strength effect for eliminations from 1 and $ArCH_2CH_2X$ may in part be attributed to the lower free energy of activation for the former.[33] If the free energy of activation is increased without changing the relative energy of any corner in the reaction coordinate diagram, the effects on parallel and perpendicular motions would become similar (Figure 3), and constant k_H/k_D and larger ρ values would be expected for the change to a stronger base, as observed for the latter.[13] Therefore, it appears that the most significant difference in transition states for related imine- and olefin-forming eliminations is a lower free energy of activation for the former which manifests itself in different base strength effects.

Experimental Section

Benzylidenemethylamines **2**, benzylmethylamines, and *N*-chlorobenzylmethylamines 1 were prepared as described previously.[6] The solvent and amines were purified by known methods.

Product studies of the reactions of *N*-chloro- and *N*-bromobenzylmethylamines with piperidine were carried out by refluxing the solution of the *N*-haloamine (2.0 mmol), piperidine (10.0 mmol), and benzene (internal standard, 2.0 mmol) in 20 mL of MeCN for 12 h. The solution was analyzed by gas chromatography on a 2 ft × $^1/_8$ in. column of 20% PEG 400 on Chromosorb P at 130 °C. The products were benzylidenemethylamine (95.0%) from **1a** and benzylidenemethylamine (22.2%) and benzylmethylamine (74.5%) from *N*-bromobenzylmethylamine. Yields of **2** from reactions of other chloroamines **1c-f** were determined by comparing the UV absorbances of the reaction products with those for authentic samples. On the basis of the starting amine concentrations, the yields of **2** were 88-95%.

Stability of *N*-haloamines in MeCN was demonstrated by the previously used method.[6]

Kinetic studies were carried out as before on a Cary 17D spectrophotometer.[6] The pseudo-first-order rate constants were divided by the base concentrations to afford the second-order rate constants, k_2. The k_2 values were found to be constant for two- tenfold variation in base concentration.

Acknowledgment. This investigation was supported by grants from the Basic Science Research Institute Program, Korea Ministry of Education (1983), the Peeres Co., and the Korea Science and Engineering Foundation.

Registry No. **1a**, 3555-71-3; **1c**, 70972-89-3; **1d**, 70972-94-0; **1e**, 70972-96-2; **1f**, 70972-95-1; Et_2NH, 109-89-7; Bu_2NH, 111-92-2; $(i\text{-}Bu)_2NH$, 110-96-3; $PhCH_2NHCH_3$, 103-67-3; D_2, 7782-39-0; piperidine, 110-89-4.

(33) Although the activation energy for elimination from $ArCH_2CH_2X$ promoted by ArO^--DMF is not available in the literature, it has been demonstrated that the $\Delta G^{\ddagger}$ for reaction 1 with MeONa-MeOH is about 6 kcal/mol lower than that for olefin-forming elimination from closely related $PhCH_2CH(Cl)CH_3$ under similar conditions.[6]

Solvolysis of 1-(1-Naphthyl)- and 1-(9-Anthryl)-2,2,2-trifluoroethyl Sulfonates

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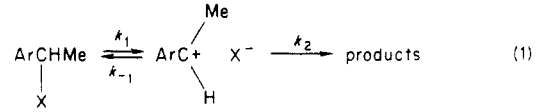
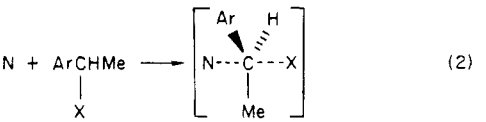
Solvolyses of $ArCH(O_3SR)CF_3$ (**13**, Ar = 1-naphthyl; R = *p*-Tol; **14**, Ar = 9-anthryl; R = Me) give *m* values for the rate dependence on solvent of 0.94 (**13**) and 0.64 (**14**) and a reactivity order **14** > **13** > Ar = *p*-Tol. The substitution products from **14** in EtOH, HOAc, or CF_3CH_2OH involve extensive or exclusive attack on the ring. The polarimetric rate constant of (*R*)-(-)-**14** in CF_3CH_2OH was 1.3 times greater than that for product formation, and in EtOH this substrate gave exclusive ring substitution with loss of optical activity. These results are interpreted in terms of initial reaction of **13** and **14** to form intimate ion pairs, which either return to reactant or form products through further steps which may involve other ion pairs. No evidence for solvent attack concurrent with sulfonate departure is observed. The strongly electron-withdrawing α-CF_3 substituent may enhance ring attack in the solvolysis of **14**.

The study of the solvolytic reactivity of 1-arylethyl systems has been of continuing utility in investigations of nucleophilic substitution.[1-5] The results of these studies have generally been interpreted that for substrates with electron-donating aryl groups in ionizing solvents the reactions involve initial formation of an ion pair that leads to products through further steps (eq 1), sometimes involving other ion pairs or free ions.[1-5] When the aryl group



(1)



(2)

1

is not a good electron donor and the resulting cation is relatively less stable and when the solvent is a reasonably good nucleophile, rate-limiting nucleophilic solvent displacement should become relatively more significant (eq

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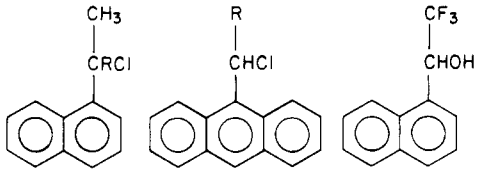
0022-3263/86/1951-1324$01.50/0

2). However in a recent study in our laboratory of optically active 1-arylethyl tosylates (Ar = C_6H_5, 3-$CF_3C_6H_4$, and 3,5-$(CF_3)_2C_6H_3$)[4] all of the results could be explained using the ion pair scheme (eq 1), and none of the data required the intervention of rate-limiting attack on the substrate to form a pentacoordinate species **1** as shown in eq 2, either as a transition state or as an intermediate.[5]

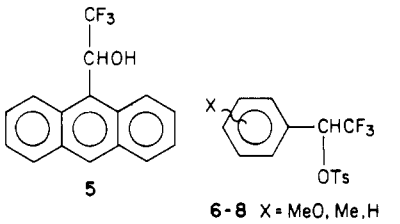
Polycyclic aromatic hydrocarbons have also been among the aryl groups used in the study of such solvolysis reactions,[6b,7] and substrates utilized include 1-(1-naphthyl)- and 1-(9-anthryl)ethyl chlorides (**2**, **3a**)[7] and 9-anthrylarylmethyl chlorides (**3b**).[8] These were of particular interest



2a, R=H
2b, R=CH_3

3a, R=CH_3
3b, R=Ar

4



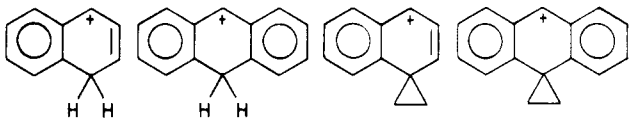
5

6-8 X = MeO, Me, H

to us because the structurally related 1-aryl-2,2,2-trifluoroethanols **4** and **5** have been finding applications as optically active NMR reagents and in optically active stationary phases in chromatography.[9] We have examined the solvolytic reactivity of the 1-aryl-2,2,2-trifluoroethyl tosylates **6–8**,[10] and so a study of solvolytic reactivity of derivatives of **4** and **5** appeared desirable.

There has been other recent interest in the effect of 1-naphthyl and 9-anthryl groups on carbocation reactivity. These include NMR and theoretical studies of long-lived benzylic cations,[11] NMR studies of the long-lived 1-naphthalenium (**9**) and 9-anthracenium ions (**10**) derived by protonation of naphthalene and anthracene, respectively,[12a] and the direct NMR study of derivatives of the 1-ethylenenaphthalenium ion **11**[12b] and the 1-ethyleneanthracenium ion **12**.[12c]

There have also been kinetic studies of the generation of **9** by tritium exchange methods, and these have been used to derive σ_{Ar}^+ parameters for the electrophilic aromatic substitution of this and other polycyclic aromatics.[13a]

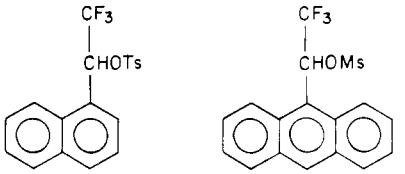


9 **10** **11** **12**

The basicities of the parent hydrocarbons to form **9** and **10** have also been used to derive these substituent parameters.[13b]

Results

The known[9] alcohols **4** and **5** were prepared by $NaBH_4$ reduction of the ketones and were converted to the toluenesulfonate (tosylate) **13** and the methanesulfonate (mesylate) **14**, respectively, by treatment with NaH fol-

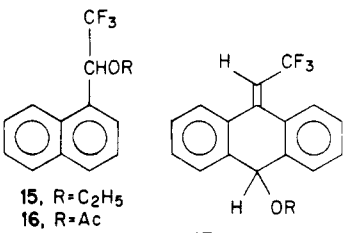


13 **14**

lowed by the appropriate sulfonyl chloride. The tosylate corresponding to **14** was also prepared but was too insoluble for satisfactory kinetic studies. The same procedure was used to prepare (*R*)-(−)-**14** from (*R*)-(−)-**5**.

The rates of solvolysis of **13** and **14** were measured in various solvents either by monitoring the change in absorption of the solutions at specific wavelengths or by titrimetric methods. First-order rate constants were obtained and are listed in Table I. The polarimetric rate of **14** in 100% CF_3CH_2OH (TFE) at 25 °C was measured as $7.50 \pm 0.09 \times 10^{-3}$ s^{-1}, and the product solution had no residual optical activity.

The formation of products from **13** and **14** was monitored by dissolving the substrates in either CD_3CD_2OD or CD_3CO_2D and measuring the spectra at intervals. These spectra indicated the formation of the corresponding ether and acetate from **13** as the only observable products, and **15** and **16** were isolated from preparative reactions of **13** in EtOH and HOAc, respectively. As described below the



15, R=C_2H_5
16, R=Ac

17, R=C_2H_5
18, R=Ac
19, R=OCH_2CF_3

solvolysis of **14** in EtOH, HOAc, and TFE led to the formation of the ring-substituted products **17–19**, respectively. Attempts to dissolve **14** in CF_3CO_2H (TFA) for NMR observation of the product led to rapid darkening of the solution and evident polymerization, and no interpretable NMR absorption was observed.

The ethyl ether **20** that would be formed by replacement of the OMs group of **14** by OEt was not observed under the solvolysis conditions. Reaction of **14** in HOAc led to variable amounts of **21**, and on prolonged standing under the reaction conditions **18** was observed to isomerize to **21**.

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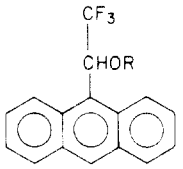

20, R = C_2H_5
21, R = Ac

An authentic sample of **21** was prepared from **5** for comparison.

The identification of **17–21** followed from their spectral properties, and the reported[8] formation of products analogous to **17–19** in solvolysis of chlorides **3b**. In particular the ^1H NMR spectra of **17–19** each displayed a singlet assignable to the CHO proton, a quartet near δ 6.1 due to $=CHCF_3$, and aromatic absorption at δ 7.1–7.9 consistent with the 1,1-diarylethylene structure but no absorption below δ 8.0 due to the anthracene moiety. The UV spectrum of **17** showed λ_{max} 254 nm (pentane), comparable to that of some related derivatives,[14b] but different from that of anthracene derivatives.

Reaction of (*R*)-(−)-**14** in EtOH gave **17** with no measurable optical activity.

Discussion

As considered in detail below the evidence indicates that both **13** and **14** are reacting by initial unimolecular ionization, presumably to an intimate ion pair (**22**). This initial ion pair reacts with solvent to form products, either directly or after formation of solvent separated ion pairs (**23**) or free ions (eq 3 and 4), and there is also evidence for some return of **22** to **14**.

$$\underset{\textbf{13 or 14}}{ArCH(CF_3)O_3SR} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\textbf{22}}{Ar\overset{+}{C}HCF_3\ {}^-O_3SR} \rightleftharpoons \underset{\textbf{23}}{Ar\overset{+}{C}HCF_3} \parallel {}^-O_3SR \quad (3)$$

$$\textbf{22 or 23} \xrightarrow[k_2]{SOH} \underset{\textbf{15–20}}{ArCH(CF_3)OS} \quad (4)$$

Even though **13** was studied as the tosylate derivative and **14** as the mesylate it is appropriate to directly compare the rates of substrates with those two different leaving groups. Thus it has been found that rates of solvolysis of mesylates and tosylates derived from the same alcohol are very similar,[15a,b] and furthermore the effect of solvent on the rates for these two leaving groups are essentially the same.[15b]

The dependence of rate on solvent are given by $\log k = 0.94Y_{OTs} - 6.56$ (r = 0.978) for **13** and $\log k = 0.64Y_{OTs} - 3.80$ (r = 0.958) for **14**, as illustrated in Figure 1. These slopes m may be compared to those of the substituted phenyl derivatives of 0.76 (**6**, *p*-MeO), 0.94 (**7**, *p*-Me), and 0.69 (**8**, H). The correlations for these latter three compounds also showed rather scattered plots of log k vs. Y_{OTs}.

Explanations of the causes of the deviations from good linearity in these log k vs. Y_{OTs} plots are rather speculative, especially since extrapolations are necessary in many cases

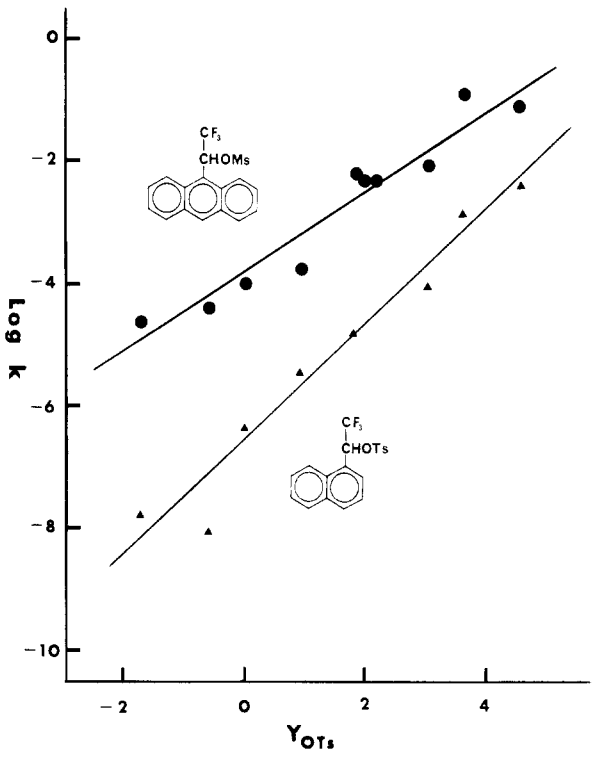

Figure 1. log k ArCH(O_3SR)CF_3 vs. Y_{OTs} for different solvents: (●) Ar = 9-anthryl; (▲) Ar = 1-naphthyl.

to compare all the rates at 25 °C. There is, however, evidence in various 1-arylethyl systems that in the less nucleophilic solvents there is ion pair return from initially formed intimate ion pairs. Thus for 1-arylethyl tosylates[4] and 1-phenyl-2,2,2-trifluoroethyl triflate[10] polarimetric rate constants in fluorinated solvents are significantly larger than rates of product formation by factors of 1.2–27, indicating that ion pairs are formed, racemize, and return to reactant. Such behavior would tend to make the rates of product formation less than the rates of ionization, and could cause deviations in log k vs. Y_{OTs} plots. For **14** the ratio k_α/k_{UV} is 1.3 in 100% TFE, so such ion pair return evidently occurs for this substrate and might well occur for **13** also. There is also recent evidence for ion pair return in a variety of other systems.[16]

For the more nucleophilic solvents the possibility of direct solvent participation in the rate-limiting ionization (eq 2) must be considered, but the current evidence and our previous studies with optically active **8**[10] and ArCH(OTs)Me[4] suggest this is not the case. Thus it was observed that any nucleophilic solvent participation in these derivatives was not strong enough to cause the formation in any case of exclusively inverted products, and it would be expected that solvent participation in **13** and **14** would be hindered by the size of the aryl groups and by the known[17] great resistance of 2,2,2-trifluoroethyl derivatives to S_N2 displacements, while the electron-donor character of the naphthyl and anthryl groups (vide infra) decrease the impetus for solvent assistance.

The relative reactivities in different solvents of 2,2,2-trifluoroethyl sulfonates **6–8** and **13–14** are summarized in Table II. The 9-anthryl-substituted compound is more

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Table I. Solvolytic Rate Constants for 1-NaphCH(OTs)CF_3 (13) and 9-AnthrylCH(OMs)CF_3 (14)[a]

substrate	solvent (*Y*)	*k*, s^{-1} (25 °C)[b]	ΔH^*, kcal/mol	ΔS^*, eu
13	TFA (4.57)	4.16×10^{-3} [c]	17.0	−12.8
	97% HFIP (3.61)	1.50×10^{-3} [d]	12.1	−30.8
	97% TFE (1.83)	1.79×10^{-5} [e,f]	19.0	−16.6
	HCO_2H (3.04)	9.52×10^{-5} [e,g]	23.0	0.2
	60% EtOH (0.92)	3.32×10^{-6} [e,h]	20.5	−14.7
	80% EtOH (0.00)	4.70×10^{-7} [e,i]	21.9	−14.1
	EtOH (−1.75)	1.71×10^{-8} [e,j]	23.5	−15.4
	HOAc (−0.61)	9.13×10^{-9} [e,k]	26.3	−7.1
14	TFA (4.57)	7.42×10^{-2} [l]		
	97% HFIP (3.61)	1.24×10^{-1}		
	50% TFE (2.14)	4.88×10^{-3}		
	70% TFE (2.00)	5.00×10^{-3}		
	97% TFE (1.83)	6.65×10^{-3}		
	TFE (1.80)	5.79×10^{-3}		
	HCO_2H (3.04)	8.43×10^{-3}		
	60% EtOH (0.92)	1.72×10^{-4}		
	80% EtOH (0.00)	9.60×10^{-5} [e,m]	19.5	−11.6
	EtOH (−1.75)	2.35×10^{-5} [e,n]	20.0	−12.7
	HOAc (−0.61)	4.06×10^{-5} [e,o]	21.6	−6.1

[a] At least two runs were made at each temperature and rate constants ±5% monitored by UV spectroscopy unless noted. TFA is CF_3CO_2H, HFIP is $(CF_3)_2CHOH$, TFE is CF_3CH_2OH, HOAc is CH_3CO_2H. Mixed solvents are diluted with H_2O. *Y* values from ref 15c given in parentheses. Maximum standard deviation: ΔH^*, 0.1 kcal/mol, ΔS^*, 0.3 eu. [b] Other measured rates and temperatures (°C) in footnotes. [c] 1.18×10^{-2} (39.0), 7.56×10^{-4} (11.4). [d] 1.00×10^{-2} (54.1); 4.02×10^{-3} (38.7). [e] Extrapolated. [f] 8.44×10^{-4} (63.1), 1.69×10^{-4} (47.8), 5.60×10^{-5} (34.6). [g] 1.68×10^{-3} (49.8), 7.00×10^{-4} (39.5), 6.56×10^{-4} (38.7), 8.77×10^{-5} (25.4). [h] 5.84×10^{-4} (74.8), 1.80×10^{-4} (63.7), 8.16×10^{-5} (53.8), measured by titration. [i] 9.10×10^{-4} (99.4), 3.80×10^{-4} (88.1), 9.94×10^{-5} (74.2). [j] 5.56×10^{-5} (99.4), 2.42×10^{-5} (89.0), 5.22×10^{-6} (74.1). [k] 4.48×10^{-4} (118.0), 8.56×10^{-5} (99.4), 2.18×10^{-5} (86.8). [l] 1.43×10^{-2} (6.0). [m] 9.59×10^{-3} (72.1), 3.32×10^{-3} (59.2), 9.34×10^{-4} (46.7). [n] 2.64×10^{-3} (72.1), 8.28×10^{-4} (58.6), 2.26×10^{-4} (46.0). [o] 6.60×10^{-3} (71.3), 1.62×10^{-3} (58.2), 5.39×10^{-4} (46.7).

Table II. Relative Reactivities of Sulfonates ArCH(O_3SR)CF_3 at 25 °C[a]

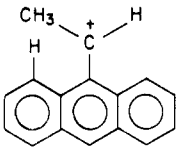
solvent	*k*(9-anth/ p-Anis)	*k*(9-anth/ 1-naph)	k(9-anth/ 4-Tol)	k(9-anth/ *Ph*)
TFA		13.1	8.9×10^3	5.0×10^5
97% HFIP	0.21	83	2.2×10^3	3.1×10^6
97% TFE	0.11	370	6.0×10^3	4.5×10^6
70% TFE	0.081			
50% TFE	0.067			
HCO_2H	0.090	89		
HOAc	0.97	4400	5.2×10^4	
60% EtOH	0.038	52	1.4×10^3	
80% EtOH	0.081	200	4.6×10^3	
100% EtOH	0.33	1400	1.2×10^5	

[a] Data for 9-anthryl and 1-naphthyl derivatives from this work, data for *p*-Anis, *p*-Tol, and Ph derivatives from ref 10. No correction applied in comparisons of tosylates and mesylates (see ref 15a,b).

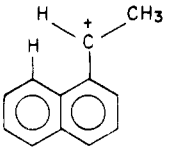
reactive than the 1-naphthyl derivative by factors of between 13 and 4400 and more reactive than the phenyl compound by factors between 5.2×10^5 and 4.5×10^6. These reactivities are qualitatively similar to the results for the 1-arylethyl chlorides **2a** and **3a**, which were found by Berliner and Shieh[7c] to be more reactive than the corresponding phenyl compound by factors of 17 and 2.4×10^4, respectively, in 80% acetone at 25 °C.

The data of Berliner and Shieh[7c] was found by Inukai and Brown[7b] to correlate with the rates of the corresponding tertiary chlorides,[18] and these latter authors used this result to derive the correlation $\log k/k_0 = -5.78\sigma^+$ for the rates of 1-arylethyl chlorides (**3a**) with σ^+ parameters of the aryl groups.[19]

Inukai and Brown[7b] did not report σ_{Ar}^+ parameters calculated by this method for the 1-naphthyl and 9-anthryl substituents because of the complicating steric interactions due to the peri hydrogens, as shown in **24** and **25**. However use of their correlation gives σ_{Ar}^+ values of −0.21 and −0.76 for these groups, respectively.



24



25

This σ_{Ar}^+ value for the 9-anthryl group is slightly less than that for the *p*-anisyl group (−0.78),[13b] and this agrees with the data in Table II in that the *p*-anisyl derivative **6** is more reactive than the 9-anthryl by factors of 1.03–26. A similarity in the reactivity of the (9-anthryl) and *p*-anisyl groups was also found in solvolysis of 2-arylethyl tosylates in which neighboring group participation by the aryl groups gives phenonium ions (**12** in the 9-anthryl case).[20]

The comparative rate data (Table II) show that the 1-naphthyl derivative **13** is more reactive than the *p*-tolyl compound by factors of 12–88. This is contrary to the result that would have been predicted from the σ_{Ar}^+ parameter of −0.21 for the 1-naphthyl group derived from solvolysis of **2a** as compared to the value of −0.31 for *p*-tolyl. Other σ_{Ar}^+ parameters that have been derived for the 1-naphthyl group are −0.35 from tritium exchange[13a] and −0.45, −0.50, and −0.51 from electrophilic nitration and chlorination and ring basicity, respectively.[13b] The latter method gave a value of −1.25 for 9-anthryl.[13b] These parameters derived from electrophilic attack on the ring would not be subject to the unfavorable peri interactions shown in **24** and **25** and suggest that such interactions tend to reduce the magnitude of the solvolytically derived σ_{Ar}^+ values.

There is also evidence for ground-state steric interactions in the molecular structures we have determined for four 1-aryl-2,2,2-trifluoroethyl tosylates including **8** by X-ray crystallography.[21] It has been argued[22] that the relief of

(18) Rates for 1-arylethyl chlorides where the position of substitution of the aryl ring is adjacent to another fused ring were not used in this correlation because the aryl group cannot attain coplanarity in the cation.

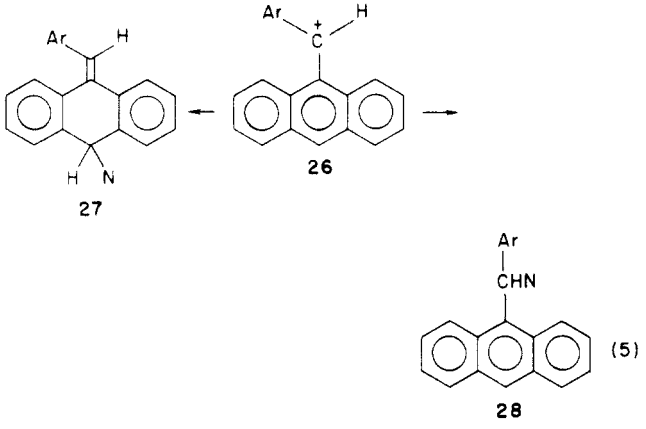
(19) These σ_{Ar}^+ values refer to the aryl group as a whole, and are the same as γ^+ constants: Peters, E. N. *J. Am. Chem. Soc.* **1976**, *98*, 5627–5632; *J. Org. Chem.* **1977**, *42*, 1419–1422. McManus, S. P.; Harris, J. M. *Ibid.* **1977**, *42*, 1422–1427.

(20) Eberson, L.; Petrovich, J. P.; Baird, R.; Dyckes, D.; Winstein, S. *J. Am. Chem. Soc.* **1965**, *87*, 3504–3506.

ground-state interactions involving tosylate leaving groups may affect rates of solvolysis of even secondary tosylates and that these effects would not be present with halide leaving groups. Quite possibly this steric repulsion would be greater for 1-naphthyl or 9-anthryl relative to phenyl substrates because the molecular structure of 8[21b] suggests there would be repulsions between the fused rings and the sulfonyl oxygens. Thus both **13** and **14** may be accelerated due to this cause. However in the case of **14** this ground-state repulsion would be replaced in the ion by an interaction between the CF_3 group and the aryl ring analogous to that shown in **24** and this effect could be more severe than the corresponding CH_3 interaction depicted in **24**. In the ion from **13** this unfavorable interaction can be avoided as shown in **25**. Thus the high reactivity of the fluorinated naphthyl derivative **13** compared to the secondary substrate **2a** may be plausibly ascribed to ground-state steric effects in **13**, which are relieved in the product ion. Similar ground-state strain is present in **14** but the product ion suffers from steric hindrance to attaining coplanarity due to the interaction of the fluorines with the 1,8-hydrogens so the net steric effects tend to cancel.

The high reactivity of **13** and **14** provide convincing evidence that these substrates react by the sequence of eq 3 and 4. Both electronic and steric factors would favor unimolecular ionization relative to less crowded and less activated analogues and steric effects would hinder bimolecular reactions involving solvent-assisted displacement (eq 2).

The formation of the products **17–19** resulting from ring substitution resembles results[8] from the ion **26**, which underwent nucleophilic substitution both at the benzylic position to give anthracene derivatives **28** or at C-10 on the ring to give exomethylene products **27** (eq 5). The



relative amounts of the two products depended on the substrate structure, the method of generation, and the reaction medium, and it was proposed that intimate ion pairs were prone to attack on the ring, whereas free ions or solvent-separated ion pairs favored substitution at the benzylic position.[8]

The intimate ion pair from ionization of (*R*)-(−)-**14** would still be chiral and so attack by solvent to form **17–19** could occur to produce optically active product. However the product **17** from reaction of (*R*)-(−)-**14** with EtOH displayed no measurable optical activity, and so either racemization of this ion pair is particularly facile or the position of addition is so remote from the anion that there is no directing influence on the stereochemistry of addition. In view of the bulky nature of the cationic part of the ion pair it would appear that ion pair racemization would not be particularly facilitated, and so the latter explanation appears preferable.

The interesting proposal has been made[5,15b,c] that there can be merging of the classic S_N1 and S_N2 mechanisms so that attack by solvent can occur to produce a pentacoordinate species as depicted in eq 2 that is an actual intermediate. The existence of *m* values for the dependence of reaction rates on polarity that are less than 1.0 has been suggested[5,15b,c] as evidence for this mechanism, in that a nucleophilic role for the solvent is manifested. Thus **14**, which has a rather low *m* value, is a good candidate for such a process, and the tendency of this substrate to undergo substitution on the ring offers a unique possibility for this "S_N2-intermediate" mechanism to be revealed. If solvent attack on **14** were concerted with leaving group departure then a stereoelectronic preference for either syn or anti attack might result, analogous to that proposed for the S_N2' mechanism,[24] and the generation of significant optical activity in **17** could be taken as evidence for a role for this process. However **17** was not optically active, and it is our belief that since the ion pair mechanism of eq 3 and 4 provides a satisfactory explanation of the data this is to be preferred. Many solvent molecules are undoubtedly involved in the stabilization of **13** and **14** during ionization, including electrophilic interactions with the sulfonate group, but evidence for a specific interaction with a particular solvent molecule leading to a covalent bond in the product has not been found.

The lesser effect of Ph in comparison to CF_3 in directing substitution to the ring may be seen in the fact that **26** gave a preference for **27** over **28** (Ar = Ph, N = OEt) of 74:26 with NaOEt/EtOH and 67:33 with EtOH,[8a] whereas **14** gave the ring-substituted product **17** as the only observable product on ethanolysis. Both steric and electronic factors can be imagined to influence the position of attack. The Ph and CF_3 groups are so dissimilar that a quantitative assessment of their relative effective sizes in this particular system would not appear to be reliable, but it is probable that Ph is at least as large as CF_3, and it appears certain that the electron demand of the carbocationic center is much greater for the CF_3-substituted system, as we have presented extensive evidence of the destabilizing influence of CF_3 on carbocation systems.[7,21,25] Thus it is reasonable to postulate that there is greater delocalization of positive charge into the ring in the carbocation derived from **14** compared to **26** (Ar = Ph) and that this factor would operate in the transition state for ethanolysis to favor ring substitution more for the CF_3-substituted ion, as is observed. If phenyl does have a larger effective size than CF_3 then steric factors alone would predict the opposite result.

Experimental Section

Liquid chromatographic separations were carried out with a Chromatotron centrifugal radial thin-layer chromatograph from Harrison Research using silica gel plates and 15/85 EtOAc/petroleum ether as eluent. NMR spectra were obtained with a Varian T-60 instrument with Me_4Si as internal standard. Elemental analyses were done by Galbraith Laboratories.

9-Anthryl trifluoromethyl ketone was obtained from Aldrich, as were the fluorinated solvents, which were purified as reported previously.[4,10,23] The alcohols **3**[9] and **4**[9d] were prepared by $NaBH_4$

(21) (a) Allen, A. D.; Kanagasabapathy, V. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1983**, *105*, 5961–5962. (b) Kanagasabapathy, V. M.; Sawyer, J. R.; Tidwell, T. T. *J. Org. Chem.* **1985**, *50*, 503–509.

(22) Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3189–3199.

(23) Allen, A. D.; Jansen, M. P.; Koshy, K. M.; Mangru, N. N.; Tidwell, T. T. *J. Am. Chem. Soc.* **1982**, *104*, 207–211.

(24) Bach, R. D.; Wolber, G. J. *J. Am. Chem. Soc.* **1985**, *107*, 1352–1357 and references therein.

(25) Tidwell, T. T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 20–32.

reduction of the ketones and converted to the tosylate **13** and mesylate **14**, respectively, by treatment with NaH and the appropriate sulfonyl chloride by the methods used for similar substrates.[4,10,23] The preparation of (*R*)-(−)-**14** from (*R*)-(−)-**4** (Aldrich) was carried out by the same method.

1-(1-Naphthyl)-2,2,2-trifluoroethyl tosylate (**13**) was recrystallized from pentane–ether: mp 84–85 °C; ^{1}H NMR (CCl_4) δ 2.22 (s, 3, CH_3), 6.45 (q, 1, J = 6 Hz, $CHCF_3$), 6.8–8.1 (m, 11 aryl H). Anal. Calcd for $C_{19}H_{15}F_3O_3S$ (M_r 380.39): C, 59.99; H, 3.97. Found: C, 59.99; H, 4.11.

1-(9-Anthryl)-2,2,2-trifluoroethyl mesylate (**14**) was purified by chromatography and gave mp 90 °C dec: ^{1}H NMR (CCl_4) δ 2.50 (s, 3, CH_3), 7.2–8.4 (m, 10, aryl H and $CHCF_3$); mass spectrum, m/e (rel intensity) 354 (M^+, 82), 285 ($M^+ - CF_3$, 9) 259 (M^+ – OMs, 100). The optically active sample gave $[\alpha]_{25}$ ($CHCl_3$) −46.7° (436 nm), −22.4 (546 nm), −19.4 (578 nm), −17.8 (589 nm).

Product Studies. A sample of 0.2 g of tosylate **13** was heated in 20 mL of EtOH 30 h at 100 °C in a sealed ampule. The product was poured into H_2O, extracted with ether, washed with $NaHCO_3$, dried, and evaporated and the product ethyl 1-(1-naphthyl)-2,2,2-trifluoroethyl ether (**15**) isolated by VPC (10 mm × 3 m Carbowax 20 M, 215 °C): ^{1}H NMR ($CDCl_3$) δ 1.22 (t, 3, J = 7 Hz, CH_3), 3.60 (q, 2, J = 7 Hz, OCH_2), 5.45 (q, 1, J = 7 Hz, $CHCF_3$), 7.2–8.3 (m, 7, naphthyl). A similar spectrum less the ethyl signals was observed when the tosylate **13** was reacted in CD_3CD_2OD and the spectrum measured directly after complete solvolysis: high-resolution mass spectrum, M^+ 254.0920, calcd for $C_{14}H_{13}F_3O$ 254.0963.

In a similar way there was obtained 1-(1-naphthyl)-2,2,2-trifluoroethyl acetate (**16**) from the reaction of **13** in AcOH: mp 55–56 °C; IR (CCl_4) 1770 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 3, CH_3), 6.96 (q, 1, J = 7 Hz, $CHCF_3$), 7.2–8.3 (m, 7, naphthyl). Anal. Calcd for $C_{14}H_{11}F_3O_2$ (M_r 268.24) C, 62.69; H, 4.13. Found: C, 62.83; H, 4.16. The same downfield shift of the $CHCF_3$ resonance could be observed on solvolysis of **13** in CD_3CO_2H at 100 °C in an NMR tube.

Solvolysis of 64 mg (0.18 mmol) of the 9-anthryl mesylate **14** in 15 mL of absolute EtOH for 16 h at 96 °C followed by chromatography gave **17** as a yellow oil (40 mg, 0.13 mmol, 73%): ^{1}H NMR ($CDCl_3$) δ 1.26 (t, 3, J = 7 Hz, CH_3), 3.68 (q, 2, J = 7 Hz, CH_2), 5.20 (s, 1, C*H*OEt), 6.06 (q, 1, J = 9 Hz, $CHCF_3$), 7.1–7.9 (m, 8, Ar); UV (pentane) λ_{max} 254 nm (ϵ 15 400); mass spectrum, m/e (relative intensity) 304 (M^+, 15), 2.75 ($M^+ - C_2H_5$, 6), 259 ($M^+ - OC_2H_5$, 100); high-resolution mass spectrum, M^+ 304.1061, calcd for $C_{18}H_{15}F_3O$ 304.1120.

A similar reaction using (*R*)-(−)-**14** gave **17** with no measureable optical activity.

Similarly reaction of **14** with HOAc for 5 min at 91 °C gave **18**: IR (CCl_4) 1760 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.08 (s, 3, CH_3), 6.14 (q, 1, J = 9 Hz, $CHCF_3$), 6.84 (s, 1, C*H*OAc), 7.2–7.6 (m, 8, Ar). When the solvolysis of **14** was carried out in CD_3CO_2D in an NMR tube and the ^{1}H NMR measured at intervals the signals at δ 6.1 and 6.8 were observed to appear and then to both disappear. At the same time aryl signals below δ 8.0 diminished and then increased in size, suggesting the initial formation of **18** followed by isomerization to **21**.

Authentic **21** was obtained by reaction of **5** with either NaH/Ac_2O or pyridine/AcCl: mp 97–98 °C; ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 3, CH_3), 7.2–9.0 (*m*, 10, C*H*OAc and Ar). Anal. Calcd for $C_{18}H_{13}F_3O_2$ (M_r 318.30): C, 67.92; H, 4.12. Found: C, 68.14, H, 4.31. Reaction of **14** with HOAc for 25 min at 100 °C and chromatographic separation gave **18** and **21** further characterized by their mass spectra. **18**: mass spectrum, m/e (relative intensity) 318 (M^+, 100), 276 ($M^+ - C_2H_2O$, 50), 259 (M^+ – AcO, 83), 207 ($M^+ - CF_3 - C_2H_2O$, 100). **21**: mass spectrum, m/e (relative intensity) 318 (88), 275 (M^+ – Ac, 5), 259 (24), 207 (100).

Reaction of **14** (54 mg, 0.15 mmol) in 60 mL of 100% TFE at 25 °C for 10 min was followed by workup and chromatography as before to give **19** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 3.80 (q, 2, J = 9 Hz, OCH_2CF_3), 5.42 (s, 1, CHO), 6.12 (q, 1, J = 10 Hz, $CHCF_3$), 7.0–8.0 (m, 8, Ar); mass spectrum, m/e (relative intensity) 358 (M^+, 15), 259 ($M^+ - OCH_2CF_3$, 100).

Kinetics were measured by typically injecting 5 μL of a 0.1 M solution of the substrate in CH_3CN into 1.2 mL of the solvent in a UV cell and monitoring the change in the absorption at an appropriate wavelength for **13** [280 nm (TFA), 278 (TFE), 281 (HCO_2H), 244 (HFIP)] or for **14** [246 nm (TFE), 254 (EtOH and HOAc), 265 (HCO_2H), 250 (HFIP)]. Titrimetric runs for **13** in ethanol and acetic acid were carried out with 1-mL aliquots of 0.01 M solutions in sealed ampules. Ethanol solutions were titrated with 0.02 M NaOH to phenolphthalein end points, and HOAc solutions were titrated with 0.02 M NaOAc in HOAc to bromophenol blue end points.

The rate for **13** in CD_3CO_2D at 99.4 °C was also measured by ^{1}H NMR by integrating the tosyl CH_3 signal at δ 2.20 and 2.40 in the reactant and product, respectively. The rate constant was 8.18 ± 0.56 × 10^{-5} s^{-1} for two runs at 99.4 °C, as compared to the value of 8.56 × 10^{-5} s^{-1} obtained for HOAc by titration.

The polarimetric rate for (*R*)-(−)-**14** in 100% TFE was measured by observing the decrease in the rotation at 436 nm using a Perkin-Elmer 141 polarimeter. Duplicate runs were reproducible to ±1%.

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Registry No. **4**, 62509-74-4; **5**, 65487-67-4; (*R*)-(−)-**5**, 53531-34-3; **13**, 90775-16-9; **14**, 90775-17-0; (*R*)-(−)-**14**, 100814-48-0; **15**, 100814-49-1; **16**, 100814-50-4; **17**, 100814-51-5; **18**, 100814-52-6; **19**, 100814-54-8; **21**, 100814-53-7; 9-anthryl trifluoromethyl ketone, 53531-31-0; 1-naphthyl trifluoromethyl ketone, 6500-37-4.