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SOLVOLYTIC STUDIES OF THE HIGHLY CROWDED 1-ARYL-1-PHENYL-1-(TRIFLUOROMETHYL)METHYL BROMIDE AND TOSYLATES

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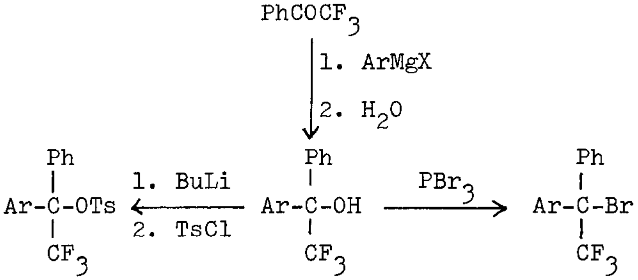
Summary: In the titled system the remarkably high tosylate/bromide solvolysis rate ratio of 1.56×10^6 : 1 indicates a highly strained ground state, and the reverse order of reactivity for substrate having 1-(4-trifluoromethyl)phenyl vs. that having 1-(3-trifluoromethyl)phenyl suggests the twisting of the aryl group from coplanarity in the cationic transition state.

The interaction of an electron-withdrawing α-substituent with the carbenium ion center developed in ionic reactions is a recent subject of active research.[1] Solvolysis of systems containing one α-trifluoromethyl group and one α-aryl group have been extensively studied by Tidwell and coworkers,[2] and by us.[3] We now wish to report the interesting results from our recent studies of the diaryl(trifluoromethyl)methyl system[4] that the ground state is highly strained and the aryl groups in the cationic transition state cannot be coplanar.

1-Aryl-1-phenyl-1-(trifluoromethyl)methanols 1a-1f were obtained from the addition of the appropriate Grignard reagents to α,α,α-trifluoroacetophenone. These alcohols were converted into tosylates 2a-2f and bromide 3a, respectively, by the conventional methods.[3] The assigned structures of these compounds were confirmed by satisfactory elemental analyses(C, H, F, S, Br) and/or by spectral data(IR, PMR, MS). The rates of solvolysis were followed titrimetrically in duplicate. The tosylate 2a was too reactive in 80% ethanol for an accurate measurement that the solvolysis was carried out in absolute ethanol, and from this the rate constant in 80% ethanol was estimated. The conversion factor was determined from 2b in these two solvents. The results are shown in Table I.

Several interesting points were revealed from these rate data A high tosylate/bromide rate ratio of about 5000 : 1 was attributed to the release of the nonbonded interaction between bulky leaving group and the cationic moiety, and was considered as a criterion for limiting S_N1 process.[5] The ratio would be



Ar			
Ar = C_6H_5	2a	1a	3a
= $3\text{-}ClC_6H_4$	2b	1b	
= $3\text{-}CF_3C_6H_4$	2c	1c	
= $4\text{-}CF_3C_6H_4$	2d	1d	
= $3,5\text{-}Cl_2C_6H_3$	2e	1e	
= $3,5\text{-}(CF_3)_2C_6H_3$	2f	1f	

Table I. Rates of Solvolysis for 1-Aryl-1-phenyl-1-(trifluoromethyl)methyl Bromide and Tosylates

	k, s^{-1} [a]			
Substrate	in EtOH		in 80% EtOH	
	at (°C)	at 25°C	at (°C)	at 25°C
2a		1.19×10^{-4}		1.47×10^{-3} [b]
2b	7.72×10^{-5}(50)			
	2.61×10^{-5}(40)	4.48×10^{-6} [c]		5.54×10^{-5}
2c				1.17×10^{-5}
2d				1.28×10^{-5}
2e			1.75×10^{-4}(60)	
			4.67×10^{-5}(50)	2.41×10^{-6} [c]
2f			1.74×10^{-4}(75)	
			2.96×10^{-5}(60)	2.39×10^{-7} [c]
3a			1.99×10^{-4}(125)	
			1.61×10^{-5}(100)	
			6.03×10^{-6}(90)	9.45×10^{-10} [c]

[a] ± 2%. [b] Calculated from k in ethanol by multiplying a factor of 12.4 derived from 2b. [c] Extrapolated from data at higher temperature.

higher for the more strained substrate. Indeed we have found a very high ratio of $3.94 \times 10^4 : 1$ for 1-phenyl-1-(trifluoromethyl)ethyl system in 80% ethanol.[3a] Similarly, a mesylate/bromide ratio of $8.01 \times 10^4 : 1$ was also observed for 1-aryl-1-cyanoethyl derivatives in buffered trifluoroethanol.[6] In the present work the remarkably high rate ratio of $1.56 \times 10^6 : 1$ for $k_{\mathbf{2a}}/k_{\mathbf{3a}}$ indicates an extremely large ground state strain due to the bulky trifluoromethyl and phenyl groups in this system. Consequently, the tosylates **2** were strongly accelerated in solvolysis by releasing of this strain. This is also accounted for the recent finding of an unexpectedly high reactivity of the arylbistrifluoromethyl analogy.[7]

The Hammett-Brown plots,[8] $\log(k/k_0) = \rho\sigma^+$, of the rate data give a linear correlation with $\rho = -3.98 (r = 0.992)$ despect the fact that the substrate containing 4-trifluoromethylphenyl group, **2d**, is more reactive than the one, **2c**, containing 3-trifluoromethylphenyl group. The correlation will be even better if the data for **2d** is omitted($\rho = -4.04$, $r = 0.999$). It is known that for electrophilic reactions 4-CF_3 is the more deactivating group than 3-CF_3 in all of the σ scales,[10] and that the σ^+ constants for both 3-CF_3 and 4-CF_3 group has been successfully employed to the correlation of rate data for a large number of systems.[3, 9, 11] Moreover, the nonplanarity of the fully developed 1-aryl-1-phenyl-1-ethyl cations in super acid has been realized.[12] Thus, a plausible explanation for the kinetic anomaly observed in the present study would be the distortion of the deactivated aryl ring from the plane of the carbenium ion developed in the transition state. The unexpected order of reactivities for **2c** vs. **2d** could be due to the increasing importance of the inductive contribution of CF_3 group, although no detailed analysis of inductive constant σ_I for substituents at different positions on aromatic ring has yet been made.[10b, 13] Additional work to assure the nonplanar transition state and to evaluate the importance on inductive effect on solvolytic reactivity is in progress.

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Footnotes and References

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