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Substituent Effect on the Solvolysis of α-t-Butyl-α-methylbenzyl Chlorides

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Abstract: *The substituent effect on the solvolysis rates of α-t-butyl-α-methylbenzyl chlorides in 80% aq. acetone was correlated to give* $\rho=-4.3$ *and* $r=0.91$ *in terms of the LArSR Eq. (1). This slightly reduced r value relative to full conjugation corresponds to a deviation by* $\theta=24.5^o$ *from the coplanarity of the benzylic π-system.*

For describing the substituent effect on the benzylic carbenium ion solvolyses, the Yukawa-Tsuno (LArSR) Eq. (1)1) has generally been employed successfully,

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

where the parameter r is a measure of the additional resonance effect with the reaction center and changes depending upon the resonance demand of benzylic transition state.2-5) The r value has been found to change widely from reaction to reaction. In general, there is a continuous spectrum of varying resonance demands characteristic of solvolyzing substrates, ranging from non-conjugative carbenium ion reactions r=0.0,6) via the Hammett σ reactivities r=0.267) and the so-called σ^+ category of r=1.00, up to an apparent ceiling r value of 1.5 observed in solvolyses forming extremely electron-deficient carbenium ion.5)

The r value should be related most closely to the degree of π-overlapping between the aryl-π-orbital and incipient benzylic carbenium vacant orbital. Hence the examination of the dependence of r-value upon the dihedral angle for both p-orbitals will provide convincing evidence for the real origin of the empirical resonance demand parameter r in Eq. (1). We have recently studied the benzylic solvolysis systems where the incipient carbenium vacant p-orbital is sterically twisted out of the coplanarity with the aryl ring.6-8) The best example of complete absence of benzylic resonance (r=0.0) has been experimentally provided by benzobicyclo[2.2.2]octenyl solvolysis where the incipient benzylic orbital in the transition state is exactly orthogonal to the benzene π-orbital.6) The solvolysis of α,α-di-t-butylbenzyl system ($I_{\alpha\text{-t-Bu},\alpha\text{-t-Bu}}$) afforded a remarkably diminished r value of r=0.26 due to steric resonance inhibition.7) The r value for this sterically twisted system is remarkably small compared with $r_{max}=1.00$ of the coplanar reference, α,α-dimethylbenzyl system ($I_{\alpha\text{-Me},\alpha\text{-Me}}$). The efficiency, r/r_{max}, is a measure of the degree of resonance interaction which is, to the first approximation, proportional to the overlap integral S between the carbenium reaction site and benzene π-system. When we use S_o as the overlap integral at the planar structure of molecule, S is given by $S=S_o\cos\theta$ where θ is the torsional angle between the benzylic site and benzene system, and the torsional angle θ in the transition state is calculated to be 75° for I $_{\alpha\text{-t-Bu},\alpha\text{-t-Bu}}$ since cos θ=0.26.[7,9)]

As a congested system of intermediate coplanarity between I $_{\alpha\text{-Me},\alpha\text{-Me}}$ and I $_{\alpha\text{-t-Bu},\alpha\text{-t-Bu}}$, we have recently reported the substituent effect on the solvolysis of α,α-diisopropylbenzyl system (I $_{\alpha\text{-i-Pr},\alpha\text{-i-Pr}}$) to provide r=1.0 expected for full conjugation.[10)] Because of similar polar effects of methyl and isopropyl groups,[11)] we will have to conclude that the through-conjugation interaction may be almost fully operative in I $_{\alpha\text{-i-Pr},\alpha\text{-i-Pr}}$. This insignificant deviation from the coplanarity for I $_{\alpha\text{-i-Pr},\alpha\text{-i-Pr}}$ is in sharp contrast to the significant twisting in I $_{\alpha\text{-t-Bu},\alpha\text{-t-Bu}}$. The isopropyl group in place of the methyl group in I should not be sterically bulky enough to deviate from the coplanarity of the sp^2 reaction center unlike I $_{\alpha\text{-t-Bu},\alpha\text{-t-Bu}}$. In the present study we have chosen another intermediate congested system, α-t-butyl-α-methylbenzyl system (I $_{\alpha\text{-t-Bu},\alpha\text{-Me}}$) where one methyl group in the α,α-dimethylbenzyl is replaced by a bulky t-butyl group.

The m, p-substituted α-t-butyl-α-methylbenzyl alcohols were mostly synthesized from the reactions of the corresponding aryllithium with pinacolone and subjected to chlorination with dry HCl gas.[12)] Several strongly deactivated I $_{\alpha\text{-t-Bu},\alpha\text{-Me}}$ chlorides were obtained from the chlorination of the corresponding 1-butenes.[12,13)] Solvolysis rates of chlorides in 80%(v/v) aqueous acetone (80A) were determined conductimetrically, and the data at 45°C are summarized in Table 1.

All para π-donor substituents deviate slightly but systematically below the ρ_m line while the logarithmic rates in 80 A are practically related linearly with σ^+ parameters, suggesting a lower resonance demand than unity in this system. In fact, the application of Eq. (1) to the present data affords an excellent correlation, as shown in Fig. 1, log $(k/k_0) = (-4.28\pm0.08)[\sigma^0 + (0.91\pm0.03)\Delta\overline{\sigma}_R^+]$, with correlation coefficient 0.9986 and SD=±0.088. The r value of 0.91 is not very much different from but still believed to be statistically distinguished from

Table 1. Solvolysis Rates of α-t-Butyl-α-methylbenzyl Chlorides in 80% aq. Acetone at 45°C

Subst.	$10^5k/s^{-1}$	Subst.	$10^5k/s^{-1}$
p-MeO-m-Me	7232[a)]	3,5-Me$_2$	4.117
p-MeO	2927[a)]	2-Naph	4.016
p-MeS	224.2	m-Me	2.332
p-PhO	134.0	p-F	1.859
3,4,5-Me$_3$	65.87	H	1.323
p-MeO-m-Cl	59.42	p-Cl	0.3053
3,4-Me$_2$	37.87	p-Br	0.2859
p-Me	19.69	m-F	0.06016[a)]
p-t-Bu	13.21	m-Cl	0.03931[a)]
p-MeS-m-Cl	7.385	m-CF$_3$	0.009720[b)]
p-Ph	5.760	p-CF$_3$	0.008376[b)]

a) Extrapolated from other temperatures.
b) Estimated from rate data in 50A based on the linear logarithmic rates relation between 80A and 50A.

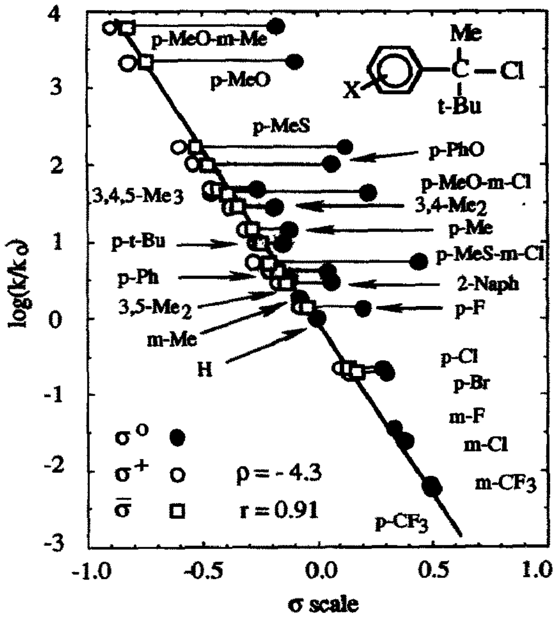

Fig. 1. LArSR plot of the solvolysis of α-t-butyl-α-methylbenzyl chlorides in 80A at 45°C.

r=1.00 of I$_{\alpha\text{-Me},\alpha\text{-Me}}$. This should be ascribed to a slight loss of the resonance interaction between the carbenium center and the benzene π-system in the solvolysis transition state, but still 90% of maximum conjugation is operative in the present system.

The intrinsic r value may be as a reasonable approximation taken to be unity for solvolyses to form a coplanar tertiary α,α-dialkylbenzylic carbenium ion.[14] The torsional angle in the transition state is calculated to be 24.5° from cos θ=0.91. This small loss of coplanarity corresponding to at most one-tenth the full resonance stabilization contrasts sharply with the remarkable twisting (θ=75°) corresponding to a 74% loss of resonance observed in the I$_{\alpha\text{-t-Bu},\alpha\text{-t-Bu}}$.[7]

It is surprising that the through-conjugation interaction with the benzylic cation site in the transition state is not significantly reduced in the I$_{\alpha\text{-t-Bu},\alpha\text{-Me}}$ solvolysis as well as in I$_{\alpha\text{-i-Pr},\alpha\text{-i-Pr}}$. These solvolyses have shown a degree of deceleration associated with steric congestion; nevertheless this steric effect does not effectively prevent from exerting its maximum resonance effect on stabilizing the incipient carbenium ion.

In Table 2 are compared rates of tert. benzylic solvolyses for a series of α-alkyl groups together with the r value and dihedral angle (θ). The distinctly diminished solvolysis rate of I$_{\alpha\text{-t-Bu},\alpha\text{-Me}}$ compared with the I$_{\alpha\text{-Me},\alpha\text{-Me}}$ and I$_{\alpha\text{-Et},\alpha\text{-Me}}$ (k=6.185x10^{-4} s^{-1} in 80A at 25°C),[10] may of course be attributed to the steric hindrance to attaining an essentially coplanar transition state as well as in I$_{\alpha\text{-i-Pr},\alpha\text{-i-Pr}}$. The stabilization attained by entire π-delocalization within the whole benzylic π-system should be an important driving force to promote ionization in the ordinary benzylic solvolysis,[15] and the enforced coplanarity brings about the distinct steric distortion around the carbenium center to reflect in the significant rate retardation.

The r values for the solvolyses of benzylic precursors are found to be exactly the same as the values for the intrinsic stabilities of the corresponding benzylic cations in the gas phase.[16] The present r value for the solvolysis transition state is also in good agreement with r=0.87 for the intermediate I$_{\alpha\text{-t-Bu},\alpha\text{-Me}}$ cation determined from the intrinsic gas-phase stabilities.[12,17] Therefore, the twisted structures of the transition states of benzylic solvolyses remain unchanged from the deviation from coplanarity of the related cations in the gas phase. This identity of empirical r values for the solvolysis transition state and the corresponding gas phase cation leads to important conclusion that the structure of the cation derived from theoretical calculation can model structure of the transition state as well as the reaction intermediate that follows closely the transition state. Ab initio calculation using a 6-31G* basis set revealed that in the optimized structure of the cation, the torsional angle between the benzylic carbenium center and benzene system was calculated to be 24°,[9] which is in very

Table 2. Tertiary Benzylic Solvolyses

Solvolysis systems	PhCMe$_2$	PhC(i-Pr)$_2$	PhCMe(t-Bu)	PhC(t-Bu)$_2$	Benzobicyclooctenyl[a]
$10^5 k$/s^{-1} (80A, 25°C)	191.4	0.0512	0.09407		
Rel. rate	1.0	0.0003	0.0005	0.1 [b]	10^{-14} [e]
r value in Eq. (1)	1.0	1.0–0.97[c]	0.91	0.26[d]	0.0
$\theta_{exp.}$[f]	0°	0–14°	24.5°	75°	90°
$\theta_{theor.}$[g]	0°	10°	24°	76°	90°

a) 4-Methylbenzobicyclo[2.2.2]octen-1-yl system (ref. 6). b) Estimated from the rate of the p-nitrobenzoate (OPNB) in 70A at 100°C (ref. 18). c) Ref. 10. d) Ref. 7. e) Approximate value estimated from rate constants for PhCMe$_2$-OPNB, 2.26x10^{-4}s^{-1} (ref. 19) and 4-methylbenzobicyclo[2.2.2]octen-1-yl-OTf, 2.61x10^{-5}s^{-1} (ref. 6) in 80E at 75°C. f) Based on cos θ=r/r$_{max}$ where r$_{max}$=1.00. g) Calcd by RHF/6-31G* (ref. 9).

good agreement with the above experimental evaluation $\theta_{obs}=24.5^{\circ}$ for the transition state of the solvolysis and the torsional angle $\theta=29.5^{\circ}$ of the gas phase cation. Moreover, results of ab initio calculation revealed that the C(t-butyl)-C^{+}-C(benzene) angle is expanded to 125° so as to be distorted away from the benzene ring, and 40% of a positive charge is transferred to the benzene ring from the benzylic cation center.9) These results support that the resonance stabilization with the phenyl group in this delocalized benzylic cation overwhelms the internal steric strain of distorted structure due to congestion. Compared with the rather sharp potential energy minimum for twisted conformation of α,α-di-t-butylbenzyl cation ($\theta=76^{\circ}$), the energy difference between the conformations at $\theta=0^{\circ}$ (coplanar) and $\theta=24^{\circ}$ (twisted) calculated for this cation is not very large, because of a rather flat potential well around the optimized structure.9)

This is a first example to demonstrate the essential identity of resonance structure between the transition state in solvolysis and the corresponding intermediate in gas phase in sterically twisted benzylic system as well as in various planar ones. The identity of the theoretically calculated dihedral angle and the empirical one assigned from r value for the twisted benzylic system provides strong support to the real significance of through-conjugative parameter r value in the LArSR Eq. (1).

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