fluxed again for 17 hr. The reaction mixture was cooled and washed with dilute acid. The almost colorless heptane solution was then extracted with concentrated hydrochloric acid and the acid layer diluted with water to give the bright yellow adduct. Traces of dimethyl fumarate were removed by chromatographing the crude product over a short column of acid-washed alumina (or silica gel). This gave 0.264 g. (48.5%)[7] of III, m.p. 126–127.5°. Recrystallization from methanol gave an analytical sample.

The methylenecyclopropene is a stable yellow solid, m.p. 127.0–127.5°. *Anal.* C, 75.39; H, 5.66; mol. wt., 350. The infrared spectrum (KBr) shows strong peaks at 5.4 μ (cyclopropene) and at 5.75 and 5.98 μ (unconjugated and conjugated ester). Its ultraviolet spectrum (acetonitrile) shows maxima at 244 mμ (ϵ 21,600), 252 (22,000), 268 (18,200), 298 (19,600), and at 378 (6850). In the presence of fluoroboric acid, the spectrum shows absorptions at 249 mμ (ϵ 16,600), 294 (29,800), and at 308 (31,000). This spectrum is strikingly similar to the reported spectra of the diphenylcyclopropenyl cation[8] and 1,2-diphenyl-3-propylcyclopropenyl fluoroborate[9] and suggests the following reaction.
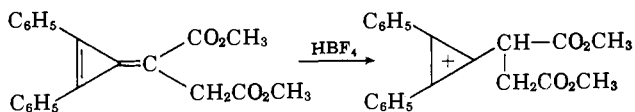
The n.m.r. spectrum of the methylenecyclopropene is also interesting. The phenyl resonances appear as three peaks, each of which appears to have some fine structure. These peaks appear at τ 1.65, 2.08, and 2.44 (from tetramethylsilane) and have relative areas of 1.97:2.47:5.85 (the latter two are not completely resolved). The methyl hydrogens and the methylene hydrogens could not be completely resolved although they could be very easily assigned resonance values, the two methyls appearing at τ 6.18 and 6.28 and the methylene at τ 6.34.

Final evidence for the suggested methylenecyclopropene structure resides in the alternate synthesis of a similar compound by Battiste[10] according to the following reaction.[11] The ultraviolet spectra of III and IV are virtually identical. In the phenyl region, the
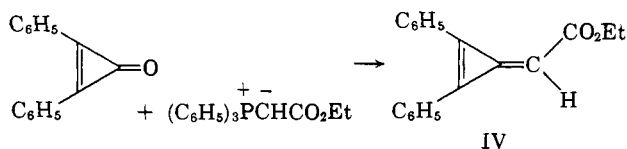
n.m.r. spectra are also strikingly similar.[12]

We are presently engaged in experiments that we

(7) It is interesting that low yields (6–7%) of adduct III can be obtained by thermally decomposing the nitrosourea in the presence of dimethyl fumarate but in the absence of the base. This reaction, as well as the details of the reaction with potassium *t*-butoxide, will be discussed in detail in a forthcoming publication.

(8) D. G. Farnum and M. Burr, *J. Am. Chem. Soc.*, **82**, 2651 (1960); R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961).

(9) R. Breslow, H. Hover, and H. W. Chang, *ibid.*, **84**, 3168 (1962).

(10) M. A. Battiste, *ibid.*, **86**, 942 (1964).

(11) Preliminary attempts to alternately synthesize adduct III by reaction of the appropriate ylide with diphenylcyclopropenone according to the method of Battiste[10] were met with only limited success. Thus, for example, reaction of the ylide with the ketone in refluxing heptane for 2 weeks followed by column chromatography and by thin layer chromatography gave a trace of yellow material, which showed an ultraviolet spectrum that had all of the peaks of the adduct contaminated with an appreciable amount of some other material.

(12) See ref. 10 for details.

hope will shed some light on the mechanism of this reaction.

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The Conformational Dependence of Secondary Deuterium Isotope Effects in Solvolytic Reactions[1]

Sir:

β-Deuterium effects on the rates of a large number of carbonium ion solvolyses can be satisfactorily correlated by the postulate that the governing mode of interaction between the sites of reaction and isotopic substitution is hyperconjugation.[2] This postulate requires that the maximum rate retardation be observed when the β C–D bond axis is parallel to the axis of the developing vacant p-orbital. We now wish to report the first *direct* observation of such an effect in the aqueous ethanolysis of a conformationally homogeneous sytem,[3,4] *cis*-4-*t*-butylcyclohexyl bromobenzenesulfonate (brosylate), I.

A comparison of the isotope effect caused by a single axial β-deuterium atom with that caused by *four* β-deuterium atoms on the rate of solvolysis of ester I was presented earlier.[1] We now wish to present a more valid comparison: The isotope effects on the rate of solvolysis of *cis*-4-*t*-butylcyclohexyl brosylate-*trans*-2-*d* (single axial β-deuterium) and *cis*-4-*t*-butylcyclohexyl brosylate-*cis*-2-*d* (single equatorial β-deuterium.)

The conformations of the initial and transition states for this reaction may be represented as Ia and II in which the dihedral angle between the carbon-leaving

Ia   II
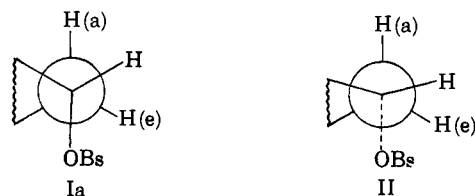
group axis and the β-carbon–hydrogen bond axis is 180° for an axial (a) hydrogen atom and 60° for 'an equatorial (e) hydrogen atom in both the initial and transition states. It is possible that some change in the extent of ring puckering accompanies transition state formation; if the ring flattens, 1,3 steric interactions involving the leaving group would be reduced, the dihedral angle with the axial hydrogen would become less than 180°, and that with the equatorial hydrogen less than 60°.

cis- and *trans*-4-*t*-butylcyclohexanol-1-*d* were prepared by lithium aluminum deuteride reduction of 4-*t*-butylcyclohexanone and separated by elution chromatography on activated alumina. *cis*-4-*t*-Butylcyclohexanol-*trans*-2-*d* was prepared by lithium aluminum deuteride reduction of a mixture of *cis*- and *trans*-4-*t*-butylcyclohexene oxide followed by separation of the desired alcohol by fractional crystallization of the *p*-nitrobenzoates. *cis*-4-*t*-Butylcyclohexanol-*cis*-2-*d* was

(1) Presented in part at 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

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

(3) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

(4) E. L. Eliel and C. A. Lukach, *ibid.*, **79**, 5986 (1957).

prepared by deuterioboration of 4-t-butylcyclohexene with deuteriodiborane, oxidation with alkaline hydrogen peroxide, separation of axial and equatorial alcohols by elution chromatography and preparative v.p.c., and separation of the desired alcohol by fractional crystallization of the axial p-nitrobenzoates. Combustion analyses indicated that the deuterated alcohols were about 98% isotopically pure. The brosylates of the various alcohols were prepared by the usual Tipson procedure.[5]

A determination of the products of the solvolysis of cis-4-t-butylcyclohexyl brosylate is complicated by insolubility of the substrate and volatility of the olefin fraction of the product. Direct analysis for olefin concentration relative to cis-decalin as internal standard was found to be possible at substrate concentrations of ca. 2.5×10^{-3} M by v.p.c. with flame ionization detection. Such an analysis on the products of solvolysis of ester I in 60 vol. % aqueous ethanol at 45° in a sealed tube with suspended calcium carbonate indicated the olefin yield to be 86%. Analysis of the products of solvolysis of a more concentrated solution at higher temperature showed the yield of alcohols to be 11% and ethers 3%. The alcohol fraction consisted of 79% trans-4-t-butylcyclohexanol (inversion) and 21% cis-4-t-butylcyclohexanol (retention). This pattern of substitution and elimination is similar to that observed by Winstein and Holness[3] for the acetolysis of cis-4-t-butylcyclohexyl tosylate and is in accord with a carbonium ion reaction rather than a solvent-assisted bimolecular elimination reaction.

The rate data, collected in Table I, were obtained by a precise conductometric determination[6] of the first-order solvolysis rate constants of the brosylates at 35° in 50 vol. % aqueous ethanol. The precision of the method, without the determination of conductance parameters, is ±0.1%. The sensitivity of the conductometric method is such that we were able to measure the solvolysis rates at a substrate concentration of 5×10^{-4} M. Thus, the solubility problem which usually requires that solvolysis rates of arenesulfonate esters measured titrimetrically be done in organic acid media at higher temperatures was circumvented.

TABLE I

SOLVOLYSIS RATES OF DEUTERATED cis-4-t-BUTYLCYCLOHEXYL BROSYLATES

Deuteration	$k_1 \times 10^4$, sec.$^{-1}$	k_H/k_D
None	3.938 ± 0.004	...
α-deuterium, equatorial	3.275 ± 0.004	1.202 ± 0.002
β-deuterium, axial	2.743 ± 0.001	1.436 ± 0.002
β-deuterium, equatorial	3.593 ± 0.003	1.096 ± 0.002

The axial β-deuterium slows the solvolysis rate by a factor of 1.436 which is the largest reported secondary isotope rate effect attributable to a single deuterium atom. Furthermore, it is almost ten times larger than the average steric isotope effect per deuterium atom calculated by Bartell[7] for the t-butyl chloride solvolysis. On the other hand, the equatorial β-deuterium atom slows the solvolysis rate by the dramatically reduced factor of 1.096.

Thus, the conformational dependence of the β-deuterium effect, predicted by the hyperconjugation postulate, is confirmed in this reaction.

The possibility exists that the axial isotope effect is due to neighboring hydrogen participation, which in our view is simply an extreme manifestation of a

type of electronic interaction also associated with hyperconjugation. One consequence of hydrogen participation would be a nonequivalence of the 2- and 6-axial hydrogens in the solvolytic transition state. Should this be the case, the solvolytic rate retardation caused by 2,6-diaxial deuteration would exceed the square of 1.436. Although this interesting question remains to be settled, there seems to be no doubt that the present results cannot be explained in terms of the simple steric model proposed by Bartell.[7]

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Free-Radical Cycloadditions to cis,cis-1,5-Cyclooctadiene

Sir:

Although ionic reactions in the cyclooctane series[1] frequently lead to transannular rearrangements, and the reactions involving carbene intermediates have also been shown[2] to result in transannular rearrangements, the corresponding free-radical rearrangements are unknown.[3] We provide here the first example of a free-radical cycloaddition in the cyclooctane series.

Addition of a mixture of 35.6 g. (0.33 mole) of cis,cis-1,5-cyclooctadiene and 5.11 g. (0.035 mole) of di-t-butyl peroxide to 1010 g. (10.0 mole) of t-butylformamide[4] at 135–140° and distillation of the reaction mixture gave 35 g. (51%) of a liquid, b.p. 115° (0.08 mm.)–165° (0.25 mm.), which, after solidification, was recrystallized from aqueous methanol, then from petroleum ether (b.p. 45–60°), to give exo,cis-N-t-butylbicyclo[3.3.0]octane-2-carboxamide[5] (I), m.p. 134–135°, λ_{max} 3.08, 3.30, 6.11, and 6.48 μ. The amide (I) did not absorb any hydrogen (5% Pd on charcoal,

I, R = CONHC(CH₃)₃
II, R = COCH₃
III, R = CCl₃
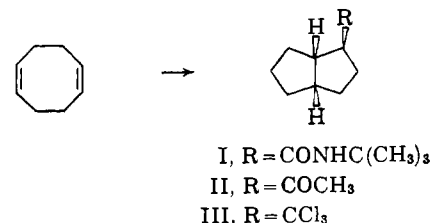
50 p.s.i.) and was recovered unchanged. All attempts at its saponification, including heating it with potassium hydroxide at 200° and fusing it with a mixture of potassium and sodium hydroxides at 200°, failed to give the acid.[6] The authentic amide (I) was prepared from exo,cis-bicyclo[3.3.0]octane-2-carboxylic acid[7] (via its acid chloride) and t-butylamine. The two compounds were indistinguishable in their infrared spectra and melting points, and the melting point of the mixture was undepressed.

cis,cis-1,5-Cyclooctadiene and acetaldehyde[8] gave,

(1) E.g., A. C. Cope, J. N. Grisar, and P. E. Peterson, J. Am. Chem. Soc., **82**, 4299 (1960).

(2) L. Friedman and H. Shechter, ibid., **83**, 3159 (1961).

(3) A. N. Nesmeyanov, R. Kh. Freidlina, V. N. Kost, and M. Ya. Khorlina, Tetrahedron, **16**, 94 (1961).

(4) L. Friedman and H. Shechter, Tetrahedron Letters, 238 (1961).

(5) Satisfactory elemental analyses were obtained for all new compounds reported here.

(6) Compound I may be one of the most difficultly saponifiable amides known.

(7) A. C. Cope and M. Brown, J. Am. Chem. Soc., **80**, 2859 (1958).

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

(6) B. L. Murr, Jr., and V. J. Shiner, Jr., J. Am. Chem. Soc., **84**, 4672 (1962).

(7) L. S. Bartell, ibid., **83**, 3567 (1961).