A Study of Solvent Effects on the Rates of Solvolyses of Pinacolyl Derivatives

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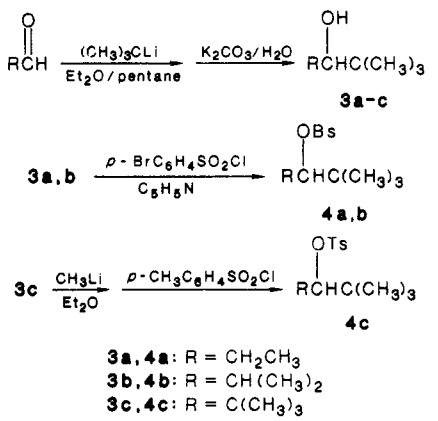
The solvolysis rates of $RCH(O_3SAr)C(CH_3)_3$ (**4a**, R = Et, Ar = *p*-BrPh; **4b**, R = *i*-Pr, Ar = *p*-BrPh; **4c**, R = *t*-Bu, Ar = *p*-Tol) and $CF_3CH(O_3SR)C(CH_3)_3$ (**6**-OBs, R = *p*-BrPh; **6**-OTf, R = CF_3) have been determined in mixtures of ethanol and water (the E–W solvent series) and acetic acid and formic acid (the A–F solvent series). Correlations of the rate data by eq 1 [$\log k = b \log k_{\text{neophyl-OTs}} + c$] showed that **4a,b** responded similarly to pinacolyl brosylate (1) to the examined solvent effect, yielding separate E–W, A–F regression lines, but with decreased dispersion with increased steric bulk of R. For compound **4c** a linear correlation with eq 1 was obtained. These results are interpreted in terms of steric hindrance to electrostatic solvation of the incipient carbocation. The reactivity of the CF_3-substituted sulfonate **6**-OBs is greatly depressed. The substrate failed to react in the E–W solvent series. Added salt produced enhanced rates of solvolysis of **6**-OBs in 25% AcOH–75% HCOOH. These results suggest an S_N2-like mechanism with very strong electrophilic solvent assistance in the transition state. However, since the solvolysis reactions of **6**-OBs are attended with kinetic complexities, the data do not allow a detailed mechanistic interpretation. The solvolytic behavior of **6**-OTf stands in sharp contrast to that of **6**-OBs. For example, added nucleophilic salts cause only small increases in the rates of solvolysis of **6**-OTf in both 70% EtOH–30% H_2O and 25% AcOH–75% HCOOH. Furthermore, the solvolysis rate constants of **6**-OTf in all solvents examined correlate with those of 2-adamantyl triflate. These data support a k_Δ mechanism for **6**-OTf and are discussed in terms of the decreased importance of electrostatic solvation of the forming carbocation from **6**-OTf than from pinacolyl brosylate.

Introduction

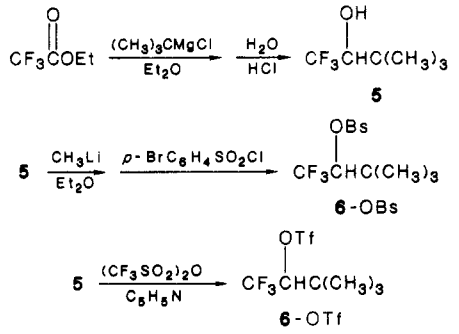
In our study[1] of solvent effects upon rates of solvolysis of primary and secondary alkyl arenesulfonates, we observed a solvent effect response by pinacolyl brosylate (1) different from that of neophyl tosylate (2)—a generally accepted model for basing a scale of ionizing power for arenesulfonates.[2] We interpreted this difference in terms of the relative importance of "cation solvation"[3,4] of the developing carbocationic center. Since this interaction depends on the distance between the solvent molecules and the reaction center,[6] the bridged structure of the intermediate generated from the neophyl tosylate substrate should preclude significant cation solvation of the ion-pair-like transition-state complex.[7] On the other hand, the more open structure of the pinacolyl system should be accessible to significant cation solvation. As a result pinacolyl derivatives would fail, as they do, to correlate with the rates of solvolysis of neophyl tosylate.

To test the above hypothesis, we designed two experiments which would reduce the importance of cation solvation in the solvolyses of pinacolyl-like substrates. In the first one, we used the tool of increasing steric hindrance[8] and in the second we use the tool of increasing electron

Scheme I



Scheme II



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(3) (a) Bunton, C. A.; Mhala, M. M.; Moffatt, J. R. *J. Org. Chem.* **1984**, *49*, 3639. (b) Swain, C. G.; Swain, M. S.; Powell, A. L.; Alunni, S. *J. Am. Chem. Soc.* **1983**, *105*, 502. (c) Parker, A. J.; Mayer, U.; Schmid, R.; Gutmann, V. *J. Org. Chem.* **1978**, *43*, 1843.

(4) (a) We define "cation solvation" as a local electrostatic interaction between solvent and the polar center of the developing carbocation (solvent–dipole interaction) as distinct from a specific covalent bonding (nucleophilic assistance) interaction as proposed in the "S_N2-intermediate" mechanism.[5a] (b) Although the difference between these two solvent interaction schemes at the transition state, i.e., dipole–dipole and partial covalent bonding, is somewhat blurred at longer interaction distances, the difference between the proposed values for cation solvating tendency[3b,c] and those for nucleophilicity[5b] in the two solvent series used in this study (E–W and A–F) is significant. Thus one can experimentally distinguish between the two solvent interaction schemes by studies of reactivity in the E–W and A–F solvent series.[1f]

(5) (a) For leading references, see: Bentley, T. W.; Carter, G. E. *J. Org. Chem.* **1983**, *48*, 579. (b) For leading references, see: Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1–67.

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(7) Ando, T.; Kim, S.-G.; Matsuda, K.; Yamstaka, H.; Yukawa, Y.; Fry, A.; Lewis, D. E.; Sims, L. B.; Wilson, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 3505.

(8) For pertinent references, see: (a) Bartlett, P. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1968**, *90*, 4421. (b) Dubois, J.-E.; Lomas, J. S. *Tetrahedron Lett.* **1973**, 1791. (c) Tidwell, T. T. *J. Org. Chem.* **1974**, *39*, 3533.

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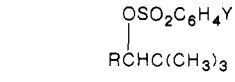
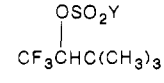
demand[9] to enhance neighboring group participation in the transition state. The first experiment involved the study of the solvolysis of the following series where the α-methyl group of the pinacolyl system was successively replaced by ethyl, isopropyl, and *tert*-butyl groups. The



4a: R = CH_2CH_3; Y = *p*-Br
b: R = $CH(CH_3)_2$; Y = *p*-Br
c: R = $C(CH_3)_3$; Y = *p*-CH_3

second experiment involved the study of the solvolysis of the following compounds where the α-methyl group of the pinacolyl system was replaced with a trifluoromethyl group.



6-OBs: Y = *p*-BrC_6H_4
6-OTf: Y = CF_3

Results

The synthesis of **4a–c** and their alcohol precursors (**3a–c**) was accomplished according to Scheme I. Preparation of **6**-OBs, **6**-OTf, and their alcohol precursor (**5**) was carried out as shown in Scheme II.

The solvolytic rate constants of **4a–c**, **6**-OBs, and **6**-OTf are collected in Table I. Each ester[10] was allowed to solvolyze in two hydroxylic solvent systems: namely, aqueous ethanol and acetic–formic acid. The reaction was followed by titrating the liberated sulfonic acid. The reactions of **4a–c** were observed to be first order up to at least 75% conversion. Some of the solvolysis reactions of both **6**-OBs and **6**-OTf were attended with kinetic complexities. In the case of both substrates, the generation of titrable acid in some solvents was complicated by an equilibrium reaction between the solvolysis products and the sulfonate starting material (cf. Experimental Section for details). As a result some of the solvolyses of **6**-OBs and **6**-OTf followed first-order kinetic law up to 25% conversion or less (cf. Table I for details). The kinetic effect of the added salt HCO_2Na on the rates of **6**-OBs and of **6**-OTf in 25/75 acetic–formic acid were measured at 45 °C and 65 °C, respectively, and are reported in Table II along with the effect of NaN_3 on the rates of **6**-OTf in 70% aqueous ethanol at 45 °C and 65 °C.

Product studies for the reactions of **6**-OBs and **6**-OTf were carried out in 25% acetic–75% formic acid solvent, and, in the case of **6**-OTf, in 80% aqueous ethanol as well. No detectable products were isolated from the solvolysis of **6**-OBs in the mixed acid solvent at 45 °C. Instead, after reacting for times equal to 1.0 and 3.5 half-lives, respectively, with and without sodium formate buffer, only starting material was recovered. It is interesting to note that from 0% to 20% conversion (a 27-day reaction time), titrable acid was liberated at a rate in accord with first-order kinetic law. On the other hand, after 20% conversion the acid titer decreased over a 40-day period to less than 1% of theoretical.[11] These results suggest that at least three competing reaction processes are taking place: one involving the production of titrable acid; a second one involving an equilibrium reaction between solvolysis product(s) and starting material; and a third process involving the consumption of titrable acid. Exhaustive analysis of the data indicates a complex reaction scenario whose unraveling would require a greatly extended investigation of the problem.

Solvolysis of **6**-OTf in 25/75 acetic–formic acid proceeded cleanly and gave mostly 2-methyl-3-(trifluoromethyl)-2-butyl formate (**7a**). Solvolysis of **6**-OTf in 80% aqueous ethanol also proceeded cleanly and gave about a

Table I. Solvolysis Rate Constants Determined in This Study

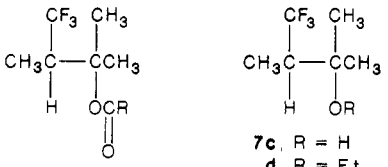
compound[a]	solvent[b]	temp, °C	k,[c] s^{-1}
t-BuEtCar-OBs (**4a**)	100E–W	25.0	$(1.14 \pm 0.02) \times 10^{-6}$
	90E–W	25.0	$(8.4 \pm 0.1) \times 10^{-6}$
	80E–W	25.0	$(2.9 \pm 0.1) \times 10^{-5}$
	70E–W	25.0	$(8.3 \pm 0.1) \times 10^{-5}$
	60E–W	25.0	$(1.46 \pm 0.05) \times 10^{-4}$
	50E–W	25.0	$(3.0 \pm 0.2) \times 10^{-4}$
	40E–W	25.0	$(1.3 \pm 0.3) \times 10^{-3}$
	100A–F	25.0	$(4.2 \pm 0.2) \times 10^{-6}$
	75A–F	25.0	$(7.8 \pm 0.2) \times 10^{-5}$
	65A–F	25.0	$(1.67 \pm 0.01) \times 10^{-4}$
	50A–F	25.0	$(4.0 \pm 0.1) \times 10^{-4}$
	0A–F	25.0	$(3.5 \pm 0.2) \times 10^{-3}$
t-Bu-*i*-PrCar-OBs (**4b**)	100E–W	25.0	$(7.16 \pm 0.2) \times 10^{-7}$
	90E–W	25.0	$(4.55 \pm 0.05) \times 10^{-6}$
	80E–W	25.0	$(1.20 \pm 0.03) \times 10^{-5}$
	70E–W	25.0	$(3.9 \times 0.1) \times 10^{-5}$
	60E–W	25.0	$(7.9 \pm 0.2) \times 10^{-5}$
	50E–W	25.0	$(1.72 \pm 0.02) \times 10^{-4}$
	40E–W	25.0	$(5.1 \pm 0.2) \times 10^{-4}$
	100A–F	25.0	$(1.82 \pm 0.05) \times 10^{-6}$
	75A–F	25.0	$(3.5 \pm 0.1) \times 10^{-5}$
	50A–F	25.0	$(1.29 \pm 0.02) \times 10^{-4}$
	0A–F	25.0	$(1.7 \pm 0.2) \times 10^{-3}$
di-*t*-BuCar-OTs (**4c**)	90E–W	25.0	$(6.9 \pm 0.2) \times 10^{-6}$
	70E–W	25.0	$(6.7 \pm 0.2) \times 10^{-5}$
	60E–W	25.0	$(1.7 \pm 0.1) \times 10^{-4}$
	50E–W	25.0	$(3.3 \pm 0.15) \times 10^{-4}$
	75A–F	25.0	$(2.3 \pm 0.2) \times 10^{-4}$
t-BuCF_3Car-OBs (**6**-OBs)	100A–F	45.0	$(2.6 \pm 0.1) \times 10^{-9}$
		65.0	$(8.0 \pm 0.1) \times 10^{-9}$
	75A–F	25.0	$(5.3 \pm 0.1) \times 10^{-9}$
		45.0	$(2.2 \pm 0.1) \times 10^{-8}$
		65.0[d]	$(9.0 \pm 0.1) \times 10^{-8}$
	65A–F	25.0[e]	$(1.0 \pm 0.1) \times 10^{-8}$
	50A–F	25.0[d]	$(1.6 \pm 0.2) \times 10^{-8}$
	25A–F	25.0[e]	$(5.0 \pm 0.2) \times 10^{-8}$
		45.0[e]	$(1.2 \times 0.2) \times 10^{-7}$
	0A–F	25.0[d]	$(1.0 \pm 0.5) \times 10^{-7}$
t-BuCF_3Car-OTf (**6**-OTf)	80E–W	65.0	$(9.0 \pm 0.1) \times 10^{-8}$
	70E–W	65.0[d]	$(1.4 \pm 0.2) \times 10^{-7}$
	60E–W	65.0	$(2.3 \pm 0.2) \times 10^{-7}$
	50E–W	65.0[f]	$(4.5 \pm 0.2) \times 10^{-7}$
	100A–F	65.0	$(1.8 \pm 0.3) \times 10^{-8}$
	75A–F	65.0[f]	$(8.0 \pm 0.2) \times 10^{-8}$
	50A–F	65.0	$(1.4 \pm 0.1) \times 10^{-7}$
	25A–F	65.0	$(2.0 \pm 0.1) \times 10^{-7}$
	0A–F	65.0[f]	$(3.0 \pm 0.2) \times 10^{-7}$

[a] *t*-BuEtCar = *tert*-butylethylcarbinyl, *t*-Bu-*i*-PrCar = *tert*-butylisopropylcarbinyl, di-*t*-BuCar = di-*tert*-butylcarbinyl, *t*-BuCF_3Car = *tert*-butyltrifluoromethylcarbinyl, -OBs = *p*-bromobenzenesulfonate, -OTf = trifluoromethanesulfonate. [b] Percent by volume. For example, 90E–W means 90 volumes of ethanol plus 10 volumes of water, both at 25 °C before mixing; 75A–F means 75 volumes of acetic acid plus 25 volumes of formic acid, both at 25 °C before mixing. [c] Errors reported as one standard deviation from the mean. [d] Calculated from initial slope of rate constant. [e] Conversions up to which reactions of **6**-OBs in 65A–F and 25A–F followed first-order rate law are 25% and 30%, respectively, at 25 °C, and 20% at 45 °C. [f] Conversion up to which reactions of **6**-OTf in 50E–W, 75A–F, and 0A followed first-order rate law is 30%.

(9) For leading references, see: (a) Brown, H. C. *The Nonclassical Ion Problem*; Plenum: New York, 1977; Chapter 10. (b) Gassman, P. G.; Tidwell, T. T. *Acc. Chem. Res.* **1983**, *16*, 279–285.

(10) In the case of the solvolysis of **6**-OBs in aqueous ethanol solvents, no titrable acid was detected up to 18 months reaction time at 65 °C.

(11) Solvolysis of **6**-OBs in both acetic acid and 75/25 acetic acid–formic acid solvents was unattended by any decrease in titrable acid over at least a 16-month reaction time at 45 °C.



7a, R = H
b, R = Me

7c, R = H
d, R = Et

60/40 mixture of 2-methyl-3-(trifluoromethyl)-2-butanol (**7c**) and its ethyl ether **7d**.

Discussion

Solvent Response to Increasing Steric Hindrance. To evaluate the solvent-effect response to steric hindrance to solvation of the forming carbocation, we used eq 1.[1f,2]

$$\log k_{\text{reaction}} = b \log k_{\text{neophyl-OTs}} + c \qquad (1)$$

Plots of the $-\log k_t$ values (Table III) for solvolysis of 1 and **4a–c** against log $k_{\text{neophyl-OTs}}$ in both ethanol–water (E–W) and acetic–formic acid (A–F) solvent series using eq 1 were carried out. The logarithmic rate–rate plots for **4a** and **4b** produce plots similar to that of **1**, i.e., a "dispersion"[12] of data yielding correlation lines of different slopes (b_{EW} and b_{AF}, cf. Table IV) for the E–W and A–F solvent series respectively. The relative magnitude of the dispersions as measured by the solvent parameter $[k_{EW}/k_{50AF}]_Y$ is noteworthy. Proceeding from R = methyl (**1**) to ethyl (**4a**) to isopropyl (**4b**) is attended by a decrease in dispersion (cf. Table IV) until R = *tert*-butyl (**4c**); a linear correlation is observed for all solvents considered. Trends of this sort are commonly attributed to increasing steric hindrance to nucleophilic solvent assistance.[13,14] However, it should be noted that the generally accepted mechanism for the solvolysis of pinacolyl brosylate (**1**)—k_c[15] or possibly k_Δ[1f]—plus the fact that **1** gives almost exclusively rearranged products[16] rules out all but very weak nucleophilic solvent assistance. The slope values collected in Table IV are quite similar for **1** and **4a–c** as are the dispersion patterns (divergent),[17] indicating that all four substrates solvolyze by a rate-limiting ionization mechanism. The m values derived from the Winstein–Grunwald expression, eq 3, are also collected in Table IV.[18] As can be seen from the similar m_{EW} and m_{AF} values, compounds **1** and **4a–c** respond similarly to changes in solvent ionizing power. This result indicates that charge development in the transition states of these four compounds is similar. There is also abundant evidence that bulky carbocations are not strongly solvated.[8,19] The results discussed above are consistent with this view.

Clearly these findings demonstrate that the solvent-effect response of pinacolyl-like substrates can be modified by steric effects to parallel that of neophyl tosylate (**2**), a generally accepted model for a rate-limiting ionization process.[2] Furthermore, they strengthen our proposal[1f] that the difference in solvent-effect response between pinacolyl brosylate (**1**) and **2** can be attributed to the greater importance of electrostatic solvation of the forming carbocation from **1** than from **2**.[20]

Solvent Response to Deactivation. For the deactivated pinacolyl brosylate $CF_3CH(OBs)C(CH_3)_3$, **6-OBs**, no solvolysis reaction was observed in the aqueous alcohol solvents. In the A–F solvents, the response of the solvolysis rate of **6-OBs** to changing solvent composition was low, varying by only 312 over the entire solvent range. The reactivity of **6-OBs** is enhanced some 2.32 times by sodium formate[22] (cf. Table II). These results suggest that **6-OBs** solvolyzes via an S_N2-like mechanism with very strong electrophilic assistance by the solvent in the transition state. However, since the precise nature of the electrophilic assistance[23] as well as exactly what fraction of the solvolysis rate is being measured is not known, the data do not allow a mechanistic interpretation of the solvolytic behavior of **6-OBs**.

The solvolytic behavior of the triflate (**6-OTf**) is much less complicated than that of the brosylate (**6-OBs**). Relatively satisfactory first-order kinetic behavior was observed in both solvent series investigated (cf. Table I). The reaction rates of **6-OTf** are correlated well against Y_{OTf} values[24] (eq 2, $r = 0.99$) over the entire range of solvents

$$\log (k/k_0) = mY_{OTf} \qquad (2)$$

studied. The slope of the correlation ($m_{OTf} = 0.40$) indicates a much lower dependence upon solvent ionizing power for **6-OTf** than for 2-adamantyl triflate, a result which is characteristic of substrates solvolyzing by the k_Δ pathway.[25-27] Interestingly, the rate data for the solvolysis of **6-OTf** are correlated equally well ($r = 0.99$) by the original Winstein–Grunwald expression,[28] eq 3. This suggests that the solvation requirements of the developing trifluoromethanesulfonate anion in acetic acid, formic acid, and ethanol/water are somewhat similar to that of the chloride ion.[29]

$$\log (k/k_0) = mY \qquad (3)$$

The dependence of the rates of solvolysis of **6-OTf** in 25/75 acetic acid–formic acid and 70% aqueous ethanol in the presence of added salts is also consistent with a rate-limiting ionization process such as k_Δ. Thus for both HCO_2Na and highly nucleophilic NaN_3, only a slight in-

(12) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1957**, *79*, 1608.
(13) For a review, see: Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1969; Chapter 7.
(14) Streitwieser, A. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962.
(15) For leading references, see: Harris, J. M.; Mount, D. L.; Smith, M. R.; Neal, W. C., Jr.; Dukes, M. D.; Raber, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 8147.
(16) Henderson, N. G.; Narayanan, K.; Pillai, C. N. *Indian J. Chem.* **1975**, *13*, 552.
(17) Recently[1f] we reported the following correlation between dispersion pattern and solvolytic mechanism: (1) parallel E–W line/A–F line dispersion, k_s process; (2) E–W line/A–F line dispersion which diverged with increasing ionizing power, k_Δ (hyperconjugation).
(18) Y values used were taken from Table 8-14 of: Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; Wiley: New York, 1963.
(19) (a) Orolovic, M.; Kronja, O.; Humski, K.; Borcic, S.; Polla, E. *J. Org. Chem.* **1986**, *51*, 3253. (b) Abraham, M. H.; Taft, R. W.; Kamlet, M. J. *J. Org. Chem.* **1981**, *46*, 3053. (c) Staley, R. H.; Wreting, R. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 5964.
(20) Differing "internal return" processes are ruled out on the basis that ion-pair return appears not to be significant in the solvolysis of pinacolyl brosylate (and by implication **4a–c**) in acetic acid, formic acid, and ethanol/water.[15,21]
(21) (a) Shriner, V. J., Jr.; Tai, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 436. (b) Paradisi, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1985**, *107*, 8223.
(22) Salt solutions were prepared by the addition of the requisite amount of Na_2CO_3 to the solvent (25/75 acetic acid–formic acid).
(23) Swain has recently shown that hydrogen-bonding acidity of a solvent parallels an anion-solvating parameter such as Y; see ref 3b.
(24) (a) Kevill, D. N.; Anderson, S. W. *J. Org. Chem.* **1985**, *50*, 3330. (b) Bentley, T. W.; Roberts, K. *J. Org. Chem.* **1985**, *50*, 4821. (c) For a set of Y_{OTf} values based on 7-norbornyl triflate, see: Creary, X.; McDonald, S. R. *J. Org. Chem.* **1985**, *50*, 474.
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(27) Raber, D. J.; Bingham, R. C.; Harris, J. M.; Fry, J. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 5977.
(28) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846.
(29) Attempts to correlate the rates of solvolysis of triflate esters against Y values have met with varying success: see ref 24.
(30) Calculated from the equation $k_t = k_t^0[1 + b(\text{salt})]$: see ref 14.

Table II. Solvolysis Rate Constants of *tert*-Butyl(trifluoromethyl)carbinyl Sulfonates in the Presence of Salts

compd	solvent,[a]	temp, °C	10^2[ester]	salt	10^2[salt]	k,[b] s^{-1}	b value[c]
6-OBs	25A–F	45.0	2.0	none		$(1.2 \pm 0.5) \times 10^{-7}$	
	25A–F	45.0[d]	2.0	HCO_2Na	2.0	$(2.2 \pm 0.2) \times 10^{-7}$	
	25A–F	45.0[d]	2.0	HCO_2Na	3.0	$(2.5 \pm 0.2) \times 10^{-7}$	
6-OTf	25A–F	65.0	1.0	none		$(2.0 \pm 0.1) \times 10^{-7}$	
	25A–F	65.0[e]	1.0	HCO_2Na	2.0	$(2.1 \pm 0.2) \times 10^{-7}$	
	25A–F	65.0[e]	1.0	HCO_2Na	3.0	$(2.2 \pm 0.5) \times 10^{-7}$	3
	70E–W	65.0	1.0	none		$(1.4 \pm 0.4) \times 10^{-7}$	
	70E–W	65.0[f]	1.0	NaN_3	1.0	$(1.5 \pm 0.4) \times 10^{-7}$	
	70E–W	65.0[f]	1.0	NaN_3	2.0	$(1.5 \pm 0.4) \times 10^{-7}$	5
	50E–W	45.0	1.0	none		$(3.69 \pm 0.05) \times 10^{-8}$	
	50E–W	45.0	1.0	NaN_3	1.0	$(3.70 \pm 0.05) \times 10^{-8}$	

[a] Percent by volume. For example, 25A–F means 25 volumes of acetic acid plus 75 volumes of formic acid, both at 25 °C before mixing; 70E–W means 70 volumes of ethanol plus 30 volumes of water, both at 25 °C before mixing. [b] Errors reported as one standard deviation from the mean. [c] Calculated from the equation $k_t \equiv k_c^\circ$ [1 + b(salt)]: see ref 14. [d] Conversion up to which reactions of 6-OBs in salt solutions of 25A–F followed first-order rate law is 40%. [e] Conversion up to which reactions of 6-OTf in salt solutions of 25A–F followed first-order rate law is 40%. [f] Conversion up to which reactions of 6-OTf in salt solutions of 70E–W followed first-order rate law is 20%.

Table III. Solvolysis Rates ($-\log k_t$)[a] and Y_{OTf} Values Used in Solvent LFE Analyses

	solvent[b]												
compd[c] or Y	100E–W	90E–W	80E–W	70E–W	60E–W	50E–W	40E–W	100A–F	75A–F	65A–F	50A–F	25A–F	0A–F
neophyl-OTs[d,e] (**2**)	8.12	7.45	7.10	6.70	6.49	6.23	5.72	7.60	6.40	6.08	5.87	5.32	4.94
pin-OBs[d,e] (**1**)	6.68	5.71	5.20	4.74	4.37	4.00	3.37	6.16	4.85		4.10	3.53	3.07
t-BuEtCar-OBs[e] (**4a**)	5.94	5.08	4.54	4.08	3.84	3.52	2.89	5.38	4.11	3.78	3.40		2.46
t-Bu-*i*-PrCar-OBs[e] (**4b**)	6.15	5.34	4.92	4.41	4.10	3.76	3.29	5.74	4.46		3.89		2.77
di-*t*-BuCar-OTs[e] (**4c**)		5.16	4.67[f]	4.17	3.77	3.48		5.26[f]	3.64				1.93[f]
t-$BuCF_3$Car-OBs[e] (**6-OBs**)								9.50[g]	8.28	8.00	7.80	7.30	7.00
t-$BuCF_3$CAR-OTf[h]	7.80[i]		7.05	6.85	6.64	6.35		7.70	7.10		6.85	6.70	6.52
Y_{OTf}[j]	−1.76		0.00	0.53	0.94			−1.66					1.49[k]

[a] In s^{-1}. [b] E–W series = aqueous ethanol mixtures; A–F series = acetic acid–formic acid mixtures. For example, 90E–W means 90 volumes of ethanol plus 10 volumes of water, both at 25 °C before mixing; 75A–F means 75 volumes of acetic acid plus 25 volumes of formic acid, both at 25 °C before mixing. [c] Neophyl = 2-methyl-2-phenyl-1-propyl, pin = pinacolyl, *t*-BuEtCar = *tert*-butylethylcarbinyl, *t*-Bu-*i*-PrCar = *tert*-butylisopropyl, di-*t*-BuCar = di-*tert*-butylcarbinyl, *t*-$BuCF_3$Car = *tert*-butyl(trifluoromethyl)carbinyl. [d] Taken from Table II, ref 1f. [e] At 25 °C. [f] Reference 46. [g] Calculated from data at higher temperatures. [h] At 65 °C. [i] Obtained from a plot of log k_t(6-OTf) vs. log k_t(neophyl-OTs) for E–W series solvents. [j] Reference 24a. [k] Reference 24c.

Table IV. Summary of Solvent Parameters Derived from Correlation Equations[a]

compd	solvent[b]	b values[c]	r	$[k_{EW}/k_{50AF}]_Y$[d]	m values[e]	r
1[f]	EW	1.38 ± 0.02	0.99+		0.73 ± 0.01	0.99+
	AF	1.17 ± 0.03	0.99+	4.2	0.83 ± 0.01	0.99+
4a	EW	1.27 ± 0.02	0.99+		0.70 ± 0.03	0.99+
	AF	1.11 ± 0.03	0.99+	2.5	0.80 ± 0.05	0.99+
4b	EW	1.22 ± 0.03	0.99+		0.67 ± 0.02	0.99+
	AF	1.11 ± 0.03	0.99+	2.2	0.80 ± 0.04	0.99+
4c	EW+AF	1.28 ± 0.03	0.99+	1.0	0.78 ± 0.16	0.89
6-OBs	AF	0.94 ± 0.02	0.99+			
6-OTf	EW+AF	0.37 ± 0.14	0.71		0.33 ± 0.02	0.99
	EW+AF	0.40 ± 0.01[g]	0.99+			
	EW+AF	0.29 ± 0.07[h]	0.84			

[a] Errors reported as standard error of the gression coefficient. [b] EW = aqueous ethanol series; AF = acetic acid–formic acid series. [c] Calculated from rate data listed in Table III by the method of least squares, using the equation $\log k_t = b \log k_{\text{neophyl-OTs}} + c$. [d] Calculated from data taken from plots of log k_t vs log $k_{\text{neophyl-OTs}}$; k_{50AF} taken from A–F correlation line at 50% A–F point, and k_{EW} taken from the vertical intersect on the E–W correlation line from that point. [e] Calculated by use of eq 3: $\log k_t = mY + \log k_0$. [f] Taken from Table IV of ref 1f. [g] Calculated by use of eq 2: $\log k_t = mY_{OTf} + \log k_0$. [h] Calculated by use of equation $\log k_t = mY_{OTs} + \log k_0$.

crease (7% to 10%, cf. Table II) in rate is observed.

Taken in total, the above evidence firmly establishes that the solvent-effect response of pinacolyl substrates can be modified by deactivation to parallel that of another generally accepted model for rate-limiting ionization processes[31] —the corresponding 2-adamantyl sulfonate—which due to steric hindrance[32] should also show little sensitivity to what Parker[3c] and Swain[3b] call the cation solvating power of the solvent. Moreover, the evidence further strengthens our proposal[1f] that the difference in solvent-effect response between pinacolyl brosylate (**1**) and neophyl tosylate (**2**) can be attributed to the greater importance of electrostatic solvation of the forming carbocation from **1** than from **2**.

Conclusion

A dispersion of solvolysis rate constants for pinacolyl brosylate against log $k_{\text{neophyl-OTs}}$ into two correlation lines does not appear to be caused by nucleophilic solvent as-

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(32) It is generally thought that the cage structure of the 2-adamantyl system prevents back-side nucleophilic solvent attack.[33-35]

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sistance. A linear correlation with log $k_{\text{neophyl-OTs}}$ can be obtained by replacing the α-methyl group of pinacolyl tosylate with a *tert*-butyl group. Similarly, a linear correlation with Y_{OTf} values can be obtained by replacing the α-methyl group of pinacolyl triflate with a trifluoromethyl group. These two findings establish the importance of "cation solvation" in the solvolysis reactions of pinacolyl substrates. Moreover, by accounting for the above-described dispersion phenomenon, these results support a recent study[1d-f] in which a similar interpretation was deduced from solvent LFE correlations for the solvolysis reactions of cyclopropylcarbinyl, cyclobutylcarbinyl, and *exo*-2-norbornyl arenesulfonates.

Experimental Section

All melting points and boiling points are uncorrected for stem exposure. Melting points were determined on a Thomas-Hoover capillary melting point apparatus. Infrared spectra were obtained on a Bausch & Lomb Shimadzu Spectronic 270 IR spectrometer using neat samples. Vapor-phase chromatograms were obtained on a Hewlett-Packard 5700A gas chromatograph using a 6-ft column packed with either 10% OV-1 (100% methyl silicon) or 10% diethylene glycol succinate on 80/100 (mesh) W-HP (Johns-Manville Chromosorb). Proton magnetic resonance spectra were obtained on a Hitachi Perkin-Elmer R-24 high resolution NMR spectrometer. All microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

***tert*-Butylethylcarbinol (3a).** The general procedure of Buhler[36] for the reaction of alkyllithiums with aldehydes was used to prepare **3a**. Thus *tert*-butyllithium (125 mL, 200 mmol, 1.6 M in pentane) was syringed under a nitrogen atmosphere in a glovebox into a 500-mL, three-necked, round-bottomed flask equipped with a gas inlet tube, a 250-mL addition funnel, a mechanical stirrer, a thermometer, and a West condenser capped with a calcium chloride drying tube. The flask was removed from the glovebox and then under a nitroen atmosphere was cooled to −78 °C by means of a dry ice–acetone bath. To the stirred solution was added dropwise 15 mL (200 mmol) of propionaldehyde in 150 mL of anhydrous ether[37] over a period of 50 min, while maintaining a temperature of −10 to −5 °C. The stirred reaction mixture was allowed to warm to room temperature over a period of 20 min; then the organic salt was hydrolyzed by the addition of 125 mL of 15% aqueous K_2CO_3 over a 10-min period, while maintaining a temperature of 3 to 6 °C. After the mixture was stirred an additional 10 min at room temperature, the aqueous phase was separated and extracted once with 100 mL of ether. The combined organic phases were dried over anhydrous $MgSO_4$ and most of the ether was removed by simple distillation. The residue was distilled at 10 mmHg to yield 20 g (86%) of the alcohol: bp 136 °C (lit.[38] bp 136 °C/10 mm); IR (neat) 3420, 2965, 2880, 1475, 1360, 1309, 1098, 1055, 969 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 0.9 (9 H, s), 0.9 (3 H, t), 1.4 (2 H, m), 3.1 (1 H, t). Its phenylurethane was recrystallized from hexane, mp 83.5–84.5 °C (lit.[39] mp 83 °C).

***tert*-Butylisopropylcarbinol (3b).** The procedure described for the preparation of **3a** was used to prepare *tert*-butylisopropylcarbinol in 71% yield: bp 151 °C (lit.[38] bp 150.9–151.1 °C); IR (neat) 3480, 2955, 2870, 1482, 1472, 1392, 1369, 1118, 1033, 986, 972 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 0.95 (6 H, d), 0.95 (9 H, s), 1.9 (1 H, m), 3.1 (1 H, d). Its phenylurethane was crystallized from hexane, mp 88.0–89.0 °C (lit.[40] mp 89 °C).

Di-*tert*-butylcarbinol (3c). The procedure described for the preparation of **3a** was used to prepare di-*tert*-butylcarbinol in 70% yield: mp 49–50 °C (lit.[41] mp 50 °C); IR (neat) 3490, 2910, 1470, 1380, 1270, 1240, 1180, 1040, 980, 850, 750 cm^{-1}. Its phenylurethane was crystallized from hexane, mp 121–122 °C (lit.[41] mp 121–122 °C).

Trifluoroacetamide. This compound was prepared in 83% yield by the method of Swarts.[42] Accordingly, a cold solution of 114.5 g (810 mmol) of ethyl trifluoroacetate in 100 mL of anhydrous ether[37] was treated with ammonia over a 90-min period. After an additional hour at room temperature, the organic phase was separated and dried over anhydrous $MgSO_4$, and most of the ether was removed by simple distillation. The residue was fractionally distilled to yield 75.5 g of product. Recrystallization once from $CHCl_3$ gave the purified amide: mp 73.5–74.5 °C (lit.[42] mp 74.8 °C).

***tert*-Butyl Trifluoromethyl Ketone.** This compound was prepared in 71% yield by the methods of Gilman[43] and Mosher.[44] Thus a 2-L three-necked, round-bottomed flask was equipped with a condenser connected to a series of traps: first, an ice–salt trap; next, a dry ice–acetone trap; finally, another dry ice–acetone trap. The flask was charged with 73.5 g (650 mmol) of trifluoroacetamide and 173 g (1.22 mol) of phosphorus pentoxide. After heating the flask at 145–150 °C for 3 h, 43.7 g (71%) of trifluoroacetonitrile was collected in the dry ice–acetone traps. The trapped trifluoroacetonitrile (43.7 g, 460 mmol) was poured into a 500-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, an addition funnel, and a condenser capped with a calcium chloride drying tube, containing 190 mL of anhydrous ether,[37] and cooled to about −78 °C by means of a dry ice–acetone bath. While maintaining a nitrogen blanket, *tert*-butylmagnesium chloride (230 mL, 460 mmol, 2.0 M in ether) was added to the stirred solution over a 22-min period, followed by the addition of 0.7 g of cuprous chloride. The resulting mixture was stirred at −78 °C for 2 h and then for 9 h at room temperature. After the usual workup, the mixture was distilled at atmospheric pressure to yield 7.4 g of a fraction boiling at 56 to 78 °C (identified as the ketone by infrared and by its 2,4-DNP derivative) and a fraction boiling at 88–110 °C (identified as the carbinol by infrared).

***tert*-Butyl(trifluoromethyl)carbinol (5). Method A.** The procedure of Mosher[44] was used to prepare **5** from *tert*-butyl trifluoromethyl ketone in 67% yield. **Method B.** Ethyl trifluoroacetate (26.8 mL, 32 g, 225 mmol) was added to 200 mL of anhydrous ether[37] in a 500-mL three-necked, round-bottomed flask equipped with two Claisen adapters, a gas inlet tube, a thermometer, a 125-mL addition funnel, a mechanical stirrer, and a West condenser capped with a calcium chloride drying tube. While maintaining a nitrogen blanket and a temperature of 25 °C, *tert*-butylmagnesium chloride (200 mL, 400 mmol, 2.0 M in ether) was added with stirring over a 35-min period. During the addition the reaction mixture turned a deep purple. The mixture was stirred for an additional 40 min at 20–25 °C. Then 50 mL of cold water was added slowly to the stirred mixture followed by the addition of 125 mL of 6.0 N hydrochloric acid while still maintaining a temperature of 20–25 °C. After the aqueous and organic phases were separated, the aqueous phase was extracted once with 30 mL of ether and the combined ether layers dried over K_2CO_3/$MgSO_4$ for 1 h. Distillation at 10 mmHg yielded 17.8 g (51%) of a fraction boiling at 102–106 °C. This fraction was dissolved in 30 mL of petroleum ether (bp 30–60 °C) and the solution chilled in a dry ice–acetone bath at −78 °C. The mother liquor was then decanted from the precipitate to yield 13.5 g (38%) of *tert*-butyl(trifluoromethyl)carbinol (**5**): n^{24}_D 1.3670 (lit.[44] n^{24}_D 1.3668); IR (neat) 3475, 3000, 1492, 1376, 1281, 1171, 1126, 1039, 933, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 1.1 (9 H, s), 2.1 (1 H, s), 3.6 (1 H, q).

***tert*-Butylethylcarbinyl Brosylate (4a). Method A.**[45] Methyllithium (12 mL, 15 mmol, 1.4 M in ether) was syringed into a 250-mL, three-necked, round-bottomed flask under a nitrogen blanket and equipped with a gas inlet tube, a 125-mL addition funnel, a magnetic stirring bar, and a West condenser capped with a calcium chloride drying tube. The flask was then cooled to 5 °C by means of an ice–water bath. To the stirred solution was added dropwise a solution of 1.74 g (15 mmol) of *tert*-butylethylcarbinol in 25 mL of anhydrous ether[37] over a

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15-min period, while maintaining a temperature of 5 to 10 °C. The reaction mixture was stirred at 0 °C for an additional 30 min. Then, while maintaining a temperature of 5 to 10 °C, a solution of 5.44 g (15 mmol) of *p*-bromobenzenesulfonyl chloride in 40 mL of anhydrous ether[37] was added dropwise over a 15-min period. After the mixture was stirred an additional 24 h at room temperaure, the lithium chloride was removed by filtration through a sintered glass funnel. The filtrate was treated twice with saturated aqueous sodium bicarbonate and dried over 3A molecular sieves, and the ether was removed by rotovaporization. The crude product was recrystallized from petroleum ether (bp 30–60 °C) to yield 4.3 g (87%) of the brosylate **4a**: mp 39.5–40.0 °C; ^{1}H NMR ($CDCl_3/Me_4Si$) δ 0.9 (9 H, s), 0.9 (3 H, t), 1.6 (2 H, m), 4.4 (1 H, t), 7.7 (4 H, d). Anal. Calcd for $C_{13}H_{19}BrO_3S$: C, 46.57; H, 5.71; Br, 23.83. Found: C, 46.37; H, 5.60; Br, 23.75.

Method B.[1f] Pyridine (25 mL, redistilled) was added to a 125-mL Erlenmeyer flask charged with *tert*-butylethylcarbinol (2.32 g, 20 mmol), while maintaining a temperature at 5 to 10 °C by means of an ice–water bath. To the cold solution was then added 7.25 g (20 mmol) of *p*-bromobenzenesulfonyl chloride. After being allowed to stand 72 h at 5–10 °C, the mixture was hydrolyzed at 5 to 10 °C by the slow addition of 20 mL of cold water, followed by the addition of sufficient cold, dilute aqueous HCl to acidify the mixture. The precipitated ester was collected on a Buchner funnel and after air drying yielded 5.0 g (75%) of the brosylate. Recrystallization from 35 mL of hot petroleum ether (bp 30–60 °C) gave 3.5 g (50%) of the brosylate **4a**: mp 39.5–40.0 °C.

***tert*-Butylisopropylcarbinyl Brosylate (4b). Method A.** The procedure used by Brown[45] for the preparation of various benzyl tosylates was used to prepare *tert*-butylisopropylcarbinyl brosylate in 10% yield. Recrystallization from hot petroleum ether (bp 30–60 °C) gave an analytical sample: mp 72.0–72.5 °C; ^{1}H NMR ($CDCl_3/Me_4Si$) δ 0.9 (9 H, s) 1.0 (6 H, d), 7.7 (4 H, d). Anal. Calcd for $C_{14}H_{21}BrO_3S$: C, 48.14; H, 6.06; Br, 22.88. Found: C, 48.00; H, 5.98; Br, 22.86. **Method B**: The procedure used by Roberts[1f] for the preparation of various alkyl arenesulfonates was used to prepare *tert*-butylisopropylcarbinyl brosylate in 85% yield: mp [after recrystallization from hot petroleum ether (bp 30–60 °C)] 72.0–72.5 °C.

Di-*tert*-butylcarbinyl Tosylate (4c). Method A. The method of Brown[45] was used to prepare di-*tert*-butylcarbinyl tosylate in 29% yield: mp (after recrystallization from hot pentane) 68–69 °C (lit.[46] mp 68–69 °C); ^{1}H NMR ($CDCl_3/Me_4Si$) δ 1.0 (18 H, s), 7.2 (4 H, s). **Method B.** The method of Roberts[1f] was used to prepare di-*tert*-butylcarbinyl tosylate in 11% yield: mp [after recrystallization from hot petroleum ether (bp 30–60 °C)] 68–69 °C.

***tert*-Butyl(trifluoromethyl)carbinyl Brosylate (6-OBs). Method A.** The method of Brown[45] was used to prepare *tert*-butyl(trifluoromethyl)carbinyl brosylate in 84% yield. Recrystallization three times from petroleum ether (bp 30–60 °C) gave an analytical sample: mp 91–92 °C; ^{1}H NMR ($CDCl_3/Me_4Si$) δ 1.1 (9 H, s), 4.8 (1 H, q), 7.7 (4 H, s). Anal. Calcd for $C_{12}H_{14}BrF_3O_3S$: C, 38.41; H, 3.76; Br, 21.30; F, 15.19; Found: C, 38.57; H, 3.98; Br, 21.34; F, 15.08. **Method B.** The method of Roberts[1f] was used to prepare *tert*-butyl(trifluoromethyl)carbinyl brosylate in 23% yield: mp [after recrystallization twice from petroleum ether (bp 30–60 °C)] 92–93 °C.

***tert*-Butyl(trifluoromethyl)carbinyl Triflate (6-OTf).** The general procedure used by Gassman[47] for the preparation of various alkyl triflates was used to prepare 6-OTf. Pyridine (15 mL, redistilled) was added to a 250-mL, three-necked, round-bottomed flask charged with *tert*-butyl(trifluoromethyl)carbinol (1.6 g, 10 mmol) under a nitrogen blanket and equipped with a gas inlet tube, a magnetic stirring bar, a 125-mL addition funnel, and a West condenser capped with a calcium chloride drying tube. After the stirred mixture was cooled to 0 °C by means of an ice–water bath, triflic anhydride (3.2 mL, 4.2 g, 15 mmol) was added over a 15-min period while maintaining a temperature of 5 to 10 °C. The mixture was stirred an additional 20 min at 5 to 10 °C, and then the deep-orange solution was kept at 5–10 °C for 4 days (after the first day, the color of the mixture changed to dark brown). Ice-cold water (20 mL) was then added to the reaction mixture, followed by extraction 4 times with 40-mL portions of ether, to destroy any unreacted anhydride. The combined ether extracts were washed with 40-mL portions of 0.1 M aqueous $KHSO_4$ until the washings remained acidic to pHydrion paper. The ether was then removed by distillation to yield 0.52 g (18%) of an oil. On the basis of titers of solvolysis reactions at 10 half-lives, the oil was shown to be 97–99% *tert*-butyl(trifluoromethyl)carbinyl triflate (6-OTf): IR (neat) 2940, 1470, 1405, 1360, 1270, 1240, 1210, 1175, 1130, 1020, 960, 935, 845 cm^{-1}; ^{1}H NMR ($CDCl_3/Me_4Si$) δ 1.1 (9 H, s), 4.8 (1 H, q).

Determination of Equilibrium Reaction between Carboxylate–Ester Product and Sulfonate–Ester Starting Material. A. Product Study in 25% Acetic–75% Formic Acid Solvent. This study was replicated three times. In a typical run, *tert*-butyl(trifluoromethyl)carbinyl brosylate (6-OBs) (0.6 g, 1.6 mmol) was dissolved in 100 mL of 25/75 (v/v) acetic–formic acid solvent. The solution was placed in a constant-temperature bath at 45 °C for 57 days. Then it was poured into 500 mL of water, the aqueous phase was extracted 5 times with 100-mL portions of ether, and the combined ether extracts were treated with powdered $NaHCO_3$ until there was no evidence of CO_2 evolution. The ether phase was then separated, dried over K_2CO_3, and concentrated on a rotovaporizer, and the remaining ether was removed by distillation to yield 0.54 g (90%) of 6-OBs. Identification was established by spectroscopy: ^{1}H NMR ($CDCl_3/Me_4Si$) δ 1.1 (9 H, s), 4.8 (1 H, q), 7.7 (4 H, s).

B. Equilibrium Reaction of *tert*-Butyl(trifluoromethyl)carbinyl Acetate with *p*-Bromobenzenesulfonic Acid in 25% Acetic–75% Formic Acid Solvent. To a 25-mL solution of *tert*-butyl(trifluoromethyl)carbinyl acetate[48] (49.3 mg, 0.25 mmol) in 25/75 (v/v) acetic–formic acid solvent was added 59.3 mg (0.25 mmol) of *p*-bromobenzenesulfonic acid. The mixture was placed in a constant-temperature bath at 65 °C for 105 days. Periodically, 2-mL aliquots were removed from the mixture and titrated with standardized base (0.02 N NaOAc in AcOH) to a bromophenol blue endpoint. After 35 days, 40% of the sulfonic acid had been consumed, an amount which remained unchanged after an additional 70 days in the bath. Workup[50] of the last 5 mL of the mixture yielded a small amount of residue which was identified by ^{1}H NMR as *tert*-butyl(trifluoromethyl)carbinyl brosylate (6-OBs).

Product Study of *tert*-Butyl(trifluoromethyl)carbinyl Triflate in 25/75 (v/v) Acetic–Formic Acid. *tert*-Butyl(trifluoromethyl)carbinyl triflate (288 mg, 1.0 mmole) was dissolved in sufficient 25/75 (v/v) acetic–formic acid solvent to give a 10-mL solution. To the mixture was added 64 mg (1.2 mequiv, 0.6 mmol) of Na_2CO_3. The resulting mixture was placed in a constant-temperature bath at 65 °C. After 2.5 half-lives (59 days), the mixture was removed from the bath, diluted with 3 mL of $CDCl_3$ and 3 mL of water, and treated with $NaHCO_3$ until there was no evidence of CO_2 evolution. The organic layer was then separated and dried over $Na_2CO_3/MgSO_4$. Most of the solvent was removed by distillation. The ^{1}H NMR spectrum of this liquid was relatively uncomplicated. With use of the chemical shifts of known structures,[51] characteristic resonance frequencies in the spectrum were assigned as follows: δ 1.05 (s), $C(CH_3)_3$; 1.45 (s), $HCO_2C(CH_3)_2$; 1.45 (d), CF_3CHCH_3; 4.8 (m), CF_3CHCH_3; 7.9 (s), HCO_2C. By analysis of the integration, we estimate that **7a** is about 75% of the product mixture and unreacted starting material (6-OTf) most of the remainder.

Product Study of *tert*-Butyl(trifluoromethyl)carbinyl Triflate in 80% Aqueous Ethanol. *tert*-Butyl(trifluoromethyl)carbinyl triflate (288 mg, 1.0 mmol) was dissolved in sufficient 80% aqueous ethanol solvent to give a 25-mL solution. The mixture was placed in a constant-temperature bath at 65 °C for 174 days. The mixture was then removed from the bath,

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(50) Used same workup procedure as described in part A.

(51) The deshielding constant for a β-formate group varies from δ 0.4 to 0.6; the deshielding constant for a β-trifluoromethyl group varies from δ 0.4 to 0.6.

diluted with 150 mL of water, and extracted 5 times with 15-mL portions of methylene chloride. The combined extracts were dried over a mixture of Na_2SO_4–$NaHCO_3$, and most of the solvent was removed by distillation to yield 0.1 g (30%) of residue. The residue on analysis by gas chromatography (6 ft × $^1/_8$ in., 15% DEGS on 80/100 Chrom WHP column, 75 °C, 38 mL/min He flow rate) in addition to the solvent peak gave rise to one minor peak, A (t_R 1.9 min), and two major peaks, B (t_R 2.9 min) and C (t_R 3.5 min) with 1.0:1.3 relative peak areas. On the basis of retention times, as compared to known samples, peak B was identified as ethyl 2-methyl-3-(trifluoromethyl)butyl ether and peak C was identified as 2-methyl-3-(trifluoromethyl)-2-butanol.

Solvents. Acetic acid solvent was prepared from 994.9 mL of glacial acetic acid (J. T. Baker Chemical Company) and 5.1 mL of acetic anhydride. Formic acid solvent was prepared by storing practical grade formic acid (Matheson, Coleman, & Bell, 97–100%) over boric anhydride for several days, decanting, and distilling from fresh anhydride. Ethanol solvent was prepared according to the method of Fieser.[52] The water solvent was purified by passage through a mixed bed deionizer to produce water of 17 μΩ or better quality.

Rate Measurements. The rates of solvolysis were followed titrimetrically. In a typical run, the requisite amount of sulfonate ester was accurately weighed into a 25-mL volumetric flask and then sufficient solvent was added rapidly to give a 25-mL reaction solution volume.[53] Reaction time commenced with the addition of the solvent. At appropriate times, 2-mL aliquots were analyzed for liberated sulfonic acid. The titrating solutions were as follows: for acetic–formic acid solvents, 0.02 N sodium acetate in acetic acid; and for the aqueous ethanol solvents, 0.02 N sodium methoxide in methanol. The indicators used were as follows: for acetic–formic acid solvents, bromophenol blue in acetic acid (2–3 drops); for aqueous ethanol solvents, bromothymol blue in water (2 drops).

Treatment of Kinetic Data. First-order rate constants were calculated by using the integrated first-order rate equation[54,55]

$$k_t = 1/t \ln (mL_\infty/mL_\infty - mL_t)$$

Multiple determinations (6–12) were made for each kinetic run. The slope values recorded in Table IV were obtained by regression analysis[56] of log k_t(Y) versus: log k_t(neophyl-OTs) values,[1f] Y_{OTf} values,[24] Winstein–Grunwald Y values,[18] and Y_{OTs} values[57] as indicated in the table.

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(53) For reactions whose half-lives were longer than a few weeks, rate measurements were accomplished by the ampule technique.[1f]

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Ion Pairing and Reactivity of the Alkali-Metal and Alkaline-Earth-Metal Derivatives of Ethyl (5-Bromopentyl)acetoacetate

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The effect of added alkali-metal and alkaline-earth-metal salts on the rate of intramolecular alkylation of the title compound has been investigated in 99% aqueous Me_2SO. It was found that the rate is practically insensitive to Et_4N^+ and K^+ ions and it is slightly decreased by Na^+ ion, but it is strongly depressed by Li^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, and Mg^{2+} ions, the observed effects ranging over nearly 5 powers of ten. Analysis of rate data was carried out by means of a self-consistent approach, as based on the classical Acree hypothesis of independent contributions of free ions and ion pairs to the overall rate. In most cases it was possible to measure the ion pairing association constants (K_{ip}) together with the specific rates for reactions of the ion pairs (k_{ip}), even when the latter are much lower than the specific rate for reaction of the free ion (k_i). The results show that ion pairing decreases in the order Li > Na > K and Mg > Ca > Sr > Ba, which clearly suggests that association is dominated by coulombic interactions. The strong inhibition caused by ion pairing is due to a greater cation interaction with the anionic reactant than with the transition state, where a significant fraction of the available negative charge is concentrated in the C–C bond-forming region.

It has been recognized for many years that cation association may greatly affect the reactivities of anionic nucleophiles such as alkoxides, aryloxides, and enolates in nucleophilic substitution and addition reactions.[1-3] It is worth noting, however, that knowledge in the field is mainly based on evidence which is qualitative in nature, or semiquantitative at best. Relatively few quantitative studies have been reported in recent years.[4-9] It has been

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