

## The Importance of Resonance Stabilization in the Benzylic Solvolysis. Substituent Effects on the Solvolysis of $\alpha,\alpha$ -Diisopropylbenzyl Chlorides

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**Abstract:** The substituent effect on the solvolysis of  $\alpha,\alpha$ -diisopropylbenzyl chlorides can be described in terms of  $\sigma^+$  value. No significant steric loss of resonance was observed by introducing two bulky isopropyl groups into benzylic reaction center.

The substituent effect on the benzylic carbocationic solvolyses has generally been described most successfully by the Yukawa-Tsuno (LArSR) Eq. (1),<sup>1</sup>

$$\log(k/k_0) = \rho(\sigma^0 + r\Delta\sigma_R^+) \quad (1)$$

where the parameter  $r$  is a measure of the additional resonance effect of para  $\pi$ -donor substituents on the reaction center and changes depending upon the resonance demand at the benzylic transition state.<sup>2</sup>

The origin of variations of  $r$  parameter, as evaluated by Eq.(1), has been discussed in terms of the varying extent of resonance interactions between substituent and reaction site from one reaction series to another.<sup>2</sup> The resonance demand of a benzylic cation should have a theoretical significance as the effective overlapping of the  $\alpha$ -carbenium  $\pi$ -orbital with the benzene  $\pi$ -ring, and the  $r$  value should be reduced by sterically twisting out of the coplanarity of extended benzene  $\pi$ -system in the transition state.

In the course of studies on the solvolysis of the benzylic system twisted out of the coplanarity,<sup>3-5</sup> a convincing example is afforded by the solvolysis of  $\alpha,\alpha$ -di-*t*-butylbenzyl *p*-nitrobenzoates.<sup>4</sup> A diminished  $r$  value of  $r=0.26$  for this system compared with  $r=1.00$  of the coplanar reference,  $\alpha,\alpha$ -dimethylbenzyl system, can reasonably be ascribed to a significant loss of the resonance interaction of the carbocation center in the solvolysis transition state.<sup>4</sup> The efficiency of resonance interaction should be in parallel with  $\cos^2 \theta$  where  $\theta$  is the dihedral angle of two overlapping *p*-orbitals.<sup>6</sup> The torsional angle  $\theta$  in the transition state is calculated to be  $60^\circ$  from  $\cos^2 \theta=0.26$ .<sup>4</sup> The ab initio calculation of the structure of  $\alpha,\alpha$ -di-*t*-butylbenzyl carbenium ion indicates that the aryl group is twisted out of the coplanarity by a dihedral angle of  $55^\circ$ .<sup>4,7</sup>

As the ideal system where any exalted  $\pi$ -delocalization interaction may be completely prohibited for structural reasons, we have studied the solvolysis of 4-methylbenzobicyclo[2.2.2]octen-1-yl system.<sup>8</sup> In the transition state, the vacant orbital developed at the bridgehead of the bicyclic skeleton is rigidly oriented to be orthogonal to the  $\pi$ -orbital of the fused benzene ring and there should be no resonance exaltation caused by the  $\pi$ -*p* overlapping interaction. In fact the substituent effect on this system follows the  $\sigma^0$  scale;  $r=0.0$  in Eq. (1). Resonance demand in the benzylic solvolysis series can arrive at  $r=0.0$ , the lowest extreme of exalted  $\pi$ -delocalization. These two conformationally reduced resonance systems provide strong evidence for our

Table 1. Solvolysis Rates of  $\alpha,\alpha$ -Diisopropylbenzyl and  $\alpha$ -Ethyl- $\alpha$ -methylbenzyl Chlorides in Aqueous Acetone and Aqueous Ethanol

Subst.	$10^5 k_t$ (s <sup>-1</sup> )		
	$\alpha,\alpha$ -di- <i>i</i> -Pro-benzyl Cl 80E, 25°C	80A, 45°C	$\alpha$ -Et- $\alpha$ -Me-benzyl Cl 90A, 25°C
p-MeO	4130 <sup>a)</sup>	2880 <sup>a)</sup>	62890 <sup>a)</sup>
p-MeS	336.7	288.1	3951 <sup>a)</sup>
p-PhO	194.2	178.2	1418
3-Cl, 4-MeO	67.97	77.97	768.2
3,4-Me <sub>2</sub>	25.08	31.12	200.4
p-Me	12.78	16.02	107.8
p- <i>t</i> -Bu	8.408	9.698	65.56
3,5-Me <sub>2</sub>	1.587	2.478	19.38
m-Me	0.7319	1.312	8.909
H	0.3855	0.6949	4.283
p-Cl	0.107 <sup>a)</sup>	0.1640	1.256
m-Cl	0.00427 <sup>a)</sup>	0.00726 <sup>a)</sup>	0.0500 <sup>b)</sup>
m-CF <sub>3</sub>	0.00112 <sup>a)</sup>	0.00241 <sup>a)</sup>	0.0132 <sup>b)</sup>
p-CF <sub>3</sub>			0.00534 <sup>b)</sup>

a) Extrapolated from rate data at other temperatures. b) Estimated from rate data in 80A based on the linear logarithmic rates plot between 80A and 90A.

characterization of the  $r$  value as a parameter reflecting the degree of resonance ( $\pi$ -delocalization) interaction between the aryl and the reaction site.

As a moderately congested system intermediate between  $\alpha,\alpha$ -dimethylbenzyl and twisted  $\alpha,\alpha$ -di-*t*-butylbenzyl ones, we have chosen here for study the solvolysis of  $\alpha,\alpha$ -diisopropylbenzyl system, which may suffer from a moderate loss of coplanarity between the  $sp^2$  reaction center and the benzene  $\pi$ -system. Furthermore, the substituent effect on the solvolysis of  $\alpha$ -ethyl- $\alpha$ -methylbenzyl chlorides, expected for a negligibly congested system, has been studied to confirm the invariant polar effect of different  $\alpha$ -alkyl groups.

The ring-substituted  $\alpha,\alpha$ -diisopropylbenzyl chlorides were synthesized through the condensation of aryllithium and 2,4-dimethyl-3-pentanone, and subsequent chlorination. The solvolysis rates were determined conductimetrically in 80 vol% aqueous ethanol (80E) and 80 vol% aqueous acetone (80A) as summarized in Table 1. In Fig. 1, displayed is the Hammett plot of the present solvolysis in 80E at 25°C. Para  $\pi$ -donor substituents are correlated well with  $\sigma^+$ , suggesting a resonance demand of unity in this system as in the  $\alpha,\alpha$ -dimethylbenzyl system. In fact, the application of Eq. (1) to the data in 80E at 25°C affords an excellent correlation

$$\log(k/k_0) = -4.88(\sigma^0 + 1.01\Delta\sigma_R^+)$$

with correlation coefficient 0.9995 and  $SD = \pm 0.11$ , and an identical result,  $\log(k/k_0) = -4.66(\sigma^0 + 0.97\Delta\sigma_R^+)$ , is obtained in 80A at 45°C. The  $r$  value of 1.0 assigned for this system is also identical with that defined for the reference solvolysis of  $\alpha,\alpha$ -dimethylbenzyl chlorides in 90 vol% aqueous acetone (90A) at 25°C. The coplanarity of the carbenium  $sp^2$  center in the present  $\alpha,\alpha$ -diisopropylbenzyl solvolysis is not decreased at all.

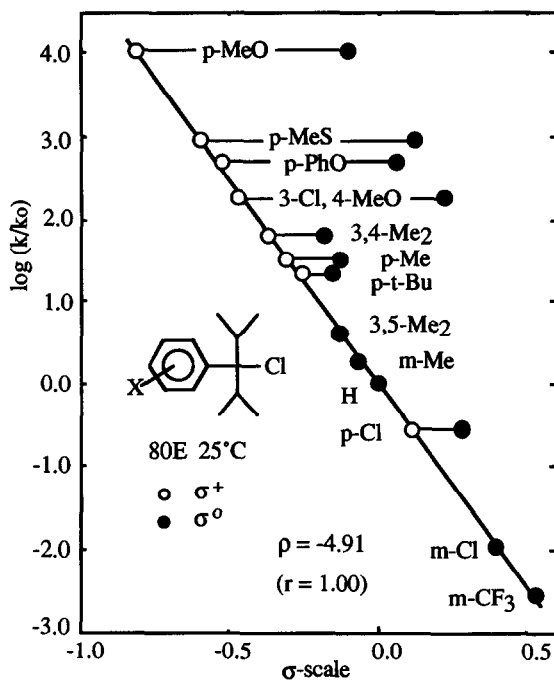


Fig. 1. LArSR plot of substituent effect on the solvolysis of  $\alpha,\alpha$ -diisopropylbenzyl chlorides in 80% aq. EtOH at 25°C: Open circles,  $\sigma^+$  and closed,  $\sigma^0$ .

overcome the large steric strain required for the derivation from the most preferred conformation.

The solvolysis rates of relevant  $\alpha,\alpha$ -dialkylbenzyl systems in 80E at 25°C were compared in summary in Table 2 for a series of  $\alpha$ -alkyl groups. If there is no steric interaction, change in alkyl chain does not cause remarkable rate change, as shown by the comparison of the  $\alpha$ -Me and the  $\alpha$ -Et systems. It has been reported that there is no significant change in solvolysis rates with increased alkyl chain length in secondary  $\alpha$ -alkylbenzyl series.<sup>9</sup> On the other hand, the rate deceleration of  $\alpha,\alpha$ -diisopropylbenzyl precursor is very significant; the rate ratio is ca. 0.0002 relative to the  $\alpha,\alpha$ -dimethylbenzyl analogue. This extremely low reactivity in the present system appears likely to reflect large internal strain to attain the coplanarity between the  $sp^2$  reaction center and benzene  $\pi$ -orbital. The stabilization by extended  $\pi$ -delocalization should be the predominant driving force to promote ionization in the ordinary benzylic solvolysis. Support for this view is provided by the fact that the free energy of the rotation of the phenyl- $C_\alpha$  bond of benzylic cations under the stable ion condition is found to be 10–20 kcal mole<sup>-1</sup>.<sup>10</sup> This strong  $\pi$ -delocalization interaction overwhelms the steric repulsion interaction with two  $\alpha$ -isopropyl groups in the present system. This fact will caution to generally plausible explanation that the rate retardation in the solvolysis for these highly congested carbocation systems is ascribed to the result of steric loss of resonance stabilization due to twisting out of coplanarity. It is noteworthy that the twisted  $\alpha,\alpha$ -di-*t*-butylbenzyl system shows only a little significantly reduced rate because of release of steric strain in the expense of serious loss in resonance energy by twisting out of coplanarity.

The torsional angle  $\theta$  at benzyl cation of the above tertiary benzylic systems can be calculated to be 10° for

The  $\alpha$ -ethyl- $\alpha$ -methylbenzyl chloride solvolysis in 90A at 25°C (in Table 1) was analyzed similarly, affording a correlation,  $\log(k/k_0) = -4.7(\sigma^0 + 1.04\Delta\sigma_R^+)$ . The  $r$  value for this system should be, to a first approximation, referred to as the value of unity characteristic of planar tertiary benzylic carbenium ion which is essentially coplanar and capable of exerting essentially maximum conjugative stabilization interaction with the carbenium site, independent of varying polar effects of  $\alpha$ -alkyl groups.

It is rather surprising that the through conjugation interaction can be fully attained in the transition state of the present  $\alpha,\alpha$ -diisopropylbenzyl solvolysis. The present solvolysis should suffer from a degree of destabilization associated with steric congestion; nevertheless this steric effect does not prevent the aryl group from exerting its maximum resonance effect on stabilizing the incipient carbenium ion. The transition state should be able to attain the maximum stabilization to

Table 2. Relative Rate constants of Solvolysis of Various Benzylic Substrates

Solvolysis Systems	PhCMe <sub>2</sub> Cl	PhC(Me)EtCl	PhC(i-Pr) <sub>2</sub> Cl	PhC(t-Bu) <sub>2</sub> OPNB
10 <sup>5</sup> k/s (80E, 25°C)	1730 <sup>a)</sup>	509	0.3855	
Relative Rate	1.0	0.3	0.0002	0.1 <sup>b)</sup>

a) Ref. 11. b) p-Nitrobenzoate in 70% aq. acetone at 100 °C, Ref. 12.

$\alpha,\alpha$ -diisopropylbenzyl and 2<sup>o</sup> for  $\alpha$ -ethyl- $\alpha$ -methylbenzyl, and 0<sup>o</sup> for  $\alpha,\alpha$ -dimethylbenzyl based on *ab initio* calculation.<sup>7</sup> These values were negligibly small compared with  $\theta=55^\circ$  for the  $\alpha,\alpha$ -di-*t*-butylbenzyl.<sup>4,7</sup> This is in line with the above experimental results based on the LArSR analysis. The resonance stabilization of benzene ring is large enough to compensate the destabilization from inner strain for attaining the most preferred conformation in the  $\alpha,\alpha$ -diisopropyl system.

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