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Communications

9-(Trifluoromethyl)fluorenyl Cation: A New Doubly Destabilized Carbocation[†]

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Summary: 9-(Trifluoromethyl)fluorenyl tosylate (**5**) undergoes solvolysis to the corresponding carbocation **3**, which is destabilized both by the electron-withdrawing CF_3 group and by its potentially antiaromatic fluorenyl cation character.

Ten years ago we reviewed the field of destabilized carbocations.[1] Examples of such carbocations include those substituted with groups more electron withdrawing than hydrogen, such as trifluoromethyl,[1b,c] and also carbocations destabilized by the presence of *anti*-aromaticity effects, such as the cyclopentadienyl cation (**1**). Subsequent work has included the study of "doubly destabilized" carbocations, specifically those bearing two electron withdrawing groups. These studies include the direct observation by NMR of bis(carbethoxy)benzyl cations **2a**,[2a] and the solvolytic generation of α,α-bis(trifluoromethyl)benzyl cations **2b**.[2b] Recently it has been reported by Johnston, Lee-Ruff, and co-workers[2c] that the 9-carbomethoxyfluorenyl cation (**3a**) could be generated as a long-lived species and directly observed spectroscopically.[2c] We now report the solvolytic generation and capture of the 9-trifluoromethylfluorenyl cation (**3b**), which is destabilized both by the presence of a trifluoromethyl group, and by the potential *anti*-aromatic character of the fluorenyl carbocation.[3]

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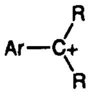
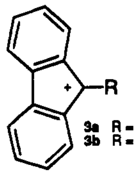


2a R = CO_2Et
2b R = CF_3



3a R = CO_2Me
3b R = CF_3

Recent studies of fluoroalkyl substituted carbocations have included salt[4a] and solvent[4b] effects on their generation, their slow reaction with nucleophiles,[4b] generation of these ions in the gas phase,[4c] analysis of the effects of aryl substituents on their generation,[4d] fragmentation of bicyclic derivatives,[4e] theoretical studies of α-CF_3 substituted vinyl cations,[4f] and the effect of ground state

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[†] Dedicated to the memory of Paul Gassman.

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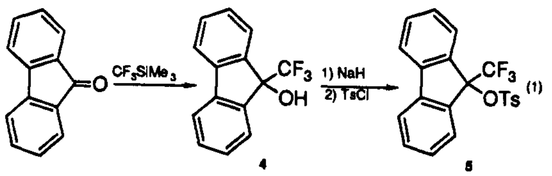
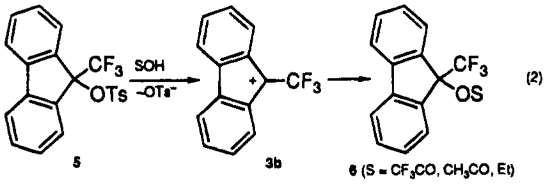
destabilization in enhancing their formation.[5] The stability of the 9-fluorenyl cation has been recently examined,[3e] as has the generation by laser flash photolysis and direct observation by ultraviolet spectroscopy of **3** with R = Ph, alkyl, and Me_3SiCH_2.[3g]

For the generation of **3b** the known carbinol **4**[6a] was prepared from fluorenone and Me_3SiCF_3[6b] and converted by reaction with NaH and TsCl[2] to the tosylate **5** (eq 1).[6c]



(1)

This underwent solvolysis in trifluoracetic acid, acetic acid, and ethanol to yield the corresponding substitution products **6** (eq 2), which were isolated and characterized spectroscopically.[7] The rates of solvolysis of **5** in a variety



(2)

of solvents were measured by UV spectroscopy as we have done in other cases,[2b,4a,5a] as given in Table 1. The rate constants give a good correlation with the solvent ionizing parameter Y_{OTs} by the relation $\log k = 1.23Y_{OTs} - 5.70$, $r = 0.991$, and are also correlated with the rates of solvolysis of $PhC(CH_3)(CF_3)OTs$ (**7**):[8] [a] $\log k$ (**5**) = 1.22 $\log k$ (**7**) + 2.16, $r = 0.996$. The effect of added CF_3CO_2Na on the reactivity in CF_3CO_2H was also examined for comparison to the recently discovered very large special salt effects of α-(trifluoromethyl)benzylic derivatives in this medium.[4a]

Table 1. Solvolysis Rates of 5[a]

solvent (Y_{OTs})	k_{obs} (s^{-1})
CF_3CO_2H (4.57)	0.308
97% HFIP (3.61)	0.133
HCO_2H (3.04)	8.26×10^{-3}
97% CF_3CH_2OH (1.83)	8.90×10^{-4}
80% EtOH (0.00)	2.40×10^{-6}[b]
HOAc (−0.61)	1.75×10^{-7}[c]
CF_3CO_2H, $[NaO_2CCF_3]$[d] (M)	
0.0588	0.210
0.0501	0.199
0.0402	0.171
0.0251	0.163
0.0161	0.128
0.00805	0.105
0.00402	0.0794
0.0	0.0387

[a] At 25 °C unless otherwise noted. Average of duplicate runs measured by UV except for HOAc at 90.2 °C, which was measured by ^1H NMR with a single run. [b] Extrapolated from data at higher temperatures. k_{obs} ($s^{-1} \times 10^{-4}$), (T, °C): 11.6 (74.6); 1.12 (53.8); 0.604 (49.6). $\Delta H^{\ddagger} = 25.3$ kcal/mol, $\Delta S^{\ddagger} = 0.4$ eu. [c] Extrapolated from data at higher temperatures. k_{obs} ($s^{-1} \times 10^{-5}$), (T, °C): 57.0 (90.2); 14.4 (73.5); 1.79 (59.7). $\Delta H^{\ddagger} = 26.5$ kcal/mol, $\Delta S^{\ddagger} = -0.4$ eu. [d] $[CF_3CO_2Na]$ in CF_3CO_2H, 6.1 °C.

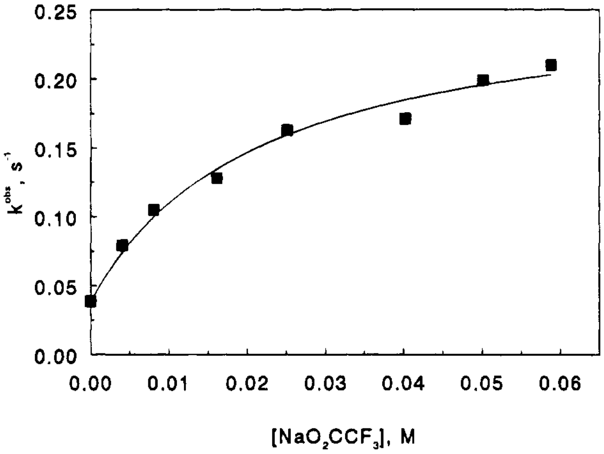


Figure 1. Effect of $[NaO_2CCF_3]$ on the reactivity of **5** (curve drawn using eq 3).

The intermediacy of the carbocation **3b** in the solvolysis of **5** is established by the strong dependence of the reaction rates on the solvent ionizing power, and by the formation of the substitution products **6**. Further evidence for this intermediate is the very strong effect of added NaO_2CCF_3 on the trifluoroacetolysis, with an acceleration by a factor of 5.4 induced by the addition of 0.059 M salt at 6.1 °C (Table 1). This acceleration is comparable to those we have recently reported for a series of other fluoroalkyl substituted benzylic substrates,[4a] which showed accelerations of 5.0 to 14.3 for 0.2 M salt. These accelerations show the characteristics of a special salt effect with an initial steep acceleration with added salt that becomes less marked at higher [salt], and these are quantitatively correlated by eq 3, which was derived for systems which involve initial reversible ionization to an ion pair or pairs which undergo competitive product formation by solvolysis (eq 4) or scavenging by added salt (eq 5).[4a] The data for **5** also give a good fit to eq 3, as shown in Figure 1, with derived values of $k_o = 0.0387$ s^{-1}, $k_1 = 0.263$ s^{-1}, $K_{app} = (k_{-1} + k_s)/k_t = 0.0215$, and correlation coefficient r = 0.993. The ratio of return to solvent capture = (k_{-1}/k_s) has a value of 5.80. These results are supportive of **5** reacting by a similar process.

$$k^{obs} = \frac{(k_0 K_{app} + k_1[\text{salt}])}{(K_{app} + [\text{salt}])} \tag{3}$$

$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+||X^- \xrightarrow{k_s} \text{products} \tag{4}$$

$$R^+||X^- \xrightarrow{k_t[\text{salt}]} \text{products} \tag{5}$$

Comparison of the rate of acetolysis of **5** to that of 2.06×10^{-3} s^{-1} for 9-fluorenyl tosylate (**8**)[3a] at 25 °C reveals that **5** is 1.2×10^4 times less reactive, showing a strong decelerating effect for the CF_3 group. Comparison of the

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(7) The major products **6** from the solvolysis of **5** by CF_3CO_2H, CH_3CO_2H, and EtOH were isolated and purified by chromatography, and characterized by ^1H NMR, IR, EIMS, and HRMS. The trifluoroacetate **6**-O_2CCF_3 was unstable under the reaction conditions, and formed unidentified products on prolonged reaction times.

rate constant measured for **5** in 80% EtOH to that of 1.47 × 10^{-3} s^{-1} estimated for $Ph_2C(OTs)CF_3$ (**9**)[8b] indicates that **5** is 610 times less reactive at 25 °C. This lower reactivity of the fluorenyl derivative compared to the diphenylmethyl analog is similar to that of 9-fluorenyl tosylate (**8**), which is about 3000 times less reactive than Ph_2CHOTs.[3a] The approximate correspondence of these factors suggests that the effects causing the retardation in the reactivity of **8** relative to Ph_2CHOTs are also operative in the CF_3 substituted analogues. The comparisons are not exact because of the influence of steric factors, which are expected to be most important for Ph_2CHOTs and $Ph_2C(OTs)CF_3$ (**9**). These effects might cause both enhanced reactivity due to ground state strain, and decreased activity due to interference with aryl conjugation in the transition state, but the net result appears to be rather modest. Combination of the reactivity comparisons of **5** relative to **8** (1/1.2 × 10^4) and that of Ph_2CHOTs relative to **8** (3000) leads to an estimate that **5** is 4 × 10^7 times less reactive than Ph_2CHOTs.

$$\begin{array}{c}CH_3\\|\\PhCOTs\\|\\CF_3\end{array}$$

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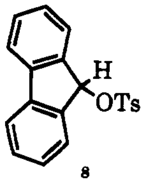

8

$$\begin{array}{c}Ph\\|\\PhCOTs\\|\\CF_3\end{array}$$

9

The very high dependence of the reactivity of **5** on the solvent ionizing power with an *m* value of 1.23 is unusual, and indicates a high demand for solvent stabilization by this developing carbocation. The implications of this observation for the demand for solvent stabilization in the potentially antiaromatic 12 π-electron cationic system of **3b** are under further study.

There is general agreement that the 9-fluorenyl cation 9-Fl^+ is destabilized relative to the benzhydryl cation Ph_2CH^+, and that this destabilization can be quantitatively expressed by their respective pK_R^+ values of −15.9 and −11.7, which correspond to a 5.7 kcal/mol destabilization of Fl^+ relative to FlOH as compared to the Ph_2CH^+/Ph_2CHOH pair.[3e] This greater ease of formation of Ph_2CH^+ apparently does not result from steric crowding in the alcohol, because the difference in the pK_R^+ values of the more crowded tertiary derivatives 9-Me-9-Fl^+ and $Ph_2C^+CH_3$ of −11.1 and −9.3, respectively, is less than for the secondary derivatives.[3e] The hydride affinity in DMSO ($-\Delta G_{\text{hydride}}$) of Ph_2CH^+ is 4 kcal/mol less than that for the fluorenyl carbocation, and this difference has also been attributed to destabilization of the fluorenyl carbocation.[3j]

Antiaromaticity is the accepted[2a,3a,d,i] explanation for the long-known destabilization of the fluorenyl cation, and it is plausible that residual effects of this phenomenon, which are stronger in the cyclopentadienyl[3i] and indenyl[9] cations, would be manifested in the fluorenyl cation. However, this view has recently been challenged[3e] in that it is "misleading" and "incorrect" to classify the fluorenyl cation as antiaromatic. The bases of this argument[3e] were (1) that the apparent destabilization of the cation was too small for such an effect,and (2) that a molecular orbital study of the cations and the corresponding alcohol produced "no evidence that this is true." In our view 5.7 kcal/mol is not a small amount but a large one, and only a significant chemical phenomenon could give rise to such a difference. Furthermore the MO studies cited[3e] do not appear to be a proven method for examining such questions.[10] However the current results do not provide direct evidence as to the origin of the destabilization of the fluorenyl cation, and further discussion of this fascinating question will be deferred. This problem is under examination by different means.

In conclusion there is strong evidence that $9\text{-CF}_3\text{-9-Fl}^+$ (**3b**) is a genuine doubly destabilized carbocation, and the substrate **5** is about 4 × 10^7 times less reactive than Ph_2CHOTs. Both the CF_3 group and the fluorenyl ring system contribute to the low reactivity of **5** and the destabilization of the cation **3**, and by approximately equal amounts. This behavior is in contrast to the substrates $ArCR(CF_3)(OTs)$, where R is CF_3 or CN. In these latter compounds the influence of the second destabilizing group is greatly attenuated relative to the first, and this behavior has been attributed[2b] to extensive delocalization into the aryl ring Ar. In the fluorenyl cation **3** such delocalization may be counterproductive due to the antiaromatic character of the delocalized ion, and no such attenuation of the destabilization is observed.

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Supplementary Material Available: Copies of ^1H NMR spectra of **5** and **6** (4 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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