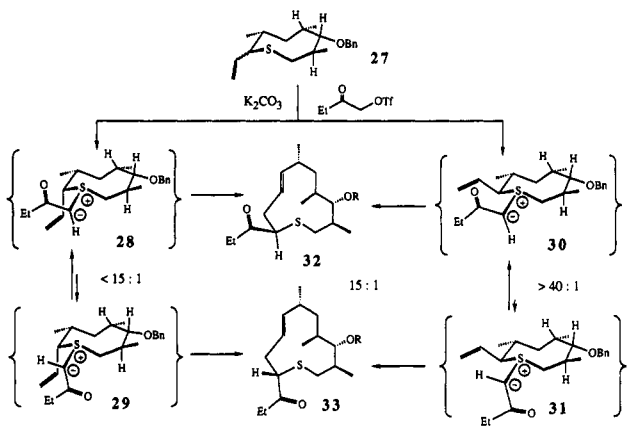
Scheme III



Vedejs et al. can also be rationalized.[2] As shown in Scheme III, Vedejs et al. observed that the α-monosubstituted ylides derived from a 1:1 mixture of diastereomers (27) gave 32 and 33 in a ratio of 15:1. Significantly higher stereoselectivity (>40:1, 32:33) was observed with one of the separated isomers.[20] Vedejs et al. proposed that the isomer corresponding to 30 is responsible for the high >40:1 preference for 32. This means that the stereoselectivity derived from 28 and 29 is less than 15:1. This is consistent with our findings. Structures 28 and 30 are more stable than 29 and 31, respectively, because the α-propanoyl group is anti to the S-CH_2 to minimize steric interactions. The structure 30 is further favored by having an endo propanoyl group, while 28 is disfavored by having an exo propanoyl group.

In summary, the transition structures for [2,3]-sigmatropic rearrangements of sulfur ylides correspond to concerted reaction pathways. The forming C---C bond is formed to a small extent, indicating a very asynchronous transition structure. Ylide-stabilizing substituents such as the formyl group make the transition structure more advanced along the reaction coordinate. There is a general tendency for the two partially formed bonds to be eclipsed, which promotes maximal orbital overlap at both termini of the allyl fragment; this tendency is stronger with ylide-stabilizing substituents. The sulfur lone pair prefers to be exo with respect to the allyl moiety; methyl and formyl substituents at the anionic center favor the exo and endo orientations, respectively. The formation of the *Z* ring expansion product from a five-membered ylide is favored to minimize ring strain in the five-membered ring. The formation of the *E* product from a six-membered ylide benefits from ring strain and sulfur lone-pair orientation effects.

Acknowledgment. We are grateful to the National Institutes of Health for financial support of this research and to Professor Edwin Vedejs for helpful comments. This work was supported in part by a grant of computer time made possible under a joint study with the IBM Corporation on the IBM 3090/600J Supercomputer at the UCLA Office of Academic Computing.

Registry No. 1a, 10152-76-8; 1b, 5296-62-8; 1c, 120983-16-6; 1d, 135285-63-1.

(20) The reasoning for conformation of the eight-membered ring and the equatorial alkylation of 27 can be found in ref 2.

Electron-Donating Ability of the Cyclopropyl Substituent in the Solvolyses of an α-CF_3-Substituted Secondary-Alkyl Tosylate

Donald D. Roberts

Department of Chemistry, Louisiana Tech University, Ruston, Louisiana 71272

Received May 10, 1991

The solvolysis rates of cyclopropyl(trifluoromethyl)carbinyl tosylate (1) have been determined in a series of aqueous alcohol, aqueous trifluoroethanol, and carboxylic acid solvents. Analysis of the rate data for % internal-return isomerization and salt effects and correlation with Y_{OTs} values indicates that 1 underwent solvolysis by the k_Δ pathway. Comparison of the relative ability [k(c-Pr)/k(Ph)] of cyclopropyl and phenyl groups to stabilize carbocation-like transition states in solvolysis reactions of the secondary systems RCH(Y)CH_3 and RCH(Y)CF_3 reveals that replacement of phenyl with cyclopropyl increases the rate in both systems by a factor of 10^2.

Introduction

The unusual electron-donating ability of the cyclopropyl group to an adjacent electron-deficient center is well-known.[1,2] In solvolysis reactions, the rate enhancements observed for a cyclopropyl substituent at the α position have been used in support of a mechanism involving neighboring-group participation by the three-membered ring.[3,4] In earlier papers from this laboratory,[5] we measured, in a wide range of solvents, the response of the cyclopropyl substituent effect to solvent ionizing power. The results clearly supported the contention that cyclopropylcarbinyl sulfonates undergo solvolysis by a k_Δ pathway. As an extension of our study of the substituent effect–solvent response relationship, we became interested

(1) For recent reviews, see: (a) de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809-826. (b) Tidwell, T. T. In *The Chemistry of The Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; Part 1, Chapter 10.

(2) (a) Brown, H. C.; Peters, E. N. *J. Am. Chem. Soc.* **1973**, *95*, 2400-2401 and references cited therein. (b) Allen, A. D.; Gong, L.; Tidwell, T. T. *J. Am. Chem. Soc.* **1990**, *112*, 6396-6397.

(3) For a review, see: (a) Richey, H. G., Jr. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 25. (b) Wiberg, K. B.; Hess, B. A., Jr.; Ashe, A. J., In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 26.

(4) Roberts, D. D.; Snyder, R. C., Jr. *J. Org. Chem.* **1979**, *44*, 2860-2863 and references cited therein.

(5) (a) Roberts, D. D. *J. Org. Chem.* **1964**, *29*, 294-297. (b) Roberts, D. D.; Watson, T. M. *J. Org. Chem.* **1970**, *35*, 978-981. (c) Roberts, D. D. *J. Org. Chem.* **1970**, *35*, 4059-4062. (d) Roberts, D. D. *J. Org. Chem.* **1984**, *49*, 2521-2526.

0022-3263/91/1956-5661$02.50/0

Table I. Solvolysis Rate Constants Determined in This Study

compd[a]	solvent	T, °C	k,[b] s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
c-PrCH(OTs)CF_3	EtOH	50.0	$(2.10 \pm 0.05) \times 10^{-8}$	25.8 (±0.2)	−14.0 (±0.4)
		70.0	$(2.4 \pm 0.1) \times 10^{-7}$		
		85.0	$(1.17 \pm 0.02) \times 10^{-6}$		
	80E–W[c]	35.0	$(7.8 \pm 0.2) \times 10^{-8}$	25.5 (±0.3)	−11.5 (±0.5)
		40.0	$(1.48 \pm 0.05) \times 10^{-7}$		
		50.0	$(4.8 \pm 0.09) \times 10^{-7}$		
		85.0	$(2.30 \pm 0.03) \times 10^{-5}$		
	60E–W[c]	35.0	$(3.99 \pm 0.07) \times 10^{-7}$	25.5 (±0.2)	−5.3 (±0.3)
		40.0	$(7.60 \pm 0.07) \times 10^{-7}$		
		50.0	$(2.80 \pm 0.02) \times 10^{-6}$		
		70.0	$(3.16 \pm 0.01) \times 10^{-5}$		
	97TFE[d]	35.0	$(3.10 \pm 0.04) \times 10^{-7}$	21.9 (±0.1)	−17.3 (±0.2)
		40.0	$(5.70 \pm 0.02) \times 10^{-7}$		
		50.0	$(1.70 \pm 0.05) \times 10^{-6}$		
		60.0	$(5.04 \pm 0.06) \times 10^{-6}$		
		70.0	$(1.32 \pm 0.02) \times 10^{-5}$		
	70TFE[d]	35.0	$(5.06 \pm 0.06) \times 10^{-7}$	26.7 (±0.1)	−0.7 (±0.1)
		40.0	$(1.09 \pm 0.05) \times 10^{-6}$		
		50.0	$(3.9 \pm 0.1) \times 10^{-6}$		
		60.0	$(1.46 \pm 0.04) \times 10^{-5}$		
		85.0	$(2.60 \pm 0.03) \times 10^{-4}$		
	AcOH	40.0	$(5.8 \pm 0.1) \times 10^{-8}$	23.8 (±0.1)	−15.7 (±0.2)
		50.0	$(2.0 \pm 0.1) \times 10^{-7}$		
		60.0	$(6.4 \pm 0.1) \times 10^{-7}$		
		70.0	$(1.79 \pm 0.05) \times 10^{-6}$		
	50A-F[c]	35.0	$(2.4 \pm 0.1) \times 10^{-6}$	21.3 (±0.2)	−15.1 (±0.4)
		40.0	$(4.2 \pm 0.1) \times 10^{-6}$		
		50.0	$(1.28 \pm 0.02) \times 10^{-5}$		
	HCOOH	35.0	$(3.00 \pm 0.03) \times 10^{-5}$	23.0 (±0.2)	−4.7 (±0.4)
		40.0	$(6.00 \pm 0.03) \times 10^{-5}$		
		50.0	$(1.92 \pm 0.04) \times 10^{-4}$		
		60.0	$(5.50 \pm 0.05) \times 10^{-4}$		
neophyl tosylate	97TFE[d]	35.0	$(1.31 \pm 0.02) \times 10^{-5}$	19.4 (±0.4)	−18.1 (±0.6)
		40.0	$(2.15 \pm 0.03) \times 10^{-6}$		
		50.0	$(5.3 \pm 0.1) \times 10^{-5}$		
		60.0	$(1.56 \pm 0.02) \times 10^{-4}$		
	70TFE[d]	35.0	$(9.46 \pm 0.3) \times 10^{-6}$	22.3 (±0.1)	−9.1 (±0.3)
		40.0	$(1.64 \pm 0.05) \times 10^{-5}$		
		50.0	$(5.25 \pm 0.04) \times 10^{-5}$		
		60.0	$(1.56 \pm 0.01) \times 10^{-4}$		

[a] c-PrCH(OTs)CF_3 = cyclopropyl(trifluoromethyl)carbinyl tosylate. [b] Errors reported as one standard deviation from the mean. [c] Percent by volume. For example, 80E–W means 80 volumes of ethanol plus 10 volumes of water, both at 25 °C before mixing. [d] Percent by weight. For example, 97TFE means 97 g of trifluoroethanol plus 3 g of water.

in substrates strongly deactivated by a trifluoromethyl group at the α position. To this end, we investigated the solvolyses of *tert*-butyl(trifluoromethyl)carbinyl tosylate.[6] We found that the β-methyl substituent in this strongly deactivated pinacolyl system, in contrast to its behavior in the parent compound,[7] also responded to solvent ionizing power in a manner consistent with a k_{Δ} process. In the light of this finding and the recent interest[8-12] in solvolytic mechanisms involving electron-deficient carbocations, it occurred to us that a reaction involving such a high electron-demand species would be appropriate for furthering our study of the cyclopropyl substituent effect–solvent response relationship. Also, it would be appropriate for comparison, under high electron-demand conditions, of the relative ability of the cyclopropyl and phenyl groups to delocalize the positive charge from an electron-deficient center.[13,14] Thus, in this paper we report

Table II. % Internal-Return Isomerization[a]

solvent	compds	
	c-PrCH(OTs)CF_3	c-PrCH_2OSO_2Ar
AcOH	32[c]	51,[d] 48,[e] 50[f]
50A/F	37[g]	31[d]
HCO_2H	25[g]	28,[d] 23[e]
EtOH	0[h]	5,[d] 7,[e] 10[f]
80E–W	21[g]	20[d]
60E–W	25[g]	28[d]
97TFE	30[g]	30,[e] 32[f]
70TFE	25[g]	

[a] Calculated from the following equation: % internal-return isomerization = [100 − (mol % infinity titer[b])]. [b] Infinity titer = mole % of arylsulfonic acid liberated at 10 half-lives. [c] At 40 °C. [d] *p*-Toluenesulfonate at 20 °C, unpublished results for kinetic data contained in ref 5a,d. [e] Pentamethylbenzenesulfonate, 15–30 °C, ref 4. [f] β-Naphthalenesulfonate at 30 °C, unpublished results for kinetic data contained in ref 31. [g] At 35 °C. [h] At 50 °C.

(6) Roberts, D. D.; Hall, E. W. *J. Org. Chem.* **1988**, *53*, 2573–2579.
(7) 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*, 8147–8156 and references cited therein.
(8) For a review, see: Gassman, P. G.; Tidwell, T. T. *Acc. Chem. Res.* **1983**, *16*, 279–285.
(9) (a) Gassman, P. G.; Harrington, C. K. *J. Org. Chem.* **1984**, *49*, 2258–2273. (b) Gassman, P. G.; Harrington, C. K. *J. Org. Chem.* **1984**, *49*, 2258–2273.
(10) Richard, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 6819–6820.
(11) Liu, K.-T.; Kuo, M.-Y.; Shu, C.-F. *J. Am. Chem. Soc.* **1982**, *104*, 211–215.
(12) (a) Allen, A. D.; Jansen, M. P.; Koshy, K. M.; Mangru, N. N.; Tidwell, T. T. *J. Am. Chem. Soc.* **1982**, *104*, 207–211. (b) Allen, A. D.; Ambridge, I. C.; Che, C.; Michael, H.; Muir, R. J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1983**, *105*, 2343–2350. (c) Allen, A. D.; Kanagasabapathy, V. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1983**, *105*, 5961–5962. (d) Jansen, M. P.; Koshy, K. M.; Mangru; Tidwell, T. T. *J. Am. Chem. Soc.* **1981**, *103*, 3863–3867. (e) Allen, A. D.; Girdhar, R.; Jansen, M. P.; Mayo, J. D.; Tidwell, T. T. *J. Org. Chem.* **1986**, *51*, 1324–1329. (f) Koshy, K. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1980**, *102*, 1216–1218.
(13) For a summary and discussion of the relative electron-donating abilities of the cyclopropyl and phenyl substituents, see: Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2889–2895.

Table III. Summary of m Values Derived from the mY_{OTs} Equation

compd	m values[a]	no. of solvents	r^b
c-PrCH(OTs)CF_3 (1)	0.83[c]	6[d]	0.999
neophyl tosylate (2)	0.70[e]	13	0.996
c-PrCH$_2$OTs (3)	0.81[e]	10	0.995
c-buOBs (4)	0.80[e]	12	0.990
pinacolyl brosylate (5)	0.82[e]	9	0.995
PhCH(OTs)CF_3 (6)	0.69[f]	3	0.990
p-AnCH(OTs)CF_3 (7)	0.76[f]	9	0.993

[a] Calculated by use of eq 1: $\log k/k_0 = mY_{OTs}$. [b] Correlation coefficient for the regression analysis. [c] Calculated from rate data listed in Table I, this study. [d] Points for TFE solvents excluded (see ref 38). [e] Calculated from rate data listed in Table II, ref 5d. [f] Reference 12b.

the kinetic investigation of the solvolytic reactions of cyclopropyl(trifluoromethyl)carbinyl tosylate (1) in a series of solvents ranging in ionizing power from ethanol to formic acid.

Results and Discussion

The substrate c-PrCH(OTs)CF_3 (1) was prepared from the corresponding alcohol by reaction of CF_3CHO with c-PrMgBr. The kinetics of reaction of 1 in various solvents and of neophyl tosylate (2) in aqueous trifluoroethanol solvents were followed titrimetrically as reported in Table I. The reactions for 1 in all solvents were accompanied by internal-return isomerization[4,15,16] to less reactive, rearranged starting material,[17,18] and consequently the apparent first-order rate constants, k_t, were computed on the basis of the infinity titer.[19,20] The extent of internal-return isomerization in various solvents for 1 and its parent compound, cyclopropylcarbinyl tosylate (3), are presented in Table II. In Table III we have listed the correlation of the rate data given in Table I vs Y_{OTs} values.[21] The effects of added salt on the reactivity of 1 and 2 in both 80% aqueous ethanol and acetic acid are summarized in Table IV.

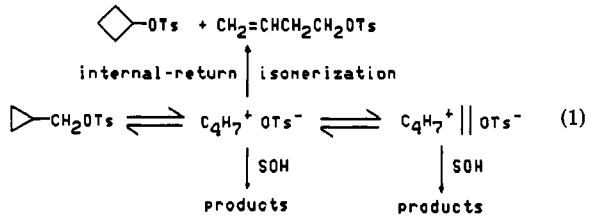
In solvolytic reactions, the presence of the trifluoromethyl substituent at the α position leads to significant rate depressions compared to hydrogen. The reported values[8,12a,d,f] of the $k(H)/k(CF_3)$ rate ratio vary from 10^{-4} to 10^{-7}, depending on solvent. Comparison of rate data given for 1, in Table I, with that previously reported[5a] for cyclopropylcarbinyl tosylate (3) permits the calculation of a $k(H)/k(CF_3)$ rate ratio of 1.06×10^{-4} at 20 °C in 80% aqueous EtOH. This value fits within the range given above. Comparison of rates for c-PrCH(OTs)CF_3 and c-PrCH(OTs)CH_3[22] gives a $k(CF_3)/k(CH_3)$ rate ratio of 2.6×10^{-8} at 20 °C in 50% aqueous EtOH. This value compares well with the $k(CF_3)/k(CH_3)$ rate ratio of 1.6×10^{-8} calculated[24] for the secondary system PhCH(OTs)R at 25 °C in 97% TFE. These results indicate that there is a high degree of destabilization of the cationic transition state by the CF_3 group in the solvolysis reactions of 1.[12d,e]

Table IV. Salt Effects on the Solvolysis of c-PrCH(OTs)CF_3 and Neophyl Tosylate at 60 °C

solvent	salt	concn (M)	k_{obsd}[a] (s^{-1})
AcOH[b]	$NaClO_4$	0.00	$(6.36 \pm 0.1) \times 10^{-7}$
		0.02	$(7.54 \pm 0.1) \times 10^{-7}$
		0.04	$(8.47 \pm 0.1) \times 10^{-7}$
		0.06	$(9.80 \pm 0.05) \times 10^{-7}$
80E-W[b]	NaN_3	0.00[d]	$(1.79 \pm 0.05) \times 10^{-6}$
		0.02[d]	$(1.89 \pm 0.03) \times 10^{-6}$
		0.04[d]	$(1.96 \pm 0.05) \times 10^{-6}$
		0.06[d]	$(2.06 \pm 0.04) \times 10^{-6}$
80E-W[c]	NaN_3	0.00[e]	$(8.39 \pm 0.05) \times 10^{-6}$
		0.02[e]	$(8.86 \pm 0.04) \times 10^{-6}$
		0.04[e]	$(9.40 \pm 0.07) \times 10^{-6}$
		0.06[e]	$(9.90 \pm 0.07) \times 10^{-6}$

[a] Errors reported as one standard deviation from the mean. [b] For c-PrCH(OTs)CF_3. [c] For neophyl tosylate. [d] Infinity titers were 81, 77, 76, and 74% of the theoretical values for 0.00, 0.02, 0.04, and 0.06 M NaN_3, respectively. [e] Infinity titers were 100, 94, 91, and 88% of the theoretical values for 0.00, 0.02, 0.04, and 0.06 M NaN_3, respectively.

The data in Table II show that, as to the extent of internal-return isomerization and its response to solvent change, there is a noticeable difference between 1 and 3. For example, in the solvolysis reactions of 3, we found[4] that the change from acetic acid to 97% TFE solvent led to a significant decrease in the amount of internal-return isomerization. Such a finding can be interpreted[26] in terms of the multiple ion-pair mechanism.[27] Here (eq 1), solvent

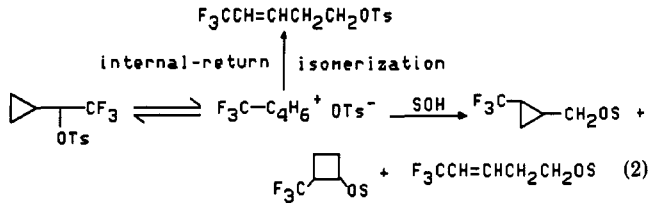


(1)

induced shifts in equilibrium between the different types of ion pair intermediates (intimate to solvent-separated) could account for the variation in the extent of internal-return isomerization with solvation changes.[27-29] On the

(14) For leading references, see: Farcasiu, D.; Sharma, S. *J. Org. Chem.* **1991**, *56*, 126–128.
(15) Caserio, M. C.; Graham, W. H.; Roberts, J. D. *Tetrahedron* **1960**, *11*, 171–182.
(16) Roberts, D. D. *J. Org. Chem.* **1966**, *31*, 2000–2003.
(17) Largely $CF_3CH{=}CHCH_2CH_2OTs$ based on kinetic analysis and the product study of Hanack.[18]
(18) Hanack, M.; Meyer, H. *Liebigs Ann. Chem.* **1968**, *720*, 81–97.
(19) Servis, K. L.; Roberts, J. D. *Tetrahedron Lett.* **1967**, *1369*.
(20) Macomber, R. S. *J. Org. Chem.* **1971**, *36*, 2182–2184.
(21) Bentley, T. W.; Llewellyn, G. *Prog. Phys. Org. Chem.* **1990**, *17*, 121–158.
(22) The rate constant for 1 in 50% aqueous EtOH (1.4×10^{-7} at 20 °C) was derived from a mY_{OTs} correlation. The rate constant for c-PrCH(OTs)CH_3 in 50% aqueous EtOH (5.4 at 20 °C) was derived as follows: k[c-PrCH(OTs)CH_3] = k[c-PrCH(Cl)CH_3][23a](OTs/Cl) where an OTs/Cl ratio of 103 was derived by comparing the rate of 3 with that of c-PrCH$_2$Cl[23b] at 20 °C in 80% aqueous EtOH.
(23) (a) Nikoletic, M.; Borcic, S.; Sunko, D. E. *Tetrahedron* **1967**, *23*, 649–660. (b) Extrapolated from data at higher temperatures given in ref 15 and 23c. (c) Brown, H. C.; Borkowski, M. *J. Am. Chem. Soc.* **1952**, *74*, 1894–1902.
(24) The rate constant for PhCH(OTs)CF_3 was taken from ref 12b, and the rate constant for PhCH(OTs)CH_3 was derived as follows: k-[PhCH(OTs)CH_3] = k[PhCH(Cl)CH_3][25](OTs/Cl) where the same value calculated in ref 22 was used for the OTs/Cl ratio.
(25) Shiner, V. J.; Fisher, R. D.; Dowd, W. *J. Am. Chem. Soc.* **1969**, *91*, 7748–7749.
(26) Paradisi, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1985**, 107, 8223–8233.
(27) For a review of the Winstein solvolysis scheme, see: Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1–67.
(28) (a) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 4829–4834. (b) Harris, J. M.; Clark, D. C.; Becker, A.; Fagan, J. F. *J. Am. Chem. Soc.* **1974**, *96*, 4478–4484.
(29) The long-standing controversy[30] over the nature of the electron-donating interaction between the cyclopropyl group and an adjacent electron-deficient center greatly increases the interpretational difficulty. It may be that the initially formed ion pairs have sufficiently different sensitivities to solvation changes to account for the change in the extent of internal-return isomerization, but it seems more likely, based on the composition of the isomerized starting material,[5a,31] that this would be the case for shifts in equilibrium between two types of ion pairs (intimate, involving a rapidly equilibrating set of cations in the bisected geometry, and solvent-separated, involving a set of rapidly equilibrating cations in the σ-bridged form).
(30) For a recent study on this subject, see: Brittain, W. J.; Squillacote, M. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1984**, *106*, 7280–7282. (b) Myhre, P. C.; Webb, G. G.; Yannoni, C. S. *J. Am. Chem. Soc.* **1990**, *112*, 8992–8994.

other hand, we find for the solvolysis reactions of 1 that the extent of internal-return isomerization changes little when the solvent is changed from acetic acid to 97% TFE. This result, as expected for such a highly destabilized carbocation as $(c\text{-}PrCHCF_3)^+$,[12d,32] is consistent with internal-return isomerization from the first-formed ion pair, most likely an intimate ion-pair type as shown in eq 2.



The effect of solvent on the rate of reaction of a substrate has proven to be a very useful criterion for assignment of reaction mechanism.[6,7,27,33-37] Accordingly we list, for I and other selected arenesulfonates, m_{OTs} values obtained from correlations of log k/k_0 against Y_{OTs},[21,38] based on solvolysis of 2-adamantyl tosylate. Neophyl tosylate (2) is thought[5d,40,41] to solvolyze with aryl participation uncomplicated by either internal return[26,42] or nucleophilic solvent assistance,[27] cyclopropylcarbinyl arenesulfonates (3) with cyclopropyl participation complicated by internal return,[5] cyclobutyl[4,43] and pinacolyl[7] brosylates (4 and 5) with neighboring-group participation,[44] and the 1-aryl-2,2,2-trifluoroethyl tosylates (6 and 7) via a k_c process.[12b] The data in Table III show that the m_{OTs} value for 1 is significantly less than 1.00, but quite similar to those for 2–7. Substrates reacting with neighboring-group participation are known[33,41a,45,46] to give m values significantly less than 1.00, most likely due to delocalization of positive charge.[21] These results are consistent with a rate-limiting ionization mechanism for the solvolyses of 1. The fact that the solvolyses of 1 yield largely rearranged products[18] plus the observation that these reactions are accompanied by internal-return isomerization supports a k_Δ mechanism as shown in eq 2.

Table V. k(c-Pr)/k(Ph) Rate Ratios for the Secondary Systems $RCH(Y)CH_3$ and $RCH(Y)CF_3$

system	Y	solvent	temp, °C	k(c-Pr)/k(Ph)[a]
CH_3	-Cl	50% aq EtOH	20	100[b]
CH_3	-OPNB	60% aq acetone	60	150[c]
CF_3	-OTs	97% aq TFE	25	60[d]
H[e]	-OTs	97% aq TFE	25	90[f]

[a] Comparison of the solvolysis rate of the cyclopropyl-substituted compound with that of the phenyl-substituted substrate. [b] Rate constant for c-PrCH(Cl)CH_3 (5.2×10^{-2} s^{-1}) taken from ref 23a; that for PhCH(Cl)CH_3 (5.0×10^{-4}) taken from ref 52. [c] Rate constant for c-PrCH(OPNB)CH_3 (9×10^{-7}) calculated from data taken from ref 53; that for PhCH(OPNB)CH_3 (9×10^{-9}) calculated from data taken from ref 54. [d] Rate constant for c-PrCH(OTs)CF_3, this study; for PhCH(OTs)CF_3, ref 12b. [e] For the primary system RCH_2Y. [f] Rate constant for c-$PrCH_2OTs$ (4.0×10^{-2}) calculated from a 16-point mY_{OTs} plot; that for $PhCH_2OTs$ taken from ref 55, using the well-known OTs/OBs ratio of 3.

Additional support for a rate-limiting ionization mechanism for the solvolysis of 1 comes from the effects of salts on rate of reaction. Thus, the nonnucleophilic salt, $NaClO_4$, as reported in Table IV, causes a significant increase in rate (54% for 0.06 M salt). This sensitivity to ion-atmosphere parallels that of both cyclopropylcarbinyl and cyclobutyl nasylates[5c] and is expected for a k_c or k_Δ process. More importantly, 1 shows very little rate enhancement due to added azide ion (15% for 0.06 M salt). This result is similar to that observed for neophyl tosylate (18% for 0.06 M salt) and 2-adamantyl tosylate[47] (16% for 0.06 M salt) and contrasts with the marked rate enhancement (294% for 0.06 M salt) observed for the solvolysis of 2-propyl tosylate[47] in 80% aqueous EtOH. Since it is generally agreed that both neophyl tosylate and 2-adamantyl tosylate[48] react by a rate-limiting carbocation formation and 2-propyl tosylate by a k_s process,[48] a rate-limiting ionization mechanism such as that given in eq 2 can be assigned to the solvolysis reactions of 1.

The relative ability of neighboring cyclopropyl and phenyl substituents to delocalize charge in carbocations is a subject of current interest.[1b,14,49] Opposite conclusions concerning this subject—based on studies of solvolysis rate measurements[50] and on determinations of ^{13}C chemical shift values of carbocations in superacidic media[51]—prompted these studies. Recently, in a study[14] involving ^{13}C chemical shift measurements of 2,6-disubstituted pyrylium cations, it was concluded, in agreement with solvolytic studies, that the cyclopropyl group is a more powerful electron donor than phenyl. In Table V, we compare the relative ability [k(c-Pr)/k(Ph)] of cyclopropyl and

(31) Roberts, D. D. *J. Org. Chem.* **1971**, *36*, 1913–1915.
(32) On the basis of product studies for the solvolysis reactions of 1,[18] Hanack proposed a bridging interaction between the cyclopropyl group and the adjacent highly electron-deficient center.
(33) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466–5475.
(34) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5741–5747.
(35) Bunton, C. A.; Mhala, M. M.; Moffatt, J. R. *J. Org. Chem.* **1984**, *49*, 3639–3641.
(36) Allen, A. D.; Kanagasabapathy, V. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4513–4519.
(37) Kevill, D. N.; Anderson, S. W. *J. Am. Chem. Soc.* **1986**, *108*, 1579–1585.
(38) The exclusion of the points for 97 and 70% TFE, which lie significantly below the regression line and have approximately the same value, is justified by the following observations: (1) in a study[39] of the solvolysis of mustard chlorohydrin, a substrate known to react via a k_Δ process, abnormally low rates were shown in aqueous TFE as compared to rates in aqueous ethanol and aqueous acetone solvents and (2) neophyl tosylate, another compound known to react via a k_Δ pathway, also demonstrates anomalous behavior in aqueous TFE solvents.[40]
(39) McManus, S. P.; Neamati-Mazraeh, N.; Hovanes, B. A.; Paley, M. S.; Harris, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 3393–3395.
(40) Shiner, V. J., Jr.; Seib, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 862–864.
(41) (a) Smith, S. G.; Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1961**, *83*, 620–625. (b) Diaz, A.; Lazdins, I.; Winstein, S. *J. Am. Chem. Soc.* **1968**, *90*, 6546–6548. (c) Ando, T.; Kim, S.-G.; Matsuda, K.; Yamataka, H.; Yukawa, Y.; Fry, A.; Lewis, D. E.; Sims, L. B.; Wilson, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 3505–3516.
(42) McManus, S. P.; Smith, M. R.; Shankweiler, J. M.; Hoffman, R. V. *J. Org. Chem.* **1988**, *53*, 141–148.
(43) Roberts, D. D. *J. Org. Chem.* **1972**, *37*, 1510–1513.
(44) For a review, see: Capon, B.; McManus, S. P. *Neighboring Group Participation*; Plenum: New York, 1976; Vol. 1, pp 167–168.
(45) Schadt, F. L., III; Lancelot, C. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 228–246.
(46) Roberts, D. D.; Snyder, R. C., Jr. *J. Org. Chem.* **1980**, *45*, 4052–4055.
(47) Raber, D. J.; Harris, J. M.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 4821–4828.
(48) For leading references, see ref 33.
(49) Murata, A.; Sakaguchi, S.; Fujiyama, M.; Mishima, M.; Fujio, M.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1138.
(50) (a) Brown, H. C.; Ravindranathan, M.; Peters, E. N. *J. Org. Chem.* **1977**, *42*, 1073–1076. (b) Brown, H. C.; Peters, E. N. *J. Am. Chem. Soc.* **1977**, *99*, 712–1716.
(51) (a) Olah, G. A.; Porter, R. D.; Kelly, D. P. *J. Am. Chem. Soc.* **1971**, *93*, 464–466. (b) Olah, G. A.; Westerman, P. W.; Nishimura, J. *J. Am. Chem. Soc.* **1974**, *96*, 3548–3559.
(52) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1957**, *79*, 1597–1602.
(53) Sneen, R. A.; Baron, A. L. *J. Am. Chem. Soc.* **1961**, *83*, 614–617.
(54) Goering, H. L.; Briody, R. G.; Sandrock, G. *J. Am. Chem. Soc.* **1970**, *92*, 7401–7407.
(55) Shiner, V. J., Jr.; Ropp, M. W.; Pinnick, H. R., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 232–233.

phenyl groups to stabilize carbocation-like transition states in solvolysis reactions of the secondary systems RCH(Y)CH_3 and RCH(Y)CF_3. The data reveal that replacement of phenyl with cyclopropyl increases the rate in both systems by a factor of 10^2. Clearly, in keeping with previous studies,[1b,56] cyclopropyl is more effective than phenyl in stabilizing an electron-deficient site, even with the α-trifluoromethyl-substituted system where the electron demand for stabilization is unusually high. Moreover, the relative ability of these two groups to conjugate with the electron-deficient center, as evidenced by the data in Table V, is nearly insensitive to marked differences in electron demand. In this regard, it is of interest to note that the value of k(c-Pr)/k(Ph) for the primary system RCH(Y)H is also about 10.[2] While the rate data used in the calculation of this value are somewhat soft,[57] it is generally accepted[58] that TFE is a suitable solvent for promoting neighboring-group assistance over that by solvent.

Experimental Section

Cyclopropyl(trifluoromethyl)carbinol. This compound was prepared in 43% yield by a modification of the method of Hanack.[18] Accordingly, trifluoroacetaldehyde (prepared by adding 50 g (0.32 mol) of trifluoroacetaldehyde ethyl hemiacetal to a mixture of 300 g of polyphosphoric acid, 94 g of P_2O_5, and 300 g of *o*-phosphoric acid maintained at 170 ± 5 °C), was passed into a cooled solution of cyclopropylmagnesium bromide (prepared from 31.2 g (0.25 mol) of cyclopropyl bromide and 6.2 g (0.13 g equiv) of magnesium turnings in 300 mL of dry ether), with the assistance of a slow stream of dry nitrogen, over a 75-min period. After the solution was stirred 3 h at room temperature and the usual workup, fractional distillation gave 15.1 g (0.11 mol) of a single product, as determined by gas chromatography: bp 73–75 °C (100 Torr) [(lit.[18] bp 73–75 °C (100 Torr)]. The FTIR and ^{1}H NMR spectra were consistent with those reported in the literature for cyclopropyl(trifluoromethyl)carbinol.[18]

Cyclopropyl(trifluoromethyl)carbinyl Tosylate (1). The general procedure used by Tidwell[12b] for the preparation of various alkyl tosylates was used to prepare 1. In a dry three-neck 100-mL, round-bottom flask equipped with a magnetic stirring bar, a $CaCl_2$ drying tube, a septum inlet, and an inlet tube through which a slow stream of dry nitrogen was passed was placed 1.06 g (35 mmol) of NaH (80% in mineral oil), which was washed three times by injecting and withdrawing 10-mL portions of pentane by syringe, followed by two washes with 10-mL portions of dry ether (<0.0006% water). Next, a solution of 2.0 g (14 mmol) of cyclopropyl(trifluoromethyl)carbinol in 10-mL of dry ether was added via a syringe over a 25 min period to the stirred reaction mixture. This was followed by stirring at room temperature for 1 h. Then 2.6 g (14 mmol) of *p*-toluenesulfonyl chloride in 25 mL of dry ether was added via a syringe to the reaction mixture, followed by additional stirring at room temperature for 4 h. Then, 40 mL of water was added, the layers were separated, and the aqueous layer was extracted twice with 40-mL portions of ether. The combined ether layers were washed once with 40 mL of 5% aqueous $NaHCO_3$, dried over a mixture of Na_2CO_3 and $MgSO_4$, and gravity filtered, and the ether was removed by rotovaporization. The resulting oil, after standing a few minutes at −10 °C, yielded 2.8 g of an off-yellow solid. Recrystallization from 25 mL of hot pentane–benzene (90:10) gave 1.6 g of white feathers: mp 45.5–46 °C (lit.[18] mp 46–46.5 °C).

Solvents were prepared as previously described.[4]

Rate Measurements. The rates of solvolysis were followed titrimetrically. In a typical kinetic run, the requisite amount of 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.[59] Reaction time commenced with the addition of half the solvent. The solvent used for each kinetic run was thermostated in a constant temperature bath held at ±0.05 °C at least 5 min prior to a run. At appropriate times, 2-mL aliquots were analyzed for liberated *p*-toluenesulfonic acid. The titrating solutions were as follows: for acetic acid–formic acid solvents,[61] 0.020 N sodium acetate in acetic acid; and for the aqueous alcohol solvents, 0.016–0.021 N sodium hydroxide in 95% aqueous methanol. The indicators used were as follows: for acetic acid–formic acid solvents, bromophenol blue (in acetic acid), 2–3 drops; and for aqueous alcohol 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:[62,63] $k_t = 1/t \ln (mL_\infty/mL_\infty - mL_t)$. Multiple determinations (6–12) were made for each kinetic run. The activation parameters recorded in Table I were obtained by regression analysis[64] of ln (k_t/T) versus $1/T$,[65] and the m values listed in Table III were also obtained by regression analysis of log k_t versus Y_{OTs} values.[21]

Registry No. 1, 22581-19-7; neophyl tosylate, 21816-03-5; cyclopropyl(trifluoromethyl)carbinol, 2516-33-8.

(56) (a) Brown, H. C.; Ravindranathan, M. *J. Am. Chem. Soc.* **1975**, *97*, 2895–2898. (b) Brown, H. C.; Ravindranathan, M.; Rao, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 1218–1222. (c) Peters, E. N.; Brown, H. C. *J. Am. Chem. Soc.* **1973**, *95*, 2397–2398.

(57) Experimental data for solvolyses of cyclopropylcarbinyl arenesulfonates in solvents of low nucleophilicity–high ionizing power (i.e., fluorinated alcohols) are scarce—these data are difficult to obtain because of the high reactivity of cyclopropylcarbinyl substrates.

(58) Bentley, T. W. In *Nucleophilicity*; Harris, J. M., McManus, S. P., Eds; ACS Advances in Chemistry Series 215; American Chemical Society: Washington, DC, 1987; pp 255–268.

(59) For reactions whose half-lives were greater than 72 h and whose reaction temperatures were greater than 50 °C, rate measurements were obtained by the ampule technique.[60]

(60) Roberts, D. D. *J. Org. Chem.* **1982**, *47*, 561–564.

(61) For reactions in formic acid or acetic–formic acid mixtures, it was necessary to dilute the 2-mL aliquots with 2 mL of acetic anhydride–acetic acid (75:25) to obtain a sharp end point.

(62) (a) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*, 2nd ed.; Wiley: New York, 1961. (b) Carpenter, R. G. *Determination of Organic Reaction Mechanisms*; Wiley: New York, 1984; Chapter 4.

(63) The parameter mL_∞ = measured titer at 10 half-lives or theoretical titer at 100% conversion calculated from known quantity of tosylate ester present in the reaction mixture; mL_t = measured titer at time t.

(64) Edwards, A. L. *An introduction to Linear Regression and Correlation*; Freeman: San Francisco, 1976; pp 21–32.

(65) Reference 62b, Chapter 7.