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Silicon Effects. VI.[1] β-Silicon Effect of Various Silyl Groups in Solvolysis for α-Alkylbenzyl and α-Silybenzyl Systems

Nobujiro Shimizu,* Sin-ichiro Watanabe, Fumie Hayakawa, Sigefumi Yasuhara,
Yuho Tsuno,† and Takahiko Inazu
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka 812
†Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Fukuoka 812

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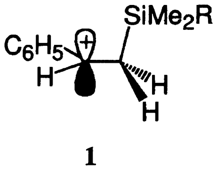
The kinetic β-silicon effects of various silyl groups including Me_3Si, Me_3SiMe_2Si, $(C_6H_5)Me_2Si$, (i-PrO)Me_2Si, and $(CH_3OCH_2)Me_2Si$ were measured in k_c solvolysis of two different benzylic systems of the types, $ArCH(OCOCF_3)CH_2R$ (**3**: Ar=phenyl or 3,5-dichlorophenyl, R=silyl group) and $C_6H_5CH(Cl)SiMe_2R$ (**4**: R=silyl group). The relative β-silyl accelerations were 1.0 : 5.57 : 0.309 for R=Me_3Si; Me_3SiMe_2Si, and $(C_6H_5)Me_2Si$, respectively, for the system **3**, and 1.0 : 7.65 : 0.502 : 0.289 for R=Me_3Si, Me_3SiMe_2Si, (i-PrO)Me_2Si, and $(CH_3OCH_2)Me_2Si$, respectively, for the system **4**. The variation of the β-silicon effect with γ-substituents was interpreted as reflecting changes in hyperconjugating abilities of β-C–Si and β-Si–Si σ-bonds mainly due to the inductive effect of the γ-substituent groups.

The interaction of silicon substituents with a positive charge on a carbon atom β to the silicon has received wide interests in mechanistic and theoretical organic chemistry.[2—9] We previously measured the kinetic β-silyl acceleration by a trimethylsilyl group relative to a β-t-butyl group in the solvolysis of benzylic systems of the two different types, $C_6H_5CH(OCOCF_3)CH_2R$ (R=Me_3Si and t-Bu) and $C_6H_5CH(Br)SiMe_2R$ (R=Me_3Si and t-Bu); $k^{\beta-Me_3Si}/k^{\beta-t-Bu}$ rate ratios at 25 °C were 2.99×10^5 and 1.07×10^5 for the former (in 30% aqueous dioxane) and the latter (in 97% 2,2,2-trifluoroethanol) systems, respectively.[10,11] A simple ionization mechanism (k_c) via an open benzylic cation was established for the R=Me_3Si compound in each system, on the basis of various mechanistic criteria including the Winstein–Grunwald solvent analysis, α-deuterium isotope effects, and the substituent effect of aromatic groups.[10—12] Thus, in solution, a β-Me_3Si group is more effective in a stabilizing a carbenium ion than is a corresponding alkyl group by approximately 6—7 kcal mol^{-1} for the benzylic cations **1** (R=Me) and **2** (R=Me) (Chart 1). Despite the marked β-silyl acceleration for the open system $C_6H_5CH(Br)SiMe_2SiMe_3$, no kinetic β-silyl acceleration was measured in the k_c solvolysis of a cyclic analog, 1,1,2,2-tetramethyl-1,2-disilaindan-3-yl chloride, in which the Si_α–Si_β σ-bond is orthogonal to a vacant p-orbital developed on the benzylic carbon, indicating that the kinetic β-silicon effect is exclusively hyperconjugative in origin.[11]

Although the hyperconjugative stabilization of a carbenium ion by C_α–Si_β or Si_α–Si_β σ-bonds depends on the dihedral angles between the β-silicon and the vacant p-orbital on the carbenium carbon,[6,9,11] the hyperconjugative interaction may also depend on the ionization potentials of these σ-bonds. In order to get quantitative information concerning the electronic effect on the hyperconjugation abilities of C_α–Si_β and Si_α–Si_β σ-bonds, we have measured the kinetic β-silicon effects of various silyl groups including Me_3SiMe_2Si, $(C_6H_5)Me_2Si$, $(CH_3OCH_2)Me_2Si$, and (i-PrO)Me_2Si in addition to Me_3Si in the solvolysis of α-alkylbenzyl and α-silylbenzyl systems, **3** (X=trifluoroacetate; abbrev. to OTFA) and **4** (X=Cl) (Chart 2). This paper deals with both kinetic and product studies on the solvolysis of 1-(3,5-dichlorophenyl)-2-(pentamethyldisilanyl)ethyl trifluoroacetate (**3a-OTFA**), 2-(dimethylphenylsilyl)-1-phenylethyl trifluoroacetate (**3b-OTFA**), α-(heptamethyltrisilanyl)benzyl chloride (**4a-Cl**), α-(2-methoxymethyl-1,1,2,2-tetramethyldisilanyl)benzyl chloride (**4b-Cl**), and α-(2-isopropoxy-1,1,2,2-tetramethyldisilanyl)benzyl chloride (**4c-Cl**).



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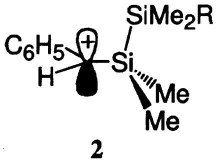

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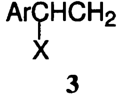
Chart 1.

Results and Discussion

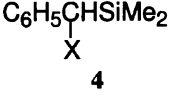
The esters **3a-OTFA** and **3b-OTFA** were obtained in a similar procedure to that described previously for the preparation of 1-phenyl-2-(trimethylsilyl)ethyl tri-



$$\underset{\displaystyle X}{Ar\overset{\displaystyle SiMe_2\text{-}R}{C}HCH_2}$$

3

a: R = Me_3Si, Ar = 3,5-$Cl_2C_6H_3$
b: R = C_6H_5, Ar = C_6H_5
c: R = Me, Ar = C_6H_5
d: R = Me, Ar = 3,5-$Cl_2C_6H_3$



$$\underset{\displaystyle X}{C_6H_5\overset{\displaystyle SiMe_2\text{-}R}{C}HSiMe_2}$$

4

a: R = Me_3Si
b: R = CH_3OCH_2
c: R = i-PrO
d: R = Me

Chart 2.

fluoroacetate (**3c-OTFA**),[10] via the addition of corresponding (silylmethyl)magnesium chlorides to 3,5-dichlorobenzaldehyde and benzaldehyde, respectively, and the subsequent treatment of the resulting alcohols with trifluoroacetic anhydride. The chlorides **4a-Cl** and **4b-Cl** were prepared via the reaction of benzylchloride with lithium diisopropylamide (LDA) at −78 °C in the presence of 1-chloro-1,1,2,2,3,3,3-heptamethyltrisilane and 1-chloro-2-methoxymethyl-1,1,2,2-tetramethyldisilane, respectively, in the same procedure as that described previously for the preparation of α-(pentamethyldisilanyl)benzyl chloride (**4d-Cl**).[11] A related reaction using 1,2-dichloro-1,1,2,2-tetramethyldisilane gave α-(2-chloro-1,1,2,2-tetramethyldisilanyl)benzyl chloride, which was converted into **4c-Cl** via a treatment with isopropyl alcohol in the presence of triethylamine.

The rates of solvolysis for **3a-OTFA**, **3b-OTFA**, **4a-Cl**, **4b-Cl**, and **4c-Cl** were measured spectrophotometrically at 25±0.05 °C by the same method as that described previously[10—12] using $(0.1—1.0)\times10^{-4}$ M (1 M=1 mol dm^{-3}) solutions in aqueous acetone and aqueous dioxane. All the solvolyses followed excellent first-order kinetics over three to four half-lives (correlation coeficient > 0.9999), and the results are given in Tables 1 and 2, which include the rate data for **3c-OTFA**, 1-(3,5-dichlorophenyl)-2-(trimethylsilyl)ethyl trifluoroacetate (**3d-OTFA**) and **4d-Cl** for comparison.[10,11]

The methanolysis of **3a-OTFA** quantitatively gave a mixture of 3,5-dichlorostyrene (**5**) and 1-(3,5-dichlorophenyl)-1-methoxy-2-(pentamethyldisilanyl)ethane (**6**) in a ratio of 60 : 40, while the solvolysis of **3b-OTFA** in aqueous acetone exclusively gave styrene (Chart 3). These findings are consistent with the results previously reported for the k_c solvolysis of **3c-OTFA** via the α-(trimethylsilylmethyl)benzyl cation **1** (R=Me), i. e., both β-silyl-elimination and substitution occurred in methanolysis, while the elimination proceeded exclusively in aqueous acetone.[10] The solvolysis of **4a-Cl** in 80% aqueous acetone involved a skeletal rearrangement affording α-[dimethyl(hydroxy)silyl]-α-(pentamethyldisilanyl)toluene (**7a**; Y=OH) as a single product in 95% yield. Similarly, the ethanolysis of **4b-Cl** cleanly gave 4,4,6,6-tetramethyl-5-phenyl-2,7-dioxa-4,6-disilanonane (**7b**: Y=OEt), and the methanolysis of **4c-Cl** afforded α,α-bis[dimethyl(methoxy)silyl]toluene (**7e**; Y=OMe) as a single product; in the latter case, an isopropoxyl group on the β-silicon atom in the starting material (**4c-Cl**) was also replaced with a methoxyl group under solvolysis conditions. The 1,2-silyl-rearrangement from the α-silicon atom to the carbenium carbon has already been established for **4d** (X=Br); it solvolyzes via the rate-determining formation of α-(pentamethyldisilanyl)benzyl cation **2** (R=Me), which reacts with water, methanol, ethanol, and trifluoroethanol yielding the corresponding silanol or silyl ethers **7d** (Y=OH, OMe, OEt, and OCH$_2$CF$_3$, respectively) after the skeletal rearrangement irrespective of nucleophilicity of solvents.[11] Thus, the product study suggests that a replacement of a β-silyl group from Me$_3$Si to Me$_3$SiMe$_2$Si, (C$_6$H$_5$)Me$_2$Si, (CH$_3$OCH$_2$)Me$_2$Si, or (*i*-PrO)Me$_2$Si does not cause changes in the mechanism of the solvolysis for the two systems **3** and **4**.

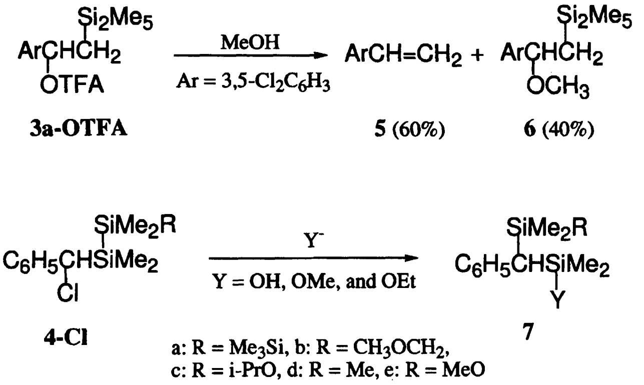


Chart 3.

The β-silyl accelerations by various silicon substituents relative to a β-trimethylsilyl group in the two benzylic systems are summarized in Tables 3 and 4, as $k_{\rm rel}(=k^{\beta\text{-silyl}}/k^{\beta\text{-Me}_3\text{Si}})$. Although the kinetic influences of γ-substituents are relatively small, a γ-Me$_3$Si group enhances the β-silicon effect relative to a γ-Me group by a factor of ca. 6—8, whereas C$_6$H$_5$, *i*-PrO, and CH$_3$OCH$_2$ groups reduce the β-silyl acceleration by factors of 2—3 relative to methyl. We previously quantified the kinetic β-silyl acceleration by a β-Me$_3$Si group relative to a β-*t*-butyl group in the α-alkylbenzyl and α-silylbenzyl systems, i. e., $k^{\beta\text{-Me}_3\text{Si}}/k^{\beta\text{-}t\text{-Bu}}$ rate ratios were 2.99×10^5 for **3c** (X=OTFA) and 1.07×10^5 for **4d** (X=Br), respectively.[10,11] From these rate ratios and the $k_{\rm rel}$ values, kinetic β-silyl accelerations by various silyl groups can be estimated, i. e., $k^{\beta\text{-silyl}}/k^{\beta\text{-}t\text{-Bu}}$ rate ratios were 1.7×10^6 and 6.2×10^4 for Me$_3$SiMe$_2$Si and (C$_6$H$_5$)Me$_2$Si, respectively, in the system **3**, and 8.2×10^5, 5.9×10^4, and 3.1×10^4 for Me$_3$SiMe$_2$Si, (*i*-PrO)Me$_2$Si, and (CH$_3$OCH$_2$)Me$_2$Si, respectively, in the system **4**; the results are included in Tables 3 and 4.

The steric factor should be taken into consideration in interpreting the effect of γ-substituents, because the solvolysis rates markedly decrease with increasing steric size of α-substituent groups for benzylic compounds.[13] However, this steric effect must be very small or negligible for γ-substituents in view of the fact that the steric effect is insignficant even for β-substituents in the systems **3** and **4**. For example, 3,3-dimethyl-1-phenyl-1-butyl trifluoroacetate (**8a**: X=OTFA) was less reactive than α-methylbenzyl trifluoroacetate (**8b**; X=OTFA) by a factor of 1.8 in 30% aqueous acetone, corresponding to a $k^{\beta\text{-}t\text{-Bu}}/k^{\beta\text{-H}}$ rate ratio of only 0.6 in the system **3**, while α-(*t*-butyldimethylsilyl)benzyl *p*-toluenesulfonate (**9a**; X=OTs) was less reactive than α-(trimethylsilyl)-

Table 1. Rates of Solvolysis for **3-OTFA**[a)]

Compound	Aryl group	Solvent[b)]	k/s^{-1}
3a−OTFA	3,5-Dichlorophenyl	80D	$(1.96\pm0.06)\times10^{-3}$ c)
3b−OTFA	Phenyl	90D	$(2.32\pm0.06)\times10^{-3}$ d)
3c−OTFA	Phenyl	90D	7.52×10^{-3} e)
3d−OTFA	3,5-Dichlorophenyl	80D	3.52×10^{-4} e)

a) At 25 °C. b) 80D: 80/20 (v/v) dioxane/water and 90D: 90/10 (v/v) dioxane/water mixtures. c) Average of three runs. d) Average of two runs. e) Data taken from Ref. 10.

Table 2. Rates of Solvolysis for **4-Cl**[a)]

Compound	Solvent[b)]	k/s^{-1}
4a−Cl	50A	$(3.98\pm0.04)\times10^{-4}$ c)
4b−Cl	30A	$(4.42\pm0.02)\times10^{-4}$ d)
4c−Cl	30A	$(8.44\pm0.10)\times10^{-4}$ c)
4d−Cl	50A	5.20×10^{-5} e)
	30A	1.53×10^{-3} e)

a) At 25 °C. b) 50A and 30A: 50/50 and 30/70 (v/v) acetone/water mixtures. c) Average of two runs. d) Average of three runs. e) Data taken from Ref. 11.

Table 3. Kinetic β-Silicon Effects of Various Silyl Groups in Solvolysis for the α-Alkylbenzyl System **3**[a)]

β-Silyl group	k_{rel}	$k^{\beta\text{-silyl}}/k^{\beta\text{-}t\text{-Bu}}$
$\mathrm{Me_3Si}$	1.0	2.99×10^{5} b)
$\mathrm{Me_3SiMe_2Si}$	5.57	1.67×10^{6} c)
$\mathrm{(C_6H_5)Me_2Si}$	0.309	6.15×10^{4} c)

a) At 25 °C. b) Reported previously (Ref. 10). c) Calculated from k_{rel} values and a $k^{\beta\text{-silyl}}/k^{\beta\text{-}t\text{-Bu}}$ ratio of 2.99×10^{5} for **3c** (X=OTFA).

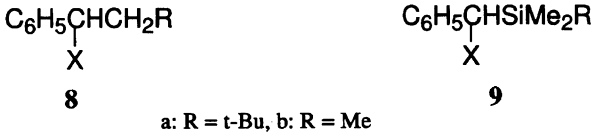
Table 4. Kinetic β-Silicon Effects of Various Silyl Groups inSolvolysis for the α-Silylbenzyl System **4**[a)]

β-Silyl group	k_{rel}	$k^{\beta\text{-silyl}}/k^{\beta\text{-}t\text{-Bu}}$
$\mathrm{Me_3Si}$	1.0	1.07×10^{5} b)
$\mathrm{Me_3SiMe_2Si}$	7.65	8.19×10^{5} c)
$(i\text{-PrO})\mathrm{Me_2Si}$	0.552	5.91×10^{4} c)
$\mathrm{(CH_3OCH_2)Me_2Si}$	0.289	3.09×10^{4} c)

a) At 25 °C. b) Reported previously (Ref. 11). c) Calculated from k_{rel} values and a $k^{\beta\text{-silyl}}/k^{\beta\text{-}t\text{-Bu}}$ ratio of 1.07×10^{5} for **4d** (X=Br).

benzyl *p*-toluenesulfonate (**9b**; X=OTs) by a factor of 1.4 in 40% aqueous acetone, indicating a $k^{\beta\text{-}t\text{-Bu}}/k^{\beta\text{-Me}}$ ratio of only 0.7 in the system **4** (Chart 4).[10,12)]

Vencle et al. reported negative Hammett ρ values in the solvolysis for the system of the type, $\mathrm{ArMe_2SiCH_2CH_2Cl}$, indicating a buildup of some positive charge on the β-silicon atom in the transition state.[14)] The analysis of the substituent effects for the two systems, $\mathrm{ArCH(OTFA)CH_2SiMe_3}$ and $\mathrm{ArCH(Cl)\text{-}SiMe_2SiMe_3}$, in terms of the Yukawa–Tsuno equation[15)] revealed significantly reduced ρ values, i. e., $\rho=-3.05$ and -3.71, respectively, compared to typical values around -5 in the k_{c} solvolysis of secondary α-alkylbenzyl compounds, indicative of extensive delocalization of a positive charge to the β-silicon atom via σ–π interactions.[10,11)] The γ-substituent effect shown in Tables 3 and 4, therefore, indicates that a phenyl and an alkoxyl groups are less effective in stabilizing the partial positive charge built up on the β-silicon atom than is a methyl group, whereas the effect of a γ-$\mathrm{Me_3Si}$ group is stabilizing relative to methyl. This is in sharp contrast to the situation for carbenium ion, i. e., α-substitution by alkoxyl and phenyl groups causes enormous stabilization, whereas α-silicon substituents relative to methyl destabilize a carbenium ion.[2,3,12)] Theoretical calculations[16)] indicated that the effect of α-substituents on stability of silicenium ion is small compared to that for carbenium ion, e. g., stabilization energies of $\mathrm{R\text{-}SiH_2^+}$ relative to $\mathrm{H_3Si^+}$ are 36.8, 17.9, 15.1, and 12.6 kcal mol^{-1} for $\mathrm{R=NH_2}$, OH, $\mathrm{CH_3}$,and $\mathrm{SiH_3}$, respectively. Mayr et al. quantified relative stabilities of various silicenium ions in solution based on the rates of hydride transfer from hydrosilanes to carbenium ions.[17)] They revealed that the α-substitution effects of a $\mathrm{Me_3SiO}$ and a $\mathrm{Me_3Si}$ groups are both comparable with that of methyl, while a phenyl group is destabilizing relative to methyl. The order of the rate acceleration with respect to γ-substituents in the present case, i. e., $\mathrm{Me_3Si>Me>C_6H_5}\cong$alkoxyl$\cong$methoxymethyl, is different from the substituent effect on stability of silicenium ions, and is best interpreted as reflecting changes in hyperconjugative abilities of the β-C–Si or β-Si–Si σ-bonds mainly due to inductive effect of the groups attached to the β-silicon atom.

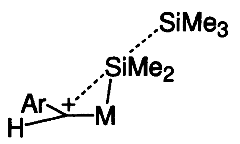


$\mathrm{C_6H_5\underset{X}{C}HCH_2R}$ **8** $\mathrm{C_6H_5\underset{X}{C}HSiMe_2R}$ **9**

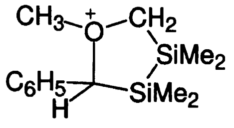
a: R = t-Bu, b: R = Me

Chart 4.

Shiner and co-workers reported distinct evidence for direct 1,3-interactions between silicon and a positive charge γ to the silicon.[18)] Such interactions, depicted in structure **10**, may account for the enhanced reactivities for the γ-silyl-substituted compounds **3a** and



10; M = CH_2 and $SiMe_2$



11

Chart 5.

4a (Chart 5). However, the absence of any products anticipated from the direct 1,3-interaction (such as 1, 3-elimination products)[18] indicates that the γ-silicon substituent exerts not a direct but an indirect influence on the ionization of the present benzylic systems probably through an inductive electron supply from the γ-Me_3Si group to the β-silicon atom resulting in enhancement of hyperconjugative abilities of the β-C–Si and β-Si–Si σ-bonds.

It is also worth nothing that **4c-Cl** bearing a γ-MeO group was less reactive than **4d-Cl**. A γ-methoxyl group is well known to accelerate the rate of ionization via anchimeric assistance, as observed in the solvolysis of γ-methoxyalkyl systems.[19] The reduced reactivity of **4c-Cl** compared to **4d-Cl** reveals essentially no contribution from the γ-MeO-participation toward ionization, depicted in structure **11**; this is also in agreement with the quantitative formation of the β-silyl-rearranged product (**7c**), indicative of the exclusive occurrence of the β-silicon-promoted solvolysis in the α-(disilanyl)benzyl system **4**. The absence of the γ-MeO-anchimeric assistance undoubtedly reflects a superior cation-stabilizing ability of a β-silicon substituent compared to a γ-methoxyl group. In connection with the competition between β-silicon effect and participation by other neighboring groups, it is worth stating that a β-Me_3Si group completely inhibits the aryl-participation in the ionization of 2-aryl-2-(trimethylsilyl)ethyl chlorides,[1] while the ionization of 1-(pentamethyldisilanyl)-2-phenylcyclopropyl bromide involves competitive σ(SiSi)- and σ(CC)-assisted processes.[20]

Experimental

Proton NMR spectra were recorded at 60 MHz on a Hitachi R-20B spectrometer in carbon tetrachloride, and the chemical shifts were reported in ppm downfield from tetramethylsilane. Infrared spectra were recorded on a Hitachi R-215 spectrophotometer. Mass spectra were recorded on a Hitachi M-60 mass spectrometer. Purification of solvents used in solvolysis and the procedure for rate measurements using a Hitachi 220A spectrophotometer were described previously.[10—12]

1-(3,5-Dichlorophenlyl)-2-(pentamethyldisilanyl)-ethyl Trifluoroacetate (3a-OTFA). To a stirred solution of (pentamethyldisilanyl)methylmagnesium chloride prepared from (pentamethyldisilanyl)methyl chloride (3.01 g, 16.6 mmol) and magnesium (465 mg) in THF (30 cm^3) was added a solution of 3,5-dichlorobenzaldehyde (3.07 g) in ether (25 cm^3) at room temperature. The mixture was stirred for 30 min at ambient temperature. A crude oil obtained after the usual workup was purified by means of column chromatography (SiO_2) affording 1-(3,5-dichlorophenyl)-2-(pentamethyldisilanyl)ethanol (2.86 g, 59%) as a colorless oil: IR (neat) 3350, 1245, and 850 cm^{-1}; ^1H NMR $\delta=-0.07$ (15H, as a single peak), 1.04—1.18 (2H, m), 1.99 (1H, br. s, OH), 4.71 (1H, t, $J=7.8$ Hz), 7.17 (3H, almost as a single peak). The alcohol was converted into the corresponding trifluoroacetate, **3a-OTFA**, in a similar procedure to that described previously:[10] IR (neat) 1775, 1250, 1220, 1170, 1140, and 855 cm^{-1}; ^1H NMR $\delta=-0.05$ (3H, s), 0.05 (9H, s), 0.03 (3H, s), 1.34—1.50 (2H, m), 5.71—5.90 (1H, m), and 7.23—7.36 (3H, m). Found. C, 43.35; 5.01%. Calcd for $C_{15}H_{21}Cl_2F_3O_2Si_2$: C, 43.17; H, 5.07%.

2-(Dimethylphenylsilyl)-1-phenylethyl Trifluoroacetate (3b-OTFA). Into an ethereal solution of (dimethylphenylsilyl)methylmagnesium chloride prepared from (chloromethyl)dimethylphenylsilane (5.00 g) and magnesium (0.76 g) in ether (50 cm^3), was added a solution of benzaldehyde (3.52 g) in ether (25 cm^3) at room temperature. The mixture was stirred for 1 h. The usual workup followed by purification of a crude oil by means of column chromatography (SiO_2) gave 2-(diemthylphenylsilyl)-1-phenylethanol (7.0 g): ^1H NMR $\delta=0.11$ (6H, s), 1.52—1.77 (2H, m), 5.69—6.02 (1H, m), and 7.20—7.48 (10H, m). Found: C, 75.26; H, 7.91%. Calcd for $C_{16}H_{20}OSi$: C, 74.95; H, 7.86%. The alcohol was converted into the corresponding trifluoroacetate in a similar procedure to that described previously:[10] ^1H NMR $\delta=0.20$ (3H, s), 0.22 (3H, s), 1.19—1.53 (2H, m), 4.55—4.90 (1H, m), 7.14—7.60 (10H, m).

α-(Heptamethyltrisilanyl)benzyl Chloride (4a-Cl). Into a stirred solution of 1-chloro-1,1,2,2,3,3,3-heptamethyltrisilane (5.84 g, 26 mmol) and lithium diisopropylamide (LDA) prepared from butyllithium (1.7 M in hexane, 15 cm^3, 26 mmol) and diisopropylamine (3.10 g) in THF (25 cm^3) was added a solution of benzyl chloride (3.23 g, 26 mmol) in THF (5 cm^3) at −78 °C under argon. The mixture was stirred for 36 h at that temperature, diluted with pentane (50 cm^3), and poured into water. Organic phase was washed with 10% sulfuric acid, aq $NaHCO_3$, and aq NaCl, and dried ($MgSO_4$). After evaporation of the solvent, the residual oil was distilled affording **4a-Cl** (3.99 g, 51%) as a colorless oil: Bp 93—94 °C (ca. 50 Pa): ^1H NMR (400 MHz, $CDCl_3$) $\delta=0.015$ (3H, s), 0.067 (3H, s), 0.089 (9H, s), 0.092 (3H, s), 0.182 (3H, s), 4.470 (1H, s), and 7.260 (5H, almost as a single peak). Found: C, 52.99; H, 8.44%. Calcd for $C_{14}H_{27}ClSi_3$: C, 53.37; H, 8.46%.

α-(2-Methoxymethyl-1,1,2,2-tetremethyldisilanyl)benzyl Chloride (4b-Cl). In a similar procedure to that described for the preparation of **4a-Cl**, benzyl chloride (2.66 g) was treated with LDA (1.1 equiv) in the presence of 1-chloro-2-methoxymethyl-1,1,2,2-tetramethyldisilane (4.57 g)[21] (−78 °C, 21 h). A crude oil obtained after a workup was distilled, affording **4b-Cl** (4.12 g, 67%): Bp 88—90 °C (ca. 30 Pa); IR (neat) 1590, 1450, 1250, 1100, 830, and 790cm^{-1}; ^1H NMR $\delta=0.0$ (3H, s), 0.03 (3H, s), 0.08 (3H, s), 0.15 (3H, s), 3.17 (2H, s), 3.27 (3H, s), 4.42 (1H, s), and 7.19 (5H, almost s). Found: C, 54.35; H, 8.06%. Calcd for $C_{13}H_{23}ClOSi_2$: C, 54.42; H, 8.08%.

α-(2-Isopropoxy-1,1,2,2-tetramethyldisilanyl)benzyl Chloride (4c-Cl). In a similar procedure to that described for the preparation of **4a-Cl**, benzyl chloride (4.48

g) was treated with LDA (1.1 equiv) in the presence of 1,2-dichloro-1,1,2,2-tetramethyldisilane (7.89 g)(−78 °C, 20 h). A crude mixture obtained after evaporation of the solvent was distilled to give 2.82 g (30%) of α-(2-chloro-1,1,2,2-tetramethyldisilanyl)benzyl chloride, bp 89—95 °C (ca. 300 Pa). The chloride was added to a solution of isopropyl alcohol (5 cm^3) and triethylamine (10.7 g) in ether (35 cm^3) at 0 °C. The mixture was stirred for 15 min at 0 °C, washed with aq $NaHCO_3$, and dried ($MgSO_4$). After evaporation of the solvent, the residual oil was distilled to give **4c-Cl** (0.61 g, 20%): Bp 92—93 °C (ca. 300Pa); ^1H NMR $\delta=0.07$ (6H, s), 0.14 (6H, s), 1.10 (6H, d, $J=6$ Hz), 3.87 (1H, sep, $J=6$ Hz), 4.40 (1H, s), and 7.20 (5H, almost as a single peak). Found: C, 55.96; H, 8.57%. Calcd for $C_{14}H_{25}ClOSi_2$: C, 55.88; H, 8.37%.

Product Studies. Solvolysis products were determined for **3a-OTFA**, **4a-Cl**, **4b-Cl**, and **4c-Cl** using 0.05—0.1 M solutions in the presence of equivalent amounts of 2,6-lutidine. The solvolysis of **3a-OTFA** in methanol (25 °C, 3 h) quantitatively gave a mixture of 3,5-dichlorostyrene (**5**) and 1-(3,5-dichlorophenyl)-1-methoxy-2-(pentamethyldisilanyl)ethane (**6**) in a ratio of 60 : 40. **6**: ^1H NMR $\delta=-0.06$ (15H, s), 0.97—1.18 (2H, m), 3.24 (3H, s), 4.10—4.25 (1H, m), and 7.29 (3H, almost as a single peak). Found: C, 48.05; H, 7.49%. Calcd for $C_{13}H_{24}Cl_2OSi_2$: C, 48.28; H, 7.48%. The solvolysis of **4a-Cl** in 80% aqueous acetone (50 °C, 8 h) gave α-[dimethyl(hydroxy)silyl]-α-(pentamethyldisilanyl)toluene (**7a-OH**) in 95% yield: IR (neat) 3400, 1245, and 830 cm^{-1}; ^1H NMR $\delta=-0.17$ (9H, s), 0.04 (3H, s), 0.11 (3H, s), 0.06 (3H, s), 0.20 (3H, s), 1.40 (1H, s, disappeared on addition of D_2O), 1.61 (1H, s), and 6.99—7.05 (5H, m). Found: C, 56.33; H, 9.27%. Calcd for $C_{14}H_{28}OSi_3$: C, 56.69; H, 9.51%. The solvolysis of **4b-Cl** in ethanol (80 °C, 10 d) quantitatively gave 4,4,6,6-tetramethyl-5-phenyl-2,7-dioxa-4,6-disilanonane (**7b-OEt**): IR (neat) 1590, 1250, 1200, 1100, 1080, 1030, 930, 830, and 700 cm^{-1}; ^1H NMR $\delta=0.0$ (6H, s), 0.07 (6H, s), 1.15 (3H, t, $J=6.6$ Hz), 1.69 (1H, s), 2.91 (2H, s), 3.22 (3H, s), 3.61 (2H, q, $J=6.6$ Hz), and 6.81—7.25 (5H, m). Found: C, 60.06; H, 9.44%. Calcd for $C_{15}H_{28}O_2Si_2$: C, 60.75; H, 9.52%. The solvolysis of **4c-Cl** in methanol (50 °C, 8 h) quantitatively gave α,α-bis[dimethyl(methoxy)silyl]toluene (**7e-OMe**): MS m/z (rel intensity) 268 (M^+, 28), 253 (27), 237 (23), 207 (20), 179 (9), 163 (46), 148 (100), 133 (48), 89 (47), 75 (52), 73 (62), 59 (38); ^1H NMR $\delta=0.07$ (12H, s), 1.64 (1H, s), 3.35 (6H, s), 7.02 (5H, almost s).

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