# Stereoselective Synthesis of (*E*)- and (*Z*)-2-Alkenyltrimethylsilanes from 1,2-Epoxy-1,3-bis(trimethylsilyl)propane[1)]

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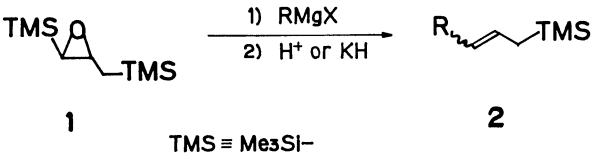
Stereoselective synthesis of various (*E*)- and (*Z*)-2-alkenyltrimethylsilanes ($RCH{=}CHCH_2SiMe_3$; R=Me, Et, *n*-Bu, *i*-Pr, *c*-hexyl, *t*-butyl, and phenyl) has been accomplished by a reaction of 1,2-epoxy-1,3-bis(trimethylsilyl)propane with Grignard reagents (RMgX) followed by subsequent Peterson olefination reactions of resulting 1,2-bis(trimethylsilyl)-3-alkanols [$RCH(OH)CH(SiMe_3)CH_2SiMe_3$]; the acid ($BF_3OEt_2$ or $HClO_4$)-catalyzed olefination yields the (*E*)-isomer, while the base (KH or NaH)-induced olefination yields the (*Z*)-isomer in more than 95% stereochemical purity in most cases.

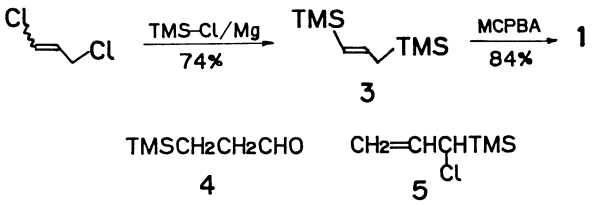
The chemistry of allylsilanes has received continuing synthetic and mechanistic interests.[2,3)] Synthetic methods for acyclic allylsilanes include coupling reactions between allyl-metal species and halosilanes,[4,5)] between silyl-metal species and allyl halides,[6)] or between allyl methyl ethers and halosilanes with the aid of sodium,[7)] Wittig condensation of 2-trimethylsilylethylidenetriphenylphosphorane with carbonyl compounds,[8)] hydrosilylation or reductive silylation of 1,3-dienes,[9)] a Ramberg-Backlund olefination,[10,11)] and transition metal-catalyzed reaction between allylic halides and disilanes.[12)] These methods are generally nonstereospecific and give a mixture of stereoisomers which are usually not readily separable from each other. Furthermore, some of these methods are not regiospecific. During the course of our study on the ene reactions of allylsilanes,[13,14)] we needed a series of (*E*)- and (*Z*)-2-alkenylsilanes in high stereochemical purity. 2-Alkenylsilanes may be prepared stereoselectively from 1-alkynes via hydroboration[15)] and from vinyl triflates via palladium-catalyzed coupling with tris(trimethylsilylmethyl)aluminum.[16)] We describe here a new stereoselective method for (*E*)- and (*Z*)-2-alkenyltrimethylsilanes (**2**) via a Grignard reaction of *trans*-1,2-epoxy-1,3-bis(trimethylsilyl)propane (**1**) followed by the Peterson olefination reaction.[17)]




## Results and Discussion

The requisite oxirane **1** was obtained in 84% yield by epoxidation of (*E*)-1,3-bis(trimethylsilyl)propene (**3**) with *m*-chloroperbenzoic acid in dichloromethane at −15 °C. The oxirane was labile and decomposed to 3-trimethylsilylpropanal (**4**) on exposure to acids; however, it could be stored for years in a refrigerator without appreciable decomposition. The precursory olefin **3** can be prepared from allyltrimethylsilane,[18)] but we prepared it more conveniently in 74% yield from 1,3-dichloropropene by in situ coupling with chlorotrimethylsilane with the aid of magnesium in THF under reflux. Although commercial 1,3-dichloropropene was a mixture of (*E*) and (*Z*) isomers in the ratio 45 : 55, the coupling reaction led to almost stereospecific formation of (*E*)-**3**. This arose from the silylation via double rearrangement of the allylic double bonds. The first silylation yields (1-chloroallyl)trimethylsilane (**5**) and the subsequent silylation occurs at the 3-position of allyl group to give (*E*)-**3** from steric reason. Indeed, a controlled reaction afforded **5** in good yield.[19)]

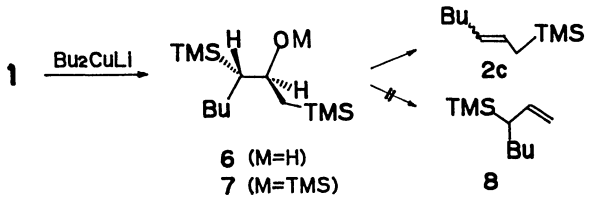
Lithium dibutylcuprate(I) reacted relatively slowly with **1** in ether at −40 °C affording 1,3-bis(trimethylsilyl)-2-heptanol (**6**) together with a small amount of its trimethylsilyl ether **7** in a combined 75% yield, the products of the anticipated α cleavage.[20)] A sodium hydride-induced olefination of the resulting alcohol stereoselectively gave [(*E*)-2-heptenyl]-trimethylsilane [**2c**, (*E*)/(*Z*)=98/2] consistent with syn-elimination[21)] from a configuration shown in **6**. On the other hand, a $BF_3OEt_2$-catalyzed olefination of **6** proceeded without significant stereoselectivity yielding a 48 : 52 mixture of the (*E*) and (*Z*) isomers in 88% yield. This is presumably due to the steric strain imposed on the anti-oriented transition state. The regiochemistry of this olefination reaction is worth



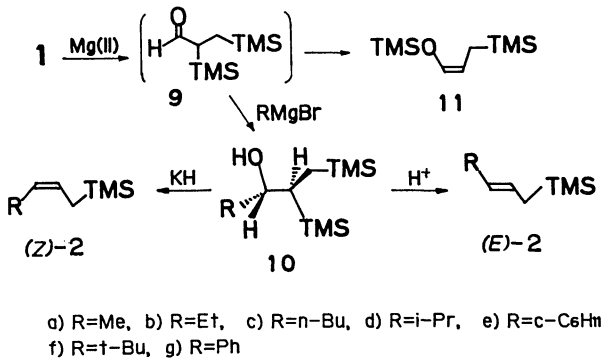

Scheme 1.

stating. Predominant (>95%) formation of **2c** instead of its regioisomer **8** indicates that the internal $SiMe_3$ is more reactive than the terminal one either in the acid-catalyzed or base-induced reaction. Stability of the producing alkenes appears to play a dominant role in the regiocontrol.

The oxirane **1** smoothly reacted with alkyl and phenyl Grignard reagents (RMgX) in ether at room temperature to give 1,2-bis(trimethylsilyl)-3-alkanols **10a—g** in good yields except for the reaction with *t*-butylmagnesium bromide, as shown in Table 1 which includes the results of the subsequent olefination reactions as well. The reaction obviously involves an initial skeletal rearrangement of **1** to 2,3-bis(trimethylsilyl)propanal (**9**) probably effected by magnesium halides,[22] as shown in Scheme 3. The acid-catalyzed olefination of **10** by use of $BF_3OEt_2$ or 70% perchloric acid gave the (*E*) isomer of 2-alkenyltrimethylsilanes (**2a—g**), while the sodium hydride- or potassium hydride-induced reaction afforded the (*Z*) isomer with more than 97% stereoselectivity in most cases. These stereochemical results indicate that the alcohol **10** was formed in high diastereomeric purity almost as a single diastereomer of a configuration shown in **10**. The structure of the alcohol is predictable from the Cram's rule[23] if we assume that $SiMe_3$ is larger than $CH_2SiMe_3$. Relatively low stereoselectivities in the olefination of the alcohol **10a** are presumably attributed to contamination of an alternative diastereoisomer of **10a**. The reaction between **1** and *t*-butylmagnesium bromide




Scheme 2.




Scheme 3.

Table 1. Reaction of **1** with Grignard Reagents and Subsequent Olefination

| Reaction of **1** | | | Olefination | | |
|---|---|---|---|---|---|
| Reagent | product | Yield[a]/% | Conditions[b] | Product [(*E*)/(*Z*)] | Yield[a]/% |
| MeMgI | **10a** | 89,97[c] | A[d] | **2a** (94/6) | 92[c] |
| | | | D | **2a** (11/89) | 58[c] |
| EtMgBr | **10b** | 88 | A | **2b** (97/3) | 71 |
| | | | B[e] | **2b** (97/3) | 86 |
| | | | C | **2b** (2/98) | 76 |
| *n*-BuMgBr | **10c** | 85 | A | **2c** (97/3) | 90 |
| | | | B | **2c** (95/5) | 92 |
| | | | C | **2c** (2/98) | 85 |
| | | | D | **2c** (2/98) | 73[c] |
| *i*-PrMgCl | **10d** | 87,94[c] | A | **2d** (98/2) | 92[c] |
| | | | B | **2d** (98/2) | 81 |
| | | | C | **2d** (2/98) | 62 |
| | | | D | **2d** (2/98) | 45[c] |
| *c*-$C_6H_{11}$MgCl | **10e** | 86 | A[d] | **2e** (98/2) | 96 |
| | | | D | **2e** (2/98) | 55 |
| *t*-BuMgBr | **10f** | 10[c] | A | **2f** (98/2) | 75[c] |
| | | | B | **2f** (98/2) | 53 |
| | | | C | **2f** (2/98) | 43 |
| | | | D | **2f** (2/98) | 50[c] |
| PhMgBr | **10g** | 92 | A[f] | **2g** (98/2) | 88 |
| | | | B[g] | **2g** (98/2) | 65 |
| | | | C[d,g] | **2g** (9/91) | 55 |
| | | | D[h] | **2g** (6/94) | 94[c] |

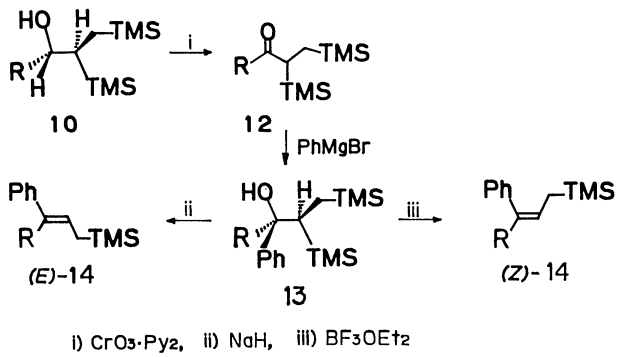
a) Isolated yield unless otherwise noted. b) Reaction conditions are as follows: (A) with ca. 1 equiv $BF_3OEt_2$ at 0 °C for 30 min in ether; (B) with 3 equiv 70% $HClO_4$ at 0 °C for 30 min in ether; (C) with 2 equiv KH in THF under reflux for 30 min; (D) with 2 equiv NaH in 1,2-dimethoxyethane under reflux for 3—5 h. c) GLC yield. d) At room temperature. e) Reflux for 90 min. f) Stirred for 15 min. g) Stirred for 5 min. h) Reflux for 20 min.

gave the alcohol **10f** in only 10% yield; the major reaction in this case was the formation of (*Z*)-1-trimethylsiloxy-3-trimethylsilyl-1-propene (**11**) which was isolated in 72% yield, indicating that **9** decayed to **11** more rapidly than it reacted with the bulky Grignard reagent.

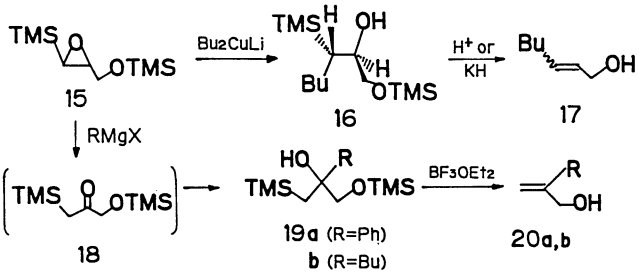
The stereochemistry of **2a—g** was deduced from IR spectra. The (*E*) and (*Z*) stereoisomers of **2a—g** appeared on GLC at different retention times and exhibited the C=C stretching vibration at different wavenumbers; one showed an absorption near 1660 $cm^{-1}$ together with a strong out-of-plane deformation band near 960 $cm^{-1}$, while the other showed an absorption near 1645 $cm^{-1}$ together with a weak band near 720 $cm^{-1}$ but no significant band near 960 $cm^{-1}$. These differences in the IR spectra allow us to assign the former to the (*E*) and the latter to the (*Z*) isomers, respectively.[24] Both (*E*) and (*Z*) stereoisomers exhibited very complicated NMR spectra for olefinic protons which were not readily resolvable except for (*Z*)-**2g**.

The oxidation of the alcohols **10** to the corresponding ketones **12** and the subsequent Grignard reaction followed by olefination may provide a stereoselective route to (3,3-disubstituted allyl)trimethylsilanes. This was exemplified by preparation of (*E*) and (*Z*) isomers of (3-phenyl-2-butenyl)trimethylsilanes (**14a**; R=$CH_3$) from **10a** via a ketone **12a** and an alcohol **13a**, as shown in Scheme 4. The $BF_3OEt_2$-catalyzed reaction almost stereospecifically gave (*Z*)-**14a** in 92% yield, while the NaH-induced reaction did (*E*)-**14a** in 78% yield. The stereochemical assignment for **14a** was deduced from the NMR analysis and from the fact that **13a** gave (*E*)-2-phenyl-2-butene instead of **14a** on prolonged treatment with NaH. The stereochemical results suggest that PhMgBr added to the ketone **12a** exclusively in an anti-Cram fashion.

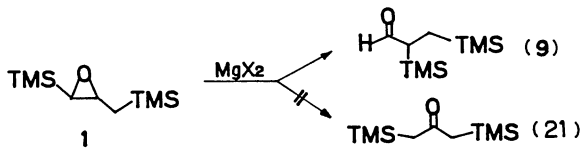
In connection with the stereoselective preparation of allylsilanes from **1**, we briefly examined reactions of a related oxirane **15**. Reaction with ($n$-Bu)$_2$CuLi gave an expected alcohol **16** which on treatment with perchloric acid and with KH respectively gave (*Z*)- and (*E*)-2-hepten-1-ol (**17**) almost in a stereospecific




Scheme 4.




Scheme 5.




Scheme 6.

manner in each case. On the other hand, phenylmagnesium bromide reacted with **15** yielding 2-phenyl-1-trimethylsiloxy-3-trimethylsilyl-2-propanol (**19**), which on treatment with $BF_3OEt_2$ afforded 2-phenylallyl alcohol (**20a**) in 91% yield. Similarly, reaction with butylmagnesium bromide and subsequent olefination gave 2-butylallyl alcohol (**20b**). The formation of the alcohol **19** indicates an initial rearrangement of **15** to 1-trimethylsiloxy-3-trimethylsilyl-2-propanone (**18**), as shown in Scheme 5.

Magnesium halide-induced rearrangement of 1-silyl-1,2-epoxyalkanes generally gives 1-silyl-2-alkanones instead of 2-silylalkanals via a regioselective ring-opening through the $\alpha$-cleavage followed by migration of hydrogen rather than alkyl groups.[25] In addition, a group *cis* to silicon is in general more labile than the corresponding *trans* group.[26] This was indeed true for the oxirane **16**. Accordingly, the magnesium halide-induced rearrangement of **1** might produce 1,3-bis(trimethylsilyl)-2-propanone (**21**) instead of the aldehyde **9**. The absence of **21** suggests either a large migratory aptitude for $CH_2SiMe_3$ as compared to hydrogen or the selective $\beta$ ring-opening followed by a 1,2-$SiMe_3$ shift, although we have no compelling evidence for the latter pathway.

## Experimental

IR spectra were recorded on a Hitachi 260-10 spectrophotometer. NMR spectra were recorded on a Hiatachi R-600 (60 MHz) spectrometer in carbon tetrachloride using TMS as internal standard except otherwise noted. Mass spectra were recorded on a Hiatchi M-60 mass spectrometer. UV spectra were recorded on a Hitachi 220A spectrophotometer. Analytical and preparative GLC were performed on a Hitachi 163 gas chromatograph equipped with the following columns: (A): 4 mm×25% Apiezon Grease L on Chamelite CK, (B): 4 mm×3 m; 25% Silicone oil SE-30 on Chromosorb W (A.W), and (C): 4 mm×2 m; 25% Silicone DC 550 on

Chromosorb W (A.W), and DMCS.

**1,3-Bis(trimethylsilyl)propene (3).** To a mixture of chlorotrimethylsilane (49 g) and magnesium (30 g) in THF (100 $cm^3$) heated to ca. 60 °C was added dropwise a mixture of 1,3-dichloropropene (50 g) and chlorotrimethylsilane (49 g) in THF (200 $cm^3$) over a period of 8 h at such a rate as to maintain gentle reflux. After completion of the addition, the mixture was stirred for 2 h under reflux and was allowed to cool to room temperature. Hexane (500 $cm^3$) was then added and inorganic material was filtered off. The filtrate was washed with water, with 10% aq NaOH, and with water, and dried over $MgSO_4$. Fractionation using an efficient column gave 62 g (74%) of 1,3-bis(trimethylsilyl)propene, bp 68—69 °C (20 Torr; 1 Torr=133.3 Pa) [lit,[18a] bp 171 °C].

**1,2-Epoxy-1,3-bis(trimethylsilyl)propane (1).** To a stirred mixture of *m*-chloroperbenzoic acid (85% purity, 25 g) in dichloromethane (100 $cm^3$) cooled to −15 °C was added **3** (21 g, 0.113 mol) over a period of 10 min and the mixture was stirred for 3 h at that temperature. Pentane (100 $cm^3$) was added and a solid was removed by filtration. The solid was washed with pentane and the combined pentane solution was washed three times with every 15 $cm^3$ of 10% cold aq NaOH, with cold water, and dried over $MgSO_4$. Solvent was removed on a rotary evaporator and the residual oil was distilled to give 19 g (83%) of **1** as a colorless oil: Bp 69—70 °C (9 Torr); IR (neat) 1255, 1185, 870, 840 $cm^{-1}$; $^1H$ NMR $\delta$=0.03 (9H, s), 0.05 (9H, s), 0.58 (1H, double d, $J$=14 and 7.5 Hz), 1.15 (1H, double d, $J$=14 and 5.5 Hz), 1.71 (1H, d, $J$=3.2 Hz), 2.62 (1H, m). Found: C, 53.18; H, 10.71%. Calcd for $C_9H_{22}OSi_2$: C, 53.41; H, 10.96%. Acidic workup should be avoided; in a separate experiment, washing a crude pentane solution with 10% aq HCl led to the formation of 3-trimethylsilylpropanal (**4**, 51%) instead: Bp 90—91 °C (118 Torr); IR (neat) 1730, 1250, 860, 840 $cm^{-1}$; $^1H$ NMR $\delta$=0.0 (9H, 5), 0.58—0.90 (2H, m), 2.29 (1H, t ($J$=8.5 Hz) of d ($J$=1.5 Hz)), 9.60 (1H, t, $J$=1.5 Hz).

**Reaction of 1 with Lithium Dibutylcuprate(I).** To a solution of $Bu_2CuLi$ prepared from BuLi (1.73 mol $dm^{-3}$ in hexane, 12 $cm^3$) and CuI (1.9 g) in ether (20 $cm^3$) cooled to −78 °C was added the oxirane **1** (1.01 g, 5.0 mmol) and the mixture was stirred for 1 d at ca. −40 °C. Usual workup gave an oil (1.1 g), bp 105—110 °C (7 Torr), which was shown to be a mixture of 1,3-bis(trimethylsilyl)-2-heptanol (**6**) and its trimethylsilyl ether **7** in the ratio 8 : 1.

**6:** IR 3480 (broad), 1255, 855, 840 $cm^{-1}$; $^1H$ NMR $\delta$=0.0 (18H, s), 0.5—1.0 (6H, m), 1.0—1.5 (6H, m), 1.8 (1H, disappeared on addition of $D_2O$), 3.8 (1H, broad m). Found: C; H, 12.39%. Calcd for $C_{13}H_{32}OSi_2$: C, 59.24; H, 12.24%.

**7:** IR 1255, 1030, 850, 835 $cm^{-1}$; $^1H$ NMR $\delta$=0.0 (18H, s), 0.06 (9H, s), 0.5—1.0 (6H, m), 1.0—1.4 (6H, m), 4.05 (1H, t ($J$=7 Hz) of d ($J$=1.5 Hz)).

**Preparation of 1,2-Bis(trimethylsilyl)-3-alkanols 10. General Procedure.** A small portion (ca. 1 $cm^3$) of a solution of the oxirane **1** (5.05 g, 25 mmol) in ether (5 $cm^3$) was added to a solution of a Grignard reagent (30 mmol) in ether (25 $cm^3$) at room temperature. After an exothermic reaction had commenced, the rest of the epoxide solution was added over a period of 10 min and the resulting mixture was stirred for 1 h at ambient temperature. The mixture was cooled to 0 °C and aq ammonium chloride was added. Organic layer was separated, washed with aq $NaHCO_3$, and dried over $MgSO_4$. A crude product was purified by distillation or by column chromatography over alumina.

**3,4-Bis(trimethylsilyl)-2-butanol (10a):** Bp 110—111 °C (27 Torr): IR 3420, 1250, 1110, 1080, 850, 840 $cm^{-1}$; $^1H$ NMR $\delta$=−0.02 (18H, s), 0.4—1.2 (3H, m), 1.09 (3H, d, $J$=6.5 Hz), 1.52 (1H, broad s, disappeared on addition of $D_2O$), 3.86 (1H, q ($J$=6.5 Hz) of d ($J$=4.5 Hz)). Found: C, 55.10; H, 12.21%. Calcd for $C_{10}H_{26}OSi_2$: C, 54.98; H, 12.00%.

**1,2-Bis(trimethylsilyl)-3-pentanol (10b):** Bp 87—88 °C (4 Torr); IR 3475, 1250, 840 $cm^{-1}$; $^1H$ NMR $\delta$=0.0 (9H, s), 0.02 (9H, s), 0.51 (2H, d, $J$=5.4 Hz), 0.81—1.04 (4H, m), 1.43 (3H, m including OH proton), 3.61 (1H, m).

**1,2-Bis(trimethylsilyl)-3-heptanol (10c):** Bp 89—90 °C (1 Torr); IR 3480, 1250, 1020, 990, 840 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=0.0 (9H, s), 0.03 (9H, s), 0.44—0.55 (2H, m), 0.81—0.97 (3H, m), 1.38 (8H, m), 3.71 (1H, m). Found: C, 59.21; H, 12.35%. Found: $C_{13}H_{32}OSi_2$: C, 59.24; H, 12.24%.

**4-Methyl-1,2-bis(trimethylsilyl)-3-pentanol (10d):** Bp 86—87 °C (3 Torr) IR 3500, 1250, 1000, 840 $cm^{-1}$; $^1H$ NMR $\delta$=0.0 (18H, s), 0.4—0.6 (2H, m), 0.80 (3H, d, $J$=7 Hz), 0.87 (3H, d, $J$=7 Hz), 0.7—1.3 (1H, m), 1.60 (2H, m, including OH proton), 3.19 (1H, m). Found: C, 58.35; H, 12.25%. Calcd for $C_{12}H_{30}OSi_2$: C, 58.47; H, 12.27%.

**1-Cyclohexyl-2,3-bis(trimethylsilyl)-1-propanol (10e):** After purification by column chromatography: IR 3490, 1250, 995, 840 $cm^{-1}$; $^1H$ NMR $\delta$=0.0 (18H, s), 0.53 (2H, m), 0.7—2.05 (13H, m), 3.22 (1H, broad m).

**4,4-Dimethyl-1,2-bis(trimethylsilyl)-3-pentanol (10f):** IR 3600, 1250, 1055, 1000, 840 $cm^{-1}$; $^1H$ NMR $\delta$=0.0 (9H, s), 0.04 (9H, s), 0.86 (9H, s), 0.3—1.3 (3H, m), 3.43 (1H, d, $J$=10.5 Nz).

**1-Trimethylsiloxy-3-trimethylsilyl-1-propene (11):** Bp 65—66 °C (22 Torr); IR 1645, 1250, 1155, 1090, 860, 840 $cm^{-1}$; $^1H$ NMR $\delta$=0.0 (9H, s), 0.19 (9H, s), 1.37 (2H, double d, $J$=8.4 and 1.5 Hz), 4.35 (1H, d ($J$=8.4 Hz) of t ($J$=5.6 Hz)), 6.02 (1H, broad d, $J$=5.6 Hz).

**1-Phenyl-2,3-bis(trimethylsilyl)-1-propanol (10g):** IR 3460, 1255, 1050, 1010, 860, 840, 760, 700 $cm^{-1}$; $^1H$ NMR $\delta$=−0.18 (9H, s), −0.15 (9H, s), 0.58 (2H, m), 0.94—1.21 (1H, m), 1.37 (1H, d, $J$=3.6 Hz, disappeared on addition of $D_2O$), 4.68 (1H, double d, $J$=6.6 and 3.6 Hz), 7.22 (5H, almost s). Found: C, 64.48; H, 10.25%. Calcd for $C_{15}H_{28}OSi_2$: C, 64.23; H, 10.16%.

**Preparation of 2-Alkenyltrimethylsilanes 2.** 1,2-Bis(trimethylsilyl)-3-alkanols (**10**) were olefinated by the following methods under conditions listed in Table 1. Crude product obtained after workup was purified by distillation or by column chromatography.

**Procedure A.** To a stirred solution of an alcohol **10** (10 mmol) in ether (25 $cm^3$) cooled to 0 °C was added 0.6 ml of fresh boron trifluoride-diethyl ether. The mixture was stirred for 30 min at 0 °C. Aq 10% NaOH solution was added and organic layer was separated, washed with saturated aq NaCl and dried ($MgSO_4$).

**Procedure B.** Procedure was the same as the Procedure A except for the use of 70% perchloric acid (0.25 g per 10 mmol of **10**) instead of boron trifluoride-diethyl ether.

**Procedure C.** Potassium hydride (3.2 g, ca. 25% slurry in oil) was washed three times with pentane, dried under argon, and was weighed. To the residue (ca. 0.8 g) was added THF (10 $cm^3$) followed by addition of an alcohol **10** (10 mmol) in THF (2 $cm^3$) at 0 °C. After evolution of gas had ceased, the mixture was heated under reflux for 15 to 30 min.

**Procedure D.** Sodium hydride (0.87 g, 55% dispersion in

oil, ca. 20 mmol) was washed three times with hexane and dried under argon. To the residue was added a solution of an alcohol **10** (10 mmol) in 1,2-dimethoxyethane (10 cm³) at room temperature and the mixture was stirred under reflux for 3 to 5 h.

**2-Butenyl(trimethyl)silane (2a):** IR and NMR spectra of (*E*) and (*Z*) isomers [GLC retention time $t_R$ (Column B, 60 °C): 16.4 and 19.6 min, respectively] were identical to those reported.[27]

**2-Pentenyl(trimethyl)silane (2b):** (*E*)-**2b:** Bp 73 °C (100 Torr) ; IR 1660, 1250, 960, 845, 690 cm⁻¹ $^1$H NMR $\delta$=−0.04 (9H, s), 0.93 (3H, t, *J*=7.8 Hz), 1.29—1.39 (2H, m), 1.66—2.20 (2H, m), 5.16—5.35 (2H, m); MS *m/z* 142 ($M^+$, 13), 73 (100).

(*Z*)-**2b:** Bp 76—77 °C (98 Torr); IR 1640, 1250, 850, 720 cm⁻¹; $^1$H NMR $\delta$=−0.01 (9H, s), 0.92 (3H, t, *J*=7.2 Hz), 1.34—1.46 (2H, m), 1.60—2.22 (2H, m), 5.12—5.35 (2H, m); MS *m/z* 142 ($M^+$, 10), 73 (100).

Retention times for (*E*)-**2b** and (*Z*)-**2b** were 16.2 and 19.4 min, respectively (Column A, 100 °C).

**2-Heptenyl(trimethyl)silane (2c):** (*E*)-**2c**: Bp 102—103 °C (58 Torr); IR 1660, 1250, 960, 850, 690 cm⁻¹; $^1$H NMR $\delta$=0.0 (9H, s), 0.90 (3H, m), 1.28—1.43 (6H, m), 1.94—2.02 (2H, m), 5.21—5.42 (2H, m); MS *m/z* 170 ($M^+$, 8), 73 (100).

(*Z*)-**2c**: Bp 104—105 °C (55 Torr): IR 1640, 1250, 850, 720 cm⁻¹; $^1$H NMR $\delta$=0.02 (9H, s), 0.91 (3H, m), 1.12—1.6 (6H, m), 1.8—2.15 (2H, m), 4.95—5.6 (2H, m); MS *m/z* 170 ($M^+$, 6), 73 (100).

Retention times for (*E*)-**2c** and (*Z*)-**2c** were 23.6 and 25.6 min, respectively (Column B, 100 °C).

**Trimethyl(4-methyl-2-pentenyl)silane (2d):** (*E*)-**2d**: Bp 76—77 °C (66 Torr); IR 1660, 1250, 1155, 1020, 960, 855, 840 cm⁻¹; $^1$H NMR $\delta$=−0.04 (9H, s), 0.91 (6H, d, *J*=8.4 Hz), 1.31 (2H, d, *J*=6 Hz), 2.15 (1H, m), 4.87—5.32 (2H, m); MS *m/z* 156 ($M^+$, 6), 73 (100).

(*Z*)-**2d**: Bp 79—80 °C (65 Torr); IR 1645, 1250, 1150, 855, 840, 730 cm⁻¹; $^1$H NMR $\delta$=0.0 (9H, s), 0.91 (6H, d, *J*=6.4 Hz), 1.42 (2H, d, *J*=7.2 Hz), 2.5 (1H, m), 4.83—5.24 (2H, m); MS *m/z* 156 ($M^+$, 5), 73 (100).

Retention times for (*E*)-**2d** and (*Z*)-**2d** were 15.5 and 16.0 min, respectively (Column B, 100 °C).

**(3-Cyclohexylallyl)trimethylsilane (2e):** (*E*)-**2e**: IR 1660, 1250, 1155, 960, 850 cm⁻¹; $^1$H NMR $\delta$=−0.03 (9H, s), 0.6—2.3 (13H, m), 4.91—5.51 (2H, m); MS *m/z* 196 (*m/z* 4), 73 (100).

(*Z*)-**2e**: IR 1645, 1250, 1150, 850, 725 cm⁻¹; $^1$H NMR 0.0 (9H, s), 0.6—2.5 (13H, m), 4.85—5.5 (2H, m). MS *m/z* 196 ($M^+$, 8), 73 (100).

Retention times for (*E*)-**2e** and (*Z*)-**2e** were 49.6 and 45.4 min, respectively (Column B, 120 °C).

**(4,4-Dimethyl-2-pentenyl)trimethylsilane (2f):** (*E*)-**2f**: IR 1250, 1155, 970, 850, 840 cm⁻¹; $^1$H NMR $\delta$=−0.04 (9H, s), 0.95 (9H, s), 1.30 (2H, m), 5.22 (2H, m); MS *m/z* 170 ($M^+$, 9), 73 (100).

(*Z*)-**2f**: IR 1645, 1250, 1150, 850, 720 cm⁻¹; $^1$H NMR $\delta$=0.0 (9H, s), 1.06 (9H, s), 1.56 (2H, m), 4.9—5.2 (2H, m); MS *m/z* 170 ($M^+$, 8), 73 (100).

Retention times for (*E*) and (*Z*)-**2f** were 2.6 and 2.0 min respectively (Column C, 150 °C).

**(3-Phenylallyl)trimethylsilane (2g):** (*E*)-**2g**: Bp 70—71 °C (2 Torr); IR 1640, 1250, 1140, 1020, 960, 855, 730, 680 cm⁻¹; $^1$H NMR 0.04 (9H, s), 1.62 (2H, m), 6.02—6.30 (2H, m), 7.08—7.32 (5H, m). Found: C, 75.61; H, 9.52%. Calcd for $C_{12}H_{18}Si$: C, 75.72; H, 9.53%.

(*Z*)-**2g**: Bp 62—63 °C (2 Torr); IR 1630, 1250, 1145, 860, 840, 760, 720, 690 cm⁻¹; $^1$H NMR $\delta$=0.0 (9H, s), 1.76 (2H, double d, *J*=9.0 and 1.2 Hz), 5.61 (1H, d (*J*=11.7 Hz) of t (*J*=8.6 Hz)), 6.26 (1H, d, *J*=12 Hz), 7.18 (5H, m). Found: C, 75.70; H, 9.42%. Calcd for $C_{12}H_{18}Si$: C; 75.72; H, 9.53.

Retention times for (*E*)-**2g** and (*Z*)-**2g** were 12.8 and 10.8 min, respectively (Column C, 180 °C).

**Olefination of 6.** Treatment of **6** (260 mg) with $BF_3OEt_2$ in the Procedure A gave 149 mg (88%) of **2c** (*E*/*Z*=48 : 52). Treatment of **6** (260 mg) with NaH in the Procedure D (reflux, 5 h) gave 127 mg (75%) of (*Z*)-**2c**. A small amount (ca. 5%) of an unidentified compound, which would probably be (1-butylallyl)trimethylsilane (**8**), was also formed in both cases.

**Oxidation of 10a.** To a solution of $CrO_3 \cdot Py_2$ (3.7 g) in dichloromethane (40 cm³) was added a solution of **10a** (1.03 g) in dichloromethane (5 cm³) at room temperature and stirred for 15 min at ambient temperature. A crude oil obtained after workup was subjected to bulb-to-bulb distillation (ca. 80 °C at 6 Torr) to give 680 mg (70%) of 3,4-bis(trimethylsilyl)-2-butanone (**12a**): IR 1690, 1250, 1085, 840 cm⁻¹; $^1$H NMR $\delta$=−0.06 (9H, s), 0.06 (9H, s), 0.35 (1H, double d, *J*=15 and 1.2 Hz), 1.28 (1H, double d, *J*=15 and 1.2 Hz), 1.99 (3H, s), 2.34 (1H, d, *J*=12 Hz).

**Reaction of 12a with Phenylmagnesium Bromide and Subsequent Olefination.** To a solution of phenylmagnesium bromide (5 mmol) in ether (15 cm³) was added **12a** (680 mg) in ether (2 cm²) at room temperature and the mixture was stirred for 1 h at ambient temperature. A crude oil obtained after workup was subjected to column chromatography over alumina eluting with 5% ether in hexane containing 1% methanol gave 497 mg (51%) of 2-phenyl-3,4-bis(trimethylsilyl)-2-butanol (**13a**): IR 3500, 1600, 1250, 840, 760, 695 cm⁻¹; $^1$H NMR $\delta$=−0.15 (9H, s), −0.09 (9H, s), 1.49 (3H, s), 7.26 (5H, m). Treatment of **13a** (110 mg) with $BF_3OEt_2$ in the olefination Procedure A (0 °C, 15 min) gave 70 mg (92%) of (*Z*)-(3-phenyl-2-butenyl)trimethylsilane (**14a**) after purification by column chromatography: IR 1600, 1250, 855, 840, 760, 695 cm⁻¹; $^1$H NMR $\delta$=−0.06 (9H, s), 1.37 (2H, broad d, *J*=8.0 Hz), 1.99 (3H, s), 5.42 (1H, t, *J*=8 Hz), 6.9—7.3 (5H, m). Treatment of **13a** (240 mg) with NaH in the Procedure D (reflux, 2 h) gave 94 mg (88%) of (*E*)-2-phenyl-2-butene. $^1$H NMR 1.77 (3H, d, *J*=7 Hz), 1.99 (3H, s), 5.77 (1H, broad q, *J*=7 Hz), 7.18 (5H, m). The same treatment of **13a** (70 mg) under reflux for 15 min gave 38 mg (78%) of (*E*)-**14a** after purification by column chromatography: IR 1640, 1250, 850, 750, 690 cm⁻¹; $^1$H NMR $\delta$=0.06 (9H, s), 1.62 (2H, d, *J*=9.0 Hz), 1.95 (3H, s), 5.77 (1H, t, *J*=9 Hz), 7.0—7.25 (5H, m).

**Preparation of 1,2-Epoxyl-3-trimethylsiloxy-1-trimethylsilylpropane (15).** To a cold mixture of *m*-chloroperbenzoic acid (7.0 g, 85% purity) in dichloromethane (50 cm³) was added a solution of [(*E*)-3-trimethylsilyl-2-propenoxy]trimethylsilane (6.0 g) in dichloromethane (10 cm³) over a period of 15 min at 0 °C. Usual workup gave 5.3 g (71%) the oxirane *trans*-**15**: Bp 94—95 °C (17 Torr); IR 1255, 1145, 1100, 1020, 860, 840 cm⁻¹; $^1$H NMR $\delta$=0.05 (9H, s), 0.09 (9H, s), 1.90 (1H, d, *J*=3.5 Hz), 2.77 (1H, m), 3.50 (1H, double d, *J*=11.7 and 4.5 Hz), 3.70 (1H, double d, *J*=11.7 and 3.9 Hz). Found: C, 49.21; H, 10.01%. Calcd for $C_9H_{22}O_2Si_2$: C, 49.49; H, 10.15%.

**Reaction of 15 with Lithium Dibutylcuprate(I) and Subsequent Olefination.** To a solution of $(n\text{-Bu})_2$CuLi prepared from BuLi (34.5 mmol, 1.7 mol dm⁻³ in hexane) and

CuI (3.23 g) in ether (25 cm³) was added a solution of **15** (1.5 g, 6.9 mmol) in ether (2 cm³) at −40 °C and the mixture was stirred for 1.5 h at −40 °C. Workup followed by bulb-to-bulb distillation (ca. 130 °C at 17 Torr) gave 1.50 g (80%) of 1-trimethylsiloxy-3-trimethylsilyl-2-heptanol (**16**): IR 3480, 1255, 1105, 1085, 870, 845 cm⁻¹; ¹H NMR δ=0.03 (9H, s), 0.12 (9H, s), 0.6—1.6 (10H, m), 2.19 (1H, broad s, disappeared on addition of $D_2O$), 3.2—3.9 (3H, m). Treatment of **16** (275 mg) with 70% $HClO_4$ in the Procedure B (0 °C, 30 min) gave 135 mg (90%) of a mixture of (*Z*)-2-hepten-1-ol (**17**) [IR 1660, 1250, 990, 875, 840, 740 cm⁻¹; ¹H NMR 0.07 (9H, s), 0.91 (3H, m), 1.15—1.65 (4H, m), 2.0 (2H, m), 3.92—4.19 (2H, m), 5.24—5.56 (2H, m)] and its trimethylsilyl ether [IR 3320, 1660, 1020 cm⁻¹; ¹H NMR δ=0.7—1.7 (7H, m), 1.8—2.3 (2H, m), 4.06 (2H, broad d, *J*=4.5 Hz), 5.3—6.8 (2H, m)] in the ratio 1:1. Treatment of **16** (413 mg) with KH in the olefination Procedure C (reflux, 2 h) gave 229 mg (81%) of (*E*)-2-heptenoxytrimethylsilane: IR 1675, 1250, 1100, 1055, 970, 870, 840 cm⁻¹; ¹H NMR δ=0.07 (9H, s), 0.91 (3H, m), 1.1—1.6 (4H, m), 2.0 (2H, m), 3.95 (2H, m), 5.48 (2H, m). On treatment with methanol, this compound gave (*E*)-**17** quantitatively: IR 3330, 1675, 1085, 1000, 970 cm⁻¹; ¹H NMR δ=0.91 (3H, m), 1.1—1.6 (5H, m), 2.0 (2H, m), 3.95 (2H, m), 5.57 (2H, m).

**Reaction of 15 with Phenylmagnesium Bromide and Subsequent Olefination.** To a stirred solution of phenylmagnesium bromide (10 mmol) in ether (25 cm³) was added a solution of **15** (1.03 g) in ether (2 cm³) at room temperature and the mixture was stirred for 4 h under reflux. Usual workup gave 857 mg (62%) of 2-phenyl-1-trimethylsiloxy-3-trimethylsilyl-2-propanol (**19a**) after purification by bulb-to-bulb distillation (ca. 120 °C at 6 Torr): IR 3550, 1600, 1250, 1090, 850, 840, 750, 695 cm⁻¹; ¹H NMR δ=−0.20 (9H, s), 0.0 (9H, s), 1.08 (d, *J*=14.5 Hz), 1.24 (1H, d, *J*=14.5 Hz), 2.73 (1H, s, disappeared on addition of $D_2O$), 3.51 (2H, s), 7.29 (5H, m). Treatment of **19a** (312 mg) with $BF_3OEt_2$ in the olefination Procedure A (room temperature, 30 min) gave 195 mg (91%) of a mixture of 2-phenylallyl alcohol (**20a**) and its trimethylsilyl ether in the ratio 55:45 after purification by bulb-to-bulb distillation (ca. 120 °C at 35 Torr). Treatment of the mixture with methanol containing a small amount of potassium carbonate cleanly gave **20a**: ¹H NMR δ=2.56 (1H, s, disappeared on addition of $D_2O$), 4.34 (2H, s), 5.24 (1H, broad s), 5.34 (1H, broad s), 7.26 (5H, m).

**Reaction of 15 with Butylmagnesium Bromide and Subsequent Olefination.** To a solution of *n*-BuMgBr (6.5 mmol) in ether (25 cm³) was added a solution of **15** (722 mg) in ether (2 cm³) and the mixture was stirred for 5 h under reflux. Workup followed by bulb-to-bulb distillation gave 550 mg (61%) of 1-trimethylsiloxy-2-(trimethylsilylmethyl)-2-hexanol (**19b**): IR 3430, 1250, 1090, 860, 840 cm⁻¹; ¹H NMR δ=0.03 (9H, s), 0.11 (9H, s), 0.65—1.7 (12H, m), 3.28 (2H, s). Treatment of **19b** (270 mg) with $BF_3OEt_2$ in the Procedure A (room temperature, 15 min) gave 51 mg (45%) of 2-butylallyl alcohol (**20b**) after treatment with methanol: ¹H NMR δ=0.6—1.7 (8H, m), 1.7—2.2 (2H, m), 3.94 (2H, s), 4.77 (1H, s), 4.92 (1H, s).

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