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Substituent Effect on the Solvolysis of 2,2-Dimethylindan-1-yl Chlorides

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Abstract: The substituent effect on the solvolysis of 2,2-dimethylindan-1-yl chlorides was analyzed in terms of the LArSR Eq., to give ρ --5.81 and r-1.14. The coplanarity of α -t-butylbenzyl cation system was discussed.

The linear free energy relationship analysis is an extremely useful tool in the exploration of mechanistic hypotheses in a wide variety of situations.¹⁾ In particular the Yukawa-Tsuno LArSR Eq. $(1)^{2}$ has proved especially invaluable in solvolysis studies.¹⁻⁸⁾

 $\log (k/k_0) = \rho(\sigma^0 + r\Delta \bar{\sigma}_R^+)$

This equation can be characterized by the reaction-dependent resonance demand parameter r, accounting for the exalted resonance effect in a given reaction. The r value, a measure of resonance stabilization of the transition state, should be related most closely to the degree of N-overlapping between the aryl-N-orbital and benzylic p-orbital in the incipient carbocation. 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 the Eq. (1). We have recently studied the benzylic solvolysis systems where the incipient carbenium center p-orbital is sterically twisted out of the coplanarity with the aryl ring. $^{5-7)}$ In this course of studies, we have carried out an analysis of the substituent effect on the solvolysis of α -t-butylbenzyl tosylates (I)⁵⁾ and their highly congested analogues, o-methyl (II) and substituted series (III).⁶⁾ In these o-methyl substituted systems, o.o-dimethyl however, no significant loss of resonance has been observed; increased steric congestion around the carbenium ion center does not appear to be effective enough to cause a significant loss of the coplanarity in the transition state.⁶⁾ Nevertheless, their solvolysis rates are remarkably lower (by a factor of 10 3) than that of the lphamethylbenzyl derivative (IV).⁵⁾ In order to analyze the geometrical dependence of the resonance demand, it is of particular importance to estimate the reference r value of an ideal secondary benzylic solvolysis generating a fully coplanar carbenium ion.

In the present work, we have extended our study to the solvolysis of 2,2dimethylindan-1-yl chlorides (V) where the vacant p-orbital developed at the benzylic position is in preferred conformation to overlap with the benzene π -system. This system

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will attain a full resonance stabilization at the transition state and then provide an optimum r value anticipated for the secondary benzylic solvolysis system.

The ring-substituted 2,2-dimethylindan-1-yl chlorides were synthesized through dimethylation and reduction of appropriate indanones, and subsequent chlorination. The solvolysis rates were determined conductometrically in 80 vol% aqueous acetone. The rate data at 25° C are listed in Table 1 in comparison with the corresponding data of the solvolysis of α -t-butylbenzyl tosylates (I).⁵ In Fig. 1, displayed is the so-called LArSR plot of this solvolysis. Para π -donor substituents are not correlated well with σ^{+} but all deviate systematically upward from the $\rho_{\rm m}$ line, suggesting a higher resonance demand than unity in this system. The application of Eq. (1) to the present data affords an excellent correlation.

 $\log (k/k_0) = -5.81 \ (\text{G}^0 + 1.14 \Delta \bar{\text{G}}_R^+)$ with correlation coefficient 0.9995 and SD=±0.11.

The r value of 1.14 is identical with that observed for the solvolysis of α -methylbenzyl chlorides (IV).³⁾ This r value may be referred to as the value characteristic of open secondary benzylic carbonium ion which is essentially coplanar and capable of exerting essentially maximum conjugative stabilization interaction with the carbonium site. In the solvolysis of α -t-butylbenzyl tosylates (I), from its r value of 1.09, the steric loss of resonance in this system does not appear to be serious, and even in the case of its o-methyl (IJ) and o,o-dimethyl (III) derivatives, the coplanarity of the carbonium sp² center with the aryl ring is not effectively decreased. All these solvolyses have been found to have a degree of steric deceleration

Table 1. Solvolysis Rates of 2,2-Dimethylindan-1-yl Chlorides (V) and α -t-Butylbenzyl Tosylates (I) in 80% Aq. Acetone at 25° C

Subst. ^{a)}	$ 10^5 k_t (s^{-1})$	
	Dimethylindanyl Cl $(\check{\mathbf{V}})$	α-t-Bubenzyl OTs (I) ^{b)}
5-MeO	358000 ^C)	94580
5-MeO-6-Cl	3080 ^d)	1180
5,6-Me ₂	254.9	186.7
5-Me	102.7	95.07
6-Me	4.312	2.862
Н	1.662	1.420
5-Br	0.2350	0.252
6-B r	0.01155 ^d)	0.00659
6-C1	0.01308 ^{d)}	0.006909
6-CN	0.000476 ^{e)}	0.000720
5-CN	0,000136 ^{e)}	0.000242

a) The substituent 5- and 6-positions correspond to p- and m-positions in the benzyl system, respectively. b) Data taken from ref. 5. c) Extrapolated from rate data in 90% aq. acetone. d) Extrapolated from other temperatures. e) Estimated from the rate data in 50% aq. acetone.



Fig. 1. LARSR plot of substituent effect on the solvolysis of 2.2-dimethylindan-1-yl chloride in 80A at 25° C: Open circles, σ^{+} , closed, σ° , and squares, $\bar{\sigma}$ for r=1.14.

associated with steric congestion; nevertheless this steric effect does not significantly prevent the aryl group from exerting its maximum resonance effect on stabilizing the incipient carbenium ion.⁶) The transition state should be able to attain the maximum stabilization to overcome the large steric strain required for the most preferred conformation.

The r values for the solvolyses of relevant benzylic precursors are found to be exactly the same as the values for the intrinsic stabilization of benzylic cations in the gas phase $^{4b,8)}$ Therefore, the structures of the transition states of benzylic solvolyses should be quite close to those of cations. The r value of 1.14 may be regarded as a reference r_{max} value, i.e., an intrinsic r value characteristic of the benzylic carbocation. The efficiency of resonance interaction can be coplanar sec. accounted for in terms of $\cos^2 \theta$ where θ is the dihedral angle of twisting out of coplanarity. $^{9)}$ The ratio of the r value for a given solvolysis relative to the $r_{
m max}$ may reflect the actual efficiency of the resonance effect of that system and the r value for a twisted benzylic system can be given by Eq. (2),

$$= r_{max} \cos^2 \theta$$

r

Thus the torsional angle θ at the transition state for the solvolysis of the above relevant sec. benzylic systems can be calculated to be 0⁰ for α -methylbenzyl, 12⁰ for α -

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t-butylbenzyl, and 20⁰ for both o-Me and $o,o-Me_2 \alpha$ -t-butylbenzyl systems, based on Eq. (2). The benzylic sp² carbon is to be twisted out of the coplanarity with the aryl mring atmost by 20⁰ in the o-substituted systems. These twisting angles are not very serious compared with the remarkable twisting angle of ca. 60⁰ estimated for the α, α -dit-butylbenzyl solvolysis,⁷⁾ in which the two t-Bu groups at the reaction center should prevent from attaining the most preferred, coplanar conformation. The significantly diminished solvolysis rate of α -t-butyl compound, I, compared with the α -methyl one, IV, may of course be attributed to the steric hindrance to attaining an essentially coplanar transition state. The stabilization attained by entire M-delocalization within the benzylic M-system should be an important driving force to promote ionization in the ordinary benzylic solvolysis.

The exact straight line correlation between V and IV excludes any possibility of mechanistic involvement of the nucleophilic solvent at the rate-determining step in the solvolysis of IV. The exalted r of 1.15 value observed for α -methyl compound, IV, is not an artifact caused from the mechanistic complexity of nucleophilic solvent involvement. The r value of α -t-butyl system, I, is reduced only insignificantly from the r value of 1.14 for the coplanar system, V, as well as the value for the α -methyl analogue, IV. The r value for α -dimethylbenzyl and related stable tertiary systems.

References

1) J. Shorter, "Correlation Analysis in Chemistry," ed by N. B. Chapman and J. Shorter, Plenum Press, New York (1978); J. Shorter, "Correlation Analysis of Organic Reactivity," Wiley, Research Studies Press, Chichester (1982). 2) Y. Yukawa and Y. Tsuno, Bull. Chem. Soc. Jpn., <u>32</u>, 971 (1959); Y. Yukawa, Y. Tsuno, and M. Sawada, Bull. Chem. Soc. Jpn., <u>39</u>, 2274 (1966). 3) Y. Tsuno, Y. Kusuyama, M. Sawada, T. Fujii, and Y. Yukawa, Bull. Chem. Soc. Jpn., <u>48</u>, 3337 (1975); M. Fujio, T. Adachi, Y. Shibuya, A. Murata, and Y. Tsuno, Tetrahedron Lett., <u>25</u>, 4557 (1984). 4) a) M. Fujio, M. Goto, M. Mishima, and Y. Tsuno, Bull. Chem. Soc. Jpn., <u>63</u>, 1121 (1990); A. Murata, M. Goto, R. Fujiyama, M. Mishima, M. Fujio, and Y. Tsuno, Ibid., <u>63</u>, 1129 (1990); A. Murata, S. Sakaguchi, R. Fujiyama, M. Mishima, M. Fujio, and Y. Tsuno, ibid., <u>63</u>, 1138 (1990). b) M. Fujio, M. Goto, T. Susuki, I. Akasaka, M. Mishima, and Y. Tsuno, ibid., <u>63</u>, 1146 (1990); M. Fujio, M. Goto, T. Susuki, M. Mishima, and Y. Tsuno, J. Phys. Org. Chem., <u>3</u>, 449 (1990). 5) Y. Tsuji, M. Fujio, and Y. Tsuno, Bull. Chem. Soc. Jpn., <u>63</u>, 856 (1990). 6) M. Fujio, Y. Tsuji, T. Otsu, and Y. Tsuno, Tetrahedron Lett., <u>32</u>, 2929 (1991). 7) M. Fujio, T. Miyamoto, Y. Tsuji, and Y. Tsuno, Tetrahedron Lett., <u>31</u>, 685 (1990). 9) P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas, J. Chem. Soc., <u>1964</u>, 5317; K. Ohkata, R. L. Paquette, and L. A. Paquette, J. Am. Chem. Soc., 101, 6687 (1979).

(Received in Japan 18 October 1991)