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The γ-Silicon Effect. I.
Solvent Effects on the Solvolyses of 2,2-Dimethyl-3-(trimethylsilyl)propyl and 3-(Aryldimethylsilyl)-2,2-dimethylpropyl *p*-Toluenesulfonates

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The solvolysis rates of 2,2-dimethyl-3-(trimethylsilyl)propyl and 3-(aryldimethylsilyl)-2,2-dimethylpropyl *p*-toluenesulfonates were measured in a wide variety of solvents at 45 °C. The solvent effects were analyzed by using the Winstein–Grunwald equation. The solvent effects observed did not give simple linear correlations with the 2-adamantyl Y_{OTs} parameter, but showed dispersion behavior in a series of binary solvents. The m values of 0.59—0.67 were remarkably lower than unity for the limiting k_c solvolysis of 2-adamantyl *p*-toluenesulfonate. The deviation patterns could not be interpreted in terms of nucleophilic assistance by the solvent. The dispersion behavior with reduced m values was found to be more significant for the 3-(aryldimethylsilyl) than for the 3-(trimethylsilyl) derivatives and was compatible with the delocalization of the incipient cationic charge by participation of the Si–C$_\gamma$ bond in the rate-determining step. An extended dual-parameter treatment, $\log(k/k_{80\mathrm{E}}) = m_c Y_{\mathrm{OTs}} + m_\Delta Y_\Delta$, successfully correlated such γ-silyl assisted solvolyses. The M_Δ values of 0.24—0.49 so obtained, where $M_\Delta = 0.51 m_\Delta/(m_c + 0.51 m_\Delta)$, are a measure of the extent of charge delocalization, suggesting that the γ-silyl group in the percaudal interaction is more effective in delocalizing the cationic charge than the alkyl group in C–C σ-participation, but less so than π-assisted interaction by the β-aryl group.

The rate acceleration by silicon substituents at the γ position to the cationic reaction center has been observed in the solvolyses of several acyclic and cyclic systems and is designated as the γ-silicon effect (Chart 1).[1—6] Shiner and coworkers fully investigated this kinetic γ-silicon effect. In the acyclic system, 2,2-dimethyl-3-(trimethylsilyl)propyl brosylate (*p*-bromobenzenesulfonate) (**1**) solvolyzes 2.2×10^4 times faster than the γ-hydrogen derivative, neopentyl brosylate, in 97% (w/w) aqueous 2,2,2-trifluoroethanol (97Tw) at 25 °C.[2] In the cyclic system, the solvolysis of *cis*-3-(trimethylsilyl)cyclohexyl brosylate (**2**) was accelerated by a factor of 400 relative to the non-silylated compound, while the solvolysis of the *trans*-epimer **3** was only enhanced by a factor of 1.2.[3] In addition, the solvolysis of **2** gave a significant fraction of bicyclo[3.1.0]hexane, which was formed by 1,3-elimination. It was noted that the γ-silicon substituent facilitates ionization, especially when the silyl group has a particular geometrical orientation with respect to the leaving group. Later, Bentley and co-workers reported an additional example of the kinetic γ-silicon effect in fixed Si–C–C–C–Lv geometries in the 2-norbornyl system.[4] 6-*exo*-Trimethylsilyl-2-bicyclo[2.2.1]heptan-2-yl *exo*-mesylate (methanesulfonate) (**4**) solvolyzes 3.3×10^4 times faster than the 6-hydrogen derivative in ethanol at 25 °C, while the solvolysis rate of the corresponding 2-*endo*-brosylate (**5**) is comparable to that of the parent in 97Tw at 25 °C. From these results, one may conclude that a "W" conformation is needed for the kinetic γ-silicon effect. Moreover, the mechanism involves the formation of a carbocation (**6**) stabilized by the γ-silyl group through the so-called percaudal interaction,[7] in which the back lobe of the Si–C$_\gamma$ bond overlaps with the developing vacant p-orbital on the cationic center.[1—6]

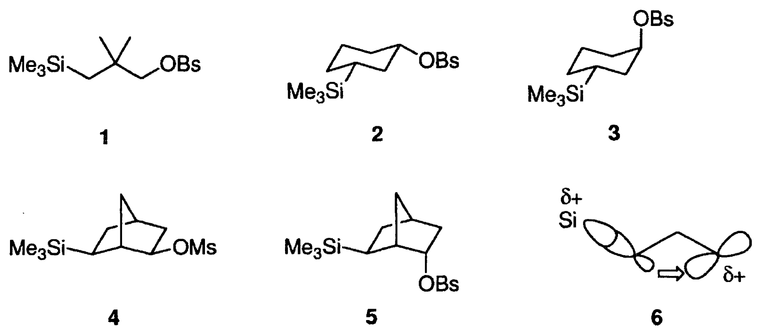


Chart 1.

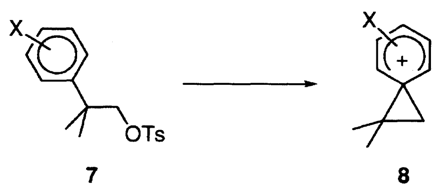
We have investigated the k_Δ solvolyses of various β-arylalkyl systems,[8—11] such as neophyl tosylates (2-methyl-2-phenylpropyl p-toluenesulfonates) (**7**), that proceed through a bridged ion (**8**) (Scheme 1), where the positive charge is delocalized by an assisting β-aryl group. Solvent effect analyses of these aryl-assisted solvolyses generally gave no simple linear relationship by using the 2-adamantyl Y_{OTs} parameter,[12] in the Winstein–Grunwald Equation 1,[13]

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

but showed significant dispersion patterns for the respective series of binary solvents exhibiting remarkably smaller m values of 0.5—0.7 less than unity for k_c solvolysis.[10,11] These split patterns are independent of solvent nucleophilicity. We concluded that the dispersion behavior and reduced m value for aryl-assisted solvolysis were explicable by the π-delocalization of the cationic charge at the reaction center by aryl ring assistance in the transition state.[10,11]

As in aryl-assisted solvolyses, solvent effects should reflect charge delocalization in the Si–C_γ assisted transition state **6**. Solvent effects on the solvolyses of the γ-silyl substituted carbocationic systems have only been performed by using binary mixtures of aq ethanol and aq 2,2,2-trifluoroethanol (TFE). Raber–Harris analysis[14] merely confirms that the solvolyses may be dependent on the solvent nucleophilicity.[1,4,5] None of these studies discussed solvent effects from the viewpoint of charge delocalization in the transition state, and none by γ-silyl group percaudal participation. We therefore decided to carry out a detailed analysis of solvent effects on the solvolyses of several γ-silicon compounds in a wide variety of binary solvents.

In order to obtain convincing evidence that charge delocalization of a carbocation into the γ-silyl group could occur through percaudal interaction, we chose a primary system where the carbocationic center might show the highest demand for stabilization. In this paper, we report the effect of solvent on the solvolyses of 2,2-dimethyl-3-(trimethylsilyl)propyl (**9**) and 3-(aryldimethylsilyl)-2,2-dimethylpropyl tosylates (**10a—c**) (Chart 2). The former system has been reported to show a large rate acceleration, presumably due to the rate-determining formation of the γ-silyl stabilized carbocation followed by migration of the (trimethylsilyl)methyl group.[2] Thus, these four tosylates are eminently suitable as candidates for the study of γ-silyl assisted solvolysis.



Scheme 1.

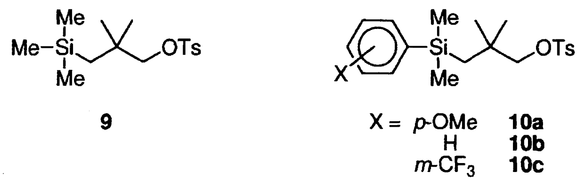


Chart 2.

Results

The rate constants for the solvolysis of **9** and **10a—c** in various solvents at 45 °C together with the solvent parameters, the Y_{OTs} and Y_Δ values, are instructive (Table 1). The methyl derivative **9** solvolyzes several times faster than the corresponding aryl derivatives **10**, where the electron-donating groups show minor rate enhancement. The solvolysis rate constant increases with the inductive polar effect of the γ-silyl substituent, in the order: Me > p-MeO–C_6H_4 > Ph > m-CF_3–C_6H_4. It should be noted that the solvolyses of these γ-silyl substituted tosylates are all markedly accelerated by a factor of 10^3—10^4 relative to the corresponding non-silylated compound, neopentyl tosylate.

The products obtained from the solvolyses of **9** and **10a—c** in 70 v/v % $(CD_3)_2CO$–D_2O at 55 °C are summarized in Scheme 2. The products were almost identical regardless of the substituents (Me, Ph, p-MeO–C_6H_4, and m-CF_3–C_6H_4 groups) on the γ-silicon atom and corresponded with those obtained for the methyl substituted brosylate **1** in 80E previously reported by Shiner.[2] Products **13**, **14**, **15**, and **16** were derived exclusively from the tertiary cation **12**, which is formed by rearrangement of the initial cation **11**. No solvent-substituted product at the primary center deriving from **11** was observed, thereby excluding an S_N2 displacement reaction. These results are in line with the rate-determining formation of the carbocation **11** stabilized by the γ-silyl group.

The Winstein–Grunwald analysis on the solvolyses of **9** using Y_{OTs} apparently gives no simple linear relationship (Fig. 1). Remarkably reduced slopes (m values) are obtained for each solvent series (Table 2). Similar results are obtained for the analysis of the solvolysis of aryl substituted derivatives **10a—c**, as exemplified by **10b** (Fig. 2). The aq ethanol and aq acetone plots fall on separate lines with different slopes. Both plots for the less nucleophilic solvent, aq TFE, and for the highly nucleophilic solvents, aq ethanol and aq methanol series lie above the aq acetone series. The dispersions between binary solvent mixtures are clearly inconsistent with any involvement of solvent nucleophilicity. For aryl substituted derivatives **10**, the extents of the dispersion between the respective solvent series were slightly greater and the m values even smaller than those seen for the methyl derivative **9**.

Consequently, we decided to evaluate the involvement of nucleophilic solvent assistance by using Eq. 2:[12]

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

where l represents the sensitivity to change in solvent nucleophilicity (N_{OTs}). Treatments with Eq. 2 gave appreciably improved correlations with negative and small contributions (l) of the solvent nucleophilicity for all the γ-silicon compounds as well as for neophyl solvolyses (Table 3). As expected, the

Table 1. Rate Constants for Solvolyses of 2,2-Dimethyl-3-(trimethylsilyl)propyl and 3-(Aryldimethylsilyl)-2,2-dimethylpropyl Tosylates at 45 °C and Solvent Parameters

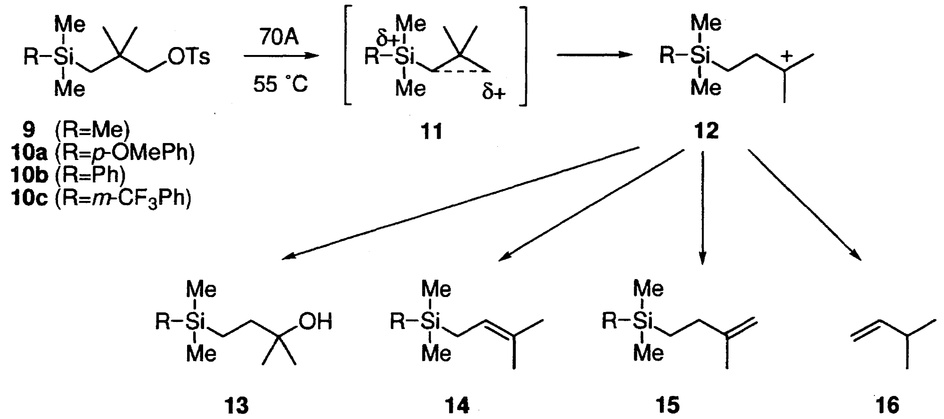
	k ($\times 10^5$/s^{-1})					
Solvent[a]	**9**	**10a**	**10b**	**10c**	Y_{OTs}[b]	Y_Δ[b,c]
100E	0.1347	0.09098	0.08676[d,e]	0.02901[d,f]	−1.749	−0.790
90E	0.4480	0.3100	0.1709	0.08186[d,g]	−0.623	−0.281
80E	1.023	0.6918	0.4488	0.1229	0.000	0.000
70E	2.279	1.203	0.7310	0.2645	0.487	0.223
60E	4.472	2.103	1.378	0.4675	0.951	0.394
50E	9.250	3.782	2.613	0.8111	1.373	0.611
40E	23.99	8.232	6.030	1.792	1.968	0.833
30E	80.57	23.10	16.97	4.305	2.665	1.117
80A	0.2773	0.1274	0.07068	0.02454[d,h]	−0.950	−0.824
70A	0.8648	0.3951	0.2221	0.09819	−0.197	−0.454
60A	2.648	0.8743	0.6089	0.1959	0.447	−0.120
50A	8.897	2.228	1.851	0.4929	1.090	0.199
40A	22.52	7.208	4.387	1.428	1.748	0.546
30A	61.30	16.06	11.25	2.343	2.412	0.909
100M	0.5304	0.3220	0.1821		−0.920	−0.368
80M	3.426	1.793	1.184	0.3893	0.470	0.298
60M	17.67	6.969	4.826	1.587	1.520	0.735
50M	39.94	14.31	9.747	3.213	2.000	0.928
TFE	53.36	16.48	14.60	4.053	1.764	1.277
97Tw	36.59	17.34	11.03	3.213	1.833	1.123
80Tv	34.15	14.05	10.99	2.855	1.919	1.092
50Tv	38.85	15.25	10.92	3.085	2.147	1.081
40Tv	44.10	16.47	11.83	3.313	2.270	1.111
30Tv	52.65	20.11	14.43	3.906	2.434	1.152
80ET	0.2833	0.1870	0.1283[d,i]	0.03692[d,j]	−1.178	−0.393
60ET	0.9709	0.5491	0.2950	0.08980	−0.437	0.015
40ET	2.902	1.778	1.049	0.2716	0.213	0.454
20ET	10.77	7.394	3.622	0.8693	0.977	0.824
90AN	0.4126	0.1819	0.1321	0.04210[d,k]	−0.796	−0.828
80AN	1.294	0.5623	0.3518	0.1340	−0.013	−0.408
60AN	5.359	2.088	1.321	0.4813	0.885	0.091
50AN	11.11	3.879	2.548	0.9906	1.307	0.320

a) Volume percent of first-named organic component, unless otherwise noted. Abbreviation, E = ethanol, A = acetone, M = methanol, AN = acetonitrile, T = TFE = 2,2,2-trifluoroethanol, and ET = ethanol–TFE mixtures (e.g., 20ET = 20 vol EtOH : 80 vol TFE). Tw and Tv mean weight percent and volue percent TFE–H_2O, respectively. b) Data taken from Refs. 10 and 11a. c) $Y_\Delta = \log (k/k_{80\mathrm{E}})_{p\text{-MeO-neophyl OTs}}$ at 45 °C. d) Extrapolated from rate data at other temperatures. e) 0.2755×10^{-5} s^{-1} (55 °C), 2.275×10^{-5} s^{-1} (75 °C). f) 0.08329×10^{-5} s^{-1} (55 °C), 0.5725×10^{-5} s^{-1} (75 °C). g) 0.2746×10^{-5} s^{-1} (55 °C), 2.508×10^{-5} s^{-1} (75 °C). h) 0.09634×10^{-5} s^{-1} (55 °C), 1.173×10^{-5} s^{-1} (75 °C). i) 0.4038×10^{-5} s^{-1} (55 °C), 3.283×10^{-5} s^{-1} (75 °C). j) 0.1327×10^{-5} s^{-1} (55 °C), 1.375×10^{-5} s^{-1} (75 °C). k) 0.1307×10^{-5} s^{-1} (55 °C), 1.037×10^{-5} s^{-1} (75 °C).

results clearly indicate that these solvolyses do not entail any nucleophilic solvent displacement and that the nucleophilic solvation toward the bridged species (**8** and **11**) decreased compared to that of the charge-localized 2-adamantyl cation. However, this interpretation is controversial because the negative l value tends to exaggerate the splitting between the aq ethanol and aq acetone series in the mY_{OTs} plots of Figs. 1 and 2.

The solvent effects observed on applying Eq. 1 to the present solvolyses were characterized by dispersion patterns for each series of binary solvents, with significantly reduced m values independent of solvent nucleophilicity. The failure of the mY_{OTs} correlation with a small m value indicates that these solvolyses do not follow a k_c mechanism, but involve finite assistance in a simple ionization step without nucleophilic assistance by the solvent.

The logarithmic rates of solvolyses of **9**, **10a**, and **10c** plotted against those for **10b** give a good linear relationship with essentially unit slope (Fig. 3) (correlation coefficients > 0.993, Table 4). These correlations may well be regarded as simple linear relationships without meaningful dispersions. The solvent behavior is similar for all the γ-silyl substrates in question, indicating similar transition states. Nevertheless, the response to solvent polarity for the methyl derivative **9**



	13	14	15	16
(R=Me)	38%	40%	20%	2%
(R=p-OMePh)	29%	51%	19%	1%
(R=Ph)	30%	48%	21%	1%
(R=m-CF₃Ph)	30%	47%	23%	0%

Scheme 2.

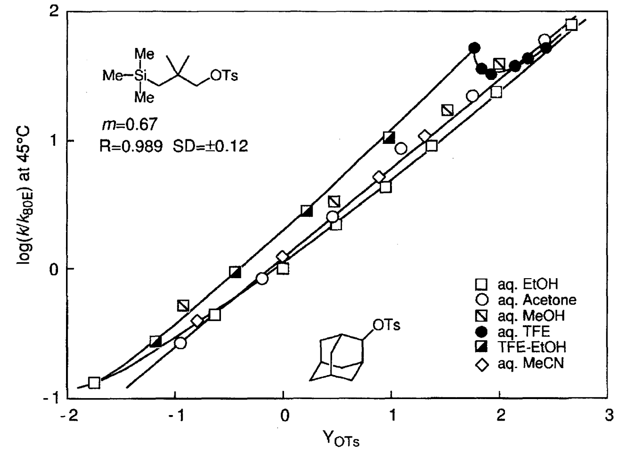


Fig. 1. The mY_{OTs} plots for the solvolysis of 2,2-dimethyl-3-(trimethylsilyl)propyl tosylate **9** at 45 °C.

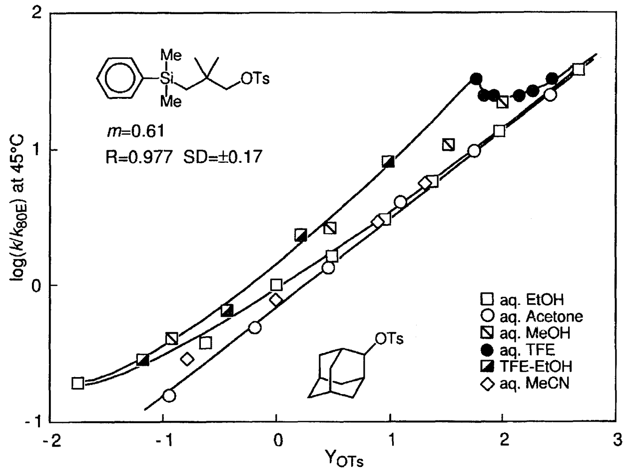


Fig. 2. The mY_{OTs} plots for the solvolysis of 3-(dimethylphenylsilyl)-2,2-dimethylpropyl tosylate **10b** at 45 °C.

is slightly larger than that for the aryl derivatives **10**.

These splitting patterns and the small m values observed for the present solvolyses are similar, though slightly less extensive, to those of the β-aryl assisted solvolysis described above.[10,11] The solvent effects on various solvolyses involving a charge-delocalized cation are found to be correlated by Eq. 3, in which the reference Y_Δ scale is based on p-methoxyneophyl tosylate that solvolyzes via p-methoxy substituted ion **8** with strong π-delocalization.[10,11,15]

$$\log(k/k_{80\mathrm{E}}) = m'Y_\Delta \qquad (3)$$

The plot of the logarithmic rates of **9** against Y_Δ revealed no simple linear relationship (Fig. 4). The dispersions observed between binary solvents were in the reverse order to those

Table 2. Correlation Analyses of Solvent Effects on Solvolyses of γ-Silicon Compounds at 45 °C by Eq. 1

Solvent series	m-Values[a)]			
	9	**10a**	**10b**	**10c**
All	0.67 (0.989)	0.60 (0.978)	0.61 (0.977)	0.59 (0.979)
aq EtOH	0.64 (0.996)	0.54 (0.998)	0.54 (0.991)	0.50 (0.994)
aq Acetone	0.71 (0.999)	0.63 (0.999)	0.66 (0.999)	0.59 (0.995)
aq MeOH	0.64 (0.999)	0.56 (0.999)	0.59 (0.999)	0.60 (0.999)
aq MeCN	0.68 (0.999)	0.63 (0.999)	0.61 (0.999)	0.65 (0.999)
aq TFE	0.10 (0.32)	0.10 (0.49)	0.04 (0.17)	0.03 (0.13)
EtOH–TFE	0.74 (0.998)	0.67 (0.997)	0.65 (0.991)	0.62 (0.988)

a) The values in parentheses are the correlation coefficients.

Table 3. Correlation Analysis of Solvent Effects on Solvolyses of Various Tosylates by Eq. 2

Substrates	m	l	$R^{a)}$	±SD$^{b)}$	$n^{c)}$
p-Methoxyneophyl	0.47	−0.15	0.969	0.16	49
10a	0.57	−0.12	0.985	0.13	32
10b	0.58	−0.12	0.985	0.14	32
10c	0.56	−0.11	0.985	0.13	31
9	0.65	−0.11	0.994	0.10	32
Neopentyl	0.67	0.01	0.997	0.09	13
Pinacolyl	0.84	0.08	0.998	0.08	25
2-*exo*-Norbornyl	0.89	0.13	0.998	0.08	36

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

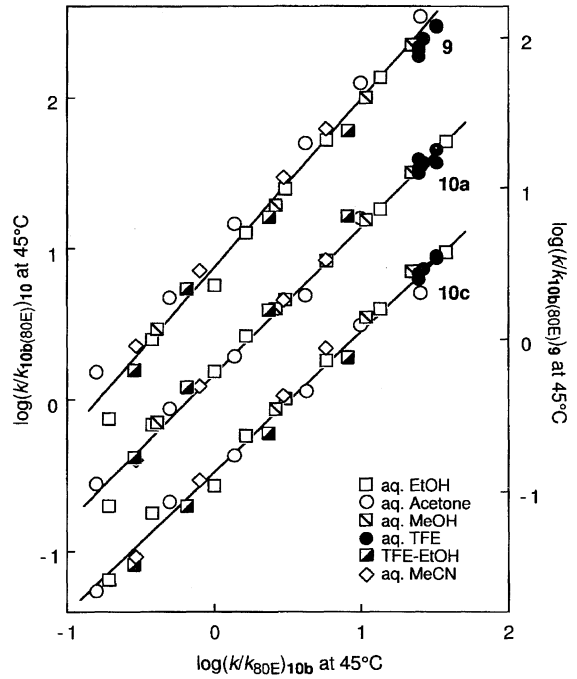


Fig. 3. The logarithmic plots for the solvolyses of **9** (Me), **10a** (*p*-MeO–Ph), and **10c** (*m*-CF$_3$–Ph) against that of **10b** (Ph) at 45 °C.

in the Y_{OTs} plot (Fig. 1). Similar results were obtained for the solvolyses of the aryl derivatives **10a**—**c**. The m' values obtained from correlation analyses of **9** and **10a**—**c** by Eq. 3 are larger than unity, except for the aq TFE series (Table 5).

Table 4. Results of Linear Logarithmic Rate Relations for Solvolyses of **9**, **10a**, and **10c** against That of **10b**

Substrates	Slope	$R^{a)}$	±SD$^{b)}$
9	1.07±0.02	0.993	0.09
10a	0.98±0.01	0.997	0.06
10c	0.94±0.02	0.996	0.06

a) Correlation coefficients. b) Standard deviations.

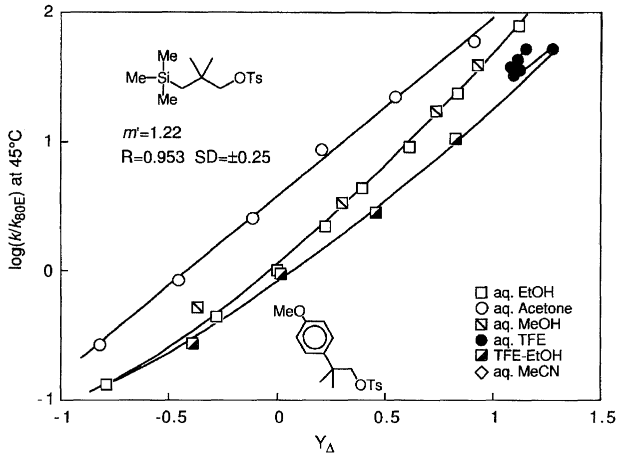


Fig. 4. The $m'Y_{\Delta}$ plots for the solvolysis of 2,2-dimethyl-3-(trimethylsilyl)propyl tosylate **9** at 45 °C.

These results show that the dispersions by the Y_{OTs} plots are not so extensive as for those of the *p*-methoxyneophyl tosylate solvolysis; i.e., the extent of charge delocalization in γ-silyl solvolysis may be smaller than that in the *p*-methoxyneophyl solvolysis.

Although the direct treatment with Y_{OTs} or Y_{Δ} does not give satisfactory correlations for all the γ-silyl substrates, solvent effects can be correlated by a linear combination of Y_{OTs} and Y_{Δ}:

$$\log(k/k_{80\mathrm{E}}) = m_{\mathrm{c}}Y_{\mathrm{OTs}} + m_{\Delta}Y_{\Delta} \qquad (4)$$

This Eq. 4 was proposed for comparing solvent effects on the solvolyses involving intermediates lying between the extremes of the localized 2-adamantyl and the π-delocalized *p*-methoxyneophyl cations. The m_{c} and m_{Δ} values change in a complementary manner with the change of the substrate. The m_{Δ} increases from 0.00 for 2-adamantyl tosylate to 1.00

Table 5. Correlation Analyses of Solvent Effects on Solvolyses of γ-Silicon Compounds at 45 °C by Eq. 3

Solvent series	m'-Values$^{a)}$			
	9	**10a**	**10b**	**10c**
All	1.22 (0.953)	1.12 (0.978)	1.13 (0.975)	1.07 (0.966)
aq EtOH	1.47 (0.993)	1.25 (0.997)	1.23 (0.987)	1.16 (0.991)
aq Acetone	1.38 (0.998)	1.23 (0.999)	1.28 (0.998)	1.15 (0.993)
aq MeOH	1.44 (0.996)	1.26 (0.998)	1.32 (0.999)	1.45 (0.999)
aq MeCN	1.24 (0.999)	1.16 (0.999)	1.12 (0.999)	1.18 (0.999)
aq. TFE	0.88 (0.75)	1.99 (0.94)	0.69 (0.82)	0.70 (0.84)
EtOH–TFE	1.26 (0.995)	1.15 (0.995)	1.09 (0.985)	1.06 (0.982)

a) The values in parentheses are the correlation coefficients.

for p-methoxyneophyl tosylate, whereas m_c decreases from 1.00 to 0.00 in parallel with the degree of π-charge delocalization in the transition state. The m_c and m_Δ values so obtained introduce the parameters of $\underline{m}$ and M_Δ which are useful for evaluating the extent of charge delocalization and the nature of the electronic structure in the transition state. The definition $\underline{m} = m_c+0.51m_\Delta$ is the response to the solvent ionizing power as a practical measure of cationic charge at the carbocationic center. The parameter M_Δ, defined by $M_\Delta = 0.51m_\Delta/\underline{m}$, describes the extent of charge delocalization in the transition state for a given solvolysis. The M_Δ value varies continuously from 0.00 for the localized 2-adamantyl to 1.00 for the π-delocalized p-methoxyneophyl cation, depending on the degree of aryl-assistance. Thus, the dispersion behavior in solvolysis can be related to the charge delocalization by Eq. 4.

The extended Winstein–Grunwald Equation 4 was applied to the solvolyses of **9** and **10a—c** and gave satisfactory correlations (correlation coefficients = 0.991—0.995) for **9** (Fig. 5) and **10b** (Fig. 6). The m_c and m_Δ values together with the $\underline{m}$ and M_Δ values provide the following observations (Table 6). The size of m_c decreases from 0.5 for the methyl derivative **9** to ca. 0.3 for the aryl derivatives **10a—c**, whereas m_Δ increases in parallel fashion from 0.3 to ca. 0.5. The degree of charge delocalization, denoted by the M_Δ values, was 0.24 and 0.4—0.5 for the solvolyses of the methyl derivative **9** and the three aryl derivatives **10a—c**, respectively. The $\underline{m}$ values decreased to 0.67 for **9** and 0.60 for **10**, while the M_Δ values increased slightly by the electron-donating aryl substituent.

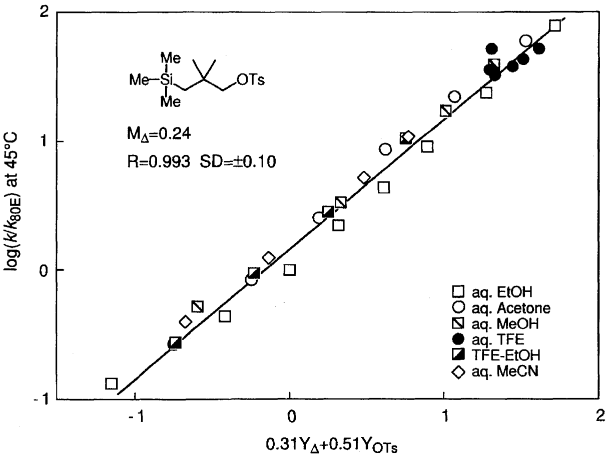


Fig. 5. The ($m_\Delta Y_\Delta$+$m_c Y_{OTs}$) plots for the solvolysis of 2,2-dimethyl-3-(trimethylsilyl)propyl tosylate **9** at 45 °C.

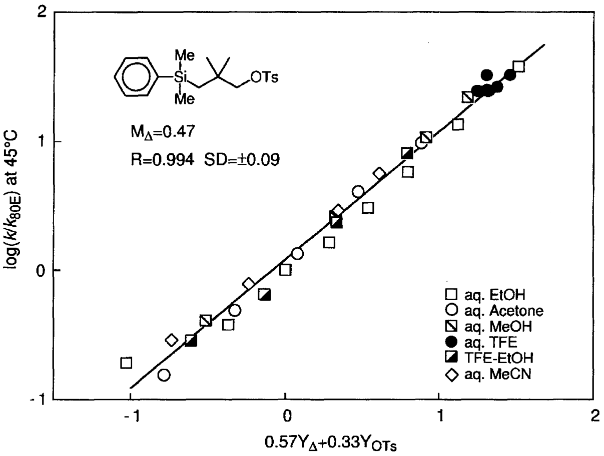


Fig. 6. The ($m_\Delta Y_\Delta$+$m_c Y_{OTs}$) plots for the solvolysis of 3-(dimethylphenylsilyl)-2,2-dimethylpropyl tosylate **10b** at 45 °C.

Table 6. Correlation Analyses of Solvent Effects on Solvolyses of Various Tosylates by Eq. 4

Substrates	m_c	m_Δ	$\underline{m}$[a]	M_Δ[b]	R[c]	±SD[d]	n[e]
p-Methoxyneophyl	0.00	1.00	0.51	1.00	(Definition)		49
Neophyl	0.16	0.95	0.64	0.75	0.998	0.06	46
10a	0.31	0.58	0.61	0.49	0.995	0.07	32
10b	0.33	0.57	0.62	0.47	0.994	0.09	32
10c	0.35	0.46	0.59	0.40	0.991	0.10	31
9	0.51	0.31	0.67	0.24	0.993	0.10	32
2-Adamantyl	1.00	0.00	1.00	0.00	(Definition)		49

a) $\underline{m} = m_c+0.51m_\Delta$. b) $M_\Delta = 0.51m_\Delta/\underline{m}$. c) Correlation coefficients. d) Standard deviations. e) Number of data points involved.

To correlate the dispersion observed in the Winstein–Grunwald plots for benzylic and related derivatives, Kevill and co-workers[16] proposed Eq. 5 containing the ring parameter (I). This equation has been successfully applied to the solvolyses of some benzyl and β-arylalkyl systems.[16,17]

$$\log(k/k_{80E}) = mY_{OTs} + hI \qquad (5)$$

The solvolyses of the present γ-silicon compounds were also treated by Eq. 5 in this work and gave results comparable to those obtained by Eq. 4, but this is not altogether surprising since there is an interrelation between Y_Δ and I; $Y_\Delta = 0.51Y_{OTs}+0.66I$.[17]

Discussion

The analyses of the solvent effects on the solvolyses of **9** and **10** by Eq. 1, uncovered some important features. 1) The 2-adamantyl Y_{OTs} parameter fails to give a simple linear correlation for the solvent effect. 2) The m values for each solvent series are remarkably lower than unity for the limiting k_c solvolysis of 2-adamantyl tosylate, and the reduced m values are more significant for the three aryl derivatives **10a—c** than for the methyl derivative **9**. 3) The pattern of deviations is not attributable to nucleophilic solvent assistance.

We observed essentially the same features from the Y_{OTs} treatments of various β-aryl assisted (k_Δ) solvolyses and concluded that the characteristic dispersions for the respective series of binary solvents with reduced m values are compatible with the π-delocalization of cationic charge by assistance of the aryl ring in the transition state.[10,11] Thus, the characteristic behavior of the γ-silicon compounds may be ascribed to the delocalization of charge by the Si–C bond participating at the vacant p-orbital at reaction center, in the rate-determining step. However, the m values of 0.59—0.67 for γ-silicon compounds **9** and **10a—c** are much larger than that observed for the solvolysis of *p*-methoxyneophyl tosylate (0.51). In addition, the dispersion pattern for the former system is smaller than that for the latter. Thus, the charge delocalization in the transition state of γ-silyl stabilized cation formation might not be so extensive as that in the aryl-bridged transition state in the standard Y_Δ system.

On the other hand, the simple alkyl-assisted (σ-participation) solvolysis gave a simple linear correlation with the Y_{OTs} parameter for the solvent effect with excellent precision ($R = 0.997$—0.991), whereas reduced m values were obtained for the solvolyses of pinacolyl (1,2,2-trimethylpropyl), 2-*exo*-norbornyl, and neopentyl tosylates (0.82, 0.83, and 0.67), respectively.[18] The m values for the present γ-silyl system are comparable to or even smaller than that for solvolyses involving σ-participation. The same m value of 0.67 was obtained for the γ-silyl derivative **9** and the parent neopentyl tosylate. Nevertheless, the characteristic dispersion behavior of the Y_{OTs} plot was observed only for the former system. On the contrary, the solvent effect of the alkyl-assisted system usually showed a slight downward deviation for the aq. fluorinated alcohol and acetic acid-formic acid mixture.[18] In fact, positive l values were observed for these substrates (Table 3). The charge delocalization in the transition state for the solvolysis of **9** owing to the γ-silicon effect is more extensive than that for neopentyl tosylate.

Thus, the mY_{OTs} plots for the solvolyses of the aryl derivatives **10a—c** show characteristic dispersions in which the plots for aq acetone series clearly lie below those for aq EtOH and aq MeOH series. In the case of the solvolysis of the methyl derivative **9**, the mY_{OTs} plot shows that the plots for the aq acetone series lie on the same line as those for aq EtOH series line, within experimental error (Fig. 1). Both enhanced charge delocalization and decreased nucleophilic solvation at the incipient cationic center may occur in the transition state. The overlap of the back lobe of Si–C_γ bond can block the backside of the cation center to effectively hinder nucleophilic solvation, and at the same time it can enhance the charge delocalization to the γ-silyl group.

The analyses based on Eq. 4 gave good correlations for the solvolyses of **9** and **10a—c** with correlation coefficients > 0.991. This treatment is equally successful for the γ-silyl- as well as for the aryl-assisted solvolyses. The mechanism of the γ-silyl-assisted solvolysis, involving intramolecular participation of the silylmethyl group dorsal to the α-carbon bearing the leaving group in the transition state structure,[1—6] is similar to that for β-aryl-assisted solvolysis. For this reason, we applied the treatment including Y_Δ (Eq. 4) to characterize the charge delocalization of a carbocation into the γ-silyl group through the percaudal interaction, rather than Eq. 5.

The degree of positive charge delocalization by γ-(trimethylsilyl), γ-(aryldimethylsilyl), and β-aryl groups is indicated by the M_Δ values. For the solvolyses of **9** and **10a—c**, the values of M_Δ are 0.24 and 0.5, respectively, compared to 1.00 for *p*-methoxyneophyl, and 0.00 for alkyl-assisted solvolysis. It can be concluded that, in the transition state for γ-(aryldimethylsilyl) assisted solvolysis, only half the positive charge is transferred to the silyl group compared to the β-*p*-methoxyphenyl analogue. Aryl substituents on the γ-Si atom result in larger M_Δ values than for the methyl derivative, the more electron-donating substituent giving slightly bigger M_Δ values. The tendency toward decreasing M_Δ values for electron-withdrawing aryl substituents on silicon atoms implies that the delocalization of positive charge should be extended not only over the Si–C_γ σ-bond, but also to the silicon atom itself. The γ-silyl group in the percaudal interaction is far more effective in delocalizing the cationic charge than is seen for σ-participation. It must be said, however, that the participation of the γ-silyl group is less important than that of the π-system in β-aryl assistance.

The analyses based on Eq. 4 showed that the differences in M_Δ and $\underline{m}$ values among the three aryl substituted derivatives **10a—c** are negligibly small, despite the wide range of substituents from *p*-MeO to *m*-CF_3. This result is in contrast to that seen for the *p*-MeO and H substituents in the neophyl system (Table 6). In other words, this distinction in charge delocalization by substituents on a phenylsilyl group and a β-phenyl group might be due to different dimensions and geometries in the two transition states. The π-orbital of the β-aryl group interacts directly with the vacant p orbital at the reaction center, whereas the phenyl group on the γ-silicon atom only indirectly interacts through the Si–C σ-bond. In fact, the effect of the aryl substituent on the solvolysis rates of **10** when correlated with unexalted σ^0 gave $\rho \cong -1.0$ in various solvents, while the same effect on the neophyl solvolysis gave $\rho = -3.8$ and $r = 0.57$ with the Yukawa–Tsuno equation.[8] The small but negative ρ values obtained confirm that an appreciable amount of positive charge resides on the Si atom at the δ position.

Experimental

Column chromatography was performed by using Silica Gel 60 (Merck, 230—400 mesh). The ^{1}H 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 (δ) downfield from TMS as an internal standard. All air- and moisture-sensitive reactions were carried out under nitrogen. Ether and tetrahydrofuran were distilled from sodium/benzophenone under nitrogen.

Materials. (Dimethylphenylsilyl)methyl Chloride. To a solution of phenylmagnesium bromide prepared from bromobenzene (12.53 g, 79.8 mmol) and Mg (1.94 g, 79.8 mmol) in 80 cm^3 of ether was added dropwise chloro(chloromethyl)dimethylsilane (11.39 g, 80.0 mmol) in 80 cm^3 of ether with stirring at 0 °C. The reaction mixture was heated under reflux with stirring overnight. After cooling, the reaction mixture was treated with NH_4Cl (8.54 g, 160 mmol) in 60 cm^3 of water, and extracted with ether. The ethereal extract was washed with aqueous saturated sodium chloride and then dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, to give 16.22 g of crude product. Purification by column chromatography afforded 10.80 g (yield, 73%) of the chloride as a colorless oil: ^{1}H NMR $\delta = 0.42$ (6H, s, Si–CH_3), 2.95 (2H, s, CH_2), 7.20—7.56 (5H, m, Ar–H). By the same procedure, the following chlorides were prepared from the corresponding bromobenzenes.

(p-Methoxyphenyldimethylsilyl)methyl Chloride: ^{1}H NMR δ = 0.39 (6H, s, Si–CH$_3$), 2.92 (2H, s, CH$_2$), 3.82 (3H, s, OCH$_3$), 6.93 (2H, d, J = 8.8 Hz, Ar–H), 7.47 (2H, d, J = 8.8 Hz, Ar–H).

[Dimethyl(m-trifluoromethylphenyl)silyl]methyl Chloride: ^{1}H NMR δ = 0.46 (6H, s, Si–CH$_3$), 2.96 (2H, s, CH$_2$), 7.49—7.77 (4H, m, Ar–H).

(Dimethylphenylsilyl)methyl Iodide. According to the method of Sommer,[19] (dimethylphenylsilyl)methyl chloride (8.00 g, 43.3 mmol) was added to a solution of sodium iodide (11.7 g, 78.1 mmol) in 80 cm^3 of acetone. The reaction mixture was heated under reflux with stirring overnight. After cooling, sodium chloride was filtered off and the filtrate was concentrated under reduced pressure. To the remaining residue was added 50 cm^3 of water, and then the mixture was extracted with ether. The ethereal extract was washed with aq saturated sodium chloride and then dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure to give 11.84 g of the iodide in quantitative yield: ^{1}H NMR δ = 0.44 (6H, s, Si–CH$_3$), 2.18 (2H, s, CH$_2$), 7.31—7.59 (5H, m, Ar–H). According to the same procedure, the following iodides were prepared from the corresponding chlorides.

(p-Methoxyphenyldimethylsilyl)methyl Iodide: ^{1}H NMR δ = 0.42 (6H, s, Si–CH$_3$), 2.16 (2H, s, CH$_2$), 3.82 (3H, s, OCH$_3$), 6.92 (2H, d, J = 8.7 Hz, Ar–H), 7.46 (2H, d, J = 8.7 Hz, Ar–H).

[Dimethyl(m-trifluoromethylphenyl)silyl]methyl Iodide: ^{1}H NMR δ = 0.48 (6H, s, Si–CH$_3$), 2.18 (2H, s, CH$_2$), 7.49—7.76 (4H, m, Ar–H).

(Trimethylsilyl)methyl Iodide: ^{1}H NMR δ = 0.15 (9H, s, Si–CH$_3$), 2.00 (2H, s, CH$_2$).

Ethyl 3-(Dimethylphenylsilyl)propionate. According to the method of Sommer,[20] ethyl acetoacetate (5.21 g, 40.0 mmol) was added to a solution of sodium (0.92 g, 40.0 mmol) in 30 cm^3 of ethanol and, after stirring for 10 min, (dimethylphenylsilyl)methyl iodide (11.06 g, 40.0 mmol) was added. The reaction mixture was heated under reflux with stirring for 44 h. After cooling, the solvent was removed under reduced pressure. To the residue was added 40 cm^3 of water, and then the mixture was extracted with ether. The ethereal extract was treated by the usual way to give 9.92 g of crude product. Purification by column chromatography afforded 6.01 g (yield, 64%) of the ester as a colorless oil: ^{1}H NMR δ = 0.25 (6H, s, Si–CH$_3$), 1.02—1.09 (2H, m, CH$_2$), 1.25 (3H, t, J = 7.2 Hz, CH$_3$), 2.20—2.26 (2H, m, CH$_2$), 4.04 (2H, q, J = 7.2 Hz, CH$_2$), 7.31—7.55 (5H, m, Ar–H). In the same procedure, the following esters were prepared from the corresponding iodides and acetoacetic ester.

Ethyl 3-(p-Methoxyphenyldimethylsilyl)propionate: ^{1}H NMR δ = 0.26 (6H, s, Si–CH$_3$), 1.03—1.08 (2H, m, CH$_2$), 1.23 (3H, t, J = 7.3 Hz, CH$_3$), 2.23—2.38 (2H, m, CH$_2$), 3.81 (3H, s, OCH$_3$), 4.08 (2H, q, J = 7.3 Hz, CH$_2$), 6.91 (2H, d, J = 8.5 Hz, Ar–H), 7.42 (2H, d, J = 8.5 Hz, Ar–H).

Ethyl 3-[Dimethyl(m-trifluoromethylphenyl)silyl]propionate: ^{1}H NMR δ = 0.33 (6H, s, Si–CH$_3$), 1.08—1.14 (2H, m, CH$_2$), 1.23 (3H, t, J = 7.3 Hz, CH$_3$), 2.24—2.29 (2H, m, CH$_2$), 4.08 (2H, q, J = 7.3 Hz, CH$_2$), 7.47—7.72 (4H, m, Ar–H).

Ethyl 3-(Trimethylsilyl)propionate: ^{1}H NMR δ = 0.01 (9H, s, Si–CH$_3$), 0.82—0.87 (2H, m, CH$_2$), 1.26 (3H, t, J = 7.0 Hz, CH$_3$), 2.25—2.30 (2H, m, CH$_2$), 4.12 (2H, q, J = 7.0 Hz, CH$_2$).

Ethyl 3-(Dimethylphenylsilyl)-2,2-dimethylpropionate. To a stirred solution of lithium diisopropylamide prepared from diisopropylamine (1.27 g, 12.55 mmol) and 1.6 M butyllithium hexane solution (7.8 cm^3, 12.50 mmol, 1 M = 1 mol dm^{-3}) in 25 cm^3 of THF at 0 °C was added dropwise a solution of ethyl 3-(dimethylphenylsilyl)propionate (2.00 g, 8.34 mmol) in 20 cm^3 of THF at −70 °C. After stirring at −70 °C for 10 min, methyl iodide (2.37 g, 16.7 mmol) in 10 cm^3 of THF was added dropwise. After stirring at −70 °C for 1 h, the reaction mixture was allowed to warm to room temperature and was stirred for 2 h. After cooling at −70 °C, lithium diisopropylamide (12.5 mmol) in 20 cm^3 of THF was added dropwise at −70 °C. After stirring at −70 °C for 10 min, methyl iodide (2.37 g, 16.7 mmol) in 10 cm^3 of THF was added dropwise. After stirring at −70 °C for 1 h, the reaction mixture was allowed to warm to room temperature, stirred 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 layers were washed with 5% hydrochloric acid, saturated sodium chloride, and dried over anhydrous magnesium sulfate. Purification by column chromatography afforded 1.82 g (yield, 83%) of the ester as a colorless oil: ^{1}H NMR δ = 0.30 (6H, s, Si–CH$_3$), 1.19 (6H, s, CH$_3$), 1.23 (2H, s, CH$_2$), 1.94 (3H, t, J = 7.5 Hz, CH$_3$), 3.95 (2H, q, J = 7.5 Hz, CH$_2$), 7.31—7.53 (5H, m, Ar–H). By the same procedure, the following esters were prepared from the corresponding propionates.

Ethyl 3-(p-Methoxyphenyldimethylsilyl)-2,2-dimethylpropionate: ^{1}H NMR δ = 0.28 (6H, s, Si–CH$_3$), 1.19 (6H, s, CH$_3$), 1.20 (2H, s, CH$_2$), 1.21 (3H, t, J = 7.3 Hz, CH$_3$), 3.80 (3H, s, OCH$_3$), 3.97 (2H, q, J = 7.3 Hz, CH$_2$), 6.90 (2H, d, J = 8.9 Hz, Ar–H), 7.43 (2H, d, J = 8.9 Hz, Ar–H).

Ethyl 3-[Dimethyl(m-trifluoromethylphenyl)silyl]-2,2-dimethylpropionate: ^{1}H NMR δ = 0.33 (6H, s, Si–CH$_3$), 1.19 (6H, s, CH$_3$), 1.19 (3H, t, J = 7.1 Hz, CH$_3$), 1.24 (2H, s, CH$_2$), 3.95 (2H, q, J = 7.1 Hz, CH$_2$), 7.43—7.72 (4H, m, Ar–H).

Ethyl 2,2-Dimethyl-3-(trimethylsilyl)propionate: ^{1}H NMR δ = 0.00 (9H, s, Si–CH$_3$), 0.98 (2H, s, CH$_2$), 1.22 (6H, s, CH$_3$), 1.25 (3H, t, J = 7.0 Hz, CH$_3$), 4.09 (2H, q, J = 7.0 Hz, CH$_2$).

3-(Dimethylphenylsilyl)-2,2-dimethyl-1-propanol. Ethyl 3-(dimethylphenylsilyl)-2,2-dimethylpropionate (1.00 g, 3.78 mmol) in 7 cm^3 of ether was added dropwise to a suspension of lithium aluminum hydride (0.30 g, 7.9 mmol) in 10 cm^3 of ether at 0 °C. After the usual work-up, the alcohol was purified by column chromatography to yield 0.68 g (81%) as a colorless oil: ^{1}H NMR δ = 0.35 (6H, s, Si–CH$_3$), 0.90 (6H, s, CH$_3$), 0.90 (2H, s, CH$_2$), 1.23 (1H, t, J = 6.3 Hz, OH), 3.20 (2H, d, J = 6.3 Hz, CH$_2$), 7.33—7.57 (5H, m, Ar–H). Similarly, the following alcohols were prepared.

3-(p-Methoxyphenyldimethylsilyl)-2,2-dimethyl-1-propanol: ^{1}H NMR δ = 0.32 (6H, s, Si–CH$_3$), 0.87 (2H, s, CH$_2$), 0.89 (6H, s, CH$_3$), 1.23 (1H, t, J = 6.1 Hz, OH), 3.19 (2H, d, J = 6.1 Hz, CH$_2$), 3.81 (3H, s, OCH$_3$), 6.90 (2H, d, J = 8.5 Hz, Ar–H), 7.45 (2H, d, J = 8.5 Hz, Ar–H).

3-[Dimethyl(m-trifluoromethylphenyl)silyl]-2,2-dimethyl-1-propanol: ^{1}H NMR δ = 0.39 (6H, s, Si–CH$_3$), 0.90 (6H, s, CH$_3$), 0.93 (2H, s, CH$_2$), 1.30 (1H, t, J = 6.1 Hz, OH), 3.23 (2H, d, J = 6.1 Hz, CH$_2$), 7.41—7.76 (4H, m, Ar–H).

2,2-Dimethyl-3-(trimethylsilyl)-1-propanol: ^{1}H NMR δ = 0.05 (9H, s, Si–CH$_3$), 0.64 (2H, s, CH$_2$), 0.88 (1H, t, J = 5.5 Hz, OH), 0.96 (6H, s, CH$_3$), 3.27 (2H, d, J = 5.5 Hz, CH$_2$).

3-(Dimethylphenylsilyl)-2,2-dimethylpropyl Tosylate (10b). To a stirred solution of 3-(dimethylphenylsilyl)-2,2-dimethyl-1-propanol (0.59 g, 2.65 mmol) in 8 cm^3 of ether was slowly added 1.6 M butyllithium (1.66 cm^3, 2.65 mmol) at 0 °C. This solution was stirred for 30 min, and then p-toluenesulfonyl chloride (0.51 g, 2.68 mmol) was added. After stirring for 18 h, the reaction mixture was treated with 10 cm^3 of water under cooling and then extracted with ether. After the usual work-up, the solvent was evaporated under reduced pressure to leave 0.91 g of the crude tosylate, which was purified by column chromatography to yield 0.81 g (81%) as a colorless oil: ^{1}H NMR δ = 0.30 (6H, s, Si–CH$_3$), 0.86 (6H, s,

CH_3), 0.86 (2H, s, CH_2), 2.44 (3H, s, CH_3), 3.57 (2H, s, CH_2), 7.31 (2H, d, $J = 8.4$ Hz, Ar–H), 7.32—7.48 (5H, m, Ar–H), 7.72 (2H, d, $J = 8.4$ Hz, Ar–H). Found: C, 63.53; H, 7.46%. Calcd for $C_{20}H_{28}O_3SSi$: C, 63.79; H, 7.49%. In the same way, the following tosylates were prepared.

3-(*p*-Methoxyphenyldimethylsilyl)-2,2-dimethylpropyl Tosylate (10a): ^{1}H NMR $\delta = 0.27$ (6H, s, Si–CH_3), 0.83 (2H, s, CH_2), 0.86 (6H, s, CH_3), 2.44 (3H, s, CH_3), 3.57 (2H, s, CH_2), 3.81 (3H, s, OCH_3), 6.88 (2H, d, $J = 8.5$ Hz, Ar–H), 7.31 (2H, d, $J = 8.5$ Hz, Ar–H), 7.37 (2H, d, $J = 8.5$ Hz, Ar–H), 7.72 (2H, d, $J = 8.5$ Hz, Ar–H). Found: C, 62.08; H, 7.44%. Calcd for $C_{21}H_{30}O_4SSi$: C, 62.03; H, 7.44%.

3-[Dimethyl(*m*-trifluoromethylphenyl)silyl]-2,2-dimethylpropyl Tosylate (10c): ^{1}H NMR $\delta = 0.34$ (6H, s, Si–CH_3), 0.87 (2H, s, CH_2), 0.88 (6H, s, CH_3), 2.44 (3H, s, CH_3), 3.58 (2H, s, CH_2), 7.32 (2H, d, $J = 8.2$ Hz, Ar–H), 7.43—7.67 (4H, m, Ar–H), 7.73 (2H, d, $J = 8.2$ Hz, Ar–H). Found: C, 56.90; H, 6.19%. Calcd for $C_{21}H_{27}F_3O_3SSi$: C, 56.73; H, 6.12%.

2,2-Dimethyl-3-(trimethylsilyl)propyl Tosylate (9): ^{1}H NMR $\delta = 0.00$ (9H, s, Si–CH_3), 0.61 (2H, s, CH_2), 0.93 (6H, s, CH_3), 2.45 (3H, s, CH_3), 3.63 (2H, s, CH_2), 7.34 (2H, d, $J = 8.3$ Hz, Ar–H), 7.79 (2H, d, $J = 8.3$ Hz, Ar–H). Found: C, 57.41; H, 8.27%. Calcd for $C_{15}H_{26}O_3SSi$: C, 57.28; H, 8.33%.

3-(Dimethylphenylsilyl)-1,1-dimethyl-1-propanol (13). To a solution of methylmagnesium iodide prepared from methyl iodide (1.41 g, 9.93 mmol) and Mg (0.24 g, 9.87 mmol) in 20 cm^3 of ether was added dropwise ethyl 3-(dimethylphenylsilyl)propionate (1.00 g, 4.23 mmol) in 5 cm^3 of ether with stirring at 0 °C. The reaction mixture was stirred overnight at room temperature. After cooling, the reaction mixture was quenched with NH_4Cl (1.06 g, 19.8 mmol) in 60 cm^3 of water, and was extracted with ether. After the usual work-up, the solvent was evaporated to give 1.11 g of crude product. Purification by column chromatography afforded 0.82 g (yield, 87%) of the alcohol as a colorless oil: ^{1}H NMR $\delta = 0.27$ (6H, s, Si–CH_3), 0.74—0.79 (2H, m, CH_2), 1.18 (6H, s, CH_3), 1.20 (1H, s, OH), 1.42—1.47 (2H, m, CH_2), 7.34—7.52 (5H, m, Ar–H).

1-(Dimethylphenylsilyl)-3-methyl-2-butene (14) and 4-(Dimethylphenylsilyl)-2-methyl-1-butene (15). A solution of 3-(dimethylphenylsilyl)-1,1-dimethyl-1-propanol (0.2 g, 0.9 mmol) was dehydrated with 5 cm^3 of concd hydrochloric acid in 30 cm^3 of aq dioxane. After reflux for 10 h, most of the solvent was evaporated. After the usual work-up, the alcohol was purified by column chromatography to yield 0.10 g (54%) of **14**; ^{1}H NMR $\delta = 0.25$ (6H, s, Si–CH_3), 1.49 (3H, s, CH_3), 1.62 (2H, d, $J = 8.5$ Hz, CH_2), 1.68 (3H, s, CH_3), 5.15 (1H, t, $J = 8.5$ Hz, CH), 7.33—7.51 (5H, m, Ar–H) and 0.02 g (11%) of **15**; ^{1}H NMR $\delta = 0.28$ (6H, s, Si–CH_3), 0.88—0.92 (2H, m, CH_2), 1.71 (3H, s, CH_3), 1.98—2.02 (2H, m, CH_2), 4.66, 4.69 (2H, ss, CH_2), 7.32—7.52 (5H, m, Ar–H).

Solvents. Solvents were purified as previously described[10,11,15,18] and binary solvents were prepared by mixing appropriate volumes or weights of pure solvents at 25 °C.

Kinetic Measurements. Solvolyses in binary solvent mixtures were followed conductimetrically.[10,11,15,18] Using a conductivity meter (CM-50AT and CM-60S equipped with an interval time unit and printer, Toa Electronics Ltd.), we followed 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. Products were analyzed by ^{1}H NMR spectroscopy (JEOL JNM-A500 FT-NMR spectrometer). A 3.9×10^{-2} M (M = mol dm^{-3}) solution of the tosylate buffered with 7.7×10^{-2} M of 2,6-lutidine in 70% aq deuterated acetone was sealed in an NMR tube and allowed to react at 55 °C in a thermostatted bath. The tube was withdrawn at appropriate intervals, cooled rapidly in an ice bath and the ^{1}H NMR spectrum of the reaction mixture was recorded. The singlet peak of the tosylated methylene group decreased with increases in the other peaks of products. After disappearance of the singlet peak of the starting tosylate, the solvolysis products were identified by comparing their ^{1}H NMR spectra with authentic samples independently prepared. 3-Methyl-1-butene (**16**) was already reported by Shiner.[2)] The relative amounts of reaction products were determined from the integral areas of the corresponding peaks (Scheme 2).

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