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Synthesis of α-Trialkylsilyl Ketones[1,2)]

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The isomerization of 2-trimethylsilyl-2,3-dialkyloxiranes occurs in the presence of MgI_2 to give α-trimethylsilyl ketones only, if one starts from (2*S**,3*S**)-isomers. In contrast, however, the reaction of (2*S**,3*R**)-oxiranes produces enol silyl ethers in addition to α-trimethylsilyl ketones. The reaction proceeds *via* the Mg salts of regio- and stereoselectively produced β-iodo-β-trimethylsilyl alcohols, each diastereomer of which behaves differently. Remarkably, Li salts of both iodohydrins [(2*S**,3*S**)- and (2*S**,3*R**)-isomers] give α-trimethylsilyl ketones exclusively. This provides efficient procedures for preparing α-trimethylsilyl ketones from a mixture of diastereomeric silyloxiranes.

Organosilicon chemistry has contributed much to the development of modern methodology of organic synthesis.[3)] Particularly, α-trialkylsilyl ketones (IV) have attracted considerable attention as precursors for olefins with predictable geometry.[4,5)] The preparation of IV usually involves acylation of α-trimethylsilyl Grignard compounds[6)] or oxidation of the β-trimethylsilyl alcohols,[4)] as direct silylation of the corresponding ketones gives none of the expected products.[7)] This article describes a synthetic route to IV including the rearrangement of silyloxiranes (II and VI) as a key step.

The rearrangement of II and VI proceeds in the presence of MgI_2.[1a,8)] The required oxiranes are readily accessible from internal olefins silylated on sp^2 carbon (I and V).[9)]

For example, oxidation of (*E*)-5-trimethylsilyl-4-decene (Ic)[9g)] with *m*-chloroperbenzoic acid gave IIc in 86% yield. Treatment of IIc with MgI_2 (10 equiv.) in ether at reflux afforded 5-trimethylsilyl-4-decenone (IVc) in 72% yield (Scheme 1 and Table 1).

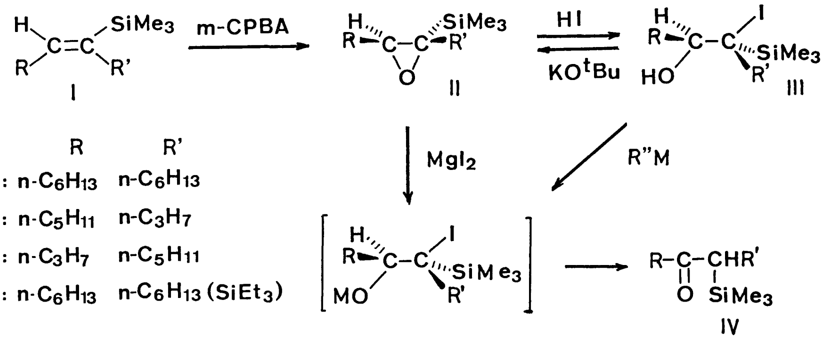
Table 1. Reaction of silyloxiranes with MgI_2

Oxirane	Isomeric purity %	Products IV (%)	Products VIII (%)
IIa	>99	93 (quant.)[a)]	0
VIa	91	48	9
IIb	>99	74	0
VIb	96	40	18
IIc	>99	72	0

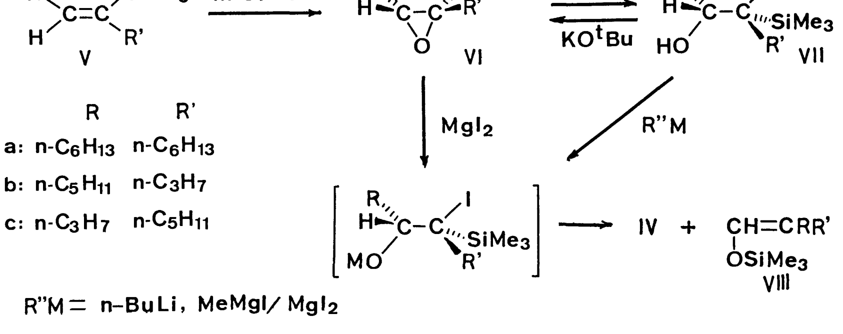
a) The yield in parentheses is that before purification.

In contrast with II the corresponding diastereomer VI gave a mixture of IV and trimethylsilyl enolate VIII (Scheme 2).

Regioselective formation of IV should be ascribed to the oxirane cleavage at the silylated carbon to oxygen bond followed by the hydride shift to that carbon. Furthermore, oxirane cleavage accompanied by R migration and the 1,3 shift of Me_3Si group from carbon to oxygen should explain the formation



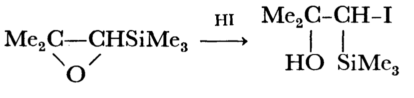
Scheme 1.



Scheme 2.

of VIII. Reasonable accounts for the observed reactivity difference between II and IV have stemmed from the following investigations.

As known already, the reaction of trimethylsilyloxiranes with $MgBr_2$ or HBr gives β-bromo-β-trimethylsilylalkanols, regio- and stereoselectively.[8,10e–g] We have found that treatment of IIa with aq HI gives iodohydrin IIIa in a quantitative yield.[13] Silyloxiranes VIa and VIc were transformed analogously into iodohydrins VIIa and VIIc, respectively. Furthermore, Scheme 3 shows that IX gives X, with the preferential cleavage of O–$CHSiMe_3$ bond.[14]



IX X

Scheme 3.

This is in contrast to the general belief that silicon stabilizes β-carbocation instead of the plus charge on the carbon directly attached to silicon.[3] The stereochemistry of the iodohydrins was established by regeneration of the starting silyloxiranes by the action of KO^{t}Bu. All observations indicate that iodide ion is attached regio- and stereoselectively to the silylated carbon upon iodohydrin formation.

The iodohydrins III and VII thus obtained were treated with an organometallic reagent R″M. For example, reaction of IIIa with *n*-BuLi (1 equiv.) in ether gave IVa in a quantitative yield (Table 2).[15] Unexpectedly analogous treatment of the diastereomer VIIa afforded the same product IVa in 90% yield. It is remarkable that both diastereomeric iodohydrins give the same α-trimethylsilyl ketone in excellent yields.[16] α-Triethylsilyl ketone (IVd) could also be obtained from IIId. These and other results are listed in Table 2.

The silylated olefins (I and V) are prepared by the alkylation of C≡CSi moiety.[9a–d,9g] Furthermore, the silylated ketones (IV) are transformed into trisubstituted ethylenes by the published procedure stereoselectively.[5] The present study, therefore, links two synthetic sequences to afford a means of preparing trisubstituted ethylenes of any desired stereochemistry starting from silylacetylenes.

Remarkably, treatment of IIIa with MeLi in THF gave predominantly the starting silyloxirane (IIa) instead of α-silyl ketone (IVa) obtained above. Solvent effect must play an important role in the reaction of Li salt of iodohydrin. The O–Li should have become more nucleophilic in THF than in ether.

Furthermore, Mg salts of diastereomeric iodohydrins behaved differently from Li salts. Treatment of IIIa with MeMgI (1 equiv.) and MgI_2 (10 equiv.) at reflux gave IVa[17] in 92% yield. The diastereomeric iodohydrin (VIIa), however, was transformed into a mixture of IVa (29%) and trimethylsilyl enolate VIIIa (43%).

The rearrangement of silyloxiranes in the presence of MgI_2 showed similar product distributions depending on the sorts of the starting diastereomers. Furthermore, treatment of IIa with MgI_2 at room temperature provided IIIa (28%) along with IVa (30%). These observations indicate that the Mg salt of iodohydrin should be an intermediate[18,19] in the MgI_2 reaction giving IV or VIII in the subsequent step.

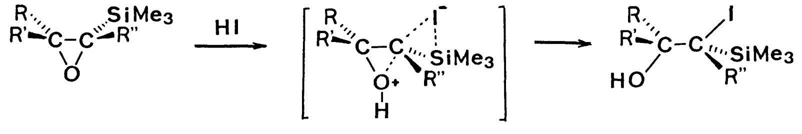
The relative orientations of the C–Si and the C–O bonds deviate markedly from the coplanar alignment which favors the β-carbocation stabilized by the C–Si bond.[3] The preference for oxirane cleavage at the silylated carbon with inversion in the iodohydrin formation suggests that the silyl group actually facilitates bimolecular nucleophilic displacements at the carbon attached to silicon.[20,21] Penta-coordinated silicon intermediate explains the observations,[22] as shown in Scheme 4.

Rearrangement of iodohydrin to α-trialkylsilyl ketone is ascribed to MI-elimination under 1,2-hydrogen

TABLE 2. CONVERSION OF SILYLOXIRANES TO IV AND VIII *via* IODOHYDRINS III AND VII

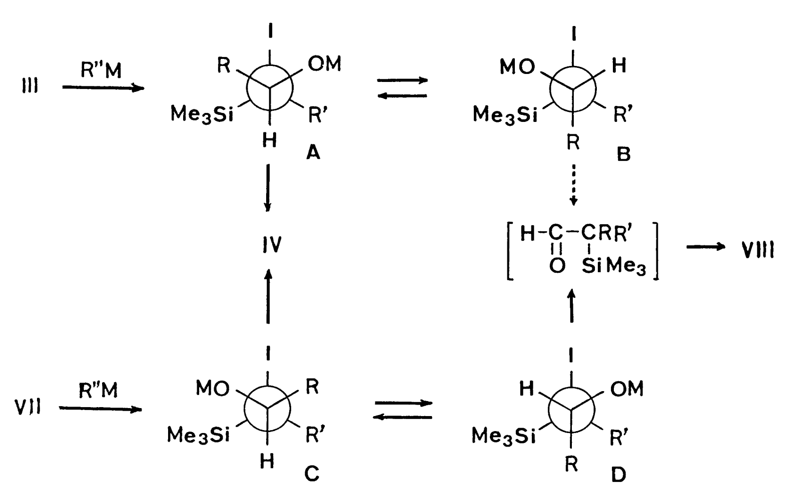
Oxirane	Isomeric purity %	Iodohydrin %	Reagent (R″M)	Products	
				IV (%)	VIII (%)
IIa	>99	IIIa, quant.	*n*-BuLi	(quant.)[a]	0
VIa	91	VIIa, 94	*n*-BuLi	90 (99)[a]	0
IIb	>99	IIIb, (92)[a]	*n*-BuLi	(quant.)[a]	0
IId	>99	IIId, (quant.)[a]	*n*-BuLi	87	0
VIc	97	VIIc, (92)[a]	*n*-BuLi	(quant.)[a]	0
IIa	>99	IIIa, quant.	$MeMgI/MgI_2$	92	0
VIa	91	VIIa, 94	$MeMgI/MgI_2$	29	43

a) Yields in parentheses are those before purification. The crude products were almost pure on GLPC, TLC, and NMR analysis.



(One of R, R', and R'' is H)

Scheme 4.

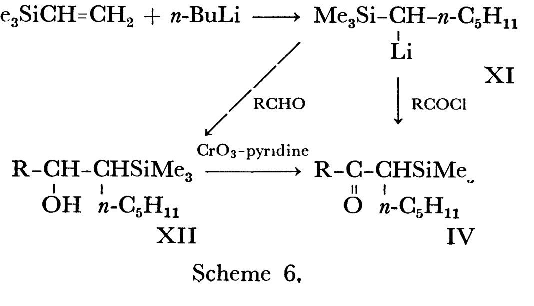


Scheme 5.

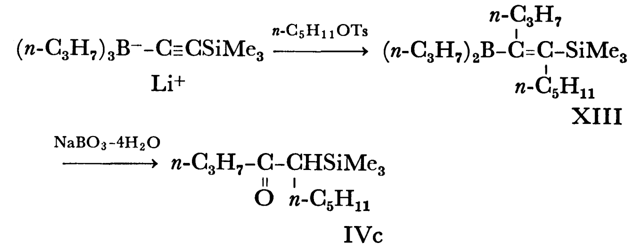
migration, while the one affording IV is accounted for by assuming MI elimination under 1,2-migration of R and the subsequent 1,3-migration of Me_3Si group (Scheme 5). The observed selectivity is explained on the following assumption: (i) migratory aptitude H>R; (ii) anti conformation of the migrating group and iodine;[23] (iii) Me_3Si>R, I in effective size; (iv) if M=Li, **A** (→IV)>**B** (→VIII) and **C** (→IV)>**D** (→VIII) in populations as R>OLi>H in effective size; (v) if M=MgI, **A**>**B** but **C**<**D** as OMgI and Me_3Si should be in anti positions each other because of the larger effective size of OMgI group. Possibly ΔF^* (**D**→VIII) is comparable with ΔF^* (**D**→**C**→IV).

Finally, other methods for obtaining α-trialkylsilyl ketones have been studied.

The procedure *via* β-trimethylsilyl alcohols XII (Scheme 6) reported by Hudrlik[4] was reinvestigated and applied to the synthesis of α-triethylsilyl ketones. Furthermore, T. H. Chan and his coworkers have reported that the reaction of α-silylalkyllithium with acid chlorides afforded, after hydrolysis with dilute hydrochloric acid, the desilylated ketones in moderate yield.[24] This reaction must proceed *via* α-silyl ketone, which is easily desilylated in acidic conditions. It was expected that careful work-up should afford α-silyl ketones. Indeed, 1-trimethylsilylhexyllithium (XI) was prepared by the addition of *n*-BuLi to $Me_3SiCH{=}CH_2$ and treated with butyryl chloride to give IVc in 45% yield (Scheme 6). Analogously 1-trimethylsilylhexylcopper obtained from XI and one equivalent of CuI afforded IVc in 71% yield. Reaction of XI with acetyl chloride gave 3-trimethylsilyl-2-octanone in 17% yield. On the other hand reaction of 1-triethylsilylhexyllithium prepared from *n*-BuLi and $Et_3SiCH{=}CH_2$ with butyryl chloride gave no desired product.



Scheme 6.



Scheme 7.

α-Trimethylsilyl ketone (IVc) has alternatively been obtained by the mild oxidation of 4-dipropylboryl-5-trimethylsilyl-4-decene (XIII)[25] with $NaBO_3$–$4H_2O$ in 57% overall yield (Scheme 7).

Experimental

Gas chromatography was performed on Shimadzu GC-4BPT with 3 m×3 mm glass column packed with 20% polyethylene glycol and 20% HVSG on Chromosorb W-AW (80—100 mesh). Mass spectra were obtained on Hitachi RMU-6L with 70V chamber voltage, NMR were measured on Varian EM-360, JEOL JNM-PMX 60, and Varian EM-390 with Me_4Si as internal standard and CCl_4 as solvent. ^{13}C-NMR on Varian CFT-20 with Me_4Si as internal standard and $CDCl_3$ as solvent. IR on Shimadzu IR-27G spectrometer. Elemental microanalyses were performed by Elemental Analyses Center of Kyoto University. All the reactions were carried out under an atmosphere of dry argon. All mass spectra were those of the samples after gas chromatographic separation.

Silylated Olefins I and V. *(*E*)-7-Trimethylsilyl-7-tetradecene (Ia, $R=R'=n\text{-}C_6H_{13}$)*: The chloroplatinic acid-catalyzed reaction of trichlorosilane and 7-tetradecyne and the following treatment with MeMgI gave Ia in 70% yield (*E*>99%).[26,27] Bp 120 °C/0.07 mmHg; IR (neat) 1611, 1200, 830, 747, 685 cm^{-1}; MS *m/e* (rel. %), 268 (M^+, 0.4), 253 (8), 194 (13), 96 (13), 73 (100), 59 (21); NMR (CCl_4) δ=0.00 (9H, s), 0.67—1.07 (6H, m), 1.07—1.70 (16H, m), 1.70—2.30 (4H, m), 5.58 (1H, br-t, J=7 Hz).

Found: C, 76.20; H, 13.46%. Calcd for $C_{17}H_{36}Si$: C, 76.03; H, 13.51%.

(E)-7-Triethylsilyl-7-tetradecene (Id, $R=R'=$ n-C_6H_{13}): Yield, 77%; $E>99\%$; IR (neat) 1610, 1232, 1010, 722 cm^{-1}; NMR (CCl_4) $\delta=0.30$—1.70 (37H, m), 1.70—2.35 (4H, m), 5.62 (1H, t, $J=6$ Hz).

Found: C, 77.39; H, 13.39%. Calcd for $C_{20}H_{42}Si$: C, 77.33; H, 13.63%.

Silylated Olefins I ($R\neq R'$). These materials were prepared by the double alkylation of $HC\equiv CSiMe_3$.[9g)]

Silylated Olefins V ($R=R'$ and $R\neq R'$). These compounds were prepared by the reductive alkylation of the corresponding $RC\equiv CSiMe_3$ according to the reported procedure.[9c,d)]

(Z)-7-Trimethylsilyl-7-tetradecene (Va, $R=R'=$ n-C_6H_{13}):[9d)] Yield, 95%; $E/Z=9/91$; bp 120 °C/0.07 mmHg.

(Z)-4-Trimethylsilyl-4-decene (Vb, $R=$ n-C_5H_{11}, $R'=$ n-C_3H_7): Yield, 79%; $E/Z=4/96$; bp 100 °C/10 mmHg; IR (neat) 1611, 1240, 830, 750, 682 cm^{-1}; MS *m/e* (rel. %), 212 (M^+, 2), 197 (24), 169 (3), 156 (4), 155 (4), 138 (20), 127 (8), 113 (8), 99 (10), 73 (100), 59 (30); NMR (CCl_4) $\delta=0.08$ (9H, s) 0.67—1.05 (6H, m), 1.05—1.67 (8H, m), 1.70—2.30 (4H, m), 5.85 (1H, br-t, $J=7$ Hz).

Found: C, 73.68; H, 13.54%. Calcd for $C_{13}H_{28}Si$: C, 73.50; H, 13.28%.

(Z)-5-Trimethylsilyl-4-decene (Vc, $R=$ n-C_3H_7, $R'=$ n-C_5H_{11}): Yield, 72%; $E/Z=3/97$; bp 118—122 °C/20 mmHg; IR (neat) 1610, 1240, 837, 758, 690 cm^{-1}; MS *m/e* (rel. %), 212 (M^+, 0.2), 197 (11), 169 (3), 155 (2), 138 (14), 127 (7), 113 (6), 101 (3), 99 (8), 95 (7), 82 (9), 74 (10), 73 (100), 59 (28), 45 (12), 43 (7), 41 (5); NMR (CCl_4) $\delta=0.10$ (9H, s), 0.90 (6H, t, $J=6$ Hz), 1.10—1.60 (8H, m), 1.80—2.25 (4H, m), 5.85 (1H, br-t, $J=7$ Hz).

Found: C, 73.45; H, 13.00%. Calcd for $C_{13}H_{28}Si$: C, 73.50; H, 13.28%.

1-Trimethylsilyl-1-alkynes. These precursors of silylated olefins V[9c,d)] were obtained by the usual trimethylsilylation of the corresponding alkynyl Grignard compounds. 1-Trimethylsilyl-1-pentyne was, however, prepared by the following procedure. To a solution of $Me_3SiC\equiv CSiMe_3$ (3.3 g, 19 mmol) in 15 ml of THF and 13 ml of HMPA was added MeLi (21 mmol, 14 ml of 1.48 M ethereal solution) at −78 °C. The mixture was warmed up to 0 °C and stirred for 1 h at 0 °C. The resulting mixture was treated with *n*-PrBr (2.0 ml, 22 mmol), stirred for 3 h at a room-temperature, and poured into aq NH_4Cl overlaid with hexane. The hexane layer was washed (aq NH_4Cl, sat. NaCl), dried ($MgSO_4$), and concentrated, affording 1.5 g (56%) of *n*-$C_3H_7C\equiv CSiMe_3$.

2-Trialkylsilyl-2,3-dialkyloxiranes II and VI. These oxiranes were prepared by *m*-CPBA oxidation of the corresponding silylated olefins.

(2S,3S*)-2-Trimethylsilyl-2-pentyl-3-propyloxirane (IIc, $R=$ n-C_3H_7, $R'=C_5H_{11}$)*: To a solution of *m*-chloroperbenzoic acid (85% purity, 1.2 g, 6.0 mmol) in CH_2Cl_2 was added (*E*)-5-trimethylsilyl-4-decene (Ic, 1.0 g, 4.9 mmol) at 0 °C. The mixture was poured into aq K_2CO_3 overlaid with ether. The ether layer was washed (aq K_2CO_3, sat. NaCl) and dried ($MgSO_4$). Chromatography of the concentrate on silica-gel column (benzene) afforded IIc (0.96 g). Yield, 86%; >99% purity; bp 72—77 °C/3 mmHg; IR (neat) 1243, 839, 752, 693 cm^{-1}; MS *m/e* (rel. %), 228 (M^+, 0.5), 213 (2), 199 (13), 185 (3), 171 (5), 143 (4), 130 (11), 113 (4), 75 (29), 73 (100), 59 (15), 43 (9); NMR (CCl_4) $\delta=0.00$ (9H, s), 0.67—1.10 (6H, m), 1.10—1.70 (12H, m), 2.45—2.70 (1H, m).

Found: C, 68.60; H, 12.62%. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35%.

(2S,3S*)-2-Trimethylsilyl-2,3-dihexyloxirane (IIa, $R=R'=$ n-C_6H_{13})*: Yield, 68%; >99% purity; oil; IR (neat) 1241, 834, 747 cm^{-1}; MS *m/e* (rel. %), 284 (M^+, 1), 269 (2), 227 (6), 213 (23), 199 (4), 185 (4), 155 (7), 143 (17), 130 (14), 129 (9), 113 (5), 95 (5), 75 (28), 73 (100), 59 (13), 43 (14); NMR (CCl_4) $\delta=0.00$ (9H, s), 0.67—1.05 (6H, m), 1.05—1.65 (20H, m), 2.40—2.70 (1H, m); ^{13}C-NMR ($CDCl_3$) $\delta=-2.94$, 14.06, 22.64, 26.34, 27.03, 28.20, 29.37, 30.08, 30.87, 31.77, 31.89, 57.16, 60.59.

Found: C, 71.91; H, 12.93%. Calcd for $C_{17}H_{36}OSi$: C, 71.76; H, 12.75%.

(2S,3S*)-2-Trimethylsilyl-2-propyl-3-pentyloxirane (IIb, $R=$ n-C_5H_{11}, $R'=$ n-C_3H_7)*: Yield, 86%; >99% purity; bp 70—75 °C/3 mmHg; IR (neat) 1239, 830, 746 cm^{-1}; MS *m/e* (rel. %), 228 (M^+, 0.4), 213 (2), 199 (1), 185 (1), 171 (29), 143 (8), 130 (7), 113 (15), 75 (28), 73 (100), 59 (13), 43 (9); NMR (CCl_4) $\delta=0.00$ (9H, s), 0.65—1.13 (6H, m), 1.13—1.65 (12H, m), 2.45—2.73 (1H, m).

Found: C, 68.37; H, 12.61%. Calcd for $C_{13}H_{28}OSi$: C, 68.37; H, 12.61%.

(2S,3S*)-2-Triethylsilyl-2,3-dihexyloxirane (IId, $R=R'=$ n-C_6H_{13})*: Yield, 98%; 99% purity; oil; IR (neat) 1230, 1005, 720 cm^{-1}; NMR (CCl_4) $\delta=0.40$—1.70 (41H, m), 2.50—2.70 (1H, m).

Found: C, 73.81; H, 13.18%. Calcd for $C_{20}H_{42}OSi$ C, 73.54; H, 12.96%.

(2S,3R*)-2-Trimethylsilyl-2,3-dihexyloxirane (VIa, $R=R'=$ n-C_6H_{13})*: Yield, 93%; 91% purity; oil; IR (neat) 1249, 842, 757 cm^{-1}; MS *m/e* (rel. %), 284 (M^+, 1), 269 (2), 227 (5), 213 (20), 199 (6), 185 (6), 155 (9), 143 (16), 130 (12), 129 (11), 113 (6), 95 (6), 75 (33), 73 (100), 59 (15), 43 (13); NMR (CCl_4) $\delta=0.08$ (9H, s), 0.65—1.05 (6H, m), 1.05—1.70 (20H, m), 2.37—2.67 (1H, m); ^{13}C NMR ($CDCl_3$) $\delta=-1.08$, 14.08, 22.67, 26.05, 27.25, 29.33, 29.74, 30.47, 31.93, 37.93, 57.14, 64.04.

Found: C, 71.71; H, 12.93%. Calcd for $C_{17}H_{36}OSi$: C, 71.76; H, 12.75%.

(2S,3R*)-2-Trimethylsilyl-2-propyl-3-pentyloxirane (VIb, $R=$ n-C_5H_{11}, $R'=$ n-C_3H_7)*: Yield, 93%; 96% purity; oil; IR (neat) 1243, 840, 756, 693 cm^{-1}; MS *m/e* (rel. %), 228 (M^+, 1), 213 (2), 199 (2), 185 (2), 171 (27), 157 (3), 143 (10), 130 (7), 113 (20), 75 (32), 73 (100), 59 (15), 43 (10); NMR (CCl_4) $\delta=0.08$ (9H, s), 0.70—1.10 (6H, m), 1.10—1.80 (12H, m), 2.40—2.67 (1H, m).

Found: C, 68.23; H, 12.47%. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35%.

(2S,3R*)-2-Trimethylsilyl-2-pentyl-3-propyloxirane (VIc, $R=$ n-C_3H_7, $R'=$ n-C_5H_{11})*: Yield, 68%; 97% purity; oil; IR (neat) 1240, 840, 755, 690 cm^{-1}; MS *m/e* (rel. %), 228 (M^+, 0.3), 213 (1), 199 (12), 185 (3), 171 (7), 157 (2), 143 (4), 141 (11), 130 (10), 129 (7), 115 (5), 113 (5), 99 (7), 85 (5), 81 (5), 75 (31), 74 (10), 73 (100), 59 (18), 45 (12); NMR (CCl_4) $\delta=0.10$ (9H, s), 0.90 (3H, t, $J=6$ Hz), 0.98 (3H, t, $J=6$ Hz), 1.13—1.70 (12H, m), 2.46—2.62 (1H, m).

Found: C, 68.64; H, 12.55%. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35%.

Isomerization of 2-Trimethylsilyl-2,3-dialkyloxiranes II and VI in the Presence of MgI_2. *5-Trimethylsilyl-4-decanone (IVc, $R=$ n-C_3H_7, $R'=$ n-C_5H_{11})*: To a solution of MgI_2 (10 mmol) in 10 ml of ether was added trimethylsilyloxirane IIc ($R=C_3H_7$, $R'=C_5H_{11}$, 0.23 g, 1 mmol dissolved in 5 ml of ether). The resulting mixture was stirred at reflux for 2 h and then treated with 6 ml of 1,4-dioxane at 0 °C overnight. The solution was freed from solids by filtration. The solids were washed with hexane several times and the combined organic layer was washed (sat. $NaHCO_3$, sat. NaCl) and dried ($MgSO_4$). Chromatography of the concentrate on silica-gel column (benzene) afforded 0.16 g (72%) of IVc. Bp 110—

120 °C/23 mmHg; IR (neat) 1686, 1249, 837, 750, 690 cm^{-1}; NMR (CCl_4) δ=0.00 (9H, s), 0.87 (6H, t, J=6 Hz), 1.00—1.90 (10H, m), 1.90—2.33 (3H, m).

Found: C, 68.85; H, 12.11%. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35%.

Attempted purification of IVc by GLPC resulted in 1,3-migration of Me_3Si group affording the respective silyl enol ether; IR (neat), 1671, 1243, 838, 749 cm^{-1}; MS *m/e* (rel. %), 228 (M^+, 5), 213 (8), 185 (7), 171 (59), 158 (10), 143 (12), 130 (35), 75 (31), 73 (100), 43 (10).

8-Trimethylsilyl-7-tetradecanone (IVa, $R=R'=$n-C_6H_{13}): Yield, 93% based on IIa; oil; IR (neat) 1686, 1240, 833, 747 cm^{-1}; NMR (CCl_4) δ=0.00 (9H, s), 0.60—1.03 (6H, m), 1.03—1.80 (18H, m), 1.80—2.45 (3H, m).

Found: C, 69.37; H, 12.97%.[28] Calcd for $C_{17}H_{36}OSi$: C, 71.76; H, 12.75%.

Purification of IVa by GLPC afforded the silyl enol ether; IR (neat) 1670, 1242, 836, 747 cm^{-1}; MS *m/e* (rel. %), 284 (M^+, 10), 269 (13), 255 (2), 241 (4), 227 (83), 213 (100), 200 (20), 185 (14), 157 (13), 143 (53), 140 (70), 75 (23), 73 (81); NMR (CCl_4) δ=0.13 (9H, s), 0.67—1.05 (6H, m), 1.05—1.67 (16H, m), 1.67—2.30 (4H, m), 4.15—4.65 (1H, m).

4-Trimethylsilyl-5-decanone (IVb, $R=$n-C_5H_{11}, $R'=$n-C_3H_7): Yield, 74% based on IIb; bp 120—130 °C/16 mmHg; IR (neat) 1686, 1245, 840, 754, 694 cm^{-1}; NMR (CCl_4) δ=0.00 (9H, s), 0.65—1.03 (6H, m), 1.03—1.80 (10H, m), 2.00—2.45 (3H, m).

Found: C, 68.30; H, 12.65%. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35%.

Purification of IVb by GLPC gave the enol silyl ether; MS *m/e* (rel. %), 228 (M^+, 13), 213 (8), 199 (47), 185 (48), 171 (8), 157 (5), 143 (16), 130 (72), 75 (28), 73 (100), 45 (10), 43 (4).

Isomerization of Trimethylsilyloxirane Va to α-Trimethylsilyl Ketone IVa and 1-Trimethylsilyloxy-2-hexyl-1-octene (VIIIa, $R=R'=$n-C_6H_{13}): The mixture containing 48% of IVa and 9% of VIIIa was separated by chromatography on silica-gel column (hexane and benzene). VIIIa: Oil; IR (neat) 1661, 1251, 1190, 1156, 1100, 881, 845, 757 cm^{-1}; MS *m/e* (rel. %), 284 (M^+, 10), 269 (3), 255 (1), 227 (1), 213 (38), 199 (5), 157 (9), 143 (79), 81 (16), 75 (20), 73 (100), 67 (15), 55 (16), 43 (20); NMR (CCl_4) δ=0.13 (9H, s), 0.60—1.05 (6H, m), 1.05—1.65 (16H, m), 1.65—2.30 (4H, m), 5.90 (1H, br-s).

Found: C, 72.06; H, 13.04%. Calcd for $C_{17}H_{36}OSi$: C, 71.76; H, 12.75%.

Isomerization of Trimethylsilyloxirane Vb to α-Trimethylsilyl Ketone IVb and 1-Trimethylsiloxy-2-propyl-1-heptene (VIIIb, $R=$n-C_5H_{11} $R'=$n-C_3H_7): The products contained 40% of IVb and 18% of VIIIb. VIIIb: Oil; IR (neat) 1664, 1245, 1154, 1092, 874, 838, 748 cm^{-1}; MS *m/e* (rel. %), 228 (M^+, 10), 213 (4), 171 (50), 157 (8), 143 (35), 129 (5), 75 (20), 73 (100), 45 (13), 43 (7); NMR (CCl_4) δ=0.13 (9H, s), 0.65—1.07 (6H, m), 1.07—1.63 (8H, m), 1.63—2.30 (4H, m), 5.93 (1H, br-s).

Found: C, 68.49; H, 12.48%. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35%.

β-Iodo-β-trialkylsilyl Alcohols III and VII. (7S,8S*)-8-Iodo-8-trimethylsilyl-7-tetradecanol (IIIa, $R=R'=$n-C_6H_{13})*: To a solution of trimethylsilyloxirane IIa (0.28 g, 1 mmol) in 5 ml of ether was added 1 ml of 57% HI at 0 °C. After stirring for 1 h, the mixture was poured into sat. $NaHCO_3$ overlaid with ether. The ether layer was washed (10% $Na_2S_2O_3$, sat. $NaHCO_3$, sat. NaCl) and dried ($MgSO_4$). Chromatography of the concentrate on silica-gel column (benzene) gave 0.41 g (quantitative yield) of IIIa. Oil; IR (neat) 3475, 1240, 840, 756, 690 cm^{-1}; NMR (CCl_4) δ=0.23 (9H, s), 0.90 (6H, t, J=6 Hz), 1.07—1.80 (20H, m), 1.50 (1H, d, J=6.6 Hz, CH-O$\underline{\text{H}}$), 3.44 (1H, m, C$\underline{\text{H}}$-OH). Hydroxyl proton was checked by D_2O-added NMR as well as double resonance irradiated at 3.44 which induced singlet at 1.50.

Found: C, 49.40; H, 9.23%. Calcd for $C_{17}H_{37}OSiI$: C, 49.50; H, 9.04%.

(7S,8S*)-8-Iodo-8-triethylsilyl-7-tetradecanol (IIId, $R=R'=$n-C_6H_{13})*: Quant. yield based on IId; oil; IR (neat) 3475, 1230, 1003, 725 cm^{-1}; NMR (CCl_4) δ=0.40—1.15 (21H, m), 1.15—2.15 (20H, m), 1.52 (1H, d, J=6.8 Hz), 3.45 (1H, m). IIId was used for the successive reaction without purification.

(7R,8S*)-8-Iodo-8-trimethylsilyl-7-tetradecanol (VIIa, $R=R'=$n-C_6H_{13})*: Yield, 94% based on VIa; oil; IR (neat) 3500, 1367, 1240, 840, 758, 690 cm^{-1}; NMR (CCl_4) δ=0.23 (9H, s), 0.90 (6H, t, J=6 Hz), 1.10—1.87 (18H, m), 1.37 (1H, d, J=8.3 Hz), 1.87—2.20 (2H, m), 3.00 (1H, m).

Found: C, 49.27; H, 8.83%. Calcd for $C_{17}H_{37}OSiI$: C, 49.50; H, 9.04%.

(4R,5S*)-5-Iodo-5-trimethylsilyl-4-decanol (VIIc, $R=$n-C_3H_7, $R'=$n-C_5H_{11})*: Crude yield, 92% based on VIc; oil; IR (neat) 3500, 1369, 1240, 840, 755, 690 cm^{-1}; NMR (CCl_4) δ=0.23 (9H, s), 0.76—1.13 (6H, m), 1.13—1.87 (10H, m), 1.38 (1H, d, J=9 Hz), 1.87—2.30 (2H, m), 3.05 (1H, m). VIIc was used for the successive reaction without purification.

Reaction of (4R,5S*)-5-Iodo-5-trimethylsilyl-4-decanol (VIIc) with KO^{t}Bu.* To a solution of KO^{t}Bu (1.0 g, 9 mmol) in 5 ml of THF was added VIIc (0.16 g, 0.92 mmol) in 5 ml of THF at 0 °C. The resulting mixture was warmed up to a room-temperature, stirred for 1 h, and poured into aq NH_4Cl overlaid with ether. The ether layer was washed (aq NH_4Cl, sat. NaCl) and dried ($MgSO_4$), affording 97 mg (92%) of (2*S**,3*R**)-2-trimethylsilyl-2-pentyl-3-propyloxirane (VIc, 96% purity) after chromatography of the concentrate on silica-gel column (benzene).

Reaction of β-Iodo-β-trialkylsilyl Alcohols III and VII with n-BuLi. 8-Trimethylsilyl-7-tetradecanone (IVa): To a solution of (7*S**,8*S**)-8-iodo-8-trimethylsilyl-7-tetradecanol (IIIa, 0.35 g, 0.85 mmol) in 5 ml of ether was added *n*-BuLi (0.85 mmol, 1.12 ml of 0.76 M hexane solution) at −20 °C. The reaction mixture was warmed up to a room-temperature, stirred for 1.5 h, and poured into aq NH_4Cl overlaid with ether. The ether layer was washed (aq NH_4Cl, sat. NaCl) and dried ($MgSO_4$), yielding 0.24 g (quantitative) of IVa.

8-Triethylsilyl-7-tetradecanone (IVd, $R=R'=$n-C_6H_{13}): Yield, 87% based on IIId; oil; IR (neat) 1687, 1230, 1130, 1002, 725 cm^{-1}; NMR (CCl_4) δ=0.40—1.10 (21H, m), 1.10—1.90 (18H, m), 2.00—2.45 (3H, m).

Found: C, 73.77; H, 12.77%. Calcd for $C_{20}H_{42}OSi$: C, 73.54; H, 12.96%.

Purification of IVd by GLPC gave the enol silyl ether; MS *m/e* (rel. %), 326 (M^+, 10), 297 (16), 269 (44), 255 (48), 241 (10), 227 (11), 213 (18), 185 (33), 157 (42), 143 (25), 116 (15), 115 (90), 104 (12), 103 (100), 87 (75), 75 (40), 59 (42), 43 (17), 41 (17), 29 (29).

Reaction of 8-Iodo-8-trimethylsilyl-7-tetradecanol (IIIa and VIIa) with MeMgI/MgI$_2$. To a solution of (7*S**,8*S**)-8-iodo-8-trimethylsilyl-7-tetradecanol (IIIa, 0.40 g, 0.96 mmol) in 4 ml of ether was added MeMgI (1 mmol, 0.79 ml of 1.27 M ethereal solution) at −20 °C. The reaction mixture was warmed to a room-temperature and treated with MgI_2 (10 mmol) in 10 ml of ether. The resulting mixture was stirred at reflux for 2 h and then treated with 6 ml of 1,4-dioxane at 0 °C followed by stirring at a room-temperature overnight. The solution was freed from solids by filtration. The solids were washed with hexane several times and the combined organic layer was washed (sat. $NaHCO_3$, sat. NaCl) and dried ($MgSO_4$). Chromatography of the concentrate on silica-gel column (benzene) gave 0.25 g (92%) of 8-trimethylsilyl-7-tetradecanone (IVa). The same treatment of ($7R^*,8S^*$)-isomer (VIIa) afforded 1-trimethylsilyloxy-2-hexyl-1-octene (VIIIa, 43%) along with IVa (29%) after chromatography on silica-gel column (hexane and benzene).

Further Methods for Obtaining α-Trialkylsilyl Ketones. *Preparation of 5-Trimethylsilyl-4-decanone (IVc)* via *5-Trimethylsilyl-4-decanol (XIIc)*: To a solution of $Me_3SiCH{=}CH_2$ (2.0 g, 2.9 ml, 20 mmol) in 60 ml of THF was added *n*-BuLi (26 mmol, 20 ml of 1.28 M hexane solution) at −78 °C and the reaction mixture was stirred for 1 h at a room-temperature.[29] The resulting mixture was treated with butyraldehyde (1.6 g, 1.8 ml, 22 mmol) at −78 °C and overnight at a room-temperature. The whole mixture was worked up with aq NH_4Cl, washed (aq NH_4Cl, sat. NaCl), and dried (Na_2SO_4). Chromatography of the concentrate on silica-gel column (hexane/THF=10/1) gave 4.0 g of 5-trimethylsilyl-4-decanol (yield, 87%; bp 89—91 °C/1 mmHg). To a mixture of CrO_3 (15 g, 150 mmol) and pyridine (24 ml, 300 mmol) in 300 ml of CH_2Cl_2 was added the above alcohol (4.0 g) in 16 ml of CH_2Cl_2 and the resulting mixture was stirred at a room-temperature for 15 min. After filtration, the filtrate was washed (aq NH_4Cl, 1M-HCl, sat. $NaHCO_3$, sat. NaCl) and dried (Na_2SO_4). Chromatography of the concentrate on silica-gel column (benzene) gave 3.1 g (77%) of IVc.

Preparation of 3-Trimethylsilyl-2-octanone via *3-Trimethylsilyl-2-octanol*: Yield, 36% based on $Me_3SiCH{=}CH_2$; bp 102 °C/20 mmHg; NMR (CCl_4) δ=0.06 (9H, s), 0.70—1.80 (11H, m), 1.80—2.45 (1H, m), 1.99 (3H, s).

Found: C, 65.87; H, 12.07%. Calcd for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07%.

Purification by GLPC gave the enol silyl ether; MS *m/e* (rel. %), 200 (M^+, 8), 185 (6), 171 (11), 157 (5), 144 (12), 143 (75), 130 (7), 115 (8), 75 (30), 73 (100), 45 (14).

Preparation of 5-Triethylsilyl-4-decanone via *5-Triethylsilyl-4-decanol*: A solution of 1-triethylsilylhexyllithium prepared from $Et_3SiCH{=}CH_2$ (2.8 g, 20 mmol) and *n*-BuLi (26 mmol) in 30 ml of THF, was treated with butyraldehyde (1.8 ml, 22 mmol) at −78 °C and then at a room-temperature for 3 days. The same treatment as described above gave 4.2 g (77%) of 5-triethylsilyl-4-decanol.[30] The oxidation of this alcohol (3.5 g, 13 mmol) with CrO_3-pyridine afforded 3.0 g (86%) of 5-triethylsilyl-4-decanone. Oil; IR (neat) 1687, 1235, 1137, 1004, 723 cm^{-1}; NMR (CCl_4) δ=0.25—2.00 (31H, m), 2.00—2.57 (3H, m).

Found: C, 71.29; H, 12.59%. Calcd for $C_{16}H_{34}OSi$: C, 71.04; H, 12.67%.

Purification by GLPC gave the enol silyl ether; IR (neat) 1670, 1230, 1170, 998, 730 cm^{-1}; MS *m/e* (rel. %), 270 (M^+, 3), 255 (2), 241 (5), 227 (5), 213 (30), 185 (10), 171 (9), 157 (19), 115 (35), 103 (37), 87 (30), 75 (27), 59 (25), 55 (14), 40 (100).

Preparation of 5-Trimethylsilyl-4-decanone (IVc) by the Acylation of 1-Trimethylsilylhexyllithium (XI): To a solution of butyryl chloride (0.55 ml, 5.0 mmol) in 5 ml of THF was added XI, prepared from $Me_3SiCH{=}CH_2$ (5.0 mmol) and *n*-BuLi (6.5 mmol) in 30 ml of THF, at −78 °C. The reaction mixture was stirred at a room-temperature overnight, washed (aq NH_4Cl, sat. $NaHCO_3$, sat. NaCl), and dried over Na_2SO_4. Chromatography of the concentrate on silica-gel column (benzene) gave 0.51 g (45%) of IVc.

Preparation of 5-Trimethylsilyl-4-decanone (IVc) by the Acylation of 1-Trimethylsilylhexylcopper: To a suspension of CuI (2.1 g, 11 mmol) in 10 ml of THF was added XI prepared from $Me_3SiCH{=}CH_2$ (10 mmol) and *n*-BuLi (13 mmol), at −30—−40 °C. The mixture was gradually warmed up to −20 °C and stirred for 0.5 h at −20 °C. The resulting mixture was treated with butyryl chloride (10 mmol, 1.1 ml) at −78 °C and overnight at a room-temperature. The whole was poured into aq NH_4Cl overlaid with ether. The ether layer was washed (aq NH_4Cl, sat. $NaHCO_3$, sat. NaCl) and dried ($MgSO_4$). Chromatography of the concentrate on silica-gel column (benzene) gave 1.6 g (71%) of IVc.

Preparation of 5-Trimethylsilyl-4-decanone (IVc) by the Oxidation of 4-Dipropylboryl-5-trimethylsilyl-4-decene (XIII): To a solution of $LiC\equiv CSiMe_3$, prepared from $HC\equiv CSiMe_3$ (0.54 ml) and *n*-BuLi (3.3 mmol, 4.2 ml of 0.78 M hexane solution) in 10 ml of THF, was added *n*-Pr_3B (0.66 ml, 3.3 mmol) at 0 °C. The mixture was stirred at a room-temperature for 1 h and at reflux for 16 h. The resulting mixture was treated with $NaBO_3$–$4H_2O$ (2.0 g, 13 mmol) at a room-temperature for 5 h and poured into aq NH_4Cl overlaid with ether. The ether layer was washed (aq NH_4Cl, sat. NaCl) and dried ($MgSO_4$). Distillation of the concentrate afforded 0.30 g (57%) of IVc.

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12) Products resulting from both cleavage at silylated carbon and cleavage at β carbon were formed in the reactions of triphenylsilylethylene oxide with HCl, with $MgBr_2$, and with amines.[10d)]

13) The structure of iodohydrins was determined by NMR.

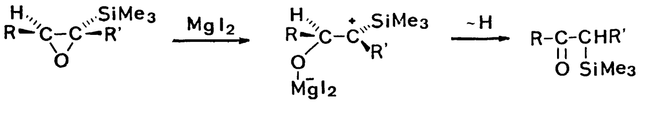
14) Yield of X, 61% based on 2-trimethylsilyl-3,3-dimethyloxirane (IX); NMR (CCl_4) δ=0.23 (9H, s), 1.39 (3H, s), 1.41 (3H, s), 1.60—1.80 (1H, m), 3.42 (1H, s). The structure of X was determined by selective formation of 1-iodo-2-methylpropene (yield 77%) by the action of BF_3–etherate.[10g)] NMR (CCl_4) δ=1.83 (3H, s), 1.92 (3H, s), 5.83 (1H, br-s).

15) Direct treatment of VIa with LiI in ether gave no rearranged product. This fact excludes another path through the starting silyloxirane VIa.

16) No product resulting from the reaction of IVa with *n*-BuLi[5)] was observed. This fact means the rearrangement of iodohydrin is sufficiently slower than the addition of *n*-BuLi to α-silyl ketones.

17) Reaction of IVa with *i*-Bu_2AlH in hexane,[4)] after acidic work-up, gave 7-tetradecene in 70% yield based on IIa.

18) The following scheme seems unprobable.



According to this scheme, 1-trimethylsilylcyclohexene oxide would afford 2-trimethylsilylcyclohexanone. Such a product, however, was not formed but trimethylsiloxymethylenecyclopentane was obtained in 12% yield. NMR (CCl_4) δ=6.06 (1H, br-s).[8)]

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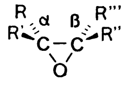

R	R′	R″	R‴	α-C	β-C
H	*n*-Hex	*n*-Hex	$SiMe_3$	57.16	60.59
n-Hex	H	*n*-Hex	$SiMe_3$	57.14	64.04
Me	Me	H	$SiMe_3$	58.55	58.20
Et	H	*n*-Hex	*n*-Pr	63.18	64.66

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28) This α-silyl ketone could not be obtained in a pure form.

29) At −30 °C the addition was incomplete.[4)]

30) The reaction of 1-triethylsilylhexyllithium with acetaldehyde gave no addition product.

31) Reaction of (2*S**,3*R**)-2-trimethylsilyl-2-propyl-3-pentyloxirane (VIb, 96% purity) with $KSiMe_3$ gave predominantly (*Z*)-4-trimethylsilyl-4-decene (Vb, *E*/*Z*=17/83).[32)]

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