The β-Silicon Effect. II. Substituent Effects on the Solvolysis of 1-Aryl-2-(aryldimethylsilyl)ethyl 3,5-Dinitrobenzoates

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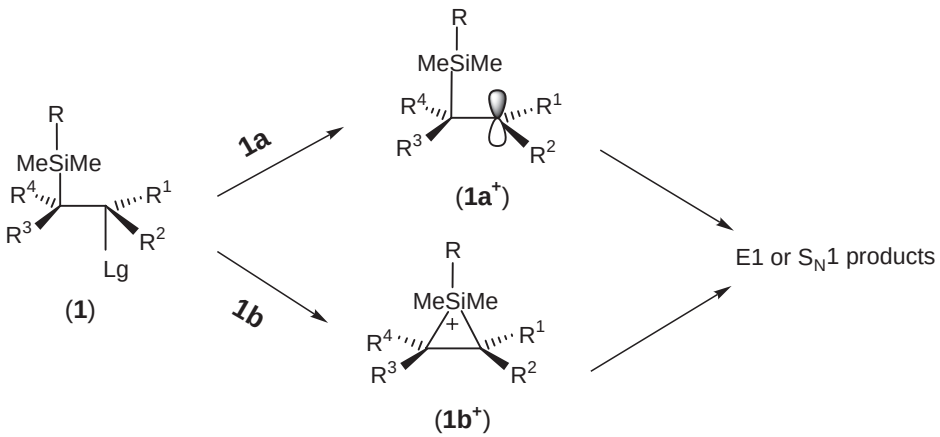
Solvolysis rates of 2-(dimethylphenylsilyl)-1-(Y-phenyl)ethyl 3,5-dinitrobenzoates were determined conductimetrically in 60% (v/v) aqueous ethanol. In order to clarify the nature of the β-Si participation quantitatively, the effects of α-aryl substituents on the rates were analyzed by means of the Yukawa–Tsuno Eq. The α-aryl (Y)-substituent effect at 25 °C was correlated with $r \cong 1.0$ and $\rho = -3.0$, which is significantly reduced compared with that of −5.45 for the non-silylated 1-arylethyl system. There is a linear relationship between $\log k_Y/k_H$ of silylated and non-silylated substrates: $\log(k_Y/k_H)_{Si} = 0.52 \log(k_Y/k_H)_{non\text{-}Si}$. This is the same form as the extended Brønsted relationship. The Brønsted coefficient $\alpha = 0.52$ appeared to be consistent with the neighboring silyl-participation in the silyl-bridged transition state.

It is well known that the β-silicon substituent greatly facilitates the heterolysis of the C–Lg bond, which is caused by a trimethylsilyl group in an antiperiplanar conformation.[2] Stabilization of this electron deficiency was interpreted in terms of either the open form (**1a**$^+$) stabilized by σ–π hyperconjugation or by the Si-bridged form (**1b**$^+$) of the cationic intermediate,[2–5] as shown in Scheme 1.

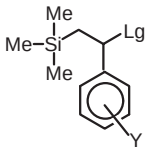
The conformational dependence of the β-silicon effect in the solvolysis of cyclic secondary systems[2,4b] was taken as convincing evidence for the Si–C_β hyperconjugation mechanism. Numerous results can be explained satisfactorily by either the non-classical (bridged) or the classical (open cation) transition state (TS). For stable substrate systems (sec. and tert. cations, and also α-phenyl-substrates), in fact, various mechanistic criteria[2,4,5] suggested the simple ionization mechanism (k_C) via the open carbocation **1a**$^+$, while in the case of primary systems, the silyl-bridged pathway (**1b**) was instead supported.[1] Thus, the relative importance of these two pathways still remains substantially unresolved. A question then arises as to whether or not the k_C pathway **1a** can be distinguished from the silyl-bridged k_Δ pathway **1b** via the silyl-bridged TS for the ionization of β-silylated substrates.

Whatever the mechanism of enormous β-silyl participation, the overall participation measured by the reactivity ratio of silylated/non-silylated substrates is anti-proportional to the cation-stabilities of the non-silylated substrates. Nevertheless, the silyl-assisted reactivities are proportional to the stabilities of non-silylated cations. In order to deal quantitatively with such a relationship as regards the β-silyl-assisted reactions, we have chosen for study the solvolysis of 2-trimethylsilyl-1-(Y-phenyl)ethyl trifluoroacetates (**2**),[5] and for the present further extended study, the solvolysis of 2-[dimethyl(X-phenyl)silyl]-1-

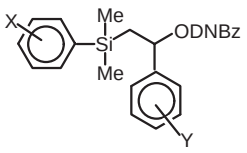


Scheme 1. β-Silicon effect in the carbocationic solvolysis.

Published on the web July 4, 2006; doi:10.1246/bcsj.79.1091



(**2**)



(**3**) X and Y variable
(**4**) X = H fixed Y variable
(**5**) X = 3,5-$(CF_3)_2$ Y variable

Chart 1. Structures of β-Si-α-Ar-ethyl systems.

(Y-phenyl)ethyl 3,5-dinitrobenzoates (**3**) (Chart 1).

One of the major interests underlying our investigation is to establish how to use the structure–reactivity relationship and relevant parameters as mechanistic criteria in order to clarify the structure(s) of the TS(s). The β-silyl-assisted reaction is especially attractive for us, because of its enormous rate-acceleration as well as the high dependency on substrate structures. Furthermore, it is most interesting if we can distinguish between the two silyl-assisted pathways, the vertical (open) ion and the nonvertical (silyl-bridged) pathways, (**1a**) and (**1b**), respectively.

The detailed analysis of the substituent effects in these systems was carried out by the Yukawa–Tsuno (Y–T) Eq. 1:[6]

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

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. Symbol σ^0 is the normal substituent constant that involves no additional π-electronic interaction between the substituent and the reaction center, and $\Delta\bar{\sigma}_R^+$ is the resonance substituent constant, defined by $\sigma^+ - \sigma^0$, measuring the capability for π-delocalization of a p-π-donor substituent.

In an earlier study concerning the β-Me_3Si-α-phenyl substrate system **2**, correlation analysis studies on the substituent effect lent some support for Lambert's interpretation, in which the mechanism via the open cationic TS is stabilized by enhanced C_β–Si hyperconjugation.[5]

In this paper, we will deal with the α-aryl (Y)-substituent effects on the silicon-participation solvolysis of **4** with a fixed silyl moiety (X = H), especially aiming at the distinction between the silyl-hyperconjugation and the neighboring silyl-group participation mechanisms (**1a**) and (**1b**).

Results

Rates of Solvolysis. The solvolysis rates of 2-(dimethylphenylsilyl)-1-(Y-phenyl)ethyl 3,5-dinitrobenzoates (**4**) were determined conductimetrically in 60% (v/v) aqueous ethanol (60E) for a wide range of aryl substituents from p-MeO to 3,5-$(CF_3)_2$. The rate for the highly reactive 1-(p-methoxyphenyl) derivative was obtained for the less reactive leaving benzoate and was converted to k_{ODNBz} by the k_{ODNBz}/k_{OBz} ratio of 76.8 derived from the rate ratio for the 1-(p-methylphenyl)-ethyl derivative. The solvolysis rates of 1-aryl-2-[3,5-bis(trifluoromethyl)phenyldimethylsilyl]ethyl 3,5-dinitrobenzoates (**5**) were also measured for several electron donating Y-derivatives. Kinetic data are listed in Table 1. The solvolysis rates for the parent **3** (X = Y = H) 3,5-dinitrobenzoate were determined in various solvents at 25.0 °C (in Table 2). Activation parameters in the present data were of quite normal magnitude for the S_N1 reaction mechanism.

Product Analysis. The product analysis for the solvolyses of 2-(dimethylphenylsilyl)-1-phenylethyl 3,5-dinitrobenzoate was carried out in CD_3CD_2OD in the presence of excess 2,6-lutidine at 55 °C by using a ^{1}H NMR method. The products of complete reaction were found to be styrene (64%) accompa-

Table 1. Solvolysis Rates of 2-[Dimethyl(X-substituted phenyl)silyl]-1-(Y-substituted phenyl)ethyl 3,5-Dinitrobenzoate in 60% Aqueous Ethanol

Substituent		$10^5 \times k/s^{-1}$		$\Delta H^{\ddagger}_{25\,°C}$ [a]	$\Delta S^{\ddagger}_{25\,°C}$ [a]
Y	X	25 °C	(Temp/°C)	/kcal mol^{-1}	/e.u.
p-MeO	H	2.3×10^4 [b]			
		301[c]	33.0 (5)[c]		
	3,5-$(CF_3)_2$	3.5×10^3 [b]			
		46.0[c]	454 (45)[c]		
m-Cl-p-MeO	H	1.9×10^3			
	3,5-$(CF_3)_2$	363	27.3 (5)	20.7	−0.2
p-Me	H	676			
		8.80[c]			
	3,5-$(CF_3)_2$	68.9	782(45)	22.3	1.8
m-Me	H	149.1	10.56(5)	21.2	−0.3
H	H	72.9	652(45)	20.1	−5.6
	3,5-$(CF_3)_2$	5.96	70.8(45), 198.7(55)	22.2	−3.3
p-Cl	H	31.3	313(45)	21.1	−3.8
m-Cl	H	5.07	61.6(45)	22.9	−1.2
m-CF_3	H	2.69	32.7(45)	22.9	−2.5
	3,5-$(CF_3)_2$	0.169	2.44(45), 7.72(55)	24.2	−3.6
3,5-Cl_2	H	0.528	7.88(45)	24.9	0.8
3,5-$(CF_3)_2$	H	0.0897[d]	4.14(55), 36.9(75)	24.2	−4.9

a) 1 cal = 4.184 J. b) Estimated value from the rate data for the benzoate based on the 3,5-dinitrobenzoate/benzoate ratio for Y = p-Me. c) Rate data for the benzoate. d) Extrapolated from the rate data at other temperatures.

Table 2. Solvolysis Rates of 2-(Dimethylphenylsilyl)-1-phenylethyl 3,5-Dinitrobenzoate at 25 °C

Solvent[a)]	$10^5 \times k$ /s^{-1} at 25 °C	Solvent[a)]	$10^5 \times k$ /s^{-1} at 25 °C
90E	8.19	50A	56.8
80E	22.5[b)]	40A	142.2
70E	39.9	97T[b)]	1200
60E	72.9	80T	1143
50E	112.4	MeOH	10.35
80A	2.22	80M	64.0
70A	6.60	60M	264
60A	22.1	50M	555

a) Volume percent (v/v) of first named organic component unless otherwise noted. Abbreviations: E = EtOH, M = MeOH, A = Acetone, T = 2,2,2-trifluoroethanol. b) Weight % (w/w) of organic component.

nied with the substitution product, ethyl ether (36%), and the composition of the products did not change during the course of reaction. This indicates that the rate-determining ionization leads to the benzylic cation followed by the elimination of the phenylsilyl moiety or displacement of the solvent. The substitution product is sufficient to support that this reaction proceeds through the β-Si carbocation, not through the nucleophilic solvent attack to a Si atom. In the solvolysis in 60E, styrene was obtained as the sole product.

The Solvent Effect. The studies of the solvent effects provide important information to estimate the TS structure, especially regarding the charge-delocalization. The solvent effect on the solvolyses of 2-(dimethylphenylsilyl)-1-phenylethyl 3,5-dinitrobenzoate at 25 °C was analyzed in terms of the Winstein–Grunwald (W–G) equation, Eq. 2:[7]

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

where Y_{Lg} is the ionizing power parameter of respective solvents based on rates of k_c solvolysis of the common reference substrate 1-adamantyl–Lg, and m is its susceptibility of a given solvolyzing substrate. Because of the lack of an appropriate set of Y parameters for leaving 3,5-dinitrobenzoate (Y_{ODNB}), we employed Y_{Cl} instead of Y_{ODNB}. As shown in Fig. 1, the solvent effect exhibited a poor correlation against Y_{Cl} with significant splittings for the respective binary solvent series and an m value of 0.54, indicating a significant decrease in cationic charge at the reaction center carbon in the TS. The scatterings from the correlation line were observed for the respective binary solvent series, indicating the dissimilarity of the present delocalized carbocationic TS to the standard 1-adamantyl system with the localized cationic TS. We made no further efforts to delineate the overall plot in this paper. For a precise discussion, it is necessary to compare the W–G correlations for related systems with the common leaving group –ODNB. Nevertheless, it is enough to conclude the absence of nucleophilic solvent assistance in the rate-determining step.

α-Aryl Substituent Effects. The substituent effects of the α-aryl group of **4** and the related systems were analyzed routinely based on the Y–T Eq. 1. As shown in Fig. 2, the substituent effects of the α-aryl group in **4** at 25 °C in 60E was linearly correlated with $r = 1.04$ and $\rho = -2.95$: R = 0.9995 and SD = ±0.055,

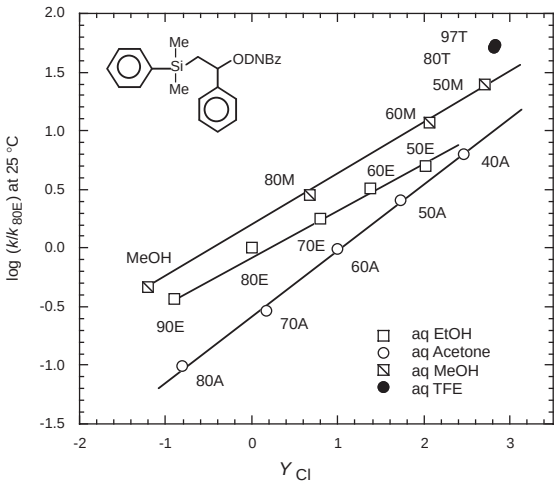


Fig. 1. The W–G plots against Y_{Cl} for the solvolysis of 2-(dimethylphenylsilyl)-1-phenylethyl 3,5-dinitrobenzoate at 25 °C.

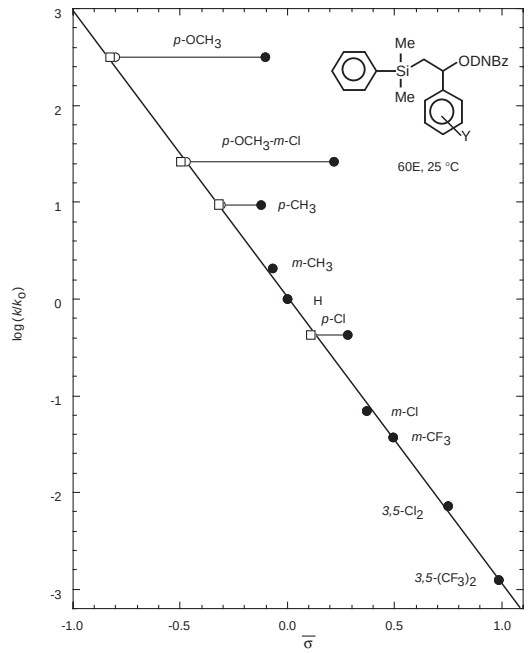


Fig. 2. Substituent effect on the solvolysis of 1-aryl-2-(dimethylphenylsilyl)ethyl 3,5-dinitrobenzoates (**4**) in 60% (v/v) aq EtOH at 25 °C: Closed circles for σ^0, open circles for σ^+, and open squares for $\bar{\sigma}$ with $r = 1.04$.

$$\log(k_Y/k_H)_{\mathbf{4}} = (-2.95 \pm 0.06)[\sigma^0 + (1.04 \pm 0.05)\Delta\bar{\sigma}_R^+]. \quad (3)$$

The Y–T correlation for the corresponding β-Me$_3$Si series **2** was reported[5a] to have closely the same ρ and r values as those in the correlation (3) for the β-dimethylphenylsilyl series **4**, while the leaving group and also the solvent were different.

$$\log(k/k_0)_{\mathbf{2}} = -3.05(\sigma^0 + 1.05\Delta\bar{\sigma}_R^+). \quad (4)$$

There existed a linear log–log relationship (5) between **4** (X = H) and **5** (X = 3,5-(CF$_3$)$_2$) subsets as shown in Fig. 3, with a slope of 1.12 (R = 0.998, SD = ±0.11):

$$\log(k_Y/k_H)_{\mathbf{5}} = (1.12 \pm 0.04)\log(k_Y/k_H)_{\mathbf{4}} - 0.04, \quad (5)$$

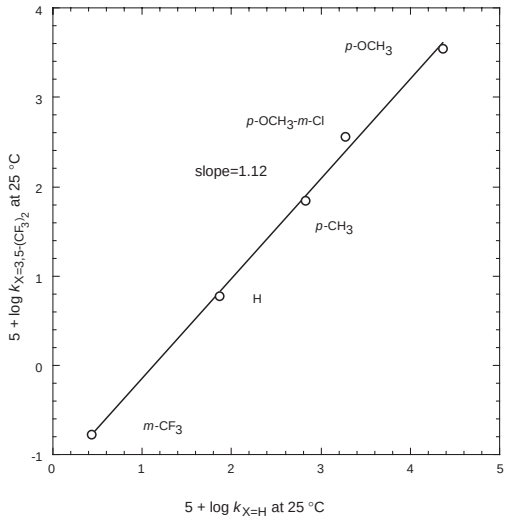


Fig. 3. Linear logarithmic plots $(k_Y)_4$ vs $(k_Y)_5$ between **4** (X = H) and **5** (X = 3,5-$(CF_3)_2$) for 2-[dimethyl(X-substituted phenyl)silyl]-1-(Y-substituted phenyl)ethyl solvolyses.

indicating that the ρ_Y value for the X = 3,5-$(CF_3)_2$ subset is −3.29, as the r remains the same.

The ρ values vary less significantly (from −2.95 to −3.29) with a change of silyl moieties, but all were different distinctly from the reference ρ value ($\rho_{\mathbf{3n}} = -5.45$) for the non-silylated 1-phenylethyl system (**3n**).[8]

Discussion

The solvolysis rates of β-silylated α-arylethyl substrates were found to be remarkably higher than the rates of the non-silylated **3n** or the corresponding β-*t*-Bu-derivative. The β-silicon effects or the overall silyl participation may be assessed most reasonably by rate accelerations, $k_{Si}/k_{t\text{-Bu}}$ or k_{Si}/k_H, for the respective Y-derivatives. The β-silicon effects in the α-phenyl system **4** were assessed to be at least of 10^5 order of magnitude or ca. 7 kcal mol^{-1} for the parent substrate **4** (Y = H).[5] Nevertheless, the silyl participation in the α-phenyl system **4** is distinctly less important compared with the participation of up to 10^{12}-fold rate acceleration observed in the other β-silylated systems **1**.[2]

As shown in Fig. 2, the substituent (Y) effect in regards to the substrate **4** was linearly correlated with a $(\rho_Y)_{Si}$ value of −2.95 against $\bar{\sigma}$ ($r = 1.04$). Essentially, the same correlation ($(\rho_Y)_{Si} = -3.05$ and $r = 1.05$) was found for the β-trimethylsilyl subset **2**.[5a] The excellent linearity of the correlation indicates the absence of a significant mechanistic change for the whole range of Y-substituents. However, the ρ_Y value of the β-silylated system is distinctly lower than that in the non-silylated 1-phenylethyl system (**3n**). The size of ρ is commonly believed to reflect the extent of charge development at the reaction site directly involved in the bond-breaking process of Lg at the TS.[9]

As shown in Fig. 4, there is a precise linear relationship between the silylated (**Si**) and non-silylated (**n**) reactivities, $\log(k_Y/k_H)_{\mathbf{Si}}$ and $\log(k_Y/k_H)_{\mathbf{3n}}$:

$$\log(k_Y/k_H)_{\mathbf{Si}} = \alpha \log(k_Y/k_H)_{\mathbf{3n}}, \quad (6)$$

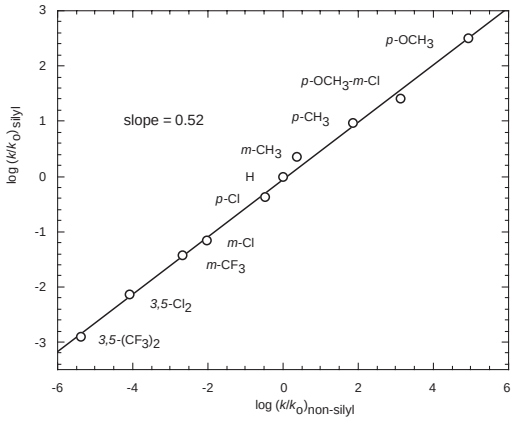


Fig. 4. Brønsted plot for 1-aryl-2-(dimethylphenylsilyl)-ethyl solvolyses.

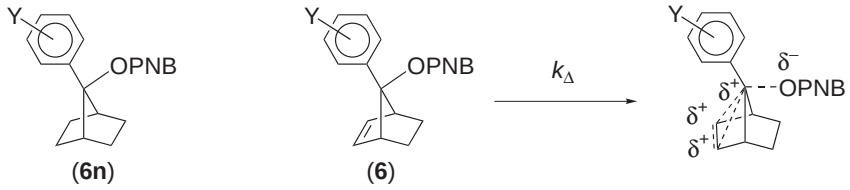
with a coefficient $\alpha = 0.52$ for **4**; practically the same α value was generally obtained for other β-silyl subsets **2** and **5**. Equation 6 is exactly the same form as the extended Brønsted relationship,[10] provided that the $\log(k_Y/k_H)_{\mathbf{3n}}$ is practically identical to ΔpK_R+ of the non-silylated system **3n** (and further to that of the silylated system **3** without silyl-participation).

The overall silyl participation was manifested by 1) the σ–π hyperconjugation mechanism (**1a**) between the highly polarizable C_β–Si bond and the empty p-orbital, and 2) the silyl-bridging mechanism (**1b**), where the silicon atom forms a partial C–Si bond to the carbon atom from which the nucleofuge departs. The bridging (Si–C_α bond-forming) may be in concert with nucleofuge departure, so that the reaction pathway **1b** should be analogous to the so-called neighboring group participation process.

The neighboring π-participation of a remote double bond occurs in the solvolyses of *syn*-7-aryl-*anti*-7-norbornenyl *p*-nitrobenzoates (**6**).[11] While the corresponding saturated system **6n** gave a linear Y–T correlation for the whole substituent range with a ρ value of −5.3 ($r = 1.0$) pointing to the ordinary k_C mechanism,[6b,11] the unsaturated **6** gave a clearly bisected plot; one falling on the **6n** line with the same ρ for strong electron donating (ED) *p*-Me_2N, and another for the range less ED than the *p*-MeO group with a reduced ρ value of −2.3 against the same $\bar{\sigma}$ scale (at $r = 1.0$) (Fig. 5), indicating competition from the C=C assisted mechanism ($\alpha = 0.43 = -2.3/(-5.3)$) (Scheme 2).

Similar participation of a neighboring electron-rich group occurs significantly in the solvolysis of 1-aryl-5-methyl-hepten-5-yl chlorides (**7**).[12] In the hexen-5-yl series **7**, the *p*-anisyl derivative solvolyzes practically at the same rate as that in the corresponding saturated series **7n** (Scheme 3).

Thus, if the stabilization of the TS is enhanced by the electron-donating *p*-MeO group, the neighboring group participation of the 5-double bond becomes insignificant. Below this leveling point of reactivity, the compounds of the unsaturated series **7** solvolyze faster than the corresponding compounds of the saturated series **7n** (Fig. 5). The acceleration, $\log(k_\Delta/k_C)$, for the respective Y derivatives appears to be significant and becomes more important as Y becomes more electron withdrawing. Equation 6 applies also to the π-participation of the remote double bond with a similar α-value of 0.4.



Scheme 2. Solvolysis of *syn*-7-aryl-*anti*-7-norbornenyl system.

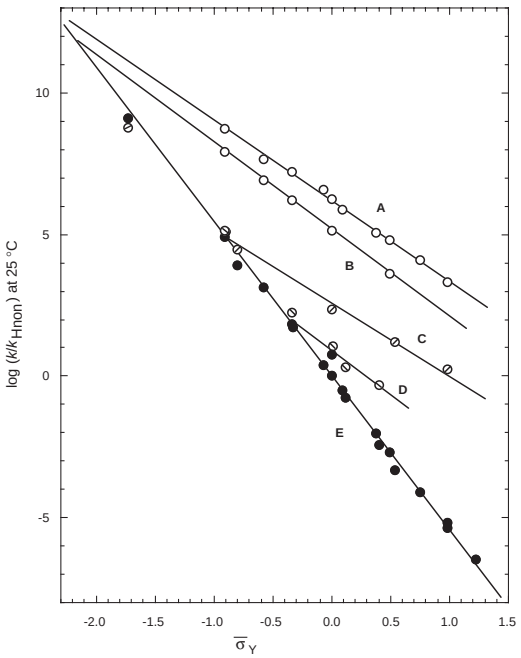


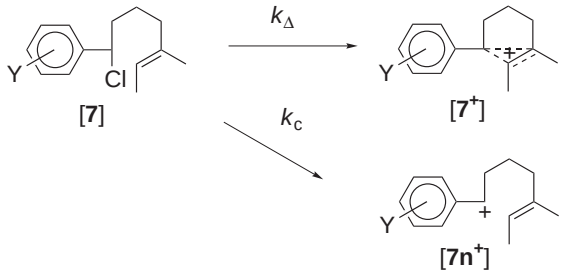
Fig. 5. Y–T plots for 1-aryl-2-(dimethylphenylsilyl)ethyl (**A**), 1-aryl-2-[3,5-bis(trifluoromethyl)phenyldimethylsilyl]ethyl (**B**), *syn*-7-aryl-*anti*-7-norbornenyl (**C**), and 1-arylhexen-5-yl (**D**) substrates, for the reference (**E**), solvolyses of **3n** and **6n**.

In order to detect the neighboring group participation, Brown applied the tool of increasing electron demand to the related systems to the above,[13] so that the $\Delta\rho$ ($=\rho_C - \rho_\Delta$) was used as the criteria instead of the coefficient α in Eq. 6. Both criteria can be related for the present system as Eq. 7,

$$(\Delta\rho)_{\mathbf{Si}} = (1-\alpha)\rho_{\mathbf{3n}}. \quad (7)$$

In Fig. 5, the Brønsted-type correlations are shown as in the form of the Y–T correlations for the above β-silyl and neighboring electron-rich group participation systems.

In the overall β-silyl participation mechanism in Scheme 1, the bridged (nonvertical) pathway (**1b**) can be referred to the concerted nucleophilic displacement mechanism with an internal nucleophile (Si-moiety), while the vertical pathway (**1a**) may be referred to the internal nucleophile (Si)-unassisted mechanism. The latter pathway involving the σ–π hyperconjugative stabilization will presumably be compatible with the so-called k_C mechanism in the solvolysis of the corresponding non-silylated substrate, α-arylethyl precursor (**3n**). On the other hand, the silyl-bridged pathway **1b** may be just compared with a concerted (S_N2) mechanism, such as the Menschutkin reaction of α-phenylethyl (**3n**) substrates with pyridine in acetonitrile, for which the Y–T correlations were assigned for



Scheme 3. Solvolysis of 1-arylhexen-5-yl substrates.

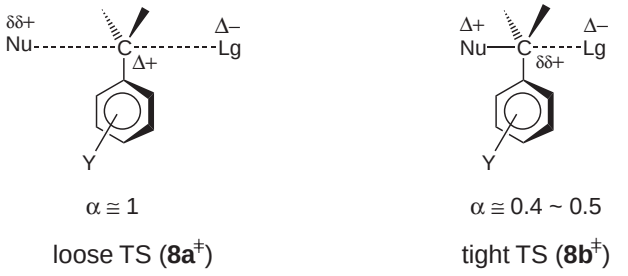
unimolecular ($\rho_1 = -5.0$, $r = 1.15$) and bimolecular ($\rho_2 = -2 - -3$, $r = 1.1$) processes, respectively.[14]

The Brønsted-type treatment (Eq. 6) is employed as the most useful tool for mechanistic investigation of the concerted nucleophilic substitution reactions, which involve varying degrees of nucleophilic participation at the TS. The criterion for the change in mechanism should be only a significant change in the α-coefficient or the magnitude of ρ. Thus, it is most essential of either the Brønsted-type treatment (Eq. 6) or Brown's tool of increasing electron demand that the substituent effect correlations are based on essentially the same $\bar{\sigma}$ scale as for the k_C solvolysis of the parent substrate, regardless of whether or not the participation of the neighboring group (or nucleophile) takes place.

In earlier studies,[5] the linear σ^+ correlation of **2** was taken as evidence for the k_C mechanism without nonvertical silyl-participation; the observed $r \cong 1$ was considered to be not in line with the silyl-bridged mechanism via a siliconium ion (**2b**$^+$) in which the resonance interaction should be largely or totally inhibited. Hence, the α-phenyl-β-silylethyl system **3** was referred to as a system of an open cation mechanism and the aryl (Y)-substituent effect will offer a measure of the k_C mechanism via (**1a**$^+$) without bridging.[5] However, this earlier conclusion was grossly misleading.

In the general case of the concerted nucleophilic substitution reactions, the benzylic substituent effects are correlated though appreciably concave by the same $\bar{\sigma}$ scale,[14,15] which is referred to that for pK_{R^+} of the substrate cations. The structure of the concerted displacement TS changes from the loose structure (**8a**‡), where a large positive charge Δ^+ resides on α-C$^+$, to the tight one (**8b**‡), where a small positive charge δ^+ resides on α-C$^+$; **8a**‡ resulted in a large negative $\rho = -5$ and **8b**‡ a much reduced $\rho = -2 - -3$.[14,15] The former TS involving weak nucleophilic participation indicates an α-coefficient close to 1, but the latter involving strong nucleophilic participation indicates α as small as 0.4–0.5 (Scheme 4).

The α-coefficient of 0.52 in the present β-silyl system **3** is consistent with the tight structure of the displacement TS, implying that an appreciable degree of Si–C$_\alpha$ bond-forming is



Scheme 4. The structure of transition state.

achieved at the TS in the silyl-assisted reactions of β-silylated systems. Consequently, we prefer to conclude that the β-silyl-assisted reaction should proceed by the silyl-bridged pathway **1b**. A sufficiently low α-coefficient may not be decisive evidence for the silyl-bridging, unless it is confirmed that the α-coefficient for the σ–π hyperconjugation process is close to unity. Perhaps, we have to still be careful in interpreting the magnitudes of the α value and linking it with the degree of bond-formation in the TS.

Experimental

Column chromatography was performed by using 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 ^{1}H NMR spectra were taken in $CDCl_3$ on a JEOL JNM-A500 (or -ECA500) FT-NMR spectrometer operating at 500 MHz 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 or argon. Ether and tetrahydrofuran were distilled from sodium/benzophenone under nitrogen.

Material. The following 1-aryl-2-(dimethylphenylsilyl)ethanols or 1-aryl-2-[3,5-bis(trifluoromethyl)phenyldimethylsilyl]-ethanols were obtained by the reactions of dimethylphenylsilylmethylmagnesium chloride or [3,5-bis(trifluoromethyl)phenyldimethylsilyl]methylmagnesium chloride reported previously[1] and substituted benzaldehydes, which are commercially available except for 3-chloro-4-methoxybenzaldehyde. The alcohols were converted to 3,5-dinitrobenzoate or benzoate using butyllithium and acid chloride.

3-Chloro-4-methoxybenzaldehyde. According to the literature method,[16] a solution of *N*-methylformanilide (4.8 g, 35.5 mmol) in 10 cm^3 of ether was added dropwise to the Grignard solution prepared from 3-chloro-4-methoxybromobenzene (8 g, 35.5 mmol) and Mg (0.86 g, 35.5 mmol) in 60 cm^3 of ether at 0 °C, and the reaction mixture was stirred at room temperature for 3 h. The solution was treated with H_2O (40 cm^3) and then with 10% HCl (40 cm^3), and extracted with ether. After the usual work-up, purification by SiO_2 column chromatography gave the colorless crystal, mp 55–56 °C: ^{1}H NMR δ 4.00 (3H, s, OCH_3), 7.05 (1H, d, J = 8.6 Hz, Ar-H), 7.78 (1H, dd, J = 8.6, 2.0 Hz, Ar-H), 7.92 (1H, d, J = 2.0 Hz, Ar-H), 9.86 (1H, s, CHO). Anal. Found: C, 56.08; H, 4.13%. Calcd for $C_8H_7ClO_2$: C, 56.32; H, 4.14%.

2-(Dimethylphenylsilyl)-1-phenylethanol. To the Grignard solution prepared from (chloromethyl)dimethylphenylsilane (2.0 g, 10.83 mmol) and Mg (0.25 g, 10.83 mmol) in 40 cm^3 of ether was added dropwise a solution of benzaldehyde (1.16 g, 10.93 mmol) in 20 cm^3 of ether with stirring at 0 °C.[5c] After stirring overnight, the reaction mixture was treated with H_2O (50 cm^3), and extracted with ether. The ethereal extract was washed with aq $NaHCO_3$ and aq saturated sodium chloride, and then dried over anhydrous magnesium sulfate. Purification by column chromatography afforded 1.1 g (yield, 40%) of the alcohol as a colorless liquid: ^{1}H NMR δ 0.20 (6H, s, $SiCH_3$), 1.39 (1H, dd, J = 14.5, 6.7 Hz, CH_2), 1.51 (1H, dd, J = 14.5, 8.0 Hz, CH_2), 1.73 (1H, d, J = 3.0 Hz, OH), 4.80 (1H, ddd, J = 8.0, 6.7, 3.0 Hz, CH), 7.29–7.51 (10H, m, Ph-H).

By the same procedure, the following α-aryl derivatives (all colorless liq.) were prepared from the corresponding substituted benzaldehyde.

2-(Dimethylphenylsilyl)-1-(*p*-methoxyphenyl)ethanol: ^{1}H NMR δ 0.19 (6H, s, $SiCH_3$), 1.38 (1H, dd, J = 14.3, 7.3 Hz, CH_2), 1.51 (1H, dd, J = 14.3, 7.6 Hz, CH_2), 1.67 (1H, brs, OH), 3.79 (3H, s, OCH_3), 4.76 (1H, dd, J = 7.6, 7.3 Hz, CH), 6.81–7.49 (9H, m, Ar-H).

1-(3-Chloro-4-methoxyphenyl)-2-(dimethylphenylsilyl)ethanol: ^{1}H NMR δ 0.21 and 0.23 (6H, ss, $SiCH_3$), 1.34 (1H, dd, J = 14.5, 7.0 Hz, CH_2), 1.47 (1H, dd, J = 14.5, 7.9 Hz, CH_2), 1.67 (1H, d, J = 3.0 Hz, OH), 3.87 (3H, s, OCH_3), 4.80 (1H, ddd, J = 7.9, 7.0, 3.0 Hz, CH), 6.81–7.47 (8H, m, Ar-H).

Since the *p*-methoxy-substituted alcohols were decomposed to the *p*-methoxy-substituted styrenes during SiO_2 column chromatography, these were esterified without further purification.

2-(Dimethylphenylsilyl)-1-(*p*-methylphenyl)ethanol: ^{1}H NMR δ 0.19 (6H, s, $SiCH_3$), 1.37 (1H, dd, J = 14.5, 6.9 Hz, CH_2), 1.50 (1H, dd, J = 14.5, 7.9 Hz, CH_2), 1.65 (1H, d, J = 3.3 Hz, OH), 2.32 (3H, s, CH_3), 4.78 (1H, ddd, J = 7.9, 6.9, 3.3 Hz, CH), 7.09–7.49 (9H, m, Ar-H).

2-(Dimethylphenylsilyl)-1-(*m*-methylphenyl)ethanol: ^{1}H NMR δ 0.21 and 0.22 (6H, ss, $SiCH_3$), 1.35 (1H, dd, J = 14.5, 6.6 Hz, CH_2), 1.50 (1H, dd, J = 14.5, 8.0 Hz, CH_2), 1.69 (1H, brs, OH), 2.32 (3H, s, CH_3), 4.77 (1H, dd, J = 8.0, 6.6 Hz, CH), 7.04–7.50 (9H, m, Ar-H).

1-(*p*-Chlorophenyl)-2-(dimethylphenylsilyl)ethanol: ^{1}H NMR δ 0.21 and 0.23 (6H, ss, $SiCH_3$), 1.34 (1H, dd, J = 14.5, 6.7 Hz, CH_2), 1.47 (1H, dd, J = 14.5, 8.0 Hz, CH_2), 1.72 (1H, brs, OH), 4.77 (1H, dd, J = 8.0, 6.7 Hz, CH), 7.18–7.48 (9H, m, Ar-H).

1-(*m*-Chlorophenyl)-2-(dimethylphenylsilyl)ethanol: ^{1}H NMR δ 0.22 and 0.25 (6H, ss, $SiCH_3$), 1.33 (1H, dd, J = 14.5, 6.4 Hz, CH_2), 1.45 (1H, dd, J = 14.5, 8.0 Hz, CH_2), 1.81 (1H, brs, OH), 4.75 (1H, dd, J = 8.0, 6.4 Hz, CH), 7.13–7.49 (9H, m, Ar-H).

2-(Dimethylphenylsilyl)-1-[*m*-(trifluoromethyl)phenyl]ethanol: ^{1}H NMR δ 0.22 and 0.26 (6H, ss, $SiCH_3$), 1.33 (1H, dd, J = 14.3, 6.4 Hz, CH_2), 1.45 (1H, dd, J = 14.3, 8.2 Hz, CH_2), 1.81 (1H, d, J = 2.7 Hz, OH), 4.85 (1H, ddd, J = 8.2, 6.4, 2.7 Hz, CH), 7.34–7.53 (9H, m, Ar-H).

1-(3,5-Dichlorophenyl)-2-(dimethylphenylsilyl)ethanol: ^{1}H NMR δ 0.26 and 0.30 (6H, ss, $SiCH_3$), 1.30 (1H, dd, J = 14.5, 6.0 Hz, CH_2), 1.42 (1H, dd, J = 14.5, 9.0 Hz, CH_2), 1.74 (1H, brs, OH), 4.73 (1H, dd, J = 9.0, 6.0 Hz, CH), 7.14–7.49 (8H, m, Ar-H).

1-[3,5-Bis(trifluoromethyl)phenyl]-2-(dimethylphenylsilyl)-ethanol: ^{1}H NMR δ 0.26 and 0.33 (6H, ss, $SiCH_3$), 1.37 (1H, dd, J = 14.7, 6.0 Hz, CH_2), 1.48 (1H, dd, J = 14.7, 8.6 Hz, CH_2), 4.92 (1H, dd, J = 8.6, 6.0 Hz, CH), 7.34–7.70 (8H, m, Ar-H).

The following 1-aryl-2-[3,5-bis(trifluoromethyl)phenylsilyl]-ethanols were obtained in a similar way by the [3,5-bis(trifluoromethyl)phenylsilyl]methylmagnesium chloride[1] and substituted benzaldehydes.

2-[3,5-Bis(trifluoromethyl)phenyldimethylsilyl]-1-phenylethanol: ^{1}H NMR δ 0.31 and 0.32 (6H, ss, $SiCH_3$), 1.43 (1H, dd, J = 14.7, 7.0 Hz, CH_2), 1.55 (1H, dd, J = 14.7, 7.9 Hz, CH_2), 1.79 (1H, brs, OH), 4.81 (1H, brt, J = 7.0 Hz, CH), 7.26–7.27

(5H, m, Ph-H), 7.80 (1H, s, Ar-H), 7.83 (2H, s, Ar-H).

2-[3,5-Bis(trifluoromethyl)phenyldimethylsilyl]-1-(*p*-methoxyphenyl)ethanol: ^{1}H NMR δ 0.29 and 0.31 (6H, ss, $SiCH_3$), 1.43 (1H, dd, J = 14.5, 7.5 Hz, CH_2), 1.55 (1H, dd, J = 14.5, 7.5 Hz, CH_2), 1.69 (1H, d, J = 2.6 Hz, OH), 3.77 (3H, s, OCH_3), 4.76 (1H, ddd, J = 7.5, 7.5, 2.6 Hz, CH), 6.77 (2H, d, J = 8.6 Hz, Ar-H), 7.16 (2H, d, J = 8.6 Hz, Ar-H), 7.80 (3H, s, Ar-H).

2-[3,5-Bis(trifluoromethyl)phenyldimethylsilyl]-1-(*p*-methylphenyl)ethanol: ^{1}H NMR δ 0.30 and 0.32 (6H, ss, $SiCH_3$), 1.43 (1H, dd, J = 14.5, 7.5 Hz, CH_2), 1.54 (1H, dd, J = 14.5, 7.5 Hz, CH_2), 1.74 (1H, d, J = 2.6 Hz, OH), 2.28 (3H, s, CH_3), 4.77 (1H, ddd, J = 7.5, 7.5, 2.6 Hz, CH), 7.04 (2H, d, J = 8.0 Hz, Ar-H), 7.12 (2H, d, J = 8.0 Hz, Ar-H), 7.80 (3H, s, Ar-H).

2-[3,5-Bis(trifluoromethyl)phenyldimethylsilyl]-1-(3-chloro-4-methoxyphenyl)ethanol: ^{1}H NMR δ 0.33 and 0.35 (6H, ss, $SiCH_3$), 1.39 (1H, dd, J = 14.6, 7.2 Hz, CH_2), 1.52 (1H, dd, J = 14.6, 7.8 Hz, CH_2), 1.75 (1H, d, J = 2.6 Hz, OH), 3.86 (3H, s, OCH_3), 4.74 (1H, ddd, J = 7.5, 7.5, 2.6 Hz, CH), 6.80 (1H, d, J = 8.6 Hz, Ar-H), 7.09 (1H, dd, J = 8.6, 2.0 Hz, Ar-H), 7.25 (1H, d, J = 2.0 Hz, Ar-H), 7.82 (3H, s, Ar-H).

2-[3,5-Bis(trifluoromethyl)phenyldimethylsilyl]-1-[*m*-(trifluoromethyl)phenyl]ethanol: ^{1}H NMR δ 0.35 and 0.38 (6H, ss, $SiCH_3$), 1.41 (1H, dd, J = 14.7, 6.3 Hz, CH_2), 1.54 (1H, dd, J = 14.7, 8.5 Hz, CH_2), 1.88 (1H, s, OH), 4.89 (1H, brt, J = 7.3 Hz, CH), 7.34–7.82 (7H, m, Ar-H).

1-Aryl-2-(aryldimethylsilyl)ethanols with butyllithium in ether were converted into the corresponding 3,5-dinitrobenzoate or benzoate by the reaction of 3,5-dinitrobenzoyl chloride or benzoyl chloride.

2-(Dimethylphenylsilyl)-1-phenylethyl 3,5-Dinitrobenzoate. The alcohol (0.2 g, 0.78 mmol) in 5 cm^3 of ether was esterified with the addition of 0.62 cm^3 (0.93 mmol) of butyllithium (1.5 mol dm^{-3} hexane solution), and then 0.20 g (0.85 mmol) of 3,5-dinitrobenzoyl chloride in 10 cm^3 of ether at 0 °C under a N_2 atmosphere. Water was added to the reaction mixture and extracted with ether. The ether extract was washed with $NaHCO_3$ and sat NaCl solution, and then dried over anhydrous $MgSO_4$. The crude ester was recrystallized from ether–hexane; mp 95–96 °C: ^{1}H NMR δ 0.16 and 0.24 (6H, ss, $SiCH_3$), 1.66 (1H, dd, J = 14.5, 8.0 Hz, CH_2), 1.89 (1H, dd, J = 14.5, 7.6 Hz, CH_2), 6.18 (1H, dd, J = 8.0, 7.6 Hz, CH), 7.20–7.50 (10H, m, Ph-H), 8.91 (2H, d, J = 2.1 Hz, Ar-H), 9.14 (1H, t, J = 2.1 Hz, Ar-H).

The following 3,5-dinitrobenzoates or benzoates were obtained in a similar way by the corresponding alcohols and 3,5-dinitrobenzoyl chloride or benzoyl chloride.

1-(3-Chloro-4-methoxyphenyl)-2-(dimethylphenylsilyl)ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.22 and 0.26 (6H, ss, $SiCH_3$), 1.63 (1H, dd, J = 14.5, 8.0 Hz, CH_2), 1.86 (1H, dd, J = 14.5, 7.6 Hz, CH_2), 3.88 (3H, s, OCH_3), 6.09 (1H, dd, J = 8.0, 7.6 Hz, CH), 7.13–7.42 (8H, m, Ar-H), 8.90 (2H, d, J = 2.1 Hz, Ar-H), 9.14 (1H, t, J = 2.1 Hz, Ar-H).

2-(Dimethylphenylsilyl)-1-(*p*-methylphenyl)ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.16 and 0.24 (6H, ss, $SiCH_3$), 1.65 (1H, dd, J = 14.7, 7.9 Hz, CH_2), 1.87 (1H, dd, J = 14.7, 7.6 Hz, CH_2), 2.33 (3H, s, CH_3), 6.15 (1H, dd, J = 7.9, 7.6 Hz, CH), 7.13–7.42 (9H, m, Ar-H), 8.89 (2H, d, J = 2.0 Hz, Ar-H), 9.13 (1H, t, J = 2.0 Hz, Ar-H).

2-(Dimethylphenylsilyl)-1-(*m*-methylphenyl)ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.18 and 0.25 (6H, ss, $SiCH_3$), 1.63 (1H, dd, J = 14.5, 7.6 Hz, CH_2), 1.87 (1H, dd, J = 14.5, 7.9 Hz, CH_2), 2.33 (3H, s, CH_3), 6.15 (1H, dd, J = 7.9, 7.6 Hz, CH), 7.11–7.42 (9H, m, Ar-H), 8.91 (2H, d, J = 2.1 Hz, Ar-H), 9.14 (1H, t, J = 2.1 Hz, Ar-H).

1-(*p*-Chlorophenyl)-2-(dimethylphenylsilyl)ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.21 and 0.25 (6H, ss, $SiCH_3$), 1.62 (1H, dd, J = 14.3, 7.6 Hz, CH_2), 1.86 (1H, dd, J = 14.3, 7.9 Hz, CH_2), 6.11 (1H, dd, J = 7.9, 7.6 Hz, CH), 7.21–7.41 (9H, m, Ar-H), 8.89 (2H, d, J = 2.1 Hz, Ar-H), 9.15 (1H, t, J = 2.1 Hz, Ar-H).

1-(*m*-Chlorophenyl)-2-(dimethylphenylsilyl)ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.22 and 0.27 (6H, ss, $SiCH_3$), 1.61 (1H, dd, J = 14.3, 7.3 Hz, CH_2), 1.90 (1H, dd, J = 14.3, 8.3 Hz, CH_2), 6.11 (1H, dd, J = 8.3, 7.3 Hz, CH), 7.17–7.41 (9H, m, Ar-H), 8.89 (2H, d, J = 2.1 Hz, Ar-H), 9.15 (1H, t, J = 2.1 Hz, Ar-H).

2-(Dimethylphenylsilyl)-1-[*m*-(trifluoromethyl)phenyl]ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.23 and 0.25 (6H, ss, $SiCH_3$), 1.64 (1H, dd, J = 14.5, 7.6 Hz, CH_2), 1.90 (1H, dd, J = 14.5, 7.9 Hz, CH_2), 6.19 (1H, dd, J = 7.9, 7.6 Hz, CH), 7.17–7.59 (9H, m, Ar-H), 8.90 (2H, d, J = 2.1 Hz, Ar-H), 9.15 (1H, t, J = 2.1 Hz, Ar-H).

1-(3,5-Dichlorophenyl)-2-(dimethylphenylsilyl)ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.28 (6H, s, $SiCH_3$), 1.65 (1H, dd, J = 14.5, 7.5 Hz, CH_2), 1.91 (1H, dd, J = 14.5, 8.2 Hz, CH_2), 6.20 (1H, dd, J = 8.2, 7.5 Hz, CH), 6.96–7.77 (8H, m, Ar-H), 8.90 (2H, d, J = 2.0 Hz, Ar-H), 9.17 (1H, t, J = 2.0 Hz, Ar-H).

1-[3,5-Bis(trifluoromethyl)phenyl]-2-(dimethylphenylsilyl)-ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.28 and 0.31 (6H, ss, $SiCH_3$), 1.65 (1H, dd, J = 14.5, 7.5 Hz, CH_2), 1.91 (1H, dd, J = 14.5, 8.2 Hz, CH_2), 6.20 (1H, dd, J = 8.2, 7.5 Hz, CH), 7.18–7.77 (8H, m, Ar-H), 8.90 (2H, d, J = 2.1 Hz, Ar-H), 9.17 (1H, t, J = 2.1 Hz, Ar-H).

2-[3,5-Bis(trifluoromethyl)phenyldimethylsilyl]-1-(3-chloro-4-methoxyphenyl)ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.35 (6H, s, $SiCH_3$), 1.81 (1H, dd, J = 14.3, 9.8 Hz, CH_2), 1.87 (1H, dd, J = 14.3, 6.3 Hz, CH_2), 3.86 (3H, s, OCH_3), 6.05 (1H, dd, J = 9.8, 6.3 Hz, CH), 6.80 (1H, d, J = 8.3 Hz, Ar-H), 7.21 (1H, dd, J = 8.3, 2.3 Hz, Ar-H), 7.30 (1H, d, J = 2.3 Hz, Ar-H), 7.71 (2H, s, Ar-H), 7.77 (1H, s, Ar-H), 9.01 (2H, d, J = 2.1 Hz, Ar-H), 9.19 (1H, t, J = 2.1 Hz, Ar-H).

2-[3,5-Bis(trifluoromethyl)phenyldimethylsilyl]-1-(*p*-methylphenyl)ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.311 and 0.315 (6H, ss, $SiCH_3$), 1.85 (1H, d, J = 9.2 Hz, CH_2), 1.86 (1H, d, J = 6.9 Hz, CH_2), 2.27 (3H, s, CH_3), 6.10 (1H, dd, J = 9.2, 6.9 Hz, CH), 7.05 (2H, d, J = 8.0 Hz, Ar-H), 7.21 (2H, d, J = 8.0 Hz, Ar-H), 7.69 (2H, s, Ar-H), 7.75 (1H, s, Ar-H), 9.02 (2H, d, J = 2.0 Hz, Ar-H), 9.18 (1H, t, J = 2.0 Hz, Ar-H).

2-[3,5-Bis(trifluoromethyl)phenyldimethylsilyl]-1-phenylethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.29 and 0.32 (6H, ss, $SiCH_3$), 1.83 (1H, dd, J = 14.3, 9.5 Hz, CH_2), 1.90 (1H, dd, J = 14.3, 6.4 Hz, CH_2), 6.13 (1H, dd, J = 9.5, 6.4 Hz, CH), 7.26–7.35 (5H, m, Ph-H), 7.72 (2H, s, Ar-H), 7.75 (1H, s, Ar-H), 9.02 (2H, d, J = 2.1 Hz, Ar-H), 9.18 (1H, t, J = 2.1 Hz, Ar-H).

2-[3,5-Bis(trifluoromethyl)phenyldimethylsilyl]-1-[*m*-(trifluoromethyl)phenyl]ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.35 (6H, s, $SiCH_3$), 1.82 (1H, dd, J = 14.3, 9.2 Hz, CH_2), 1.93 (1H, dd, J = 14.3, 6.7 Hz, CH_2), 6.17 (1H, dd, J = 9.2, 6.7 Hz, CH), 7.41–7.56 (4H, m, Ar-H), 7.70 (2H, s, Ar-H), 7.75 (1H, s, Ar-H), 9.00 (2H, d, J = 2.1 Hz, Ar-H), 9.20 (1H, t, J = 2.1 Hz, Ar-H).

2-(Dimethylphenylsilyl)-1-(*p*-methoxyphenyl)ethyl Benzoate: ^{1}H NMR δ 0.14 and 0.19 (6H, ss, $SiCH_3$), 1.59 (1H, dd, J = 14.5, 8.5 Hz, CH_2), 1.80 (1H, dd, J = 14.5, 7.0 Hz, CH_2), 3.76 (3H, s, OCH_3), 6.04 (1H, dd, J = 8.5, 7.0 Hz, CH), 6.81 (2H, d, J = 8.5 Hz, Ar-H), 7.28–7.48 (10H, m, Ph-H), 7.93 (2H,

Table 3. Physical and Analytical Data of 2-[Dimethyl(X-substituted phenyl)silyl]-1-(Y-substituted phenyl)ethanols and the 3,5-Dinitrobenzoates

Substituents		Mp/°C	Carbon/%		Hydrogen/%		Nitrogen/%	
Y	X		Found	Calcd	Found	Calcd	Found	Calcd
Alcohols								
p-Me	H	Liq	75.38	75.50	8.22	8.20		
m-Me	H	Liq	75.56	75.50	8.28	8.20		
H	H	Liq	75.16	74.95	7.81	7.86		
p-Cl	H	Liq	66.19	66.07	6.71	6.58		
m-Cl	H	Liq	65.87	66.07	6.65	6.58		
m-CF_3	H	Liq	63.16	62.94	5.92	5.90		
3,5-Cl_2	H	Liq	59.19	59.07	5.68	5.58		
3,5-$(CF_3)_2$	H	Liq	55.11	55.09	4.83	4.62		
p-MeO	3,5-$(CF_3)_2$	Liq	54.11	54.02	4.80	4.77		
p-Me	3,5-$(CF_3)_2$	Liq	56.19	56.15	5.02	4.96		
m-Cl-*p*-MeO	3,5-$(CF_3)_2$	Liq	49.76	49.95	4.14	4.19		
H	3,5-$(CF_3)_2$	Liq	55.21	55.09	4.77	4.62		
m-CF_3	3,5-$(CF_3)_2$	Liq	49.59	49.57	3.82	3.72		
3,5-Dinitrobenzoates								
H	H	95–96	61.42	61.32	4.96	4.92	6.16	6.22
p-Cl	H	Liq	56.58	56.96	4.37	4.36	5.56	5.78
m-CF_3	H	96–97	55.39	55.59	4.08	4.13	5.40	5.42
3,5-$(CF_3)_2$	H	Liq	51.52	51.20	3.59	3.44	4.76	4.78
m-Cl-*p*-MeO	3,5-$(CF_3)_2$	Liq	47.70	47.97	3.29	3.25	4.02	4.30
p-Me	3,5-$(CF_3)_2$	Liq	51.79	52.00	3.80	3.69	4.39	4.66
m-CF_3	3,5-$(CF_3)_2$	Liq	48.11	47.71	2.95	2.93	4.28	4.28

d, $J = 8.5$ Hz, Ar-H).

2-[3,5-Bis(trifluoromethyl)phenyldimethylsilyl]-1-(*p*-methoxyphenyl)ethyl Benzoate: ^{1}H NMR δ 0.28 and 0.32 (6H, ss, $SiCH_3$), 1.68 (1H, dd, $J = 14.5$, 8.9 Hz, CH_2), 1.84 (1H, dd, $J = 14.5$, 6.9 Hz, CH_2), 3.75 (3H, s, OCH_3), 6.05 (1H, dd, $J = 8.9$, 6.9 Hz, CH), 6.75 (2H, d, $J = 8.9$ Hz, Ar-H), 7.25 (2H, d, $J = 8.9$ Hz, Ar-H), 7.35–7.52 (3H, m, Ph-H), 7.73 (3H, s, Ar-H), 7.88–7.91 (2H, m, Ph-H).

2-(Dimethylphenylsilyl)-1-(*p*-methylphenyl)ethyl Benzoate: ^{1}H NMR δ 0.14 and 0.19 (6H, ss, $SiCH_3$), 1.57 (1H, dd, $J = 14.3$, 8.2 Hz, CH_2), 1.80 (1H, dd, $J = 14.3$, 7.6 Hz, CH_2), 2.31 (3H, s, CH_3), 6.05 (1H, t, $J = 7.8$ Hz, CH), 7.09 (2H, d, $J = 7.9$ Hz, Ar-H), 7.09–7.51 (10H, m, Ph-H), 7.93 (2H, d, $J = 7.9$ Hz, Ar-H).

Physical constants and elemental analysis data of the alcohols and the esters are listed in Table 3.

Solvents. Solvents were purified and binary solvents were prepared by mixing appropriate volumes or weights of pure solvents at 25 °C, as previously described.[1]

Kinetic Measurements. The solvolysis rates were determined conductimetrically as reported previously[1] at initial concentrations of ca. 10^{-5} for benzoates. CM-60S and CM-50AT (Toa Electronics Ltd.) conductivity meters were equipped with an interval time unit and printer, and those of CM-60V, CM-40G, and CM-40V were connected to a high speed personal computer. Solvolyses were monitored 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. As described before,[1] a solution of 2-(dimethylphenylsilyl)-1-phenylethyl 3,5-dinitrobenzoate buffered with ca. 2 equiv of 2,6-lutidine in deuterated ethanol (CD_3CD_2OD) or deuterated 60% (v/v) aqueous ethanol (CD_3CD_2OD–D_2O) was allowed to react at 55 °C in an NMR tube, and the solvolysis products at ten half-lives were identified by the ^{1}H NMR spectra. The relative amounts of reaction products, styrene and 2-(dimethylphenylsilyl)-1-phenylethyl ethyl ether, were determined from the integral areas of the corresponding peaks, as follows: styrene 1: the ether 0.56 in absolute ethanol and styrene only in 60% ethanol. Olefin peaks of ^{1}H NMR in ethanol-d_6 were δ 5.18 (1H, d, $J = 10.9$ Hz), 5.72 (1H, d, $J = 17.8$ Hz), 6.69 (1H, dd, $J = 17.8$, 10.9 Hz) and characteristic peaks of 2-(dimethylphenylsilyl)-1-phenylethyl ethyl ether were δ 0.16 and 0.21 (6H, ss, $SiCH_3$), 1.22 (1H, dd, $J = 14.9$, 6.3 Hz, CH_2), 1.43 (1H, dd, $J = 14.9$, 8.6 Hz, CH_2), 4.23 (1H, dd, $J = 8.6$, 6.3 Hz, CH).

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