Inverse Order of Solvolytic Reactivity for Benzylic Substrates Containing Electron-attracting Aromatic Substituents. A Probe for the Absence of Resonance Contribution of the α-Aryl Group to the Cationic Transition State

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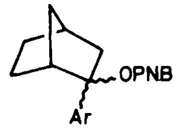
An inverse order of reactivities, $k_p/k_m > 1$, for electron-attracting α-aryl substituents was observed in the solvolysis of highly crowded toluene-*p*-sulphonates (**5**) and *p*-nitrobenzoates (**6**), which could be used as a probe for the lack of significance of resonance contribution in the cationic transition state.

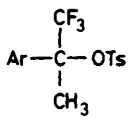
The correlations of reactivities with the modified Hammett substituent constants σ^+, either by the simple Hammett–Brown (HB) treatment[1] or by the dual-parameter Yukawa–Tsuno (YT) treatment,[2] have been widely employed in mechanistic studies of reactions involving the development of cationic transition states α to aryl groups. For any $-I$ or $-I-M$ substituent[3] the σ^+_p constant is always more positive than the σ^+_m constant.[4,5] Indeed, higher reactivities for substrates bearing a *meta*-CF_3 substituent on the α-aryl rings than those bearing *para*-CF_3, *i.e.* $k_p/k_m < 1$, have been observed in the solvolysis of a variety of systems such as 2-aryl-*exo*- and *endo*-norbornyl *p*-nitrobenzoates (**1**) and (**2**),[6] 1-aryl-1-trifluoromethylethyl toluene-*p*-sulphonates (**3**),[7] and 1-aryl-1-cyanoethyl methanesulphonates (**4**).[8] However, studies on the solvolysis of highly crowded tertiary benzylic substrates reveal inverse orders of reactivities for those containing a cyano and/or trifluoromethyl group on the α-aryl ring. This anomaly can be used as a probe to detect the effectiveness of the resonance contribution of the aryl ring in cationic transition states.

In a recent study[9] we noticed that the rate of solvolysis for the *m*-trifluoromethylphenyl compound (**5a**) was slower than that for the *p*-trifluoromethylphenyl isomer (**5b**), *i.e.* $k_p/k_m > 1$ for CF_3. This inverse order of reactivity was attributed to the distortion of the deactivated aryl ring from the plane of the carbenium ion developed in the transition state. To explore whether or not this phenomenon is general for highly crowded tertiary substrates, the cyanophenyl analogues (**5c**) and (**5d**), and the trifluoromethylphenyl derivatives (**6a**) and (**6b**), and (**7a**) and (**7b**) have been prepared from the corresponding ketones with a newly developed one-pot procedure.[10] The rates of solvolysis in 80% acetone [(**6a**), (**6b**), (**7a**), and (**7b**)] and in 80% ethanol [(**5c**) and (**5d**)] were followed titrimetrically in duplicate (±1%) at suitable temperature. The results are shown in Table 1. The higher reactivity of the *para*-substituted substrate than the *meta*-isomer in the isomeric pairs is realized for the toluene-*p*-sulphonates (**5**) and *p*-nitrobenzoates (**6**), but not for the *p*-nitrobenzoates (**7**).

It has been proposed that the aryl ring and the carbenium sp^2 orbital in the cationic transition state for the solvolysis of the *m*-phenyl derivative (**6c**) are not coplanar, based on the observation that the reactivity increases as the phenyl group is replaced by a methyl group, *i.e.* $k_{Ph}/k_{Me} < 1$.[11] The present observation that $k(\mathbf{6b})/k(\mathbf{6a})$ is greater than unity is clearly in line with this proposal. However, in comparing the solvolytic reactivities for the phenyl derivatives of (**3**) and (**5**), *i.e.* Ar =

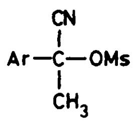


(1) *exo* OPNB
endo Ar
(2) *exo* Ar
endo OPNB



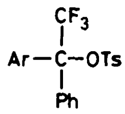
$\mathrm{Ar{-}C(CF_3)(CH_3){-}OTs}$

(3)



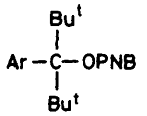
$\mathrm{Ar{-}C(CN)(CH_3){-}OMs}$

(4)



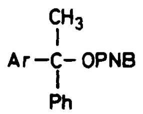
$\mathrm{Ar{-}C(CF_3)(Ph){-}OTs}$

(5)



$\mathrm{Ar{-}C(Bu^t)(Bu^t){-}OPNB}$

(6)



$\mathrm{Ar{-}C(CH_3)(Ph){-}OPNB}$

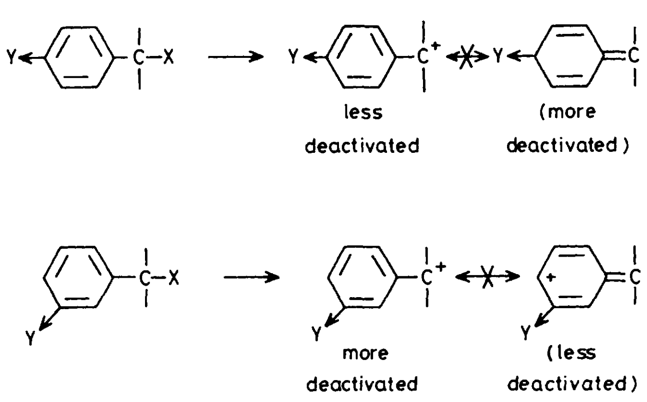
(7)

(5) a; Ar = m-$CF_3C_6H_4$
b; Ar = p-$CF_3C_6H_4$
c; Ar = m-NCC_6H_4
d; Ar = p-NCC_6H_4

(6) a; Ar = m-$CF_3C_6H_4$
b; Ar = p-$CF_3C_6H_4$

(7) a; Ar = m-$CF_3C_6H_4$
b; Ar = p-$CF_3C_6H_4$

PNB = p-$O_2NC_6H_4CO$; Ts = p-$MeC_6H_4SO_2$; Ms = $MeSO_2$.



Scheme 1. Y = CF_3, CN, *etc.*

Ph, a normal k_{Ph}/k_{Me} rate ratio of 1940 was observed,[7,9†] although k_p/k_m for both CF_3 and CN substituents was greater than unity in (**5**). Therefore, the k_p/k_m ratio is likely to be a better probe than the k_{Ph}/k_{Me} ratio for detecting the effectiveness of the contribution of the resonance of the α-aryl group with the incipient cationic centre in the transition state. In the highly crowded transition state the aryl ring in (**6**) and the deactivated aryl ring in (**5**) deviate appreciably from the plane of the cationic centre. The resonance interaction between such an aryl group and the reaction centre will be negligible, so that the $-I$ inductive effect of the substituent such as CF_3 becomes the dominant factor governing reactivities (Scheme 1). The σ_I value for CN, 0.58, is larger than that for CF_3, 0.43,[4] and in fact the reactivity order (**5b**) > (**5a**) > (**5d**) > (**5c**) is as predicted. The two aryl rings in the 1-aryl-1-phenylethyl cation could hardly be coplanar and the deactivated ring would be twisted,[12,13] but the resonance effect of the latter was not completely eliminated in the transition state for the solvolysis of (**7**) because a normal k_p/k_m ratio for CF_3 was observed.

Table 1. Rate constants for solvolysis of some tertiary benzylic substrates.

Substrate	$10^6 k/s^{-1}$	$T/°C$	k_p/k_m (25 °C)
(**5a**)[a]	11.7	25[b]	1.09
(**5b**)[a]	12.8	25[b]	
(**5c**)[a]	7.76	25	1.28
(**5d**)[a]	9.91	25	
(**6a**)[c]	52.7	125	1.52
	3.39	100	
(**6b**)[c]	68.9	125	
	4.57	100	
(**7a**)[c]	157	125	0.394
	12.6	100	
(**7b**)[c,d]	111	125	
	7.54	100	

[a] Solvent: $EtOH-H_2O$ (8:2) for (**5**); Me_2CO-H_2O (8:2) for (**6**) and (**7**). [b] Ref. 9. [c] Values extrapolated to 25 °C: 3.69×10^{-11} for (**6a**); 5.70×10^{-11} for (**6b**); 2.28×10^{-8} for (**7a**), and $8.99 \times 10^{-9}\ s^{-1}$ for (**7b**). [d] Lit.[15] 1.07×10^{-4} (100 °C), 7.36×10^{-6} (75 °C), and $8.95 \times 10^{-9}\ s^{-1}$ (25 °C).

It is interesting that both HB and YT treatments give satisfactory to excellent correlations[14] for (**5**)—(**7**). That is, for (**5**) $\rho_{HB} = -3.90$, $r = 0.983$ and $\rho_{YT} = -3.88$, $r = 0.984$, $r^+ = 1.09$ (8 points); for (**6**) $\rho_{HB} = -1.30$, $r = 0.979$ and $\rho_{YT} = -1.79$, $r = 0.993$, $r^+ = 0.491$ (5 points);[11] for (**7**) $\rho_{HB} = -3.34$, $r = 0.999$ and $\rho_{YT} = -3.50$, $r = 0.999$, $r^+ = 0.870$ (5 points).[15] Thus, neither treatment is good enough for detecting the insignificance of resonance interaction in the transition state due to an aryl group. At least one isomeric pair containing $-I$ or $-I-M$ substituent, such as CF_3 or CN, should be included in the kinetic study for this purpose. Further research on the relationship between the solvolytic rate ratio k_p/k_m and the cationic transition state structure, and the applicability of the HB or YT treatment is in progress.

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† Rate constants for solvolysis in 80% ethanol at 25 °C are $k = 1.47 \times 10^{-3}\ s^{-1}$ for (**5**) (Ar = Ph),[9] and $7.57 \times 10^{-7}\ s^{-1}$ for (**3**) (Ar = Ph).[7]