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Substituent Effects on the Solvolysis of 1,1-Diphenyl-2,2,2-trifluoroethyl Tosylates: Comparison between Symmetrically Disubstituted and Monosubstituted Systems

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The solvolysis rates of 1-(substituted phenyl)-1-phenyl-2,2,2-trifluoroethyl and 1,1-bis(substituted phenyl)-2,2,2-trifluoroethyl tosylates or bromides were conductimetrically measured at 25.0 °C in 80% aqueous ethanol. The substituent effects on these solvolyses were analyzed on the basis of the Yukawa–Tsuno equation. The former monosubstituted diphenyl system did not show a single linear Yukawa–Tsuno correlation; a bilinear correlation was observed with $\rho = -4.33$ and $r = 1.26$ for substituents more deactivating than *p*-methyl, and $\rho = -6.08$ and $r = 1.45$ for the substituent range more reactive than 3,4-dimethyl. The bilinear correlation was explicable in terms of the changing coplanarity of the respective benzene rings.

On the other hand, the symmetrically disubstituted diphenyl substrates gave an excellent linear Yukawa–Tsuno correlation for the whole substituent range with a ρ value of $-8.3/2$ and an r value of 1.19. The substituent effect correlation leads to the conclusion that the two aryl rings in this symmetrical system remain in the equivalent propeller-shape conformation with respect to deviations from coplanarity with the carbenium ion center in the transition state.

In a variety of aromatic side-chain reactions, exemplified by benzylic solvolyses, where direct π-delocalization of the cationic charge into the ring is possible, the substituent effect can be most appropriately described by the Yukawa–Tsuno (Y–T) equation :[1)]

$$\log(k/k_o) = \rho(\sigma^\circ + r\Delta\bar{\sigma}_R^+). \qquad (1)$$

The r value in this equation is a parameter characterized as the resonance demand, measuring the degree of resonance interaction between the aryl group and the reaction site in the rate-determining transition state.[1—5)] The resonance substituent constant $\Delta\bar{\sigma}_R^+$ is defined by $\sigma_p^+ - \sigma_p^\circ$,[1b)] and hence r=0 refers to σ° and r=1.00 to the Brown σ^+, as found for the α,α-dimethylbenzyl system (**1**).[6)] By the Y–T relationship, we introduced the concept of varying resonance demand of reactions into the substituent effect analysis.[3—5)] In the general application of this equation, the r value has been found to change widely with the reaction, not only within a range lower than unity ($0<r<1$), but to be also significantly higher than unity ($r>1$) in many cases. This fact clearly indicates that the Brown σ^+ value (r=1.0) does not reflect the highest extreme of benzylic resonance exaltation but is rather a point in a continuous r scale of resonance exaltation effects. This r scale permits evaluation of the nature of the transition state, and has been widely applied to the assignment and interpretation of reaction mechanisms.[1—5)]

Substituent effects in the solvolyses of benzylic substrates carrying strongly electron-withdrawing α-substituents, which generate highly electron-deficient carbocations, have been intensively investigated in the last ten years;[7)] solvolyses of this class of substrates are anticipated to show highly exalted resonance demand. We also undertook intensive investigations of substituent effects on the solvolyses of α-(trifluoromethyl)benzyl compounds leading to highly electron-deficient carbocations,[5)] such as the 1-phenyl-1-(trifluoromethyl)ethyl (**2**)[8)] and α-(trifluoromethyl)benzyl (**3**)[9)] systems, based on the Y–T equation (Eq. 1). Solvolyses of these extremely electron-deficient carbocationic systems also gave good linear Y–T relationships with particularly high r values; e.g., 1.39 for **2** and 1.53 for **3**.[8,9)] In the solvolysis of **2**, the strong destabilization of the carbocationic transition state by the α-CF_3 group provides a high demand for positive charge delocalization into the α-aryl π-system. The r value of 1.39 assigned for **2** can be distinguished statistically from the value of unity required for the σ^+ correlation. Exalted resonance contributions, indicated by extremely high r values compared with the r values close to unity for solvolyses forming stable tertiary benzylic carbocations,[10)] provided strong evidence for the enhanced π-delocalization between the aryl π-system and the deactivated carbenium center in the rate-determining transition state of solvolysis.[5,8,9)] Substituent effects on the solvolysis of **3** may be similarly interpreted based on the Y–T equation. This would be an even more highly deactivated system having a secondary reaction center.

Contrary to the success of the Y–T analysis, Liu and coworkers have suggested in their studies on related systems that both the Brown and the Y–T correlations showed equal predicting ability of rates, and that the better correlations obtained from the Y–T treatment are likely to be due to the statistical advantage of using two adjustable parameters instead of only one parameter in the Brown equation.[11] They also concluded that the observed superiority in the linear Y–T plots might not reflect the reliability of the Y–T relationship, but might be merely a computational artifact.[12]

Through our extensive studies regarding substituent effects on various resonance-exalted solvolyses, we have generalized the concept of varying resonance demand in benzylic carbocationic solvolyses.[3—5] This concept should apply also to the solvolyses of diphenylmethyl systems. The stability of the carbenium transition state can be widely changed by changing the substituent in the two aryl groups in the diarylmethyl system, while keeping the basic framework of the structure essentially uncharged. In this situation, the substituent effect on the solvolysis of the deactivated 1,1-diaryl-2,2,2-trifluoroethyl system promises to afford important evidence regarding the intrinsic relation between Y–T *r* values and the stabilities of benzylic systems uncomplicated by steric factors.

While the substituent effect on this solvolysis has been studied recently also by Liu et al.,[12] their elucidation was based only on the linearity of the correlation analysis for the system. Moreover, the conclusion they reach appears to arise from a misapplication of the Y–T equation, especially on the basis of an insufficient data set.

Accordingly, we now report the results of our studies of substituent effects on the solvolysis of the monosubstituted 1,1-diphenyl-2,2,2-trifluoroethyl system (**4**) as the simplest diaryl system and the symmetrically disubstituted 1,1-diphenyl-2,2,2-trifluoroethyl system (**5**), the analysis of which is particularly straightforward. In this paper, the substituent effects on both systems are treated with the Y–T equation and are discussed in comparison with substituent effects on the solvolyses of the α-(trifluoromethyl)benzyl analogue of **2** and **3** (Chart 1).

Results

Rate constants for solvolysis of the tosylates (*p*-toluenesulfonates) **4** and **5**, and the corresponding bromides (or chlorides) were measured conductimetrically at 25.0 °C in 80 vol% aqueous ethanol (80E) at the initial concentrations of ca. 10^{-4} mol dm^{-3} of substrates under the same conditions as those employed for the solvolysis of **2** in the previous paper.[8] All kinetic runs accurately followed first-order kinetics over 2.5 half-lives, and the reproducibility of rate constants from repeated runs was estimated to be within 1%. The rates of more reactive substrates than **4**(*p*-*t*-Bu) and **5**(*p*-*t*-Bu) were determined for the corresponding bromides and were converted into the rates for the corresponding tosylates on the basis of the tosylate/bromide rate ratio=4.243×10^5, which is evaluated from the data obtained for **5**(3,5-Me$_2$). The rates for **5**(*p*-MeO) and **5**(p-MeS) were measured only for the corresponding chlorides because of their high reactivity, and were converted into the tosylate reactivities with the aid of the bromide/chloride rate ratio obtained from the halide derivatives of **5**(*p*-PhO). Rate constants obtained are listed in Tables 1 and 2. Several data were reported in the literature[12,13] and agree with our results within experimental uncertainty.

As shown in Table 1, the solvolysis rate varies over a range of 10^9 in reactivity with the substituents of **4** ranging from *p*-methoxy to 3,5-dichloro in 80E at 25 °C, indicating that the solvolysis is highly sensitive to substituent change.

The rate change of the symmetrically disubstituted series **5** in Table 2 covers a wide range of reactivity, ca. 10^{11} from *p*-MeO to *m*-Cl, even wider than that of the monosubstituted series **4** or of the system **2**, which is generally taken as a reference for substituent effects in the electron-deficient benzyl carbocationic solvolyses. The rate enhancement by two *m*-methylphenyls in **5**(*m*-Me) is approximately as large as that of the 3,5-dimethylphenyl in **4**(3,5-Me$_2$), and the same is true in the comparison of the **4**(3,4-Me$_2$) and the 1-(*m*-methylphenyl)-1-(*p*-methylphenyl)-2,2,2-trifluoroethyl tosylate, as shown in Table 1.

This comparison may lead to the conclusion that the total substituent effect for the two aryl groups in the diaryl series **5** should be twice as large as the effect for a single aryl group in series **4**. That is, both aryl groups in the series **5** are equally effective in stabilizing the rate-determining transition state by delocalization of the positive charge.

Correlation Analysis. Figure 1 shows the substituent effect on the solvolysis rates of **4** and **5** plotted against σ^+ (or $2\sigma^+_\mathrm{X}$ for **5**). While the *m*-substituents afford a single linear plot (*meta* correlation) without any notable deviation, σ^+_p plots of all *p*-π-donor substituents exhibit significant deviations in the direction of rate enhancement from the meta correlation line, indicating exalted substituent-resonance of *p*-π-donors with the carbenium center. The effects may be reasonably accounted for by the exalted resonance contribution, as in the Y–T equation. However, from the apparent pattern of deviations, there is evidently no simple additivity of two aryl-substituent effects nor any single common Y–T correlation between them.

Correlation analysis of the substituent effects has been carried out by the ordinary least-squares procedure based on Eq. 1 and also on the Brown $\rho^+\sigma^+$ equation, as summarized in Table 3. Substituent parameters, σ°, $\Delta\overline{\sigma}^+_\mathrm{R}$, and σ^+, employed in the present analysis are mostly the standard values, except for the correction of 0.03—0.04 σ unit applied for the resonance parameters of *p*-MeS derivatives characteristic of highly electron-deficient systems, as already noted.[8,9] An application of the Brown $\rho^+\sigma^+$ equation gives a less satisfactory correlation for all the substrates (both **4** and **5**) and also for the respective series, while it gives an excellent correlation only for the nonconjugative class of substituents, i.e., meta substituents and the para π-acceptor one (CF$_3$), for which the ρ value is the ρ_m value common to both **4** and **5** series (Entry 5 in Table 3).

The Y–T equation results in an excellent correlation with $r=1.26\pm0.08$ for the range of less activating substrates, except for significant deviations of six strong π-donor sub-

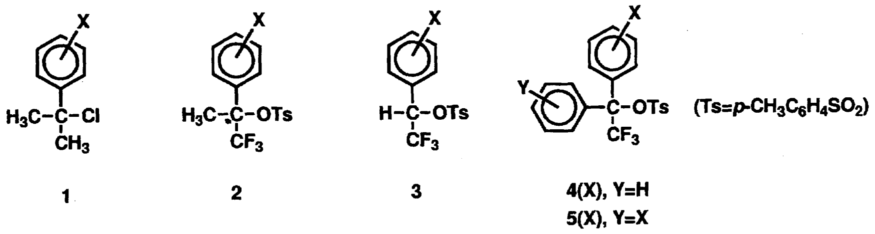

Chart 1.

Table 1. Solvolysis Rates of 1-Aryl-1-phenyl-2,2,2-trifluoroethyl Tosylates **4**(X) in 80% Aqueous Ethanol

Subst.	Temp	10^5k_t/s^{-1}		$\Delta H^{\ddagger}_{25}$ [a]	$\Delta S^{\ddagger}_{25}$ [a]
X	°C	Tosylates	Bromides	kcal mol^{-1}	cal K^{-1} mol^{-1}
p-MeO	25.0	198000000[b]	466.6	20.0	−2.2
	5.0		38.37		
p-MeS	25.0	52300000[b]	123.3	20.7	−2.3
	5.0		9.266		
p-PhO	25.0	2235000[b]	5.267, 5.38[d]		
p-MeO–*m*-Cl	25.0	1292000[b]	3.045	23.2	−1.3
	45.0		38.08		
p-MeS–*m*-Cl	25.0	426400[b]	1.005	23.4	−2.8
	45.0		12.86		
3,4-Me$_2$	25.0	25760[b]	0.06070[c]	25.0	−3.2
	45.0		0.9164		
	75.0		29.95		
p-Me	25.0	8046[b]	0.01896,[c] 0.0239[e]	26.0	−2.0
	55.0		1.155		
	75.0		12.06		
p-*t*-Bu	25.0	4247[b]	0.01001[c]	26.2	−2.8
	55.0		0.6371		
	65.0		1.997		
	75.0		6.744		
3,5-Me$_2$	25.0	998.7			
	5.0	68.54		(21.5	4.4)
p-F	25.0	607.8			
m-Me	25.0	517.0			
H	25.0	267.7		(22.0	3.6)
	5.0	17.15			
p-Cl	25.0	144.8			
m-F	25.0	8.367		(23.5	1.5)
	45.0	107.5			
m-Cl	25.0	5.279, 5.54[f]		(23.7	1.5)
	45.0	69.83			
p-CF$_3$	25.0	1.418, 1.28[f,g]		(24.3	0.7)
	45.0	19.85			
m-CF$_3$	25.0	1.265, 1.17[f,g]		(24.7	1.8)
	45.0	18.48			
3,5-Cl$_2$	25.0	0.2736, 0.241,[f] 0.184[h]		(25.8	2.6)
	45.0	4.504			
m-Me, *p*′-Me[i]	25.0	18180[b]	0.04285[c]	24.8	−4.4
	45.0		0.6366		
	55.0		2.162		
	65.0		6.869		

a) Activation parameters in parentheses are those for tosylates and 1 cal=4.184 J. b) Estimated from bromides reactivities based on the ratio of tosylate/bromide=4.2432×10^5 for **5**(3,5-Me$_2$) in Table 2. c) Extrapolated from other temperatures. d) Ref. 12. e) Ref. 13d. f) Ref. 13a. g) Ref. 13b. h) Ref. 13c. i) 1-(*m*-Methylphenyl)-1-(*p*-methylphenyl)-2,2,2-trifluoroethyl derivative.

stituents in the monosubstituted series **4** in Fig. 2 (Entry 8 in Table 3). Nevertheless, the Y–T plots for *p*-π-donors (open squares) against a Y–T $\bar{\sigma}$-scale with r=1.45 (Entry 9 in Table 3) does not appear to be satisfactorily linear but still seems to be significantly concave upward, as shown in Fig. 2.

It is therefore remarkable that there is an excellent linear Y–T correlation for a particularly limited series of the

Table 2. Solvolysis Rates of 1,1-Bis(substituted phenyl)-2,2,2-trifluoroethyl Tosylates **5**(X) in 80% Aqueous Ethanol

Subst.	Temp	$10^5k_t/\mathrm{s}^{-1}$		$\Delta H^{\ddagger}_{25}$[a]	$\Delta S^{\ddagger}_{25}$[a]
X	°C	Tosylates	Bromides	kcal mol^{-1}	cal K^{-1} mol^{-1}
p-MeO	25	13280000000[f]	646.6[e]		
p-MeS	25	974000000[f]	47.44[e]		
p-PhO	25	78190000[b]	184.3, 170[d]	21.6	1.4
			3.809,[e] 3.19[d,e]		
	5		12.45		
p-MeO–*m*-Cl	25	19520000[b]	46.00	22.7	2.4
	5		2.713		
p-MeS–*m*-Cl	25	2497000[b]	5.885	23.0	−0.8
	45		71.74		
3,4-Me$_2$	25	652500[b]	1.538	24.4	1.1
	45		21.64		
	55		72.20		
p-Me	25	164700[b]	0.3882	25.2	1.1
	45		5.960		
p-*t*-Bu	25	59100[b]	0.1393[c]	25.0	−1.6
	45		2.105		
	55		7.133		
	65		23.00		
3,5-Me$_2$	25	3364.5[c]	0.0079292[c]	26.1	−3.6
	55		0.4830	(21.8	7.8)
	65		1.644		
	75		5.058		
	−10	22.68			
	0	110.3			
	10	514.0			
p-F	25	1194		(20.7	2.1)
	5	90.06			
m-Me	25	936.6			
p-Cl	25	82.02			
m-Cl	25	0.07169[c]		(25.0	−2.7)
	45	1.091			
	55	3.722			
	75	35.85			

a,b,c,d) See footnotes a, b, c, and d of Table 1. e) Rate constant of chlorides. f) Estimated from chloride reactivities using the bromide/chloride rate ratio=48.39 for the halide derivatives of **5**(*p*-PhO) and the tosylate/bromide one (footnote b of Table 1).

symmetrically disubstituted system **5** in Fig. 3. The ρ_m correlation line defined by nonconjugative meta substituents passes through the points dividing at a constant external ratio (higher than 1.0) the resonance line-segments $2\times(\sigma^+-\sigma^\circ)$ for all para π-donor substituents. An application of Eq. 1 to the rate at 25.0 °C in Table 2 results in an excellent correlation (Entry 11 in Table 3). The Y–T plot (squares) with an r value of 1.19 ± 0.04 in Fig. 3 is excellently linear, indicating the absence of significant mechanistic change within the whole range of substituents employed.

Discussion

The solvolytic reactivity of the present systems indicates that the deactivation by α-CF_3 substitution of the benzhydryl system should be ca. 10^7, which is comparable to the α-CF_3 deactivation in **2** over the 1-phenylethyl system. Thus the present system may be classified in the category of so-called "extremely electron-deficient carbocation solvolyses", even though the reactivity of **4**(H) is more than 10^3 fold higher than that of **2**(H). Whereas remarkably high ρ^+ values in the range of −10 to −12 for the Brown $\rho^+\sigma^+$ correlations have been emphasized in the literature[14] as a characteristic feature of highly electron-deficient carbocation reactions, we have already pointed out that this characterization is rather misleading.[9] There is convincing evidence supporting the contention that the extremely electron-deficient carbocation reaction should be characterized by a high resonance demand r of 1.4—1.5 in the Y–T equation, with a ρ value of ordinary magnitude of −6 — −7.[5,8,9]

The solvolysis of **2**, which is typical of highly electron-deficient system, was correlated by Eq. 1,[8] with excellent precision:

$$\log(k/k_o)_2=-6.29(\sigma^\circ+1.39\Delta\bar{\sigma}_R^+). \tag{2}$$

It was also confirmed that a particular set of apparent substituent constant $\bar{\sigma}$-scales, with a high resonance demand $r=1.4$ derived from $\log(k/k_o)_2$ for the solvolysis of **2**, was capable of linearly describing the substituent effects in these extremely electron-deficient benzylic systems.[9]

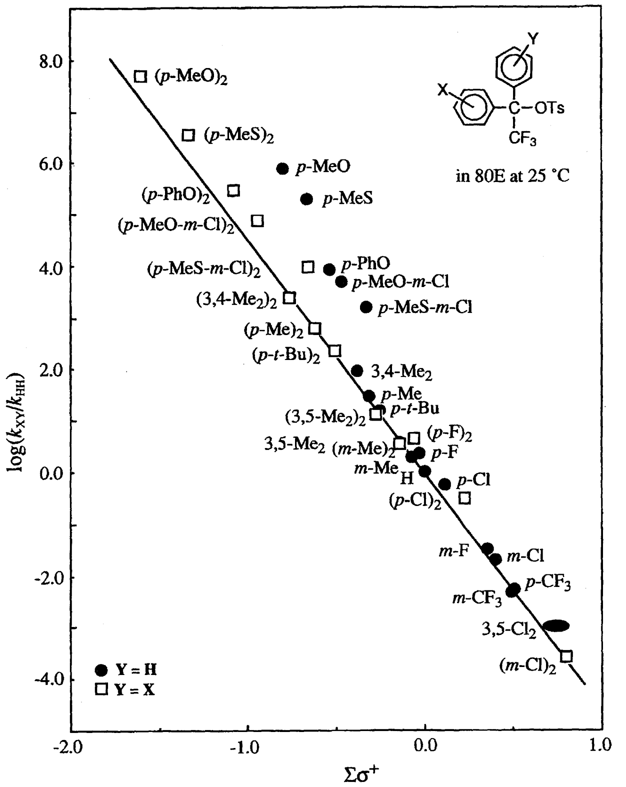

Fig. 1. σ^+ plots for solvolyses of 1,1-diaryl-2,2,2-trifluoroethyl tosylates; **4**, Y=H (closed circles) and **5**, Y=X (open squares) in 80% aq EtOH at 25.0 °C.

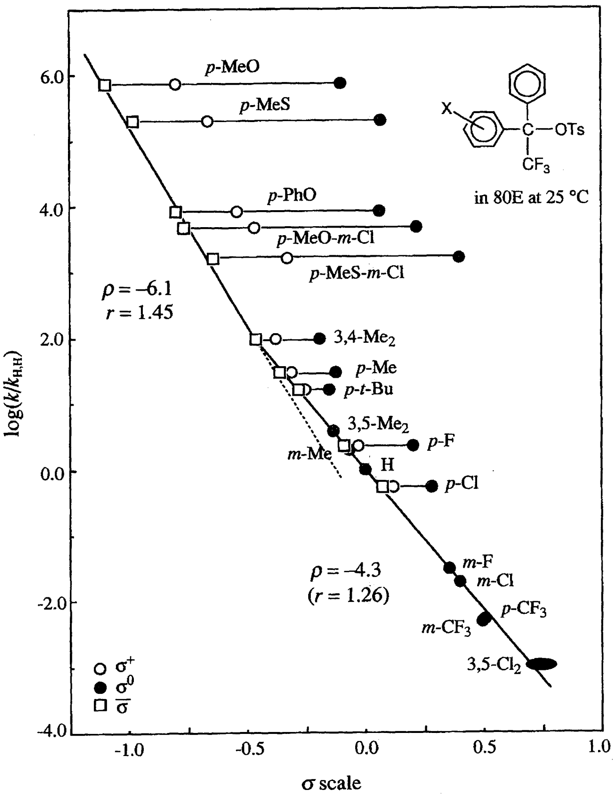

Fig. 2. Bilinear Y–T plot of the solvolysis of 1-aryl-1-phenyl-2,2,2-trifluoroethyl tosylates (**4**) in 80% aq EtOH at 25 °C: Open circles, σ^+, closed circles, σ°, and open squares, $\bar{\sigma}$ (r=1.45 for strong p-π-donors and r=1.26 for weak ones).

The bilinear plot of log $(k/k_o)_4$ vs. log $(k/k_o)_2$ in Fig. 4 manifests the different characteristics of the sets of reactivities for **2** and **4**. Substituents more electron-donating than *p*-alkyl are correlated linearly with unit slope, while substrates with electron-withdrawing substituents are described by a separate linear correlation with the distinctly different slope of 0.68. The bisected correlation indicates the occurrence of mechanistic changeover within the range of substituents involved. On the other hand, while the set of log $(k/k_o)_5$ values for the symmetrical diaryl series **5** does not give a single linear correlation against log $(k/k_o)_2$, it gives an excellent correlation, if a correction for different resonance contributions is applied, as in the following equation:

$$\log(k/k_o)_5 = 1.38\log(k/k_o)_2 + 1.94\Delta\bar{\sigma}_R^+ \qquad (3)$$

which has a precision of SD=±0.16 and R=0.9988.

These results, $\rho_5=-8.68/2$ and $r_5=1.17$, are consistent

Table 3. Correlation Analysis of Substituent Effects[a)]

No.	System		ρ	r	n	R	SD
1.	(4) + (5)	All	−4.99±0.21	(1.00)[b)]	31	0.976	±0.64
2.			−4.39±0.32	1.20±0.14	31	0.980	±0.60
3.		ex. Sπ-Ds[c)]	−4.74±0.08	(1.00)[b)]	26	0.996	±0.25
4.			−4.25±0.06	1.17±0.03	26	0.9993	±0.12
5.		m-correl[d)]	−4.35±0.06		11	0.999	±0.07
6.	(4)	All	−5.94±0.33	(1.00)[b)]	18	0.976	±0.60
7.			−4.37±0.21	1.67±0.13	18	0.996	±0.24
8.		<3,4-Me₂[e)]	−4.33±0.08	1.26±0.08	12	0.999	±0.07
9.		≧3,4-Me₂[f)]	−6.08±0.42	1.45±0.17	6	0.996	±0.12
10.	(5)	All	−4.74±0.14	(1.00)[b)]	14	0.995	±0.33
11.			−4.15±0.08	1.19±0.04	14	0.9994	±0.12

a) Correlation for single aryl substituent effects. The literature value of σ^+ of 0.701 for 3,5-dichloro substituent (X. Creary, *J. Am. Chem. Soc.*, **103**, 2463 (1981)) was used. b) Brown $\rho^+\sigma^+$ equation. c) Excluding five strong *p*-π-Donors; *p*-MeO, *p*-MeS, *p*-PhO, *p*-MeO–*m*-Cl, and *p*-MeS-*m*-Cl. d) *p*-π-acceptor and *m*-substituents. e) Less reactive substituents than *p*-Me. f) More reactive substituents than 3,4-Me₂.

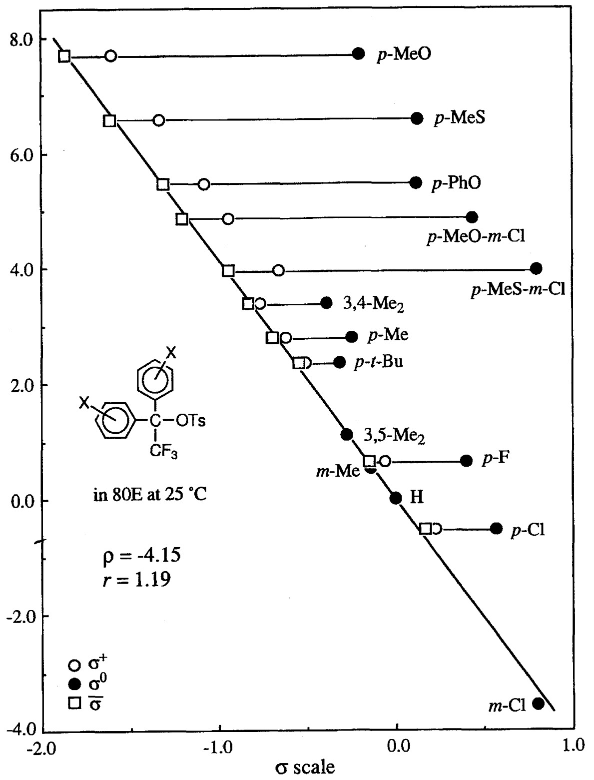

Fig. 3. Y–T plot for the solvolysis of 1,1-bis(substituted phenyl)-2,2,2-trifluoroethyl tosylates (**5**) in 80% aq EtOH at 25.0 °C: Open circles, $2\sigma^+$, closed circles, $2\sigma^\circ$, and open squares, $2\bar{\sigma}$ for r=1.19.

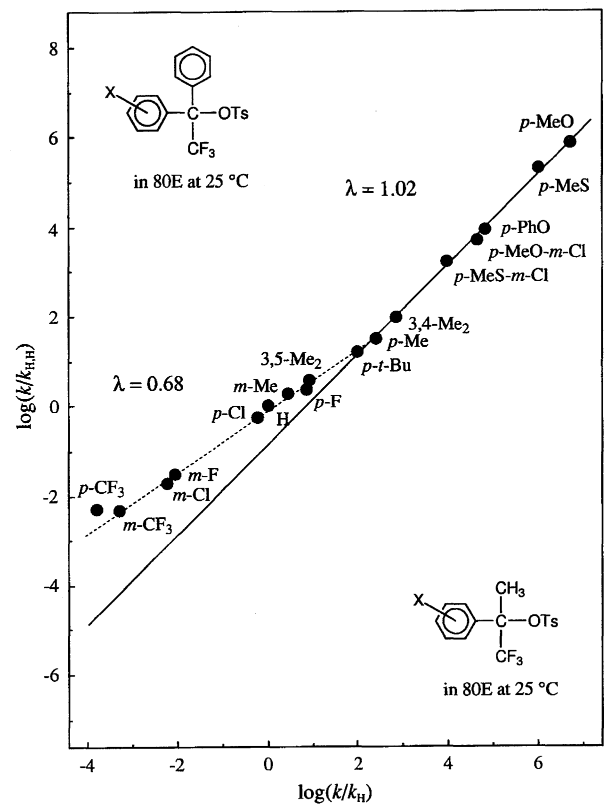

Fig. 4. Log k–log k plot between solvolyses of 1-aryl-1-phenyl-2,2,2-trifluoroethyl tosylates (**4**) and 1-aryl-(1-trifluoromethyl) ethyl tosylates (**2**) in 80% aq EtOH at 25 °C.

with the results from the Y–T correlation analysis (Entry 11 in Table 3). In particular, a single linear correlation provides strong evidence for a constant mechanism for the diaryl series **5** over the whole range of substituents involved, and thus the nonlinear Y–T correlation for **4** should lead to the conflicting conclusion. Here, substituent effects on respective range of substrates should be described by different Y–T correlations as in Fig. 2. It seems rather serious that, within the same range of reactivities where the electron-deficience of the reaction center should remain the same in both series, only the specified, unsymmetrical monosubstituted series **4** appears to involve a significant mechanistic changeover.

Most importantly, the ρ and r values for the separate Y–T correlation obtained for six strongly electron-donating p-substituents, but not for all the other substituents of **4**, are essentially identical to those of the reference system **2**.

Such non-equivalent behavior between the monosubstituted **4** and the symmetrically disubstituted **5** has also been observed in the correlations of pK_{R^+} or solvolysis rates of triarylmethyl system.[15)] The substituent effects on the pK_{R^+}'s for symmetrically trisubstituted triphenylmethanols were reported to give a completely linear Y–T correlation with an r value of 0.79 for the substituent range from p-dimethylamino to p-nitro, and similar behavior has been observed for triphenylmethyl solvolyses.[1b,3b,15a)] On the other hand, less satisfactory Y–T correlations were obtained for the pK_{R^+} values of monosubstituted triphenylmethanols or for the solvolyses of monosubstituted triphenylmethyl chlorides;[15b)] in these correlations, only strong π-donor substituents such as p-methoxy show a high r-value, and more weakly electron-donating groups give a lower value. The three aryl rings in the triarylmethyl cation are twisted out of the coplanarity with the carbocation center, to give a propeller conformation; for the symmetrical triarylmethyl cation, the loss of coplanarity equally prevents the three aryl groups from exerting their maximum effect in stabilizing the carbocation. However, in monosubstituted triphenylmethyl cations, only the strong π-donor substituted aryl can be coplanar with the cationic orbital, exerting its maximum π-effect.

The two aryl groups in the present α-CF_3–benzhydryl systems (both **4** and **5**) also can not simultaneously attain the coplanar conformation of full conjugation, because of the congestion in this tertiary diarylcarbenium transition state. In these diphenylcarbenium ions, the molecule adopts a propeller-shaped twisted conformation to overcome steric repulsion, but the twist angle will be a minimum to favor the positive charge delocalization into the ring. For unsymmetrically substituted diphenylcarbenium ions the propeller shape is probably not symmetrical and the deviation from coplanarity is related to the electron-releasing ability of the p-substituent. The diphenylmethyl cation has the two phenyl groups twisted equally out of the plane of C^+. The symmetry will be destroyed by replacing the p-hydrogen atom on one phenyl by an electron-donating substituent, causing the substituted ring to become more coplanar with the trigonal cationic carbon, due to the increased delocalization of the ring electrons. This will lower the electron demand on the other phenyl ring, which in turn will be forced further out of the plane.

The deviant behavior of the two aryl groups in **4**, when one is substituted and the other unsubstituted, should be ascribed to loss of coplanarity with the carbocation, depending largely on their different resonance capabilities (Fig. 5).

The aryl groups having sufficiently electron-donating substituents enter into full conjugation in the transition state, and such compounds predominantly have a conformation with the substituted X-phenyl being coplanar; in these conformers, the substituent X in the coplanar aryl exerts its maximum resonance effect on the solvolysis rate. On the other hand, when the substituents in the substituted X-phenyl are sufficiently deactivating, the unsubstituted phenyl (rather than substituted one) tends to enter into dominant (or full) conjugation, while constraining the substituted phenyl to be twisted more out of coplanarity. The apparent solvolysis rates for such compounds, therefore, exhibit the reduced substituent effect from the twisted aryl group.

Whereas we see precise Y–T correlations for solvolyses of a series of α,α-dialkylbenzylic substrates having two bulky alkyl groups at the reaction center, the more congested ones result in more significantly reduced r values, which should be ascribed to the loss of resonance interaction between the carbocation center and the aryl π-system in the solvolysis transition state.[3b,16)] The efficiency of this resonance interaction should be a function of the dihedral angle θ between the two overlapping p-orbitals, as described by Eq. 4 :[17,18)]

$$r = r_{\max}\cos^2\theta, \qquad (4)$$

where $r_{\max}$ is the "intrinsic" r value for the coplanar system. However, it should be particularly noted that a significant decrease of ρ value also is accompanied by a decreased r value in the sterically twisted systems.[16b)]

The bilinear correlation of **4** against **2** (in Fig. 4) appears to arise as a result of a change in coplanarity of the solvolysis transition state with aryl substituent, since the reference system **2** must be retained in entire coplanarity in the carbocationic transition state. This nonlinear correlation can thus be ascribed to the substituent-induced rotation around the aryl–C$_\alpha$ bond axis from coplanarity of either the unsubstituted or substituted phenyl ring with the carbenium center in **4**. The linear plot of unit slope for the electron-donating range of substituents in **4** as in Fig. 4 implies that r and ρ values identical with those for **2** should be characteristic values of the substituent effect of the coplanar aryl-ring under full conjugation. On the other hand, the correlation for the remainder, the range of non-activating to deactivating substituents, should correspond to the substituent effect from the twisted aryl-ring in **4**, in which the unsubstituted phenyl-ring tends to enter into coplanarity. The correlation parameters (Entry 8 in Table 3) are significantly diminished from the ordinary values obtained in the extremely electron-deficient solvolyses, such as **2**, under the same conditions.

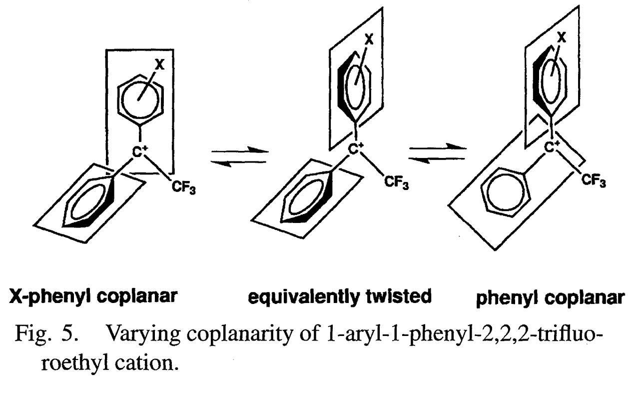

Fig. 5. Varying coplanarity of 1-aryl-1-phenyl-2,2,2-trifluoroethyl cation.

The r value of 1.19 given for the symmetrical diaryl series **5** must be related to the resonance demand characteristic of the ionizing process to produce the diarylcarbenium ion **5C$^+$** where both aryls are equivalently displaced from coplanarity with the reaction center. The reduced resonance demand r compared with the exalted resonance stabilization of the transition state characteristic of a deactivated benzyl cation is ascribed to a reduced coplanarity of both benzene rings. Thus the degree of deviation of the aryl-ring from coplanarity in the transition state, $\theta \fallingdotseq 25^\circ$ can be estimated based on Eq. 4, from the r-values, taking r_5 for **5** as r_{twist} and r_4 for the strong electron-donor range of **4** as r_{plan} :

$$\cos^2\theta = r_{\text{twist}}/r_{\text{plan}} = 1.19/1.45. \qquad (5)$$

This value of the dihedral angle θ is in good accordance with those assigned for α-methyldiphenylcarbenium and α-hydroxydiphenylcarbenium ions.[19)]

While our interpretation in terms of changing coplanarity reasonably applies to the variation of resonance effect, the effect of twisting the aryl ring from coplanarity causes a significant change in ρ value. In either the **4** or the **5** series, there should be no change in the geometrical factors at the transition state with changing substituents, except for the rotation around the Ar–C$_\alpha$ bond. The enhanced π-delocalization of the incipient carbenium p-orbital in the transition state or the exalted π-bond order of Aryl–C$_\alpha$ bond should also play an important part in the transmission of the polar effect.

Our investigation of α-CF$_3$–benzhydryl system was initially carried out with the aim of exploring the effects of highly enhanced resonance demand by the second electron-withdrawing aryl group. Accordingly, we have extended our investigation to the substituent effects in a single ring of the α-CF$_3$–benzhydryl system where the fixed ring is the more deactivating *m*-chlorophenyl or 3,5-dichlorophenyl rather than the phenyl group. The substituent effect, especially effects of increased resonance demand, will be discussed in more detail for all series including these electron-attracting Y series.

Experimental

Materials: Most of the α,α,α-trifluoroacetophenones required for preparation of alcohol precursors of solvolysis substrates were synthesized according to Stewart's procedure of Grignard reaction of substituted bromobenzenes with trifluoroacetic anhydride at −78 °C in a dry ice–acetone bath.[8,20]

Trifluoroacetophenones were converted into the corresponding 1,1-diaryl-2,2,2-trifluoroethanols by the Grignard reaction with substituted phenylmagnesium bromide at ice-bath temperature. 1,1-Bis(substituted phenyl)-2,2,2-trifluoroethanols were prepared by the addition of trifluoroacetic anhydride into ethereal solutions of substituted phenyl Grignard solution at ice-bath temperature. The tertiary alcohols obtained were purified by column chromatography on silica gel.

1,1-Diaryl-2,2,2-trifluoroethyl tosylates were synthesized according to Tidwell's method.[14,21] 0.020 mol of tertiary alcohol in 25 cm^3 of ether was added to 0.046 mol of NaH in 50 cm^3 of ether under nitrogen atmosphere at ice-bath temperature. The mixture was stirred overnight, and then 0.020 mol of *p*-toluenesulfonyl chloride in 140 cm^3 of ether was added dropwise. After stirring for 2 d, the mixture was filtered and the filtrate was concentrated under vacuum, to give the solid tosylate, which was purified by recrystallization from ether–hexane.

Table 4. Physical and Analytical Data of 1-Aryl-1-phenyl-2,2,2-trifluoroethyl Alcohols, Tosylates, and Bromides

Subst.	Mp	Carbon/%		Hydrogen/%	
X	°C	Found	Calcd	Found	Calcd
Alcohols					
p-MeO	Liq.	63.64	63.83	4.61	4.64
p-MeS	Liq.	60.26	60.39	4.59	4.39
p-PhO	87.2—87.6	69.82	69.76	4.50	4.39
3,4-Me_2	Liq.	68.55	68.56	5.64	5.39
3,5-Me_2	68.6—68.9	68.56	68.56	5.39	5.39
p-Me	Liq.	67.72	67.66	4.95	4.92
p-*t*-Bu	Liq.	70.27	70.12	6.33	6.21
p-F	Liq.	62.13	62.23	3.77	3.73
m-Me	Liq.	67.55	67.66	4.91	4.92
H	75.0—75.5[a]	66.65	66.67	4.45	4.40
p-MeO–*m*-Cl	95.0—96.0	56.83	56.88	3.83	3.82
p-Cl	Liq.	58.71	58.66	3.47	3.52
m-F	Liq.	62.27	62.23	3.79	3.73
m-Cl	53.4—54.0	58.51	58.66	3.51	3.52
p-CF_3	Liq.	56.06	56.26	3.25	3.15
m-CF_3	34.5—35.9	56.25	56.26	3.22	3.15
3,5-Cl_2	73.8—75.0	52.60	56.36	2.86	2.82
m-Me,*p*′-Me[b]	Liq.	68.46	68.56	5.48	5.39
Tosylates					
3,5-Me_2	56.3—59.3	63.71	63.58	4.94	4.87
m-Me	47.6—48.8	62.77	62.85	4.55	4.55
H	49.2—50.0[c]	62.02	62.06	4.39	4.22
p-F	41.1—43.8	59.43	59.43	3.97	3.80
m-Cl	73.2—73.5	56.95	57.21	3.69	3.66
3,5-Cl_2	137—139.2[d]	53.07	53.07	3.38	3.18
m-F	72.6—73.5	59.15	59.43	3.79	3.80
m-CF_3	99.7—100.8	55.56	55.70	3.50	3.40
p-CF_3	100.5—103.2	55.68	55.70	3.51	3.40
Bromides					
p-MeO-*m*-Cl	61.2—62.3	47.86	47.76	2.98	2.92
3,4-Me_2	Liq.	56.08	56.00	4.15	4.11
p-Me	Liq.	54.93	54.73	3.74	3.67
p-*t*-Bu	23.8—25.0	58.13	58.24	4.94	4.89
m-Me,*p*′-Me[b]	Liq.	56.08	56.00	4.13	4.11

a) Lit, mp 74.3—75.2 °C (K. T. Dishart and R. Levine, *J. Am. Chem. Soc.*, **78**, 2268 (1956)); lit, mp 74.5—75.0 °C (A. Kaluszyner, S. Reuter, and F. D. Bergmann, *J. Am. Chem. Soc.*, **77**, 4164 (1955)). b) See footnote i of Table 1. c) Lit, mp 53 °C (T. Netscher and H. Prinzbach, *Syntheses*, **1987**, 683). d) Lit,[13c] mp 117—118 °C.

1,1-Diaryl-2,2,2-trifluoroethyl bromides were prepared by essentially the same procedure as that reported by Liu et al.[11] Phosphorus tribromide (34 mmol) was added slowly to 20 mmol of alcohol in CCl_4 10 cm^3 with stirring in an ice bath. After stirring at 40 °C for 2 d, the reaction mixture was poured into ice–water, extracted with ether, and washed with $NaHCO_3$ solution and sat. NaCl solution. The bromide was purified through column chromatography on alumina. Some of bromides were not easily purified and were directly utilized for kinetic measurements.

The *p*-phenoxy, *p*-methylthio, and *p*-methoxy derivatives of 1,1-bis(substituted phenyl)-2,2,2-trifluoroethyl chlorides were obtained by the treatment of the alcohols (0.03 mol) and thionyl chloride (0.1 mol) in the presence of pyridine (1 cm^3) at ice-bath temperature.

Physical constants and analytical data are summarized in Tables 4 and 5.

Solvents: Commercial 95% ethanol was dehydrated twice by heating under reflux with magnesium ethoxide and then was distilled. Deionized water was reflux with $KMnO_4$ and the distillate was redistilled immediately before use. 80% aqueous ethanol (80E) was prepared by mixing corresponding volumes of absolute ethanol (80) and water (20) at 25 °C.

Table 5. Physical and Analytical Data of 1,1-Bis(substituted phenyl)-2,2,2-trifluoroethyl Alcohols, Tosylates, and Bromides

Subst.	Mp	Carbon/%		Hydrogen/%	
X	°C	Found	Calcd	Found	Calcd
Alcohols					
p-MeO	Liq.	61.70	61.54	4.95	4.84
p-MeS	Liq.	55.57	55.80	4.43	4.39
p-PhO	Liq.	71.26	71.56	4.51	4.39
3,4-Me_2	62.1—63.3	69.98	70.12	6.27	6.21
p-Me	Liq.	68.43	68.56	5.26	5.39
p-*t*-Bu	141—142.9	72.75	72.50	7.57	7.47
p-F	Liq.	58.49	58.34	3.17	3.15
3,5-Me_2	88.5—89.0	70.18	70.12	6.36	6.21
m-Me	Liq.	68.53	68.56	5.46	5.39
p-MeO–*m*-Cl	76.2—78.0	50.60	50.42	3.56	3.44
p-MeS–*m*-Cl	115.3—116.8	46.59	46.50	3.25	3.17
p-Cl	Liq.	52.50	52.36	2.86	2.82
m-Cl	61.1—62.0	52.55	52.36	2.85	2.82
Tosylates					
3,5-Me_2	39.1—40.0	64.75	64.92	5.47	5.45
m-Me	45.6—46.5	63.83	63.58	4.80	4.87
p-F	38.1—40.5	57.07	57.01	3.43	3.42
p-Cl	60.6—61.5	53.14	53.07	3.22	3.18
m-Cl	104.0—105.3	53.00	53.07	3.21	3.18
Bromides					
3,4-Me_2	85.5—86.3	58.41	58.24	4.95	4.89
p-Me	61.5—63.0	56.05	56.00	4.14	4.11
p-*t*-Bu	132.1—135.0	61.91	61.83	6.22	6.13
3,5-Me_2	104.0—105.6	58.47	58.24	4.97	4.89

Kinetic Measurement: Solvolysis rates were measured by a conductimetric method described before.[8] The first-order rate constants were determined by the least-squares computer program; the precision of fit to first-order kinetics was generally satisfactory over 2.5 half-lives with correlation coefficient >(0.99998).

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