Articles

3-(Trifluoromethyl)indenyl Cation: Ion Pair Return in the Formation of an Antiaromatic and Electron-Deficient Doubly Destabilized Carbocation

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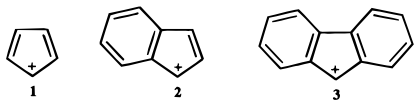
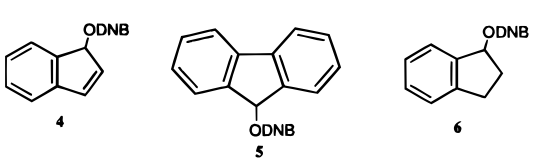
The solvolysis of 3-(trifluoromethyl)-3-indenyl tosylate (**15**) occurs with extensive isomerization to 1-(trifluoromethyl)-3-indenyl tosylate (**16**), which reacts in a slower process to give the substitution product **17**. Kinetic analysis of a model involving an intermediate allyl cation/tosylate ion pair **18** gave a partitioning ratio in CD_3CO_2D at 99.6 °C for **18** of 7.7 for return with allylic rearrangement compared with solvent capture. Studies of **15** with specific ^{18}O labeling show no scrambling in recovered **15** and partial scrambling in rearrangement to **16**. The *m* value measuring the dependence of the reactivity of **15** on the solvent-ionizing parameter Y_{OTs} is 0.78, which is significantly less than that of 1.23 for the analogous 9-(trifluoromethyl)-9-fluorenyl tosylate **7**. Normal salt effects in CF_3CO_2H predominate for **15**, and the special salt effect involves no more than 14% capture of solvent-separated ion pairs by 0.551 M KO_2CCF_3. The substrate **15** has a net diminution in reactivity of more than 10^9 relative to the secondary indanyl tosylate **22**, with factors of 10^6 and 10^3 attributable to antiaromaticity and to the electron-withdrawing CF_3 group, respectively. The solvolysis of **15** is proposed to occur by formation of an ion pair with significant nucleophilic solvation at the relatively unhindered allylic carbon, but internal return occurs in preference to solvent or salt capture. Solvolysis of the rearranged tosylate **16** occurs with a strong rate retardation by the γ-CF_3 group, a large extent of internal return, and with a normal salt effect.

There has been increasing interest in the concepts of aromaticity and antiaromaticity,[1] and the study of carbocations and carbanions that display these properties continues to be a particularly challenging area for both theoretical[2] and experimental[3] studies. Because of our interest in destabilized carbocations,[4,5] we have been attracted to the study of the cyclopentadienyl (**1**),[5h] indenyl (**2**), and fluorenyl (**3**)[5g] cations. Of these, **1** has received particular attention,[1,2a,c,d,5h] and there have been recent studies of **3**,[3b,5g] but **2** has been comparatively neglected. We now report the results of our studies of a doubly destabilized indenyl carbocation.



1 2 3

The solvolytic generation of the indenyl cation (**2**) has been studied by Friedrich and co-workers.[6] The relative solvolytic reactivities of **4, 5**, and **6** were estimated as 1, 10, and 10^5−10^6, respectively, and on the basis of these data, rate retardations due to antiaromatic destabilization by factors of 10^{11} and 10^8 were estimated for formation of **2** and the 9-fluorenyl cation, using the cyclopentyl system as a reference.[6]



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We have been interested in the destabilizing effects of CF_3 and C_2F_5 groups on carbocationic reactivity,[5] including the effects on the reactivity of molecules substituted with two such groups to produce doubly destabilized

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(6) (a) Friedrich, E. C.; Taggart, D. B. *J. Org. Chem.* **1978**, *43*, 805−808. (b) Friedrich, E. C.; Tam, T. M. *J. Org. Chem.* **1982**, *47*, 315−319.

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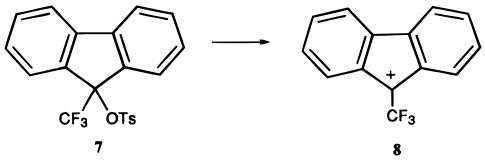
carbocations.[5f] Recently, we have extended this approach to include double destabilization by antiaromaticity and electron-withdrawing α-substitution and have examined the solvolysis of tosylate **7** to generate the 9-(trifluoromethyl)fluorenyl cation **8**.[5g] The results indicated that **7** is 4×10^7 times less reactive than Ph_2CHOTs, and rate factors of 10^4 and 10^3 may be attributed to the effect of the electron-withdrawing effect of the CF_3 group and the destabilizing effect of the 12 π-electron antiaromatic[1] system, respectively, in the generation of cation **8**.

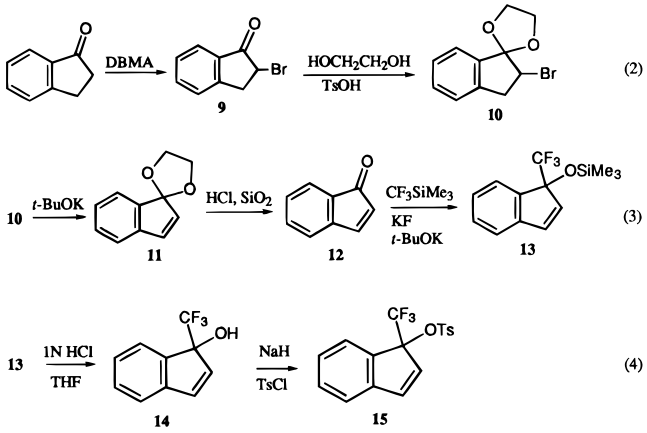


7 8 (1)

The tosylate **7** was also found to have a very high dependence of reactivity on the solvent ionizing power Y_{OTs}, with an *m* value of 1.23, and was found to display very large accelerations of trifluoroacetolysis on addition of NaO_2CCF_3. The effects were attributed to a high demand for solvent stabilization and a special salt effect with scavenging of solvent-separated ion pairs by the added salt.[5g] We have now extended these studies to the potentially more highly destabilized indenyl system, which shows markedly different behavior from **7**.

Results

The indenyl tosylate **15** was prepared using a modification[7a] of the Marvel and Hinman synthesis of indenone (**12**),[7b,c] followed by CF_3 transfer using CF_3SiMe_3 (eqs 2−4).[7d]



The solvolysis of **15** in trifluoroacetic acid or acetic acid gave rearrangement to the secondary tosylate **16**, which reacted further in a slower process to the corresponding substitution products **17** (eq 5). These processes could

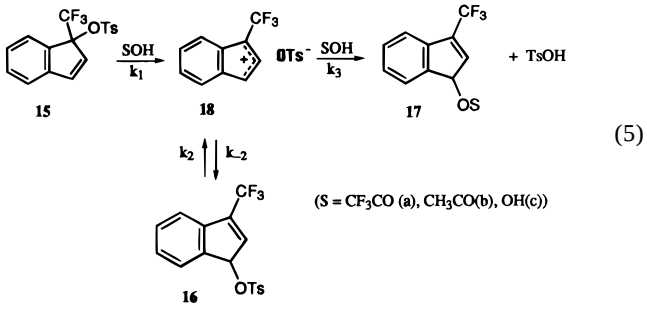


Table 1. Solvolysis Rate Constants for 15 and 16 at 25 °C

solvent	[salt]	k_1 (s^{-1})[a] **15**	k (s^{-1})[a] **16**	k **7**/k **15**	k **15**/k **16**
TFA		2.06×10^{-3}	8.30×10^{-5}	149[e]	24.8
	0.0587[b]	2.59×10^{-3}	1.12×10^{-4}		23.1
	0.0588[c]	2.66×10^{-3}	1.19×10^{-4}		22.4
	0.201[c]	4.38×10^{-3}	2.14×10^{-4}		20.5
	0.201[d]	3.61×10^{-3}	1.86×10^{-4}		19.4
	0.421[c]	5.82×10^{-3}	3.13×10^{-4}		18.6
	0.592[c]	7.00×10^{-3}	3.56×10^{-4}		19.7
97 HFIP		5.89×10^{-4}[f]	1.15×10^{-5}[g]	226[e]	51.2
HCO_2H		9.57×10^{-5}		86[e]	
97 TFE		1.61×10^{-5}[h]		55[e]	
50 TFE		2.27×10^{-5}[i]	(4.59×10^{-4})[i]		4.2[i]
80 EtOH		(3.20×10^{-5})[j]		7.7[j]	
HOAc		2.00×10^{-7}[k]		0.87	1.5[l]

[a] Duplicate runs measured by UV unless noted at each temperature, reproducible ±5%. [b] NaO_2CCF_3. [c] KO_2CCF_3; for **15** $k_1 = (8.52 \pm 0.35) \times 10^{-3}$ M^{-1} s^{-1} $[KO_2CCF_3] + (2.18 \pm 0.11) \times 10^{-3}$ s^{-1}, for **16** $k = (4.88 \pm 0.24) \times 10^{-4}$ M^{-1} s^{-1} $[KO_2CCF_3] + (9.16 \pm 0.77) \times 10^{-5}$ s^{-1}. [d] NaO_3SCF_3. [e] Derived using redetermined values of k (**7**). [f] k_{obs}($s^{-1} \times 10^3$), (*T*, °C): 5.30 (56.6), 2.78 (45.9), 1.28 (35.8); $\Delta H^{\ddagger} = 13.0$ kcal/mol; $\Delta S^{\ddagger} = -29.6$ cal K^{-1} mol^{-1}. [g] k_{obs} ($s^{-1} \times 10^5$), (*T*, °C): 21.0 (56.6), 8.83 (45.9), 3.24 (35.8); $\Delta H^{\ddagger} = 17.4$ kcal/mol; $\Delta S^{\ddagger} = -22.6$ cal K^{-1} mol^{-1}. [h] k_{obs} ($s^{-1} \times 10^4$), (*T*, °C): 7.61 (62.7), 1.95 (47.6); $\Delta H^{\ddagger} = 19.8$ kcal/mol, $\Delta S^{\ddagger} = -14.1$ cal K^{-1} mol^{-1}. [i] k_{obs} **15** (65.1 °C) $= 1.94 \times 10^{-3}$ s^{-1}; k_{obs} **16** (65.1 °C) $= 4.59 \times 10^{-4}$ s^{-1}, k **15**/k **16** = 4.2. [j] 60.8 °C. [k] Extrapolated value from measurements at higher temperatures, k_{obs} $s^{-1} \times 10^5$ (*T*, °C) 40.0 (99.6), 4.86 (75.4), 1.31 (63.0); $\Delta H^{\ddagger} = 22.6$ kcal/mol, $\Delta S^{\ddagger} = -13.9$ cal K^{-1} mol^{-1}. Rate at 99.6 °C measured by ^1H NMR in CD_3CO_2D. [l] See text.

be monitored by UV and by NMR, and **16** could be obtained on a preparative scale by stopping the reaction at a suitable time and then isolating and characterizing the purified material. After extended reaction times, the acetates **17a** and **17b** were isolated and characterized, along with small amounts of the alcohol **17c**.

Rate constants for the reaction of **15** and for the subsequent solvolysis of **16** to **17** were measured by both UV and NMR spectroscopy, as collected in Table 1. The rates for both processes could be measured by continuous monitoring of the same sample, and good agreement in the rates was found by using isolated and purified **16** to measure the rate of the second step.

For the reaction of **15** in acetic acid the reaction mixture in CD_3CO_2D was sealed in an NMR tube and heated at 99.6 °C. The tube was cooled at intervals, and the ^1H NMR spectrum was measured. The change in the CH_3 peak of **16** with time as a function of the total tosylate concentration (**15** + **16** + TsOH) was measured, as collected in Table 2 (Supporting Information), and illustrated in Figure 1.

The effects of added salts on the rates of trifluoroacetolysis of **15** and **16** as measured by UV are reported in Table 1. Addition of NaO_2CCF_3, KO_2CCF_3, and NaO_3SCF_3 gave similar changes in the reactivity of **15**, and linear correlations of the dependence on $[KO_2CCF_3]$ of the rates of **15** and **16** gave slopes (s^{-1} M^{-1}) of $(8.52 \pm 0.35) \times 10^{-3}$ and $(4.88 \pm 0.24) \times 10^{-4}$. A plot for **15** at 25 °C is shown in Figure 2, along with comparative data[5g] for 9-(trifluoromethyl)fluorenyl tosylate (**7**) at 6.1 °C. For direct comparison the latter rates have been multiplied by 0.0532 to give the same rates at [salt] = 0.0.

To determine the effect of added salt on the competition between rearrangement of **15** to **16** and solvolysis to **17**, solutions of **15** in CF_3CO_2D without salt and with 0.551 M KO_2CCF_3 were observed at intervals by ^1H NMR (400 MHz) at 22 °C, as reported in Table 3 (Supporting Material). Kinetic analysis of the data in the absence of salt gave similar rate constants of 1.24×10^{-3} and 1.48

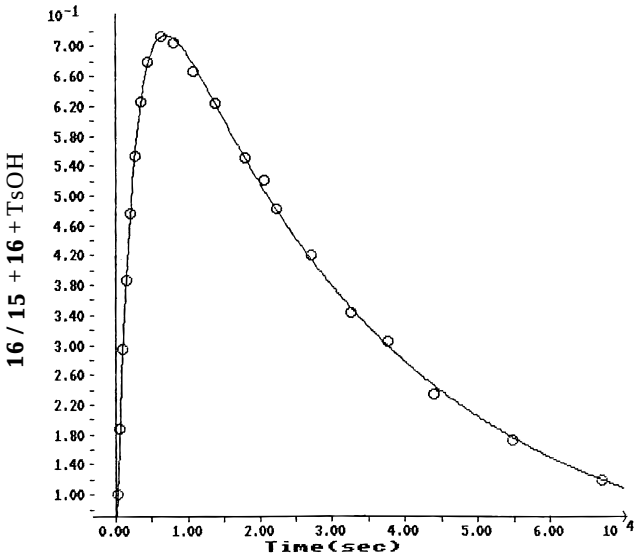


Figure 1. Fraction of 1-(trifluoromethyl)-3-indenyl tosylate (**16**) vs time in the acetolysis of 3-(trifluoromethyl)-3-indenyl tosylate (**15**) in CD_3CO_2D at 99.9 °C (curve fit by eq 6).

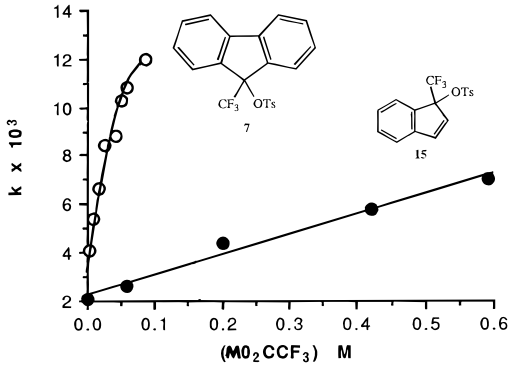


Figure 2. Effects of added salts MO_2CCF_3 on the trifluoroacetolysis of 9-(trifluoromethylfluorenyl)tosylate **7** (NaO_2CCF_3 at 6.1 °C, k × 0.517) and 3-(trifluoromethyl)-3-indenyl tosylate **15** (KO_2CCF_3 at 25 °C).

$\times 10^{-3}$ s^{-1} for the disappearance of **15** and the appearance of **16** at 22 °C, respectively, in reasonable agreement with the UV rate 2.06×10^{-3} s^{-1} at 25 °C for reaction of **15**. For the data in the presence of 0.551 M KO_2CCF_3, a value of k_1 of 3.3×10^{-3} s^{-1} at 22 °C was estimated, which is 2.6 times greater than the value in the absence of salt, and this acceleration in the rate is comparable to that of 3.4 observed by UV for 0.592 M KO_2CCF_3 (Table 1).

To examine the extent of oxygen equilibration during the reaction in CF_3CO_2H, a sample of **15** with sulfonyl-$^{18}O_2$ labeling was prepared using sulfonyl-$^{18}O_2$-labeled 4-tosyl chloride made using $H_2{}^{18}O$ with 98.8% ^{18}O, as we have done previously.[5d] The solvolysis was carried out for 9 min (1.6 half-lives) at 25 °C and then quenched,[5d] and the ^1H NMR spectrum showed the presence of the starting tosylate **15** and the rearranged tosylate **16** in a ratio of 1:1.5. The ^{13}C NMR spectrum of the recovered tosylate **15** showed no detectable ^{18}O-induced isotope shift in the peak for the alkoxy carbon at δ 90.6, indicating no ^{18}O scrambling had occurred. The ^{13}C NMR spectrum of the rearranged tosylate **16** showed signals for ^{13}C bonded to ^{16}O at δ 80.089 and to ^{18}O at 80.058 ppm, in a ratio of 1.142:1.000, respectively (Figure 3), corresponding to 53% bonding of ^{16}O-labeled oxygen to the allylic carbon.

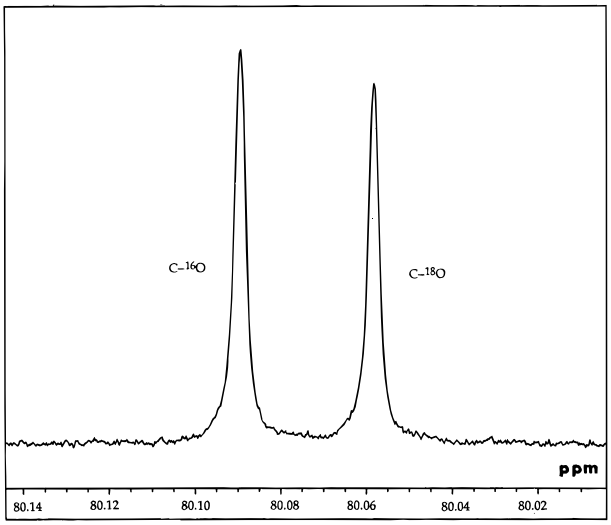


Figure 3. ^{13}C NMR signal for the carbinyl carbon of partially scrambled 1-(trifluoromethyl)-3-indenyl tosylate-$^{18}O_2$ (**16**-$^{18}O_2$).

Discussion

These results are consistent with the solvolysis of **15** proceeding to an ion pair **18** that can partition between return to the rearranged tosylate **16** and solvent capture to form **17**, but without return to the less stable starting tosylate **15** (eq 5). There have been numerous previous demonstrations of return in allylic systems,[8ab] but the conversion of **15** to **16** is unusual in that there is an isomerization of a tertiary to a secondary substrate.

The kinetic rate expressions for the reaction scheme corresponding to eq. 5 have been derived previously.[9] For the reaction in CD_3CO_2D (Table 2, Supporting Information), the appropriate expression for the measured quantity [**16**]/([**15**] + [**16**] + [**17**]) is given in eq 6, and fitting this equation to the measured results (Figure 1) gave $k_a + k_b$ ($= k_1$) of $(4.00 \pm 0.07) \times 10^{-4}$ s^{-1}, $k_a/(k_a + k_b) = 0.886 \pm 0.005$, and $k_c = (3.09 \pm 0.04) \times 10^{-5}$ s^{-1}, and these give values $k_a = 3.54 \times 10^{-4}$ s^{-1} and $k_b = 4.60 \times 10^{-5}$ s^{-1}. The fraction k_a/k_b is 7.7 and is equal to k_{-2}/k_3, which is the extent to which the initial ion pair partitions between rearranged tosylate **16** and solvent capture. The value of k_2 ($= k_1k_ck_b^{-1}$, eq 5), is 2.69×10^{-4} s^{-1}, so the ionization rate ratio $k_1/k_2 = 1.5$, considerably less than the rate ratio $(k_a + k_b)/k_c$ of 13 for product formation from **15** and **16**.

$$\mathbf{15} \xrightarrow{k_a} \mathbf{16}$$

$$\mathbf{15} \xrightarrow{k_b} \mathbf{17}$$

$$\mathbf{16} \xrightarrow{k_c} \mathbf{17}$$

$$[\mathbf{16}]/([\mathbf{15}] + [\mathbf{16}] + [\mathbf{17}]) = k_a[\exp(-(k_a + k_b)t) - \exp(-k_ct)](k_c - k_a - k_b)^{-1} \quad (6)$$

For the kinetic data (Table 1) in CF_3CO_2H k(**15**) ($= k_a + k_b$) is 2.06×10^{-3} s^{-1} and k(**16**) ($= k_c$) is 8.30×10^{-5} s^{-1}. From the product data in CF_3CO_2D (Table 3, Supporting Information) the first observed product ratio [**16**]/([**16**] + [**17**]) [$= k_a/(k_a + k_b)$] is 0.88, giving values for k_a of 1.80×10^{-3} s^{-1}, k_b of 2.6×10^{-4} s^{-1}, k_1/k_2 ($= k_b/k_c$) of 3.1, and k_a/k_b ($= k_{-2}/k_3$) of 6.9.

The trifluoroacetolysis of **15** labeled with 98.8% sulfonyl-$^{18}O_2$ for 1.6 half-lives showed no scrambling of the label in recovered **15**, consistent with the absence of return of the ion pair **18** to **15**, as shown in eq 5. The rearranged tosylate **16** showed the oxygen bonded to the allylic carbon contained 53% ^{16}O, while complete scrambling of the ^{18}O label would result in 34% ^{16}O incorporation at this position, and selective migration of the ^{16}O at C-3 of **15** to the allylic carbon would result in 100% ^{16}O at this position. This result indicates a preference (memory effect) for rebonding of the originally carbon-bonded oxygen to the extent of 30%, with 70% scrambling of the oxygens. For comparison, in one previous study[8d] of an allylic rearrangement of a *p*-nitrobenzoate ester ^{18}O equilibration to the extent of 90−100% was observed, while for 2-pent-3-enyl *p*-nitrobenzoate there was a preference for bonding of the carbonyl oxygen during the symmetrical allylic rearrangement[8e] by a factor of 3.8 to 4.9. Preferential return of an original tertiary carbon bonded oxygen to a secondary carbon following Wagner−Meerwein rearrangement to the extent of 6.1:1 in an ^{18}O-labeled hexafluorobutyrate ester has also been observed.[8f]

The values of k_1 for the initial reaction of **15** in 6 solvents (Table 1) are well correlated by Y_{OTs} values at 25 °C by the relation $\log k_1 = (0.78 \pm 0.03)Y_{OTs} - 6.25 \pm 0.09$, $r = 0.997$. The initial ion pair presumably has the tosylate anion in proximity to the original point of attachment, and there is likely to be a barrier to the movement of the tosylate to the γ-position, as it has been demonstrated by Nordlander and Gassman *et al.*,[10] that allylic ion pairs in which the termini differ only in isotopic labeling and the initial position of the counterion do not undergo equilibration as fast as collapse to covalent products. A plausible contributing factor for this barrier is the presence of a node at C_β in the HOMO of the allylic carbocation, which causes an impediment to the movement of the counterion. Despite this barrier the extent of tosylate internal return with rearrangement is still quite large. The fraction return in CD_3CO_2D at 99.6 °C $k_a/(k_a + k_b)$ is 0.88, and in CF_3CO_2D in the absence of salt the initial observed fraction of return observed is also 0.88 (Table 3, Supporting Information). In the presence of 0.551 M KO_2CCF_3 the initial observed fraction of rearrangement to **16** decreases to 0.74, and the change of 14% caused by the salt may be interpreted as a very modest special salt effect in which solvent separated ion pairs are captured by salt. The similarity of the extent of ion pair return in CF_3CO_2D and CD_3CO_2D is suggestive that there is only a similar and small extent of formation of solvent separated ion pairs in both of these media, so that the nucleophilic CD_3CO_2D or the added salts in CF_3CO_2D do not capture major portions of the initial ion pair.

Added KO_2CCF_3 in CF_3CO_2H gives normal salt effects on the rates of both **15** and **16**, with increases of 3.4 and 4.3, respectively, for 0.592 M salt. These increases are, however, much less than those observed for either secondary or tertiary substrates $ArCH(OTs)CF_3$[5d] and $ArC(OTs)(CH_3)CF_3$;[5c] for example, in the latter case[5d] 0.586 M KO_2CCF_3 gives a rate acceleration of 27.1, which is 8.0 times greater than the effect on **15**. Similarly, for the fluorenyl tosylate **7**, a concentration of KO_2CCF_3 of 0.059 M produces a rate acceleration of 5.4,[5g] 4.2 times greater than for **15**. For the indenyl tosylate **15** the added salts cause mainly normal salt effects and intercept no more than 14% of solvent separated ion pairs, and predominant internal return to rearranged tosylate **16** still occurs, even at 0.59 M salt. By contrast, the much larger salt effects for the fluorenyl tosylate **7** have been characterized kinetically as special salt effects[5g] and result in formation of solvolysis product. The comparative salt effects on the trifluoroacetolysis of **7** and **15** are shown in Figure 2. The different behavior of the indenyl tosylate **15** is due to the availability of the unhindered allylic position, which provides a ready point of return for the tosylate anion. The steep initial curvature of rate *vs* [salt] plots characteristic of the special salt effect is too weak in the case of **15** to be reliably observed.

The strikingly different *m* values of 1.23 and 0.78 for the fluorenyl tosylate **7** and the indenyl tosylate **15**, respectively, lead to a steady decrease in the fluorenyl/indenyl rate ratio k **7**/k **15** with decreasing solvent polarity from 226 (HFIP) to 0.87 (HOAc). The large *m* value for the fluorenyl tosylate **7** was attributed[5g] to destabilization due to antiaromaticity effects, which therefore led to a rather localized carbocation that showed enhanced stabilization by polar solvents.

The significantly lower *m* value for **15** may be explained on the basis of extensive charge delocalization to the relatively unhindered allylic carbon, which undergoes significant nucleophilic interaction with the solvent. However, this solvation does not advance to the stage of nucleophilic solvent participation, as even in the rather nucleophilic acetic acid formation of the rearranged tosylate exceeds solvent capture by a factor of 7.7 (*vide supra*).

The alternative mechanism of formation of the rearranged tosylate **16** without ionization but by a sigmatropic rearrangement of **15** appears highly unlikely, as the strong dependence of the reaction rate on solvent polarity, and the significant normal salt effect, indicate a very polar transition state, and such pathways have not been demonstrated in other allylic rearrangements.[8]

The rates of solvolysis of the rearranged secondary tosylate **16** in TFA (25 °C), 97% HFIP (25 °C), 50% TFE (65.1 °C), and CD_3CO_2D (99.6 °C) are 25, 51, 4.2, and 13 times slower, respectively, than the rate of rearrangement of **15** to **16**. The lower rate ratios in the more nucleophilic 50% TFE and CD_3CO_2D are consistent with some nucleophilic solvent assistance in the case of **16**, which is not unexpected for this secondary substrate. In CD_3CO_2D the kinetic analysis shows that the ionization rate ratio k_1/k_2 is only 1.5, but because of the extensive reformation of **16** by ion pair return the rate of consumption of the reactant is considerably less.

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(8) (a) Goering, H.; Koerner, G. S.; Linsay, E. C. *J. Am. Chem. Soc.* **1971**, *93*, 1230−1233. (b) Goering, H. L.; Anderson, R. P. *J. Am. Chem. Soc.* **1978**, *100*, 6469−6474. (c) Gassman, P. G.; Harrington, C. K. *J. Org. Chem.* **1984**, *49*, 2258−2273. (d) Goering, H. L.; Linsay, E. C. *J. Am. Chem. Soc.* **1969**, *91*, 7435−7439. (e) Goering, H. L.; Pombo, M. M.; McDaniel, K. D. *J. Am. Chem. Soc.* **1963**, *85*, 965−970. (f) Wilgis, F. P.; Neumann, T. E.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4435−4446.

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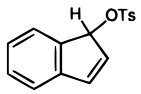
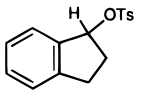
As described above, the kinetic analysis indicates that the rate ratio k_{-2}/k_3 for internal return relative to solvent capture for the ion pair **18** is 7.7, even in the highly nucleophilic solvent CD_3CO_2D. This is rather larger than values that have been obtained for other allylic systems, for example, a value of 2.1 in 90/10 acetone/H_2O found using ^{18}O equilibration.[8a] The value of 7.7 is remarkable since this is a relatively unhindered substrate that should be rather accessible for backside solvent attack. This substrate has the advantage that the ratio of ion pair return and solvent capture can be assessed from the kinetic analysis.

Comparison of the rate of rearrangement in trifluoroethanol of 1.61×10^{-5} s^{-1} for the tertiary CF_3-substituted indenyl tosylate **15** to the rate of trifluoroethanolysis of 2.1×10^{-2} s^{-1} estimated for the secondary indenyl tosylate **21**[6b,11a] reveals that **15** is 1.3×10^3 less reactive, showing a strong decelerating effect for the CF_3 group. The magnitude of this rate ratio k_H/k_{CF3} is comparable to those reported for some substrates $ArCH(OTs)CF_3$.[5f] A trifluoroethanolysis rate of 2.3×10^4 s^{-1} may be estimated for the indanyl tosylate **22**,[6b,11b] which implies a retardation in rate by a factor of 1.1×10^6 for **21** relative to **22**, and this was attributed[6b] to destabilization of the cation **2** derived from **21** due to the potentially antiaromatic 8π-electron cation system of the indenyl moiety. Thus, there are major decelerating effects of both the CF_3 substituent and the antiaromatic effect of the extra double bond in **15**, resulting in a net deceleration of more than 10^9 for **15** compared to **22**.



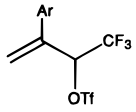
21



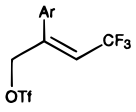
22

From the rates of solvolysis of the rearranged tosylate **16** in TFA and 97% HFIP a rate of reaction in TFE at 25 °C of 2×10^{-7} s^{-1} may be estimated, and comparison of this rate to that for **21**[11c] shows that the allylic CF_3 group decreases the reactivity of **16** by a factor of 10^5. This may be contrasted to the effect of a γ-CH_3 group in accelerating the solvolysis of indenyl dinitrobenzoate (**4**) by a factor of 10^3 at 21 °C,[6a] so the γ-CH_3 group is 10^8 more effective than γ-CF_3 in promoting the reactivity of these indenyl substrates. The greater effect of a γ as compared to a α-trifluoromethyl group in decreasing the reactivity of the allylic tosylate is a strong argument for the importance of geminal ground-state destabilization of α-trifluoromethyl tosylates partially counterbalancing the electronic destabilization of the carbocation and thus giving k_H/k_{CF_3} rate ratios greater than would be expected in the absence of this effect. We have previously argued that such ground-state destabilization led to enhanced k_H/k_{CF_3} rate ratios in 2-(trifluoromethyl)-2-adamantyl tosylate[5b] and 2-(pentafluoroethyl)-*exo*-2-norbornyl brosylate.[5a] Both of these substrates rearrange to less reactive secondary sulfonates in reactions suggested[5a] to be accelerated by the ground-state destabilizing effect caused by the presence of electron-withdrawing fluoroalkyl and sulfonate groups on the same carbon.

In contrast to **15** and **16**, studies by Gassman and Harrington[8c] of the solvolysis of acylic (trifluoromethyl)-allylic triflates **23** and **24** showed that the α-(trifluoromethyl) isomers **23** were 50−100 times less reactive than the primary γ-(trifluoromethyl) isomers **24**, and the trifluoroethanolysis of **23** gave the *E*/*Z* stereoisomeric trifluoroethyl ethers of general structure **24**, while triflates **24** gave only the corresponding ethers. Evidently, solvent displacement in the solvolysis is a major contributor to the higher reactivity of **24**. The solvolyses of **23** were interpreted as involving largely rate-limiting ionization with solvent substitution at the γ-carbon of the ion pair.



23



24

In summary, the doubly destabilized indenyl tosylate **15** shows a strong rate retardation by a factor of more than 10^9 due to the combined effects of antiaromaticity and the electron-withdrawing CF_3 group. In contrast to the relatively localized ion from fluorenyl tosylate **7**, the indenyl tosylate undergoes allylic delocalization permitting nucleophilic solvation at the relatively unhindered allylic carbon resulting in a much less marked dependence of rate on solvent ionizing power compared to **7**, so that **15** is slightly more reactive than **7** in the rather weakly ionizing HOAc solvent. The initial ion pair from **15** undergoes predominantly internal return to the secondary allylic tosylate **16**, even in the rather nucleophilic solvent CD_3CO_2D, or in the presence of 0.59 M added salt in CF_3CO_2D, and the lower reactivity of **16** provides further evidence for the importance of geminal ground-state destabilization in the reactivity of α-(trifluoromethyl) tosylates.

Experimental Section

Reagents for preparative experiments were obtained from commercial suppliers and used as received unless noted. Procedures and solvents for kinetics measurements have been described previously.[5]

Ether and THF for use as reaction solvents were dried by refluxing over Na/benzophenone and distilling. Glassware was either dried in an oven at 150 °C and then cooled under N_2 or Ar, or flame dried under N_2 or Ar before use.

2-Bromoindanone (9).[7a,b] To indanone (6.0 g, 0.045 mol) in 150 mL of CCl_4 was added 5,5-dibromo-2,2-dimethyl-4,6-dioxo-1,3-dioxane (dibromo Meldrum's acid, DBMA) (14.5 g, 0.047 mol), and the solution was refluxed for 3.5 h. Analysis of the mixture by ^1H NMR revealed the presence of 6% starting material, 78% **9**, and 16% 2,2-dibromoindanone. The solution was extracted with saturated $NaHCO_3$ solution, and the aqueous layer was extracted twice with ether. The combined organic layers were dried over $CaSO_4$, and the solvent was evaporated to give a bluish viscous solution, which was purified twice eluting on a column of silica gel with 3/2 CH_2Cl_2/hexane and final purification by radial chromatography with the same solvent to give **9** (3.71 g, 39%) as a pale yellow solid: mp 32−34 °C; ^1H NMR ($CDCl_3$) δ 3.43 (dd, 1, J = 3.2 Hz, 18.1 Hz), 3.85 (dd, 1, J = 7.5, 18.1 Hz), 4.66 (dd, 1, J = 3.2, 7.5 Hz), 7.4−7.9 (m, 4).

2-Bromoindanone Ethylene Ketal (10).[7a,b] A solution of **9** (3.71 g, 0.0176 mol), ethylene glycol (17 mL, 0.305 mol), and toluenesulfonic acid monohydrate (0.10 g, 0.53 mmol) in 200 mL of toluene was refluxed in a 500 mL round-bottomed flask

(11) (a) Multiplying the rate constant for **21**-ODNB in TFE at 25 °C of 8.32×10^{-12} s^{-1} (extrapolated from data in ref 6b) by the *k*(ROPNB)/*k*(ROTs) conversion factor of 2.5×10^9 (Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; p 374) gives 2.08×10^{-2} s^{-1} for **21** in TFE at 25 °C. (b) Based on the rate constant of 9.4×10^{-6} s^{-1} for **22**-ODNP in TFE at 25 °C extrapolated from data in ref 6b. (c) Solvolysis rates are compared since the ionization rate of **21** has not been determined.

equipped with a Dean−Stark trap for 5 h. Workup of a small sample showed 7% **9** remained, so additional toluenesulfonic acid (0.022 g, 0.12 mmol) and ethylene glycol (10 mL, 0.18 mol) were added and the solution was refluxed for an additional 8 h. The organic layer was washed with $NaHCO_3$ and NaCl solutions, dried over $CaSO_4$, and evaporated to give crude **10** (3.9 g, ca. 87%), which contained 6% **9** by ^{1}H NMR. The identity of **10** was confirmed by ^{1}H NMR ($CDCl_3$) δ 3.26 (dd, 1, J = 7.3, 16.1 Hz), 3.48 (dd, 1, J = 7.3, 16.1 Hz), 4.2−4.4 (m, 4), 4.55 (t, 1, J = 7.3 Hz), 7.1−7.5 (m, 4).

2-Indenone Ethylene Ketal (11).[7a,b] The crude ketal **10** (1.0 g, ca. 3.9 mmol) was added to freshly opened potassium *tert*-butoxide (0.84 g, 7.5 mmol) in a flame-dried three-neck round-bottomed flask. After an initial exothermic reaction, the mixture was heated for 3 h at 90 °C, cooled, added to aqueous NH_4Cl solution, and extracted three times with ether. The combined ether layers were washed with NaCl, dried, and evaporated to give crude **11** (0.502 g, ca. 73%) as a brown oil: ^{1}H NMR ($CDCl_3$) δ 4.1−4.4 (m, 4), 6.14 (d, 1, J = 5.8 Hz), 6.64 (d, 1, J = 5.8 Hz), 7.02−7.35 (m, 4).

2-Indenone (12).[7b] The crude ketal **11** (0.474 g, 2.72 mmol) was added with stirring to 1.5 g of silica gel (70−230 mesh), 4.5 mL of $CHCl_3$, and 5 drops of 1 N HCl. After 30 min of stirring, $NaHCO_3$ (0.054g) was added, and after 5 min of stirring the mixture was filtered through silica gel on a sintered glass funnel to give a bright yellow solution. Analysis by ^{1}H NMR showed the presence of 30% residual **11** with the product **12**, and so the above procedure was repeated with 7 drops of 1 N HCl to give a solution shown to contain only **12** by ^{1}H NMR:^{1}H NMR ($CDCl_3$) δ 5.89 (d, 1, J = 5.9 Hz), 7.2−7.5 (m, 4), 7.58 (d, 1, J = 5.9 Hz): IR ($CDCl_3$) 1736 (m), 1711 (s, C═O), and 1607 (m, CH═CH) cm^{-1}. For the next step it was essential to remove all $CHCl_3$, and this was done by drying the solution first with Drierite and then with 4A molecular sieves, evaporating, and adding CCl_4 followed by evaporation again.

3-(Trifluoromethyl)-3-[(trimethylsilyl)oxy]-1-indene (13). A solution of indenone **12** (0.123 g, 0.945 mmol) in 3 mL of THF was added to KF (0.011 g, 0.189 mmol) in 12 mL of THF cooled to −78 °C in a 25 mL round-bottomed three-neck flask, followed by the addition of CF_3SiMe_3 (0.30 mL, 2.0 mmol). Then, 10 drops of a saturated solution of *t*-BuOK in THF was added with a syringe. After 10 min TLC (10/90 EtOAc/hexane on silica gel) showed **13** (R_f = 0.6), and no residual **12** (R_f = 0.3). The solution was warmed to room temperature, water was added, and the solution was extracted three times with hexanes. The combined organic layers were dried over $CaSO_4$ and evaporated to give **13** (0.23 g, 0.84 mmol, 90%, at least 95% pure by ^{1}H NMR), which was purified by VPC (OV-17, 170 °C, t_R 5 min): ^{1}H NMR ($CDCl_3$) δ −0.07 (s, 9), 6.28 (d, 1, J = 5.8 Hz), 6.88 (d, 1, J = 5.8 Hz), 7.2−7.6 (m, 4); ^{13}C NMR ($CDCl_3$) δ 1.4, 85.5 (q, $^2J_{CF}$ = 31.0 Hz), 122.0, 124.4, 124.8 (q, $^1J_{CF}$ = 284.1 Hz), 126.8, 129.9, 134.2, 136.6, 141.8, 142.6; ^{19}F NMR ($CDCl_3$) δ −79.4; EIMS m/z 274 (M^+, 34), 203 ($M^+ - CF_3$, 44), 180 ($M^+ - Me_3SiF$, 30), 161 ($M^+ - Me_3Si$, F_2, 48), 133 ($M^+ - Me_3SiO$, CF_2, 100), 73 (Me_3Si^+, 56); HRMS m/z calcd for $C_{13}H_{15}F_3OSi$ 272.0844, found 272.0853.

3-(Trifluoromethyl)-3-indenol (14). In a 10 mL flask was stirred **13** (0.023 g, 0.09 mmol) overnight in 2 mL of THF and 3 mL 1 M HCl until TLC revealed no starting material remained. The reaction mixture was added to H_2O and extracted three times with ether, the combined ether layer was washed with H_2O and saturated NaCl and dried over $CaSO_4$, and the solvent was evaporated. The product was purified by radial chromatography with 20/80 EtOAc/hexane to give **14** (12 mg, 0.058 mmol, 66%), which after recystallization from pentane gave mp 46.5−47 °C: ^{1}H NMR ($CDCl_3$) δ 2.53 (bs, 1, OH), 6.29 (d, 1, J = 5.7 Hz), 6.90 (d, 1, J = 5.7 Hz); ^{13}C NMR ($CDCl_3$) δ 84.0 (q, $^2J_{CF}$ = 30.7 Hz), 122.3, 123.6, 124.8 (q, $^1J_{CF}$ = 283.4 Hz), 127.2, 130.4, 133.1, 137.2, 140.9, 142.8; ^{19}F NMR ($CDCl_3$) δ −78.5; IR ($CDCl_3$) 3592 cm^{-1} (OH); EIMS m/z 200 (M^+, 67), 180 (M^+ − HF, 31), 152 (35), 151 (29), 131 ($M^+ - CF_3$, 100), 103 ($M^+ - CF_3CO$, 52), 77 (43); HRMS m/z calcd for $C_{10}H_7F_3O$, 200.0449, found 200.0450. Anal. Calcd C, 59.99; H, 3.53. Found C, 60.06; H, 3.61.

3-(Trifluoromethyl)-3-indenyl Tosylate (15). To a cooled suspension of NaH (0.3 g, 6.3 mmol), previously washed with pentane, in 8 mL of ether was added alcohol **14** (0.0252 g, 0.126 mmol) in 2 mL of ether. After the mixture was stirred for 1 h, TsCl (0.023 g, 0.121 mmol) in 2 mL ether was added, the solution was stirred for 30 min, and the TLC showed no trace of residual TsCl. Ice and H_2O were added, the solution was extracted three times with ether, and the combined ether layers were washed with $NaHCO_3$ and NaCl solution, dried over $CaSO_4$, and evaporated to give crude **15** (0.047 g, 0.13 mmol, ca. 100%), which after radial chromatography (10/90 EtOAc/hexanes) and recrystallization from pentane gave mp 72.5−73 °C: ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3, CH_3), 6.31 (d, 1, J = 5.8 Hz, C═CH), 6.94 (d, 1, J = 5.8 Hz), 7.08−7.63 (m, 8, Ar); ^{13}C NMR ($CDCl_3$) δ 21.6, 90.6 (q, $^2J_{CF}$ = 32.2 Hz), 122.4, 122.8 (q, $^1J_{CF}$ = 283.4 Hz), 124.7, 127.2, 128.0, 128.8, 129.4, 130.8, 133.9, 136.3, 139.4, 142.6, 145.0; ^{19}F NMR ($CDCl_3$) δ −77.5; EIMS m/z 354 (M^+, 20), 334 (M^+ − HF, 6), 199 (M^+ − Ts, 100), 183 (M^+ − TsO, 43), 164 (M^+ − TsO, F, 46), 155 (Ts^+, 61); HRMS m/z calcd for $C_{17}H_{13}F_3O_3S$ 354.0537, found 354.0523.

1-(Trifluoromethyl)-3-indenyl Tosylate (16). A solution of tosylate **15** (20.1 mg, 0.0568 mmol) in 3 mL of CF_3CO_2H was left at 25 °C for 35 min and then poured into ice−water and extracted twice with ether, and the ether layers were washed with $NaHCO_3$ and NaCl, dried over $CaSO_4$, filtered, and evaporated to give 14.1 mg of crude product that by ^{1}H contained 10% of trifluoroacetate **17a** and 90% **16**. Radial chromatography (20/80 EtOAc/hexanes) gave **17a** (R_f = 0.56) and **16** (R_f = 0.35), which after recrystallization from pentane gave white needles: mp 92.5-93 °C; ^{1}H NMR ($CDCl_3$) δ 2.49 (s, 3, CH_3), 5.88 (broad quintet, 1, J = 1.5, 2.0 Hz), 6.63 (quintet, 1, J = 1.9 Hz, CF_3C═CH), 7.24−7.95 (m, 8); ^{13}C NMR ($CDCl_3$) δ 21.7, 80.1, 121.3 (2), 121.4 (q, $^1J_{CF}$ = 270.9 Hz), 125.1, 128.1, 130.0, 130.1, 133.1, 133.5 (q, $^3J_{CF}$ = 5.1 Hz), 136.4, 137.9 (q, $^2J_{CF}$ = 35.2 Hz), 139.9, 145.5; ^{19}F NMR ($CDCl_3$) δ −65.70 (t, J_{HF} 1.9 Hz); EIMS m/z 354 (M^+, 9), 334 (M^+ − HF, 13), 290 ($M^+ - SO_2$, 23), 199 (M^+ − Ts, 46), 183 (M^+ − OTs, 34), 164 (M^+ − OTs − F, 100), 155 (Ts^+, 65), 91 ($C_7H_7^+$, 100); HRMS m/z calcd for $C_{17}H_{13}F_3O_3S$ 354.0537, found 354.0541.

1-(Trifluoromethyl)-3-indenyl Trifluoroacetate (17a). Reaction of tosylate **15** in CF_3CO_2H as above for 25 h gave after workup a product containing alcohol **17c** and **17a** in a 1/4 ratio. On separation by radial chromatography **17a** decomposed to some extent, and only a small sample of slightly impure material was obtained: ^{1}H NMR ($CDCl_3$) δ 6.38 (broad quintet, 1), 6.80 (quintet, 1, $^3J_{CF}$ = 1.9 Hz), 7.00−7.60 (m, 4); ^{19}F NMR ($CDCl_3$) δ −65.8, −74.9; IR ($CDCl_3$) 1788 cm^{-1} (C═O); EIMS m/z 296 (M^+, 43), 199 ($M^+ - COCF_3$, 100), 151 ($M^+ - O_2CCF_3$, 66), 69 (CF_3^+, 74); HRMS m/z calcd for $C_{12}H_6F_6O_2$ 296.0272, found 296.0259. **1-(Trifluoromethyl)-3-indenol (17c)**: ^{1}H NMR ($CDCl_3$) δ 1.71 (d, 1, J = 10.0 Hz, OH), 5.31 (broad quintet, 1, $^2J_{CF}$ = 11.5, 2 Hz, CHO), 6.84 (quintet, 1, J = 1.8, 1.9 Hz, C═CH), 7.0−7.6 (m, 4, Ar); ^{13}C NMR ($CDCl_3$) δ 76.2, 121.0, 124.0, 127.6, 129.0, 138.6, 145.1 (3 C not visible); IR ($CDCl_3$) 3690 cm^{-1} (OH); EIMS m/z 200 (M^+, 77), 180 (M^+ − HF, 31), 131 ($M^+ - CF_3$, 100), 103 ($M^+ - CF_3CO$, 41); HRMS m/z calcd for $C_{10}H_7F_3O$ 200.0449, found 200.0447.

Trifluoroacetolysis of 15. A solution of **15** (4 mg, 0.011 mmol) and KO_2CCF_3 (83.7 mg, 0.550 mmol) in 1 mL of CF_3CO_2D was observed at intervals by ^{1}H NMR (400 mHz) at 22 °C. The signals due to the vinyl protons of **15**−**17** were integrated and used to calculate the relative amounts of **15**−**17** present. A similar experiment was carried out in the absence of salt. The amounts of **15**−**17** could also be evaluated from the integration of the CH_3 protons of the tosylate group, and sample spectra are included in the Supporting Information.

Acetolysis of 15. Kinetics. A solution of tosylate **15** (6.1 mg) in 650 μL of CD_3CO_2D in a sealed NMR tube was heated at 99.6 °C, and 24 data points were measured for the change in the ^{1}H NMR spectrum of the CH_3 in the tosylate group **16** at δ 2.4 and of **15** plus TsOH (corresponding to **17**), which were both near δ 2.5. The rate constant for formation of the rearranged tosylate **16** was 4.00 × 10^{-4} s^{-1}, and this disappeared to form the acetate **16b**-O_2CCD_3 with a rate constant

of 3.09×10^{-5} s^{-1}. Kinetic analysis as reported in the text using the programs ENZFITTER, distributed by Elsevier-BIOSOFT, and Sigma Plot, from Jandel Scientific, gave rate ratios of the individual steps. **Products.** A solution of **15** (19.8 mg, 0.0559 mmol) in 2 mL of CH_3CO_2H was heated at 100 °C for 26 h, and after workup the ^1H NMR of the product showed the presence of the rearranged acetate **17b** and the corresponding alcohol **17c** in a 4/1 ratio. Radial chromatography (1/9 EtOAc/hexanes) gave 3-(trifluoromethyl)-1-indenyl acetate (**17b**): mp near 0 °C; ^1H NMR ($CDCl_3$) δ 2.18 (s, 3), 6.31 (br quintet, 1), 6.81 (quintet, 1, J = 1.9 Hz), 7.25−7.54 (m, 4); ^{13}C NMR ($CDCl_3$) δ 20.9, 75.6, 121.1, 121.7 (q, $^1J_{CF}$ = 270.3 Hz, CF_3), 124.8, 127.7, 129.4, 134.6 (q, $^3J_{CF}$ = 5.1 Hz, CF_3CC), 137.0, 137.2 (q, $^2J_{CF}$ = 35.1 Hz, CCF_3), 141.7, 170.9; IR ($CDCl_3$) 1739 cm^{-1} (C=O); ^{19}F NMR ($CDCl_3$) δ −65.58; EIMS m/z 242 (M^+, 13), 200 ($M^+ - CH_2CO$, 100), 183 ($M^+ -$ AcO, 24), 131 (69); HRMS m/z calcd for $C_{12}H_9F_3O_2$ 242.0555, found 242.0548.

Kinetic measurements were carried out by injecting 10 μL of a 0.028 M solution of **15** in CH_3CN into 1.2 mL of solvent in the UV cell and monitoring the change in the absorption at 310 nm. Solvolysis rate constants for the disappearance of **15** were derived by fitting the observed absorbance data to a double exponential linear least-squares fit and correspond to the initial rate process observed. Rates for the reaction of **16** were obtained beginning with pure **16** and gave reasonable agreement with those obtained for the second process observed beginning with **15**.

3-(Trifluoromethyl)-3-indenyl Tosylate-*sulfonyl*-$^{18}O_2$. The labeled tosylate was prepared from indenol **14** and 4-tosyl-*sulfonyl*-$^{18}O_2$ chloride[5d] following the procedure for unlabeled **15**.

^{18}O Exchange. The reaction of **15** in TFA at 25 °C was carried out for 9 min and quenched and worked up for ^{13}C NMR analysis in $CDCl_3$ by the procedure utilized previously.[5d] The tosylate-bonded carbon in residual **15** appeared at 90.6 ppm, with no detectable signal due to an isotope shift from bonding to ^{18}O, while the tosylate-bonded carbon in the rearranged tosylate **16** showed a signal at 80.089 ppm due to bonding to ^{16}O and a signal at 80.058 ppm due to bonding to ^{18}O in a ratio of 1.142:1.00, respectively.

Acknowledgment. Financial support by the Natural Sciences and Engineering Research Council of Canada and helpful discussions regarding the kinetic analysis with Professors R. A. McClelland and O. S. Tee are gratefully acknowledged.

Supporting Information Available: Copies of ^1H NMR spectra and Tables 2 and 3, kinetic derivation (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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