 (96:4)	85 (5:95)
C_2H_5	C_6H_5	89 (96:4)	78 (6:94)

In summary, use of 2-chloroacyltrimethylsilanes has made it feasible to prepare 3-(trimethylsilyl)-2-alkanones or 2-(trimethylsilyl)-1-alkanols, depending on the Grignard reagent employed, in completely regio-controlled manner. The latter alcohols can be oxidized to the corresponding silyl ketones[12a)] in good yield.

Although we failed to explore a method for regiospecific preparation of enol silyl ethers by a sequence described above,[13] these silyl ketones[12,14] obtained undergo a facile isomerization to the corresponding enol silyl ethers regiospecifically.[15] Further, these silyl ketones themselves have been proved to be especially useful for regioselective aldol formation because the silyl group has played dual roles for selective generation of two types of enolates as described already.[16]

Experimental

General Methods. Boiling points are uncorrected. Infrared (IR) spectra were recorded on a Hitachi EPI-G3 spectrometer; absorptions are reported in reciprocal centimeters. Proton nuclear magnetic resonance spectra (^1H NMR) were obtained on a Hitachi R-24B spectrometer; chemical shifts (δ) are expressed in part per million downfield from tetramethylsilane. Analytical gas-liquid chromatography (GLC) was performed on a Hitachi 163 instrument with a flame ionization detector and nitrogen carrier gas (1.0—1.3 kg/cm^2) using a OV-101 fused silica 20 m capillary column (Hitachi Chemi-Column). Microanalysis were performed with a Perkin-Elmer 240 at the Micro-analytical Laboratory, Tokyo Institute of Technology.

Reactions involving air- or moisture-sensitive compounds were carried out in appropriate round-bottomed flasks with stirring bars under nitrogen or argon atmosphere. Bulb-to-bulb distillation was performed with a Büchi Kugelrohr apparatus.

Preparative thin-layer chromatography (TLC) was carried out on glass plates (20×20 cm) coated with Merck silica gel PF 254 (1 mm thick).

Hexane was distilled from sodium. Ether and tetrahydrofuran (THF) were distilled from sodium-benzophenone ketyl immediately before use.

Materials. Enol trimethylsilyl ethers of acyltrimethylsilanes were prepared from the corresponding enol trimethylsilyl ethers of benzenethiol or methanethiol esters according to the procedure developed in our laboratory.[6]

Preparation of 2-Chloro- or 2-Bromoacyltrimethylsilanes. General Procedure: An enol trimethylsilyl ether of acyltrimethylsilane (1 mmol) in carbon tetrachloride (1.5 ml) was added to a carbon tetrachloride (4.5 ml) solution of chlorine or bromine (1.1 mmol) at −20 °C and it was stirred for 5—10 min at that temperature under argon. Then, the solvent was removed on a rotary evaporator, and the residual oil was separated by preparative TLC using a mixture of hexane and ether (5:1) as a solvent to give the title compound.

2-Chlorohexanoyltrimethylsilane **1a**: IR(neat): 1650, 1250, 855 cm^{-1}; NMR(CCl_4) δ=0.30 (s, 9H), 0.77—2.33 (m, 9H), 4.11 (t, J=6 Hz, 1H); Calcd for $C_9H_{19}OClSi$: C, 52.27; H, 9.26. Found: C, 52.40; H, 9.05.

2-Bromohexanoyltrimethylsilane **1a'**: IR (neat): 1652, 1250, 855 cm^{-1}; NMR(CCl_4) δ=0.40 (s, 9H), 0.76—2.33 (m, 9H), 4.33 (t, J=7 Hz, 1H); Calcd for $C_9H_{19}OBrSi$: C, 43.03; H, 7.62. Found: C, 43.21; H, 7.50.

2-Chlorooctanoyltrimethylsilane **1b**: IR (neat): 1650, 1250, 855 cm^{-1}; NMR(CCl_4) δ=0.33 (s, 9H), 0.66—2.43 (m, 13H), 4.15 (t, J=5 Hz, 1H); Calcd for $C_{11}H_{23}OClSi$: C, 52.26; H, 9.87. Found: 52.43; H, 9.59.

2-Bromooctanoyltrimethylsilane **1b'**: IR (neat): 1650, 1250, 855 cm^{-1}; NMR(CCl_4) δ=0.33 (s, 9H), 0.66—2.43 (m, 13H), 4.37 (t, J=7 Hz, 1H).

2-Chloro-3-phenylpropionyltrimethylsilane **1c**: IR (neat): 1645, 1250, 845 cm^{-1}; NMR(CCl_4) δ=0.33 (s, 9H), 2.99 (dd, J=14 and 8 Hz, 1H), 3.40 (dd, J=14 and 6 Hz, 1H), 4.50 (dd, J=8 and 6 Hz, 1H), 7.20 (s, 5H); Calcd for $C_{12}H_{17}OClSi$: C, 59.85; H, 7.12. Found: C, 60.06; H, 6.97.

2-Bromo-3-phenylpropionyltrimethylsilane **1c'**. IR (neat): 1640, 1250, 845 cm^{-1}; NMR (CCl_4) δ=0.20 (s, 9H), 3.05 (dd, J=14 and 7 Hz, 1H), 3.53 (dd, J=14 and 7 Hz, 1H), 4.70 (t, J=7 Hz, 1H), 7.23 (s, 5H).

2-Chloro-10-undecenoyltrimethylsilane **1d**: IR (neat): 1652, 1250, 855 cm^{-1}; NMR(CCl_4) δ=0.30 (s, 9H), 1.15—2.25 (m, 14H), 4.23 (t, J=6 Hz, 1H), 4.94 (d, J=13 Hz, 1H), 4.99 (d, J=17 Hz, 1H), 5.78 (m, 1H); Calcd for $C_{14}H_{27}OClSi$: C, 61.17; H, 9.90. Found: C, 61.05; H, 10.08.

2-Bromo-10-undecenoyltrimethylsilane **1d'**. IR (neat): 1651, 1250, 855 cm^{-1}; NMR(CCl_4) δ=0.30 (s, 9H), 1.00—2.50 (m, 14H), 4.40 (t, J=6 Hz, 1H), 4.94 (d, J=13 Hz, 1H), 4.99 (d, J=17 Hz, 1H), 5.78 (m, 1H).

The Reaction of 2-Chloroacyltrimethylsilane with Methylmagnesium Iodide. General Procedure: An ethereal solution of methylmagnesium iodide (21.8 ml of 0.95 M solution (1 M=1 mol dm^{-3})) was added to a THF (20 ml) solution of 2-chloroacyltrimethylsilane (20 mmol) at −78 °C and it was stirred for 30 min at that temperature under argon. Hexane (200 ml) pre-cooled to −60 °C was added directly to the reaction mixture and the resulting solution was washed with satd aq NH_4Cl (20 ml). After drying the organic layer with anhyd $MgSO_4$ and removal of the solvent, fractional distillation of the residual oil gave the corresponding 3-(trimethylsilyl)-2-alkanone.

3-(Trimethylsilyl)-2-heptanone **4a**: Bp 78—83 °C/5 mmHg (1 mmHg≈133.322 Pa); IR (neat): 2950, 2920, 2845, 1693, 1253, 843 cm^{-1}; NMR (CCl_4) δ=−0.11 (s, 9H), 1.63—4.70 (m, 9H), 1.83 (s, 3H), 2.06—2.43 (m, 1H); Calcd for $C_{10}H_{22}OSi$: C, 64.45; H, 11.90. Found: C, 64.28; H, 12.13.

3-(Trimethylsilyl)-2-nonanone **4b**: Bp 86—90 °C/2 mmHg; IR (neat): 2950, 2920, 2845, 1693, 1253, 843 cm^{-1}; NMR (CCl_4) δ=−0.10 (s, 9H), 0.57—1.60 (m, 16H), 1.87 (s, 3H), 2.13—2.50 (m, 1H); Calcd for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22. Found: C, 67.09; H, 12.07.

4-Phenyl-3-(trimethylsilyl)-2-butanone **4c**: Bp 117—120 °C/1 mmHg; IR (neat): 3020, 1920, 1690, 1605, 1497, 1255, 845 cm^{-1}; NMR (CCl_4) δ=0.00 (s, 9H), 1.77 (s, 3H), 2.35—3.38 (m, 3H), 7.05 (s, 5H); Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15. Found: C, 70.62; H, 9.03.

3-(Trimethylsilyl)-11-dodecen-2-one **4d**: Bp. 117—120 °C/1 mmHg; IR (neat): 3070, 2925, 2850, 1695, 1645, 1255, 985, 910, 840 cm^{-1}; NMR (CCl_4) δ=−0.11 (s, 9H), 0.90—1.40 (m, 12H), 1.75—2.40 (m, 3H), 4.87 (d, J=11 Hz, 1H), 4.92 (d, J=16 Hz, 1H), 5.12—6.00 (m, 1H); Calcd for $C_{15}H_{30}OSi$: C, 70.79; H, 11.88. Found: C, 70.92; H, 12.03.

2-Methyl-5-(trimethylsilyl)-2-nonen-4-one **4e**: IR (neat): 1670, 1620 cm^{-1}; NMR (CCl_4) δ=0.07 (s, 9H), 0.70—1.50 (m, 9H), 1.70—2.40 (m, 2H), 1.87 (s, 3H), 2.13 (s, 3H), 5.90 (m, 1H).

The Reaction of 2-Chloroacyltrimethylsilane with a Grignard Reagent Bearing β-Hydrogen. General Procedure: An ethereal solution of the Grignard reagent (5.2 mmol) was added to a THF (2.5 ml) solution of 2-chloroacyltrimethylsilane (2.5 mmol) at −78 °C and it was stirred for 30 min at that temperature. Then, the reaction mixture was quenched with satd aq NH_4Cl and the aqueous layer was extracted with ether. After drying the combined extracts over anhyd $MgSO_4$ and removal of the solvent, purification of the residual oil with TLC using a mixture of hexane and ether (20:1) afforded the corresponding 2-(trimethylsilyl)-1-alkanol.

5-(Trimethylsilyl)-6-dodecanol **5b**: IR (neat): 3440, 2950, 2920, 1240, 836 cm^{-1}; NMR (CCl_4) δ=−0.07 (s, 9H), 0.7—1.62 (m, 23H), 2.06 (br s, 1H), 3.63 (m, 1H); Calcd for $C_{15}H_{34}OSi$: C, 69.69; H, 13.26. Found: C, 69.42; H, 13.38.

6-(Trimethylsilyl)-7-tetradecanol **5c**: IR (neat): 3450, 2920, 2850, 1247, 836 cm^{-1}; NMR (CCl_4) δ=0.03 (s, 9H), 0.77—1.73 (m, 27H), 1.97 (br s, 1H), 3.77 (m, 1H); Calcd for $C_{17}H_{38}OSi$: C, 71.25; H, 13.37. Found: C, 71.07; H, 13.16.

1-Phenyl-2-(trimethylsilyl)-3-heptanol **5d**: IR (neat): 3430, 1250, 840 cm^{-1}; NMR (CCl_4) δ=0.10 (s, 9H), 0.90—1.80 (m, 11H), 2.83 (d, J=7 Hz, 2H), 3.85 (m, 1H), 7.26 (s, 5H).

1-Phenyl-2-(trimethylsilyl)-3-nonanol **5e**: IR (neat): 3450, 3060, 3030, 3000, 2940, 2900, 2835, 1600, 1490, 1245, 835 cm^{-1}; NMR (CCl_4) δ=0.03 (s, 9H), 0.7—1.9 (m, 14H), 2.01 (br s, 1H), 2.95 (d, J=7 Hz, 2H), 3.95 (m, 1H), 7.38 (s, 5H); Calcd for $C_{18}H_{32}OSi$: C, 73.90; H, 11.03. Found: C, 73.68; H, 10.89.

8-(Trimethylsilyl)-16-heptadecen-7-ol **5f**: IR (neat): 3420, 3070, 2925, 2850, 1645, 1255, 910, 840; NMR (CCl_4) δ=−0.07 (s, 9H), 0.6—1.67 (m, 26H), 1.67—2.17 (m, 2H), 2.83 (br s, 1H), 4.87 (d, J=11 Hz, 1H), 4.92 (d, J=16 Hz, 1H), 5.12—6.00 (m, 1H); Calcd for $C_{20}H_{42}OSi$: C, 73.54; H, 12.96. Found: C, 73.33; H, 13.04.

Conversion of 6-(Trimethylsilyl)-5-decanol to (E)- and (Z)-5-Decene. 2-Chlorohexanoyltrimethylsilane (412 mg, 2 mmol) was treated with butylmagnesium bromide (4.4 mmol) in a similar manner as described above and 6-(trimethylsilyl)-5-decanol **5a** (462 mg, 85%) was obtained. IR (neat): 3450, 2960, 1680, 835 cm^{-1}; NMR(CCl$_4$) δ=−0.06 (s, 9H), 0.77—1.67 (m, 19H), 3.70 (m, 1H). To a THF (2 ml) solution of the alcohol **5a** (230 mg, 1 mmol) was added KH (3 mmol) in THF (1 ml) at 0 °C and it was stirred for 1 h at room temperature. Then, the reaction mixture was quenched with sat aq NH$_4$Cl and the aqueous layer was extracted with ether. The combined extracts were dried over anhyd MgSO$_4$, and the resulting solution was analyzed by GLC using decane as an internal standard, which showed formation of a mixture of (*E*)- and (*Z*)-5-decene in 82% yield. Ratio of (*E*)- to (*Z*)-isomer was determined to be 4:96 by comparison with the authentic sample.

The same alcohol (216 mg, 0.94 mmol) was treated with BF$_3$OEt$_2$ (0.4 ml) in dichloromethane (5 ml) at room temperature for 1 h. Similar analysis of the reaction mixture indicated formation of (*E*)- and (*Z*)-5-decene in 85% yield in a ratio of 95:5, respectively.

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