Kinetics. Solvents were prepared as described previously,[2a] except for TFA. Titrimetric rates were usually measured on 0.04 to 0.08 M solutions. The reactions in TFE and HFIP were carried out in volumetric flasks by adding solid **2** to the solvent preequilibrated to the reaction temperature. Samples (0.5 mL) were withdrawn at intervals with pipets and discharged into cold acetone and titrated with 0.02 M NaOH using methyl red indicator. For reactions in HCO_2H, aliquots were added to a 60:40 mixture of HOAc and Ac_2O and titrated with NaOAc in HOAc. Reactions in HOAc, 80% EtOH, and 100% EtOH were carried out using sealed tubes and were titrated using 0.05 M NaOAc in HOAc and bromophenol blue in the former case and 0.02 M NaOH and methyl red in the latter two cases. For salt effect measurements 0.01 M solutions of **2** were measured using the ampule technique and titration with 0.02 M NaOH and bromthymol blue indicator.

Trifluoroacetic acid was distilled immediately before use. Trifluoroacetic anhydride was not added to the solution as has been done previously[2a,16a] because the strong UV absorption of the anhydride interfered with the kinetic measurements. The solvent was made 0.20 M in NaO_2CCF_3.[2a]

For measurements of the kinetics in TFA and for observing the isotope effects in TFA, HFIP, TFE, HCO_2H, and 80% EtOH, the rates were followed by injecting 4 μL of **2** (0.5 M in CH_3CN) into the solvent preequilibrated in 1-cm UV cells to give 10^{-3} M solutions and observing the decrease in absorption at 262 nm.[16a,26]

The rate of **2** in TFA with 0.125 M NaO_2CCF_3 was measured as 4.33×10^{-2} s^{-1}, as compared to 5.10×10^{-2} s^{-1} with 0.20 M salt. The rate of *i*-PrOTs in 0.125 M NaO_2CCF_3 at 53.6 °C was measured as 4.95×10^{-4} s^{-1} by UV. This compares to the value of 4.85×10^{-4} s^{-1} calculated from data at other temperatures and 0.060 M salt[16a] using a correction factor of 1.16 to convert rates in 0.06 M to 0.125 M salt.[16a,b] It should be noted that the rate of *i*-PrOTs at 55.0 °C is 5.09×10^{-4} s^{-1} (J. E. Norlander, private communication), and the published rate constant at 50.0 °C[16a] is a typographical error.

Products were measured by sealing 50 mg (0.145 mmol) of **2** in 0.5 mL of deuterated solvent in an NMR tube and heating for 10 half-lives, and then observing the spectrum. In TFA the product showed signals at δ 2.30 (CH_3CCF_3), 2.48 ($CH_3C_6H_4$), 5.82 and 6.00 ($C{=}CH_2$). In 95% ethanol-d_6 the chemical shift difference between the CH_3 groups was more (0.52 ppm) and between the vinyl H was less (0.14 ppm). These signals were integrated to calculate the product yields. No signals attributable to any other products were observed.

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Registry No. 2, 73572-26-6; **2**-d_3, 73572-27-7; 2-adamantyl tosylate, 25139-43-9; $PhC(CF_3)MeOH$, 426-54-0.

Solvolytic Studies of the Highly Deactivated 1-Aryl-1-(trifluoromethyl)ethyl Tosylates

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Abstract: The rates of solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates **1b–i** and 1-aryl-1-(trifluoromethyl)ethyl bromides **3a,b** in 80% ethanol, and of 1-phenyl- and 1-(3-chlorophenyl)-1-(trifluoromethyl)ethyl tosylates (**1e** and **1g**) in a variety of solvents, were measured. Linear mY_{OTs} plots with $m = 1.09$ for **1e** and $m = 1.03$ for **1g** were observed. These and the very high tosylate/bromide rate ratio, 3.94×10^4, for 1-(4-methylphenyl) derivatives **1b** vs. **3b** indicate a rate-limiting ionization process without intervention of solvent participation. The rate-retarding effect of the α-trifluoromethyl group is so large that a highly negative reaction constant, −7.46, results from a Hammett–Brown $\rho\sigma^+$ treatment of the rate data. Moreover, the 1-phenyl derivative **1e** is even less reactive than benzyl tosylate in trifluoroethanol. The rate data can also be correlated with the Yukawa–Tsuno equation, $\log (k/k_0) = \rho(\sigma + r(\sigma^+ - \sigma))$. The choice of these two treatments and possible mechanistic complexities are discussed.

The electronic effect of substituents on the reactivity of organic compounds involving the formation of carbenium ion intermediates is a theme which has received intense and continuous attention ever since the beginning of mechanistic studies on these systems.[1] Although the importance of the rate-retarding effect of strongly electron-withdrawing substituents β to cationic centers in solvolysis has been realized for more than a decade,[2] studies on the α effect of such substituents became a subject of active research only recently.[3-7] Decreases in rates on the order of 10^7 for the α-carbonyl relative to the α-methylene group,[3] and of 10^2–10^6 for the α-cyano[4] and of 10^{-4}–10^{-6} for the α-trifluoromethyl group[5-7] relative to α-hydrogen were observed, respectively.

The electron-withdrawing influence of the trifluoromethyl group on a cationic intermediate through the aromatic ring is already known.[8] The deactivating effect of this group in solvolysis has also been noted when it is at the C-1[5] and C-3[5,9] positions of allyl sulfonates. Tidwell and co-workers have studied the electrophilic addition to substituted α-trifluoromethylstyrenes[10] and the solvolysis of α-trifluoromethyl sulfonate esters.[6] From the observed

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Table I. Rates of Solvolysis of 1-Aryl-1-(trifluoromethyl)ethyl Tosylates and Bromides

substrate	solvent	k, s^{-1} T_1 (°C)	k, s^{-1} T_2 (°C)	k, s^{-1} 25 °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1a	80% EtOH			5.08[a]		
3a	80% EtOH			1.29×10^{-4}		
1b	80% EtOH			1.73×10^{-4}		
3b	80% EtOH	3.83×10^{-5} (100)	2.83×10^{-6} (75)	4.40×10^{-9}[b]	26.2	−8.39
1c	80% EtOH			1.38×10^{-4}		
1d	80% EtOH			2.10×10^{-6}		
1e	HOAc	5.92×10^{-4} (100)	3.83×10^{-5} (75)	4.12×10^{-8}[b]	27.6	0.49
	80% EtOH	3.47×10^{-4} (75)	2.05×10^{-5} (50)	7.57×10^{-7}[b]	24.7	−3.35
	70% EtOH			1.95×10^{-6}		
	60% EtOH			5.24×10^{-6}		
	97% TFE			5.07×10^{-5}		
	HCOOH			6.08×10^{-4}		
1f	80% EtOH	2.38×10^{-4} (75)	1.32×10^{-5} (50)	4.56×10^{-7}[b]	25.3	−2.83
1g	HOAc	1.26×10^{-4} (125)	8.90×10^{-6} (100)	2.18×10^{-10}[b]	30.7	0.21
	80% EtOH	4.38×10^{-4} (125)	4.38×10^{-5} (100)	4.48×10^{-9}[b]	26.6	−7.55
	70% EtOH	1.06×10^{-4} (100)	7.55×10^{-6} (75)	1.01×10^{-8}[b]	26.6	−5.70
	60% EtOH	2.24×10^{-4} (100)	1.60×10^{-6} (75)	2.16×10^{-8}[b]	26.6	−4.02
	97% TFE	5.48×10^{-4} (100)	5.89×10^{-5} (75)	2.21×10^{-7}[b]	23.0	−11.4
	HCOOH			2.15×10^{-6}		
1h	80% EtOH	7.62×10^{-5} (125)	6.15×10^{-6} (100)	2.57×10^{-10}[b]	29.2	−4.74
1i	80% EtOH	3.85×10^{-5} (125)	3.08×10^{-6} (100)	1.27×10^{-10}[b]	29.1	−5.37

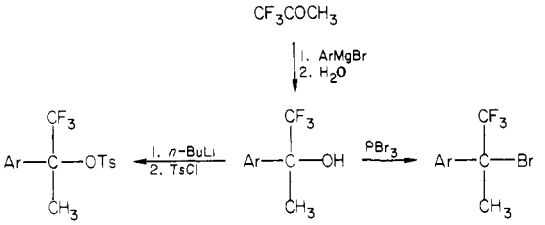
[a] Calculated by multiplying the rate constant of 3a by a factor of 3.94×10^4 (k_{1b}/k_{3b}). [b] Calculated from data at higher temperature.

solvent, salt, and β-deuterium isotope effects, they conclude that the solvolysis of 2-trifluoromethyl-2-propyl triflate proceeds with a rate-limiting solvent or salt attack on the intimate ion pair,[6b] and a limiting ionization mechanism is involved in the solvolysis of 1-phenyl-1-(trifluoromethyl)ethyl tosylate.[6c]

We have independently carried out studies in this area, and have reported part of our results in a preliminary communication.[7] For a series of 1-aryl-1-(trifluoromethyl)ethyl tosylates (**1**) we have observed a very strong dependence on the rates of solvolysis on the aryl substituents, and have also shown the insignificance of solvent participation for the 1-phenyl substrate (**1e**). The correlation of rates with σ^+ constants did not result in a perfectly straight line. Additional work with the aim of clarifying this deviation was undertaken. In the present paper and details of our kinetic study are reported.

Results

1-Aryl-1-(trifluoromethyl)ethanols **2a–i** were prepared from Grignard addition of the corresponding arylmagnesium bromide to 1,1,1-trifluoroacetone. These alcohols were converted into



Ar = 4-$CH_3OC_6H_4$	1a	2a	3a
= 4-$CH_3C_6H_4$	1b	2b	3b
= 4-$C_6H_5C_6H_4$	1c	2c	
= 3-$CH_3C_6H_4$	1d	2d	
= C_6H_5	1e	2e	
= 4-ClC_6H_4	1f	2f	
= 3-ClC_6H_4	1g	2g	
= 3-$CF_3C_6H_4$	1h	2h	
= 4-$CF_3C_6H_4$	1i	2i	

tosylates **1b–i** by reaction with *n*-butyllithium and then with *p*-toluenesulfonyl chloride, and into bromides **3a,b** by treating with phosphorus tribromide. Satisfactory elemental analyses and spectral data agreed with the assigned structures of these substrates.

The rates of solvolysis of tosylates **1b–i** and bromides **3a,b** were followed titrimetrically. Since 1-(4-methoxyphenyl)-1-(trifluoromethyl)ethyl tosylate was too unstable to be obtained in a pure state and was too reactive for an accurate kinetic measurement, the bromide **3a** was employed instead. The conversion factor for the relative rates of tosylate vs. bromide was determined from the 4-methylphenyl compounds **1b** and **3b**. The first-order rate constants were measured from duplicate runs and were calculated by means of the least-squares method. The results are summarized in Table I. The rates for 1-phenyl-1-(trifluoromethyl)ethyl tosylate (**1e**) in acetic acid, 80% ethanol, and 97% trifluoroethanol are in good agreement with those reported by Tidwell and co-workers.[6,11] The Hammett–Brown plots, log $(k/k_0) = \rho\sigma^+$,[12] of the rate data are shown in Figure 1, in which the special value of −0.219 for the *p*-phenyl group in a polar solvent

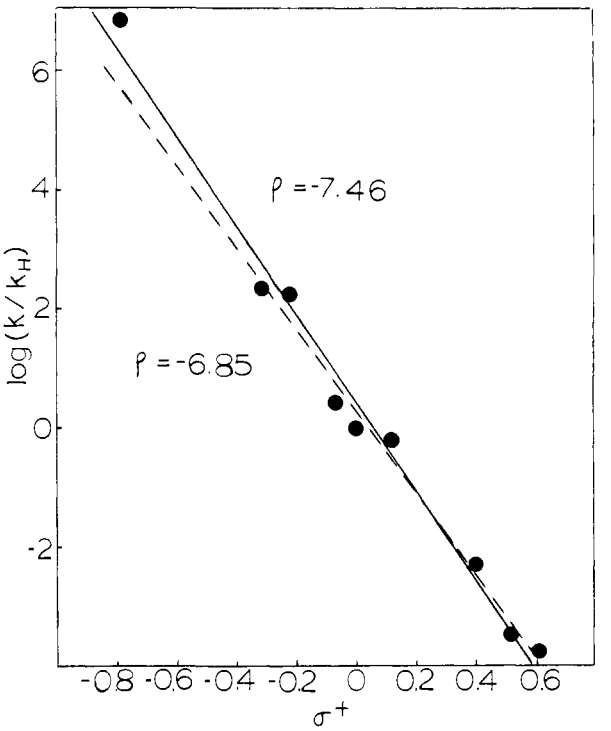


Figure 1. Hammett–Brown plots of the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates in 80% ethanol at 25 °C.

(11) For the rate of formolysis, though the difference between our data and that reported by Tidwell and co-workers, (3.90×10^{-4} s^{-1}) is comparatively large, it will not affect the *mY* plot significantly.

(12) Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *1*, 34–154.

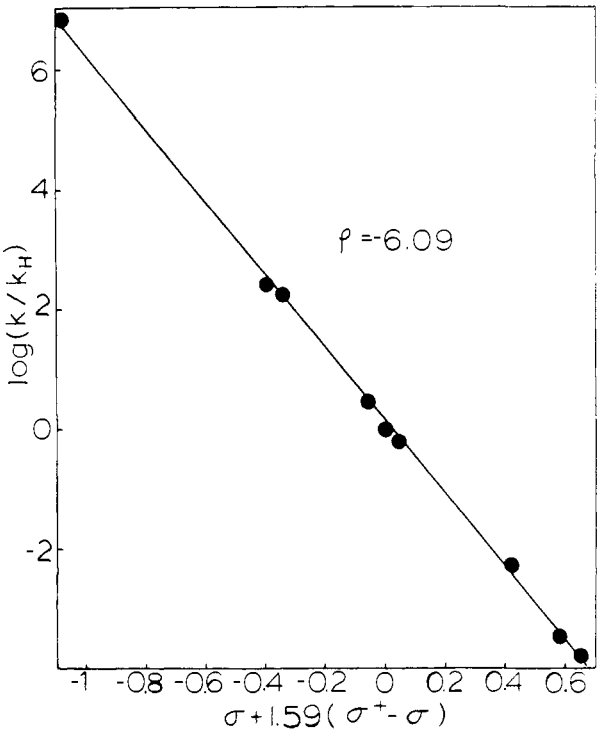


Figure 2. Yukawa–Tsuno plot of the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates in 80% ethanol at 25 °C.

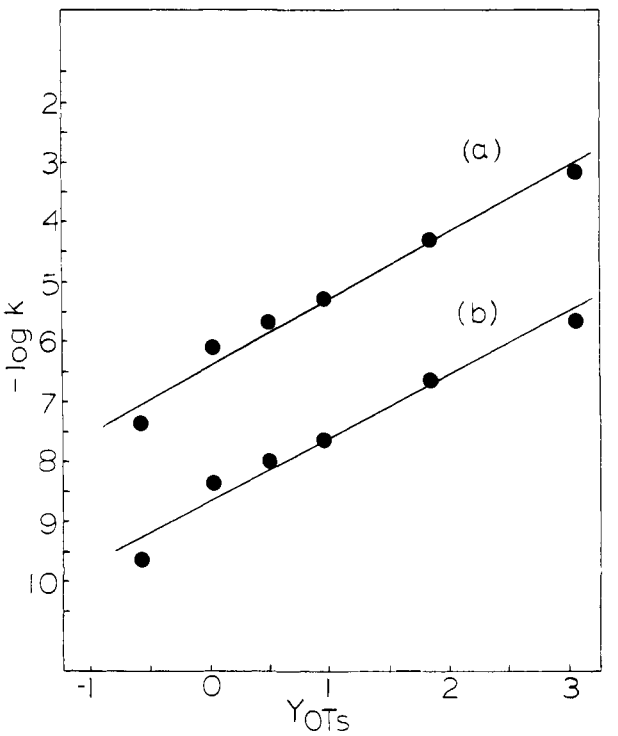


Figure 3. Correlations of logarithms of solvolysis rate constants against Y_{OTs} at 25 °C for (a) 1-phenyl-1(trifluoromethyl)ethyl tosylate and (b) 1-(3-chlorophenyl)-1-(trifluoromethyl)ethyl tosylate.

was used.[13] The Yukawa–Tsuno treatment, $\log (k/k_0) = \rho(\sigma + r(\sigma^+ - \sigma))$,[14] is shown in Figure 2. In Figure 3 the logarithms of the rates for **1e** and **1h** in different solvents are plotted against Y for 2-adamantyl tosylate (Y_{OTs}).[15]

Discussion

Considerable attention has been paid to the solvolysis of a variety of tertiary benzylic systems of mechanistic interest.[16] With the exception of the highly hindered aryl di-*tert*-butylcarbinyl derivative,[17,18] the Hammett–Brown treatment of rate data with σ^+ constants generally displays a very good linear coorelation in every system studied. The dependence of the ρ value on the extent of charge transmission into the aromatic ring was noted.[19] Recently the tool of increasing electron demand was extensively exploited for the study of solvolytic mechanisms, and the structural effect on the ρ value was examined in detail.[16] For 1-aryl-1-(trifluoromethyl)ethyl tosylates the rates of solvolysis observed in the present study also give a straight line in the Hammett–Brown plot. ρ is −7.46 with a correlation coefficient of 0.993 (solid line, Figure 1), which, as expected, reveals a very high electron demand induced by the trifluoromethyl group.

The deactivating effect of the α-trifluoromethyl group is so profound that the reactivity of the tertiary tosylate **1e** becomes even less than that of benzyl tosylate in the absence of solvent participation. The rate of solvolysis of benzyl brosylate in 97% trifluoroethanol is 1.55×10^{-3} s^{-1}.[20] Dividing this value by 3[21] will give the estimated rate of the corresponding tosylate, $k = 5.17 \times 10^{-4}$ s^{-1}. Therefore, in this very poorly nucleophilic solvent the solvolytic reactivity of the tertiary tosylate **1e**, $k = 5.07 \times 10^{-5}$ s^{-1}, is only about one-tenth of that of the primary analogue.

However, from Figure 1 it can be noticed that points are more scattered than those commonly observed in correlations involving solvolytic processes.[22,23] Apparently the point associated with the estimated rate for the 1-(4-methoxyphenyl) derivative **1a** deviates appreciably from the line. It could be due to the unverified assumption[24] that the tosylate/bromide rate ratios are the same for both 4-methoxyphenyl and 4-methylphenyl compounds; i.e., $k_{1a}/k_{3a} = k_{1b}/k_{3b}$. With the omission of the rate data for **1a**, a better fit with a ρ of −6.85 results (broken line, Figure 1). It is still very close to the value of −7.07 for the solvolysis of 1-aryl-1-cyclopropyl 3,5-dinitrobenzoate,[25] the most negative one for the solvolysis of benzene derivatives recorded to date.[26]

On the other hand, the multiparameter treatment proposed by Yukawa and Tsuno[14,27] has also been received much attention.[28] It is often considered to be more suitable than the Hammett–Brown treatment especially when a considerable resonance stabilization of the transition state is required.[28,29] Indeed, the rates of solvolysis for tosylates **1a**–i in 80% ethanol were found to give an excellent correlation (correlation coefficient 0.999) with a Yukawa–Tsuno plot: $\log (k/k_0) = -6.09(\sigma + 1.59\ (\sigma^+ - \sigma))$, which is shown in Figure 2. The reason for this better correlation might be considered the superiority of the Yukawa–Tsuno treatment for reactions with very high electron demand in the transition state. However, the question as to whether the reactivity is more validly examined by using the Yukawa–Tsuno method

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(22) For examples see references cited in ref 16.
(23) With six rate data a nonlinear correlation was previously suggested.
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(25) Brown, H. C.; Rao, C. G.; Ravindranathan, M. *J. Am. Chem. Soc.* **1978**, *100*, 7946.
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(28) For recent work, see for examples: (a) Ando, T.; Yamawaki, J.; Saito, Y.; Takai, Y.; Yamataka, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2348–2356, (b) Bly, R. S.; Ni, E. K.; Tse, A. K. K.; Walace, E. *J. Org. Chem.* **1980**, *45*, 1362–1366.
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rather than by other methods has arisen.[19a,30] In some cases, e.g., the monosubstituted benzhydryl chlorides,[31] the simple Hammett-Brown treatment was found to work better. Furthermore, on examination of the literature we have found that most systems favored by the Yukawa–Tsuno treatment are secondary substrates in nucleophilic solvents such as aqueous acetone or ethanol.[32] In these circumstances solvent involvement in the rate-determining step may occur. Consequently, we prefer not to draw a conclusion until more evidence is obtained.

The importance of solvent intervention in the solvolysis of primary and secondary substrates has been well studied.[33] Recently, the evidence for solvent participation in the solvolysis of *tert*-butyl halides was also recognized.[34] The possibility of direct solvent attack on the highly deactivated tosylates **1b–i** should thus be considered. Although the attack of salt and solvent in the solvolysis of 2-trifluoromethyl-2-propyl triflate has already been confirmed,[6b] the very high tosylate/bromide rate ratio for the 1-(4-methylphenyl)-1-(trifluoromethyl)ethyl derivatives, 3.94×10^4, as compared with that for *tert*-butyl derivatives,[35] reveals that the back strain in the 1-aryl-1-(trifluoromethyl)ethyl system is likely quite large.[7] Indeed, the observations of a linear mY correlation between the rate data for **1e** vs. Y_{OTs} with an m value of 1.09 (line a, Figure 3) rules out any significant solvent assistance in this case. More remarkably, a linear mY plot is also observed for the even less reactive 3-chlorophenyl derivative **1g** (line b, Figure 3) with $m = 1.03$. Clearly the intervention of solvent participation is unimportant in the whole series of tertiary tosylates **1a–i**.

In comparing the rates of solvolysis for tertiary benzylic and alkyl systems, both Peters[36] and also McManus and Harris[37] concluded that a methyl group might be regarded as a deactivating aryl group with σ^+ (γ^+) about 0.63–0.79. It is interesting to note that the estimated rate constant for 2-trifluoromethyl-2-propyl tosylate in 80% ethanol, 1.36×10^{-10} s^{-1},[38] is very close to that for **1i**. That is, the γ^+ for the methyl group is about 0.61 in this case. The two systems, 2-trifluoromethyl-2-propyl and **1**, can thus be incorporated as in the above-mentioned tertiary alkyl and benzylic substrates even though solvent participation is present in 2-trifluoromethyl-2-propyl but is absent in the other three systems. Therefore, some mechanistic complexities might exist in the deactivated 1-aryl-1-(trifluoromethyl)ethyl compounds. Hyperconjugative stabilization by the methyl group might be an explanation, since a decrease in secondary isotope effect with ionizing power of solvent has been observed.[6c] Additional work toward a solution is in progress.

Experimental Section

General Remarks. Melting points, measured in capillaries, and boiling points are uncorrected. Elemental analyses were done by Chung-Shan Institute of Technology, Lung-Tan, Taiwan. Infrared spectra were recorded with Perkin-Elmer Model 137 or JASCO Model S-G5 spectrometers. Proton NMR spectra were taken with Varian Model T-60 or JEOL Model C-60HL instruments using tetramethylsilane as internal standard. Mass spectral analyses were obtained with a Hitachi Model RMS-4 spectrometer.

Materials. Reagents for the preparations, which were obtained from commerical sources were used without further purification: 3-bromotoluene, 3-bromobenzotrifluoride, 4-bromobenzotrifluoride, and 1,1,1-trifluoroacetone from Aldrich; 4-bromoanisole and 4-bromochlorobenzene from BDH Chemicals; 4-bromoaniline and 4-toluenesulfonyl chloride from E. Merck; magnesium turnings from Fisher; bromobenzene, 4-bromotoluene, 3-bromochlorobenzene, and *n*-butyllithium from Tokyo Kasei. 4-Bromobiphenyl was prepared by diazotization of 4-bromoaniline followed by coupling with benzene.[39] Solvents for the rate studies were purified according to standard methods.[40]

Preparation of 1-Aryl-1-(trifluoromethyl)ethanols 2a–i. Alcohols **2a**,**2b**, and **2d–i** were prepared by the addition of the appropriate arylmagnesium bromide to 1,1,1-trifluoroacetone following the general procedure. A 250-mL three-necked flask, fitted with a mechanical stirrer, a condenser with drying tube, and a pressure-equalizing dropping funnel with nitrogen-inlet tube, was flame-dried under nitrogen. In this, the arylmagnesium bromide was made by slow addition of the aryl bromide (60–90 mmol) to an equivalent amount of magnesium turnings in 20 mL of anhydrous ether. All of the magnesium was dissolved after the mixture has been stirred at room temperature for 2 h. A solution of 1,1,1-trifluoroacetone (50–75 mmol) in 20 mL of anhydrous ether was added dropwise to a stirred solution of the Grignard reagent under nitrogen at ice-bath temperature. The stirring was continued at room temperature overnight. It was then hydrolyzed with 5–7.5 mL of an ice-chilled saturated solution of ammonium chloride. This mixture was filtered and the inorganic residue was washed twice with 20 mL of ether. The combined ether solution was dried (Na_2SO_4) and decolorized. The alcohol was isolated by distillation.

For 1-(4-biphenylyl)-1-(trifluoromethyl)ethanol (**2c**) the Grignard reagent was made in tetrahydrofuran solution at 40–50 °C with a drop of bromine in carbon tetrachloride as catalyst, and the addition was also carried out in tetrahydrofuran. The product was obtained by crystallization.

Alcohols **2a–i** exhibit characteristic infrared absorptions for O–H stretching in the region between 3430 and 3410 cm^{-1}. The yield, boiling point or melting point, and pertinent spectral data of these compounds are listed as follows.

1-(4-Methoxyphenyl)-1-(trifluoromethyl)ethanol (**2a**): yield 64%; bp 98–99 °C (1.5 Torr); ^{1}H NMR($CDCl_3$) δ 1.75 (s, 3, CF_3CCH_3), 3.36 (s, 1, OH), 3.85 (s, 3, OCH_3), 7.06 and 7.60 (A_2B_2, 4, $J = 7.5$ Hz, C_6H_4); MS (60 eV) m/z 220 (M^+), 151 (base peak, $M^{+\cdot} - CF_3$).

1-(4-Methylphenyl)-1-(trifluoromethyl)ethanol (**2b**): yield 67%; bp 51 °C (0.7 Torr); ^{1}H NMR ($CDCl_3$) δ 1.73 (s, 3, CF_3CCH_3), 2.36 (s, 3, $ArCH_3$), 3.07 (s, 1, OH), 7.26 and 7.54 (A_2B_2, 4, $J = 7.5$ Hz, C_6H_4); MS (60 eV) m/z 204 (M^+), 135 (base peak, $M^{+\cdot} - CF_3$).

1-(4-Biphenylyl)-1-(trifluoromethyl)ethanol (**2c**): yield 48%; mp 89–89.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.70 (s, 3, CF_3CCH_3), 2.50 (s, 1, OH), 7.05–7.40 (m, 9, ArH); MS (70 eV) m/z 266 (M^+), 197 (base peak, $M^{+\cdot} - CF_3$).

1-(3-Methylphenyl)-1-(trifluoromethyl)ethanol (**2d**): yield 72%; bp 43 °C (0.1 Torr); ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 3, CF_3CCH_3), 2.38 (s, 3, $ArCH_3$), 3.28 (s, 1, OH), 7.15–7.40 (m, 4, C_6H_4); MS (12 eV) m/z 204 (M^+), 135 (base peak, $M^{+\cdot} - CF_3$).

1-Phenyl-1-(trifluoromethyl)ethanol (**2e**): yield 86%; bp 56–58 °C (3 Torr) (lit.[41] 62–66 °C (4.5 Torr)); ^{1}H NMR($CDCl_3$) δ 1.70 (s, 3, CF_3CCH_3), 2.45 (s, 1, OH), 7.20–7.50 (m, 5, C_6H_5); MS (70 eV) m/z 190 (M^+), 121 (base peak, $M^{+\cdot} - CF_3$).

1-(4-Chlorophenyl)-1-(trifluoromethyl)ethanol (**2f**): yield 71%; bp 80 °C (2.4 Torr); ^{1}H NMR ($CDCl_3$) δ 1.78 (s, 3, CF_3CCH_3), 3.30 (s, 1, OH), 7.49 and 7.62 (A_2B_2, 4, $J = 7.5$ Hz, C_6H_4); MS (60 eV) m/z 226, 224 (M^+), 155 (base peak, $M^{+\cdot} - CF_3$).

1-(3-Chlorophenyl)-1-(trifluoromethyl)ethanol (**2g**): yield 63%; bp 71 °C (2 Torr); ^{1}H NMR ($CDCl_3$) δ 1.78 (s, 3, CF_3CCH_3), 2.60 (s, 1, OH), 7.33–7.50 (m, 3, ArH), 7.64 (bs, 1, ArH); MS (70 eV) m/z 226, 224 (M^+), 155 (base peak, $M^{+\cdot} - CF_3$).

1-(3-Trifluoromethylphenyl)-1-(trifluoromethyl)ethanol (**2h**): yield 64%; bp 34 °C (0.1 Torr) (lit[41] 87.5–88.0 °C (4 Torr); ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 3, CF_3CCH_3); 2.68 (s, 1, OH), 7.30–7.70 (m, 4, C_6H_4); MS (12 eV) m/z 258 (M^+), 189 (base peak, $M^{+\cdot} - CF_3$).

1-(4-Trifluoromethylphenyl)-1-(trifluoromethyl)ethanol (**2i**): yield 59%; bp 62–64 °C (2.5 Torr); ^{1}H NMR($CDCl_3$) δ 1.80(s, 3, CF_3CCH_3), 3.88 (s, 1, OH), 7.81 (s, 4, C_6H_4); MS (70 eV) m/z 239 ($M^{+\cdot} - F$), 189 (base peak, $M^{+\cdot} - CF_3$).

Preparation of 1-Aryl-1-(trifluoromethyl)ethyl Tosylates 1b–i. The following general proceudre was employed for the preparation of tosylates. A 100-mL round-bottom flask with a serum-capped side arm was flame-dried under nitrogen. To this, 6 mmol of an alcohol in 6 mL of

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tetrahydrofuran was added. *n*-Butyllithium in hexane, 4.5 mL (ca. 7 mmol), was added dropwise at 0 °C with magnetic stirring. This mixture was allowed to stir for 0.5 h and was then cooled to −40 °C. Tosyl chloride (6 mmol) in 6 mL of tetrahydrofran was added, and the solution was then allowed to warm to room temperature. The solution was stirred overnight, and then the solvent was stripped off. The residue was extracted with ether, and the ethereal solution was washed with ice-chilled 5% sodium bicarbonate. It was dried (Na_2SO_4) and then evaporated to dryness. The solid was recrystallized from benzene–hexane (1:4). The infrared spectrum (KBr) showed the absence of O–H stretching frequency at 3430–3410 cm^{-1} and the presence of two very strong absorptions for $-SO_2-$ at 1370–1340 and at 1190–1150 cm^{-1}. The yield, melting point, proton NMR spectral data, and analyses for the eight tosylates prepared are summarized as follows.

1-(4-Methylphenyl)-1-(trifluoromethyl)ethyl tosylate (**1b**): yield 62%; mp 73 °C; ^1H NMR ($CDCl_3$) δ 2.04 (s, 3, CF_3CCH_3), 2.20 (s, 3, $ArCH_3$), 2.29 (s, 3, $ArCH_3$), 6.90 and 7.12 (A_2B_2, 4, J = 7.5 Hz, C_6H_4), 6.87 and 7.45 (A_2B_2, 4, J = 8.5 Hz, $MeC_6H_4SO_3$). Anal. ($C_{17}H_{17}F_3O_3S$) C, H, F, S.

1-(4-Biphenylyl)-1-(trifluoromethyl)ethyl tosylate (**1c**): yield 55%; mp 88.5 °C; ^1H NMR($CDCl_3$) δ 2.15 (s, 3, CF_3CCH_3), 2.32 (s, 3, $ArCH_3$), 7.08 and 7.51 (A_2B_2, 4, J = 8 Hz, MeC_6H_4), 7.22–7.42 (m, 9, ArH). Anal. ($C_{22}H_{19}F_3O_3S$) C, H, F.

1-(3-Methylphenyl)-1-(trifluoromethyl)ethyl tosylate (**1d**): yield 45%; mp 75.5–76.5 °C; ^1H NMR ($CDCl_3$) δ 2.19 (s, 3, CF_3CCH_3), 2.32 (s, 3, $ArCH_3$), 2.43 (s, 3, $ArCH_3$), 7.28 (bs, 4, 3-MeC_6H_4), 7.28 and 7.70 (A_2B_2, 4, J = 8.0 Hz, 4-MeC_6H_4). Anal. ($C_{17}H_{17}F_3O_3S$) C, H, S.

1-Phenyl-1-(trifluoromethyl)ethyl tosylate (**1e**): yield 78%; mp 103.5 °C; ^1H NMR ($CDCl_3$) δ 2.20 (s, 3, CF_3CCH_3), 2.43 (s, 3, $ArCH_3$), 7.30 and 7.74 (A_2B_2, 4, J = 8.3 Hz, MeC_6H_4), 7.37–7.46 (m, 3, C_6H_5). Anal. ($C_{16}H_{15}F_3O_3S$) C, H, F, S.

1-(4-Chlorophenyl)-1-(trifluoromethyl)ethyl tosylate (**1f**): yield 74%; mp 93-93.5 °C; ^1H NMR ($CDCl_3$) δ 2.19 (s, 3, CF_3CCH_3), 2.45 (s, 3 $ArCH_3$), 7.36 and 7.44 (A_2B_2, 4, J = 9.5 Hz, ClC_6H_4), 7.34 and 7.73 (A_2B_2, 4, J = 8.3 Hz, MeC_6H_4). Anal. ($C_{16}H_{14}ClF_3O_3S$) C, H, Cl, F, S.

1-(3-Chlorophenyl)-1-(trifluoromethyl)ethyl tosylate (**1g**): yield 80%; mp 81.5 °C; ^1H NMR ($CDCl_3$) δ 2.25 (s, 3, CF_3CCH_3), 2.47 (s, 3, $ArCH_3$), 7.40 (s, 4, ClC_6H_4), 7.36 and 7.78 (A_2B_2, 4, J = 8 Hz, MeC_6H_4). Anal. ($C_{16}H_{14}ClF_3O_3S$) C, H, Cl, F, S.

1-(3-Trifluoromethylphenyl)-1-(trifluoromethyl)ethyl tosylate (**1h**): yield 55%; mp 70–70.5 °C; ^1H NMR ($CDCl_3$) δ 2.26 (s, 3, CF_3CCH_3), 2.44 (s, 3, $ArCH_3$), 7.54 and 7.70 (A_2B_2, 4, J = 8 Hz, MeC_6H_4), 7.66 (s, 1, ArH), 7.25–7.34 (m, 3, ArH). Anal. ($C_{17}H_{14}F_6O_3S$) C, H, S.

1-(4-Trifluoromethylphenyl)-1-(trifluoromethyl)ethyl tosylate (**1i**): yield 59%; mp 89 °C; ^1H NMR ($CDCl_3$) δ 2.24 (s, 3, CF_3CCH_3), 2.45 (s, 3, $ArCH_3$), 7.33 and 7.74 (A_2B_2, 4, J = 8.5 Hz, MeC_6H_4), 7.64 (s, 4, $CF_3C_6H_4$). Anal. ($C_{17}H_{14}F_6O_3S$) C, H, F.

Preparation of 1-Aryl-1-(trifluoromethyl)ethyl Bromides 3a and 3b. In a 25-mL round-bottom flask with a serum-capped side arm cooled in an ice bath was placed 7 mmol of **2a** or **2b**. Phosphorus tribromide, 8 mmol, was added slowly through the side arm with stirring. After 30 min the reaction mixture was heated to 40 °C and stirring was continued for 2 h. The product was extracted with ether, and the ethereal solution was washed with 5% sodium bicarbonate and then with water. The solution was dried (Na_2SO_4) and the solvent was stripped off. The resultant bromide was purified by using column chromatography on alumina, with *n*-hexane–benzene(3:2) as eluent. No O–H stretching frequency was observed in the infrared spectrum. The yield, pertinent spectral data, and analyses for **3a** and **3b** are shown as follows.

1-(4-Methoxyphenyl)-1-(trifluoromethyl)ethyl bromide (**3a**): yield 64%; ^1H NMR ($CDCl_3$) δ 2.8 (s, 3, CF_3CCH_3), 3.65 (s, 3, OCH_3), 6.64 and 7.37 (A_2B_2, 4, J = 9 Hz, C_6H_4); MS (70 eV) m/z 283, 281 (M^+), 202 ($M^{+\cdot}$ − Br), 133 (base peak, $M^{+\cdot}$ − Br − CF_3). Anal. ($C_{10}H_{10}BrF_3O$) C, H.

1-(4-Methylphenyl)-1-(trifluoromethyl)ethyl bromide (**3b**): yield 86%; ^1H NMR ($CDCl_3$) δ 2.28 (s, 3, CF_3CCH), 2.34 (s, 3, $ArCH_3$), 7.16 and 7.76 (A_2B_2, 4, J = 8 Hz, C_6H_4); MS (70 eV) m/z 268, 266 (M^+), 187 (base peak, $M^{+\cdot}$ − Br). Anal. ($C_{10}H_{10}BrF_3$) C, H.

Kinetic Experiments. In general, a 0.01 M solution of the tosylate or bromide was prepared at room temperature and aliquots of 5 mL were sealed in Pyrex tubes under nitrogen. The ampules were placed in the thermostat with a temperature variation of ±0.02°, and nine to ten of them were successively removed after certain intervals of time. For the solvolysis in aqueous ethanol or trifluoroethanol at high temperature the ampule was quickly cooled in ice–water, and two 2-mL aliquots were separately discharged into 10 mL of chilled ethanol. The solution was titrated with a 0.01 M aqueous sodium hydroxide using methyl red as indicator. The averages of these two, and of the infinity titer, were taken to make a plot of log $(a - x)$ against time using least-squares calculation. The first-order rate constant was then obtained from the slope with a correlation coefficient of 0.997 to 0.999. For acetolysis the 5-mL aliquot was directly titrated with 0.01 M sodium acetate in acetic acid using bromothymol blue as indicator. For formolysis the aliquot was diluted with cold dioxane before titration. If the reaction proceeded too fast at room temperature to apply the ampule technique, the solvolysis was carried out in a long-necked flask and the rate was followed by pipetting 2-mL aliquots into 10 mL of 95% ethanol or dioxane for titration.

All rates were followed to 70–80% completion of solvolysis. Duplicate runs generally differed by less than 5%. The mean values of rate constants are listed in Table I.

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