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Silicon Effects. II.[1] Structure and Stability of 1-Phenyl-2-(trimethylsilyl)ethyl Cation in Solution

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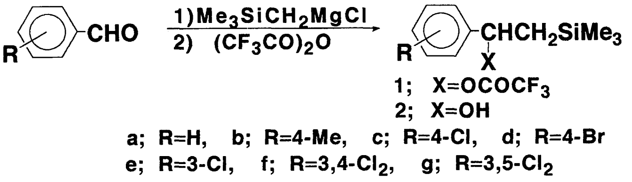
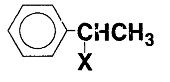
Solvolysis rates have been measured in various solvents at 25 °C for 1-(substituted phenyl)-2-(trimethylsilyl)ethyl trifluoroacetates (**1a**—**1g**; R=H, 4-Me, 4-Cl, 4-Br, 3-Cl, 3,4-Cl$_2$, and 3,5-Cl$_2$, respectively) and structurally related compounds, 1-phenylethyl-, 3,3-dimethyl-1-phenylbutyl-, and 1-(4-methylphenyl)ethyl trifluoroacetates (**3a**, **4**, and **5**). In dioxane/water mixtures **1g** solvolyzes with the same sensitivity to the change in solvent ionizing power as that for a k_c substrate **5**. The solvolyses of **1e** and **5** exhibit almost identical α-deuterium kinetic isotope effects (k_H/k_D) of 1.18—1.19 in aq dioxane. Substituent effect on the solvolysis of **1** in 90% aq dioxane is expressed by an LArSR equation: $\log k^X/k^H=-3.05\ (\sigma^\circ+1.05\Delta\bar{\sigma}_R^+)$ (R=0.9997). These findings are consistent with k_c mechanism for the solvolysis of **1**. Relative rates for the solvolysis of **1a**, **3a**, and **4** in 30% aq dioxane are 2.99×10^5 : 2.84 : 1.0 indicating solvolytic generation of α-(trimethylsilylmethyl)benzyl cation to be about 7 kcal mol^{-1} energetically more favorable than that of the corresponding α-alkylbenzyl cations.

Previously[2] we have shown in a preliminary report that α-(pentamethyldisilanyl)benzyl bromide solvolyzes 2×10^5 times more rapidly than does α-trimethysilybenzyl bromide indicative of a marked β-silicon effect of the disilanyl group. It is of interest to compare the effect of the Si–Si bonds on stability of adjacent carbocations with the effect of the corresponding carbon–silicon bonds. Lambert and co-workers have shown that an anti β-SiMe$_3$ group exerts a rate-acceleration effect of 2.4×10^{12} relative to hydrogen in the solvolysis of cyclohexyl derivatives suggesting a β-SiMe$_3$ group to stabilize cyclohexyl cation by about 17 kcal mol^{-1} (1 cal=4.184 J) relative to hydrogen.[3] Seemingly, the β-silicon effect appears much less effective in a $R^1R^2C^+$–Si–SiMe$_3$ system than in a $R^1R^2C^+$–C–SiMe$_3$ system, although the Si–Si single bonds possess low ionization potentials as compared to the C–Si bonds.[4] However, a direct comparison of the β-silicon effects in the benzylic and cyclohexyl solvolyses is not justified. There is a marked difference in the electronic demands at the carbenium carbon in the two systems. Theoretical study[5] indicates marked dependence of the β-silicon effect on the electronic demands of the carbocations as well as on the stereoelectronic restraint for the β-silicon group. In order to discuss the effect of the disilanyl group, it is therefore desirable to estimate the β-silicon effect of the corresponding silylmethyl group in the same benzylic system. This paper describes kinetic details on the solvolysis of 1-aryl-2-(trimethylsilyl)ethyl trifluoroacetates (**1a**—**1g**) and related α-alkylbenzyl trifluoroacetates **3**—**5**, and discusses mechanistic implications on the β-silicon effect in the benzylic solvolysis.

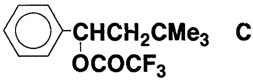
Results





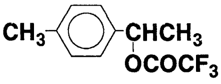
$C_6H_5CH(X)CH_3$

3a; X=OCOCF$_3$
b; X=Cl



$C_6H_5CH(OCOCF_3)CH_2CMe_3$

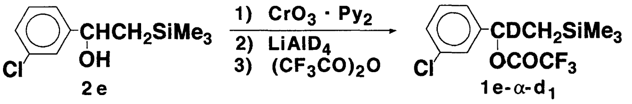
4



$CH_3C_6H_4CH(OCOCF_3)CH_3$

5

The trifluoroacetates **1a**—**1g** were prepared by treatment of the corresponding alcohols **2** with trifluoroacetic anhydride in the presence of pyridine.[3] The trifluoroacetates **1** were labile at room temperature and a crude product was directly used for kinetic measurements. We used three α-alkylbenzyl trifluoroacetates as alkyl reference standards. They were 1-phenylethyl trifluoroacetate (**3a**), 3,3-dimethyl-1-phenylbutyl trifluoroacetate (**4**), and 1-(4-methylphenyl)ethyl trifluoroacetate (**5**). Oxidation of **2e** followed by reduction with LiAlD$_4$ gave corresponding α-deuterated alcohol, which was converted into its trifluoroacetate **1e**-α-d_1.



Solvolysis reactions were followed spectrometrically at 25.0±0.05 °C by measuring either increase in produced trifluoroacetic acid as its acridinium salt[1] or increase in styrene derivatives which were formed practically as a single product under solvolytic conditions. All the solvolyses followed good first-order kinetics over 3 to 4 half-lives (correlation coefficient R>0.9999) and both methods gave identical rate constants within experimental error (±3%). We also compared spectrometric rates with conductimetric rates in several cases; for example, a spectrometric rate for the solvolysis of **1e** in

Table 1. Solvolysis Rates for **1**, **3a**, **4**, and **5** at 25.0±0.05 °C

Substrate	Solvent a)	$10^{-5}\ k/\mathrm{s}^{-1}$ b)	$\Delta H^{\ddagger}_{298}$ kcal mol^{-1}	$\Delta S^{\ddagger}_{298}$ cal K^{-1} mol^{-1}
1a	90D	752 ±11 c)	17.8 d)	−8.5 d)
	95D	128 ±0.5		
1b	90D	7450 e)	17.1 f)	−6.3 f)
	95D	1200±0.3		
1c	90D	371 ±3 g)		
1d	90D	306 ±0.1		
1e	90D	52.6 ±0.8 h)		
	80D	374 ±5.1 c)		
	90A	277 ±0.1		
	EtOH	225 ±0.2		
1f	90D	41.6 ±0.02		
1g	90D	5.45 ±0.02 g)	20.4 i)	−9.6 i)
	80D	35.2 ±0.02		
	70D	154 ±0.1		
	60D	618 ±0.2		
	50D	2570±23 j)	16.1 k)	−11.6 k)
	90A	31.3 ±0.1		
	80A	135 ±0.2		
	70A	413 ±0.3		
	60A	1210±1.0		
	EtOH	24.9 ±0.06		
	80E	355 ±0.8		
	MeOH	171 ±0.05		
3a	30D	35.2 ±0.3 g)		
4	30D	12.3 ±0.2 g)		
5	60D	4.40 ±0.002		
	50D	19.1 ±0.02	18.9 l)	−12.3 l)
	40D	59.8 ±0.8 g)	18.4 m)	−11.3 m)
	30D	200 ±0.5		
	20D	567 ±1.0 g)		
	97T	91.5 ±0.02		
	60A	5.80 ±0.02		
	40A	75.8 ±0.1		
	30A	236 ±0.5		
	20A	657 ±1.0		
	50E	37.3 ±0.3 g)		
	40E	130 ±0.1		
	30E	495 ±0.4		

a) A: acetone/water (v/v), D: dioxane/water (v/v), E: ethanol/water (v/v), and 97T: 97/3 (w/w) trifluoroethanol/water mixtures. b) Single run except otherwise noted. c) Average of four runs. d) Calculated from the following rates: $10^5\ k/\mathrm{s}^{-1}$ (temp/°C) 113 (7.6), 189 (11.7), 296 (16.0), 494 (20.5), and 752 (25.0). e) Extrapolated value from other temperatures. f) Calculated from the following rates: $10^5\ k/\mathrm{s}^{-1}$ (temp/°C) 4680 (20.5), 2890 (16.0), 1920 (11.7), 1130 (7.6), and 687 (2.9). g) Average of two runs. h) Average of six runs. i) Calculated from the following rates: $10^5\ k/\mathrm{s}^{-1}$ (temp/°C) 5.45 (25.0), 60.3 (46.2), and 451 (67.4). j) Average of three runs. k) Calculated from the following rates: $10^5\ k/\mathrm{s}^{-1}$ (temp/°C) 696 (11.7), 1071 (16.0), 1733 (20.5), and 2570 (25.1). l) Calculated from the following rates: $10^5\ k/\mathrm{s}^{-1}$ (temp/°C) 19.1 (25.0), 47.5 (33.8), and 127 (43.2). m) Calculated from the following rates: $10^5\ k/\mathrm{s}^{-1}$ (temp/°C) 14.4 (11.7), 23.8 (16.0), 59.8 (25.0), 161 (34.3), and 418 (43.2).

90% aq acetone at 25.0 °C measured by the acridine method, $k=(2.765\pm0.003)\times10^{-3}\ \mathrm{s}^{-1}$, was identical to a conductimetric rate, $k=(2.772\pm0.001)\times10^{-3}\ \mathrm{s}^{-1}$. The conductimetric method could not be successfully applied to the solvolyses in 90% aq dioxane because of a poor conductimetrical response of trifluoroacetic acid. Table 1 summarizes solvolysis rates for **1a**—**1g**, **3a**, **4**, and **5** in various solvents including 20/80 to 95/5 (v/v) dioxane/water (D series), 20/80 to 90/10 (v/v) acetone/water (A series), 30/70 to 100/0 (v/v) ethanol/water (E series), 97/3 (w/w) 2,2,2-trifluoroethanol (TFE)/water (T series) binary mixtures and methanol. Table 2 shows the β-silicon effect in the α-alkylbenzyl solvolysis.

α-Deuterium kinetic isotope effects (KIE) were measured for the solvolysis of **1e** in 80D and in 90D. We also measured KIE for the solvolysis of the reference compound **5** in 40D for comparison. The results are given in Table 3.

Solvent effects were examined for **1g**. Unfortunately, a solvent ionizing power scale for the trifluoroacetoxy

Table 2. β-Silicon Effect in Benzylic Solvolysis[a)]

$ArCHCH_2R$ (OCOCF$_3$)		Solvent	k/s^{-1}	k_{rel}
Ar	R			
4-$CH_3C_6H_4$	$SiMe_3$	50D	35.2[b)]	1.84×10^5
	H	50D	1.91×10^{-4}	1.0
C_6H_5	$SiMe_3$	30D	36.8[c)]	2.99×10^5
	H	30D	3.52×10^{-4}	2.86
	t-Bu	30D	1.23×10^{-4}	1.0

a) At 25.0 °C. b) Extrapolated value from *k*(**1g**) in 50D and a rate ratio $k(\mathbf{1b})/k(\mathbf{1g})=1.37\times10^3$ in 90D. c) Extrapolated value from *k*(**1g**) in 50D and rate raios $k(\mathbf{1a})/k(\mathbf{1g})=138$ in 90D and $k_{30D}/k_{50D}=10.4$ for **4**.

Table 3. α-Deuterium Kinetic Isotope Effects[a)]

Substrate	Solvent	$10^5k/s^{-1}$	k_H/k_D
1e	80D	347.5 ±2.6[b)]	
1e-α-d_1		293.2 ±2.3[c)]	1.185±0.018
1e	90D	52.63±0.76[d)]	
1e-α-d_1		44.57±1.00[e)]	1.181±0.044
5	40D	59.81±0.78[e)]	
5-α-d_1		50.76±0.07[e)]	1.178±0.017

a) At 25.0±0.05 °C. b) Average of seven runs. c) Average of six runs. d) Average of four runs. e) Average of two runs.

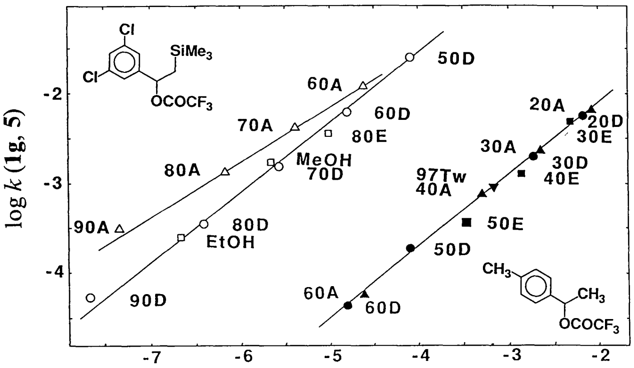


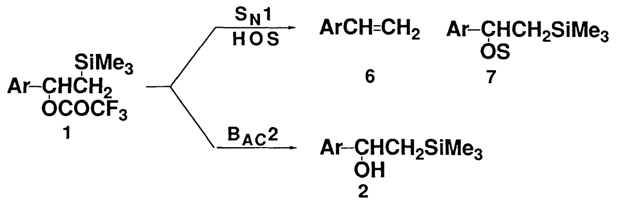
Fig. 1. Plots of log *k* for **1g** (open circles, triangles, and squares) and **5** (closed circles, triangles, and squares) vs. log *k* (1-phenylethyl chloride **3b**) in various solvents.

Table 4. Comparison of Solvent Effect

Substrate	m'[a)]	
	For aq dioxane	For all solvents
1g	0.80 (n=4, R=0.999)[b)]	0.78 (n=7, R=0.999)[c)]
5	0.79 (n=4, R=0.999)	0.80 (n=12, R=0.999)

a) Slope for a plot of log *k* vs. log *k* (1-phenylethyl chloride) (Ref. 6). b) Except for 90D. c) Except for aq acetone and 90D.

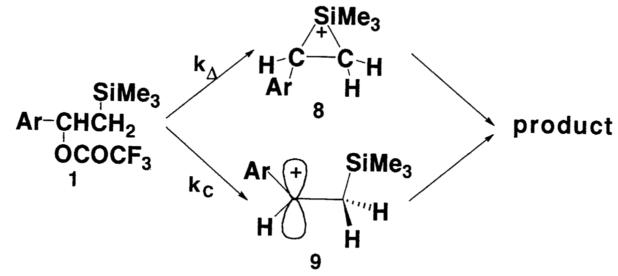
leaving group is not available; so we chose 1-phenylethyl chloride (**3b**) as a standard benzylic substrate undergoing k_c solvolysis.[6,7)] Figure 1 represents a plot of the rates (log *k*) for **1g** against log *k* for **3b**[6)] in various solvents. Aq dioxane and alcoholic solvents show a single linear response with a slope (m') of 0.78, while acetone/water mixtures exhibit a separate line (m'=0.61). Figure 1 includes a log *k*–log *k* plot for **5** for comparison. Judging from a comparable nucleofugality of the trifluoroacetoxy leaving group to that of Cl,[8)] we can assume k_c mechanism for the solvolysis of **5**. This is consistent with the fact that the solvolysis rates for **5** exhibit a linear response to those for **3b** for a range of solvents of varying solvent nucleophilicity and ionizing power including aq dioxane, aq acetone, aq ethanol, and aq trifluoroethanol. A significantly reduced slope for **5**, m'=0.80 relative to the chloride **3b**, should be ascribed to the leaving group effect. Since trifluoroacetate ion is a highly delocalized species, it must be less strongly solvated hence less sensitive to the change in solvent ionizing power than chloride ion. Table 4 shows a comparison of the solvent effect between the solvolyses of **1g** and **5**.



Solvolytic reactions of **1** in aq dioxane and ethanol gave the corresponding styrenes (**6**) exclusively. In the case of the reaction of **1e** in methanol, a significant amount (14%) of a methanolysis product **7** was also formed. Under basic conditions, however, was produced the alcohol **2** as the major product instead. For example, a reaction of **1e** in methanol containing sodium methoxide (0.09 M; 1 M=1 mol dm^{-3}) gave **2e** in 93% yield. The formation of **2** undoubtedly arises from a $B_{AC}2$ reaction of the trifluoroacetates. Amines promoted this process and hence accelerated the rate of reaction; the presence of 0.01 M triethylamine accelerated the reaction rate of **1g** in 70D by a factor of 4.85. Thus, the amine-induced $B_{AC}2$ reaction may become a serious problem in the rate measurement for the solvolysis of the trifluoroacetates **1** when acridine is used as a monitoring base. Fortunately, however, we found that acridine did not affect significantly the rate of the solvolysis under solvolytic conditions at acridine concentrations around 10^{-4} M; for instance, the solvolyses of **1g** in 70D in the presence of 1.0×10^{-3} M acridine showed an identical rate constant to that measured in the absence of acridine within experimental error: $k=1.58\times10^{-3}$ and 1.54×10^{-3} s^{-1} at 25 °C, respectively.

Discussion

Table 2 indicates that a β-SiMe$_3$ group exerts a rate-acceleration effect of (1—3)$\times 10^5$ relative to hydrogen or *t*-Bu in the α-alkylbenzyl solvolysis. Although the solvolysis of α-alkylbenzyl derivatives is subjected to the steric effect of the α-alkyl groups,[2,9,10] a rate ratio of **1a** and a structurally related compound **4** provides a reasonable estimate for the β-silicon effect in the benzylic solvolysis. The rate acceleration by the β-silicon can be interpreted either by a σ-participation mechanism (k_Δ) via a bridged siliconium ion intermediate **8** or by a simple ionization mechanism (k_c) via an open 1-aryl-2-(trimethylsilyl)ethyl cation **9**.[3,11-15]



The following kinetic features are informative on the structure of the transition state. First, the KIE for **1g**, i.e., k_H/k_D=1.18—1.19 in aq dioxane, is comparable to the KIE, k_H/k_D=1.18, for the reference compound **5** which can be assumed to be a k_c substrate (Table 3). These isotope effects can be compared with KIE values for the typical k_c solvolysis of α-alkylbenzyl derivatives e.g., k_H/k_D=1.157 for the solvolysis of 1-(4-methoxyphenyl)ethyl chloride in aq ethanol.[16] Apparently, the isotope effect indicates a striking resemblance in the structures of the transition state for the solvolysis of **1g** and **5**.

Second, solvolytic reactivities of a series of 1-aryl-2-(trimethylsilyl)ethyl trifluoroacetates **1a**—**1g** were well linearly correlated with σ^+[17] affording a ρ^+ value of -3.07 (R=0.9997). The application of the LArSR equation (Eq. 1)[18] gave an almost identical expression with a resonance parameter close to unity, r=1.05, and a reaction constant ρ=-3.05 (R=0.9997, SD=0.029).[19]

$$\log k^X/k^H = \rho(\sigma^\circ + r\Delta\bar{\sigma}_R^+) \qquad (1)$$

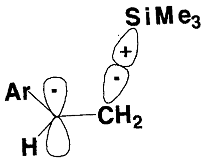
The limited number of π-donor substituents may not give us a precise r value; nevertheless, a rather high r value around 1.0 is apparently inconsistent with the bridged siliconium ion intermediate **8**. The result is interestingly compared with the substituent effect for the α-alkylbenzyl solvolysis which has been characterized by r close to 1.15 and ρ around -5.[20] A reduced r value for **1** is quite reasonable judging from the anticipated high stability of the cation **9a** as compared to 1-phenylethyl cation. It has been shown that r decreases with increasing stability of the benzylic cations ArC$^+$R^{1}R^2.[20] The rate ratio, k(**1a**)/k(**3a**)=1.1$\times 10^5$, would suggest the electronic demand of the carbenium carbon in the cation **9a** to be comparable to that in the α,α-dimethylbenzyl cation which is characterized by r=1.0 by definition.[18]

It is also instructive to note that **1g** and **5** showed very similar activation entropies in their solvolyses in a common solvent. For example, it is clear from Table 1 that a rate ratio of **1g** to **5** observed in 50D at 25 °C of a factor of 135 is entirely attributable to a 2.8 kcal mol^{-1} low enthalpy of activaion for **1g** relative to **5**. Again the result is more in accord with thr k_c mechanism than with the k_Δ mechanism which must involve substantial restraint of rotational motions at the transition state.

Finally it should be noted that in a log k–log k (**3b**) plot (Fig. 1), **1g** showed an identical slope to that for **5** (Table 4). This means that **1g** solvolyzes with the same susceptibility to the change in solvent ionizing power as that for **5** indicative of a marked resemblance in mechanism for ionization of the two substrates. Obviously, the solvent effect support the k_c solvolysis for **1**, although we do not understand quite well the origin for deviations of aq acetone at present.

Thus, the combined results lead us to conclude that **1** solvolyzes via rate-determining formation of a classical 1-aryl-2-(trimethylsilyl)ethyl cation **9**. The cation must be effectively stabilized by the β-SiMe$_3$ group through hyperconjugation.[5,21] It is worth stating that the k_c mechanism has been proposed also for the solvolysis of α-(pentamethyldisilanyl)benzyl halides which cleanly give 1,2-SiMe$_3$ rearranged products seemingly suggestive of σ-participation.[2] Extensive hyperconjugative interactions between the β-C–SiMe$_3$ σ-bond and the carbenium carbon would naturally involve changes in bond angles and bond lengths associated with the β-silicon atom.[5] However, the absence of compelling evidence suggesting bond-forming interactions between the β-silicon and the benzylic carbon leads us at present to prefer a simple k_c mechanism to a σ-participated ionization. The k_c mechanism for **1** is compatible with the recent theoretical[5] and experimental results in the gas phase[22] that an open structure of β-silyl-substituted alkyl cations is energetically more favorable than a bridged form except for the primary cation which preferably takes a bridged form. It can thus be said that the solvolytic generation of 1-phenyl-2-(trimethylsilyl)ethyl cation is about 7 kcal mol^{-1} energetically more favorable than that of the corresponding α-alkylbenzyl cations.

Noteworthy is a marked reduction in ρ value for the k_c solvolysis of **1** indicative of substantial dispersion of the positive charge on the benzylic carbon to the β-C–SiMe$_3$ σ-bond in the transition state without significant bridging of the β-silicon. This would undoubtedly result from the electronic interaction between the empty 2p orbital and the β-C–Si bond, although it is not clear at present whether such the interaction is purely hyperconjugative or includes intramolecular charge or electron transfer interaction as illustrated by the structure **10**.



10

The β-silicon effects in the present α-alkylbenzyl system as well as in the α-silylbenzyl system[2)] are obviously much smaller than would be expected from a reported rate-acceleration of 2.4×10^{12} in the cyclohexyl solvolysis corresponding to a reduction of activation energy by 17 kcal mol^{-1} by a β-$SiMe_3$ group relative to hydrogen.[3)] The reduced β-silicon effect would undoubtedly arise from the low electronic demands at the carbenium carbon for benzylic cations as compared to cyclohexyl cation. Li and Stone[22)] have shown from the gas-phase experiments that the stabilization of the carbocations afforded by a β-$SiMe_3$ group relative to hydrogen markedly decreases with increasing stability of the parent carbocations from 38 kcal mol^{-1} for isopropyl cation to 22 kcal mol^{-1} for 1-phenylethyl cation. The difference in the β-silicon effect between the secondary alkyl and 1-phenylethyl cations by 16 kcal mol^{-1} in the gas phase reasonably accounts for the observed ca. 10 kcal mol^{-1} difference in the β-silicon effect between the α-alkylbenzyl and cyclohexyl solvolyses.

Experimental

IR spectra were recorded on a Hitachi R-215 spectrophotometer. NMR spectra were taken on a Hitachi R-20B spectrometer in carbon tetrachloride using TMS as internal standard. GLC were performed with a Hitachi 163 gas chromatograph using a 4 mm×2 m column packed with 5% Silicone GE SE-30 on Chamelite CS. UV spectra were recorded on a Hitachi 220A spectrophotometer equipped with a programmed data printer.

Dioxane was refluxed first with potassium hydroxide for 3 days, then with sodium for 3 days, and distilled. Acetone was refluxed with potassium permanganate and the distillate was dried over potassium carbonate and fractionated. Ethanol was distilled twice over sufficient amounts of magnesium ethoxide.

1-Aryl-2-(trimethylsilyl)ethyl Trifluoroacetates (1a—1g). These trifluoroacetates were prepared from the corresponding alcohols **2** according to the literature method.[3)] The alcohols **2** were prepared by the Grignard reaction between the corresponding benzaldehyde and (trimethylsilyl)methylmagnesium chloride. A typical example is shown below:

To a stirred solution of (trimethylsilyl)methylmagnesium chloride prepared from trimethylsilylmethyl chloride (4.88 g, 40 mmol) and Mg (1.07 g) in ether (50 cm^3) was added a solution of 3-chlorobenzaldehyde (5.07 g, 36 mmol) in ether (25 cm^3) at room temperature. The mixture was stirred for 3 h at ambient temperature. A crude oil obtained after workup was distilled to give 4.75 g (93%) of 1-(3-chlorophenyl)-2-(trimethylsilyl)ethanol (**2e**) as a colorless oil: Bp 121—121.5 °C (1.5 Torr; 1 Torr=133.3 Pa); IR (neat) 3350, 1250, 860, 840, 785 cm^{-1}; ^1H NMR δ=0.0 (9H, s), 1.03—1.17 (2H, m), 2.32 (1H, broad s, OH), 4.72 (1H, t, J=7.2 Hz), 7.20—7.29 (4H, m). Found: C, 57.66; H, 7.46%. Calcd for $C_{11}H_{17}ClOSi$: C, 57.75; H, 7.49%. To a stirred solution of **2e** (286 mg, 1.3 mmol) and pyridine (2.5 mmol) in ether (4 cm^3) precooled in an ice-salt bath was added slowly trifluoroacetic anhydride (525 mg, 2.5 mmol) in ether (2 cm^3) and the mixture was stirred for 30 min at that temperature. Pentane (15 cm^3) was added. Organic layer was decanted, washed first with 10% hydrochloric acid, then with aq $NaHCO_3$, and dried. Solvent was removed under reduced pressure affording a crude oil which was shown to be a practically pure 1-(3-chlorophenyl)-2-(trimethylsilyl)ethyl trifluoroacetate (**1e**; 353 mg, 87%) by ^1H NMR analysis: IR 1780, 1255, 1220, 1150, 860, 840, 780 cm^{-1}; ^1H NMR δ=−0.06 (9H, s), 1.33—1.47 (2H, m), 5.89 (1H, t, J=7.8 Hz), 7.27 (4H, broad s). Found: C, 48.33; H, 4.97%. Calcd for $C_{13}H_{16}ClF_3O_2Si$: C, 48.07; H, 4.97%.

In a similar procedure, the following alcohols and their trifluoroacetates were prepared.

1-Phenyl-2-(trimethylsilyl)ethanol (**2a** in 98% yield): IR 3350, 1250 cm^{-1}; ^1H NMR δ=−0.09 (9H, s), 1.00—1.13 (2H, m), 1.74 (1H, s, OH), 4.68 (1H, t, J=7.8 Hz), 7.18 (5H, broad s). Found: C, 67.81; H, 9.19%. Calcd for $C_{11}H_{18}Si$: C, 67.98; H, 9.38%. **1a**: ^1H NMR δ=−0.11 (9H, s), 1.45 (2H, d, J=7.8 Hz), 5.93 (1H, t, J=7.8 Hz), 7.33 (5H, broad s).

1-(4-Methylphenyl)-2-(trimethylsilyl)ethanol (**2b**; 98%): IR 3350, 1250, 860, 820 cm^{-1}; ^1H NMR δ=−0.06 (9H, s), 1.08 (2H, d, J=6.6 Hz), 1.50 (1H, s, OH), 4.70 (1H, t, J=6.6 Hz), 7.08 (4H, broad s). Found: C, 69.11; H, 9.80%. Calcd for $C_{12}H_{20}OSi$: C, 69.17; H, 9.67%. **1b**: ^1H NMR δ=−0.11 (9H, s), 1.44 (2H, d, J=7.8 Hz), 2.35 (3H, s), 5.89 (1H, t, J=7.8 Hz), 7.18 (4H, broad s).

1-(4-Chlorophenyl)-2-(trimethylsilyl)ethanol (**2c**, 95%): ^1H NMR δ=−0.04 (9H, s), 1.03—1.17 (2H, m), 1.68 (1H, s, OH), 4.73 (1H, t, J=7.2 Hz), 7.22 (4H, broad s). Found: C, 57.96; H, 7.49%. Calcd for $C_{11}H_{17}ClOSi$: C, 57.75; H, 7.49%. **1c**: ^1H NMR δ=−0.07 (9H, s), 1.33—1.47 (2H, m), 5.90 (1H, t, J=8.4 Hz), 7.31 (4H, broad s).

1-(4-Bromophenyl)-2-(trimethylsilyl)ethanol (**2d**, 96%): IR 3350, 1250, 860, 825 cm^{-1}; ^1H NMR δ=0.03 (9H, s), 1.00—1.13 (2H, m), 1.71 (1H, s, OH), 4.72 (1H, t, J=7.2 Hz), 7.06—7.48 (4H, m). Found: C; 48.20, H; 6.27%. Calcd for $C_{11}H_{17}BrOSi$: C; 48.35, H; 6.27%. **1d**: ^1H NMR δ=−0.07 (9H, s), 1.32—1.47 (2H, m), 5.89 (1H, t, J=7.8 Hz), 7.16—7.58 (4H, m).

1-(3,4-Dichlorophenyl)-2-(trimethylsilyl)ethanol (**2f**, 93%): IR 3350, 1250, 1130, 860, 840 cm^{-1}; ^1H NMR δ=−0.02 (9H, s), 0.97—1.11 (2H, m), 1.97 (1H, s, OH), 4.70 (1H, at, J=7.2 Hz), 6.97—7.42 (3H, m). **1g**: IR 1775, 1250, 1220, 1175, 855, 840, 795 cm^{-1}; ^1H NMR δ=−0.03 (9H, s), 1.31—1.48 (2H, m), 5.88 (1H, m), 7.10—7.53 (3H, m). Found: C, 43.54; H, 4.20%. Calcd for $C_{13}H_{15}Cl_2F_3O_2Si$: C, 43.46; H, 4.21%.

1-(3,5-Dichlorophenyl)-2-(trimethylsilyl)ethanol (**2g**, 92%): IR 3350, 1250, 850, 835, 795 cm^{-1}; ^1H NMR δ=0.0 (9H, s), 0.98—1.12 (2H, m), 1.70 (1H, s, OH), 4.70 (1H, t, J=7.8 Hz), 7.18 (3H, broad s). **1g**: IR 1765, 1250, 1140, 860, 840 cm^{-1}; ^1H NMR δ=0.0 (9H, s), 1.30—1.49 (2H, m), 5.87 (1H, t, J=7.8 Hz), 7.23—7.36 (3H, m). Found: C, 43.49; H, 4.23%. Calcd for $C_{13}H_{15}Cl_2F_3O_2Si$: C, 43.46; H, 4.21%.

1-Phenylethyl Trifluoroacetate (3a): Bp 33-33.5 °C (1 Torr) [lit,[8] bp 32 °C (0.5 Torr)]; IR 1785, 1230, 1160 cm^{-1}; ^{1}H NMR δ=1.68 (3H, d, J=6.6 Hz), 5.99 (1H, q, J=6.6 Hz), 7.33 (5H, broad s).

3,3-Dimethyl-1-phenylbutyl Trifluoroacetate (4): Bp 50—55 °C (1 Torr); IR 1780, 1225, 1170, 1150 cm^{-1};^{1}H NMR δ= 0.97 (9H, s), 1.76—2.07 (2H, m), 5.84—6.05 (1H, m), 7.29 (5H, broad s). Found: C, 61.44, H, 6.28%. Calcd for $C_{14}H_{17}F_3O_2$: C, 61.31; H, 6.25%.

1-(4-Methylphenyl)ethyl Trifluoroacetate (5): Bp 30—31 °C (0.5 Torr); IR 1780, 1220, 1160, 810 cm^{-1}; ^{1}H NMR δ=1.64 (3H, d, J=6.6 Hz), 2.34 (3H, s), 5.95 (1H, q, J=6.6 Hz), 7.16 (4H, broad s). Found: C, 56.94; H, 4.78%. Calcd for $C_{11}H_{11}F_3O_2$: C, 56.90; H, 4.78%.

Kinetic Procedure. Solvolyses were followed spectrophotometrically by measuring increase in trifluoroacetic acid as its acridinium ion at 402.5 nm[1] or increase in producing styrenes at 252 nm by using (0.5—2)×10^{-4} M solutions. In the former case, the solvolysis was carried out in the presence of (1—3)× 10^{-4} M acridine and 1.0×10^{-4} M of acridinium trifluoroacetate. The initial addition of the acridinium salt was necessary for linear response of absorbance to concentration of acridinium ion under solvolysis conditions.[1]

Product Studies. Solvolysis reactions were performed with 0.02—0.04 M solutions of a substrate in a given solvent at 25 °C and a crude product obtained after workup was directly analyzed by GLC using an appropriate internal standard. A reaction of **1d** in ethanol qunatitatively gave *p*-bromostyrene (**6d**). A reaction of **1e** in 90% aq dioxane gave *m*-chlorostyrene (**6e**) in 95% yield. A reaction of **1e** in methanol gave **6e** and *m*-chloro-α-ethoxy-α-(trimethylsilylmethyl)toluene (**7e**) in 86 and 14% yield, respectively. **7e**: IR 1250, 1100, 860 cm^{-1}; ^{1}H NMR δ=−0.04 (9H, s), 0.94—1.15 (2H, m), 3.10 (3H, s), 4.10 (1H, dd, J=8.5 and 6.6 Hz), 7.17 (4H, broad s). A reaction of **1e** in methanol containing sodium methoxide (0.087 M) gave a mixure of **2e**, **6e**, and **7e** in the ratio 1.0 : 0.04 : 0.03. A reaction of **1e** in methanol in the presence of equimolar amounts of lutidine gave a mixture of **6e**, **7e**, and **2e** in the ratio 1.0 : 0.37 : 0.02.

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