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# The Yukawa–Tsuno Relationship for the *β*-Silicon Effect in the Solvolysis Rates of 2-(Aryldimethylsilyl)ethyl Chlorides

**Mizue Fujio,* Mai Uchida, Ayumi Okada, Md. Ashadul Alam,**
**Ryoji Fujiyama,[1] Hans-Ullrich Siehl,[2] and Yuho Tsuno**

Institute for Materials Chemistry and Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581

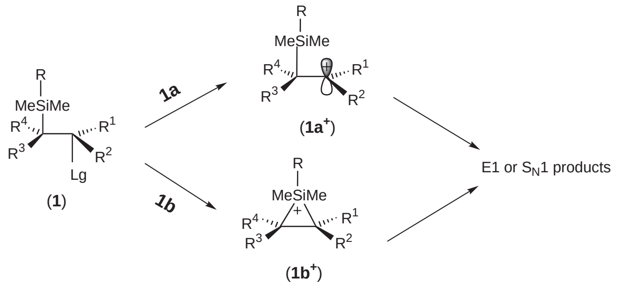
[1]Department of Material Science, Faculty of Science, Kochi University, Akebono-cho, Kochi 780-8520

[2]Division of Organic Chemistry 1, University of Ulm, D-89069 Ulm, Germany

Received March 3, 2005; E-mail: fujio@ms.ifoc.kyushu-u.ac.jp

Solvolysis rates of 2-(aryldimethylsilyl)ethyl chlorides were determined conductimetrically in 60% (v/v) aqueous ethanol. The effects of aryl substituents at the silyl atom on the solvolysis rates at 50 °C were correlated with essentially nonresonant $\bar{\sigma}$ parameters of $r = 0.10$ in terms of Yukawa–Tsuno (Y–T) Eq. 1, giving a $\rho$ value of $-1.75$. Such a high $\rho$ value may be regarded as the effect of aryl ring on the bridged Si in the rate-determining step. The Si-bridging is consistent with the fact that the solvolysis of the unsubstituted substrate with $d_2$-labeled ethylene moiety gave substitution products with label scrambling. The arylsilyl substituent effects were likewise analyzed for several relevant sets of $\beta$-silyl systems in order to ascertain significant variations of $\rho$ values from system to system; Y–T Eq. 1 correlated quite excellently with essentially nonresonant sigmas of negligible resonance demand ($r \cong 0.10$), to exhibit significant variations of $\rho$ from $-1.75$ to $-0.95$.

It is well known that the $\beta$-silicon substituent greatly facilitates the heterolysis of the C–Lg bond by $10^{12}$-fold. This improvement is caused by trimethylsilyl group in an antiperiplanar conformation.[1] The so-called $\beta$-silicon effect is manifested primarily in an E1-like mechanism, in which departure of the nucleofuge is rate-determining (Scheme 1). Stabilization of this electron deficiency was interpreted in terms of either the open form (**1a$^+$**) stabilized by $\sigma$–$\pi$ hyperconjugation or by the Si-bridged form (**1b$^+$**) of the cationic intermediate,[1–7] as shown in Scheme 1. Advanced MO calculations indicated that the two forms (**1a$^+$** and **1b$^+$**) have similar energies generally in the secondary cations ($R^1$–$R^4$ = H or Me in **1**)[6] but the bridged structure (**1b$^+$**) is somewhat more stable in the primary case, while the predictions have seldom been found experimental support in solvolytic reactions.[5b,9–13] The conformational dependences of the $\beta$-silicon effect on the dihedral angles of $C_\beta$–Si bond and on the cation p-orbital in the solvolysis of cyclic secondary systems,[1,3b] were taken as convincing evidence for the Si–$C_\beta$ hyperconjugation mechanism. Nevertheless, this conformational dependence may also be taken as evidence for the Si-bridged pathway (**1b**). Thus the relative importance of these two pathways in the primary system remains substantially unresolved. Numerous results have revealed the necessity of the antiperiplanar stereochemistry and can be explained satisfactorily by either the non-classical (bridged) or the classical (open cation) transition state.



Scheme 1. $\beta$-Silicon effect in the carbocationic solvolysis.

On the other hand, the bridged structure (**1b$^+$** in Scheme 1) has been invoked by Eaborn et al., who observed reversible ionization and migration of the $SiMe_3$ group between the two carbon atoms in the solvolysis of $Me_3SiCH_2CD_2Br$.[13] The Si-bridged pathway (**1b**) is highly plausible in the primary carbocationic system, while the question of which pathway, **1a** or **1b**, should be favored still remains open. At least the $\beta$-silyl-group bridged (silyl-participation) pathway appeared to be analogous to the neighboring aryl-group assistance in the $\beta$-arylalkyl solvolyses. The distinction between the pathways (**1a**) and (**1b**) in Scheme 1 may be made most practically by the difference in the relative position of Si atom in the transition state.

The correlation analysis of substituent effects should be an effective tool of investigation of reaction mechanisms. The Yukawa–Tsuno (Y–T) Eq. 1 has been successfully applied to the analysis of various $\beta$-aryl-assisted solvolyses; the $\rho$ and $r$ values permit one to assess the structure of the transition state:[14]

$$\log(k/k_0) = \rho(\sigma^0 + r\Delta\bar{\sigma}_R^+), \tag{1}$$

where $k$ is the rate constant for a given reaction of a ring-substituted derivative and $k_0$ is the corresponding value of the unsubstituted one. $\sigma^0$ is the normal substituent constant that excludes additional $\pi$-electronic interaction, and $\Delta\bar{\sigma}_R^+$ is the resonance substituent constant, defined by $\sigma^+ - \sigma^0$,

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Table 1. Solvolysis Rates of 2-(Aryldimethylsilyl)ethyl Chlorides in 60% (v/v) aq EtOH

| Subst. | $10^5 \times k/\mathrm{s}^{-1}$ | | | | $\Delta H^{\ddagger}_{50\,°\mathrm{C}}$ /kcal mol$^{-1}$ [a)] | $\Delta S^{\ddagger}_{50\,°\mathrm{C}}$ /e.u.[a)] |
|---|---|---|---|---|---|---|
| | 25 °C | 45 °C | 55 °C | 50 °C | | |
| *p*-MeO | 6.45 | 66.7 | | 114.3[b)] | 21.4 | −6.0 |
| *p*-Me | | | | 94.8[c)] | | |
| 3,5-Me$_2$ | | | | 79.2[c)] | | |
| *m*-Me | | | | 71.9[c)] | | |
| H | 3.43 | 34.7 | | 59.1,[b)] 59.5[c)] | 21.2 | −8.0 |
| *p*-MeO-*m*-Cl | 1.773 | 17.28 | | 29.2[b)] | 20.8 | −10.5 |
| *p*-Cl | 1.597 | 15.74 | | 24.9,[b)] 25.9[c)] | 20.7 | −11.3 |
| *m*-Cl | 0.575 | 6.431 | 19.59 | 11.33,[b)] 11.77[c)] | 22.8 | −8.0 |
| *m*-CF$_3$ | | | | 7.1[c)] | | |
| 3,5-(CF$_3$)$_2$ | | 0.661 | 1.99 | 1.157[b)] | 22.2 | −12.5 |

a) 1 cal = 4.184 J. b) Calculated from the rate data at other temperatures. c) Ref. 17.

measuring the capability of $\pi$-delocalization of $p$–$\pi$-donor substituent.

The present $\beta$-silyl group participation reactions (Scheme 1) were similarly subjected to correlation analysis by introducing X-substituted phenyls to the silyl function (R = X-C$_6$H$_4$ in **1**).[15–17] The final goal of our investigation is to establish the use of a selectivity parameter ($\rho$-value) of the arylsilyl substituent effects as a criterion to distinguish the mechanisms **1a** and **1b**.

In this paper, we have carried out determination of the solvolysis rates of a wide range of ring substituents to rationalize the aryl substituent effect on the $\beta$-Si participation in the solvolysis of the simplest $\beta$-silyl system **2**.

## Results

2-(Aryldimethylsilyl)ethyl chlorides (**2**) were synthesized according to the procedure of Vencl et al.[16] The solvolysis rates for these aryl substituents in 60% (v/v) aqueous ethanol (60E) were measured conductimetrically at appropriate temperatures in the same manner as reported before[17,18] and were extrapolated to those at 50 °C to compare with the previous data.[17] The solvolysis rates of the unsubstituted derivative **2** (X = H) were also determined in various solvents at 25 °C to analyze the solvent effect. All the solvolyses followed accurately a first-order rate law until 2.5 half-lives. Kinetic data are listed in Tables 1 and 2 together with the previous data.

The solvolysis rates were mostly in good agreement with those reported before, except for *p*-MeO and *p*-MeO-*m*-Cl derivatives, for which more than 10 times higher rate constants were reported earlier;[17] we could not reproduce these rate constants in repeated measurements in this laboratory in Kyushu University.

The solvolysis product of the chlorides (**2**) was ethylene that is given by the E1-desilylation from incipient $\beta$-silyl carbocation (Scheme 2) in all cases examined here, as reported in the literature.[16]

The solvolysis rates were faster than that of the non-silylated derivative, ethyl chloride, by ca. $10^9$-fold acceleration by PhSiMe$_2$ substitution. In this simple primary system (**2**), there seems to be the largest $\beta$-silicon effect ever reported.[1] Such a remarkable cation-stabilizing $\beta$-Si effect makes it possible for the system to undergo solvolysis by the E1 $k_\mathrm{C}$ mechanism.

Table 2. Solvolysis Rates of 2-(Dimethylphenylsilyl)ethyl Chloride at 25 °C

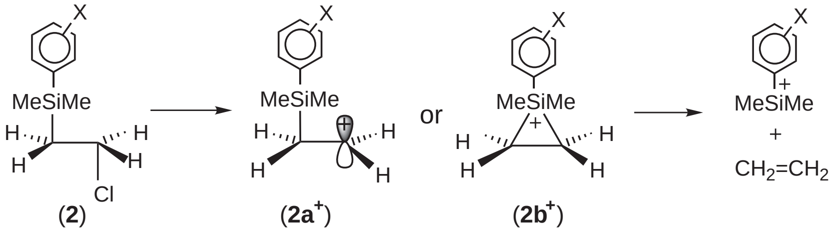
| Solv.[a)] | $10^5 \times k/\mathrm{s}^{-1}$ | Solv.[a)] | $10^5 \times k/\mathrm{s}^{-1}$ |
|---|---|---|---|
| EtOH | 0.0094[b)] | 30A | 224 |
| 90E | 0.111[b)] | MeOH | 0.102[b)] |
| 80E | 0.312 | 80M | 1.819 |
| 70E | 1.097 | 60M | 18.90 |
| 60E | 3.40 | 50M | 59.9 |
| 50E | 11.85 | TFE | 38.5 |
| 40E | 55.0 | 97T[c)] | 49.4 |
| 30E | 249 | 80T | 37.9 |
| 80A | 0.107[b)] | 50T | 59.1 |
| 70A | 0.329 | 80ET | 0.0338[b)] |
| 60A | 1.677 | 60ET | 0.1279 |
| 50A | 5.63 | 40ET | 0.807 |
| 40A | 32.7 | 20ET | 5.99 |

a) Volume percent (v/v) of first named organic component unless otherwise noted. Abbreviations; E = EtOH, M = MeOH, A = Acetone, T = TFE (2,2,2-trifluoroethanol), ET = EtOH–TFE (e.g., 20ET = 20% vol EtOH:80% vol TFE mixture). b) Extrapolated from the data at other temperatures. c) Weight % (w/w).

**Deuterium Scrambling Analysis.** In the ordinary chlorination of the $\alpha$ or $\beta$-$d_2$-labeled 2-(dimethylphenylsilyl)ethanol either with dry HCl gas or SOCl$_2$, the complete label scrambling of the ethyl moiety occurred, suggesting some involvement of Si-bridged species at least in the chlorination process.

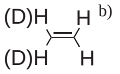
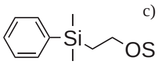
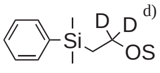
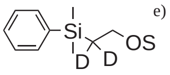
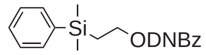
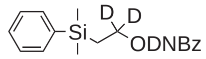
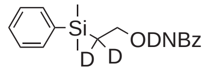
The label scrambling analysis for the solvolyses with three isotopomers (protio, 1,1-$d_2$, and 2,2-$d_2$ derivatives) of 2-(dimethylphenylsilyl)ethyl 3,5-dinitrobenzoate was carried out in CF$_3$CD$_2$OD in the presence of excess 2,6-lutidine at 125 °C, by using $^1$H NMR method. The products of these solvolyses were found to be ethylene accompanied by the substitution products of the label scrambling, as summarized in Table 3. The substitution products, 2,2,2-trifluoroethyl ether, were obtained in 32–40% yield for the 3,5-dinitrobenzoate solvolysis in this less nucleophilic solvent, while the chloride solvolysis gave exclusively the elimination product, ethylene, but no substitution product even in 60E. No $d_2$ scrambling was observed in the reactant 3,5-dinitrobenzoates but such scrambling was observed in the product 2,2,2-trifluoroethyl ether, as shown in Table 3. The unrearranged ether from both the deuterium compounds was slightly larger than the rearranged product.

**Solvent Effect.** The solvent effect on the solvolyses of 2-(dimethylphenylsilyl)ethyl chloride at 25 °C (in Table 2)



Scheme 2. Solvolysis of 2-(aryldimethylsilyl)ethyl chlorides **2**.

Table 3. Product Analyses on the Solvolyses of 2-(Dimethylphenylsilyl)ethyl 3,5-Dinitrobenzoate and Its Deuterium Compounds in $CF_3CD_2OD$ at 125 °C[a)]

| Compounds |  b) |  c) |  d) |  e) |
|---|---|---|---|---|
|  | 68% | 32% | — | — |
|  | 60% | — | 22% | 18% |
|  | 62% | — | 16% | 22% |

a) S = $CD_2CF_3$ and ODNBz = 3,5-dinitrobenzoate. b) δ 5.47 ppm (quintet, $J_{HD} = 2.4$ Hz for $CH_2{=}CD_2$). c) δ 1.27–1.38 ppm (2H, m, $SiCH_2$), 3.80–3.85 ppm (2H, m, $CH_2$). d) δ 1.38 ppm (2H, s, $SiCH_2$). e) δ 3.78–3.94 ppm (2H, m, $CH_2$).

was analyzed with the Winstein–Grunwald–Schleyer–Bentley Eq. 2:[19]

$$\log(k/k_{80E}) = mY_{Cl}, \tag{2}$$

where $Y_{Cl}$ is the solvent ionizing power parameter based on solvolyses of 1-adamantyl chloride, and $m$ is the susceptibility. Figure 1 shows the linear solvent-effects correlation against $Y_{Cl}$ with an $m$ value of $0.73 \pm 0.02$ without any serious deviation of particular solvent series ($R = 0.990$ and SD $= \pm 0.18$). The lack of any serious deviation depending on the solvent nucleophilicity, $l = 0$, indicates the absence of nucleophilic attack to either the Si atom or the carbon center in the rate-determining transition state.

While the systematic dispersion between the respective binary solvent series in the plot against $Y_{Cl}$ was slightly observed in Fig. 1, such dispersal attributable to charge delocalization is not very significant in this reaction, compared with the serious dispersion caused by the aryl-π-delocalization as in benzylic chloride solvolyses.[20] The reduced $m$ value of 0.73 suggests for this solvolysis a Si-bridged transition state that can be referred to as the intramolecular nucleophilic participation to the carbocation center, as observed similarly in the γ-silyl solvolyses of percaudal mechanism.[18]

**Substituent Effect Analysis.** The substituent effects on the solvolysis of 2-(aryldimethylsilyl)ethyl chlorides (**2**) were earlier reported to give the aryl substituent effects of $\rho = -1.4$– $-2.3$ against σ constant.[15,16]

The rate change with ring substituents in Table 1 was ca. 100-fold for the range of substituent changes from the *p*-MeO to 3,5-$(CF_3)_2$. The rate of the *p*-MeO derivative is comparable with that of the *p*-Me derivative, indicating that the substituent effect on this solvolysis can be characterized as the nonresonant $\sigma^0$ or σ reactivity, as indicated in the result of Vencl.[16] In Fig. 2, the logarithms of the relative rates at 50 °C were plotted against $\sigma^0$ (closed circles) and $\sigma^+$ (open circles). An application of Y–T Eq. 1 affords a good correlation with $r = 0.10$ ($R = 0.997$ and SD $= \pm 0.05$) for the whole range of substituents:

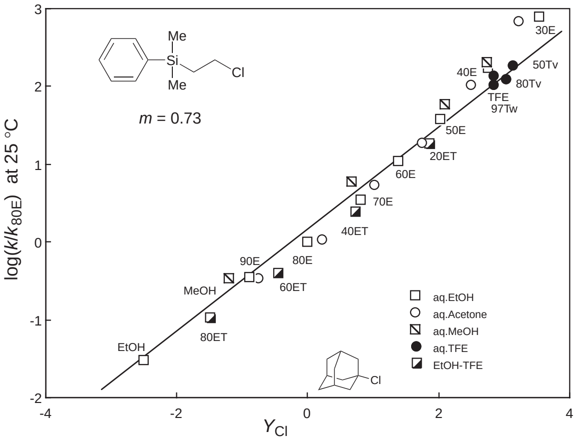


Fig. 1. The $mY_{Cl}$ plots for the solvolysis of 2-(dimethylphenylsilyl)ethyl chloride at 25 °C.

$$\log(k/k_0) = (-1.75 \pm 0.05)[\sigma^0 + (0.10 \pm 0.01)\Delta\bar{\sigma}_R^+]. \tag{3}$$

The $r$ value of 0.10 assigned for this system may be explicable if the phenyl π-system on the β-silicon atom interacts through negligibly small π-delocalization with the carbocationic reaction center in the transition state. Employment of the higher $k$ values for *p*-MeO and *p*-MeO-*m*-Cl substituents reported earlier[17] resulted in a ridiculously high $r$ value of

1.5 with unsatisfactory precision.

The arylsilyl substituent effects were likewise analyzed for several relevant sets of $\beta$-silyl systems in order to ascertain significant variations of $\rho$ values from system to system; the correlation results are summarized in Table 4. The rate data of $\beta$-silyl systems were quoted from the unpublished results in these laboratories, since no data were available in the literature other than our file of unpublished results. For all the $\beta$-silyl systems, Y–T Eq. 1 correlated quite excellently with essentially nonresonant sigmas of negligible resonance demand ($r \cong 0.10$), to exhibit significant variations of $\rho$ from $-1.75$ to $-0.96$.

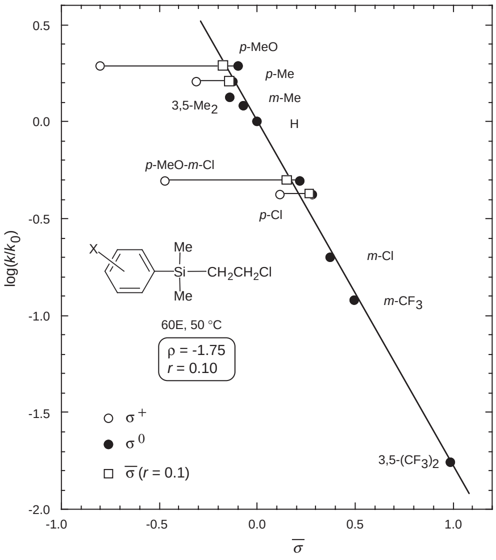


Fig. 2. Substituent effect on the solvolysis of 2-(aryldimethylsilyl)ethyl chlorides (**2**) in 60% (v/v) aq EtOH at 50 °C: Closed circles for $\sigma^0$, open circles for $\sigma^+$, and open squares for $\bar{\sigma}$ with $r = 0.10$.

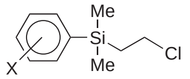
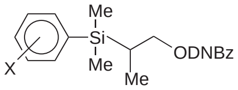
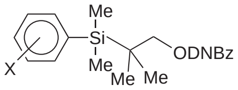
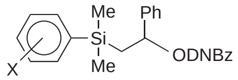
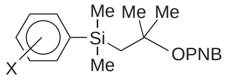
By the way, as far as we are aware of the $\beta$-aryl-silyl substituent effects, the $\beta$-silyl systems are, without exception, correlated precisely linearly against essentially nonresonant $\sigma^0$ with $r \cong 0.10$. This is the strongest support for the validity of the present rate data for *p*-MeO and *p*-MeO-*m*-Cl derivatives (in Table 1).

## Discussion

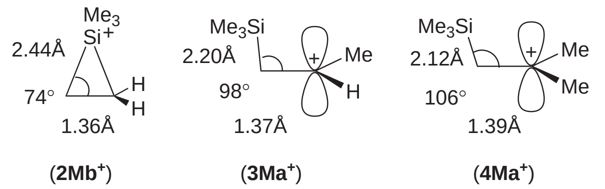
The so-called $\beta$-silicon effect, ca. $10^{12}$-fold rate enhancement, arises because the high polarizability and electropositivity of silicon enable it to stabilize the electron-deficient intermediate. The overall reaction pathway is a $\beta$-elimination (formation of an olefin by loss of the electrofuge $Me_3Si$ group and nucleofuge chloride ion). The $\beta$-silyl effects due to the trimethylsilyl group were observed as remarkable rate acceleration for systems in an antiperiplanar conformation,[1] and this was manifested primarily in an E1-like mechanism, in which departure of the nucleofuge is rate-determining (Scheme 1). Overall stabilization of this electron deficiency occurs by $\sigma$–$\pi$ hyperconjugation between the highly polarizable C–Si bond and the empty p-orbital (**1a$^+$**).

On the other hand, the silyl-bridged pathway was invoked by Eaborn et al.[13] especially for primary carbocation systems **1** ($R^1$, $R^2$ = H). In the silyl-bridged pathway (**1b**), the silicon atom forms a partial C–Si bond to the carbon atom from which the nucleofuge departs. The bridging may be in concert with nucleofuge departure, so that the reaction is analogous to neighboring group participation (anchimeric assistance). The antiperiplanar arrangement is required for the bridged pathway (**1b**) to place the internal nucleophile (silicon) backside to the breaking bond (C–Lg) during formation of the three-members ring (**1b$^+$**). Thus, two modes of stabilization differing in the geometry of the intermediate, the unbridged (vertical) and the bridged (nonvertical) structures, have been considered: Both bridged and unbridged models are consistent with the whole set of evidence.

Table 4. Correlation Analysis for 2-(Aryldimethylsilyl)ethyl Solvolyses in 60E Using Y–T Eq. 1

| Substrates[a)] | | Temp/°C | $\rho$ | $r$ | $k$(ODNBz,50 °C)[b)] |
|---|---|---|---|---|---|
|  | **2**[c)] | 50 | −1.75 | 0.10 | $9.55 \times 10^{-9}$ |
|  | **11**[d)] | 70 | −1.77 | 0.17 | $9.95 \times 10^{-7}$ |
|  | **6**[d)] | 70 | −1.54 | 0.08 | $1.63 \times 10^{-5}$ |
|  | **5**[d)] | 50 | −0.96 | 0.05 | $1.13 \times 10^{-2}$ |
|  | **4**[d)] | 50 | −1.08 | 0.15 | $8.9 \times 10^{-1}$ |

a) Cl = chloride, ODNBz = 3,5-dinitrobenzoate, and OPNB = *p*-nitrobenzoate. b) Rate constants ($/s^{-1}$) for the 3,5-dinitrobenzoates of X = H derivatives at 50 °C in 60E. c) Present study. d) To be published in separate papers.



Scheme 3. The ab initio calculation for $\beta$-silyl cations where R = Me in **1a**$^+$ or **1b**$^+$.

The ab initio calculation gave the following structures (Scheme 3) optimized at MP2/6-31G(d).[8] The progressive substitution with Me-groups at the reaction center carbon results in the increase of the $C_\alpha$–$C_\beta$ distance, decrease of $C_\beta$–Si distance, and increase of $C_\alpha$–$C_\beta$–Si angle. Furthermore, the optimized structure of $\alpha$-phenyl cation (**5Ma**$^+$) shows the larger $C_\alpha$–$C_\beta$–Si angle, indicating the most open cation form among the calculated systems.

Jorgensen's calculations found that the bridged structure (**1b**$^+$) was more stable than the open structure (**1a**$^+$) for the primary case, and that the open form was not an energy minimum.[4b] In the secondary case, however, the open form was found to be slightly more stable than the bridged form, and in this case the bridged form was not an energy minimum. Nevertheless, for 1,2-dimethyl-2-silylethyl cation, the bridged form is slightly more stable.[8] Thus, direct calculation did not provide a clear answer. Moreover, theory addresses only the fully developed carbocation, whereas the actual transition state has only a partial positive charge and an incompletely departed leaving group. Anyhow, the actual involvement of structure (**1a**$^+$) vs (**1b**$^+$) is hard to prove.

For the most fundamental case, the primary $\beta$-SiMe$_3$-ethyl system (**2M**), MO calculation indicates that the unbridged cation (**2Ma**$^+$) is not an energy minimum in the potential surface but immediately leaks to the bridged intermediate (**2Mb**$^+$). It appears therefore highly plausible that the reaction in Scheme 2 proceeds by the bridged pathway (**2b**) toward the more stable bridged cation (**2b**$^+$) but not by the unbridged pathway (**2a**) toward the corresponding vertical (unbridged) cation (**2a**$^+$). At this symmetrical intermediate (**2b**$^+$), the substrate loses the distinction between $\alpha$- and $\beta$-carbons. The solvolyses (**2M**: Lg = bromide) in acetic acid accompanied the return to the reactant from the carbocation intermediate with the $d_2$ scrambling in the ethyl moiety.[13] This means that the departure of the nucleofuge occurs before the departure of the electrofuge silyl moiety. It should be noted that the solvolysis of **2** yields the substitution products besides the commonly occurring silyl-eliminated product (ethylene). The solvolysis in TFE (Lg = 3,5-dinitrobenzoate) resulted in the substitution product 2,2,2-trifluoroethyl ether with $d_2$ scrambling in Table 3. The $d_2$ scrambling in the ethyl chain is consistent with the bridged cation (**2b**$^+$) as the key intermediate in the primary cation system. The solvent effects indicate that the nucleophilic solvent attack on either the silyl or the cationic center carbon does not take place at the rate-determining transition state. The migration of the silyl moiety had to exceed the solvent capture of the cation center.

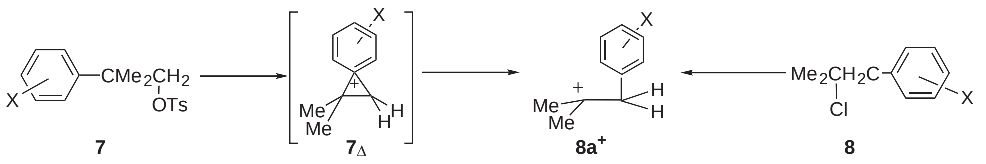
The substituent effect on the solvolysis of 2-(aryldimethylsilyl)ethyl chlorides (**2**) in Fig. 2 gave a linear Y–T correlation with $\rho = -1.75$ against essentially nonresonant $\sigma^0$ constant ($r = 0.10$). The precise linearity ($R = 0.997$) of the correlation Eq. 3 indicates a constant mechanism over the full range of substituents. For all the $\beta$-silyl systems in Table 4, linear correlations of high quality ($R > 0.994$) against essentially nonresonant $\sigma^0$ ($r \cong 0$) are obtained irrespective of structures of the ethylene chain, and no significant mechanistic change should be the case in any system with the silyl substituent perturbation.

The substituent effect of 2-(aryldimethylsilyl)ethyl system bearing 2,2-dimethyl groups (**6**) has a large $\rho$ value of $-1.54$. Most significant, all the primary systems in Table 4 provide essentially the same $\rho$ value as that for **2**. On the other hand, the $\alpha$-phenyl derivative **5** as well as 1,1-dimethyl substrate **4**, where the silyl group assistance is unnecessary because of the strong stabilization with phenyl or Me$_2$ gave a distinctly small $\rho$ value of ca. $-1.0$, as shown in Table 4. The large $\rho$ value of $-1.75$ points to the silyl bridged transition state, while the small $\rho$ value of $-1.0$ points to the open (unbridged) cation transition state.

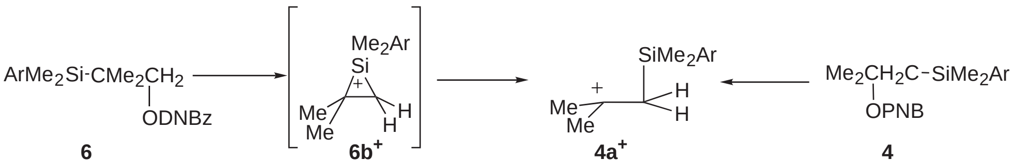
It is of particular interest to compare such a significant change in the $\rho$ values in the $\beta$-(aryldimethylsilyl)alkyl system **1** (R = X-C$_6$H$_4$) with the change in $\rho$ in the corresponding $\beta$-arylethyl systems, e.g., neophyl tosylate **7** and 2-aryl-1,1-dimethylethyl chlorides **8**. Whereas tertiary reactant (**8**) undergoes the $k_C$ solvolysis via a stable open carbocation (**8a**$^+$) as a single intermediate, the neophyl one (**7**) does not undergo the $k_C$ solvolysis to form an unstable intermediate **7a**$^+$. The extremely unstable primary cation **7a**$^+$ does not compete to act as an appropriate intermediate with other stable cations, **7**$_\Delta$ and **8a**$^+$. As the solvolysis of **7** gave exclusively the rearranged product(s) that is/are identical to the $k_C$ solvolysis product(s) from **8a**$^+$, an appropriate intermediate of the solvolysis of **7** should be a rearranged intermediate **8a**$^+$. Thus the solvolysis of **7** does not proceed through the $k_C$ pathway toward an unstable intermediate **7a**$^+$ but proceeds by the aryl-migration ($k_\Delta$) pathway to give a pseudo-intermediate cation **7**$_\Delta$ that immediately cascades down to the more stable isomeric open cation (**8a**$^+$) in Scheme 4.

It was well documented that the aryl-assisted correlation ($\rho = -3.8$; $r = 0.6$) could be observed for **7**[14b] and that the unassisted correlation ($\rho = -2.1$; $r = 0$) was obtained for **8**,[21] respectively. High $\rho_\Delta$ values of $-3.5$–$-3.8$ were generally observed for the $k_\Delta$ processes, but lower values of ca. $-2$ for the aryl-unassisted $k_C$ processes. The enhanced $\rho$ value for the $k_\Delta$ pathway is ascribed to the bond-contraction by direct bonding between aryl ring and the reaction center in the transition state.[14b]

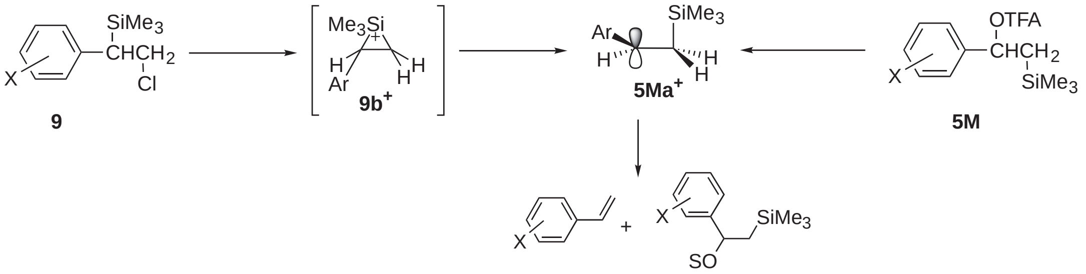
In the corresponding $\beta$-silyl systems, ArSiMe$_2$–CH$_2$CMe$_2$- (**4**) solvolyzes undoubtedly by the vertical pathway (**4a**) to form an open cation (**4a**$^+$). In the case of ArSiMe$_2$–CMe$_2$CH$_2$- (**6**), on the other hand, MO calculation indicates significantly different stabilities of the isomeric silyl-cations; **6a**$^+$ $\ll$ **6b**$^+$ $<$ **4a**$^+$. The vertical solvolysis of **6** should not proceed toward an extremely unstable primary cation (**6a**$^+$) that is presumably incapable of existing as an intermediate. The solvolysis of **6** may be rationalized to proceed through the nonvertical pathway (**6b**) to form a Si-bridged cation (**6b**$^+$), which immediately cascades downhill toward the more stable tertiary



Scheme 4. Solvolysis of 2-phenylethyl system bearing 2,2- or 1,1-dimethyl substituents.



Scheme 5. Solvolysis of 2-silylethyl system bearing 2,2- or 1,1-dimethyl substituents.



Scheme 6. Solvolyses of $\beta$-silylethyl system bearing $\alpha$- and $\beta$-phenyl groups.

cation ($4a^+$) (Scheme 5).

We showed before that the $\alpha$- and $\beta$-phenyl derivatives of $\beta$-trimethylsilyl series **1** (where R = Me) gave on solvolysis the same products as those which were derived from the open cation intermediate (**5Ma**$^+$) in the vertical solvolysis of the $\alpha$-phenyl system (**5M**).[5b,5c]

The products indicated that the solvolysis of **9** does not proceed by the unbridged pathway toward the open primary cation **9a**$^+$ but by the bridged pathway toward the silyl-migrated cation (**5Ma**$^+$) as an appropriate intermediate. Thus, the rate-determining transition state ($9^\ddagger$) has to be a nonvertical (bridged) structure (Scheme 6).[5b]

Unfortunately, however, both **6** and **4** yielded 2-methylpropene as a sole product that is incapable of discriminating rearranged and unrearranged intermediates. Most of $\beta$-silylalkyl substrates likewise yielded only desilylated olefins. The same is also true for the case of the secondary substrate that is understood to proceed by the vertical mechanism. Besides MO calculations, there is no chemical evidence to discriminate an appropriate intermediate among three possible cations; vertical (nonmigrated) cation (**2a**$^+$), nonvertical (bridged) one (**2b**$^+$), and vertical isomeric (migrated) cation. It is therefore remarkable that a quite significant difference was observed in the $\rho$ value for $\beta$-silyl substituent effect between the primary **6** and tertiary substrate **4**.

As briefly discussed above, the significant enhancement in the $\beta$-silicon effects observed in solvolysis are essentially kinetic in nature, whereas the remarkable $\beta$-silyl participations in most of preceding studies were related exclusively to the thermodynamic stabilities of the intermediates. While the structure of the transition state resembles that of the intermediate, the structures of transition state may be manifested by the continuous shift of the $\beta$-Si moiety from $sp^3$ position (open cation form) through the nonvertical (bridged) to the rearranged vertical position within the antiperiplanar phase. The kinetic parameters will be promising as a probe for discriminating the structures of intermediates. Indeed, significantly different $\rho$ values for $\beta$-silyl substituent effects on solvolyses were found for substrates of varying ethylene moieties. We then believe that the $\rho$ value should be different for systems that proceed through the rate-determining transition states of vertical (open) ion structure or the nonvertical (bridged) $\beta$-silyl cation structure. It is worthy of note that the substituent effect on the solvolysis through the percaudal interaction of $\gamma$-silyl-ester (**10**) also gave a correlation with $\rho = -1.0$ and $r \cong 0$,[18] that is expected for the transition state where the aryl-silyl function is attached at the $\beta$-position to the carbocation center.

In order to establish the use of selectivity ($\rho$) parameters as a sensitive probe for the $\beta$-silyl participation, we have to obtain more data about $\beta$-(arylsilyl) substituent effects in a series of relevant $\beta$-silylalkyl systems bearing substituents in the ethyl chain ($R^1$–$R^4$ in **1**).

## Experimental

Column chromatography was performed by using $SiO_2$ (Silica gel 60 (230–400 mesh, Merck) for flash column chromatography or LiChroprep Si 60 (25–40 µm, Merck) for middle-pressure liquid chromatography). The $^1H$ NMR spectra were taken in $CDCl_3$ on a JEOL JNM-A500 FT-NMR spectrometer operating at 500 MHz and the chemical shifts were recorded in ppm ($\delta$) downfield from TMS as an internal standard. All air- and moisture-sensitive reactions were carried out under nitrogen or argon. Ether and tetrahydrofuran were distilled from sodium/benzophenone under nitrogen.

**Material [(3,5-Bis(trifluoromethyl)phenyl)dimethylsilyl]methyl Chloride.** A solution of 3,5-bis(trifluoromethyl)phenylmagnesium bromide prepared from the 3,5-bis(trifluoromethyl)bromobenzene and Mg in THF was added dropwise to chloro(chloromethyl)dimethylsilane in THF with stirring at 0 °C and the reaction mixture was heated under reflux with stirring overnight under nitrogen atmosphere, according to the method of Vencl et al.[16] After cooling, the reaction mixture was treated with aqueous $NH_4Cl$, and extracted with ether. The ethereal extract was washed with aqueous sodium hydrogencarbonate and aqueous saturated sodium chloride, and then dried over anhydrous magnesium sulfate. The crude chloride was purified by vacuum distillation (bp 71–74 °C/1.5 mmHg (1 mmHg = 133.322 Pa)) to give a colorless oil (yield, 50%): $^1$H NMR $\delta$ 0.50 (6H, s, $SiCH_3$), 2.98 (2H, s, $CH_2$), 7.90 (1H, s, Ar-H), 7.95 (2H, s, Ar-H).

Other (aryldimethylsilyl)methyl chlorides were synthesized from arylmagnesium bromides and chloro(chloromethyl)dimethylsilane in ether as reported before.[18]

**Ethyl (Dimethylphenylsilyl)acetate.** Ethyl (dimethylphenylsilyl)acetate was synthesized by the Reformatsky reaction from the chlorodimethylphenylsilane and ethyl bromoacetate, according to the method of Vencl et al.[16] The mixture of chlorodimethylphenylsilane (5.16 g, 30.2 mmol) and ethyl bromoacetate (4.95 g, 29.6 mmol) in THF (10 mL) solution was added dropwise to Zn (1.94 g, 29.7 mmol) in THF 30 mL under reflux and the mixture was maintained under reflux until Zn completely dissolved. Then, 10% HCl 20 mL was added to the cold reaction mixture, which was extracted with ether. Ethereal extract was washed with aq sat $NH_4Cl$, aq $NaHCO_3$, and aq sat NaCl, and then dried over anhydrous $MgSO_4$. Purification by column chromatography afforded 3.35 g (yield, 50%) of the acetate as a colorless oil: $^1$H NMR $\delta$ 0.40 (6H, s, $SiCH_3$), 1.15 (3H, t, $J = 7.0$ Hz, $CH_3$), 2.10 (2H, s, $CH_2$), 4.03 (2H, q, $J = 7.0$ Hz, $OCH_2$), 7.34–7.54 (5H, m, Ph-H).

**Ethyl (*p*-Methoxyphenyldimethylsilyl)acetate.** To a Grignard solution prepared from (*p*-methoxyphenyldimethylsilyl)methyl chloride (11 g, 51 mmol) and Mg (1.24 g, 51 mmol) in 70 cm$^3$ of ether was added dropwise a solution of ethyl chloroformate (5.53 g, 51 mmol) in 60 cm$^3$ of ether with stirring at 0 °C, according to the method of Vencl et al.[16] After stirring overnight, the reaction mixture was treated with aq $NH_4Cl$, and extracted with ether. The ethereal extract was washed with aq $NaHCO_3$ and aq sat NaCl, and then dried over anhydrous $MgSO_4$. Purification by column chromatography afforded 3.57 g (yield, 27%) of the ester as a colorless oil: $^1$H NMR $\delta$ 0.37 (6H, s, $SiCH_3$), 1.17 (3H, t, $J = 7.5$ Hz, $CH_3$), 2.08 (2H, s, $CH_2$), 3.81 (3H, s, $OCH_3$), 4.03 (2H, q, $J = 7.5$ Hz, $OCH_2$), 6.92 (2H, d, $J = 8.5$ Hz, Ar-H), 7.46 (2H, d, $J = 8.5$ Hz, Ar-H). By the same procedure, the following acetates were prepared from the corresponding (aryldimethylsilyl)methyl chlorides.

**Ethyl [(3-Chloro-4-methoxyphenyl)dimethylsilyl]acetate:** $^1$H NMR $\delta$ 0.38 (6H, s, $SiCH_3$), 1.17 (3H, t, $J = 7.5$ Hz, $CH_3$), 2.08 (2H, s, $CH_2$), 3.91 (3H, s, $OCH_3$), 4.04 (2H, q, $J = 7.5$ Hz, $OCH_2$), 6.94 (1H, d, $J = 8.0$ Hz, Ar-H), 7.37 (1H, dd, $J = 8.0$ Hz, $J = 1.5$ Hz, Ar-H), 7.48 (1H, d, $J = 1.5$ Hz, Ar-H).

**Ethyl (*p*-Chlorophenyldimethylsilyl)acetate:** $^1$H NMR $\delta$ 0.39 (6H, s, $SiCH_3$), 1.16 (3H, t, $J = 7.0$ Hz, $CH_3$), 2.09 (2H, s, $CH_2$), 4.03 (2H, q, $J = 7.0$ Hz, $OCH_2$), 7.35 (2H, d, $J = 8.5$ Hz, Ar-H), 7.46 (2H, d, $J = 8.5$ Hz, Ar-H).

**Ethyl (*m*-Chlorophenyldimethylsilyl)acetate:** $^1$H NMR $\delta$ 0.40 (6H, s, $SiCH_3$), 1.16 (3H, t, $J = 7.0$ Hz, $CH_3$), 2.10 (2H, s, $CH_2$), 4.04 (2H, q, $J = 7.0$ Hz, $OCH_2$), 7.28–7.41 (4H, m, Ar-H).

**Ethyl [3,5-Bis(trifluoromethyl)phenyldimethylsilyl]acetate:** $^1$H NMR $\delta$ 0.48 (6H, s, $SiCH_3$), 1.14 (3H, t, $J = 7.0$ Hz, $CH_3$), 2.16 (2H, s, $CH_2$), 4.03 (2H, q, $J = 7.0$ Hz, $OCH_2$), 7.89 (1H, s, Ar-H), 7.95 (2H, s, Ar-H).

**2-(Dimethylphenylsilyl)ethanol.** Ethyl (dimethylphenylsilyl)acetate was reduced by $LiAlH_4$ in ether with reflux overnight. After the usual work-up, the crude alcohol was purified by column chromatography. Colorless oil: $^1$H NMR $\delta$ 0.30 (6H, s, $SiCH_3$), 1.20 (2H, t, $J = 8.5$ Hz, $SiCH_2$), 3.74 (2H, t, $J = 8.5$ Hz, $CH_2$), 7.33–7.52 (5H, m, Ph-H). Found: C, 66.54; H, 9.01%. Calcd for $C_{10}H_{16}OSi$: C, 66.61; H, 8.94%. The following ring substituted derivatives were obtained in the same way.

**2-(*p*-Methoxyphenyldimethylsilyl)ethanol:** Colorless oil: $^1$H NMR $\delta$ 0.28 (6H, s, $SiCH_3$), 1.17 (2H, t, $J = 8.5$ Hz, $SiCH_2$), 3.73 (2H, t, $J = 8.5$ 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). Found: C, 62.64; H, 8.62%. Calcd for $C_{11}H_{18}O_2Si$: C, 62.81; H, 8.63%.

**2-[(3-Chloro-4-methoxyphenyl)dimethylsilyl]ethanol:** Colorless oil: $^1$H NMR $\delta$ 0.28 (6H, s, $SiCH_3$), 1.17 (2H, t, $J = 8.5$ Hz, $SiCH_2$), 3.72 (2H, t, $J = 8.5$ Hz, $CH_2$), 3.90 (3H, s, $OCH_3$), 6.93 (1H, d, $J = 7.5$ Hz, Ar-H), 7.34 (1H, dd, $J = 7.5$ Hz, $J = 1.5$ Hz, Ar-H), 7.46 (1H, d, $J = 1.5$ Hz, Ar-H). Found: C, 53.98; H, 7.04%. Calcd for $C_{11}H_{17}ClO_2Si$: C, 53.97; H, 7.00%.

**2-(*p*-Chlorophenyldimethylsilyl)ethanol:** Colorless oil: $^1$H NMR $\delta$ 0.30 (6H, s, $SiCH_3$), 1.18 (2H, t, $J = 8.0$ Hz, $SiCH_2$), 3.73 (2H, t, $J = 8.0$ Hz, $CH_2$), 7.33 (2H, d, $J = 8.0$ Hz, Ar-H), 7.43 (2H, d, $J = 8.0$ Hz, Ar-H). Anal. Found: C, 56.28; H, 7.04%. Calcd for $C_{10}H_{15}ClOSi$: C, 55.93; H, 7.04%.

**2-(*m*-Chlorophenyldimethylsilyl)ethanol:** Colorless oil: $^1$H NMR $\delta$ 0.31 (6H, s, $SiCH_3$), 1.19 (2H, t, $J = 8.0$ Hz, $SiCH_2$), 3.74 (2H, t, $J = 8.0$ Hz, $CH_2$), 7.29–7.52 (4H, m, Ar-H). Found: C, 55.86; H, 6.93%.

**2-[3,5-Bis(trifluoromethyl)phenyldimethylsilyl]ethanol:** Colorless oil: $^1$H NMR $\delta$ 0.34 (6H, s, $SiCH_3$), 1.21 (2H, t, $J = 8.0$ Hz, $SiCH_2$), 3.78 (2H, t, $J = 8.0$ Hz, $CH_2$), 7.84 (1H, s, Ar-H), 7.91 (2H, s, Ar-H). Found: C, 45.75; H, 4.59%. Calcd for $C_{12}H_{14}F_6OSi$: C, 45.56; H, 4.46%.

**2-(Dimethylphenylsilyl)ethan-1,1-*d*$_2$-ol.** Ethyl (dimethylphenylsilyl)acetate was reduced by $LiAlD_4$ (98%D) in ether in the same way as the protio isotopomer. After the usual work-up, the crude alcohol was purified by column chromatograpy. Colorless oil: $^1$H NMR $\delta$ 0.30 (6H, s, $SiCH_3$), 1.18 (2H, s, $SiCH_2$), 7.33–7.52 (5H, m, Ph-H).

**2-(Dimethylphenylsilyl)ethan-2,2-*d*$_2$-ol.** To a stirred solution of lithium diisopropylamide prepared from diisopropylamine (1.9 cm$^3$, 13.5 mmol) and 1.6 M (M = mol dm$^{-3}$) butyllithium hexane solution (9.0 cm$^3$, 13.5 mmol) in 15 cm$^3$ of THF at 0 °C was added dropwise a solution of ethyl 2-(dimethylphenylsilyl)acetate (2.00 g, 9.0 mmol) in 5 cm$^3$ of THF at −70 °C. After stirring at −70 °C for 10 min, $D_2O$ (0.37 g, 18.0 mmol) in 5 cm$^3$ of THF was added quickly. After stirring at −70 °C for 1 h, the reaction mixture was kept at room temperature with stirring for 2 h, and then quenched with 40 cm$^3$ of water. The aqueous layer was separated from the organic layer, and then extracted with ether. The combined organic layer was washed with aq $NH_4Cl$, aq $NaHCO_3$, and sat NaCl, and dried over anhydrous $MgSO_4$. Purification by column chromatography afforded 1.0 g (yield, 83%) of the 2-*d* ester as a colorless oil: $^1$H NMR $\delta$ 0.40 (6H, s, $SiCH_3$), 1.16 (3H, t, $J = 7.0$ Hz, $CH_3$), 2.11 (1H, s, CHD), 4.03 (2H, q, $J = 7.0$ Hz, $CH_2$), 7.34–7.54 (5H, m, Ph-H). By the same procedure, 2-*d* ester was converted to 2,2-$d_2$ ester, which has 94%D content: $^1$H NMR $\delta$ 0.40 (6H, s, $SiCH_3$), 1.16 (3H, t, $J = 7.0$ Hz, $CH_3$), 4.03 (2H, q, $J = 7.0$ Hz, $OCH_2$), 7.34–7.54 (5H, m, Ph-H). The 2,2-$d_2$ ester was reduced with $LiAlH_4$ in ether to 2-(dimethylphenylsilyl)ethanol-2,2-$d_2$ as the same way as used for protio derivative: $^1$H NMR $\delta$ 0.30 (6H, s, $SiCH_3$), 3.74 (2H, s, $CH_2$), 7.35–7.52 (5H, m, Ph-H).

**2-(Dimethylphenylsilyl)ethyl Chloride.** The alcohol (1.9 g, 10 mmol) in 15 cm$^3$ of ether was chlorinated with $SOCl_2$ (7.7 cm$^3$, 105 mmol) at 0 °C. Excess $SOCl_2$ was completely removed by the distillation with fresh dry benzene added under the reduced pressure. The crude chloride was purified by distillation using Kugelrohr distillation (bp 79–81 °C/2 mmHg). Colorless oil: $^1$H NMR $\delta$ 0.33 (6H, s, $SiCH_3$), 1.42–1.46 (2H, m, $SiCH_2$), 3.60–3.64 (2H, m, $CH_2$), 7.34–7.54 (5H, m, Ph-H).

**2-(*p*-Methoxyphenyldimethylsilyl)ethyl Chloride:** Colorless oil (bp 120–125 °C/4 mmHg): $^1$H NMR $\delta$ 0.26 (6H, s, $SiCH_3$), 1.37–1.40 (2H, m, $SiCH_2$), 3.56–3.60 (2H, m, $CH_2Cl$), 3.77 (3H, s, $OCH_3$), 6.85–7.34 (4H, m, Ar-H).

**2-[(3-Chloro-4-methoxyphenyl)dimethylsilyl]ethyl Chloride:** Colorless oil (bp 115–117 °C/2 mmHg): $^1$H NMR $\delta$ 0.31 (6H, s, $SiCH_3$), 1.40–1.44 (2H, m, $SiCH_2$), 3.59–3.62 (2H, m, $CH_2$), 3.91 (3H, s, $OCH_3$), 6.90–7.43 (3H, m, Ar-H).

**2-(*p*-Chlorophenyldimethylsilyl)ethyl Chloride:** Colorless oil (bp 110–113 °C/3 mmHg): $^1$H NMR $\delta$ 0.32 (6H, s, $SiCH_3$), 1.41–1.45 (2H, m, $SiCH_2$), 3.58–3.62 (2H, m, $CH_2$), 7.35 (2H, d, $J = 8.5$ Hz, Ar-H), 7.41 (2H, d, $J = 8.5$ Hz, Ar-H).

**2-(*m*-Chlorophenyldimethylsilyl)ethyl Chloride:** Colorless oil: $^1$H NMR $\delta$ 0.34 (6H, s, $SiCH_3$), 1.43–1.46 (2H, m, $SiCH_2$), 3.59–3.63 (2H, m, $CH_2$), 7.32–7.54 (4H, m, Ar-H).

**2-[3,5-Bis(trifluoromethyl)phenyldimethylsilyl]ethyl Chloride:** Colorless oil: $^1$H NMR $\delta$ 0.43 (6H, s, $SiCH_3$), 1.50 (2H, t, $J = 8.5$ Hz, $SiCH_2$), 3.63 (2H, t, $J = 8.5$ Hz, $CH_2$), 7.88–7.95 (3H, m, Ar-H).

**2-(Dimethylphenylsilyl)ethyl 3,5-Dinitrobenzoate.** To a stirred solution of 2-(dimethylphenylsilyl)ethanol (0.300 g, 1.66 mmol) in 3 cm$^3$ of ether with pyridine (2.0 cm$^3$) was slowly added 3,5-dinitrobenzoyl chloride (0.384 g, 1.66 mmol) in 10 cm$^3$ ether at 0 °C. After stirring overnight, the reaction mixture was treated with 10 cm$^3$ of cold water under cooling and then extracted with ether. After the material was washed with dil. HCl, aq $NaHCO_3$, and sat. NaCl, and dehydrated over anhydrous $MgSO_4$, the solvent was evaporated under reduced pressure to give the crude 3,5-dinitrobenzoate, which was purified by column chromatography and recrystallized with hexane–AcOEt to yield 0.42 g (yield 67%) as needles, mp 79–80.5 °C: $^1$H NMR $\delta$ 0.39 (6H, s, $SiCH_3$), 1.45 (2H, t, $J = 8.5$ Hz, $SiCH_2$), 4.55 (2H, t, $J = 8.5$ Hz, $CH_2$), 7.37–7.52 (5H, m, Ph-H), 9.03 (2H, d, $J = 2.0$ Hz, Ar-H), 9.18 (1H, t, $J = 2.0$ Hz, Ar-H). Found: C, 54.78; H, 4.94; N, 7.49%. Calcd for $C_{17}H_{18}N_2O_6Si$: C, 54.53; H, 4.85; N, 7.48%. In the same way, the following deuterated esters were prepared.

**2-(Dimethylphenylsilyl)ethyl-1,1-$d_2$ 3,5-Dinitrobenzoate:** mp 78–80 °C: $^1$H NMR $\delta$ 0.38 (6H, s, $SiCH_3$), 1.43 (2H, s, $SiCH_2$), 7.27–7.69 (5H, m, Ph-H), 9.03 (2H, d, $J = 2.0$ Hz, Ar-H), 9.18 (1H, t, $J = 2.0$ Hz, Ar-H).

**2-(Dimethylphenylsilyl)ethyl-2,2-$d_2$ 3,5-Dinitrobenzoate:** mp 77–78.5 °C: $^1$H NMR $\delta$ 0.38 (6H, s, $SiCH_3$), 4.53–4.56 (2H, m, $CH_2$), 7.27–7.69 (5H, m, Ph-H), 9.03 (2H, d, $J = 2.0$ Hz, Ar-H), 9.18 (1H, t, $J = 2.0$ 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.[18]

**Kinetic Measurements.** The solvolysis rates of 2-(dimethylphenylsilyl)ethyl chlorides were determined conductimetrically as reported previously[18] at initial concentrations of $10^{-5}$–$10^{-4}$ M. Using conductivity meters (Toa Electronics Ltd: CM-50AT, CM-40S, and CM-60S, equipped with an interval time unit and printer, or CM-60V, CM-40V, and CM-40G, connected to a personal computer) we followed the solvolyses 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%.

**Product Analyses.** Product analyses for solvolyses of the chlorides under the buffered condition with excess 2,6-lutidine were carried out using $^1$H NMR in situ according to the same procedure as described before,[18] providing the exclusive formation of $CH_2{=}CH_2$ in the deuterated solvents of aq ethanol, aq acetone, and 2,2,2-trifluoroethanol.

A solution ($6 \times 10^{-3}$ M) of the 3,5-dinitrobenzoate buffered with 2 equiv 2,6-lutidine in deuterated 2,2,2-trifluoroethanol ($CF_3CD_2OD$) was allowed to react at 125 °C in a fused NMR tube and the solvolysis products at ten half-lives were identified by the $^1$H NMR spectra. The relative amounts of reaction products, ethylene and 2-(dimethylphenylsilyl)ethyl 2′,2′,2′-trifluoroethyl-1′,1′-$d_2$ ether, were determined from the integral areas of the corresponding peaks, as summarized in Table 3.

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