noted that, as a check, the rate effect of a single axial β-deuterium may be calculated from the other four β-effects in Table I, leading to a value of 1.458, about 2% larger than the directly observed rate retardation. This small discrepancy is barely outside combined experimental error and does not qualitatively affect the results summarized below. It may be due to the incursion of a small amount of nondiaxial opening or rearrangement in the lithium aluminum deuteride reaction with the epoxide. The effect of each different β-deuterium atom in the solvolytic transition state may be calculated using an expression of the form[5] $(k_H/k_D)_X = 2xx'/(x + x')$ where $(k_H/k_D)_X$ is the experimentally determined isotope effect for substitution of a single deuterium atom (X = axial or equatorial) while x and x' are the effects of the 2- and 6-axial or equatorial isotopic atoms in the transition state. Such an analysis leads to the isotope effects for replacement of each of the hydrogen atoms by deuterium indicated in the partial structure below.
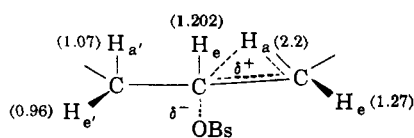
As was suggested earlier,[1] such grossly noncumulative behavior and the large isotope effect associated with one neighboring (axial) hydrogen[6] are in accord with neighboring hydrogen participation in the solvolytic transition state. Since this participation is from a secondary hydrogen to an adjacent secondary solvolytic center it is difficult to conceive of any driving force for it except the formation of a stabilized, bridged, nonclassical intermediate carbonium ion. Further, the absence of extensive rearranged substitution products indicates that this nonclassical ion is *unsymmetrically* hydrogen bridged and separated from another presumably similar unsymmetrically hydrogen-bridged, but rearranged, ion by an appreciable if not large energy barrier.

β-Deuterium isotope rate effects thus provide a sensitive probe for nonclassical carbonium ion character in solvolytic transition states *and* an operational distinction of limited but important applicability between hyperconjugation (cumulative isotope effects from equivalent initial state sites) and participation (noncumulative isotope effects from equivalent initial state sites).

(5) V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, *J. Am. Chem. Soc.*, **85**, 2413 (1963).
(6) S. Winstein and J. Takahashi, *Tetrahedron*, **2**, 316 (1958).

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Nonchair Transition State Conformation in *trans*-4-*t*-Butylcyclohexyl Brosylate Solvolysis

Sir:

As a part of our study of β-deuterium isotope effects in solvolytic reactions, we wish to report the rate retardation caused by the substitution of deuterium for *each* of the four β-hydrogen atoms in the aqueous ethanolysis of *trans*-4-*t*-butylcyclohexyl *p*-bromobenzenesulfonate (brosylate), I. Our earlier work showed that there is a strong conformational dependence of the β-effect in secondary arenesulfonate solvolyses: a maximum effect (hydrogen participation) is associated with a conformation in which the dihedral angle between the β-carbon–hydrogen bond axis and the carbon-leaving group axis is 180°; a much smaller effect is associated with a conformation in which this dihedral angle is 60°.[1] Thus, it seems that β deuterium effects may provide a sensitive probe for the determination of the structure and conformation of solvolytic transition states.

trans-4-*t*-Butylcyclohexanol and its deuterated analogs, -1-*d*, -*cis*-2-*d*, -*trans*-2,6,6-*d₃*, and -2,2,6,6-*d₄*, were obtained in reactions previously described which also afforded the deuterated *cis*-4-*t*-butylcyclohexanols.[1,2] *trans*-4-*t*-Butylcyclohexanol-*trans*-2-*d* was prepared by epimerization of *cis*-4-*t*-butylcyclohexanol-*cis*-2-*d* by the method of Eliel and Rerick.[3] Combustion and/or n.m.r. analysis indicated that, save for one, the deuterated alcohols were about 98% isotopically pure. The exception, *trans*-4-*t*-butylcyclohexanol-*trans*-2-*d* (obtained by epimerization), gave a combustion analysis corresponding to 97% isotopic purity. The brosylates of the various alcohols were prepared by the usual Tipson procedure.[4]

The products of solvolysis of ester I in 50% aqueous ethanol at reflux in the presence of suspended calcium carbonate consisted of 67% 4-*t*-butylcyclohexene, 27% *t*-butylcyclohexanols, and 6% ethers. The alcohol fraction consisted of 94% *cis*-4-*t*-butylcyclohexanol (inversion). Infrared analysis of the olefin fraction from the solvolysis of *trans*-4-*t*-butylcyclohexyl brosylate-*cis*-2-*d* indicated that the olefin-forming step of the reaction involves the loss of an *equatorial* (*trans*) β-hydrogen atom.

The rate data, collected in Table I, were obtained as previously described.[2] The precision of the conductometric method is ± 0.1%.

Table I. Solvolysis Rates of Deuterated *trans*-4-*t*-Butylcyclohexyl Brosylates, 50 Vol. % Aqueous Ethanol at 35°

Deuteration a = axial e = equatorial	$k_1 \times 10^5$ sec.$^{-1}$	k_H/k_D
None	8.652	...
α-Deuterium, a	7.382	1.172
β-Deuterium, a	7.680	1.127
β-Deuterium, e	6.458	1.340
β-Deuterium (3), e,e,a	4.145	2.087
β-Deuterium (4), e,e,a,a	3.568	2.425

(1) V. J. Shiner, Jr., and J. G. Jewett, *J. Am. Chem. Soc.*, **87**, 1382 (1965).
(2) V. J. Shiner, Jr., and J. G. Jewett, *ibid*, **86**, 945 (1964).
(3) E. L. Eliel and M. N. Rerick, *ibid.*, **82**, 1367 (1960).
(4) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

These data reveal that the isotope effects due to *equatorial* (*trans* to the leaving group) deuterium substitution are not only larger, but they are very nearly cumulative ($\sqrt{2.087/1.127} = 1.361$); that is, the two equatorial β-hydrogen atoms seem to be *equivalent* in the solvolytic transition state. The slight discrepancy may be due to loss of deuterium in the epimerization reaction. On the other hand, the two *axial* (*cis* to the leaving group) β-hydrogen atoms seem to be *nonequivalent* in the transition state; the rate retardation caused by 2,6-diaxial deuteration exceeds the square of 1.127 (the effect of the second axial β-deuterium = $2.425/2.087 = 1.164$).

The effect of each β-deuterium atom in the solvolytic transition state may be calculated as was previously described.[1] Such an analysis (assuming exactly cumulative equatorial behavior) leads to the distribution shown in partial structure II. The striking conforma-

$$(1.36)H_{e'} \quad H_a(1.172) \quad H_e(1.36)$$

II
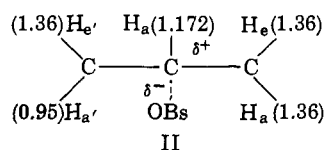
tional dependence of the β-deuterium isotope effect in this system can be explained by a solvolytic transition state which involves a nonchair (*e.g.*, twist boat)[5] conformation. The slight deviation from cumulative behavior for equatorial β-deuterium substitution can also be accommodated in terms of a twist-boat-like conformation for the activated state (*i.e.*, the *degree* of "twist" may determine this). It is difficult to see how these isotope effects and product data can be in accord with a chair conformation of the ring in the solvolytic transition state.

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(5) J. B. Hendrickson, *J. Am. Chem. Soc.*, 83, 4537 (1961).

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The Transition State in Acetolysis of Cyclohexyl Tosylate

Sir:

Some time ago we studied the acetolysis of deuterated cyclohexyl tosylates, but delayed publication because insufficient information was available to permit interpretation of our data. The results of Shiner and Jewett[1,2] point to a persuasive explanation and move us to report our work at this time.

The following deuterated cyclohexanols were prepared: 1-*d*, 2,2,6,6-*d*₄, *trans*-2-*d*, and *cis*-2-*d*. All except the last of these were obtained by the procedures used by Streitwieser[3] for the analogous cyclopentanols.

(1) V. J. Shiner, Jr., and J. G. Jewett, *J. Am. Chem. Soc.*, 87, 1382 (1965).
(2) V. J. Shiner, Jr., and J. G. Jewett, *ibid.*, 87, 1383 (1965).
(3) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *ibid.*, 80, 2326 (1958).

Table I. Rates of Acetolysis of Deuterated Cyclohexyl Tosylates at 50.00°[a]

Compd.	$k_1 \times 10^6$, sec.$^{-1}$[b]	k_H/k_D
H	2.37 ± 0.02	
1-*d*	1.95 ± 0.02	1.22[c]
H	2.38 ± 0.02	
cis-2-*d*	1.91 ± 0.02	1.25
H	2.36 ± 0.02	
trans-2-*d*	1.82 ± 0.03	1.30
H	2.39 ± 0.04	
2,2,6,6-*d*₄	1.02 ± 0.03	2.34

[a] Determined in 0.05 M solutions in anhydrous acetic acid containing 0.08 M sodium acetate. Aliquots were quenched in glacial acetic acid and titrated with 0.05 M perchloric acid in glacial acetic acid to the crystal violet end point. Temperature control was good to 0.02°. [b] Parallel runs on deuterated and undeuterated compounds in each case. Rate constants are averages of duplicate determinations with indicated deviations from the averages. [c] A value of 1.19 at 75.4° is reported by K. Mislow, S. Borčić, and V. Prelog, *Helv. Chim. Acta*, 40, 2477 (1957).

cis-Cyclohexanol-2-*d* resulted from deuterioboration of cyclohexene followed by oxidation with alkaline hydrogen peroxide.[4] The tosylates of the cyclohexanols, prepared by the Tipson method,[5] were all shown to contain 94% or more of the theoretical amount of deuterium. Rates of acetolysis and pertinent data on the procedures and results are recorded in Table 1.

The most striking feature is the close similarity of the isotope effects with the *cis*-2-*d*- and *trans*-2-*d*-tosylates. Our isotope effects are qualitatively similar to those reported by Streitwieser,[3] though the numbers are somewhat larger. This fact would seem to indicate that there is little average difference in the dihedral angle between the C–OTs and C–D bonds for the *cis* and *trans* isomers in the cyclohexyl as well as in the cyclopentyl systems. The alternative, that the isotope effect shows little or no dependence on the dihedral angle, is rendered untenable by the work of Shiner and Jewett.[1,6]

This being the case, the conventional picture of solvolysis *via* a chair conformation requires that the solvolysis go essentially entirely through the conformation having the tosyloxy group equatorial,[7] which would predict similar dihedral angles for both isomers. Further, the isotope effects for axial–equatorial or equatorial–equatorial arrangements of the C–D and C–OTs bonds would have to be near 25%.

Both conditions are sufficiently unlikely that solvolysis of the unsubstituted cyclohexyl tosylate *via* a transition state having a twist-boat conformation becomes a much more attractive explanation. Shiner and Jewett[2] offer strong evidence for such a transition state in the solvolysis of *trans*-4-*t*-butylcyclohexyl brosylate.[2] In our more conformationally mobile system, the average dihedral angles in twist-boat conformations for the *cis*- and *trans*-2-*d* isomers should show similar depar-

(4) H. C. Brown and G. Zweifel, *ibid.*, 81, 247 (1959); 83, 2544 (1961).
(5) R. S. Tipson, *J. Org. Chem.*, 9, 235 (1944).
(6) V. J. Shiner, Jr., and J. G. Jewett, *J. Am. Chem. Soc.*, 86, 945 (1964).
(7) S. Winstein and N. J. Holness [*ibid.*, 77, 5562 (1955)], however, present data suggesting that *ca.* 70% of the solvolysis goes through the equatorial conformation, assuming a chair-like transition state.