Rates and Mechanism for the Solvolyses of 2,2-Dimethyl-2-sila-1-indanyl Bromide and α-Trialkylsilylbenzyl *p*-Toluenesulfonates. α-Silicon Effect on the Stability of Benzylic Cations in Solution

Nobujiro SHIMIZU,* Erika OSAJIMA, and Yuho TSUNO
Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812
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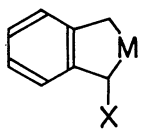
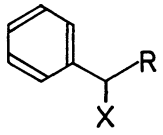
α-Silicon effect on the benzylic solvolysis has been investigated. The solvolysis of 2,2-dimethyl-2-sila-1-indanyl bromide in aq acetone exhibits a linear response to the solvent ionizing power Y_{Br} with a slope m close to unity (m=0.93) and gives the corresponding alcohol without skeletal rearrangement indicative of a k_c mechanism; it solvolyzes 4.98×10^2 times less rapidly than a carbon reference, 2,2-dimethyl-1-indanyl bromide, in 60% aq acetone at 25 °C suggesting that solvolytic generation of the α-silylated benzylic cation is electronically about 4 kcal mol^{-1} less favorable than that of the corresponding α-alkylated benzylic cation. A more pronounced rate-retardation of 1.65×10^4 by an α-$SiMe_3$ group relative to Me is observed in the solvolysis of an open benzylic system due to the additional steric effect. Mechanism for the solvolysis of α-trialkylsilylbenzyl *p*-toluenesulfonates including $SiMe_3$, $SiEt_3$, and Si(*t*-Bu)Me_2 groups has been also examined on the basis of the solvent effect, salt effect, and ethanol/water selectivity as well as product analysis; a k_c mechanism including a product forming step via preferential front side solvent attack is suggested.

The effect of silicon on the stability of adjacent carbocations has been the subjects of recent theoretical and mechanistic interests.[1] During the course of our study on the mechanism of solvolysis of α-disilanylbenzyl halides, we needed precise estimation for the α-silicon effect relative to carbon on the ionization of benzylic derivatives.[2] While strong electron-releasing property of β-silicon has been verified experimentally[3] as well as theoretically,[4] the effects of α-silicon are rather puzzling. A trimethylsilyl group, the most commonly used silyl group, sometimes acts as a weak electron-accepting group contrary to a low electronegativity of silicon.[5] Theoretical study suggests that a carbocation $SiH_3CH_2^+$ is 17 kcal mol^{-1} more stable than methyl cation but 17 kcal mol^{-1} less stable than ethyl cation.[4b] Experimental results are, however, diverse. For example, $SiMe_3$ relative to methyl accelerates the solvolysis of vinyl triflates,[6] while replacement of one of methyl groups in *t*-butyl bromide with $SiMe_3$ results in a marked rate retardation.[7] On the other hand, $SiMe_3$ exerts essentially the same effect as methyl in the solvolysis of 2-adamantyl derivatives.[8] A deactivating effect of $SiMe_3$ has been also reported in the benzylic solvolysis but the data are not quantitative.[9] These diverse results on the α-silicon effect arise in part from the steric effect which varies with the system and hence is difficult to estimate precisely. The $SiMe_3$ group is undoubtedly a bulky group as compared to methyl, although it is considered to be significantly smaller in its effective size than *t*-butyl.[10,11] Since the solvolysis of α-alkylbenzyl derivatives is susceptible to steric effect of the α-alkyl groups,[12,13] a direct comparison between the solvolysis rates for α-$SiMe_3$- and α-alkylbenzyl derivatives may not provide a reasonable estimation for the α-silicon effect relative to carbon on the stability of adjacent benzylic cations. In order to minimize the steric effect, we selected the solvolysis of 2,2-dimethyl-2-sila-1-indanyl bromide (**1a-Br**) and compared its solvolysis rates with those of a carbon reference, 2,2-dimethyl-1-indanyl bromide (**1b-Br**). Since the two substrates undergo the same structural change during the ionization, rate ratios between the two substrates would be attributable primarily to the difference in stability of the corresponding cations in solution. This paper also deals with the mechanism of the solvolysis of α-trialkylsilylbenzyl derivatives (**2a—c**) on the basis of the Winstein-Grunwald solvent analysis,[14] salt effect, ethanol/water selectivity, and product analysis.



1a: M=$SiMe_2$
1b: M=CMe_2
1c: M=CH_2



2a: R=$SiMe_3$
2b: R=$SiEt_3$
2c: R=$SiMe_2$(t-Bu)
3a: R=Me
3b: R=CMe_3

Results

1a-Br was prepared by halogenation of 2,2-dimethyl-2-silaindane with *N*-bromosuccinimide. α-Trimethylsilyl-, α-triethylsilyl-, and α-*t*-butyldimethylsilylbenzyl *p*-toluenesulfonates (**2a-OTs**, **2b-OTs**, and **2c-OTs**) were prepared by treatment of the corresponding benzyl trialkylsilyl ethers with *s*-butyllithium followed by addition of *p*-toluenesulfonyl chloride.

Table 1. Rate Constants for Solvolysis of **1**—**3** at 25.0±0.05 °C

Solvent[b]	$k\times10^5/s^{-1}$ [a]						
	1a-Br	**1b-Br**	**2a-Br**	**3a-Br**	**2a-OTs**	**2b-OTs**	**2c-OTs**
EtOH		6.70[c]			4.91, 4.96[c]	1.80	0.809[c]
90E					17.7	7.71	4.97
80E	1.00[c]	354			40.6	19.7	15.6
70E					78.4	45.5	37.5
60E					199	101	91.4
50E	32.8[c]				504, 513[c]	237	216
40E	162[c]				1790	829	791
80A		55.5			3.56	1.98	1.76
70A	0.642	373		12.6	14.1	8.33	7.41
60A	3.17	1580		50.9	49.8	36.5	31.5
50A	14.4			233	212[d]	130	114[d]
40A	81.0			876	866	598	601[d]
30A	372		0.102[c]	3100	4130		2470[d]
97T	223[c]		0.0313[e,f]	515, 518[c]	2064[d]	3050[d]	3820[d]
80T				893	2090[d]	2820[d]	3440[d]
50T	302[c]						3860[d]
40T					3730[d]	3810[d]	4570[d]

a) $k_{UV(acridine)}$ determined by measuring increase in an acid generated as its acridinium ion except otherwise noted. b) E: ethanol/water (v/v), A: acetone/water (v/v), and T: TFE/water (v/v) mixtures except for 97T which is a 97/3 (w/w) TFE/water mixture. c) k_{UV} determined by measuring decrease in a reactant. d) Average of duplicate runs. e) Conductimetric rate. f) Extrapolated: $k=(4.76\pm0.003)\times10^{-6}$ and $(4.89\pm0.001)\times10^{-5}$ s^{-1} at 50.0 and 75.0 °C, respectively; $\Delta H^{\ddagger}_{298}=20.2$ kcal mol^{-1} and $\Delta S^{\ddagger}_{298}=-20.3$ cal K^{-1} mol^{-1}.

Table 2. α-Silicon Effect on the Solvolysis Rates for Benzyl and 1-Indanyl Derivatives

Solvent	$10^5k/s^{-1}$ [a]				Ratio $k(1)/k(2)$
	Substrate (1)		Substrate (2)		
60A	**1a-Br:**	3.17	**1b-Br:**	1580	2.01×10^{-3}
70A		0.642		373	2.26×10^{-3}
80E		1.00		354	2.82×10^{-3}
97T	**2a-Br:**	0.0313	**3a-Br:**	515	6.06×10^{-5}
30A		0.102		3100	3.30×10^{-5}
97T	**2a-OTs:**	2060	**3b-OTs:**	1348[b]	1.53
60A		49.8		24.9[b]	2.00

a) At 25 °C. b) Rata data were taken from Ref. 30.

Table 3. Comparison of Solvolysis Rates between Benzyl and 1-Indanyl Derivatives[a]

Solvent	$10^5k/s^{-1}$				Ratio $k(1)/k(2)$
	Indanyl (1)		Benzyl (2)		
97T	**1a-Br:**	223	**2a-Br:**	0.0313	7130
30A		372		0.102	3650
EtOH	**1b-Cl:**	2.93[b]	**3b-Cl:**	0.0000217[c]	13500
EtOH	**1c-Cl:**	15.1[b]	**3a-Cl:**	0.0216[d]	700

a) At 25 °C. b) Ref. 14. c) Estimated from the rate constant in 80% aq ethanol (Ref. 12) and a k_{EtOH}/k_{80E} rate ratio of 0.021 for **3a-Cl**. d) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **79**, 1597 (1957).

Solvolyses were followed spectrophotometrically by measuring decrease in a reactant or increase in a liberated acid as its acridinium salt for (0.2—2)×10^{-4} M solutions (1 M=1 mol dm^{-3}). In the latter case, the solvolysis was monitored by a 402.5 nm light in the presence of 2—3 equiv acridine and (5—10)×10^{-5} M of acridinium *p*-toluenesulfonate. The initial addition of the acridinium salt was necessary to assure linear response of absorbance to the concentration of the produced acid. In several cases, the solvolysis were followed conductimetrically. In most cases, the solvolyses followed excellent first-order kinetics over a range of 3 to 4 half-lives (correlation coefficient $R>0.9999$) giving rate constants within ±3% reproducibility. Table 1 shows solvolysis rates for **1**, **2**, and α-methylbenzyl bromide (**3a-Br**) in various solvents including 30/70 to 80/20 (v/v) acetone/water (A-series), 40/60 to 100/0 (v/v) ethanol/water (E-series),

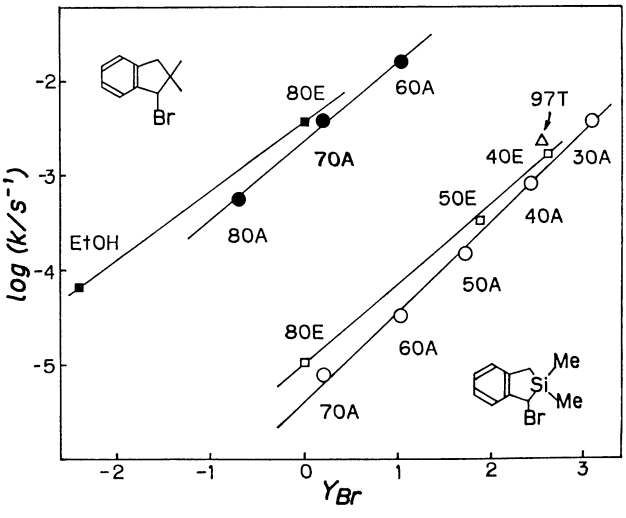


Fig. 1. Plots of log *k* for solvolyses of **1a-Br** (bottom) and **1b-Br** (top) vs. Y_{Br}.

Table 4. Grunwald-Winstein Analysis for the Solvolysis of **1** and **2**

Substrate	m[a]		Rate-increment[b]		
	For aq acetone	For all solvents	EtOH	80E	97Tw
1a-Br	0.93 (n=5, R=0.997)	0.91 (n=9, R=0.986)	0.38	0.37	
1b-Br	0.84 (n=3, R=0.998)	0.70 (n=5, R=0.991)	0.49	0.19	
2a-OTs	0.91 (n=6, R=0.993)	0.81 (n=16, R=0.979)	0.95	0.26	0.29
2b-OTs	0.92 (n=5, R=0.999)	0.90 (n=15, R=0.971)	0.72	0.15	0.64
2c-OTs	0.94 (n=6, R=0.999)	0.99 (n=18, R=0.979)	0.46	0.10	0.76

a) Based on Y_{Br} (Ref. 15) and Y_{OTs} (Ref. 16) for bromides and p-toluenesulfonates, respectively. b) Deviations from the acetone correlation line in log k unit.

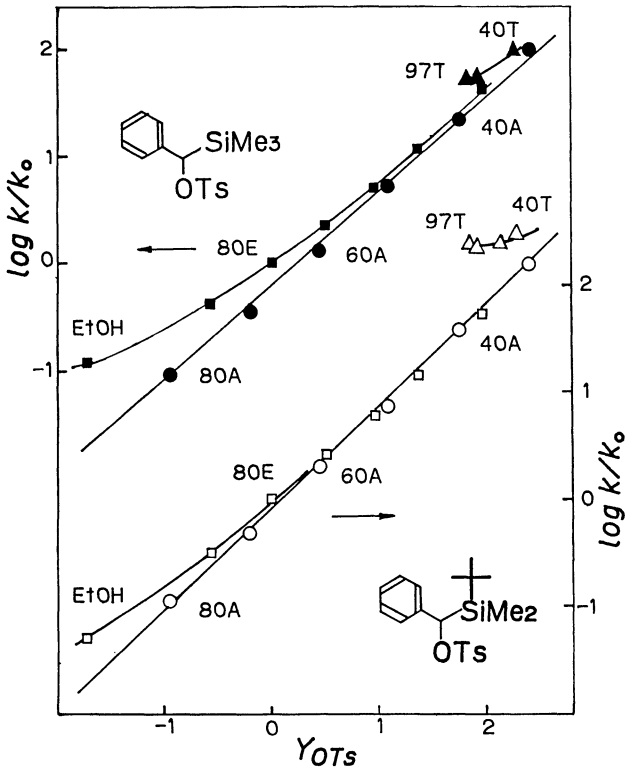


Fig. 2. Plots of log k for solvolyses of **2a-OTs** (top) and **2c-OTs** (bottom) vs. Y_{OTs}.

Table 5. Salt Effects on Hydrolysis of **2a-OTs** and **2c-OTs**[a]

Substrate	Salt	[Salt]/M	$10^5k/s^{-1}$ [b,c]	k_{rel}
2a-OTs	None		212	1.00
	NaOTs	0.100	203	0.95
		0.300	177	0.84
	NaCl	0.100	206	0.97
		0.300	186	0.88
	$LiClO_4$	0.101	240	1.13
		0.321	318	1.45
2c-OTs	None		114	1.00
	NaOTs	0.100	103	0.91
		0.300	94.9	0.84
	NaCl	0.100	108	0.95
		0.300	94.7	0.83
	$LiClO_4$	0.101	131	1.15
		0.321	184	1.62

a) In 50% acetone/water (v/v) at 25 °C. b) Average of duplicate runs. c) $k_{UV(acridine)}$; [reactant]=1.0×10^{-4} M, [acridine]=3.0×10^{-4} M, and [acridinium p-toluenesulfonate]=1×10^{-4} M.

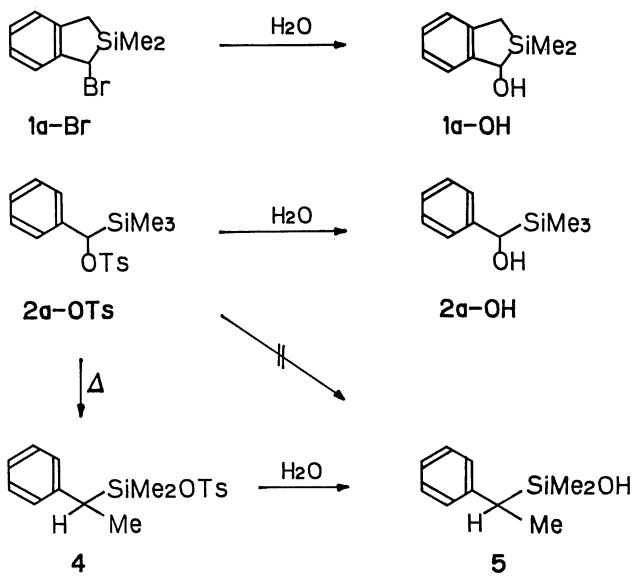
Table 6. Products, Selectivity, and Rate Increment in the Solvolysis of **2a-OTs** in aq Ethanol

Solvent	Products[a]		Selectivity[b]	Rate-increment
	2a-OH	**2a-OEt**	k_W/k_E	k_{obsd}/k_{calcd} [c]
EtOH	0%	100%		6.89
90E	36.9%	63.1%	1.62	2.34
80E	55.9%	45.1%	1.53	1.51
50E	82.1%	17.9%	1.42	0.92
40E	86.1%	13.9%	1.28	1.06

a) Determined by GLC. b) Defined by k_W/k_E=[**2a-OH**][EtOH]/[**2a-OEt**][H_2O]. c) The k_{calcd} is the rate constant expected from the mY correlation line observed for aq acetone: log k_{calcd}=$0.915Y_{OTs}$−3.648.

and 40/60 to 80/20 (v/v) and 97/3 (w/w) 2,2,2-trifluoroethanol (TFE)/water (T-series) binary solvent mixtures at 25 °C. The α-silicon effects on the solvolysis rates in 1-indanyl and benzyl systems are summarized in Table 2. Marked deactivation effects of α-silicon are apparent in both cases. Table 3 shows a comparison of the solvolysis rates between 1-indanyl and benzylic derivatives. Obviously, the indanyl system solvolyzes much more rapidly than the corresponding benzyl system. Figure 1 illustrates the dependence of solvolysis rates on the solvent ionizing power Y_{Br}[15] for the solvolyses of **1a-Br** and **1b-Br**. Since α-trimethylsilylbenzyl bromide (**2a-Br**) solvolyzed at inconveniently slow rates, we examined the solvent effect on the ionization of α-silylbenzyl derivatives by using α-trialkylsilylbenzyl p-toluenesulfonates **2a-OTs**—**2c-OTs**. Figure 2 represents the solvent dependence of the solvolyses of **2a-OTs** and **2c-OTs** on Y_{OTs}.[16] Table 4 summarizes the results of solvent mY analysis[14] for **1** and **2**. Table 5 shows salt effects on the solvolyses of **2a-OTs** and **2c-OTs**.

Hydrolysis of **1a-Br** in 50% aq acetone cleanly gave the corresponding alcohol **1a-OH**. Similarly, **1b-Br** gave 2,2-dimethyl-1-indanol as a single product on hydrolysis in 80% aq acetone. Solvolytic reactions of **2a-OTs** and **2c-OTs** with TFE, ethanol, and aq acetone cleanly gave the corresponding ethers (**2-OTFE**



and **2-OEt**) or alcohols (**2-OH**) without skeletal rearrangement in contrast to the fact that the solvolysis of 2-trimethylsilyl-2-adamantyl *p*-nitrobenzoate involves an extensive 1,2-methyl shift from the silicon to the carbenium carbon.[17] Thermally, however, **2a-OTs** rearranged to a silyl *p*-toluenesulfonate **4**, which on hydrolysis gave a rearranged alcohol **5**.[18] Product analysis for the solvolysis of **2a-OTs** in ethanol-water binary solvent mixtures was given in Table 6 which includes selectivity, $S=k_W/k_E$, defined by Eq. 1 where k_W and k_E are the rate constants for nucleophilic attack of water and ethanol respectively in the product forming step, [**2-OH**]/[**2-OEt**] is the product ratio determined by GLC analysis, and [EtOH]/[H_2O] is the molar ratio of ethanol to water in binary solvent mixtures.

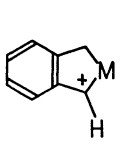
$$S=k_W/k_E=[\textbf{2-OH}][EtOH]/[\textbf{2-OEt}][H_2O] \quad (1)$$

Discussion

Table 2 shows a marked rate retardation of (1.6—3.0)×10^4 by an α-$SiMe_3$ group relative to methyl in the benzylic solvolysis. A different situation, however, arises when *t*-butyl is selected as an alkyl reference; k(**2a-OTs**)/k(**3b-OTs**) rate ratios suggest the effect of $SiMe_3$ to be comparable to that of *t*-butyl. These results in the benzylic solvolysis contrast to the α-silicon effect in the 2-adamantyl solvolysis where the rates are in the order $k(\alpha\text{-SiMe}_3):k(\alpha\text{-Me}):k(\alpha\text{-}t\text{-Bu})$=ca. $1:1.0:10^5$.[8,19] The discrepancy of the α-silicon effect between the two systems is undoubtedly associated with the steric effect. Whereas a bulky α-alkyl group facilitates the 2-adamantyl solvolysis,[19] it retards the rate of solvolysis of benzyl derivatives.[12,13] The steric rate retardation in the latter system results partly from steric strain imposed on the benzylic cations in which the α-alkyl group is coplanar to the phenyl ring or nearly so and partly from steric hindrance to solvation in the transition state. We have found a rather simple relation between the solvolysis rates of α-alkylbenzyl chlorides (PhCHRCl; R=Me, Et, *i*-Pr, and *t*-Bu) reported by Baddeley and coworkers[12] and a steric parameter *A*-value[11a] (free energy difference between axial and equatorial conformers in mono-substituted cyclohexanes) represented by Eq. 2 where k_R and k_{Me} are the rate constants for α-R and α-methylbenzyl chlorides, and A_R and A_{Me} are *A* values for R and methyl groups respectively. This relationship suggests the α-alkyl effect to be largely steric in the benzylic solvolysis, although this steric rate-retardation effect seems to be complicated by an opposing rate-acceleration effect arising from the release of B-strain for a bulky group larger than *t*-Bu.[12] If an *A* value of 2.5 is used for $SiMe_3$,[10a] a

$$\log k_R/k_{Me}=1.73\,(A_R-A_{Me})^{1/3} \quad (2)$$
(R = Me, Et, *i*-Pr, *t*-Bu; $R=0.999$)

rate retardation by the steric effect of $SiMe_3$ can be estimated to be by a factor of 40 relative to methyl. Obviously, the steric effect alone is insufficient to account for the observed low reactivity of **2a-Br**. Provided the observed k(**3a-Br**)/k(**2a-Br**) rate ratio includes a steric rate retardation of 40 by $SiMe_3$, a rate ratio of (4—8)×10^2 of the total rate difference should be ascribed to the electronic deactivation effect of $SiMe_3$ relative to methyl on the ionization step. In connection with this, α-silicon effect on the solvolysis of the indanyl system is informative. Table 2 shows that the replacement of a C_2 group from CMe_2 to $SiMe_2$ results in a rate retardation by a factor of (3—5)×10^2. A high sensitivity (m) to the solvent ionizing power Y_{Br}, i.e., m=0.93 for aq acetone (Fig. 1 and Table 3), together with the clean formation of the hydrolysis product without skeletal rearrangement is indicative of k_c mechanism for **1a-Br**. Since **1a-Br** and **1b-Br** are structurally close to each other and undergo practically the same structural change during the ionization, the difference in electronic effects between the $SiMe_2$ and the CMe_2 groups must be primarily responsible for the rate difference between the two substrates. The fact that the ethanolysis of **1b-Cl** proceeds ca. 50 times less rapidly than that of **1c-Cl**[20] implies small steric effect to be still operative in the indanyl system probably due to the steric hindrance to solvation in the transition state. Since $SiMe_2$ must have a small effective size as compared to CMe_2,[10a] a slightly more pronounced α-silicon effect than the observed k(**1b-Br**)/k(**1a-Br**) rate ratio would result, if the steric effect is taken into consideration. It is thus concluded that in solution, the α-silicon group destabilizes the adjacent benzylic cation by about 4 kcal mol^{-1} relative to the corresponding carbon group. This is in agreement with the theoretical study.[1,4b] A similar α-silicon effect of $SiMe_3$ relative to *t*-Bu has been reported in the formation of α-



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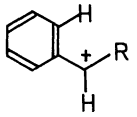

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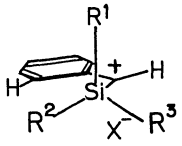

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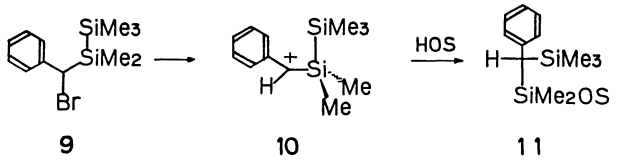
methoxycarbenium ions via acid-catalyzed hydrolysis of vinyl ethers.[21] The above conclusion also provides a major reason for the markedly low reactivity of **2a-Br** as compared to **3a-Br** compatible with the discussion mentioned earlier.

Table 3 indicates that indanyl derivatives solvolyze 10^2 to 10^4 times as rapidly as the corresponding benzyl derivatives. Major factors attributable to the rate differences between the two systems include ortho-alkyl effect and difference in conformational requirements of the corresponding cations **6** and **7**. The ortho effect can be estimated from the substituent effect. Provided ρ value is around -5 for the solvolysis of α-alkylbenzyl derivatives[22] and the electronic effect of *o*-alkyls is comparable to *p*-Me ($\sigma^+=-0.31$), *o*-alkylation would lead to a rate acceleration of about 40. Apparently, the *ortho*-effect alone does not explain the observed large rate differences, particularly those between **1a-Br** and **2a-Br**, and between **1b-Cl** and **3b-Cl**, even if we consider anticipated difference in inductive effect between *o*- and *p*-alkyls. Conformational factor must be the chief reason for the rate difference in these cases. 1-Indanyl derivatives ionize probably without significant increase in steric strain yielding the corresponding cations **6** which can receive the maximal resonance stabilization from the aromatic ring, while the formation of planar α-alkylbenzyl cations **7** must involve substantial steric strain because of proximity of *ortho* hydrogens to the α-alkyl group. The k(indanyl)/k(benzyl) rate ratios increase with increasing steric size of the α-groups in the order k(**1b**)/k(**3b**)>k(**1a**)/k(**2a**)>k(**1c**)/k(**3a**); this arises from the fact that the benzylic solvolysis is more sensitive to the steric effect than the indanyl solvolysis.[12,20]

The solvolyses of α-trialkylsilylbenzyl *p*-toluenesufonates **2-OTs** in A, E, and T solvent series do not show a single linear response to the solvolysis of the reference compound, 2-adamantyl *p*-toluenesulfonate, as shown in Fig. 2. Similarly, the solvolysis of **1a-Br** exhibits a diverging response to the solvent ionizing power Y_{Br} for the three solvent series. It should be noted, however, that each substrate shows a straight line with a slope m close to unity (m>0.9) for acetone/water mixtures which are nearly isonucleophilic in a wide range of water contents (Table 4). The high m values together with the absence of skeletal rearrangement during the solvolysis are indicative of the k_c mechanism for these α-silyl substrates. Lithium perchlorate showed normal salt effect on the solvolyses of **2a-OTs** and **2c-OTs**, as shown in Table 5. On the other hand, addition of sodium *p*-toluenesulfonate significantly retarded the solvolysis rate. It is questionable, however, whether this is the common ion effect because external chloride ion also caused a similar rate depression. We do not understand the origin for these rate depression quite well but intervention of the free cation is unlikely because of the following observation on product selectivity. The solvolysis through the free cation is considered to exhibit normal water/ethanol selectivity ($S=k_W/k_E<1$), as has been demonstrated by the solvolysis of diphenylmethyl chloride, e.g., S=0.36 in 80% aq ethanol.[23] **2a-OTs**, however, exhibited small but negative selectivities (S=1.28—1.65) in the solvolysis in 40% to 90% aq ethanol (Table 6). Interestingly, these selectivities are rather close to those observed in the 1- and 2-adamantyl solvolyses (s=1.6—2.2) which include a product formation step exclusively from the solvent-separated ion pair through the front side solvent attack.[24-26] One explanation for the negative selectivity in the present case is to assume a restricted conformation **8** for an intermediate ion pair. It is likely that during the ionization, one of alkyl groups of the α-trialkylsilyl group, probably the largest group of the three alkyls, takes the anti position to the leaving group to minimize the steric interaction between ortho hydrogens and the alkyl groups on the silicon. Such a conformation interferes with solvent attack from the rear side; hence, the product formation would preferentially occur from the front side.

It is worth stating a diverging mY plot pattern for **2-OTs** shown in Fig. 2. Both E- and T-series deviate substantially above the aq acetone line. The deviations for three typical solvents, ethanol, 80E, and 97T, are listed in Table 4 as rate-increments defined by log k_{obsd}/k_{calcd} where k_{obsd} and k_{calcd} are the rate constants observed and calculated from the acetone correlation line, respectively. The rate-increment for ethanol decreases with increasing steric size of the α-silyl group in the order $SiMe_3$, $SiEt_3$, and $SiMe_2$(*t*-Bu), while the rate-increment for 97T increases in this order. Although k_Δ processes often encounter diverging mY plot patterns,[27] the absence of the skeletal rearrangement in the present case eliminates such a possibility. Since α-silicon enhances S_N2 reactivity,[28] the upward deviation for E solvents seems to suggest nucleophilic solvent assistance; however, this is not the case either. Such solvent interaction would lead to downward deviations for T solvents which are much less nucleophilic than aq acetone, clearly against the observation. In fact, the mY correlation for the solvolysis of **2c-OTs** in the A, E, and T solvents was not improved at all by application of the extended Winstein-Grunwald equation[29] which includes a solvent nucleophilicity term. A diverging mY plot is not confined to the present α-silylbenzyl derivatives. α-Alkylbenzyl derivatives, for example, **3a-Cl** and **3b-OTs**, have been shown to exhibit diverging patterns as



9 10 11

well.[22,30] Interestingly, α-(pentamethyldisilanyl)benzyl bromide (**9**), structurally close to **2c-OTs**, exhibits a very similar mY pattern to that for **2c-OTs**.[2] The bromide **9** has been classified as a k_c substrate solvolyzing via α-(pentamethyldisilanyl)benzyl cation **10** despite the fact that it solvolyzes 2×10^5 times more rapidly than the corresponding α-silyl substrate, **2a-Br**, and cleanly gives 1,2-$SiMe_3$ rearranged solvolysis products **11**.[2] Thus, the diverging mY plot does not necessarily mean a mechanistic shift from the k_c solvolysis. Different responses to the solvent ionizing power between adamantyl derivatives and the present α-silylbenzyl substrates are presumably responsible for the apparent diverging solvent effect. Nevertheless, the decreasing deviation for E-solvents with increasing steric hindrance of the α-silyl groups appears to suggest unattested rear side solvent interaction. The fact that the k_W/k_E ratios increase with increasing rate-increment suggest this interaction to be purely kinetic and different from the k_s process; if the rate-increments of E-solvents are related with the k_s interaction, the k_W/k_E ratios should decrease with increasing ethanol content of the E-solvents against the observation.

Experimental

IR spectra were recorded on a Hitachi R-215 spectrophotometer. NMR spectra were recorded on a Hitachi R-20B spectrometer. GLC were performed with a Hitachi 163 gas chromatograph by using glass columns (6 mm×1.5, and 2.0 m) packed with 10% Silicone oil SE-30 on Chamelite CS or 25% Apiezon Grease L on Chromosorb W.

2,2-Dimethyl-2-sila-1-indanyl Bromide (1a—Br). Into a mixture of Mg (6.10 g) and HMPA (20 cm^3) in THF (75 cm^3) was added slowly a solution of α,α′-dichloro-*o*-xylene (20.0 g 0.114 mol) and dichlorodimethylsilane (16.2 g, 0.126 mol) in THF (50 cm^3) during a period of 8 h at ambient temperature. The mixture was stirred overnight at ambient temperature, heated under reflux for 3 h, and worked up. A crude oil was fractionated to give 2,2-dimethyl-2-silaindane (14.5 g), bp 100.5—101 °C (2.9 kPa). The product was heated with *N*-bromosuccinimide (14.3 g) and benzoyl peroxide (160 mg) in carbon tetrachloride (150 cm^3) for 1.5 h. Solvent was removed on a rotary evaporator. The residue was washed with pentane and filtered. The filtrate was evaporated and the remaining oil was fractionated using a spinning band column to give **1a-Br** as a colorless oil (11.5 g, 59%); bp 62—63 °C (0.13 kPa); UV (95% EtOH) 235 (log ε=3.76), 275 (3.27); ^{1}H NMR (CCl_4) δ=0.13 (3H, s), 0.48 (3H, s), 1.91 (1H, d J=16.2 Hz), 2.19 (1H, d, J=16.2 Hz), 4.31 (1H, s), 6.9—7.5 (4H, m). Found: C, 49.82; H, 5.44%. Calcd for $C_{10}H_{13}BrSi$: C, 49.80; H, 5.43%.

2,2-Dimethyl-1-indanyl Bromide (1b—Br). To a solution of LDA (0.21 mol) in ether (200 cmm^3) was added ethyl isobutyrate (21.8 g) over a period of 15 min at −78 °C and the mixture was stirred for 30 min at −78 °C. Benzyl bromide (30.5 g) was added and the mixture was heated under reflux for 2 d. Usual workup gave 2,2-dimethyl-3-phenylpropionic acid (22 g), which was converted into the acyl chloride by treatment with thionyl chloride. The crude acyl chloride was added to a mixture of $AlCl_3$ (15.7 g) in carbon disulfide (80 cm^3) and the resulting mixture was heated under reflux for 30 min. Workup gave 16.2 g of 2,2-dimethyl-1-indanone which on treatment with $LiAlH_4$ (2.0 g) gave 2,2-dimethyl-1-indanol (11.6 g); mp 55—56 °C [lit,[20] mp 56—57 °C]. The alcohol (2.9 g) was dissolved in ether (25 cm^3) and dry hydrogen bromide was bubbled into the solution for 30 min at ambient temperature. A crude oil obtained after workup was distilled to give **1b-Br** (3.0 g), bp 69—70 °C (0.27 kPa); NMR (CCl_4) δ=1.17 (3H, s), 1.28 (3H,s), 2.62 (1H, d, J=14.4 Hz), 2.89 (1H, d, J=14.4 Hz), 5.05 (1H, s), 7.04—7.4 (m, 4H). Found: C, 58.83; H, 5.76%. Calcd for $C_{11}H_{13}Br$: C, 58.69; H, 5.82%.

α-Trimethylsilylbenzyl Bromide (2a—Br). Into a cold (−78 °C) stirred mixture of LDA (16 mmol) and chlorotrimethylsilane (2.2 cm^3) in THF (20 cm^3) was added benzyl bromide (2.4 g) in THF (20 cm^3) at −78 °C and the mixture was stirred overnight at −78 °C. Usual workup gave **2a-Br** (3.0 g, 87%), bp 100—101 °C (0.5 kPa) [lit,[9] bp 98 °C (0.5 kPa)].

α-Trimethylsilylbenzyl *p*-Toluenesulfonate (2a-OTs). Into a cold (−78 °C) solution of benzyl trimethylsilyl ether (1.8 g) in THF (25 cm^3) was added *s*-BuLi (1.3 M in cyclohexane, 10 cm^3) and the mixture was stirred at −78 °C for 4 h. Then, *p*-toluenesulfonyl chloride (1.9 g) in ether (15 cm^3) was added and the mixture was allowed to worm to ca. 0 °C. The mixture was stirred for 1 h at 0 °C and worked up. Crude product was recrystallized from hexane to give **2a-OTs** (2.2 g, 66%); mp 103—104 °C; IR (Nujol) 1600, 1355, 1250, 1095, 925, 910, 860, 850, 825, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.01 (9H, s), 2.33 (3H, s), 5.27 (1H, s), 6.8—7.3 (5H, m), 7.21 and 7.59 (4H, A_2B_2, J=7.8 Hz). Found: C, 61.05; H, 6.54%. Calcd for $C_{17}H_{22}O_3SSi$: C, 61.05; H, 6.64%.

α-Triethylsilylbenzyl *p*-Toluenesulfonate (2b-OTs). In the same procedure described for the preparation of **2a-OTs**, benzyl triethylsilyl ether (2.2 g) was converted into **2b-OTs** (2.06 g, 55%); mp 32.8—33.5 °C; ^{1}H NMR (CCl_4) δ=0.3—1.2 (15H, m), 2.30 (3H, s), 5.35 (1H, 6.8—7.15 (5H, m), 6.99 and 7.46 (4H, A_2B_2, J=7.8 Hz). Found: C, 63.70; H, 7.42%. Calcd for $C_{20}H_{28}O_3SSi$: C, 63.79; H, 7.50%.

α-*t*-Butyldimethylsilylbenzyl *p*-Toluenesulfonate (2c-OTs). In the same procedure described for the preparation of **2a-OTs**, benzyl *t*-butyldimethylsilyl ether (2.2 g) was converted into **2c-OTs** (2.1 g, 55 %); mp 93—94 °C; ^{1}H NMR ($CDCl_3$) δ=−0.20 (3H, s), 0.06 (3H, s), 0.93 (9H, s), 2.28 (3H, s), 5.42 (1H, s), 6.8—7.1 (7H, m), 7.41 (2H, d, J=7.8 Hz). Found: C, 63.88; H, 7.50%. Calcd for $C_{20}H_{28}O_3SSi$: C, 63.79; H, 7.50%.

Solvents. Ethanol was distilled twice over sufficient amounts of magnesium ethoxide. Acetone was refluxed with potassium permanganate and the distillate was dried over potassium carbonate and fractionated. 2,2,2-Trifluoroethanol was dried over Molecular Sieve 4A for a week and distilled over sodium carbonate.

Kinetics. Solvolysis rates were measured in most cases spectrophotometrically by use of a Hitachi 220A spectro-

photometer equipped with a programmed data printer. Solvolyses were followed by measuring either decrease in a reactant at an appropriate wavelength [253 (**1a-Br**), 240 (**1b-Br**), 235 (**2a-OTs**), 240 (**2b-OTs** and **2c-OTs**), and 231 nm (**3a-Br**)] or increase in a liberated acid as its acridinium ion at 402.5 nm by using $(0.2—2)\times10^{-4}$ M solutions. In the latter method, each sample solution contained a reactant, 2—3 equiv acridine, and $(0.5—1)\times10^{-4}$ M of acridinium *p*-toluenesulfonate. In the absence of the acridinium salt, the first-order plot exhibited a curve for the initial ca. 25% reaction because of non-linear response of the absorbance to the concentration of the acridium ion below 10^{-5} M. For rapid reactions ($k>10^{-2}$ s^{-1}), 1 μl of a stock solution (ca. 0.3 M) of a reactant in acetonitrile was added to a given solvent (3 cm^3) which had been maintained at 25 °C in a UV cell and the reaction was immediately followed after short mixing effected by mechanical stirring or bubbling nitrogen through a syringe needle. In several cases, the rates were determined conductimetrically by using a TOA CM-50AT conductivity meter for $(5—10)\times10^{-4}$ M solutions.

Product Analysis. The following products were isolated and characterized from reactions carried out in TFE, ethanol, and aq acetone in the presence of equivalent amounts of 2,6-dimethylpyridine. The reactions in these solvents gave a single product shown below in each case.

Solvolysis in 2,2,2-Trifluoroethanol: 2a-OTFE (93% yield): IR 1600, 1280, 1250, 1150, 1110, 980, 870, 845, 750, 700 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.0 (9H, s), 3.69 (2H, m), 4.20 (1H, 5), 6.92—7.42 (5H, m). Found: C, 54.86; H, 6.33%. Calcd for $C_{12}H_{17}F_3OSi$: C, 54.94; H, 6.53%. **2c-OTFE** (100% yield): IR 1600, 1285, 1270, 1160, 1110, 980, 840, 800, 760 cm^{-1}; ^{1}H NMR (CCl_4) δ=−0.24 (3H, s) , 0.0 (3H, s) , 0.95 (9H, s) , 3.65 (2H, m), 4.37 (1H, s), 6.9—7.3 (5H, m). Found: C, 59.01; H, 7.51%. Calcd for $C_{15}H_{23}F_3OSi$: C, 59.18; H, 7.62%.

Sovolysis in Ethanol: 2a-OEt (91% yield): IR 1600, 1250, 1150, 1085, 1070, 865, 840, 745, 730 cm^{-1}; ^{1}H NMR (CCl_4) δ=−0.06 (9H, s), 1.15 (3H, t, J=6.8 Hz), 3.37 (2H, m), 3.96 (1H, s), 6.9—7.3 (5H, m). Found: C, 69.08; H, 9.63%. Calcd for $C_{12}H_{20}OSi$: C, 69.18; H, 9.68%.

Solvolysis in 50% aq Acetone. 1a-OH (87% yield): IR 3360, 1250, 1030, 940, 840, 820 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.19 (3H, s), 0.22 (3H, s), 1.90 (1H, d, J=16.8 Hz), 2.05 (1H, d, J=16.8 Hz), 4.43 (1H, s), 6.9—7.5 (4H, m). Found: C, 67.09; H, 7.68%. Calcd for $C_{10}H_{14}OSi$: C, 67.36; H, 7.91%. **1b-OH** (88% yield; from the reaction of **1b-Br** in 80% aq acetone). **2a-OH** (94% yield): IR 3410, 1600, 1250, 1000, 860, 840, 745, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.03 (9H, s), 4.53 (1H, s), 1.75 (IN, OH), 7.25 (5H, m). **2c-OH** (95% yield): ^{1}H NMR (CCl_4) δ=−0.23 (3H, s), −0.04 (3H, s), 0.95 (9H, s), 4.59 (1H, s), 7.15 (5H, almost s). Found: C, 70.20; H, 9.81%. Calcd for $C_{13}H_{22}OSi$: C, 70.21; H, 9.97%.

Water/Ethanol Selectivity. After completion of solvolysis of **2a-OTs** in aq ethanol in the presence of 1 equiv of 2,6-dimethylpyridine, the mixture was concentrated, extracted with benzene, and dried. Benzene was evaporated and the residual oil was directly analyzed by GLC (AGL, 170 °C, retention time; 10.4 and 15.2 min for **2a-OEt** and **2a-OH**, respectively).

Thermal Rearrangement of 2a-OTs. 2a-OTs (350 mg) was heated to 150 °C for 30 min in a glass ampoule. ^{1}H NMR analysis indicated the formation of two products in the ratio 2 : 1. The more abundant product was assigned to (1-phenylethyl)dimethylsilyl *p*-toluenesulfonate (**4**): ^{1}H NMR (CCl_4) δ=0.35 (6H, s), 1.40 (3H, d, J=7.2 Hz), 2.40 (3H, s), 6.8—7.8 (9H, m). A benzylic proton coalesces in the methyl peak of the tosyl group. The crude product was dissolved in ether, washed with aq sodium carbonate, and dried. Solvent was removed and the residual oil was subjected to column chromatography over silica gel. Elution with 1% methanol in benzene gave (1-phenylethyl)-dimethylsilanol (**5**) (80 mg): IR 3300, 1600, 1250, 840 cm^{-1}; ^{1}H NMR δ=0.0 (6H, s), 1.33 (3H, d, J=7.2 Hz), 1.61 (1H, disappeared on addition of D_2O), 2.12 (1H, m), 6.8—7.3 (5H, m).

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References

1) a) Y. Apeloig, "The Chemistry of Organic Silicon Compounds," ed by S. Patai and Z. Rappoport, John Wiley & Sons, Chichester (1989), Part 1, Chap.2; b) A. R. Bassindale and P. G. Taylor, *ibid.*, Part 2, Chap. 14; c) V. J. Shiner, Jr. and M. W. Ensinger, *J. Am. Chem. Soc.*, **108**, 842 (1986).

2) N. Shimizu, C. Kinoshita, E. Osajima, and Y. Tsuno, *Chem. Lett.*, **1990**, 1937.

3) a) J. B. Lambert, G. Wang, R. B. Finzel, and D. H. Teramura, *J. Am. Chem. Soc.*, **109**, 7838 (1987); b) X. Li and J. A. Stone, *ibid.*, **111**, 5586 (1989); c) D. J. Hajdasz and R. R. Squires, *J. Chem. Soc., Chem. Commun.*, **1988**, 1212.

4) a) M. R. Ibrahim and W. L. Jorgensen, *J. Am Chem. Soc.*, **111**, 819 (1989); b) S. G. Wierschke, J. Chandrasekhar, and W. L. Jorgensen, *ibid.*, **107**, 1496 (1985); c) Y. Apeloig, M. Karme, A. Stanger, H. Schwarz, T. Drewellow, and G. Czekay, *J. Chem. Soc., Chem. Commun.*, 989 (1987).

5) a) M. A. Cook, C. Eaborn, and D. R. M. Walton, *J. Organomet. Chem.*, **23**, 85 (1970); b) H. Bock, G. Brahler, G. Fritz, and E. Matern, *Angew. Chem., Int. Ed. Engl.*, **15**, 699 (1976); c) R. A. Benkeser and H. R. Krysiak, *J. Am. Chem. Soc.*, **75**, 2421 (1953).

6) M. D. Schiavelli, D. M. Jung, A. K. Vaden, P. J. Stang, T. E. Fisk, and D. S. Morrison, *J. Org. Chem.*, **46**, 92 (1981).

7) F. K. Cartledge and J. P. Jones, *Tetrahedron Lett.*, **1971**, 2193; *idem., J. Organomet. Chem.*, **67**, 379 (1974).

8) Y. Apeloig and A. Stanger, *J. Am. Chem. Soc.*, **107**, 2806 (1985).

9) M. A. Cook, C. Eaborn, and R. M. Walton, *J. Organomet. Chem.*, **29**, 389 (1971).

10) a) W. Kitching, H. A. Olszonwy, G. M. Drew, and W. Adcock, *J. Org. Chem.*, **47**, 5153 (1982); b) R. J. Quellette, D. Baron, J. Stolfo, A. Rosenblum, and P. Weber., *Tetrahedron*, **28**, 2163 (1978).

11) a) J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967); b) S. H. Onger and C. Hansch, *Progr. Phys. Org. Chem.*, **12**, 91 (1976).

12) G. Baddeley, J. Chadwick, and H. T. Taylor, *J. Chem. Soc.*, **1954**, 2405.

13) H. Tanida and H. Matsumura, *J. Am Chem. Soc.*, **95**, 1586 (1972).

14) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

15) T. W. Bentley and G. E. Carter, *J. Am. Chem. Soc.*, **104**, 5741 (1982).
16) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *J. Am. Chem Soc.*, **98**, 7667 (1976); M. Fujio, M. Goto, K. Funatsu, Y. Tsuji, S. Ouchi, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **16**(**1**), 85 (1987).
17) Y. Apeloig and A. Stanger, *J. Am. Chem. Soc.*, **109**, 272 (1987).
18) A. R. Bassindale, A. G. Brook, P. F. Jones, and J. M. Lennon, *Can. J. Chem.*, **53**, 332 (1975).
19) J. L. Fry, E. M. Engle, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 4628 (1972).
20) G. Baddeley, J. W. Rasburn, and R. Rose, *J. Chem. Soc.*, **1958**, 3168.
21) J. A. Soderquist and A. Hassner, *Tetrahedron Lett.*, **29**, 1899 (1988).
22) a) S. Usui, Y. Shibuya, T. Adachi, M. Fujio, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **14**(**2**), 355 (1984); b) Y. Tsuno, Y. Kusuyama, M. Sawada, T. Fujii, and Y. Yukawa, *Bull. Chem. Soc. Jpn.*, **48**, 3337 (1975).
23) Y. Karton and A. Pross, *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1860.
24) Y. Karton and A. Pross, *J. Chem. Soc. Perkin Trans. 2*, **1978**, 595.
25) J. M. Harris, A. Becker, J. F. Fagan, and F. A. Walden, *J. Am. Chem. Soc.*, **96**, 4484 (1974).
26) J. Kaspi and Z. Rappoport, *J. Am. Chem. Soc.*, **102**, 3829 (1980).
27) a) D. D. Roberts, *J. Org. Chem.*, **49**, 2521 (1984); b) D. J. Raber, W. C. Neal, Jr., M. D. Dukes, J. M. Harris, and D. L. Mount, *J. Am. Chem. Soc.*, **100**, 8137 (1978).
28) P. J. Stang, M. Ladika, Y. Apeloig, A. Stanger, M. D. Schiavelli, and M. Hughey, *J. Am. Chem. Soc.*, **102**, 6852 (1982).
29) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 7667 (1976).
30) Y. Tsuji, M. Fujio, and Y. Tsuno, *Mem. Fac. Sci., Kyushu University, Ser. C*, **17**(**2**), 281 (1989); **17**(**1**), 139 (1989).