The γ-Silicon Effect. IV.[1]
The Solvolysis Mechanism of 3-(Aryldimethylsilyl)propyl p-Toluenesulfonates

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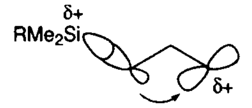
Solvolysis rates of 3-(aryldimethylsilyl)propyl p-toluenesulfonates were determined in various solvents. The reaction mechanism of this simple γ-silyl system was clarified based on the solvent effect and the substituent effect analyses. The solvent effect on this system clearly showed the nucleophilic assistance of solvent, but failed to correlate linearly with the extended Winstein–Grunwald equation, substantiating that the reaction should not proceed through either the formation of the cation intermediate or the S_N2 mechanism. This suggests that the reaction takes place in competition between γ-silyl-assisted (k_{Si}) and solvent-assisted (k_s) pathways, and that the competition ratio varies with solvents and with aryl substituents. Product analysis revealed that the former pathway gave only cyclopropane and the latter gave only the substitution products. The overall k_t value could be dissected into the partial rate constants k_{Si} and k_s for the two pathways by using product ratios. The effects of aryl substituents at the γ-silyl atom on k_{Si} pathway were correlated with unexalted σ° parameter, giving the ρ values of -1.0 in 60E and -1.32 in 97Tw, and reflecting the delocalization of incipient carbocationic charge by participation of the Si–C_γ bond. The substituent effects on the k_s pathway were negligibly small; this is in line with the remote reaction center in the concerted S_N2 mechanism.

The kinetic influences of silicon substituents at the γ-position to the reaction center have been observed in solvolyses of various secondary open-chain and cyclic systems and are denoted as the γ-silicon effect.[2—7] The kinetic γ-silicon effect is ascribed to the interaction of the back lobe of the Si–C_γ bond with the developing vacant p-orbital on the cationic center in the transition state (**1**) (percaudal interaction;[8] Scheme 1).[2—7] The interaction is orientation-dependent, favoring ionization from a W-conformation with respect to the Si–C–C–C–Lv skeleton. However, the primary open-chain system, in which the W-conformation between γ-silyl and leaving groups is unenhanced due to the flexible Si–C–C–C–Lv chain, has never been studied in detail.[3,8]



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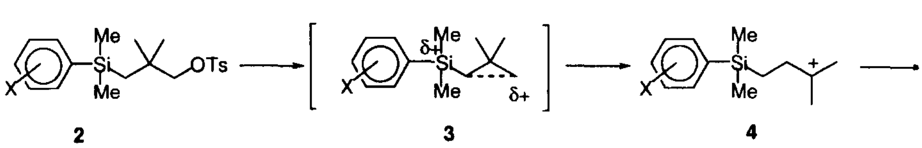
Scheme 1.

Recently, we have elucidated the characteristic feature of the γ-silyl-assisted solvolyses of 3-(aryldimethylsilyl)-2,2-dimethylpropyl tosylates (OTs; p-toluenesulfonates) (**2**) which showed large rate acceleration of 10^3—10^4 compared with the γ-H derivative, neopentyl (2,2-dimethylpropyl) OTs.[9] The solvent effect on this γ-silyl-assisted solvolysis has been analyzed by using the Winstein–Grunwald equation.[9a] The result demonstrates a significant degree of the delocalization of developed cationic charge by the γ-silyl group via the assisting Si–C_γ bond in the transition state (**3**). Products were derived exclusively from the tertiary cation (**4**), which is formed by rearrangement of the (aryldimethylsilyl)methyl group (Scheme 2).[9] The effect of aryl substituents at the Si atom on this solvolysis was correlated with unexalted σ° parameter, giving the ρ value of -1.0.[9b] This indicates that there exists a certain extent of positive charge on the γ-silicon atom, reflecting the delocalization of incipient carbocationic charge by participation of the Si–C_γ bond. More important, the magnitude of ρ value can be regarded as the effect of aryl ring on γ-Si via percaudal interaction in the rate-determining step. All these results were in line with the rate-determining formation of the bridged transition state **3** stabilized by the γ-silyl group.



Scheme 2.

In the case of the secondary open-chain system, the percaudal interaction was favored by methyl substitution at the β position, as is evident from the stepwise increase in reaction rate of 1 : 7 : 57 with methyl substitution at C_β for the solvolysis of 1-methyl-3-(trimethylsilyl)propyl system in 80% (v/v) aq ethanol (80E) at 25 °C.[3] In order to substantiate the γ-silicon effect in the primary system, which has flexible Si–C–C–C–Lv geometry, we have undertaken detailed studies on the solvolysis mechanism of 3-(aryldimethylsilyl)propyl tosylate (**5**(X)) (Chart 1). In this paper, the solvolysis of **5** is discussed based on the effects of substituents, solvents, and deuterium isotope, in comparison with the γ-silyl-assisted solvolysis of 3-(aryldimethylsilyl)-2,2-dimethylpropyl system **2** reported in previous papers.[9]

Results and Discussion

The tosylates **5** were synthesized for a wide range of ring substituents X from 3-(aryldimethylsilyl)propyl chlorides which were prepared by the reaction of 3-(chlorodimethylsilyl)propyl chloride with arylmagnesium bromides, followed by the reaction of their Grignard reagents with oxygen gas and esterification of the corresponding propanols. The α-d_2 alcohols were prepared by lithium aluminum deuteride (lithium tetradeuterioaluminate) reduction of ethyl 3-(aryldimethylsilyl)propionates, which were synthesized as described in the previous paper.[9a]

The solvolysis rates of **5** with various ring substituents were determined conductimetrically in 60% (v/v) aq ethanol (60E), 70% (w/w) aq 2,2,2-trifluoroethanol (70Tw) at 70 °C, and 97% (w/w) aq 2,2,2-trifluoroethanol (97Tw) at 75 °C. The rate constants are listed in Table 1. The solvolysis rates of p-MeO, H, and m-CF_3 derivatives were measured in various binary solvents at 45 °C in order to examine the solvent effect and are summarized in Table 2 together with solvent parameters.

Table 1. Rate Constants for Solvolysis of 3-(Aryldimethylsilyl)propyl Tosylates **5**

	$10^5 \times k/s^{-1}$		
Substituent	60E[a)] at 70 °C	70Tw[b)] at 70 °C	97Tw[c)] at 75 °C
p-MeO	6.269	5.845	4.297
p-Me	6.024	5.952	5.191
m-Me	5.798	5.171	4.291
H	5.749	4.204	3.317
m-Cl-p-MeO	5.680	2.906	1.687
p-Cl	5.785	2.519	1.552
m-CF_3	5.204	1.480	0.7452

a) 60% (v/v) aq ethanol. b) 70% (w/w) aq 2,2,2-trifluoroethanol. c) 97% (w/w) aq 2,2,2-trifluoroethanol.

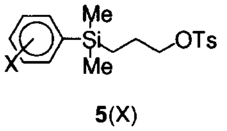
Table 2. Rate Constants for Solvolyses of 3-[p-Methoxyphenyl(dimethyl)silyl]-, 3-(Dimethylphenylsilyl)-, and 3-[Dimethyl(m-trifluoromethylphenyl)silyl]propyl Tosylates at 45 °C and Solvent Parameters

	$10^5 \times k/s^{-1}$				
Solvent[a)]	p-MeO	H	m-CF_3	Y_{OTs}[b)]	N_{OTs}[b)]
100E	0.1361	0.1093	0.1102	−1.749	0.00
90E	0.2383	0.1844	0.2259	−0.623	0.01
80E	0.2725	0.2525	0.3024	0.000	0.00
70E	0.3798	0.3528	0.3281	0.487	−0.05
60E	0.4609	0.4260	0.4202	0.951	−0.09
50E	0.6942	0.5604	0.5420	1.373	−0.11
40E	1.030	0.9515	0.7618	1.968	−0.22
30E	1.812	1.754	1.364	2.665	−0.31
80A		0.0214		−0.950	−0.42
70A		0.0545		−0.197	−0.38
60A	0.1374	0.1176	0.1125	0.447	−0.34
50A	0.3141	0.2752	0.2163	1.090	−0.35
40A	0.5733	0.5291	0.3822	1.748	−0.39
30A	1.425	1.119	0.6666	2.412	−0.40
TFE		0.3380		1.764	−3.00
97Tw	0.3175	0.2195	0.0462	1.833	−2.79
80Tv	0.3023	0.2115	0.0682	1.919	−1.90
70Tw	0.3503	0.2739	0.0729	2.004	−1.20
50Tv	0.4433	0.3406	0.1239	2.147	−1.14
40Tv	0.5052	0.4196	0.1640	2.270	−0.92
30Tv	0.7477	0.4871	0.2401	2.434	−0.80

a) Volume percent of first-named organic component, unless otherwise noted. Abbreviation; E = ethanol, A = acetone, and TFE = T = 2,2,2-trifluoroethanol. Tw and Tv mean weight percent and volume percent of TFE–H_2O, respectively. b) Data taken from Refs. 9a and 19a.

The H derivative solvolyzes slightly slower than the nonsilylated derivative, propyl tosylate ($k = 6.804 \times 10^{-5}/s^{-1}$) in 60E at 70 °C. The absence of significant rate enhancement by the γ-silyl substitution in the propyl system might indicate that the solvolysis mechanism of γ-silylated **5**(H) is similar to that of 1-propyl tosylate in highly nucleophilic 60E. Thus, the solvolysis mechanism of **5**(H) in 60E can be regarded as an S_N2 mechanism. On the other hand, it solvolyzes 3.4 times faster than the parent tosylate ($k = 1.231 \times 10^{-5}/s^{-1}$) in 70Tw at 70 °C. In such a less nucleophilic solvent, the solvolysis of the present γ-silyl compound appears to proceed partly through the carbocationic intermediate influenced by the γ-silyl group.

The rate change with ring substituents was fairly small but varied with solvents; only 1.2-fold in highly nucleophilic 60E, while 4-fold in less nucleophilic solvent 70Tw and 7-fold in extremely less nucleophilic solvent 97Tw for a wide range of substituent changes from the p-MeO to m-CF_3 (Table 1). These facts indicate a mechanistic transition with solvent nucleophilicity.



5(X)

X = p-MeO
m-Cl-p-MeO
p-Me
m-Me
H
p-Cl
m-CF_3

Chart 1.

Solvent Effect. The solvent effect on the solvolysis of **5**(H) does not follow any simple linear relationship (Fig. 1; Table 3) by the Winstein–Grunwald equation 1[10] using the 2-adamantyl Y_{OTs} parameter:[11]

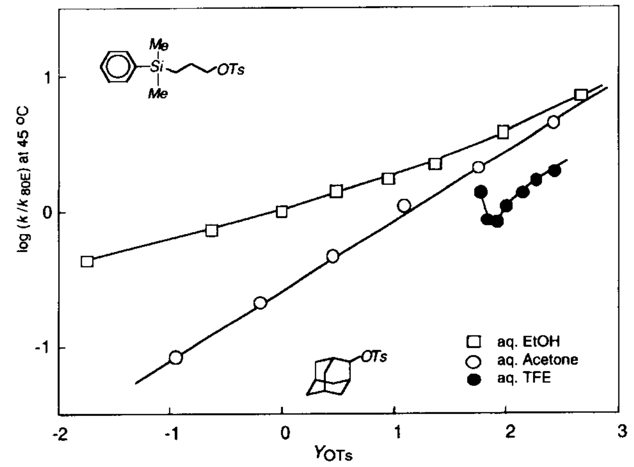


Fig. 1. The mY_{OTs} plots for the solvent effect of the solvolysis of 3-(dimethylphenylsilyl)propyl tosylate **5**(H) at 45 °C.

Table 3. Correlation Analyses of Solvent Effects on Solvolyses of **5** at 45 °C by Eqs. 1 and 2

Subst.	m	l	$R^{a)}$	± SD$^{b)}$	$n^{c)}$
p-MeO	0.19		0.75	0.21	18
	0.26	0.22	0.88	0.15	
H	0.26		0.76	0.29	21
	0.32	0.21	0.85	0.24	
m-CF_3	0.06		0.19	0.40	18
	0.22	0.52	0.89	0.19	

a) Correlation coefficients. b) Standard deviations. c) Numbers of data involved.

$$\log(k/k_{80\mathrm{E}}) = mY_{\mathrm{OTs}}. \tag{1}$$

As shown in Fig. 1, the aq ethanol and aq acetone plots fall on separate lines with remarkably reduced slopes of 0.2—0.3, similar to those observed for the typical S_N2 substrates such as methyl tosylate.[11] Plots for less nucleophilic solvents, aq TFE (2,2,2-trifluoroethanol) series, lie below the line for the aq acetone series, while the highly nucleophilic solvents, aq ethanol series, are plotted above the aq acetone line. The dispersions between binary solvent mixtures are clearly consistent with an involvement of solvent nucleophilicity. Similar results are obtained for the solvolyses of p-MeO and m-CF_3 derivatives. For the m-CF_3 derivative, the extent of the dispersion of the aq TFE from the aq acetone line in the lower direction seems to be slightly greater than those observed for the other derivatives. The results of mY_{OTs} correlations indicate that the present solvolyses proceed through the nucleophilically solvent-assisted mechanism.

Consequently, we evaluated the involvement of nucleophilic solvent assistance by using the extended Winstein–Grunwald Equation 2:[11]

$$\log(k/k_{80\mathrm{E}}) = mY_{\mathrm{OTs}} + lN_{\mathrm{OTs}}, \tag{2}$$

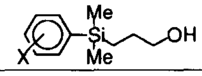
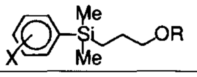
where l represents the sensitivity to changes in solvent nucleophilicity (N_{OTs}). The treatments with Eq. 2 obviously gave no simple linear relationships but negligibly improved correlations with small positive contributions (l) of the solvent nucleophilicity for these three γ-silyl compounds, as listed in Table 3. The m values (0.2—0.3) are essentially the same for all substrates, while the contribution of the solvent nucleophilicity for the m-CF_3 derivative ($l = 0.5$) is significantly larger than those ($l = 0.2$) for p-MeO and H derivatives. The failure of the correlations with Eqs. 1 and 2 for the solvolyses of **5** provides evidence for the conclusion that the reaction should not proceed through either the formation of the cation intermediate or the S_N2 mechanism. In other words, these results suggest that the solvolysis reaction takes place in competition between γ-silyl-assisted and solvent-assisted solvolyses, and that the ratio varies with solvents and with aryl substituents.

Product Analysis. Product analyses for the present solvolyses were carried out in mixed solvents of D_2O and deuterated organic components, such as 60E and ethanol (100E) regarded as highly nucleophilic solvents and 70Tw and 97Tw as less nucleophilic solvents in the presence of excess 2,6-lutidine at 75 °C, by using ^{1}H NMR method. The products from these solvolyses were found to be exclusively the substitution products and cyclopropane, as summarized in Table 4.

The substitution products were major products in 60E for all substrates, accompanied by a small amount (4—16%) of cyclopropane which slightly increased with the electron-donating aryl substituent. In 100E, a more nucleophilic and less ionizing solvent than 60E, the substitution product (the ethyl ether) was obtained exclusively for all derivatives without cyclopropane ($\leq 1\%$). On the other hand, in a less nucleophilic and highly ionizing solvent, 70Tw, the major product was cyclopropane (53—84%) along with minor substitution products. In 97Tw, a still less nucleophilic solvent, cyclopropane was formed exclusively ($\geq 94\%$).

Cyclopropane should be exclusively formed by the 1,3-elimination from the carbocation stabilized by γ-silyl group, therefore, the present solvolysis of **5** proceeds exclusively via the γ-silyl-assisted pathway in 97Tw. In the solvolyses of 1-methyl-3-trimethylsilylpropyl and 1,2-dimethyl-3-trimethylsilylpropyl brosylates (p-bromobenzenesulfonates), the solvolyses were found to proceed without nucleophilic assistance by solvent, producing mainly the substitution products accompanied by the minor product of the cyclopropane analogue.[2a,2b] As a result, the substitution products can be derived from the γ-silyl-assisted pathway. Therefore, the substitution products should be considered to arise not only from the S_N2 displacement reaction but also from the bridged cation. However, the solvent effects in solvolyses of **5** clearly showed the dependence on the solvent nucleophilicity in contrast to those of the 1-methyl-3-silylpropyl system. Thus, we carried out the product analysis of the α-d_2 labeled **5**. Although the signals of alcohol and ether were not separated in the ^{1}H NMR, the products in the solvolyses of p-MeO, H, and m-CF_3 derivatives of the α-d_2 labeled **5** appear to be essentially the same as those for undeuterated substrates in 60E and 70Tw, as shown in parentheses of Table 4. It is an important finding that the d_2 scrambled tosylates or alcohols and ethers, which should arise as a result from the internal return or the

Table 4. Products for Solvolyses of **5** at 75 °C[a)]

Solv.[b)]	Subst.			Cyclopropane[c)]
100E	*p*-MeO	—	99	1
	H	—	>99	<1
	m-CF_3	—	100	0
60E	*p*-MeO	46	38	16 (14)
	p-Me	48	39	13
	m-Me	48	40	12
	H	49	40	11 (8)
	m-Cl-*p*-MeO	52	41	7
	p-Cl	53	41	6
	m-CF_3	52	44	4 (2)
70Tw	*p*-MeO	16	0	84 (83)
	p-Me	16	0	84
	m-Me	17	0	83
	H	21	0	79 (77)
	m-Cl-*p*-MeO	28	0	72
	p-Cl	31	0	69
	m-CF_3	46	1	53 (51)
97Tw	*p*-MeO	0	0	100
	H	<1	>1	98
	m-CF_3	2	4	94

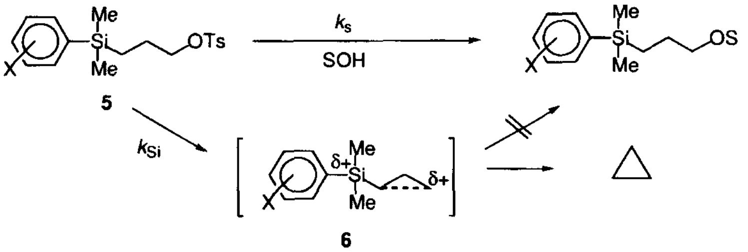
a) Products, given as percentage, were determined by ^{1}H NMR in situ. All reactions were carried out in the presence of 2,6-lutidine in deuterated solvents up to the completion. b) See footnote a of Table 2. c) Values in the parentheses are obtained for the solvolyses of α-d_2 labeled substrates.

substitution with solvent(s) at the bridged intermediate, were not observed in both solvents at all. As a conclusion, the γ-silyl-assisted pathway does not give the substitution products but exclusively the 1,3-elimination product, cyclopropane; furthermore, the substitution products should arise from the solvent-assisted pathway in the solvolyses of **5**, as depicted in Scheme 3. This is supported by the exclusive formation of the substitution product in 100E characterized as a highly nucleophilic and less ionizing solvent.

Consequently, for the solvolysis of **5** in a highly nucleophilic solvent such as aq ethanol series, the solvent-assisted pathway might be preferred to the γ-silyl-assisted pathway, but the latter pathway appears to be enhanced slightly with the increase of water content. On the other hand, in the less nucleophilic and highly ionizing solvent such as aq TFE series, the solvolysis of **5** occurs preferentially through the γ-silyl-assisted pathway, while in more aqueous solvents the reaction proceeds to a greater extent through the solvent-assisted pathway. In each solvent, an electron-donating aryl substituent at the silicon atom increases an amount of cyclopropane due to facilitating the formation of the cation stabilized by the γ-silyl group.

Kinetic Deuterium Isotope Effect. The kinetic deuterium isotope effects at α position to reaction center in the solvolyses of *p*-MeO, H, and *m*-CF_3 derivatives of **5** were measured conductimetrically in 100E, 60E, 70Tw, and 97Tw at 75 °C. The α-d_2 effects are summarized in Table 5 together with the relevant literature data.[3,12]

In 97Tw for the solvolysis of **5**, which reacts exclusively via the γ-silyl-assisted pathway without nucleophilic assistance by solvent, the α-d_2 effect was observed to be $k_H/k_D = 1.18$—1.20 per d_2. This is an intermediate value between the α-d_2 effect for a solvent-assisted solvolysis ($k_H/k_D = 1.0$)[13] and that for a limiting reaction, k_c solvolysis ($k_H/k_D = 1.22$ per d_1),[14] and is comparable to those observed in the alkyl-assisted solvolysis of neopentyl system, the β-aryl-assisted solvolysis of neophyl (2-methyl-2-phenylpropyl) system,[12] and the γ-silyl-assisted solvolysis of 2,2-dimethyl-3-(trimethylsilyl)propyl system[3] (Table 5). Since the kinetic isotope effect (KIE) depends slightly on temperature,



Scheme 3.

Table 5. α-D_2 Kinetic Isotope Effects for Solvolyses of **5** at 75 °C and Relevant Systems

System	Solv.,[a] Temp	k_H[b]	k_D[c]	k_H/k_D[d]	%Δ[e]
3-(Aryldimethylsilyl)propyl tosylates (**5**)					
p-MeO	100E, 75 °C	2.258	2.231	1.012	1
H		1.891	1.896	0.998	<1
m-CF_3		1.900	1.847	1.028	0
p-MeO	60E, 75 °C	9.028	8.525	1.059	16
H		8.640	8.229	1.050	11
m-CF_3		7.732	7.453	1.037	4
p-MeO	70Tw, 75 °C	8.713	7.444	1.170	84
H		6.683	5.747	1.163	79
m-CF_3		2.316	2.083	1.112	53
p-MeO	97Tw, 75 °C	4.297	3.630	1.184	100
H		3.317	2.804	1.183	98
m-CF_3		0.7452	0.6226	1.197	94
2,2-Dimethyl-3-(trimethylsilyl)propyl brosylate[f]					
	80E, 25 °C	0.5411		1.221	
	97Tw, 25 °C	14.37		1.221	
Neopentyl brosylate[h]					
	AcOH, 100 °C[g]	2.82		1.187	
	CF_3COOH, 65 °C	7.74		1.190	
2-Methyl-2-adamantanemethyl brosylate[h]					
	AcOH, 100 °C	17.3		1.190	
	CF_3COOH, 25 °C	3.30		1.228	
	45 °C	36.3		1.20	
Neophyl brosylate					
	70Tw, 25 °C[i]	0.3965		1.272	
	AcOH, 75 °C[h]	6.99		1.214	
	CF_3COOH, 0 °C[h]	7.62		1.247	

a) See footnote a of Table 2. b) Rate constants (10^5k (s^{-1})) for the undeuterated substrate. c) Rate constants (10^5k (s^{-1})) for the α-d_2 labeled substrate. d) Per d_2. e) Product yield (%) of cyclopropane. f) Ref. 3. g) *p*-Nitrobenzenesulfonate. h) Ref. 12b. i) Methanesulfonate; Ref. 12a.

solvent, and leaving group, as shown for the solvolysis of the neophyl system in Table 5, the α-d_2 effect for the solvolysis of **5** in 97Tw implies that the solvolysis proceeds through the transition state involving neighboring group participation of the Si–C_γ bond. On the other hand, the KIEs in 100E were almost negligible, implying the solvent-assisted mechanism. These facts are in line with the exclusive formation of cyclopropane in 97Tw and of ethyl ether derivative in 100E.

The KIE values of the present system **5** are in the range of $k_H/k_D = 1.0$ for the solvent-assisted solvolysis in 100E, and $k_H/k_D = 1.18$ for the γ-silyl-assisted solvolysis in 97Tw. The effects in 60E were similar to but a little larger than unity for solvent-assisted solvolysis, indicating that the reactions in this solvent proceed predominantly via the solvent-assisted pathway, with a minor part proceeding via the γ-silyl-assisted pathway. The effects in 70Tw were similar to but even smaller than that for γ-silyl-assisted solvolysis, implying that the γ-silyl-assisted pathway is preferable to the competing solvent-assisted pathway in this solvent. In both solvents, the introduction of a substituent on phenyl ring bearing the γ-silicon atom significantly affected the α-d_2 effect. These effects arise as a result of varying fractions of the γ-silyl-assisted pathway, which competes with the solvent-assisted pathway, due to changing the solvent and the substituent. Namely, the fraction of γ-silyl-assisted pathway increases with decrease in the solvent nucleophilicity and with the increasing electron-donating aryl substituent on γ-silyl group. The magnitudes of the KIE are parallel to product ratios (%) of cyclopropane (see last column of Table 5). Thus, the above interpretations are consistent with the results of the product analysis.

Substituent Effect. The Yukawa–Tsuno (Y–T) Equation 3 is one of the most useful tools to predict the nature of a transition state whose reaction center is modified by the benzene π-system:[15]

$$\log(k/k_0) = \rho(\sigma^\circ + r\Delta\bar{\sigma}_R^+) \qquad (3)$$

Here σ° is the normal substituent constant, which involves no additional π-electronic interaction between substituent and reaction center; $\Delta\bar{\sigma}_R^+$ is the resonance substituent constant measuring the capability for π-delocalization of *p*-π-electron-donor substituent, defined by $\sigma^+ - \sigma^\circ$.[15,16] The r value is a parameter characteristic of a given reaction, measuring the degree of resonance interaction between aryl group and reaction site in the rate-determining step.

The rate of the *p*-MeO derivative is slower than that of the *p*-Me derivative in 97Tw, indicating that the substituent effect on this solvolysis can be characterized as the resonance unexalted σ° reactivity ($r \cong 0$). As shown in Fig. 2, the logarithms of the relative rates in 97Tw at 75 °C were correlated directly with σ°, giving a ρ value of -1.32. In fact, an application of *Y–T* Eq. 3 affords good correlations with $r = -0.03\pm0.02$. The small but negative ρ value obtained suggests that a significant amount of positive charge resides on the Si atom at the γ-position. The r value of 0.0 assigned for this system may be explicable if the phenyl π-system on the γ-silicon atom interacts through the Si–C σ-bond only indirectly (by non-π-interaction mechanism) with the carbocationic reaction center in **6**. The magnitude of substituent effect obtained in 97Tw is similar to that ($\rho = -1.10$ and $r = -0.03$) for the γ-silyl-assisted solvolysis of 3-(aryldimethylsilyl)-2,2-dimethylpropyl brosylate **2** in 97Tw described in the previous paper.[9b]

Substituent effects for the solvolysis of **5** in 60E at 70 °C were plotted against σ° in Fig. 3 and the essentially horizontal plot ($\rho = -0.09$) plausibly means that the solvolysis in 60E predominantly proceeds via the solvent-assisted mechanism. This is substantiated by the major yield (96—84%) of substitution products for all substituents. On the other hand, as shown in Fig. 4, the analysis for the solvolysis of **5** in 70Tw gave $\rho = -0.95\pm0.04$ with σ° ($R = 0.997$ and SD = ±0.02) which are close to those for the solvolysis of **5** in 97Tw and also the solvolysis of **2**. This demonstrates

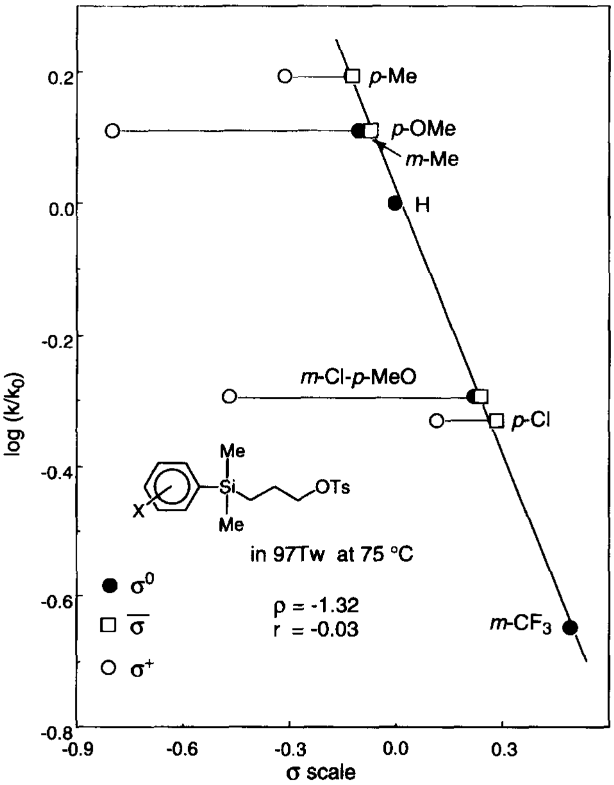


Fig. 2. *Y–T* plots for the solvolysis of 3-(aryldimethylsilyl)propyl tosylates **5** in 97% (w/w) aqueous 2,2,2-trifluoroethanol at 75 °C; open circles, σ^+, closed circles, σ°, and open squares, $\bar{\sigma}$ for $r = -0.03$.

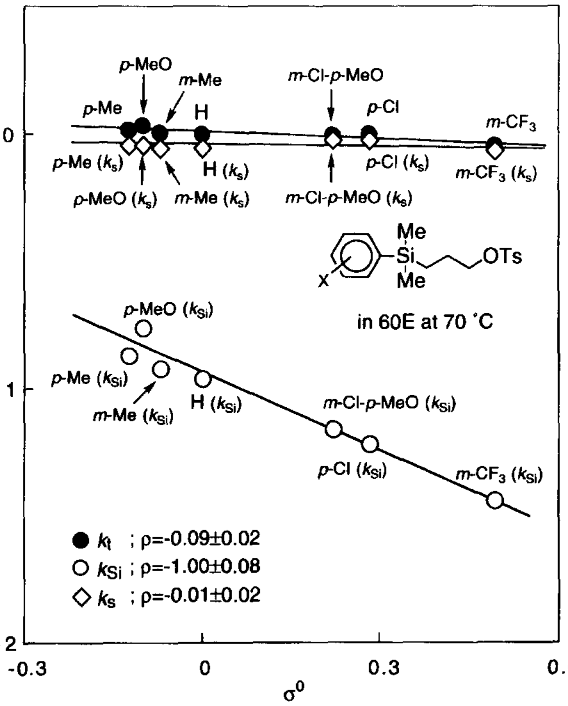


Fig. 3. σ° plots for the solvolysis of 3-(aryldimethylsilyl)propyl tosylates **5** in 60% (v/v) aqueous ethanol at 70 °C; closed circles for k_t, open circles for k_{Si}, and open diamonds for k_s.

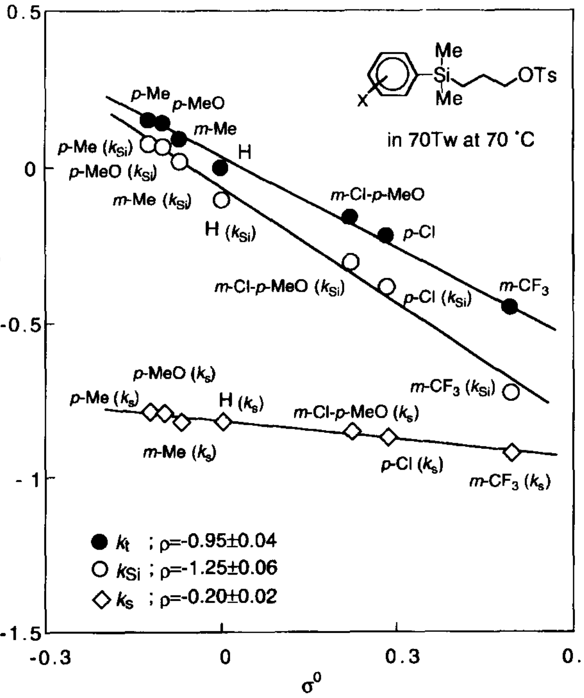


Fig. 4. σ° plots for the solvolysis of 3-(aryldimethylsilyl)propyl tosylate **5** in 70% (w/w) aqueous 2,2,2-trifluoroethanol at 70 °C; closed circles for k_t, open circles for k_{Si}, and open diamonds for k_s.

that the solvolysis of **5** in 70Tw proceeds mainly through the γ-silyl-assisted carbocation **6**. In fact, the product analysis shows the major yield (53—84%) of cyclopropane for all substituents.

However, for the solvolysis of **5** in both solvents 60E and 70Tw, the substituent effects on apparent rates might not be meaningful because of the competition between the solvent-assisted and γ-silyl-assisted mechanisms. In other words, the apparent rate constants, k_t, are expressed by the sum of the rate constants for γ-silyl-assisted (k_{Si}) and solvent-assisted (k_s) pathways; $k_t = k_{Si}+k_s$. The overall rate constants k_t should be divided into the composite rate constants k_{Si} and k_s in order to analyze the mechanism quantitatively. Assuming the products to be entirely kinetic controlled, one may represent k_{Si} and k_s as follows:

$$k_{Si} = k_t \times P_{Si}/(P_{Si}+P_s), \qquad (4)$$

$$k_s = k_t \times P_s/(P_{Si}+P_s). \qquad (5)$$

Here P_{Si} and P_s are the product percent ratios for the γ-silyl-assisted (k_{Si}) and the solvent-assisted (k_s) pathways, respectively. As cyclopropane and the substitution products were derived from the γ-silyl-assisted mechanism and the S_N2 displacement, respectively, the P_{Si} and P_s can be calculated from the amounts of cyclopropane and substitution products in Table 4, respectively. Thus, the overall k_t in Table 1 could be dissected into the partial rate constants k_{Si} and k_s by using product ratios, as summarized in Table 6.

The exact substituent effects on the solvolyses in 60E and 70Tw are displayed clearly in Figs. 3 and 4, respectively, where the logarithms of the overall k_t (closed circles), k_{Si} (open circles), and k_s (open diamonds) are plotted against σ°. The existence of linear relationships indicates that k_{Si} and k_s pathways should proceed by the mechanisms without enhanced π-delocalization interaction of the p-π-electron-

Table 6. Overall and Partial Rate Constants[a] and Product Ratios Obtained for Solvolyses of **5** in 60E and 70Tw at 70 °C

Solvent[b]	Substituent	P_{Si}/P_s[c]	k_t[d]	k_{Si}[e]	k_s[f]
60E	p-MeO	16/84	6.269	1.003	5.266
	p-Me	13/87	6.024	0.783	5.241
	m-Me	12/88	5.798	0.696	5.102
	H	11/89	5.749	0.632	5.117
	m-Cl-p-MeO	7/93	5.680	0.398	5.282
	p-Cl	6/94	5.785	0.347	5.438
	m-CF$_3$	4/96	5.204	0.208	4.996
70Tw	p-MeO	84/16	5.845	4.910	0.935
	p-Me	84/16	5.952	5.000	0.952
	m-Me	83/17	5.171	4.292	0.879
	H	79/21	4.204	3.321	0.883
	m-Cl-p-MeO	72/28	2.906	2.092	0.814
	p-Cl	69/31	2.519	1.738	0.781
	m-CF$_3$	53/47	1.480	0.784	0.696

a) 10^5k (s^{-1}). b) See footnote a of Table 2. c) At 75 °C; P_{Si} = % of cyclopropane and P_s = % of substitution products (the alcohol and the ether). d) Overall rate constants. e) $k_t \times P_{Si}/100$. f) $k_t \times P_s/100$.

Table 7. Substituent Effect Analysis for γ-Silyl-Assisted Solvolyses By Y–T Eq. 3.

System (Solv., Temp)	ρ	r	R[a]	SD[b]	n[c]
3-(Aryldimethylsilyl)propyl tosylates (**5**)					
60E, 70 °C[d]	−0.97±0.07	0.10±0.06	0.992	±0.04	7
	−1.00±0.08	0.00[e]	0.983	±0.05	7
70Tw, 70 °C[d]	−1.24±0.05	0.06±0.03	0.997	±0.03	7
	−1.25±0.06	0.00[e]	0.994	±0.04	7
97Tw, 75 °C	−1.32±0.04	−0.03±0.02	0.998	±0.02	7
	−1.32±0.04	0.00[e]	0.998	±0.02	7
3-Aryldimethylsilyl-2,2-dimethylpropyl brosylates[f]					
60E, 50 °C	−0.85±0.06	0.05±0.07	0.993	±0.03	7
	−0.87±0.05	0.00[e]	0.992	±0.03	7
97Tw, 50 °C	−1.10±0.01	−0.03±0.01	0.9998	±0.007	7
	−1.08±0.02	0.00[e]	0.9993	±0.01	7

a) Correlation coefficients. b) Standard deviations. c) Numbers of substituents involved. d) For dissected k_{Si} rates. e) Against σ°. f) Ref. 9b.

donor substituent.

The dissected partial rate constants for the k_{Si} pathway in 60E were linearly correlated with σ° to give $\rho = -1.00$. The ρ value of -1.25 was obtained by the same treatment for the k_{Si} in 70Tw. These ρ values were quite close to those for the solvolyses of **5** in 97Tw and 3-(aryldimethylsilyl)-2, 2-dimethylpropyl brosylate **2** in 60E ($\rho = -0.87$) and 97Tw ($\rho = -1.08$), respectively, as summarized in Table 7.[9b] In each solvent, the k_{Si}-correlation against unexalted σ° scale with a small ρ value is consistent with the structure of the Si–C$_\gamma$ bridged transition state **1** or **6**, as discussed in the previous paper.[9b]

The substituent effect on the partial rates for the k_s pathway was characterized by negligibly small ρ values of -0.01 ± 0.02 in 60E (SD = ±0.01) and -0.20 ± 0.02 in 70Tw ($R = 0.98$ and SD = ±0.01) with unexalted σ°. These essentially horizontal k_s-correlations which were not affected by the aryl substituent at the γ-silicon atom are compatible with those for the concerted S_N2 displacement mechanism having the remote reaction center of no significant cationic charge.

In conclusion, the solvolysis of **5** can thus be described as competing reactions of the γ-silyl-assisted (k_{Si}) and the solvent-assisted (k_s) pathways, as outlined in Scheme 3. The ratio of the two pathways depends on the solvolyzing solvent and the X-substituent on γ-silicon atom. Small rate acceleration of the γ-silylpropyl relative to 1-propyl does not imply the less effective assistance of γ-Si in the solvolysis of the present system **5**, compared with the large one (10^3—10^4) in the solvolysis of **2**. Since there are no rate data available for the S_N1 solvolysis of the parent 1-propyl system, the kinetic γ-silicon effect can not be estimated properly, because the nucleophilic solvent assistance becomes advantageous due to the less crowdedness of the reaction center carbon of **5**. As the silylmethyl in **2** shows significant percaudal acceleration comparable with the *p*-methoxyphenyl participation in the neophyl system,[17] the silyl function in **5** also shows percaudal driving force of comparable significance with the *p*-methoxyphenyl participation in the 2-arylethyl system,[18] though the significance of either participation is in fact made obscure by enhanced solvent participation in the latter simple primary system. The Si–C$_\gamma$ assistance is stronger than the solvent-assistance by the less nucleophilic solvents and weaker than the solvent-assistance by the nucleophilic solvents in the simple *n*-propyl system.

Experimental

Column chromatography was performed by using Silica Gel 60 (Merck, 230—400 mesh). The ^{1}H NMR spectra were taken on a JEOL JNM-A500 FT-NMR spectrometer operating at 500 MHz (in $CDCl_3$) or a Hitachi R-600 FT-NMR spectrometer operating at 60 MHz (in CCl_4) and the chemical shifts were recorded in ppm (δ) downfield from TMS as an internal standard. All air- and moisture-sensitive reactions were carried out under nitrogen. Ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone under nitrogen.

Materials. 3-(Dimethylphenylsilyl)propyl Chloride. To a solution of phenylmagnesium bromide prepared from bromobenzene (8.64 g, 55.0 mmol) and Mg (1.33 g, 54.7 mmol) in 50 cm^3 of ether was added dropwise a solution of 3-(chlorodimethylsilyl)propyl chloride (8.56 g, 50.0 mmol) in 50 cm^3 of ether with stirring at 0 °C. The reaction mixture was heated under reflux with stirring overnight. After cooling, the reaction mixture was treated with NH_4Cl (5.88 g, 0.11 mol) in 60 cm^3 of water, and extracted with ether. The ethereal extract was washed with aqueous saturated sodium chloride and then dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give 11.97 g of crude product. Purification by column chromatography afforded 9.57 g (yield, 90%) of the chloride as a colorless oil: ^{1}H NMR (500 MHz) δ = 0.29 (6H, s, Si–CH_3), 0.83—0.87 (2H, m, CH_2), 1.72—1.80 (2H, m, CH_2), 3.48 (2H, t, J = 6.9 Hz, CH_2), 7.35—7.51 (5H, m, Ar–H). By the same procedure, the following chlorides were prepared from the corresponding bromobenzenes.

3-[*p*-Methoxyphenyl(dimethyl)silyl]propyl Chloride: ^{1}H NMR (500 MHz) δ = 0.26 (6H, s, Si–CH_3), 0.80—0.84 (2H, m, CH_2), 1.72—1.79 (2H, m, CH_2), 3.48 (2H, t, J = 6.9 Hz, CH_2), 3.81 (3H, s, OCH_3), 6.91 (2H, d, J = 8.2 Hz, Ar–H), 7.42 (2H, d, J = 8.2 Hz, Ar–H).

3-[(*m*-Chloro-*p*-methoxyphenyl)dimethylsilyl]propyl Chloride: ^{1}H NMR (500 MHz) δ = 0.26 (6H, s, Si–CH_3), 0.80–0.85 (2H, m, CH_2), 1.73–1.79 (2H, m, CH_2), 3.48 (2H, t, J = 6.8 Hz, CH_2), 3.80 (3H, s, OCH_3), 6.87—7.45 (3H, m, Ar–H).

3-[Dimethyl(*p*-methylphenyl)silyl]propyl Chloride: ^{1}H NMR (500 MHz) δ = 0.27 (6H, s, Si–CH_3), 0.81—0.85 (2H, m, CH_2), 1.72—1.80 (2H, m, CH_2), 2.35 (3H, s, CH_3), 3.48 (2H, t, J = 6.7 Hz, CH_2), 7.18 (2H, d, J = 7.8 Hz, Ar–H), 7.39 (2H, d, J = 7.8 Hz, Ar–H).

3-[Dimethyl(*m*-methylphenyl)silyl]propyl Chloride: ^{1}H NMR (500 MHz) δ = 0.28 (6H, s, Si–CH_3), 0.82—0.86 (2H, m, CH_2), 1.73—1.80 (2H, m, CH_2), 2.36 (3H, s, CH_3), 3.48 (2H, t, J = 7.0 Hz, CH_2), 7.14—7.31 (4H, m, Ar–H).

3-(*p*-Chlorophenyldimethylsilyl)propyl Chloride: ^{1}H NMR (500 MHz) δ = 0.28 (6H, s, Si–CH_3), 0.82—0.86 (2H, m, CH_2), 1.71—1.77 (2H, m, CH_2), 3.48 (2H, t, J = 7.0 Hz, CH_2), 7.33 (2H, d, J = 8.3 Hz, Ar–H), 7.41 (2H, d, J = 8.3 Hz, Ar–H).

3-[Dimethyl(*m*-trifluoromethylphenyl)silyl]propyl Chloride: ^{1}H NMR (500 MHz) δ = 0.32 (6H, s, Si–CH_3), 0.86—0.91 (2H, m, CH_2), 1.73—1.79 (2H, m, CH_2), 3.45 (2H, t, J = 6.9 Hz, CH_2), 7.47—7.72 (4H, m, Ar–H).

3-Dimethylphenylsilyl-1-propanol. Oxygen gas was bubbled for 2 h into a solution of 3-(dimethylphenylsilyl)propylmagnesium chloride prepared from 3-(dimethylphenylsilyl)propyl chloride (3.15 g, 14.8 mmol) and Mg (0.36 g, 14.8 mmol) in 50 cm^3 of THF. The reaction mixture was treated with NH_4Cl (1.59 g, 29.6 mmol) in 40 cm^3 of water, and extracted with ether. The usual work-up gave 2.82 g of crude product. Purification by column chromatography afforded 2.05 g (yield, 71%) of the alcohol as a colorless oil: ^{1}H NMR (500 MHz) δ = 0.28 (6H, s, Si–CH_3), 0.72—0.78 (2H, m, CH_2), 1.27 (1H, broad t, J = 6.0 Hz, OH), 1.54—1.60 (2H, m, CH_2), 3.58 (2H, broad q, J = 6.3 Hz, CH_2), 7.34—7.53 (5H, m, Ar–H). By the same procedure, the following alcohols were prepared from the corresponding chlorides.

3-[*p*-Methoxyphenyl(dimethyl)silyl]-1-propanol: ^{1}H NMR (500 MHz) δ = 0.26 (6H, s, Si–CH_3), 0.70—0.85 (2H, m, CH_2), 1.26 (1H, broad t, J = 5.5 Hz, OH), 1.53—1.60 (2H, m, CH_2), 3.58 (2H, broad q, J = 6.2 Hz, CH_2), 3.81 (3H, s, OCH_3), 6.91 (2H, d, J = 8.5 Hz, Ar–H), 7.43 (2H, d, J = 8.5 Hz, Ar–H).

3-[(*m*-Chloro-*p*-methoxyphenyl)dimethylsilyl]-1-propanol: ^{1}H NMR (60 MHz) δ = 0.14 (6H, s, Si–CH_3), 0.41—0.80 (2H, m, CH_2), 1.21—1.60 (2H, m, CH_2), 3.39 (2H, t, J = 6.0 Hz, CH_2), 3.78 (3H, s, OCH_3), 6.69—7.30 (3H, m, Ar–H).

3-[Dimethyl(*p*-methylphenyl)silyl[-1-propanol: ^{1}H NMR (60 MHz) $\delta = 0.20$ (6H, s, Si–CH$_3$), 0.43—0.84 (2H, m, CH$_2$), 1.15—1.60 (2H, m, CH$_2$), 1.31 (1H, broad s, OH), 2.27 (3H, s, CH$_3$), 3.41 (2H, t, $J = 6.0$ Hz, CH$_2$), 6.93—7.36 (4H, m, Ar–H).

3-[Dimethyl(*m*-methylphenyl)silyl]-1-propanol: ^{1}H NMR (60 MHz) $\delta = 0.20$ (6H, s, Si–CH$_3$), 0.43—0.80 (2H, m, CH$_2$), 1.15—1.70 (2H, m, CH$_2$), 1.74 (1H, broad s, OH), 2.29 (3H, s, CH$_3$), 3.41 (2H, t, $J = 7.2$ Hz, CH$_2$), 6.93—7.38 (4H, m, Ar–H).

3-(*p*-Chlorophenyldimethylsilyl)-1-propanol: ^{1}H NMR (60 MHz) $\delta = 0.20$ (6H, s, Si–CH$_3$), 0.45—0.88 (2H, m, CH$_2$), 1.13—1.64 (2H, m, CH$_2$), 1.74 (1H, broad s, OH), 3.45 (2H, t, $J = 6.6$ Hz, CH$_2$), 7.01—7.53 (4H, m, Ar–H).

3-[Dimethyl(*m*-trifluoromethylphenyl)silyl]-1-propanol: ^{1}H NMR (500 MHz) $\delta = 0.31$ (6H, s, Si–CH$_3$), 0.76—0.81 (2H, m, CH$_2$), 1.29 (1H, broad t, $J = 5.2$ Hz, OH), 1.43—1.60 (2H, m, CH$_2$), 3.60 (2H, broad q, $J = 6.1$ Hz, CH$_2$), 7.44—7.73 (4H, m, Ar–H).

3-(Dimethylphenylsilyl)-1-[1,1-^{2}H$_2$]propanol. Ethyl 3-(dimethylphenylsilyl)propionate (1.00 g, 4.2 mmol) in 5 cm^3 of ether was added dropwise to a suspension of lithium aluminum deuteride (0.36 g, 8.6 mmol, 98 atom% D) in 10 cm^3 of ether at 0 °C. After the usual work-up, the alcohol was purified by column chromatography to yield 0.87 g (99%) as a colorless oil: ^{1}H NMR (500 MHz) $\delta = 0.28$ (6H, s, Si–CH$_3$), 0.72—0.77 (2H, m, CH$_2$), 1.52—1.58 (2H, m, CH$_2$), 7.33—7.53 (5H, m, Ar–H). Similarly, the following alcohols were prepared.

3-[*p*-methoxyphenyl(dimethyl)silyl]-1-[1,1-^{2}H$_2$]propanol: ^{1}H NMR (500 MHz) $\delta = 0.25$ (6H, s, Si–CH$_3$), 0.69—0.75 (2H, m, CH$_2$), 1.53—1.58 (2H, m, CH$_2$), 3.81 (3H, s, OCH$_3$), 6.91 (2H, d, $J = 8.7$ Hz, Ar–H), 7.43 (2H, d, $J = 8.7$ Hz, Ar–H).

3-[Dimethyl(*m*-trifluoromethylphenyl)silyl]-1-[1,1-^{2}H$_2$]-propanol: ^{1}H NMR (500 MHz) $\delta = 0.31$ (6H, s, Si–CH$_3$), 0.76—0.80 (2H, m, CH$_2$), 1.53—1.57 (2H, m, CH$_2$), 7.42—7.72 (4H, m, Ar–H).

3-(Dimethylphenylsilyl)propyl Tosylate. To a stirred solution of 3-dimethylphenylsilyl-1-propanol (1.25 g, 6.4 mmol) in 8 cm^3 of ether was slowly added 1.6 M butyllithium hexane solution (M = mol dm^{-3}) (4 cm^3, 6.4 mmol) at 0 °C. This solution was stirred for 30 min, and then *p*-toluenesulfonyl chloride (1.23 g, 6.5 mmol) was added. After stirring for 12 h, the reaction mixture was treated with 10 cm^3 of water at 0 °C and then extracted with ether. After the usual work-up, the solvent was evaporated under reduced pressure to leave 2.12 g of the crude tosylate which was purified by column chromatography to yield 1.05 g (47%) as a colorless oil: ^{1}H NMR (500 MHz) $\delta = 0.24$ (6H, s, Si–CH$_3$), 0.66—0.70 (2H, m, CH$_2$), 1.59—1.66 (2H, m, CH$_2$), 2.44 (3H, s, CH$_3$), 3.96 (2H, t, $J = 6.7$ Hz, CH$_2$), 7.30—7.45 (5H, m, Ar–H), 7.33 (2H, d, $J = 8.0$ Hz, Ar–H), 7.76 (2H, d, $J = 8.0$ Hz, Ar–H). Found: C, 62.03; H, 6.91%. Calcd for C$_{18}$H$_{24}$O$_3$SSi: C, 62.03; H, 6.94%. In the same way, the following tosylates were prepared.

3-[*p*-Methoxyphenyl(dimethyl)silyl]propyl Tosylate: ^{1}H NMR (500 MHz) $\delta = 0.21$ (6H, s, Si–CH$_3$), 0.63—0.67 (2H, m, CH$_2$), 1.58—1.65 (2H, m, CH$_2$), 2.44 (3H, s, CH$_3$), 3.81 (3H, s, OCH$_3$), 3.95 (2H, t, $J = 6.7$ Hz, CH$_2$), 6.89 (2H, d, $J = 8.9$ Hz, Ar–H), 7.32 (2H, d, $J = 8.1$ Hz, Ar–H), 7.36 (2H, d, $J = 8.9$ Hz, Ar–H), 7.76 (2H, d, $J = 8.1$ Hz, Ar–H). Found: C, 60.17; H, 6.97%. Calcd for C$_{19}$H$_{26}$O$_4$SSi: C, 60.28; H, 6.92%.

3-[(*m*-Chloro-*p*-methoxyphenyl)dimethylsilyl]propyl Tosylate: ^{1}H NMR (500 MHz) $\delta = 0.22$ (6H, s, Si–CH$_3$), 0.63—0.68 (2H, m, CH$_2$), 1.55—1.68 (2H, m, CH$_2$), 2.44 (3H, s, CH$_3$), 3.91 (3H, s, OCH$_3$), 3.95 (2H, t, $J = 6.8$ Hz, CH$_2$), 6.91—7.39 (3H, m, Ar–H), 7.33 (2H, d, $J = 8.2$ Hz, Ar–H), 7.77 (2H, d, $J = 8.2$ Hz, Ar–H). Found: C, 55.53; H, 6.24%. Calcd for C$_{19}$H$_{25}$ClO$_4$SSi: C, 55.26; H, 6.10%.

3-[Dimethyl(*p*-methylphenyl)silyl]propyl Tosylate: ^{1}H NMR (500 MHz) $\delta = 0.22$ (6H, s, Si–CH$_3$), 0.63—0.68 (2H, m, CH$_2$), 1.57—1.66 (2H, m, CH$_2$), 2.34 (3H, s, CH$_3$), 2.44 (3H, s, CH$_3$), 3.95 (2H, t, $J = 6.7$ Hz, CH$_2$), 7.15 (2H, d, $J = 7.9$ Hz, Ar–H), 7.32 (2H, d, $J = 8.2$ Hz, Ar–H), 7.34 (2H, d, $J = 7.9$ Hz, Ar–H), 7.76 (2H, d, $J = 8.2$ Hz, Ar–H). Found: C, 63.22; H, 7.25%. Calcd for C$_{19}$H$_{26}$O$_3$SSi: C, 62.94; H, 7.23%.

3-[Dimethyl(*m*-methylphenyl)silyl]propyl Tosylate: ^{1}H NMR (500 MHz) $\delta = 0.22$ (6H, s, Si–CH$_3$), 0.64—0.70 (2H, m, CH$_2$), 1.57—1.66 (2H, m, CH$_2$), 2.35 (3H, s, CH$_3$), 2.44 (3H, s, CH$_3$), 3.96 (2H, t, $J = 7.0$ Hz, CH$_2$), 7.17—7.27 (4H, m, Ar–H), 7.32 (2H, d, $J = 8.0$ Hz, Ar–H), 7.76 (2H, d, $J = 8.0$ Hz, Ar–H). Found: C, 62.98; H, 7.26%. Calcd for C$_{19}$H$_{26}$O$_3$SSi: C, 62.94; H, 7.23%.

3-(*p*-Chlorophenyldimethylsilyl)propyl Tosylate: ^{1}H NMR (500 MHz) $\delta = 0.23$ (6H, s, Si–CH$_3$), 0.65—0.71 (2H, m, CH$_2$), 1.56—1.64 (2H, m, CH$_2$), 2.44 (3H, s, CH$_3$), 3.95 (2H, t, $J = 6.7$ Hz, CH$_2$), 7.28—7.37 (6H, m, Ar–H), 7.76 (2H, d, $J = 8.0$ Hz, Ar–H). Found: C, 56.84; H, 6.11%. Calcd for C$_{18}$H$_{23}$ClO$_3$SSi: C, 56.45; H, 6.05%.

3-[Dimethyl(*m*-trifluoromethylphenyl)silyl]propyl Tosylate: ^{1}H NMR (500 MHz) $\delta = 0.27$ (6H, s, Si–CH$_3$), 0.69—0.75 (2H, m, CH$_2$), 1.59—1.66 (2H, m, CH$_2$), 2.44 (3H, s, CH$_3$), 3.97 (2H, t, $J = 6.7$ Hz, CH$_2$), 7.32 (2H, d, $J = 8.2$ Hz, Ar–H), 7.43-7.67 (4H, m, Ar–H), 7.73 (2H, d, $J = 8.2$ Hz, Ar–H). Found: C, 54.89; H, 5.63%. Calcd for C$_{19}$H$_{23}$F$_3$O$_3$SSi: C, 54.79; H, 5.57%.

3-(Dimethylphenylsilyl)[1,1-^{2}H$_2$]propyl Tosylate: ^{1}H NMR (500 MHz) $\delta = 0.23$ (6H, s, Si–CH$_3$), 0.65—0.70 (2H, m, CH$_2$), 1.59—1.63 (2H, m, CH$_2$), 2.43 (3H, s, CH$_3$), 7.29—7.45 (5H, m, Ar–H), 7.33 (2H, d, $J = 8.2$ Hz, Ar–H), 7.76 (2H, d, $J = 8.2$ Hz, Ar–H).

3-[*p*-Methoxyphenyl(dimethyl)silyl][1,1-^{2}H$_2$]propyl Tosylate: ^{1}H NMR (500 MHz) $\delta = 0.21$ (6H, s, Si–CH$_3$), 0.63—0.67 (2H, m, CH$_2$), 1.59—1.63 (2H, m, CH$_2$), 2.43 (3H, s, CH$_3$), 3.80 (3H, s, OCH$_3$), 6.89 (2H, d, $J = 8.5$ Hz, Ar–H), 7.31 (2H, d, $J = 8.5$ Hz, Ar–H), 7.36 (2H, d, $J = 8.5$ Hz, Ar–H), 7.76 (2H, d, $J = 8.5$ Hz, Ar–H).

3-[Dimethyl(*m*-trifluoromethylphenyl)silyl][1,1-^{2}H$_2$]propyl Tosylate: ^{1}H NMR (500 MHz) $\delta = 0.27$ (6H, s, Si–CH$_3$), 0.69—0.74 (2H, m, CH$_2$), 1.57—1.63 (2H, m, CH$_2$), 2.44 (3H, s, CH$_3$), 7.32 (2H, d, $J = 8.4$ Hz, Ar–H), 7.40—7.71 (4H, m, Ar–H), 7.73 (2H, d, $J = 8.4$ Hz, Ar–H).

Solvents. Solvents were purified and binary solvents prepared by mixing appropriate volumes or weights of pure solvents at 25 °C, as previously described.[9,17,19]

Kinetic Measurements. Solvolyses in binary solvent mixtures were followed conductimetrically.[9,17,19] Using conductivity meters (CM-50AT, CM-40V, and CM-60S equipped with an interval time unit and printer, Toa Electronics Ltd.), solvolyses were followed in a thermostatted bath controlled within ±0.01 °C by taking at least 100 readings at appropriate intervals during 2.5 half-lives, and an infinity reading after 10 half-lives. The experimental errors in respective runs were generally less than 1.0% and the reproducibility of the rate constants was within ±1.5%.

To determine the deuterium kinetic isotope effects, the solvolysis rates of both deuterated and non-deuterated compounds were measured by the conductimetric method in simultaneous runs in order to keep the same reaction condition.

Product Analyses. Products were analyzed by ^{1}H NMR spectroscopy (JEOL JNM-A500 FT-NMR spectrometer). A solution of 1.8—3.1 × 10^{-2} M of the tosylate in the presence of 2.7—5.3 × 10^{-2}

M of 2,6-lutidine in deuterated solvent was sealed in an NMR tube and allowed to react at 75 °C in a thermostatted bath. The tube was withdrawn at appropriate intervals, cooled rapidly in an ice bath and the ^{1}H NMR spectrum of the reaction mixture was recorded. The peaks of the tosylate decreased with increases in the other peaks of products. After disappearance of the peaks of the starting tosylate, the solvolysis products were identified by comparing their ^{1}H NMR spectra with the authentic samples. Cyclopropane[20] was identified by singlet peak at 0.20 ppm in aq ethanol and 0.22 ppm in aq TFE. Deuterated cyclopropane ($C_3H_4D_2$) showed a quintet peak (J_{HD} = 1.1 Hz) at 0.18 ppm in aq ethanol and 0.19 ppm in aq TFE. The relative amounts of reaction products were determined from the integral areas of the corresponding peaks. The product ratios did not change with the reaction at all. Therefore, in these conditions, all the products were stable and kinetic controlled.

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