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Silicon Effects. V.
β-Silicon Effect in the Solvolysis of 2-Phenylethyl Compounds[1)]

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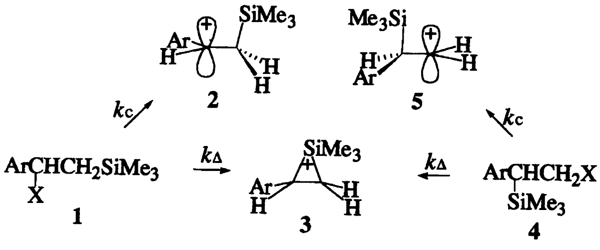
The rates of the solvolysis of 2-aryl-2-(trimethylsilyl)ethyl compounds, $ArCH(SiMe_3)CH_2X$ (**4**: X=Cl and $OCOCF_3$; $Ar=C_6H_5$ and p-$MeOC_6H_4$), have been measured in various solvents at 25°C. The solvolysis of the chloride, **4** (X=Cl; $Ar=C_6H_5$), exhibited an m value of 0.90 in aqueous dioxane consistent with rate-determining ionization; it gave (2-ethoxy-2-phenylethyl) trimethylsilane together with styrene in ethanol indicating a 1, 2-$SiMe_3$ migration during the solvolysis. The p-MeO-substitution effect, $k^{p-\mathrm{MeO}}/k^{\mathrm{H}}$, was measured with the trifluoroacetates to be 2.1, in contrast to a factor of 269 observed in solvolysis of 1-aryl-2-(trimethylsilyl)ethyl compounds (**1**), indicating that distinct intermediates are involved in ionization of the two regioisomeric systems, **1** and **4**.

The effect of organosilicon groups in carbocation-forming processes has received wide attention from theoretical and mechanistic interests in recent years.[2—9)] Theoretical calculations reported by Jorgensen and co-workers[3)] indicated that the SiH_3-bridged form for the primary cation, $SiH_3CH_2CH_2^+$, is slightly more stable than an open, bisected form by 2.4 kcal mol^{-1} (1 kcal= 4.18 kJ), while the bridged form is ca. 4 kcal mol^{-1} higher in energy than the open form for the secondary cation, $SiH_3CH_2C^+HCH_3$.

We previously reported the kinetic β-silicon effect in solvolysis of the 1-aryl-2-(trimethylsilyl)ethyl system **1**.[10)] In 30% aqueous dioxane at 25°C, 1-phenyl-2-(trimethylsilyl)ethyl trifluoroacetate (**1a-OTFA**) solvolyzed 2.99×10^5 and 1.05×10^5 times more rapidly than did corresponding 3, 3-dimethyl-1-phenylbutyl and 1-phenylethyl compounds, respectively, indicating an acceleration of ca. 10^5 by a β-$SiMe_3$ group relative to a β-hydrogen or a β-t-Bu group in ionization of the 1-phenylethyl system. The results of the various mechanistic criteria including solvent effect, substituent effect, deuterium kinetic isotope effect, and activation energies for the system **1** were consistent with the simple ionization mechanism (k_c) via the open benzylic cation **2** rather than the σ-participation mechanism (k_Δ) via the bridged siliconium ion intermediate **3**. Further evidence to confirm the mechanism of ionization of **1** may be provided from the comparison with solvolysis of the regioisomeric system, i. e., 2-phenyl-2-(trimethylsilyl)ethyl compounds (**4**), which may undergo either k_Δ ionization forming **3**, or k_c ionization leading to the primary cation **5** (Chart 1).

This paper describes both kinetic and product studies concerning the solvolysis of 2-phenyl- and 2-(p-methoxyphenyl)-2-(trimethylsilyl)ethyl trifluoroacetates (**4a-OTFA** and **4b-OTFA**) and 2-phenyl-2-(trimethylsilyl)ethyl chloride (**4a-Cl**), and discusses the β-silicon effect in the solvolysis of 1-phenyl- and 2-phenylethyl compounds.



a; $Ar=C_6H_5$, b; $Ar=p$-$MeOC_6H_4$
X=Cl, $OCOCF_3$ (OTFA), OAc

Chart 1.

i; Ar_2CuLi, ii; $SOCl_2$ or $(CF_3CO)_2O$

Chart 2.

Results and Discussion

The compounds, **4a-Cl**, **4a-OTFA**, and **4b-OTFA**, were prepared by the treatment of the corresponding alcohols, **6**, with thionyl chloride or trifluoroacetic anhydride;[5,7)] the alcohols were obtained by the reaction of 2-(trimethylsilyl)oxirane with lithium diphenylcuprate or lithium bis(p-methoxyphenyl)cuprate (Chart 2).

The rates of solvolysis were measured spectrophotometrically at 25.0°C by the method described previously.[10)] Table 1 summarizes the results of the solvolysis for **4a-Cl**, **4a-OTFA**, and **4b-OTFA** in various solvents. Table 1 includes the rates of solvolysis for 1-phenyl-2-(trimethylsilyl)ethyl acetate (**1a-OAc**) and a 2-p-methoxyphenyl derivative, **1b-OAc**, for comparison.

We previously showed that the solvolytic reactivities of **1a-OTFA** and p-Me, m-Cl, p-Br, 3, 4-dichloro, and 3, 5-dichloro derivatives were correlated with σ^+, yielding a ρ^+ value of -3.07 (correlation coefficient R=0.997).[10)] The substituent effect of a p-methoxyl group observed for the acetates, i.e., $k^{p-\mathrm{MeO}}/k^{\mathrm{H}}=269$ for **1-OAc**, is

Table 1. Rates of Solvolysis for **4-Cl**, **4-OTFA**, and **1-OAc** at 25.0±0.05°C

Substrate	Solvent [a]	$10^5\ k/\mathrm{s}^{-1}$
4a-Cl	97T	$(1.80\pm0.05)\times10^{-2}$ [b]
	60A	$(2.94\pm0.03)\times10^{-4}$ [b]
	50A	$(8.37\pm0.09)\times10^{-4}$ [b]
	40A	$(2.24\pm0.007)\times10^{-3}$
	60D	$(1.65\pm0.002)\times10^{-4}$
	50D	$(6.34\pm0.002)\times10^{-4}$
	40D	$(2.12\pm0.001)\times10^{-3}$
	80E	$(3.18\pm0.0009)\times10^{-4}$
	60E	$(1.02\pm0.0004)\times10^{-3}$
	50E	$(2.02\pm0.0008)\times10^{-3}$
	40E	$(4.54\pm0.14)\times10^{-3}$ [b]
4a-OTFA	97T	$(5.73\pm0.003)\times10^{-4}$
	30D	$(1.35\pm0.01)\times10^{-3}$ [b]
4b-OTFA	97T	$(1.21\pm0.0005)\times10^{-3}$
	30D	$(2.88\pm0.06)\times10^{-3}$ [b]
1a-OAc	40D	$(5.84\pm0.007)\times10^{-5}$
1b-OAc	40D	$(1.57\pm0.01)\times10^{-2}$

a) 97T: 97/3 (w/w) trifluoroethanol/water; 60A—40A: 60/40—40/60 (v/v) acetone/water; 60D—40D: 60/40—40/60 (v/v) dioxane/water; and 80E—40E: 80/20—40/60 (v/v) ethanol/water mixtures. b) Average of duplicate determinations.

in good agreement with a predicted value of 248 calculated from the above correlation. The Yukawa-Tsuno treatment (Eq. 1)[11] for the eight *m*- and *p*-substituents including the *p*-MeO group gave a good linear correlation expressed as Eq. 2 (R=0.998), yielding a ρ value of −3.05 and a resonance parameter r value of 0.98, indicating essentially the same resonance demand for 1-phenyl-2-(trimethylsilyl)ethyl cation (**2**) as that for the reference standard, 1-methyl-1-phenylethyl cation (r=1.0).

$$\log k^{\mathrm{X}}/k^{\mathrm{H}} = \rho(\sigma^{\circ} + r\Delta\bar{\sigma}_{\mathrm{R}}^{+}) \tag{1}$$

$$\log k^{\mathrm{X}}/k^{\mathrm{H}} = -3.05(\sigma^{\circ} + 0.98\Delta\bar{\sigma}_{\mathrm{R}}^{+}) \tag{2}$$

The products in the solvolysis of the chloride, **4a-Cl**, were determined in buffered ethanol at 50°C. The GLC and NMR analyses of a crude mixture obtained after solvolysis indicated the formation of styrene **7** and (2-ethoxy-2-phenylethyl)trimethylsilane (**8**) at a ratio of 84 : 16; the latter compound arose from a 1, 2-silyl rearrangement. The result is interestingly compared with the previous finding that the buffered methanolysis of **1-OTFA** (Ar=*m*-$\mathrm{ClC_6H_4}$) gave *m*-chlorostyrene and [2-methoxy-2-(*m*-chlorophenyl)ethyl] trimethylsilane at a ratio of 78 : 22.[10] The striking resemblance in the products in the two solvolyses suggests a common product-forming step for the two regioisomeric systems, **1** and **4**. The 2-phenylethyl compound, **4a-Cl**, may undergo phenyl-assisted solvolysis via a phenonium ion, **9**; however, the formation of any phenyl-rearranged products, such as **10**, could not be detected. No direct substitution product was formed, either (Charts 3 and 4).

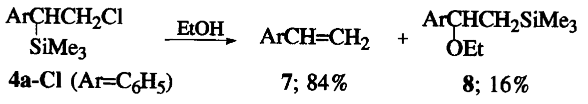


Chart 3.

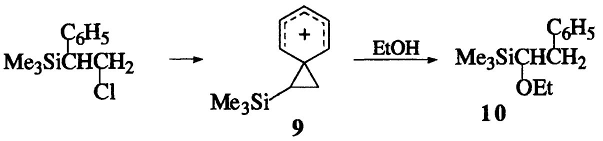


Chart 4.

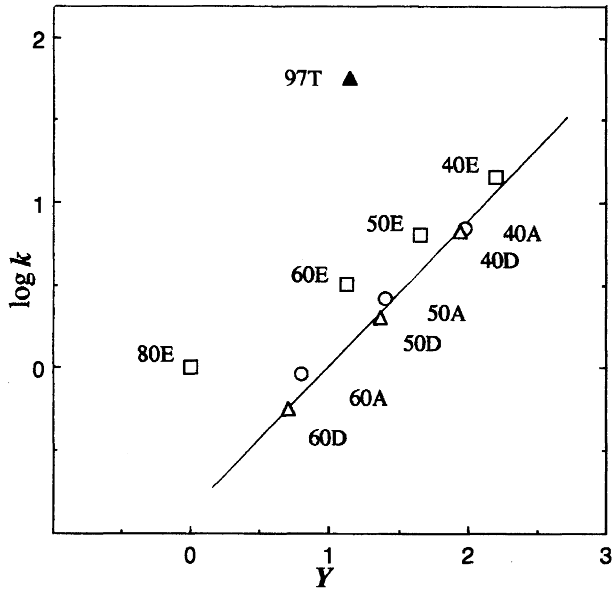


Fig. 1. Plot of log k vs. Y for solvolysis of 2-phenyl-2-(trimethylsilyl)ethyl chloride (**4a-Cl**) at 25°C in: aq acetone, ○; aq dioxane, △; aq ethanol, □; and aq 2, 2, 2-trifluoroethanol, ▲.

Figure 1 illustrates the dependence of the logarithmic rates for **4a-Cl** on solvent ionizing power Y.[12] Apparently, **4a-Cl** shows not a single linear response to Y but a dispersion for different sets of binary solvent mixtures; m values for aqueous dioxane, aqueous acetone, and aqueous ethanol were 0.90 (R=0.999), 0.74 (R=0.999), and 0.52 (R=0.995), respectively. The m value of 0.9 for the aqueous dioxane is consistent with ionization in a rate-determining step. A plot against Y_{Cl}[13] in place of Y showed a similar dispersion pattern.

The dispersion does not result from inclusion of nucleophilic solvent assistance (k_{s}, **11**). First, direct substitution did not occur even in a strongly nucleophilic solvent, ethanol. Second, 97% aqueous 2, 2, 2-trifluoroethanol (TFE), which is much less nucleophilic than aqueous ethanol, deviates not below but substantially above the aqueous ethanol line, clearly against nucleophilic solvent assistance either at $\mathrm{C_1}$ or at the silicon atom (**12**) in the rate-determining step. Although the dispersion in the solvent effect in the 2-arylethyl systems is often attributable to aryl participation,[14,15] this is not the case, either. The present system does not involve

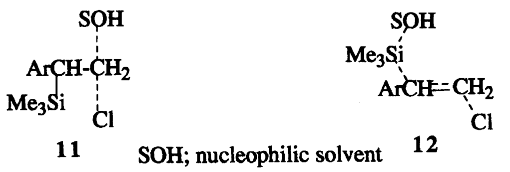


Chart 5.

Table 2. Comparison of Reactivities for **1a-OTFA** and **4a-OTFA**

Substrate	Solvent	k/s^{-1}	k_{rel}
1a-OTFA	30D	36.8 $^{a)}$	2.7×10^4
4a-OTFA	30D	1.35×10^{-3}	1.0

a) Reported previously (Ref. 10).

Chart 6.

aryl participation in view of a very small *p*-MeO-substitution effect, i. e., $k(\mathbf{4b-OTFA})/k(\mathbf{4a-OTFA})=2.1$, as well as the absence of the 1, 2-phenyl rearrangement. Thus, the dispersed solvent effect for **4a-Cl** should be interpreted as its intrinsic response to solvent ionizing power. Marked deviation of aqueous TFE above a correlation line for aqueous ethanol has been observed in k_c solvolyses of α-(trialkylsilyl)benzyl tosylates (=*p*-toluenesulfonates) and α-(pentamethyldisilanyl)benzyl halides (Chart 5).[9)]

Table 2 compares the reactivity of **4a-OTFA** with that of its regioisomer, **1a-OTFA**; the former solvolyzed 2.7×10^4 times less rapidly than did the latter in 30% aqueous dioxane at 25°C. Since the two regio isomers probably have similar ground state energies, the result suggests that the transition state for the primary system **4** is about 6 $\mathrm{kcal\,mol^{-1}}$ higher in energy than that for the benzylic system **1**.

Table 3 compares the rate for 2-phenyl-2-(trimethylsilyl)ethyl tosylate (**4a-OTs**) with the phenyl-assisted (k_Δ) and solvent-assisted (k_s) rates of solvolysis for 2-phenylpropyl tosylate (**13**) in 97% TFE reported by Raber et al.[15)] The reactivity of the tosylate, **4a-OTs**, was estimated from the rate for the chloride, $k=1.8\times10^{-2}\ \mathrm{s}^{-1}$, and a tosylate/chloride rate ratio of 3.7×10^4.[16)] As Table 3 shows, **4a-OTs** solvolyzes 1.3×10^9 times faster than does **13** via aryl participation, indicating that a β-SiMe$_3$ group is about 12 $\mathrm{kcal\,mol^{-1}}$ more effective in ionizing the ethyl system than is a β-phenyl group. Since the rate of unassisted ionization (k_c) must be significantly lower than the k_s in the primary system **13**, a $k(\mathbf{4a\text{-}OTs})/k_s(\mathbf{13})$ ratio of ca. 10^{11} provides a minimum estimate for the kinetic β-silicon effect of a SiMe$_3$ group relative to Me on ionization of the 2-phenylethyl system (Chart 6).

Table 3. β-Silicon Effects in Solvolysis of the 2-Phenylethyl- and 1-Phenylethyl Systems

Substrate	Solvent	k/s^{-1} $^{a)}$	k_{rel}	
4a-Cl	97T	1.80×10^{-2}		
4a-OTs	97T	6.7×10^{2} $^{b)}$	9.9×10^{10}	1.3×10^{9}
13 (k_Δ)	97T	5.2×10^{-7} $^{c)}$		1.0
(k_s)	97T	6.8×10^{-9} $^{c)}$	1.0	
1a-OTFA	30D	36.8 $^{d)}$	2.99×10^{5}	1.05×10^{5}
PhCH(OTFA)CH$_3$	30D	3.52×10^{-4} $^{d)}$		1.0
PhCHCH$_2$C(CH$_3$)$_3$ OTFA	30D	1.24×10^{-4} $^{d)}$	1.0	

a) At 25°C. b) Estimated from the rate for the chloride and a tosylate/chloride rate ratio of 3.7×10^4 (Ref. 16). c) Data taken from Ref. 15; the rates, k_Δ and k_s, were calculated from the observed rate at 25°C and a k_Δ/k_s ratio of 76 at 125°C. d) Reported previously (Ref. 10).

Table 4. Substitution Effect of *p*-Methoxyl Group

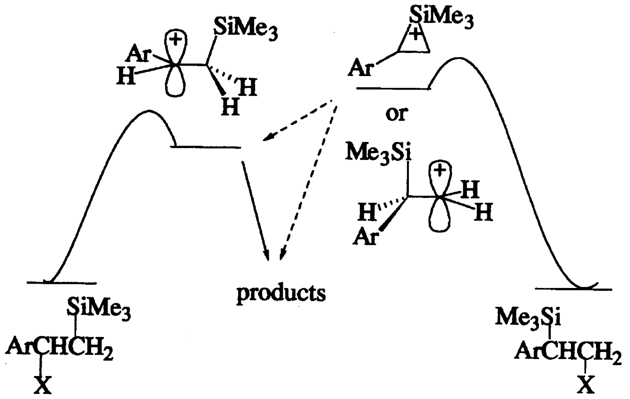
Solvent	$k^{p\text{-MeO}}/k^{\mathrm{H}}$ $^{a)}$	
	4-OTFA	**1-OTFA**
97T	2.11	
30D	2.13	
40D		269

a) At 25°C.

Table 3 includes the β-silicon effect in the 1-phenylethyl system for comparison. Accelerations by a β-SiMe$_3$ group relative to a β-hydrogen and a β-*t*-Bu group were previously quantified to be 1.05×10^5 and 2.99×10^5, respectively;[10)] the result suggests the effect of the β-SiMe$_3$-group relative to methyl to be a factor of ca. 10^5. Thus, the combined results indicate that the β-silicon effect on ionization of the 2-phenylethyl system is more than six-orders of magnitude greater than that of the 1-phenylethyl system. This is attributable to a much greater electronic demand of the primary cationic center involved in the former system than that of the benzylic cationic center involved in the latter system. Like kinetic α-methyl and α-phenyl substitution effects in k_c solvolysis,[17)] the β-silicon effect must increase with increasing the electronic demands of the relevant carbocationic centers.[3,18)]

As Table 4 shows, the substituent effect of a *p*-methoxyl group, $k^{p-\mathrm{MeO}}/k^{\mathrm{H}}$, in solvolysis of **4** is quite different from that in solvolysis of **1**, i. e., a $k^{p-\mathrm{MeO}}/k^{\mathrm{H}}$ ratio of 269 for **1-OAc**, but only 2.1 for **4-OTFA**. The striking difference in the substituent effect clearly indicates that at least two distinct intermediates are involved in ionization of the regioisomeric systems, **1** and **4**. Pronounced acceleration by the *p*-methoxyl group in the former system is consistent with the previous conclusion that solvolysis occurs by the k_c mechanism via the open benzylic cation **2**.[10)]

The small $k^{p-\mathrm{MeO}}/k^{\mathrm{H}}$ ratio of 2.1 in solvolysis of **4-OTFA** eliminates aryl-assisted ionization, since it should exhibit more pronounced $k^{p-\mathrm{MeO}}/k^{\mathrm{H}}$ ratios, i. e., a factor of ca. 10^2.[14)] The inhibition of aryl partici-



Scheme 1.

pation in the 2-arylethyl system, **4**, undoubtedly results from the presence of a β-$SiMe_3$ group, which is superior in its cation-stabilizing ability to a β-aryl group, as indicated by the k(**4a-OTs**)/k_Δ (**13**) ratio of 10^9 (Table 3).

It is instructive to note that the p-MeO-substitution effect in the system **4** is essentially the same as that observed in k_c solvolysis of 2-aryl-1, 1-dimethylethyl chlorides (**14**) reported by Brown and Kim, i. e., $k^{p\text{-MeO}}/k^{H}=1.51$ in 80% aqueous ethanol at 50°C.[19,20] This means that the positive charge on the benzylic carbon is marginal in the transition state of ionization of **4-OTFA**. The results are consistent either with σ(CSi)-assisted ionization (k_Δ) forming the $SiMe_3$-bridged species, **3**, or with unassisted (k_c) ionization forming the open primary cation **5**. In the latter cation, the C^+–C–Si bond angle must be significantly narrow compared to a normal angle (109°) as the result of strong σ(CSi)-π interaction.[3] In view of low stabilities of primary alkyl cations, σ(CSi)-assisted ionization seems more likely to occur; however, the energy difference between the two species, **3** and **5**, may be quite small. Recent theoretical calculations indicate that the SiH_3-bridged form for the primary cation, $SiH_3CH_2CH_2^+$, is slightly more stable than the open, bisected form by only 2.4 kcal mol^{-1} (even in the gas-phase), and that for the secondary cation, $SiH_3C^+HCH_3$, the open form is lower in energy than the bridged form.[3]

Whichever mechanism is really operative in solvolysis of the system, **4**, it can be concluded that ionization of the two regioisomeric systems, **1** and **4**, leads to the distinct intermediates in their rate-determining steps, as illustrated in Scheme 1; the structure of the transition state for **1** resembles the open benzylic cation **2**, which is estimated on the basis of the difference in the reactivities between **1** and **4** to be about 6 kcal mol^{-1} lower in energy than the intermediate formed from **4**, either **3** or **5**. The striking resemblance in the products in the solvolyses of the two regioisomeric systems suggests a common product-forming step from **2**.

Experimental

Proton NMR were recorded in CCl_4 at 60 MHz (Hitachi R-60) and referenced to tetramethylsilane. IR spectra were recorded on a Hitachi R-215 spectrophotometer. Absolute ethanol was distilled twice over sufficient amounts of magnesium ethoxide. Acetone was refluxed with potassium permanganate and distilled; the distillate was dried over potassium carbonate and fractionated. Dioxane was refluxed for 3 d with sodium hydroxide and distilled; the distillate was refluxed for 3 d with metallic sodium, and fractionated. Commercial 2,2,2-trifluoroethanol (Kishida Chemicals) was dried over Molecular Sieves 4A for one week, and distilled over sodium carbonate.

1-Phenyl-2-(trimethylsilyl)ethyl Acetate (1a-OAc). Into a stirred solution of 1-phenyl-2-(trimethylsilyl)ethanol[10] (948 mg) and pyridine (655 mg) in ether (10 cm^3) was added an ethereal solution of acetyl chloride (652 mg) over a period of 10 min and the mixture was stirred at ambient temperature for 3 h. A crude oil obtained after a usual workup was purified by column chromatography on silica gel to give 921 mg (82% yield) of the acetate, **1a-OAc:** IR (neat) 1740, 1250, 1220, 1050, and 840 cm^{-1}; ^{1}H NMR $\delta=-0.10$ (9H, s), 1.17—1.34 (2H, m), 1.94 (3H, s), 5.77 (1H, t, $J=7.8$ Hz), and 7.25 (5H, almost s). Found: C, 66.10; H, 8.35%. Calcd for $C_{13}H_{20}O_2Si$: C, 66.05; H, 8.53%.

1-(p-Methoxyphenyl)-2-(trimethylsilyl)ethyl Acetate (1b-OAc). Into a solution of (trimethylsilyl)methyllithium, prepared from (trimethylsilyl)methyl chloride (6.10 g) and lithium (701 mg) in ether (20 cm^3) at −50°C, was added p-methoxybenzaldehyde (6.45 g) in ether (10 cm^3) over a period of 30 min at −50°C, and the mixture was stirred for 1.5 h at that temperature. A solution of acetyl chloride (3.69 g) in ether (10 cm^3) was added and the mixture was allowed to warm to room temperature. A crude oil obtained after a usual workup was purified by a bulb-to-bulb distillation (120—130°C at 67 Pa) to give the acetate, **1b-OAc** (860 mg): ^{1}H NMR $\delta=-0.11$ (9H, s), 1.16—1.31 (2H, m), 1.90 (3H, s), 2.52 (3H, s), 5.72 (1H, t, $J=7.8$ Hz), and 6.97 (4H, aromatic). Found: C, 63.35; H, 8.21%. Calcd for $C_{14}H_{22}O_3Si$: C, 63.12; H, 8.33%.

2-Phenyl-2-(trimethylsilyl)ethyl Chloride (4a-Cl) and Trifluoroacetate (4a-OTFA). Into a stirred solution of lithium diphenylcuprate prepared from phenyllithium (0.090 mol) and copper(I) iodide (8.19 g) in ether (200 cm^3) was added dropwise 2-(trimethylsilyl)oxirane (2.99 g) at −40°C under argon. The mixture was stirred for 2 h at −40°C and overnight at −15°C. A crude oil obtained after a usual workup was purified by column chromatography on silica gel to give 2-phenyl-2-(trimethylsilyl)ethanol (**6a**, 5.19 g): Mp 65—65.9°C; IR (Nujol) 3200, 1250, 1040, 840, and 690 cm^{-1}; ^{1}H NMR $\delta=-0.06$ (9H, s), 2.27 (1H, dd, $J=9.6$ and 5.4 Hz), 3.68—4.13 (2H, m), and 6.9—7.46 (5H, m). Found: C, 67.75; H, 9.18%. Calcd for $C_{11}H_{18}OSi$: C, 67.99; H, 9.34%. The alcohol was converted into the chloride **4a-Cl** and the trifluoroacetate **4a-OTFA** by the methods described in the literature.[5a,7]

4a-Cl: ^{1}H NMR $\delta=-0.02$ (9H, s), 2.41 (1H, dd, $J=9.0$ and 5.4 Hz), 3.96—4.40 (2H, m), and 6.85—7.44 (5H, m). Found: C, 62.15; H, 8.09%. Calcd for $C_{11}H_{17}ClSi$: C, 62.09; H, 8.05%.

4a-OTFA: IR (neat) 1790, 1360, 1250, 1220, 1150, 840, and 700 cm^{-1}; ^{1}H NMR δ=0.03 (9H, s), 2.59 (1H, dd, J= 10.2 and 5.4 Hz), 4.56—5.05 (2H, m), and 6.90—7.46 (5H, m). Found: C, 53.83; H, 5.98%. Calcd for $C_{13}H_{17}F_3O_2Si$: C, 53.78; H, 5.90%.

2-(*p*-Methoxyphenyl)-2-(trimethylsilyl)ethyl Trifluoroacetate (4b-OTFA). The alcohol, 2-(*p*-methoxyphenyl)-2-(trimethylsilyl)ethanol (**6b**) was prepared in a similar procedure to that described for the preparation of **6a** using lithium bis(*p*-methoxyphenyl)cuprate in 77% yield: Mp 52.8—53.9 °C; IR (Nujol) 3350, 1250, 1200, and 840 cm^{-1}; ^{1}H NMR δ=0.0 (9H, s), 2.28 (1H, dd, J=9.0 and 5.4 Hz), 3.78 (3H, s), 3.8—4.0 (2H, m), and 6.65—7.12 (4H, aromatic). Found: C, 64.18; H, 8.90%. Calcd for $C_{12}H_{16}O_2Si$: C, 64.24; H, 8.98%. The alcohol was converted into the ester **4b-OTFA** by the method described in the literature:[5a)]^{1}H NMR δ=0.02 (9H, s), 2.50 (1H, dd, J=9.6 and 6.0 Hz), 3.73 (3H, s), 4.52—4.98 (2H, m), and 6.64—6.99 (4H, aromatic). Found. C; 52.75; H, 6.21%. Calcd for $C_{14}H_{19}F_3O_3Si$: C, 52.49; H, 5.98%.

Kinetics. Rates were determined UV spectrophotometrically using (4—8)×10^{-5} mol dm^{-3} solutions for the substrates by the same method described previously.[9,10)] All the solvolysis reactions reported followed excellent first-order kinetics; the rates listed in Table 1 were normally determined from the data points (>100) measured during the first three half-lives (R>0.99998).

Ethanolysis of 4a-Cl. Compound **4a-Cl** (0.100 g) was solvolyzed in ethanol (10 cm^3) in the presence of 2,6-lutidine (53 mg, 1.05 equiv) at 50°C for 33 h. A crude oil (83 mg) obtained after a usual workup was a mixture of two compounds in a ration of 84.1 : 15.9. Each compound was isolated by GLC. The major compound was identified as styrene, and the minor one, as (2-ethoxy-2-phenylethyl)-trimethylsilane (**8**): IR (neat) 1250, 1080, and 850 cm^{-1}; ^{1}H NMR δ=−0.03 (9H, s), 0.96—1.17 (2H, m), 1.12 (3H, t, J=7.2 Hz), 3.22 (2H, q, J=7.2 Hz), 4.24 (1H, dd, J=8.4 and 6.6 Hz), and 7.20 (5H, almost s). Found: C, 70.29; H, 10.03%. Calcd for $C_{13}H_{22}OSi$: C, 70.21; H, 9.97%.

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