2378 Bull. Chem. Soc. Jpn. Vol. 80, No. 12, 2378–2383 (2007)

The *β*-Silicon Effect. III. Substituent Effects of the *β*-Si-Aryl Moiety in the Solvolysis of 1-Aryl-2-(aryldimethylsilyl)ethyl 3,5-Dinitrobenzoates[1]

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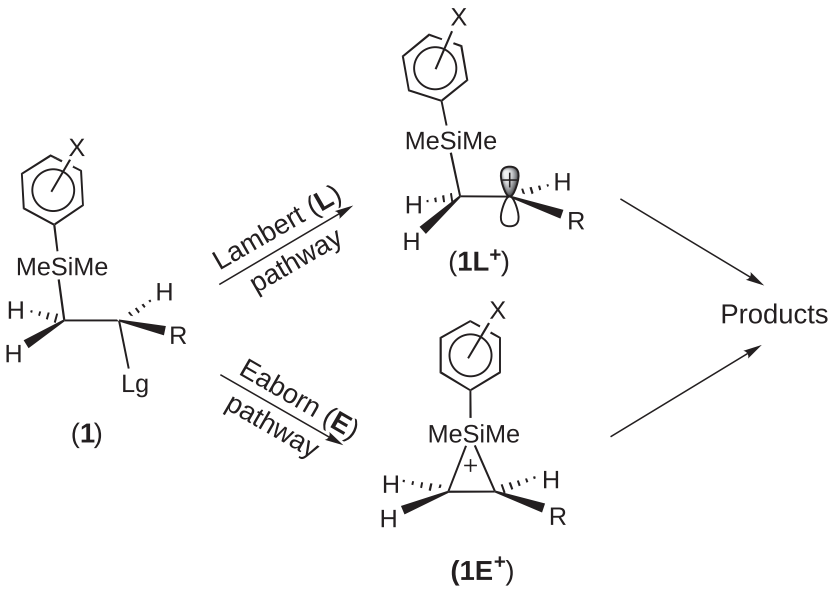
Solvolysis rates of 2-[dimethyl(X-phenyl)silyl]-1-(Y-phenyl)ethyl 3,5-dinitrobenzoates were determined conductimetrically in 60% (v/v) aqueous ethanol. The effects of substituents X in the β-arylsilyl moiety ($X\text{-}C_6H_4(CH_3)_2Si$–) were analyzed by means of the Yukawa–Tsuno Equation. The X-phenyl-Si substituent effects (at 25 °C) were correlated against a set of $\bar{\sigma}_X$ parameters of $r^+ \cong 0.1$ to give a $[(\rho_X)_{Si}]$ value of -1.06 for α-Ph (Y = H) and $[(\rho_X)_{Si}] = -1.18$ for α-(m-CF$_3$)phenyl (Y = m-CF$_3$) subsets, which are all distinctly lower than that of -1.75 for the 2-[dimethyl(X-phenyl)-silyl]ethyl solvolysis. The $\delta_Y[(\rho_X)_{Si}]_Y$ can be regarded as the effect of the aryl substituents on the β-Si moiety on the benzylic cation center in the rate-determining step. The α-aryl substituent effect $\delta_Y[\log(k_Y)_{X=H}]$ of 2-[dimethyl(X-phenyl)silyl]-1-(Y-phenyl)ethyl system was correlated against $\bar{\sigma}_Y$ scale characteristic of the benzylic cation reactions ($r^+ \cong 1.0$) to give $(\rho_Y)_{\alpha\text{-Ar}} \cong -3.0$. The $[(\rho_X)_{Si}]_Y$ values changed in parallel with the reactivities $\delta_Y[\log(k_Y)_{X=H}]$ of the α-Ar substrate.

β-Silylated substrates **1** exhibit a remarkable β-silicon effect, in which the solvolysis rate is enhanced up to 10^{12}-fold when the Si-moiety and the leaving group (Lg) are aligned in an antiperiplanar conformation. The β-silicon effect has been related to the stabilities of the intermediates $\mathbf{1}^+$, of which the structures are either the Lambert (open cation) structure $\mathbf{1L}^+$ stabilized by σ–π hyperconjugation or the Eaborn (Si-bridged) structure $\mathbf{1E}^+$ in Scheme 1.[2,3]

Previous studies on the mechanism involving the silyl group have all been focused on the dependence (δ) on the structural change (δ_R) of the reactivities $\delta_R[\log(k_{X=H})]_j$ of β-silylated substrates ***j***.

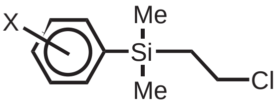
In our series of studies on the β-silicon effects,[1,4] we have employed the selectivity parameter $[(\rho_X)_{Si}]_j$ for the substituent effects $\delta_X[\log(k_X/k_H)]_j$ of the β-arylsilyl moiety β-ArMe$_2$Si– on the substrate ***j*** as a diagnostic probe of the β-silyl participation (Si) mechanisms.

Analysis of the substituent effects has been undertaken on the basis of the Yukawa–Tsuno (Y–T) Eq. 1:[5]

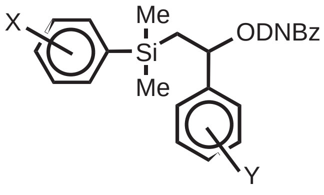


Scheme 1. β-Silicon effect in the carbocationic solvolysis.

Published on the web December 13, 2007; doi:10.1246/bcsj.80.2378



(2)



(3)

Chart 1.

$$[\log(k_X/k_H)]_j = [(\rho_X)_{Si}]_j[\sigma^0 + (r^+)_{Si}\Delta\bar{\sigma}^+_R], \qquad (1)$$

where k_X is rate constant for given reaction of a ring-substituted derivative and k_H is the corresponding value of the unsubstituted one. Symbol σ^0 is the normal substituent constant, which involves no additional π-electronic interaction between the substituent and the reaction center, and $\Delta\bar{\sigma}^+_R$ is the resonance substituent constant, measuring the capability for π-delocalization of a p-π-donor substituent.

Previous studies[1,4] have shown that the $[(\rho_X)_{Si}]_j$ value is sensitive to the overall magnitude of the β-silyl-participation. The substituent effects $\delta_X[\log(k_X/k_H)_{Si}]_\mathbf{2}$ in the solvolyses of 2-(aryldimethylsilyl)ethyl system **2** (Chart 1), in which the non-vertical (Si-bridged) mechanism evidently occurs,[2b] resulted in $[(\rho_X)_{Si}]_\mathbf{2} = -1.75$ against essentially nonresonant sigmas ($\bar{\sigma}_X$) of negligible resonance demand ($r^+ = 0.10$).[4a] To a contrary, the more stable α,α-Me$_2$ substrate system has been found to give a small $(\rho_X)_{Si}$ value of -1.34.[4b]

In the preceding study,[1] we have chosen for study the substrate α-R = Ar in Scheme 1 and the solvolysis of 2-(dimethylphenylsilyl)-1-(Y-phenyl)ethyl 3,5-dinitrobenzoates **3** (X = H) and carried out detailed analysis of the substituent (Y) effects (δ_Y) on $[\log(k_{XY}/k_{XH})_{X=H}]_\mathbf{3}$ of **3** (X = H), simplified as $\delta_Y[\log(k_Y/k_H)_{X=H}]_\mathbf{3}$ or $\delta_Y[\log(k_Y/k_H)]_{\mathbf{3}(X=H)}$, on the basis of the Y–T Eq. 1, resulting in Eq. 2,

$$[\log(k_Y/k_H)_{X=H}]_\mathbf{3} = (-2.95 \pm 0.06)[\sigma^0 + (1.04 \pm 0.05)\Delta\bar{\sigma}^+_R]. \qquad (2)$$

In the present study, we dealt with the β-arylsilyl substituent effect (δ_X) in the solvolysis of **3** and mainly with the dependence (δ_Y) of the selectivity parameters $[(\rho_X)_{Si}]_\mathbf{3}$ on the structures or the stabilities of the parent substrates, i.e., the benzylic Y substituents in $\boldsymbol{j} = \mathbf{3}$, aiming to establish the $[(\rho_X)_{Si}]_j$ parameters as effective diagnostic probes of silyl-participation.

Results

Rates of Solvolysis. The solvolysis rates of 2-(aryldimethylsilyl)-1-phenylethyl 3,5-dinitrobenzoates **3** (Y = H) and of 2-(aryldimethylsilyl)-1-[m-(trifluoromethyl)phenyl]ethyl 3,5-dinitrobenzoates **3** (Y = m-CF$_3$) were measured conductimetrically in 60% (v/v) aq ethanol (60E) for a range of β-arylsilyl substituents (X = p-MeO to 3,5-(CF$_3$)$_2$). Kinetic data are listed in Tables 1 and 2.

Table 1. Solvolysis Rates of 2-(Aryldimethylsilyl)-1-phenylethyl 3,5-Dinitrobenzoates in 60% Aqueous Ethanol

Substituent	$10^5 \times k/\text{s}^{-1}$				$\Delta H^\ddagger_{25\,°C}$	$\Delta S^\ddagger_{25\,°C}$
X	25 °C	35 °C	45 °C	55 °C	/kJ mol^{-1}	/J mol^{-1} K^{-1}
p-MeO	103.0		941		84.8	−17.8
p-Me	89.5	278	839		85.8	−15.7
m-Me	73.0		698		86.6	−14.7
H	67.0		652		87.2	−13.0
p-MeO-m-Cl	39.7		375	1128	87.9	−15.3
p-Cl	31.1		317	896	88.7	−14.5
m-Cl	25.5		261		89.2	−14.4
m-CF$_3$	19.22		199.9		89.9	−14.6
3,5-(CF$_3$)$_2$	5.96		63.2	198.7	92.3	−16.4

Table 2. Solvolyis Rates of 2-(Aryldimethylsilyl)-1-[m-(trifluoromethyl)phenyl]ethyl 3,5-Dinitrobenzoates in 60% Aqueous Ethanol

Substituent	$10^5 \times k/\text{s}^{-1}$				$\Delta H^\ddagger_{25\,°C}$	$\Delta S^\ddagger_{25\,°C}$
X	25 °C	35 °C	45 °C	55 °C	/kJ mol^{-1}	/J mol^{-1} K^{-1}
p-MeO	4.09		48.2	147.1	94.7	−11.3
p-Me	3.24[a)]	11.77	37.1	119.3	94.8	−12.7
m-Me	2.96[a)]	10.46	34.6	104.5	94.3	−15.4
H	2.54	9.43	32.7	91.6	95.2	−13.3
p-MeO-m-Cl	1.485	5.36	17.47	54.7	95.2	−18.2
p-Cl	1.117[a)]	4.06	14.07	43.0	96.8	−15.2
m-Cl	0.862[a)]	3.21	11.15	35.2	98.2	−12.5
m-CF$_3$	0.629[a)]	2.35	8.08	25.8	98.2	−15.0
3,5-(CF$_3$)$_2$	0.1719[a)]	0.658	2.44	7.72	101.1	−16.3

a) Extrapolated from rate data at other temperatures.

Aryl-Substituent Effects ($\boldsymbol{\delta_X}$) in the $\boldsymbol{\beta}$-Si Moiety. The Y–T plot for the aryl (X)-substituent effect $\delta_X[\log(k_X/k_H)_{Y=H}]_\mathbf{3}$ in the β-silyl function of the α-phenyl system **3** (Y = H) is shown in Fig. 1. For logarithms of the relative solvolysis rates $\delta_X[\log(k_X/k_H)_{Y=H}]_\mathbf{3}$ of **3** (Y = H) at 25 °C in 60E, use of the Y–T Eq. affords a linear correlation Eq. 3 with $R = 0.9982$ and SD = ±0.027:

$$[\log(k_X/k_H)_{Y=H}]_\mathbf{3} = (-1.063 \pm 0.029)[\sigma^0 + (0.082 \pm 0.035)\Delta\bar{\sigma}^+_R]. \qquad (3)$$

Application of the Y–T Eq. 1 to subset **3** (Y = m-CF$_3$) resulted in a good correlation (Fig. 2) with a $[(\rho_X)_{Si}]_{\mathbf{3}(Y=m\text{-}CF_3)}$ value of -1.18 at $r^+ = 0.09$ ($R = 0.9985$ and SD = ±0.028):

$$[\log(k_X/k_H)_{Y=m\text{-}CF_3}]_\mathbf{3} = (-1.175 \pm 0.029)[\sigma^0 + (0.092 \pm 0.033)\Delta\bar{\sigma}^+_R]. \qquad (4)$$

For all of the substrates $\boldsymbol{j}$ examined (including non-aryl α-R substrates),[1,4] precise linear Y–T correlations on $\delta_X[\log(k_X/k_H)]_j$ were obtained ($R > 0.994$) with a constant $\bar{\sigma}_X$ scale showing no increase in resonance demand ($r^+ \approx 0.10$), which is inherent in the β-arylsilyl function.

In our previous report,[1] we have obtained the solvolysis rate constants of X = 3,5-(CF$_3$)$_2$ derivatives of **3** for a wide series of Y, and moreover, have shown that the variations in the substituent effects $\delta_Y[\log(k_Y/k_H)_{X=\text{diCF}_3}]_\mathbf{3}$ are precisely linear (Eq. 5) against $\delta_Y[\log(k_Y/k_H)_{X=H}]_\mathbf{3}$ for the X = H subset of substrates **3**.

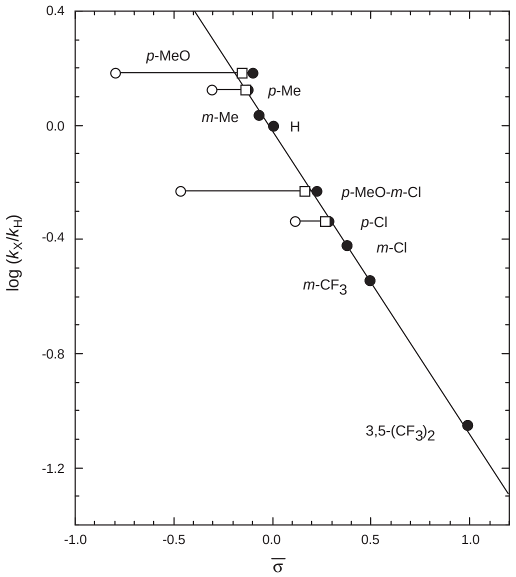


Fig. 1. Substituent effects in the solvolysis of 2-(aryldimethylsilyl)-1-phenylethyl 3,5-dinitrobenzoates **3** (Y = H) in 60% aq EtOH at 25 °C: Closed circles for σ^0, open circles for σ^+, and open squares for $\bar{\sigma}$ with $r^+ = 0.08$.

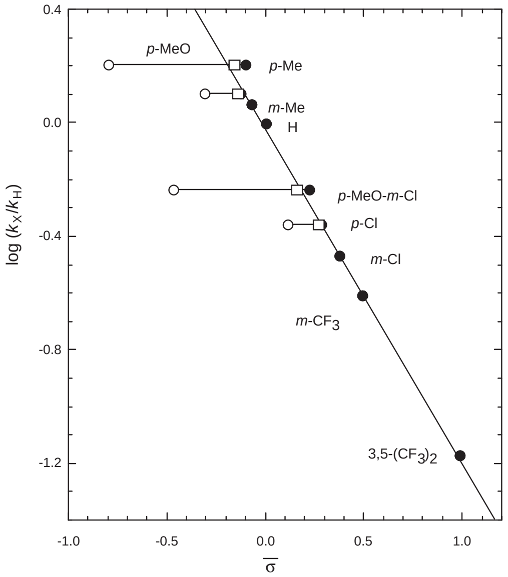


Fig. 2. Substituent effects in the solvolysis of 2-(aryldimethylsilyl)-1-[*m*-(triflluoromethyl)phenyl]ethyl 3,5-dinitrobenzoates **3** (Y = *m*-CF$_3$) in 60% aq EtOH at 25 °C: Closed circles for σ^0, open circles for σ^+, and open squares for $\bar{\sigma}$ with $r^+ = 0.09$.

$$[\log(k_Y/k_H)_{X=\text{diCF}_3}]_\mathbf{3} = (1.12 \pm 0.03)[\log(k_Y/k_H)_{X=H}]_\mathbf{3}. \quad (5)$$

Equation 5 was utilized to estimate (or extrapolate) the rate constants of the same Y-substrates in either X-subset.

The $[(\rho_X)_{Si}]_Y$ values for the respective Y-subsets of the α-Ar-substrate **3** were obtained to a good approximation by using a two-points determination based on the $\log(k_X/k_H)_Y$ values for X = H and X = 3,5-(CF$_3$)$_2$ in Table 3. The $[(\rho_X)_{Si}]_Y$ values, thus obtained, for the respective Y subsets are also listed in Table 3.

Table 3. Solvolysis Rates of **3**-ODNBz with X = H and 3,5-(CF$_3$)$_2$ and $[(\rho_X)_{Si}]_Y$ for Y-Substrates

Substituent	$10^5 \times k_X/\text{s}^{-1}$ at 25 °C[a]		$[(\rho_X)_{Si}]_Y$[b]	$\bar{\sigma}_Y$
Y	X = H	X = 3,5-(CF$_3$)$_2$		$r^+ = 1.04$
p-MeO	2.3×10^4	3.5×10^3	−0.83	−0.83
p-MeO-*m*-Cl	2.7×10^3 [c),d)]	363	−0.88	−0.50
p-Me	676	68.9	−1.00	−0.32
H	67.0[e),f)]	5.96	−1.06	0.00
p-Cl	31.3	2.57[c)]	−1.10	0.108
m-Cl	5.07	0.336[c)]	−1.18	0.375
m-CF$_3$	2.54[e),g)]	0.1719[e),h)]	−1.19	0.49
3,5-(CF$_3$)$_2$	0.0897	0.00373[c)]	−1.40	0.99

a) Data taken from Ref. 1, otherwise noted. b) $[(\rho_X)_{Si}]_Y$ parameters for the respective Y subsets, which were based on $\log k_X$s for X = H and 3,5-(CF$_3$)$_2$; see text. c) Rates estimated based on Eq. 5; see text. d) Directly observed value $1.9 \times 10^{-2}\ \text{s}^{-1}$ under the reference condition has been reported (Ref. 1). This value appears less reliable, because the solvolysis rate of the ODNBz substrate under reference conditions is too fast to follow the changes in conductivity of the solution by our equipment. e) The present work. f) Reported $7.29 \times 10^{-4}\ \text{s}^{-1}$ in Ref. 1. g) Reported $2.69 \times 10^{-5}\ \text{s}^{-1}$ in Ref. 1. h) Reported $1.69 \times 10^{-6}\ \text{s}^{-1}$ in Ref. 1.

Discussion

The β-silyl effects were analyzed using the Y–T Eq. 1 generally in terms of Y–T correlations with the $\bar{\sigma}_X$ scale of essentially unenhanced resonance demand ($r^+ \cong 0.1$) for all the relevant β-silylated systems with high precision ($R > 0.994$).

To determine the β-silyl substituent effects $\delta_X[\log(k_X/k_H)]_Y$ on the reactivity of respective Y subsets **3**, Y–T Eq. 1 was applied (cf., Figs. 1 and 2) to correlate linearly against the $\bar{\sigma}_X$ scale ($r^+ \cong 0.1$) characteristic of the β-silyl function ($R \cong 0.998$ and SD $\cong \pm 0.03$). The $[(\rho_X)_{Si}]_Y$ value for any fixed Y-subset of the α-R = Ar-substrate **3** appears to be distinctly smaller than that of the α-R = H substrate **2**.

On the other hand, in the preceding paper,[1] we have reported that the α-aryl substituent effect $\delta_Y[\log(k_Y/k_H)_{X=H}]_\mathbf{3}$ on the solvolysis of **3** is linearly correlated to yield a $[(\rho_Y)_{X=H}]_\mathbf{3}$ value of −2.95 against the $\bar{\sigma}_Y$ scale ($r^+ = 1.04$). For comparison, the substituent effect on the solvolysis of the non-silylated 1-arylethyl substrates **3N** is known to provide a linear Y–T correlation with $r^+ = 1.1$ and $\rho_Y = -5.45$.[5,6]

Furthermore, the substituent effect $\delta_Y[\log(k_Y/k_H)_{X=H}]_\mathbf{3}$ on the solvolysis of β-silyl substrate **3** was found to be linear to the substituent effect $\delta_Y[\log(k_Y/k_H)]_\mathbf{3N}$ on the solvolysis of the corresponding non-silylated parent substrate **3N**:[1]

$$\delta_Y[\log(k_Y/k_H)_{X=H}]_\mathbf{3} = 0.52\{\delta_Y[\log(k_Y/k_H)]_\mathbf{3N}\}. \quad (6)$$

Precise fit to the relationship Eq. 6 implies that the solvolysis of **3** comprising the β-silyl participation causes no significant change in $\bar{\sigma}_Y$ (or r^+), whereas there is a significant reduction in the magnitude of the reaction constant $|(\rho_Y)_\mathbf{3}|$ parameter.

β-Silyl-induced reactivity $\delta_Y[\log(k_Y)_{X=H}]_\mathbf{3}$ should be linear to the electron deficiency $\delta_Y(\log k_Y)_\mathbf{3N}$ of the non-silylated substrate cation (**3N$^+$**).

It is remarkable that $\delta_Y[(\rho_X)_{Si}]_Y$ vs. $\bar{\sigma}_Y$ relationship Eq. 7 was linear, as shown in Fig. 3.

$$[(\rho_X)_{Si}]_Y = -0.31\bar{\sigma}_Y - 1.07, \quad (7)$$

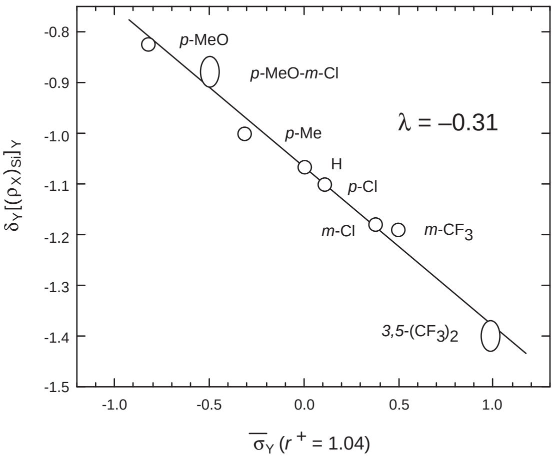


Fig. 3. The plots of $[(\rho_X)_{Si}]_Y$ against $\bar{\sigma}_Y$ ($r^+ = 1.04$) of the solvolysis of 2-[dimethyl(X-substituted phenyl)silyl]-1-(Y-substituted phenyl)ethyl 3,5-dinitrobenzoates **3** in 60% aq EtOH at 25 °C.

where $\bar{\sigma}_Y$ is the Y–T $\bar{\sigma}$ parameter ($r^+ = 1.04$). Equation 7 can also be rewritten as in the form of relationship Eq. 8:

$$[(\rho_X)_{Si}]_{\mathbf{Y}} = \lambda_3[\log(k_Y/k_H)_{X=H}]_{\mathbf{3}} - 1.07 \tag{8}$$

$$\text{or}\quad \delta_Y[(\rho_X)_{Si}]_{\mathbf{Y}} = \lambda_3\{\delta_Y[\log(k_Y/k_H)_{X=H}]_{\mathbf{3}}\}, \tag{8a}$$

where the coefficient $\lambda_3 = -0.31/[(\rho_Y)_{X=H}]_{\mathbf{3}} = 0.105$. Equation 8, which shows the linearity between δ_X-selectivity and δ_Y-reactivities of Y-substrates of **3**, can be regarded as a reactivity–selectivity relationship (RSR) in the empirical theory of physical organic chemistry.[7,8]

Lambert and his co-workers have determined the β-silyl participation effect in relation to the rate acceleration of the β-silylated substrate relative to the corresponding non-silylated substrate ***j***, i.e., the rate ratio $(k_{Si}/k_{non\text{-}Si})_j$ of substrate ***j***. In the present α-Ar system, the β-silyl participation quantities can be given by the rate ratio $(k_3/k_{3N})_Y$ for the respective Y-substituents in the β-silylated **3** relative to the non-silylated **3N** and by the $\log(k_3/k_{3N})_Y$ in the linear free energy expression. As $\log(k_3/k_{3N})_Y = \log(k_Y)_3 - \log(k_Y)_{3N}$, the β-silyl participation quantities should also be linear against $\bar{\sigma}_Y$, resulting in Eq. 9:

$$\delta_Y[\log(k_3/k_{3N})_Y] = \mu(\bar{\sigma}_Y), \tag{9}$$

where $\mu = -0.48(\rho_Y)_{3N} = 2.6$.

The β-silyl participation should also be linear against the same $\bar{\sigma}_Y$ scale, that is, the Y–T substituent constant ($\bar{\sigma}$) scale, at the r^+ characteristic of benzylic cation intermediate or TS.[4b] Furthermore, combining with Eq. 7, we obtain Eq. 10:

$$\delta_Y[(\rho_X)_{Si}]_Y = \lambda_{Si}\{\delta_Y[\log(k_3/k_{3N})_Y]\}, \tag{10}$$

where $\lambda_{Si} = -0.12$. Thus, the $[(\rho_X)_{Si}]_{\mathbf{Y}}$ values are sensitive to the overall magnitude of the β-silyl-participation. The selectivity probe $\delta_Y[(\rho_X)_{Si}]_Y$ varies inversely proportional to the β-silyl-participation quantities, $\delta_Y[\log(k_3/k_{3N})_Y]$.

This implies that the selectivity parameter $\delta_Y[(\rho_X)_{Si}]_Y$ is a sensitive probe to determine the extent of the overall silyl participation in the solvolysis of **3**, regardless of the mechanism, i.e., the Lambert or the Eaborn mechanism.

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 recycling preparative HPLC was performed on a LC-908 (Japan Analytical Co Ltd) using a JAIGEL-1H column (styrene polymer) and eluting with $CHCl_3$. The ^1H 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. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone under nitrogen.

Material. As described in the previous paper,[1] the following 2-(aryldimethylsilyl)-1-phenylethanols or -1-(*m*-CF_3-phenyl)ethanols (colorless liq.) were prepared from the reaction of the corresponding (aryldimethylsilyl)methylmagnesium chloride with benzaldehyde or *m*-CF_3-benzaldehyde.

2-[(*p*-Methoxyphenyl)dimethylsilyl]-1-phenylethanol: ^1H NMR δ 0.175 and 0.178 (6H, ss, $SiCH_3$), 1.36 (1H, dd, J = 14.7, 6.6 Hz, CH_2), 1.48 (1H, dd, J = 14.7, 8.0 Hz, CH_2), 1.70 (1H, brs, OH), 3.82 (3H, s, OCH_3), 4.80 (1H, t, J = 7.5 Hz, CH), 6.90 (2H, d, J = 8.6 Hz, Ar–H), 7.24–7.31 (5H, m, Ph–H), 7.42 (2H, d, J = 8.6 Hz, Ar–H).

2-[(3-Chloro-4-methoxyphenyl)dimethylsilyl]-1-phenylethanol: ^1H NMR δ 0.19 and 0.20 (6H, ss, $SiCH_3$), 1.36 (1H, dd, J = 14.7, 6.9 Hz, CH_2), 1.48 (1H, dd, J = 14.7, 8.0 Hz, CH_2), 1.81 (1H, brs, OH), 3.91 (3H, s, OCH_3), 4.80 (1H, ddd, J = 8.0, 6.9, 3.0 Hz, CH), 6.90–7.41 (8H, m, Ar–H).

2-[Dimethyl(*p*-methylphenyl)silyl]-1-phenylethanol: ^1H NMR δ 0.18 (6H, s, $SiCH_3$), 1.37 (1H, dd, J = 14.5, 6.7 Hz, CH_2), 1.50 (1H, dd, J = 14.5, 8.0 Hz, CH_2), 2.35 (3H, s, CH_3), 4.80 (1H, dd, J = 8.0, 6.7 Hz, CH), 7.10 (2H, d, J = 8.1 Hz, Ar–H), 7.18 (2H, d, J = 8.1 Hz, Ar–H), 7.33–7.50 (5H, m, Ph–H).

2-[Dimethyl(*m*-methylphenyl)silyl]-1-phenylethanol: ^1H NMR δ 0.189 and 0.198 (6H, ss, $SiCH_3$), 1.39 (1H, dd, J = 14.5, 6.5 Hz, CH_2), 1.51 (1H, dd, J = 14.5, 8.0 Hz, CH_2), 1.70 (1H, brs, OH), 2.35 (3H, s, CH_3), 4.82 (1H, t, J = 7.5 Hz, CH), 7.08–7.41 (9H, m, Ar–H).

2-(*p*-Chlorophenyldimethylsilyl)-1-phenylethanol: ^1H NMR δ 0.19 and 0.20 (6H, ss, $SiCH_3$), 1.37 (1H, dd, J = 14.6, 6.9 Hz, CH_2), 1.49 (1H, dd, J = 14.6, 8.0 Hz, CH_2), 1.72 (1H, d, J = 3.4 Hz, OH), 4.79 (1H, ddd, J = 8.0, 6.9, 3.4 Hz, CH), 7.19 (2H, d, J = 8.3 Hz, Ar–H), 7.25–7.32 (5H, m, Ph–H), 7.40 (2H, d, J = 8.3 Hz, Ar–H).

2-(*m*-Chlorophenyldimethylsilyl)-1-phenylethanol: ^1H NMR δ 0.21 and 0.22 (6H, ss, $SiCH_3$), 1.38 (1H, dd, J = 14.5, 6.7 Hz, CH_2), 1.50 (1H, dd, J = 14.5, 8.1 Hz, CH_2), 1.81 (1H, brs, OH), 4.80 (1H, dd, J = 8.1, 6.7 Hz, CH), 7.24–7.39 (9H, m, Ar–H).

2-{Dimethyl[*m*-(trifluoromethyl)phenyl]silyl}-1-phenylethanol: ^1H NMR δ 0.24 and 0.25 (6H, ss, $SiCH_3$), 1.40 (1H, dd, J = 14.5, 7.0 Hz, CH_2), 1.53 (1H, dd, J = 14.5, 7.9 Hz, CH_2), 1.78 (1H, d, J = 2.7 Hz, OH), 4.79 (1H, ddd, J = 7.9, 7.0, 2.7 Hz, CH), 7.22–7.67 (9H, m, Ar–H).

2-[(*p*-Methoxyphenyl)dimethylsilyl]-1-[*m*-(trifluoromethyl)phenyl]ethanol: ^1H NMR δ 0.20 and 0.24 (6H, ss, $SiCH_3$), 1.35 (1H, dd, J = 14.5, 6.5 Hz, CH_2), 1.47 (1H, dd, J = 14.5, 8.5 Hz, CH_2), 1.77 (1H, d, J = 3.5 Hz, OH), 3.82 (3H, s, OCH_3), 4.84–4.87 (1H, m, CH), 6.90 (2H, d, J = 8.5 Hz, Ar–H), 7.38–7.52 (4H, m, Ar–H), 7.40 (2H, d, J = 8.5 Hz, Ar–H).

2-[Dimethyl(*p*-methylphenyl)silyl]-1-[*m*-(trifluoromethyl)phenyl]ethanol: ^{1}H NMR δ 0.21 and 0.24 (6H, s, SiCH$_3$), 1.35 (1H, dd, $J = 14.6$, 6.3 Hz, CH$_2$), 1.47 (1H, dd, $J = 14.6$, 8.6 Hz, CH$_2$), 1.77 (1H, d, $J = 3.7$ Hz, OH), 2.35 (3H, s, CH$_3$), 4.85 (1H, ddd, $J = 8.6$, 6.3, 3.7 Hz, CH), 7.17 (2H, d, $J = 7.6$ Hz, Ar–H), 7.38 (2H, d, $J = 7.6$ Hz, Ar–H), 7.40–7.52 (4H, m, Ar–H).

2-[Dimethyl(*m*-methylphenyl)silyl]-1-[*m*-(trifluoromethyl)phenyl]ethanol: ^{1}H NMR δ 0.21 and 0.25 (6H, ss, SiCH$_3$), 1.37 (1H, dd, $J = 14.5$, 6.5 Hz, CH$_2$), 1.48 (1H, dd, $J = 14.5$, 8.5 Hz, CH$_2$), 1.81 (1H, d, $J = 2.5$ Hz, OH), 2.34 (3H, s, CH$_3$), 4.84–4.87 (1H, m, CH), 7.16–7.29 (4H, m, Ar–H), 7.37–7.52 (4H, m, Ar–H).

2-[(3-Chloro-4-methoxyphenyl)dimethylsilyl]-1-[*m*-(trifluoromethyl)phenyl]ethanol: ^{1}H NMR δ 0.21 and 0.26 (6H, ss, SiCH$_3$), 1.35 (1H, dd, $J = 14.5$, 6.4 Hz, CH$_2$), 1.47 (1H, dd, $J = 14.5$, 8.2 Hz, CH$_2$), 1.80 (1H, s, OH), 3.90 (3H, s, OCH$_3$), 4.85 (1H, brt, $J = 7.3$ Hz, CH), 6.89–7.52 (7H, m, Ar–H).

2-(*p*-Chlorophenyldimethylsilyl)-1-[*m*-(trifluoromethyl)phenyl]ethanol: ^{1}H NMR δ 0.22 and 0.27 (6H, ss, SiCH$_3$), 1.35 (1H, dd, $J = 14.3$, 6.3 Hz, CH$_2$), 1.47 (1H, dd, $J = 14.3$, 8.6 Hz, CH$_2$), 1.80 (1H, s, OH), 4.79 (1H, brt, $J = 7.5$ Hz, CH), 7.31 (2H, d, $J = 8.3$ Hz, Ar–H), 7.39 (2H, d, $J = 8.3$ Hz, Ar–H), 7.41–7.52 (4H, m, Ar–H).

2-(*m*-Chlorophenyldimethylsilyl)-1-[*m*-(trifluoromethyl)phenyl]ethanol: ^{1}H NMR δ 0.24 and 0.28 (6H, ss, SiCH$_3$), 1.36 (1H, dd, $J = 14.7$, 6.4 Hz, CH$_2$), 1.49 (1H, dd, $J = 14.7$, 8.2 Hz, CH$_2$), 1.81 (1H, s, OH), 4.86 (1H, brt, $J = 7.5$ Hz, CH), 7.25–7.53 (8H, m, Ar–H).

2-{Dimethyl[*m*-(trifluoromethyl)phenyl]silyl}-1-[*m*-(trifluoromethyl)phenyl]ethanol: ^{1}H NMR δ 0.27 and 0.32 (6H, ss, SiCH$_3$), 1.39 (1H, dd, $J = 14.8$, 6.3 Hz, CH$_2$), 1.51 (1H, dd, $J = 14.8$, 8.3 Hz, CH$_2$), 1.83 (1H, s, OH), 4.87 (1H, dd, $J = 8.3$, 6.3 Hz, CH), 7.37–7.66 (8H, m, Ar–H).

2-(Aryldimethylsilyl)-1-phenylethyl 3,5-dinitrobenzoates were obtained by the corresponding alcohols and 3,5-dinitrobenzoyl chloride, as described before.[1]

2-[(*p*-Methoxyphenyl)dimethylsilyl]-1-phenylethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.15 and 0.23 (6H, ss, SiCH$_3$), 1.60 (1H, dd, $J = 14.5$, 7.4 Hz, CH$_2$), 1.85 (1H, dd, $J = 14.5$, 8.3 Hz, CH$_2$), 3.69 (1H, s, OCH$_3$), 6.19 (1H, dd, $J = 8.3$, 7.4 Hz, CH), 6.72 (2H, d, $J = 8.6$ Hz, Ar–H), 7.30–7.37 (5H, m, Ph–H), 7.40 (2H, d, $J = 8.6$ Hz, Ar–H), 8.88 (2H, d, $J = 2.3$ Hz, Ar–H), 9.14 (1H, t, $J = 2.3$ Hz, Ar–H).

2-[(3-Chloro-4-methoxyphenyl)dimethylsilyl]-1-phenylethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.17 and 0.27 (6H, ss, SiCH$_3$), 1.60 (1H, dd, $J = 14.7$, 7.0 Hz, CH$_2$), 1.85 (1H, dd, $J = 14.7$, 8.2 Hz, CH$_2$), 3.80 (3H, s, OCH$_3$), 6.19 (1H, dd, $J = 8.2$, 7.0 Hz, CH), 7.17–7.59 (8H, m, Ar–H), 8.88 (2H, d, $J = 2.1$ Hz, Ar–H), 9.16 (1H, t, $J = 2.1$ Hz, Ar–H).

2-[Dimethyl(*p*-methylphenyl)silyl]-1-phenylethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.14 and 0.22 (6H, ss, SiCH$_3$), 1.62 (1H, dd, $J = 14.5$, 7.5 Hz, CH$_2$), 1.87 (1H, dd, $J = 14.5$, 8.1 Hz, CH$_2$), 2.20 (3H, s, CH$_3$), 6.19 (1H, dd, $J = 8.1$, 7.5 Hz, CH), 7.03 (2H, d, $J = 7.6$ Hz, Ar–H), 7.30–7.36 (5H, m, Ph–H), 7.40 (2H, d, $J = 7.6$ Hz, Ar–H), 8.90 (2H, d, $J = 2.1$ Hz, Ar–H), 9.14 (1H, t, $J = 2.1$ Hz, Ar–H).

2-[Dimethyl(*m*-methylphenyl)silyl]-1-phenylethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.15 and 0.25 (6H, ss, SiCH$_3$), 1.64 (1H, dd, $J = 14.3$, 7.5 Hz, CH$_2$), 1.87 (1H, dd, $J = 14.3$, 8.0 Hz, CH$_2$), 2.22 (3H, s, CH$_3$), 6.19 (1H, t, $J = 8.0$ Hz, CH), 7.03–7.41 (9H, m, Ar–H), 8.90 (2H, d, $J = 2.3$ Hz, Ar–H), 9.14 (1H, t, $J = 2.3$ Hz, Ar–H).

2-(*p*-Chlorophenyldimethylsilyl)-1-phenylethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.17 and 0.26 (6H, ss, SiCH$_3$), 1.63 (1H, dd, $J = 14.3$, 7.4 Hz, CH$_2$), 1.86 (1H, dd, $J = 14.3$, 8.0 Hz, CH$_2$), 6.18 (1H, dd, $J = 8.0$, 7.4 Hz, CH), 7.16 (2H, d, $J = 8.0$ Hz, Ar–H), 7.31–7.39 (7H, m, Ar–H), 8.90 (2H, d, $J = 2.3$ Hz, Ar–H), 9.17 (1H, t, $J = 2.3$ Hz, Ar–H).

2-(*m*-Chlorophenyldimethylsilyl)-1-phenylethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.18 and 0.27 (6H, ss, SiCH$_3$), 1.66 (1H, dd, $J = 14.5$, 7.6 Hz, CH$_2$), 1.87 (1H, dd, $J = 14.5$, 7.9 Hz, CH$_2$), 6.18 (1H, dd, $J = 7.9$, 7.6 Hz, CH), 7.14–7.40 (9H, m, Ar–H), 8.93 (2H, d, $J = 2.1$ Hz, Ar–H), 9.16 (1H, t, $J = 2.1$ Hz, Ar–H).

2-{Dimethyl[*m*-(trifluoromethyl)phenyl]silyl}-1-phenylethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.21 and 0.28 (6H, ss, SiCH$_3$), 1.73 (1H, dd, $J = 14.3$, 8.6 Hz, CH$_2$), 1.89 (1H, dd, $J = 14.3$, 7.3 Hz, CH$_2$), 6.15 (1H, dd, $J = 8.6$, 7.3 Hz, CH), 7.23–7.67 (9H, m, Ar–H), 8.95 (2H, d, $J = 2.1$ Hz, Ar–H), 9.15 (1H, t, $J = 2.1$ Hz, Ar–H).

2-[(*p*-Methoxyphenyl)dimethylsilyl]-1-[*m*-(trifluoromethyl)phenyl]ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.22 and 0.25 (6H, ss, SiCH$_3$), 1.59 (1H, dd, $J = 14.5$, 8.4 Hz, CH$_2$), 1.86 (1H, dd, $J = 14.5$, 7.0 Hz, CH$_2$), 3.69 (3H, s, OCH$_3$), 6.21 (1H, brt, $J = 7.8$ Hz, CH), 6.71 (2H, d, $J = 7.8$ Hz, Ar–H), 7.30 (2H, d, $J = 7.8$ Hz, Ar–H), 7.45–7.59 (4H, m, Ar–H), 8.88 (2H, d, $J = 2.1$ Hz, Ar–H), 9.16 (1H, t, $J = 2.1$ Hz, Ar–H).

2-[Dimethyl(*p*-methylphenyl)silyl]-1-[*m*-(trifluoromethyl)phenyl]ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.21 and 0.23 (6H, ss, SiCH$_3$), 1.62 (1H, dd, $J = 14.7$, 7.3 Hz, CH$_2$), 1.88 (1H, dd, $J = 14.7$, 8.2 Hz, CH$_2$), 2.20 (3H, s, CH$_3$), 6.19 (1H, brt, $J = 7.8$ Hz, CH), 7.02 (2H, d, $J = 7.8$ Hz, Ar–H), 7.28 (2H, d, $J = 7.8$ Hz, Ar–H), 7.45–7.59 (4H, m, Ar–H), 8.90 (2H, d, $J = 2.1$ Hz, Ar–H), 9.16 (1H, t, $J = 2.1$ Hz, Ar–H).

2-[Dimethyl(*m*-methylphenyl)silyl]-1-[*m*-(trifluoromethyl)phenyl]ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.23 and 0.25 (6H, ss, SiCH$_3$), 1.63 (1H, dd, $J = 14.7$, 7.3 Hz, CH$_2$), 1.88 (1H, dd, $J = 14.7$, 8.2 Hz, CH$_2$), 2.22 (3H, s, CH$_3$), 6.20 (1H, brt, $J = 7.8$ Hz, CH), 6.97–7.59 (8H, m, Ar–H), 8.90 (2H, d, $J = 2.1$ Hz, Ar–H), 9.16 (1H, t, $J = 2.1$ Hz, Ar–H).

2-[(3-Chloro-4-methoxyphenyl)dimethylsilyl]-1-[*m*-(trifluoromethyl)phenyl]ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.24 and 0.29 (6H, ss, SiCH$_3$), 1.59 (1H, dd, $J = 14.7$, 6.7 Hz, CH$_2$), 1.86 (1H, dd, $J = 14.7$, 8.5 Hz, CH$_2$), 3.80 (3H, s, OCH$_3$), 6.22 (1H, dd, $J = 8.5$, 6.7 Hz, CH), 6.80–7.60 (7H, m, Ar–H), 8.87 (2H, d, $J = 2.4$ Hz, Ar–H), 9.17 (1H, t, $J = 2.4$ Hz, Ar–H).

2-(*p*-Chlorophenyldimethylsilyl)-1-[*m*-(trifluoromethyl)phenyl]ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.24 and 0.29 (6H, ss, SiCH$_3$), 1.62 (1H, dd, $J = 14.6$, 7.5 Hz, CH$_2$), 1.88 (1H, dd, $J = 14.6$, 8.0 Hz, CH$_2$), 6.20 (1H, dd, $J = 8.0$, 7.5 Hz, CH), 7.14 (2H, d, $J = 8.0$ Hz, Ar–H), 7.31 (2H, d, $J = 8.0$ Hz, Ar–H), 7.45–7.59 (4H, m, Ar–H), 8.89 (2H, d, $J = 2.3$ Hz, Ar–H), 9.19 (1H, t, $J = 2.3$ Hz, Ar).

2-(*m*-Chlorophenyldimethylsilyl)-1-[*m*-(trifluoromethyl)phenyl]ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.25 and 0.29 (6H, ss, SiCH$_3$), 1.65 (1H, dd, $J = 14.5$, 7.5 Hz, CH$_2$), 1.89 (1H, dd, $J = 14.5$, 8.1 Hz, CH$_2$), 6.20 (1H, dd, $J = 8.1$, 7.5 Hz, CH), 7.12–7.60 (8H, m, Ar–H), 8.90 (2H, d, $J = 2.0$ Hz, Ar–H), 9.16 (1H, t, $J = 2.0$ Hz, Ar–H).

2-{Dimethyl[*m*-(trifluoromethyl)phenyl]silyl}-1-[*m*-(trifluoromethyl)phenyl]ethyl 3,5-Dinitrobenzoate: ^{1}H NMR δ 0.29 and 0.30 (6H, ss, SiCH$_3$), 1.73 (1H, dd, $J = 14.3$, 8.0 Hz, CH$_2$), 1.91 (1H, dd, $J = 14.3$, 7.4 Hz, CH$_2$), 6.18 (1H, dd, $J = 8.0$, 7.4 Hz, CH), 7.38–7.60 (8H, m, Ar–H), 8.94 (2H, d, $J = 2.3$ Hz, Ar–H), 9.18 (1H, t, $J = 2.3$ Hz, Ar–H).

Table 4. Physical and Analytical Data of 2-[Dimethyl(X-substituted phenyl)silyl]-1-(Y-substituted phenyl)ethyl Alcohols and 3,5-Dinitrobenzoates

Substituents		Mp/°C	Carbon/%		Hydrogen/%		Nitrogen/%	
Y	X		Found	Calcd	Found	Calcd	Found	Calcd
Alcohols								
H	*p*-MeO	Liq	71.04	71.28	7.67	7.74		
H	*p*-MeO-*m*-Cl	Liq	63.45	63.63	6.56	6.60		
H	*p*-Me	Liq	75.14	75.50	8.14	8.20		
H	*m*-Me	Liq	75.08	75.50	8.13	8.20		
H	*p*-Cl	Liq	65.44	66.07	6.52	6.58		
H	*m*-Cl	Liq	65.84	66.07	6.57	6.58		
H	*m*-CF_3	Liq	63.04	62.94	5.96	5.90		
m-CF_3	*p*-MeO	Liq	61.01	61.00	6.00	5.97		
m-CF_3	*p*-Me	Liq	63.85	63.88	6.24	6.25		
m-CF_3	*m*-Me	Liq	63.91	63.88	6.10	6.25		
m-CF_3	*p*-MeO-*m*-Cl	Liq	55.85	55.59	5.25	5.18		
m-CF_3	*p*-Cl	Liq	57.06	56.90	5.12	5.06		
m-CF_3	*m*-Cl	Liq	56.99	56.90	5.08	5.06		
m-CF_3	*m*-CF_3	Liq	55.03	55.09	4.66	4.62		
3,5-Dinitrobenzoates								
H	*p*-Cl	Liq	56.58	56.96	4.37	4.36	5.56	5.78
m-CF_3	*p*-MeO	104–105	54.55	54.74	4.30	4.23	5.01	5.11
m-CF_3	*p*-Me	136–137	56.37	56.38	4.47	4.35	5.17	5.26
m-CF_3	*m*-Me	96–97	56.32	56.38	4.40	4.35	5.31	5.26
m-CF_3	*p*-MeO-*m*-Cl	138–139	51.60	51.51	3.91	3.80	4.82	4.81
m-CF_3	*p*-Cl	130–131	52.40	52.13	3.81	3.65	5.04	5.07
m-CF_3	*m*-Cl	Liq	51.95	52.13	3.67	3.65	5.14	5.07
m-CF_3	*m*-CF_3	Liq	50.95	51.20	3.48	3.44	4.71	4.78

Analytical data of the alcohols and the esters were listed in Table 4.

Kinetic Measurements. The solvolysis rates were determined conductimetrically as reported in previous papers[1,4] at initial concentrations of ca. 10^{-5} mol dm^{-3} for 3,5-dinitrobenzoates. The progress of solvolysis was followed by taking at least 100 conductivity 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%.

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