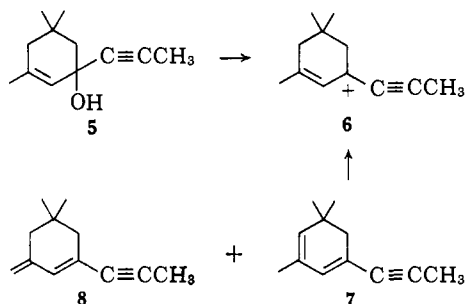


Figure 2. N.m.r. spectrum of a sulfuric acid solution of cation 6.

spectrum is assumed to be due to cation 6; the peak assignments agree closely with those reported⁴ for other carbonium ions containing a cyclohexenyl system. The absorption of the hydrogens of the propynyl methyl group (which must be either at 7.28 or



7.35 p.p.m.) is considerably downfield from the absorption of the same group at 8.22 in 5 and at 8.07 p.p.m. in the mixture of 7 and 8. In fact, the magnitude of the downfield shift of the absorption due to this group is about the same in the formation of 3 and of 6.

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Hydrogen Participation in *cis*-4-*t*-Butylcyclohexyl Brosylate Solvolysis

Sir:

In a previous communication we reported a strong conformational dependence of *cis*-4-*t*-butylcyclohexyl *p*-bromobenzenesulfonate (brosylate), I.¹ It was then suggested that the large axial β -effect, though in accord with the hyperconjugation postulate,² might be due to

(1) V. J. Shiner, Jr., and J. G. Jewett, *J. Am. Chem. Soc.*, **86**, 945 (1964).

(2) V. J. Shiner, Jr., and J. S. Humphrey, Jr., *ibid.*, **85**, 2416 (1963).

neighboring hydrogen participation which we, and others,³ view as an extreme manifestation of a type of electronic interaction also associated with hyperconjugation. In order to resolve this question, we have determined the effect of substitution of deuterium for each of the four β -hydrogen atoms on the rate of solvolysis of I.

cis-4-*t*-Butylcyclohexanol-1-*d* and *cis*-4-*t*-butylcyclohexanol-*cis*-2-*d* (equatorial β -deuterium) were prepared as previously described.¹ *cis*-4-*t*-Butylcyclohexanol-2,2,6,6-*d*₄ was prepared by base-catalyzed exchange of 4-*t*-butylcyclohexanone with deuterium oxide followed by reduction with lithium aluminum hydride and separation of the axial and equatorial alcohols by elution chromatography and preparative v.p.c. Pyrolysis of a mixture of *cis*- and *trans*-4-*t*-butylcyclohexyl-2,2,6,6-*d*₄ acetate afforded 4-*t*-butylcyclohexene-2,6,6-*d*₃. Hydroboration of this olefin followed by hydrogen peroxide oxidation and the previously described¹ separation procedure afforded *cis*-4-*t*-butylcyclohexanol-*trans*-2,6,6-*d*₃ (axial,axial,equatorial β -deuterium). *cis*-4-*t*-Butylcyclohexanol-*cis*-2,6,6-*d*₃ (axial,equatorial,equatorial β -deuterium) was obtained by epoxidation of this olefin followed by lithium aluminum hydride reduction and the previously described¹ separation procedure. Combustion and n.m.r. analysis indicated that the alcohols were about 98% isotopically pure. The brosylates of the various alcohols were prepared by the usual Tipson procedure.⁴

The products of aqueous ethanolysis of ester I consisted of 86% *t*-butylcyclohexene, 3% ethers, 9% *trans*-4-*t*-butylcyclohexanol, and 2% (axial) *t*-butylcyclohexanol (probably a mixture of 3 and 4 alcohols).¹ Complete deuteration of the β -positions did not substantially lower the olefin fraction of the product. Infrared analysis of the olefin fraction from the solvolysis of *cis*-4-*t*-butylcyclohexyl-*trans*-2-*d* brosylate indicated that the olefin-forming step of the reaction involves the loss of an axial (*trans*) β -hydrogen atom.

The rate data, collected in Table I, were obtained as previously described.¹ The precision of the conductometric method is $\pm 0.1\%$.

Table I. Solvolysis Rates of Deuterated *cis*-4-*t*-Butylcyclohexyl Brosylates^a

Deuteration ^b	$k_1 \times 10^4$, sec. ⁻¹	k_H/k_D
None	3.938	
α -Deuterium, e	3.275	1.202
β -Deuterium, a	2.743	1.436
β -Deuterium, e	3.593	1.096
β -Deuterium (3), a, a, e	1.535	2.565
β -Deuterium (3), a, e, e	2.207	1.784
β -Deuterium (4), a, a, e, e	1.376	2.862

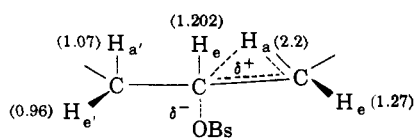
^a Aqueous ethanol (50 vol. %) at 35°. ^b a = axial, e = equatorial.

It is clear from these data that successive β -deuterium substitution at conformationally equivalent sites does not lead to cumulative isotope effects, *i.e.*, the solvolytic rate retardation caused by 2,6-diaxial deuteration exceeds the square of that caused by monoaxial deuteration ($2.565/1.096 = 2.339 > 2.062 = 1.436^2$). It should be

(3) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952).

(4) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

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 form⁵ $(k_H/k_D)_X = 2xx'/(x + x')$ 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) hydrogen⁶ 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).

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(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-*d*₃, and -2,2,6,6-*d*₄, 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 $\pm 0.1\%$.

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

Deuteration a = axial e = equatorial	$k_1 \times 10^6$ 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).