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Resonance Effects in the Solvolysis of *α*-*t*-Butyl-*α*-neopentylbenzyl and *α*-*t*-Butyl-*α*-isopropylbenzyl *p*-Nitrobenzoates

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Substituent effects on the solvolysis rates of *α*-*t*-butyl-*α*-neopentylbenzyl and *α*-*t*-butyl-*α*-isopropylbenzyl *p*-nitrobenzoates in 50% (v/v) aqueous EtOH at 75 °C were correlated with the Yukawa–Tsuno equation to give $\rho=-3.37$ and $r=0.78$, and $\rho=-3.09$ and $r=0.68$, respectively. The reduction in *r* values from $r=1.00$ characteristic of full conjugation is ascribed to deviation from coplanarity of the carbocationic center and the benzylic π-system in the transition state. The torsion angles for twisting out of coplanarity were estimated from the relationship $r/r_{\max}=\cos^2\theta$ for a series of sterically hindered tertiary dialkylbenzylic solvolyses. The torsion angles assigned for these twisted benzylic systems are in good agreement with theoretically calculated dihedral angles of the corresponding 6-31G* optimized carbenium ions. This identity provides convincing evidence for occurrence of steric inhibition of resonance through loss of coplanarity, and, in turn, provides strong support for our characterization of the *r* value as a resonance demand parameter reflecting the degree of resonance (π-delocalization) interaction between an aryl group and the reaction site.

For describing the substituent effect on the S_N1 solvolyses of benzylic precursors, the Yukawa–Tsuno (Y–T) equation, Eq. 1[1)] has generally been employed successfully:[2—4)]

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

In this equation the parameter *r* is a measure of the degree of resonance interaction between the carbocationic center and benzene π-system. This "resonance demand" parameter should be closely related to the degree of π-overlap between the aryl-π-orbital and incipient vacant orbital of the benzylic carbenium ion. Hence, examination of the dependence of the *r*-value upon dihedral angle between the two p-orbitals should provide convincing evidence as to the origin of the empirical resonance demand parameter.

Tanida et al.[5)] carried out systematic studies of the steric effects of bulky *α*-substituents in tertiary benzylic systems, based on the variation of aryl substituent effects. They pointed out that excellent Y–T correlations exist for these solvolyses, with significantly reduced *r* values. These *r* values are remarkably small compared with $r=1.00$ for solvolysis of the uncongested coplanar system, *α*,*α*-dimethylbenzyl *p*-nitrobenzoates (PNBs) (**1**), and it appears that the loss of coplanarity between the aryl and the *α*-cationic center may bring about a significant decrease in the *r* value.

Recently we have also carried out investigations of substituent effects in benzylic solvolysis systems where the vacant p-orbital of the incipient carbenium ion is sterically twisted out of coplanarity with the aryl ring.[6—10)] The solvolysis of *α*,*α*-di-*t*-butylbenzyl PNBs (**2**) afforded a remarkably diminished value of $r=0.27$ due to steric inhibition of resonance by the application of Eq. 1.[6)] The best example of the complete absence of benzylic resonance ($r=0.0$) is provided by the solvolyses of 4-methylbenzobicyclo[2.2.2]octen-1-yl trifluoromethanesulfonates (OTf) (**3**) where the incipient benzylic orbital in the transition state is fixed exactly orthogonally to the benzene π-orbital.[7)]

On the other hand, the use of the Y–T equation and the interpretation based thereon has been criticized by Johnson,[11)] who has suggested that the regular Hammett–Brown treatment[12)] is just as effective. Johnson[11)] proposed that there exists a linear "extended selectivity principle (ESP)" relationship between reactivities ($\log k/k_o$) for *p*-methoxy substituents and ρ^+ values for a series of tertiary benzylic PNB solvolyses, and emphasized that several highly congested PNBs should show a degree of steric acceleration. In particular, this led to the contradictory view that the steric effect in most of these congested systems does not prevent the aryl group from exerting its maximum effect in stabilizing the carbenium ion. Thus only deviations from the line of the ESP plot were considered to be indicative specifically of resonance loss due to twisting, e.g., solvolysis of **2** was recognized as suffering from severe restriction of resonance due to aryl twisting.[11)]

One of the most likely explanations of a rate enhancing steric effect is that based on the Brown B-strain,[5,13)] resulting from strain relief in the transition state; bulky groups at the reaction site in the *α*,*α*-dialkylbenzylic systems would similarly increase the ground state strain of this kind. However, if resonance between the developing carbenium p-orbital and the aryl-π-system plays an important part in facilitating solvolysis of these systems, an overall drop in rate may result if in the transition state this resonance is disturbed by the bulky α-groups; this is indeed just what we have observed in this solvolysis series.

As an example of a congested system of coplanarity intermediate between **1** and **2**, we have recently reported substituent effects on the solvolysis of the α-*t*-butyl-α-methylbenzyl system (**4**) to provide r=0.91.[8)] The through-conjugation interaction with the benzylic cation site in the transition state in the solvolysis of **4** is not significantly reduced from full conjugation in the transition state of **1**. This small loss of resonance stabilization contrasts sharply with the very significant loss of resonance indicated by r=0.27 in **2**.[6)]

The carbenium ion transition state of a benzylic substrate carrying two bulky α-alkyl groups may be released from steric congestion most effectively by twisting the aryl group out of coplanarity. The efficiency of resonance interaction may then be expressed as a function of $\cos^2\theta$, where θ is the dihedral angle between the two overlapping p-orbitals (Scheme 1),[4,14,15)] and the resonance energy may be considered to follow an equation of the form:

$$RE_\theta / RE_{\max} = \cos^2\theta\,. \qquad (2)$$

Here $RE_{\max}$ is the resonance energy corresponding to a situation in which the aryl group lies in the plane of the carbenium ion, and RE_θ is that when there is an angle θ between these planes. It has frequently been assumed that $r_\theta/r_{\max}$ of the Y–T equation is equivalent to $RE_\theta/RE_{\max}$ and that θ can thus be calculated. This use of r provides a new approach to the interpretation of the steric effect–resonance effect interrelation and, in turn, gives strong support for the characterization of empirical r values from the Y–T equation as resonance demand parameters.

Nevertheless, in order to discuss the precise dependence of resonance demand upon the steric bulk of α-alkyl groups, it is necessary to gather more substituent effect data for tertiary benzylic solvolyses to establish a continuous series of systems of varying extents of twisting of the aryl group out of coplanarity with the benzyl carbenium ion. In the present study, we have chosen as examples of moderately congested systems, α-*t*-butyl-α-neopentylbenzyl (**5**) and α-*t*-butyl-α-isopropylbenzyl (**6**) PNBs as having alkyl groups of intermediate bulk between the methyl and *t*-butyl groups (Chart 1).

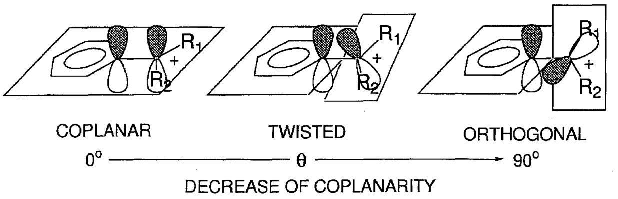
Results and Discussion

Meta and para substituted derivatives of α-*t*-butyl-α-neopentylbenzyl alcohols and α-*t*-butyl-α-isopropylbenzyl alcohols were synthesized by reaction of the corresponding aryllithium with *t*-butyl neopentyl ketone and *t*-butyl isopropyl ketone, respectively, and converted into their *p*-nitrobenzoates.

Solvolysis rates of the *p*-nitrobenzoates of **5** and **6** in 50% (v/v) aqueous ethanol (50E) were determined conductimetrically in the presence of lutidine; data are listed in Tables 1 and 2.

The substituent effects on these systems have been analyzed on the basis of Y–T equation (Eq. 1) and compared with the Brown $\rho^+\sigma^+$ equation. The correlation results are summarized in Table 3.

The solvolysis of α,α-dimethylbenzyl chlorides **1** is the σ^+ defining system[12)] and the substituent effect is also the reference standard for r=1.00 in the Y–T correlation.[1)] This unit value of r is generally valid for different leaving groups



Scheme 1. Decrease of resonance interaction.

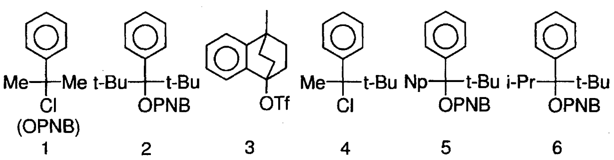


Chart 1.

Table 1. Solvolysis Rates of α-*t*-Butyl-α-neopentylbenzyl *p*-Nitrobenzoates in 50% Aq Ethanol

Subst.	$10^5\,k_t$ (s^{-1}) at 75 °C	$10^5\,k_t$ (s^{-1}) Other temp (°C)			$\Delta H^\ddagger_{75\,°C}$ kcal mol^{-1} a)	$\Delta S^\ddagger_{75\,°C}$ e.u. a)
p-MeO	9511 b)	470 (45),	163.4 (35),	46.10 (25)	21.2	−2.6
p-MeS	1646 b)	222.6 (55),	81.29 (45),	23.92 (35)	21.7	−4.6
4-MeO-3-Cl	671.0 b)	230.1 (65),	90.60 (55),	24.79 (45)	23.2	−2.3
p-Me	485.7 b)	169.5 (65),	56.28 (55),	17.07 (45)	23.9	−0.9
p-*t*-Bu	389.1	157.3 (65),	47.68 (55),	14.75 (45)	23.6	−2.1
3,5-Me$_2$	146.4	50.34 (65),	16.19 (55),	4.513 (45)	24.8	−0.6
m-Me	100.9	31.96 (65),	10.56 (55),	2.901 (45)	25.2	−0.2
p-F	67.42	20.68 (65),	6.725 (55),	1.885 (45)	25.4	−0.4
H	60.39	20.33 (65),	6.392 (55),	1.785 (45)	25.1	−1.4
p-Cl	21.41	5.805 (65),	1.830 (55),	0.493 (45)	26.7	1.1
m-Cl	3.036	0.9889 (65),	0.2736 (55),		26.6	−3.0
m-CF$_3$	1.277	0.3063 (65),	0.09107 (55),		29.3	2.7

a) 1 cal=4.184 J. b) Extrapolated from data at other temperatures.

Table 2. Solvolysis Rates of α-t-Butyl-α-isopropylbenzyl p-Nitrobenzoates in 50% Aq Ethanol

Subst.	$10^5k_t(s^{-1})$ at 75°C	$10^5k_t(s^{-1})$ at 55°C	$\Delta H^{\ddagger}_{75°C}$ kcal mol^{-1} [a]	$\Delta S^{\ddagger}_{75°C}$ e.u. [a]
p-MeO[b]	439.8	61.86	22.6	−4.7
p-MeS	63.43	6.959	24.4	−3.4
4-MeO-3-Cl	30.23	2.519	27.5	4.1
p-Me	28.87	2.190	28.6	7.1
p-t-Bu	24.73	1.876	28.6	6.8
3,5-Me$_2$	15.63	1.122	29.2	7.6
m-Me	9.111	0.6610	29.1	6.2
H	5.858	0.4145	29.4	6.2
p-F	4.262	0.3108	29.0	4.5
p-Cl	1.656			
m-Cl	0.3923			
m-CF$_3$	0.1845			

a) 1 cal=4.184 J. b) 1.807×10^{-3} s^{-1} (65 °C), 1.862×10^{-4} s^{-1} (45 °C).

and for varying solvents.[5,11,12] Insufficiently congested α-ethyl-α-methylbenzyl and α,α-diisopropylbenzyl solvolyses both gave a good linear σ^+-correlations as well as Y–T correlations with $r=1.00$.[10] The solvolysis of α-t-butyl-α-methylbenzyl chlorides **4** gave a linear Y–T correlation with a reduced r-value of 0.91, which was ascribed to the steric loss of resonance, while the σ^+ correlation was not much worse.[8]

The behavior of substituents in the solvolysis of **5** in 50E at 75 °C is illustrated by the Y–T plot in Fig. 1. The substituent effects are clearly not correlated linearly with σ^+ parameters. Although the m-substituents are correlated linearly with σ° (or σ^+) to give a reference correlation line, the σ^+ points (open circles) of para π-donor substituents consistently deviate downward from the reference m-correlation line, suggesting a lower resonance demand than unity for this system. The line-segments between σ^+ and σ° values for para π-donor substituents measure the resonance capabilities of these substituents, i.e., the $\Delta\overline{\sigma}^+_R$ values. The ρ_m correlation line divides all these line-segments at a constant internal ratio of 0.78, which represents the r value for this system. Thus, the Y–T correlation (ρ_{YT}) line, i.e., ρ_m-line, can be defined as a unique line intersecting all line-segments for para π-donors at such a constant ratio. In fact, the application of Eq. 1 to the present data affords an excellent correlation, with correlation coefficient 0.9996 and standard deviation ±0.036, as shown in Table 3. For the solvolysis of **5** in 70% aqueous acetone, Tanida et al.[5] earlier reported a Y–T correlation giving the different r value of 0.990. However, this may be attributed to a larger uncertainty in the correlation of this data set (vide infra).

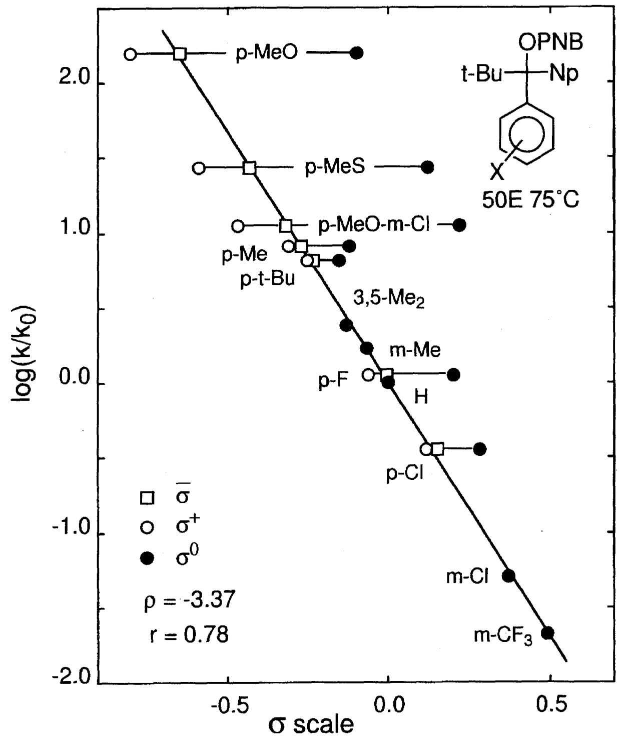


Fig. 1. The Y–T plot of substituent effect on the solvolysis of α-t-butyl-α-neopentylbenzyl p-nitrobenzoates in 50% aq ethanol at 75 °C: Open circles, σ^+, closed, σ°, and squares, $\overline{\sigma}$ for r=0.78.

The behavior of **6** in Fig. 2 is similar to that of **5**, giving an excellent Y–T correlation with the slightly lower r value of 0.68±0.04 (Table 3). The σ^+ plots are neither ran-

Table 3. Results of Correlation Analysis for α-Alkyl-α-t-butylbenzyl Solvolyses

Solvolysis systems	Correlation	ρ	r	R[a]	SD[b]	n[c]
4[d]	Y–T Eq.	−4.28±0.08	0.91±0.03	0.9986	0.088	22
	Brown Eq.	−4.06±0.06	(1.00)	0.9978	0.108	22
	meta-corr.	−4.19±0.09		0.9988	0.062	7
5[e]	Y–T Eq.	−3.37±0.05	0.78±0.02	0.9996	0.036	12
	Brown $\rho^+\sigma^+$	−2.90±0.11	(1.00)	0.9928	0.138	12
	meta-corr.	−3.37±0.05		0.9997	0.026	5
6[e]	Y–T Eq.	−3.09±0.08	0.68±0.04	0.9985	0.058	12
	Brown $\rho^+\sigma^+$	−2.46±0.15	(1.00)	0.9815	0.189	12
	meta-corr.	−3.07±0.06		0.9998	0.019	5

a) Correlation coefficient. b) Standard deviation. c) Numbers of substituents involved. d) Chlorides in 80% aq acetone at 45 °C; Ref. 8. e) p-Nitrobenzoates in 50% aq ethanol at 75 °C; present work.

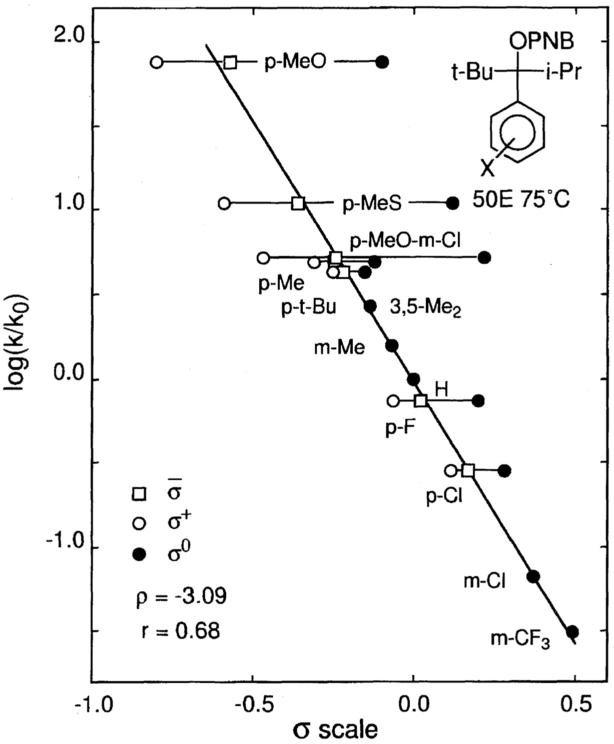


Fig. 2. The Y–T plot of substituent effect on the solvolysis of α-*t*-butyl-α-isopropylbenzyl *p*-nitrobenzoates in 50% aq ethanol at 75 °C: Open circles, σ^+, closed, σ°, and squares, $\bar{\sigma}$ for r=0.68.

domly scattered nor smooth curves; the discontinuously split pattern of the σ^+ plot in principle should be incompatible with any mechanistic interpretation other than inadequacy of substituent parameter.

Although the moderate decrease in r does not appear statistically very significant in bringing about a clear failure of the Brown σ^+ correlation, these r values lower than unity are sensibly ascribed to steric inhibition of the resonance interaction in the solvolysis transition state.

On the other hand, we showed that solvolysis of the more congested **2** gave an excellent Y–T correlation, with a significantly lower r value of 0.27. Furthermore, the solvolysis of benzobicyclooctenyl substrates **3**, where any exalted π-delocalization interaction may be completely prohibited for structural reasons, can be characterized by the resonance-unexalted reactivity value of r=0.0; the vacant orbital at the bridgehead of the bicyclic skeleton should be rigidly oriented to be orthogonal to the benzo-π-orbital.

These systems constitute a continuous spectrum of resonance demand parameters reflecting the bulk of α-alkyl substituents in the tertiary benzylic solvolysis series, which covers from the Brown σ^+ reference system **1** of entire benzylic π-delocalization to the σ° system as the lowest extreme of exalted π-delocalization, as summarized in Table 4.

Johnson, on the contrary, as we have seen, has stressed the broad applicability of the Brown $\rho^+\sigma^+$ equation to tertiary benzylic PNB solvolyses, and emphasized that the steric effect, even in most congested PNB's, does not prevent the aryl group from exerting its maximum effect in stabilizing the carbenium ion.[11] Only the solvolysis of **2** was considered to suffer from resonance loss due to twisting.[11]

In commenting on this point, it is worthy of note that the solvolysis of **2** not only fails to correlate with the Brown σ^+, but correlates excellently with the ordinary Hammett σ constant. Quite generally, the σ-correlation has been considered to be the system exerting essentially an unenhanced resonance effect ($r\doteqdot 0$). Thus the "ESP" analysis led to a conclusion that the steric inhibition of resonance in this series should be either absent (r=1) or present (r=0), and hence that there is no continuous spectrum of restricted resonance stabilization due to twisting of the coplanar transition state. Even if the relation between the aryl-rotation and varying resonance demand r may be qualitative, we do not accept the assumption that all the transition states or carbenium ion intermediates of this series of solvolyses have either the coplanar conformation (dihedral angle $\theta\doteqdot 0°$) of full resonance or the orthogonal structure (θ=90°) in which resonance stabilization is completely absent.

If this were correct, in the former class the reactivities should be affected by secondary steric effects upon the ground state destabilization but not upon resonance stabilization of the incipient carbenium ion. By constraining a constant value of r in his series of substrates, Johnson[11] obtained a decreased $|\rho^+|$. This was interpreted in terms of a Hammond shift towards an early transition state caused by steric destabilization of the ground state reactant. However, this effect should accompany a steric acceleration in the rate. On the contrary reactivities of the parent substrates decrease as the bulk of the α-substituents increases (see Table 4).[8,10] Hence, the prediction based on the anticipated effects of strain relief of reactant clearly fails. In addition, contrary to expectation, only **2** in the latter class may involve the effect of strain relief (see Table 4); even the exceptionally low ρ value found for the di-*t*-butyl system **2** cannot simply be attributed to the steric loss of resonance deduced from the failure of the Johnson ESP relation.

It should be mentioned that the Brown σ^+ correlation becomes significantly worse, regardless of the decrease in the ρ^+ value, as the reaction center becomes bulkier, and that the Y–T correlations are indeed always better than the corresponding Brown correlations for the series, as shown in Table 3.

Nevertheless, the ρ values for the Y–T correlations, i.e., ρ_{YT} values, for **5** and **6** are also substantially smaller than those observed for uncongested tertiary benzyl substrates, e.g., **1** (Table 4). The available solvolytic data reveal that the decrease in ρ value is consistent with the occurrence of an early transition state, as the ground state strain is progressively increased.[16] However, the diminution of ρ_{YT} as well as ρ_m occurs independently of the progressive change in resonance demand (r) caused by the steric loss of resonance.

The correlations of substituent effects in **4**, **5**, and **6**, bearing moderately bulky α-alkyls, should therefore be of particular importance for exploring the continuity of variation in resonance effect with varying steric effects.

Table 4. Tertiary Benzylic Solvolyses Having a Series of α-Alkyl Groups

Systems	**1**	**4**	**5**	**6**	**2**	**3**
$10^5 \times k_t^{H}$ [a]	419.5[b]	0.2698[b]	60.39	4.661	8.660	10^{-11} [c]
ρ value	−3.96,[b,d] −4.54[e]	−4.28[f]	−3.37[d]	−3.09[d]	−2.2[d,g]	−2.2[h]
r value	1.0	0.91	0.78	0.68	0.27	0.0
θ_{expt}[i] /°	0	17	28	34	59	90
θ_{calc}[j] /°						
RHF/6-31G*	5 (7)[k]	24	26	33	76 (69)[k]	90
RHF/3-21G	5	24	32	37	77	90
RHF/STO3G	0	20	21	31	55	90

a) Solvolysis rate constant for the unsubstituted α,α-dialkylbenzyl *p*-nitrobenzoate in 50% aq ethanol at 75 °C. b) Unpublished data in this laboratory. c) Approximate value; see Ref. 8. d) *p*-Nitrobenzoates in 50% aq ethanol at 75 °C. e) Chlorides in 90% aq acetone at 25 °C, Ref. 12. f) Chlorides in 80% aq acetone at 45 °C, Ref. 8. g) Ref. 6. h) Triflates in 80% aq ethanol at 75 °C, Ref. 7. i) Based on $\cos^2 \theta = r/r_{max}$ where $r_{max}=1.00$. j) Refs. 4 and 15. k) MP2/6-31G*//RHF/6-31G*.

Figure 3 shows the dependence of the standard deviations (SD) upon *r* in the least-squares fitting to Eq. 1 without constraining the ρ value, which provides a reasonable measure of the real validity of Y–T correlations. For all the solvolyses, the SD changes sensitively with varying *r*, giving a sharp wedge-shaped plot; any deviation from the best-fit *r* causes a sharp increase in the SD value. The steepness rather than the depth of the wedge plot is a more direct measure of the validity of the *r* value and therefore will be important for discussing varying resonance demand. Similar SD vs. *r* plots are seen for **5** and **6**.

Since the uncertainty of typical sets of substituent parameters, such as σ and σ^+, is generally considered to be within ±0.02, the failure of correlations with a ρ value of −4 to −3 should be judged by the criterion of a standard deviation of 0.08—0.06. The precision of *r*-value is practically evaluated from the overall SD value for the best-fit correlation at the *r* point of minimum SD in Fig. 3, so the judgment on the conformity of correlation should be based only on the requirement that the minimum SD value is within (or smaller than) the above criterion. Then, the validity of *r* may also be estimated, even though qualitatively, by the width of a standard deviation vs. *r* plot at such a level (SD=±0.06—0.08) as to provide a criterion of unacceptable conformity to Eq. 1. Thus the *r* value may be valid within a possible uncertainty of the order of ±0.06. This range of validity of *r* value is appreciably larger than the ordinary precision indices in the SD scale shown in Table 3. Even if such a large possible uncertainty in the *r* value may be allowed, the *r* value of 0.68 assigned for **6** is well outside the range of applicability of the σ^+ scale taking r=1.00. The results of the validity analysis of *r* thus contradict Johnson's argument that the Brown σ^+ treatment can be equally applied to all of these systems.

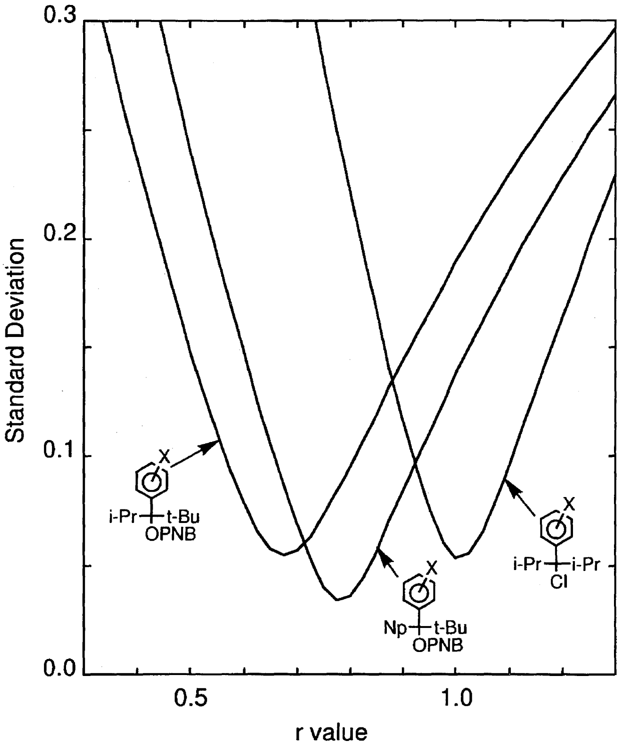
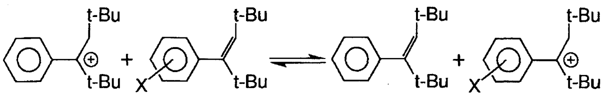


Fig. 3. The plot of standard deviations as a function of *r* values for the solvolyses of tertiary benzylic systems.

The intermediate *r* values of 0.78 for **5** and 0.68 for **6** are statistically distinguished from either r=1.00 for **1** or r=0.27 for **2**, and probably even from r=0.91 for **4**. The decrease in the *r* parameter can be understood if we assume that in the transition state the aryl group has not attained complete coplanarity with the sp^2 reaction site. Rotation of the aryl ring to increase the overlap between its orbitals and the empty p orbital would be impeded in **2** and also somewhat in **4**—**6** by steric interactions between aryl and α-substituents.

Intuitively, this interpretation can be better understood on the basis of a simplified model of the delocalization interaction of overlapping orbitals when it applies to a benzyl carbenium ion intermediate rather than the solvolysis transition state.

We have widely explored the proposal that *r* values for solvolyses of benzylic precursors are in general exactly the same as values for the carbocation stabilities of the corresponding benzylic cations in the gas phase.[4,17] The *r* value for the solvolysis transition state of **4** is in good agreement with the *r* value of 0.87 estimated for the corresponding carbenium intermediate based on the stabilities of the gas-phase cations.[18] Most recently, the substituent effect on the stability of α-*t*-butyl-α-neopentylbenzyl **5** cations has also been determined from the gas-phase proton transfer equilibrium shown below;



(3)

The gas phase stability of cation **5** can be correlated excellently with Eq. 1 to give an *r* of 0.81, which is identical, within the uncertainty verified above, to the value observed for the α-*t*-butyl-α-neopentylbenzyl solvolysis.[19] The identity of the empirical *r* values for the solvolysis transition state and the corresponding gas phase cation appears to embrace both sterically twisted[18,19] and untwisted systems.[4,17] Thus, the structures of the transition states of benzylic solvolyses should be essentially unchanged as regards reduced aryl-carbenium coplanarity from those of the corresponding gas-phase cations.

Thus the structure of the carbenium ion can model that of the transition state as well as of the solvolysis intermediate following closely after the transition state. This confirms that the observed decrease in the *r* value should be ascribed to a loss of the resonance interaction due to a deviation out of the coplanarity between the carbenium center and the benzene π-system rather than to a shift in the transition state coordinate.

The efficiency of resonance interaction can be expressed as in Eq. 2 as a function of $\cos^2\theta$, where θ is the dihedral angle between two overlapping p-orbitals.[4,14,15] An "intrinsic" $r_{\max}$ value may be taken to be unity for solvolyses forming coplanar tertiary α,α-dialkylbenzylic cations.[10,11] Thus, from the ratios $r/r_{\max}$ for these solvolyses, which can be related to the efficiency of benzylic resonance interaction, the torsion angles θ in the transition states may be estimated by Eq. 2. The torsion angles θ in the gas-phase cations **4** and **5** are identical to those derived from the corresponding solvolyses.[8,18,19] In Table 4, the *r* values and the calculated dihedral angles θ between aryl and α-carbenium sp^2 planes are compared for a series of α-alkyl groups of tertiary benzylic solvolyses.

In order to further substantiate this relationship regarding the resonance demand, these estimated torsion angles should be directly compared with dihedral angles of carbenium ions under equilibrium condition in solution. However, there are insufficient structural data available, especially for sterically congested carbenium ions, to allow us to interpret these results through comparison of geometries of the transition state and intermediate. However, the structures of carbenium ions can now be precisely and unambiguously estimated by the most advanced molecular orbital calculation. Recently we have reported the geometries of a series of benzylic carbenium ions optimized by the ab initio MO calculation at the RHF/6-31G* level.[15,20]

Table 4 reveals that the 6-31G*-optimized carbenium ions all have significantly twisted structures, and furthermore that the dihedral angles of the optimized structures are, even though slightly dependent on the basis sets, in good agreement with the "experimental" angles of the solvolysis transition states and/or of the gas-phase carbenium ions based on Eq. 2.

The value θ_{calc} of 26—32° for cation **5**[15] is in good agreement with the above experimental value of $\theta_{\mathrm{expt}}=28°$ for the solvolysis transition state and $\theta_{\mathrm{expt}}=26°$ for the gas-phase cation of **5**. Similarly, the dihedral angle of the optimized cation **6** is 33°[15] in good agreement with that (34°) obtained from the *r* valus for solvolysis.

The close agreement between theoretically calculated and empirically derived dihedral angles assigned for twisted benzylic systems provides a theoretical basis for characterization of the empirical parameter *r* in the Yukawa–Tsuno equation as reflecting the degree of π-delocalization interaction between the aryl group and the reaction site.

Finally, we return to the appreciable decrease in the ρ value that also occurs in these congested systems, compared with the value for the uncongested benzylic solvolysis. The reduced ρ value may be related to the shift of this transition state toward an earlier position along the reaction coordinate.[16] However, it should be noted that a significant decrease in the ρ value is accompanied by a decrease in *r* value in the sterically twisted bulky-formed carbenium ion system in the gas phase.[19] This argues against the Hammond shift towards an earlier transition state. It follows that either the extended π-delocalization to the incipient carbenium p-orbital or the exalted π-bond order of aryl-C$_\alpha$ bond plays an important part in the attenuation of the polar effect of substituents.

Experimental

Materials: *t*-Butyl isopropyl ketone was synthesized according to the literature method,[21] by the dropwise addition of isopropylmagnesium bromide (0.75 mol) in 500 cm^3 of ether to an ethereal suspension of pivaloyl chloride (72.3 g, 0.6 mol) and CuCl (5.9 g, 0.06 mol) at −5 °C. The ketone so obtained, which was removed from the unreacted acid chloride by alkaline hydrolysis, was distilled through a helix-packed column; bp 132—138.5 °C (lit,[21] bp 135—139 °C). Similarly, *t*-butyl neopentyl ketone was synthesized from *t*-butylmagnesium chloride and *t*-butylacetyl chloride; bp 107—110 °C/143 mmHg (lit,[22] bp 108—110 °C/150 mmHg) (1 mmHg=133.322 Pa).

Details of the conversion of the above ketones to aryl alcohols and *p*-nitrobenzoates are given for the example for α-*t*-butyl-α-isopropyl alcohol (and *p*-nitrobenzoate) which are typical of the series, according to literature methods.[5,23]

Under an argon gas atmosphere, bromobenzene (0.12 mol) in ether (100 cm^3) was added to 15% butyllithium in hexane solution (75 cm^3, 0.12 mol) at −40 °C. After stirring for 1 h at room temperature, *t*-butyl isopropyl ketone 0.12 mol in 100 cm^3 ether was added to the reaction mixture at −30 °C. The α-*t*-butyl-α-isopropylbenzyl alcohols was purified by distillation; other alcohols were purified similarly or by column chromatography or recrystallization.

Under an argon gas atmosphere, a 15% butyllithium solution in hexane (9.2 cm^3, 15 mmol) was added to the above alcohol (10 mmol) in THF 10 cm^3 at −30 °C and heated under reflux for 2 h. *p*-Nitrobenzoyl chloride (1.9 g, 10 mmol) in THF 10 cm^3 was added to the above alkoxide solution at −30 °C over 20 min with stirring; the reaction mixture was kept overnight at room temperature and then treated with ice water. The crude ester was extracted with ether and was purified through SiO_2 column chromatography and recrystallized from dichloromethane–hexane; other esters were similarly purified and recrystallized from benzene–hexane or dichloromethane–hexane.

Several *p*-nitrobenzoates were also obtained directly without isolation of alcohols. The physical data of alcohols and *p*-nitrobenzoates prepared are listed in Tables 5, 6, 7, and 8.

Solvents: Ethanol and water were purified by the established method as described before.[3] 50% (v/v) aqueous ethanol was prepared by mixing equal volumes of ethanol and water at 25 °C.

Kinetic Measurement:[3] Solvolysis rates of the *p*-nitrobenzoates in 50% (v/v) aqueous ethanol (50E) were determined

Table 5. Physical and Analytical Data of α-*t*-Butyl-α-neopentylbenzyl Alcohols

Subst.	Mp [°C] or	Carbon/%		Hydrogen/%	
X	bp (°C/mmHg)	Found	Calcd	Found	Calcd
p-MeO	[78.6—80.2]	77.25	77.23	10.63	10.67
p-MeS	[44.3—46.5]	72.68	72.80	9.97	10.06
4-MeO-3-Cl	[95.8—98.7]	68.38	68.32	9.12	9.11
p-Me	[55.9—56.5]	82.08	82.20	11.29	11.36
p-*t*-Bu	[72.4—74.3]	82.73	82.70	11.79	11.80
3,5-Me_2	(122—126/2)	82.32	82.38	11.43	11.52
m-Me	(109—112/2)	82.18	82.20	11.18	11.36
H	(93—100/2)	81.84	81.99	11.05	11.18
p-Cl	[75.6—77.8]	71.39	71.49	9.37	9.37
m-Cl	(120—122/2)	71.50	71.49	9.32	9.37
m-CF_3	(100—105/2)	67.59	67.53	8.18	8.33

Table 6. Physical and Analytical Data of α-*t*-Butyl-α-isopropylbenzyl Alcohols

Subst.	Mp [°C] or	Carbon/%		Hydrogen/%	
X	bp (°C/mmHg)	Found	Calcd	Found	Calcd
p-MeO	[89.6—90.9]	76.16	76.23	10.25	10.24
p-MeS	[41.9—44.5]	71.18	71.38	9.68	9.58
p-Me	Liq.	81.73	81.76	10.98	10.98
p-*t*-Bu	Liq.	82.37	82.38	11.34	11.52
3,5-Me_2	(120—135/2)	82.21	81.99	11.05	11.18
m-Me	(131—133/7)	81.79	81.76	10.77	10.98
H	Liq.[a]	81.50	81.50	10.62	10.75
p-Cl	(130—135/3)	69.81	69.84	8.72	8.79
m-Cl	(120—122/2)	69.87	69.84	8.71	8.79

a) Lit,[24] bp 60 °C/0.01 mmHg.

Table 7. Physical and Analytical Data of α-*t*-Butyl-α-neopentylbenzyl *p*-Nitrobenzoates

Subst.	Mp	Carbon/%		Hydrogen/%		Nitrogen/%	
X	°C	Found	Calcd	Found	Calcd	Found	Calcd
p-MeO	107—110.3[a]	69.56	69.71	7.55	7.56	3.43	3.39
p-MeS	126—129.9	67.13	67.11	7.30	7.27	3.33	3.26
4-MeO-3-Cl	148.8—151.1	64.33	64.35	6.82	6.75	3.13	3.13
p-Me	121.0—124.9[b]	72.40	72.52	7.86	7.86	3.48	3.52
p-*t*-Bu	129—134.2	73.77	73.77	8.68	8.48	3.00	3.19
3,5-Me_2	167.9—171.2	72.88	72.96	8.19	8.08	3.23	3.40
m-Me	154.4—156.0	72.45	72.52	7.87	7.86	3.43	3.52
H	153.2—155.9[c]	71.81	72.04	7.65	7.62	3.55	3.65
p-F	137.0—139.2	68.84	68.81	7.15	7.03	3.33	3.49
p-Cl	155.6—159.3[d]	66.00	66.10	6.92	6.75	3.13	3.35
m-Cl	106.0—110.5	66.31	66.10	6.89	6.75	3.35	3.35
m-CF_3	125.0—127.8	63.95	63.85	6.34	6.25	3.27	3.10

a) Lit,[5] mp 115—116 °C. b) Lit,[5] mp 131—132 °C. c) Lit,[5] mp 154—155 °C. d) Lit,[5] mp 147—148 °C.

Table 8. Physical and Analytical Data of α-*t*-Butyl-α-isopropylbenzyl *p*-Nitrobenzoates

Subst.	Mp	Carbon/%		Hydrogen/%		Nitrogen/%	
X	°C	Found	Calcd	Found	Calcd	Found	Calcd
p-MeO	142.2—143.1	68.46	68.55	7.09	7.06	3.60	3.63
p-MeS	158.0—160.2	65.51	65.81	6.72	6.78	3.49	3.49
4-MeO-3-Cl	168.2—168.9	62.98	62.93	6.29	6.24	3.28	3.34
p-Me	168.0—169.6	71.56	71.52	7.38	7.37	3.72	3.79
p-*t*-Bu	164.8—166.0	72.72	72.96	8.03	8.08	3.28	3.40
3,5-Me_2	169.6—171.3	72.07	72.04	7.67	7.62	3.65	3.65
m-Me	125.6—127.5	71.33	71.52	7.35	7.37	3.75	3.79
H	156.2—156.9[a]	70.89	70.96	7.07	7.09	3.92	3.94
p-F	152.7—155.8	67.40	67.55	6.62	6.48	3.55	3.75
p-Cl	195.2—197.0	64.70	64.70	6.14	6.20	3.51	3.59
m-Cl	121.4—122.3	64.84	64.70	6.29	6.20	3.55	3.59
m-CF_3	104.7—106.0	62.40	62.41	5.75	5.71	3.18	3.31

a) Lit,[24] mp 158 °C.

conductimetrically at 75 °C. Conductance measurements were made using approximately 50 $\mathrm{cm^3}$ of 10^{-4}—10^{-5} $\mathrm{mol\,dm^{-3}}$ solution of the starting *p*-nitrobenzoates (1—2 mg) in a thermostatted bath at the appropriate temperature controlled within ±0.02 °C in the presence of excess lutidine (2—5 μl). For the conductivity measurement in 50E, complete dissolution of substrate can be attained relatively quickly by first dissolving in a small amount of absolute ethanol and then adding starting *p*-nitrobenzoate to the 50E solvent together with the same amount of water. Conductance readings were taken automatically by using a conductivity meter (CM-60S, Toa Electronics Ltd.) connected to a computer. Solvolyses were followed by taking at least 100 readings at appropriate intervals for 2.5 half-lives; the infinity reading was taken after 10 half-lives. The precision of fit to first-order kinetics was generally satisfactory over 2.5 half-lives in the presence of lutidine ($R>0.99995$).

The experimental errors (SD of rate constants) in individual runs were generally less than 1.5% and rate constants from repeated runs were reproducible within an accuracy of 3%.

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