

Silicon Effects. VI.¹⁾ β -Silicon Effect of Various Silyl Groups in Solvolysis for α -Alkylbenzyl and α -Silylbenzyl Systems

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The kinetic β -silicon effects of various silyl groups including Me₃Si, Me₃SiMe₂Si, (C₆H₅)Me₂Si, (*i*-PrO)-Me₂Si, and (CH₃OCH₂)Me₂Si were measured in *k_c* solvolysis of two different benzylic systems of the types, ArCH(OCOCF₃)CH₂R (**3**: Ar=phenyl or 3,5-dichlorophenyl, R=silyl group) and C₆H₅CH(Cl)SiMe₂R (**4**: R=silyl group). The relative β -silyl accelerations were 1.0:5.57:0.309 for R=Me₃Si, Me₃SiMe₂Si, and (C₆H₅)Me₂Si, respectively, for the system **3**, and 1.0:7.65:0.502:0.289 for R=Me₃Si, Me₃SiMe₂Si, (*i*-PrO)Me₂Si, and (CH₃OCH₂)Me₂Si, 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, C₆H₅CH(OCOCF₃)CH₂R (R=Me₃Si and *t*-Bu) and C₆H₅CH(Br)SiMe₂R (R=Me₃Si and *t*-Bu); *k^β*-Me₃Si/*k^β*-*t*-Bu rate ratios at 25 °C were 2.99×10⁵ and 1.07×10⁵ 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=Me₃Si 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 -Me₃Si 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 C₆H₅CH(Br)SiMe₂SiMe₃, no kinetic β -silyl acceleration was measured in the *k_c* solvolysis of a cyclic analog, 1,1,2,2-tetramethyl-1,2-disila-indan-3-yl chloride, in which the Si $_{\alpha}$ –Si $_{\beta}$ 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 car-

benium ion by C $_{\alpha}$ –Si $_{\beta}$ or Si $_{\alpha}$ –Si $_{\beta}$ 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 $_{\alpha}$ –Si $_{\beta}$ and Si $_{\alpha}$ –Si $_{\beta}$ σ -bonds, we have measured the kinetic β -silicon effects of various silyl groups including Me₃SiMe₂Si, (C₆H₅)Me₂Si, (CH₃OCH₂)Me₂Si, and (*i*-PrO)Me₂Si in addition to Me₃Si 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**).

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-

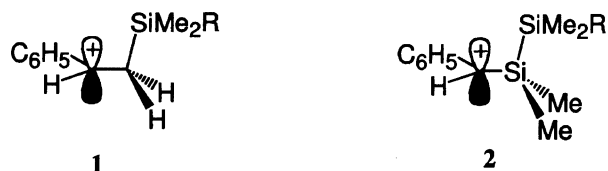


Chart 1.



- a: R = Me₃Si, Ar = 3,5-Cl₂C₆H₃
 b: R = C₆H₅, Ar = C₆H₅
 c: R = Me, Ar = C₆H₅
 d: R = Me, Ar = 3,5-Cl₂C₆H₃

- a: R = Me₃Si
 b: R = CH₃OCH₂
 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 $25 \pm 0.05^\circ\text{C}$ by the same method as that described previously^{10–12} using $(0.1\text{--}1.0) \times 10^{-4}$ 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 coefficient > 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-dioxo-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 OCH₂CF₃, respectively)

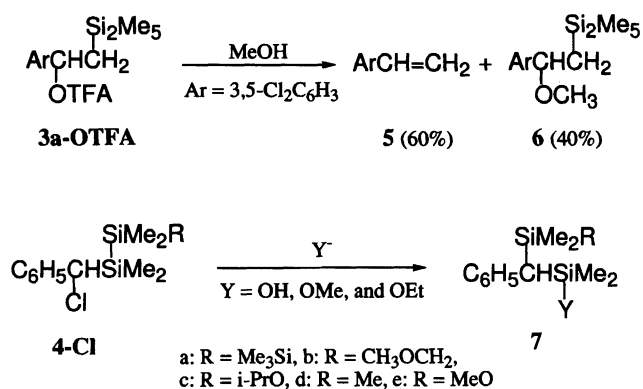


Chart 3.

after the skeletal rearrangement irrespective of nucleophilicity of solvents.¹¹ Thus, the product study suggests that a replacement of a β -silyl group from Me₃Si to Me₃SiMe₂Si, (C₆H₅)Me₂Si, (CH₃OCH₂)Me₂Si, or (*i*-PrO)Me₂Si does not cause changes in the mechanism of the solvolysis for the two systems **3** and **4**.

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 $k_{\text{rel}} (= k^{\beta\text{-silyl}} / k^{\beta\text{-Me}_3\text{Si}})$. Although the kinetic influences of γ -substituents are relatively small, a γ -Me₃Si group enhances the β -silicon effect relative to a γ -Me group by a factor of ca. 6–8, whereas C₆H₅, *i*-PrO, and CH₃OCH₂ 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 -Me₃Si 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_{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 Me₃SiMe₂Si and (C₆H₅)Me₂Si, respectively, in the system **3**, and 8.2×10^5 , 5.9×10^4 , and 3.1×10^4 for Me₃SiMe₂Si, (*i*-PrO)Me₂Si, and (CH₃OCH₂)Me₂Si, 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 insignificant 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	$(1.96 \pm 0.06) \times 10^{-3}$ ^{c)}
3b-OTFA	Phenyl	90D	$(2.32 \pm 0.06) \times 10^{-3}$ ^{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	$(3.98 \pm 0.04) \times 10^{-4}$ ^{c)}
4b-Cl	30A	$(4.42 \pm 0.02) \times 10^{-4}$ ^{d)}
4c-Cl	30A	$(8.44 \pm 0.10) \times 10^{-4}$ ^{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 **3a**^{a)}

β -Silyl group	k_{rel}	$k^{\beta-silyl}/k^{\beta-t-Bu}$
Me ₃ Si	1.0	2.99×10^5 ^{b)}
Me ₃ SiMe ₂ Si	5.57	1.67×10^6 ^{c)}
(C ₆ H ₅)Me ₂ Si	0.309	6.15×10^4 ^{c)}

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

Table 4. Kinetic β -Silicon Effects of Various Silyl Groups in Solvolysis for the α -Silylbenzyl System **4a**^{a)}

β -Silyl group	k_{rel}	$k^{\beta-silyl}/k^{\beta-t-Bu}$
Me ₃ Si	1.0	1.07×10^5 ^{b)}
Me ₃ SiMe ₂ Si	7.65	8.19×10^5 ^{c)}
(<i>i</i> -PrO)Me ₂ Si	0.552	5.91×10^4 ^{c)}
(CH ₃ OCH ₂)Me ₂ Si	0.289	3.09×10^4 ^{c)}

a) At 25 °C. b) Reported previously (Ref. 11). c) Calculated from k_{rel} values and a $k^{\beta-silyl}/k^{\beta-t-Bu}$ 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 $k^{\beta-t-Bu}/k^{\beta-Me}$ 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, ArMe₂SiCH₂CH₂Cl, 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, ArCH(OTFA)CH₂SiMe₃ and ArCH(Cl)-SiMe₂SiMe₃, in terms of the Yukawa-Tsuno equation¹⁵⁾



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

Chart 4.

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 alkoxy 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 -Me₃Si group is stabilizing relative to methyl. This is in sharp contrast to the situation for carbenium ion, i. e., α -substitution by alkoxy and phenyl groups causes enormous stabilization, whereas α -silicon substituents relative to methyl destabilize a carbenium ion.^{2,3,12)} Theoretical calculations¹⁶⁾ 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 R-SiH₂⁺ relative to H₃Si⁺ are 36.8, 17.9, 15.1, and 12.6 kcal mol⁻¹ for R=NH₂, OH, CH₃, and SiH₃, 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 Me₃SiO and a Me₃Si 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., Me₃Si > Me > C₆H₅ $\cong$ alkoxy $\cong$ 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.

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

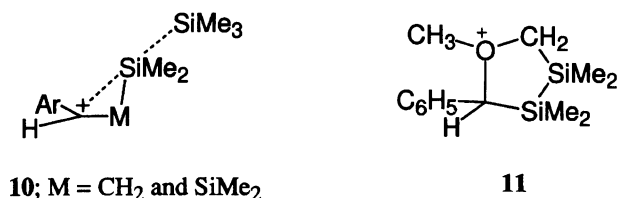


Chart 5.

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 -Me₃Si 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 noting 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 -Me₃Si 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-Dichlorophenyl)-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 cm³) was added a solution of 3,5-dichlorobenzaldehyde (3.07 g) in ether (25 cm³) 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 (SiO₂) 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 δ = -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 δ = -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 C₁₅H₂₁Cl₂F₃O₂Si₂: 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 cm³), was added a solution of benzaldehyde (3.52 g) in ether (25 cm³) 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 (SiO₂) gave 2-(dimethylphenylsilyl)-1-phenylethanol (7.0 g): ¹H NMR δ = 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 C₁₆H₂₀OSi: 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 δ = 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 cm³, 26 mmol) and diisopropylamine (3.10 g) in THF (25 cm³) was added a solution of benzyl chloride (3.23 g, 26 mmol) in THF (5 cm³) at -78 °C under argon. The mixture was stirred for 36 h at that temperature, diluted with pentane (50 cm³), and poured into water. Organic phase was washed with 10% sulfuric acid, aq NaHCO₃, and aq NaCl, and dried (MgSO₄). 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, CDCl₃) δ = 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 C₁₄H₂₇ClSi₃: C, 53.37; H, 8.46%.

α -(2-Methoxymethyl-1,1,2,2-tetramethyldisilanyl)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 790 cm⁻¹; ¹H NMR δ = 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 C₁₃H₂₃ClOSi₂: 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 $89-95^{\circ}\text{C}$ (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 $92-93^{\circ}\text{C}$ (ca. 300 Pa); $^1\text{H NMR}$ $\delta=0.07$ (6H, s), 0.14 (6H, s), 1.10 (6H, d, $J=6\text{ Hz}$), 3.87 (1H, sep, $J=6\text{ Hz}$), 4.40 (1H, s), and 7.20 (5H, almost as a single peak). Found: C, 55.96; H, 8.57%. Calcd for $\text{C}_{14}\text{H}_{25}\text{ClOSi}_2$: 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**: $^1\text{H NMR}$ $\delta=-0.06$ (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 $\text{C}_{13}\text{H}_{24}\text{Cl}_2\text{OSi}_2$: 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} ; $^1\text{H NMR}$ $\delta=-0.17$ (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 $\text{C}_{14}\text{H}_{28}\text{OSi}_3$: 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-dioxo-4,6-disilanonane (**7b-OEt**): IR (neat) 1590, 1250, 1200, 1100, 1080, 1030, 930, 830, and 700 cm^{-1} ; $^1\text{H NMR}$ $\delta=0.0$ (6H, s), 0.07 (6H, s), 1.15 (3H, t, $J=6.6\text{ Hz}$), 1.69 (1H, s), 2.91 (2H, s), 3.22 (3H, s), 3.61 (2H, q, $J=6.6\text{ Hz}$), and 6.81–7.25 (5H, m). Found: C, 60.06; H, 9.44%. Calcd for $\text{C}_{15}\text{H}_{28}\text{O}_2\text{Si}_2$: 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 (**7c-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); $^1\text{H NMR}$ $\delta=0.07$ (12H, s), 1.64 (1H, s), 3.35 (6H, s), 7.02 (5H, almost s).

References

- 1) Part V: F. Hayakawa, S. Watanabe, N. Shimizu, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **66**, 153 (1993).
- 2) J. B. Lambert, *Tetrahedron*, **46**, 2677 (1991).
- 3) Y. Apeloig, "The Chemistry of Organic Silicon Compounds," ed by S. Patai and Z. Rappoport, John Wiley & Sons, Chichester, England (1989), Part 1, Chap. 2.
- 4) N. Shimizu, *Rev. Heteroatom Chem.*, **9**, 155 (1993).
- 5) L. H. Sommer and G. A. Baughman, *J. Am. Chem. Soc.*, **83**, 3346 (1961); A. W. P. Jarvie, A. Holt, and J. Thompson, *J. Chem. Soc. B*, **1969**, 852; M. A. Cook, C. Eaborn, and D. R. M. Walton, *J. Organomet. Chem.*, **1970**, 301.
- 6) J. B. Lambert, G.-t. Wang, R. B. Finzel, and D. H. Teramura, *J. Am. Chem. Soc.*, **109**, 7838 (1987); J. B. Lambert and E. C. Chelius, *J. Am. Chem. Soc.*, **112**, 8120 (1990).
- 7) D. J. Hajdasz and R. R. Squires, *J. Chem. Soc., Chem. Commun.*, **1988**, 1212; X. Li and J. A. Stone, *J. Am. Chem. Soc.*, **111**, 5586 (1989); J. A. Stone, *Rev. Heteroatom Chem.*, **5**, 232 (1991).
- 8) J. M. White and G. B. Robertson, *J. Org. Chem.*, **57**, 4638 (1992).
- 9) S. G. Wierschke, J. Chandrasekhar, and W. L. Jorgensen, *J. Am. Chem. Soc.*, **107**, 1496 (1985); M. R. Ibrahim and W. L. Jorgensen, *J. Am. Chem. Soc.*, **111**, 819 (1989).
- 10) N. Shimizu, S. Watanabe, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **64**, 2249 (1991).
- 11) N. Shimizu, C. Kinoshita, and Y. Tsuno, *Chem. Lett.*, **1990**, 1937; N. Shimizu, C. Kinoshita, E. Osajima, F. Hayakawa, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **64**, 3280 (1991).
- 12) N. Shimizu, E. Osajima, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **64**, 1145 (1991).
- 13) G. Baddeley, J. Chadwick, and H. T. Taylor, *J. Chem. Soc.*, **1954**, 2405.
- 14) J. Vencle, J. Hetflejš, J. Čermák, and V. Chalovský, *Collect. Czech. Chem. Commun.*, **38**, 1256 (1973).
- 15) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **32**, 971 (1959); Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Jpn.*, **39**, 2249 (1966).
- 16) Y. Apeloig, "Heteroatom Chemistry," ed by E. Blook, VCH-Verlagsgesellschaft, Weinheim (1990), p. 27.
- 17) H. Mayr, N. Basso, and G. Hagen, *J. Am. Chem. Soc.*, **114**, 3060 (1992).
- 18) V. J. Shiner, Jr., M. W. Ensinger, and R. D. Rutkowski, *J. Am. Chem. Soc.*, **109**, 804 (1987); J. C. Coope, V. J. Shiner, Jr., and M. W. Ensinger, *J. Am. Chem. Soc.*, **112**, 2834 (1990); V. J. Shiner, Jr., M. W. Ensinger, J. S. Kritiz, and K. A. Haley, *J. Org. Chem.*, **55**, 653 (1990).
- 19) S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951); S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Am. Chem. Soc.*, **79**, 4146 (1957).
- 20) N. Shimizu, F. Hayakawa, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **65**, 959 (1992).
- 21) M. Kumada, M. Ishikawa, and K. Tamao, *J. Organomet. Chem.*, **5**, 226 (1966).