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STEREOELECTRONIC REQUIREMENTS FOR HYPERCONJUGATION IN SOLVOLYSIS TRANSITION STATES

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Earlier work has demonstrated that carbonium ion reactivities of bridgehead substrates may be correlated by quantitative conformational analysis.[2] Thus, the enthalpy difference between ground state and transition state as measured by the calculated strain energy difference between hydrocarbon and carbonium ion is found to be directly proportional to the log of the solvolysis rate for a wide variety of bridgehead substrates.

Applying these calculations to available acetolysis data for bridgehead tosylates (Table I) reveals that the solvolytic reactivity of 10-tricyclo[5.2.1.$0^{4,10}$]decyl tosylate (VI)[3] is abnormally low (Figure I). While seven bridgehead systems which vary in reactivity by nearly ten powers of ten are correlated satisfactorily (correlation coefficient = 0.975, average deviation = $10^{\pm 0.54}$), the experimental acetolysis rate of VI is 10^9 times slower than that predicted by the calculations! This deviation is far outside expected error limits and must indicate that a special effect is operative.

Two structural features of the 10-tricyclo[5.2.1.$0^{4,10}$]decyl system, VI, are unique relative to the other bridgehead systems studied. The backside of the molecule is not shielded from the solvent as is the case for the cage-like polycyclic systems and the nearly eclipsed torsional arrangements around the reaction center contrast with the staggered conformations involving the leaving groups in the other bridgehead substrates (Figure II).

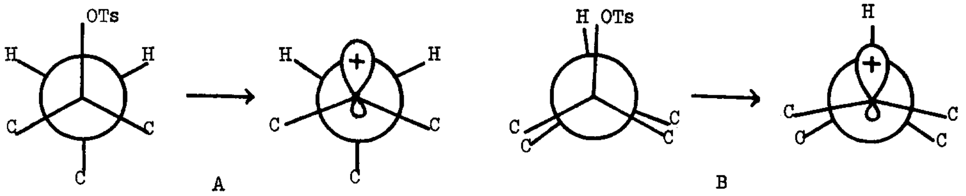


Figure II. Torsional arrangements around the reaction centers of bridgehead substrates. A. 1-Adamantyl (I). B. 10-Tricyclo[5.2.1.$0^{4,10}$]decyl (VI).

Solvation effects cannot account for the failure of VI to conform to the model established by the conformational analysis calculations. Backside solvation has been found not to play a significant role in the rate determining step of tertiary substrate solvolyses.[4] Furthermore,

Table I. Solvolysis Data for Bridgehead Tosylates in Acetic Acid at 70°.

Compound	*k* (sec^{-1})	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (e.u.)	ΔH (calc)[a]
I	1.02×10^{-1}[b]	22.8	3.0	12.3
II	1.02×10^{-4}[c]	23.4	-9.0	17.6
III	2.09×10^{-5}[d,e]	(26.2)[k]	(-1.7)[k]	16.3
IV	1.73×10^{-6}[d,f]	(28.0)[k]	(-1.4)[k]	18.7
V	3.13×10^{-7}[g]	26.9	-10.1	18.8
VI	2.33×10^{-7}[h]	30.1	-1.4	9.3
VII	3.40×10^{-9}[i]	32.6	-2.7	20.3
VIII	1.15×10^{-11}[d,j]	(31.7)[k]	(-14.3)[k]	23.5

[a] Computer calculated hydrocarbon-carbonium ion strain energy differences (see text and reference 2). [b] E. R. Thornton, private communication. *Cf.* B. R. Ree and J. C. Martin, *J. Amer. Chem. Soc.*, **92**, 1660 (1970); M. L. Sinnot, H. J. Storesund and M. C. Whiting, *Chem. Commun.*, 1000 (1969); P. v. R. Schleyer and R. D. Nicholas, *J. Amer.Chem. Soc.*, **83**, 2700 (1961). [c] R. C. Bingham, P. v. R. Schleyer, Y. Lambert and P. Deslongchamps, *Can. J. Chem.*, (in press). [d] Calculated assuming *k*(brosylate)/*k*(tosylate)=3. [e] P. v. R. Schleyer and C. W. Woodworth, *J. Amer.Chem.Soc.*, **90**, 6528 (1968). [f] R. S. Bly and E. K. Quinn, Abstracts, 153rd Meeting of the Amer. Chem. Soc., Miami Beach, Fla., April, 1967, Paper 910. [g] J. S. Wishnok, E. Funke, P. v. R. Schleyer, A. Nickon, G. D. Pandit and R. O. Williams, *J. Org. Chem.*, to be published. [h] This work. [i] P. v. R. Schleyer and E. Wiskott, *Tetrahedron Lett.*, 2845 (1967). [j] C. J. Norton, Ph.D. Dissertation, Harvard University, 1955. [k] Activation parameters for the brosylates.

backside solvation in VI should make the rate *faster* than expected, not *slower* as is observed.

We believe that the nearly eclipsed torsional arrangement around the reaction center of VI gives rise to its abnormal solvolytic behavior. The stabilization of developing cationic centers by α-alkyl groups appears to involve, at least in part, the operation of a specific *trans* effect.[5] That is, a hyperconjugative stabilization which is greatest in the *trans* periplanar arrangement (relative to the leaving group) is indicated. In VI, the β C-H bonds are particularly unfavorably disposed (Fig. II B).

This stereoelectronic requirement for hyperconjugation in carbonium ion-forming transition states is indicated by a number of other observations. The conformational dependence of deuterium isotope effects in solvolysis reactions provides a well known example.[6] The effect is also predicted by Hoffmann's extended Hückel calculations which are confirmed by recent *ab initio* molecular orbital results.[7] Both the tetrahedral ethyl and n-propyl cations are calculated to have a pronounced preference for conformation IX with a *trans* β bond. Conformation X which approximates the situation expected from the solvolysis of VI is found to be much less stable.

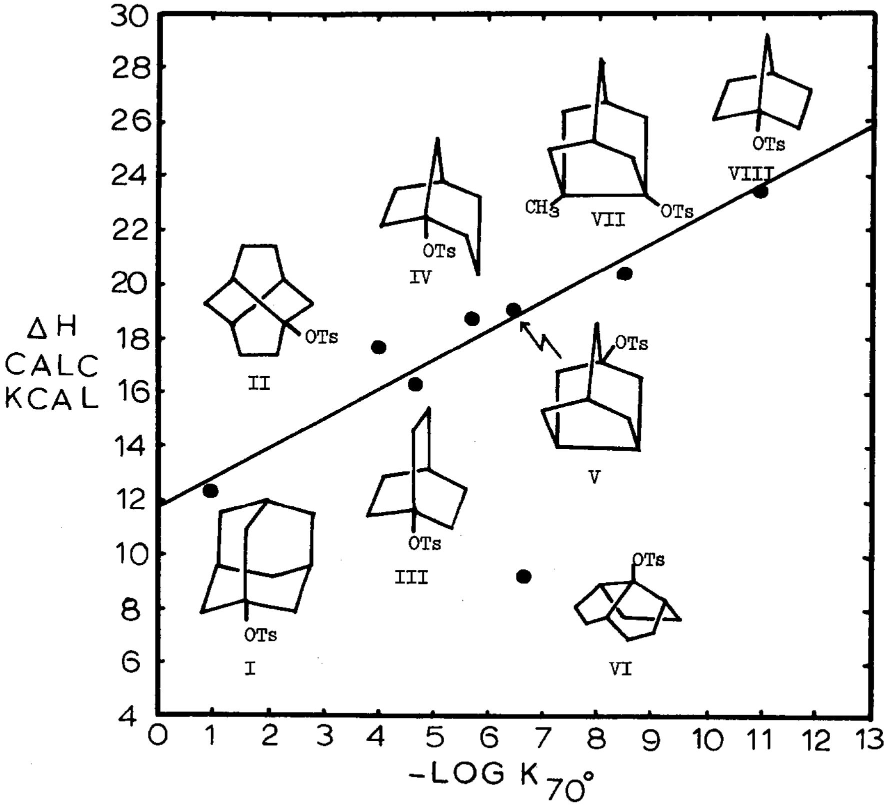
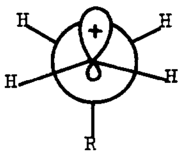
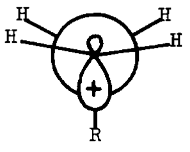


Figure I. Calculated hydrocarbon-carbonium ion strain energy differences (ΔH) plotted against -log of the experimental acetolysis rate constants at 70°.



IX

R = H, CH_3



X

The magnitude of this *trans* effect on solvolysis reactions based on the 10-tricyclo-[5.2.1.$0^{4,10}$]decyl tosylate result is quite large. At 70°, there is a 14 kcal/mole difference in activation free energies ($\Delta\Delta F^{\ddagger}$) between the predicted and experimental acetolysis rates of VI. That is, the better *trans* overlap relative to the *cis* (Figure II) apparently is lowering the transition state energies of solvolysis reactions by nearly 5 kcal/mole per bond. Further work is in progress to attempt to establish the generality of this effect.[8]

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REFERENCES AND FOOTNOTES

(1) National Institutes of Health Predoctoral Fellow, 1967-1970.

(2) G. J. Gleicher and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 582 (1967); P. v. R. Schleyer, P. R. Isele and R. C. Bingham, *J. Org. Chem.*, **33**, 1239 (1968); W. G. Dauben and C. D. Poulter, *ibid.*, **33**, 1237 (1968); R. C. Bingham, W. F. Sliwinski and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 3471 (1970); S. A. Sherrod, R. G. Bergman, G. J. Gleicher and D. Morris, *ibid.*, **92**, 3469 (1970).

(3) Prepared from the corresponding alcohol (J. W. Baum and C. D. Gutsche, *J. Org. Chem.*, **33**, 4312 (1968)) *via* the lithium alcoholate (*cf.*, H. C. Brown, R. Bernheimer, C. J. Kim and S. E. Shepple, *J. Amer. Chem. Soc.*, **89**, 370 (1967)).

(4) D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry and P. v. R. Schleyer, *ibid.*, in press; D. N. Kevill, K. C. Kolwyck and F. L. Weitl, private communication.

(5) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964) and private communication.

(6) M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962; V. J. Shiner, Jr. and J. S. Humphrey, Jr., *J. Amer. Chem. Soc.*, **85**, 2416 (1963); B. L. Murr and J. A. Conkling, *ibid.*, **92**, 3464 (1970).

(7) J. E. Williams, V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Latham, W. J. Hehre and J. A. Pople, *ibid.*, **92**, 2141 (1970); L. Radom, J. A. Pople, V. Buss and P. v. R. Schleyer, *ibid.*, in press.

(8) *Cf.* F. R. Jensen and B. E. Smart, *ibid.*, **91**, 5686, 5688 (1969); W. Hanstein, H. J. Berwin and T. G. Traylor, *ibid.*, **92**, 829 (1970); N. A. Clinton, R. S. Brown and T. G. Traylor, *ibid.*, **92**, 5228 (1970).