

TABLE I
 AUTOXIDATION OF TETRALIN (TRITIUM LABELED)^a

Run 125: concn. of di-*tert*-butyl diperoxyoxalate, 0.0952 *M*; concn. of tetralin, 2.203 *M* (15.00 ml. in 30.00 ml. of benzene); vol. reactor, 121.9 ml.; solution, 45.0 ml.; temp., 24.90°; obsd. press. at 0 time 834.4 mm.; pressure — vapor pressure, ^b 762.4; amount of gas (N_T) = 3.150×10^{-3} mole; amount of argon (N_{Ar}) = 1.770×10^{-4} mole

Time, sec.	Mass spectrometer peak heights								H_{44}/H_{40}	H_{O_2}/H_{40}
	28	32	34	36	40	44	78			
0	363	8780	37.6	144.6, 141.4 ^c	951	61.7	8	0.0649	9.43	
600	275	8810	39.3	144.6, 141.2	1032	233.4	15.6	.2261	8.72 ^c	
1800	398	6410	31.6	105.0, 102	897	434	71	.484	7.30	
3000	385	7190	40.3	117.3, 113.3	1209	876	60	.725	6.080	
4553	441	6560	43.0	104.7, 99.9	1449	1560	20	1.077	4.630	
6064	654	5700	44.2	93.0, 86.8	1866	2640	206	1.414	3.145	
8100	1104	3800	38.9	62.1, 52.1	3000	5500	138	1.832	1.298	
8520	1113	2460	27.9	43.5, 33.8	2900	5610	165	1.935	.869	

^a Experiments to be described in a subsequent paper of this series. ^b Taken as the vapor pressure of benzene at 25.9° times its mole fraction. ^c This column is corrected for Ar³⁶.

A typical set of kinetic data, on the autoxidation of tetralin, is shown in Table I and plotted in Fig. 2 as suggested by eq. 8 and 9. Plots of eq. 11 and 12 are shown in ref. 2a.

In some cases the total amount of calculating is minimized by calculating the final slopes and other quantities without the use of sensitivity and solubility corrections, then correcting them by the formulas below. Log-log plots require no corrections because all multiplicative constants drop out.

Moles of argon (N_{Ar}) without corrections

$$N'_{Ar} = \left(\frac{H_{Ar}}{H_{Ar} + \Sigma H_{O_2} + H_{N_2}} \right) (\text{total moles of gas}) \quad (13)$$

$$\text{Moles of } i, N'_i = (H_i/H_{Ar})N_{Ar}' \quad (14)$$

$$\text{Corrected } N_{Ar} = \left[\frac{H_{Ar}}{H_{Ar} + \Sigma H_{O_2}S_{O_2} + H_{N_2}S_{N_2}} \right] \times (\text{total moles of gas})$$

$$N_i = (H_iS_i/H_{Ar})N_{Ar}$$

Corrected $dN_i/dt = b$ or R ; is obtained from 15

$$\frac{dN_i}{dt} = \frac{dN'_i}{dt} \frac{S_i N_{Ar}}{N'_{Ar}} \left[\frac{V_{gas} + \alpha_i V_{soln.}}{V_{gas}} \right] \quad (15)$$

Acknowledgment.—Grateful acknowledgment is made to the National Institutes of Health for support of this work and for a post-doctoral fellowship in 1959–1961.

[CONTRIBUTION NO. 1116 FROM THE DEPARTMENT OF CHEMISTRY OF INDIANA UNIVERSITY, BLOOMINGTON, IND.]

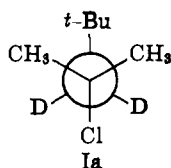
The Effects of Deuterium Substitution on the Rates of Organic Reactions. VIII. The Solvolysis of *t*-Butyl-*d*₁, -*d*₂, -*d*₃, -*d*₆ and -*d*₉ Chlorides¹

By V. J. SHINER, JR.,² B. L. MURR³ AND G. HEINEMANN

RECEIVED DECEMBER 27, 1962

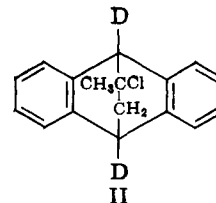
The solvolysis rate retardations caused by substitution of 1, 2 and 3 deuterium atoms in one methyl group of *t*-butyl chloride are not quite cumulative; the isotope effect per deuterium increases slightly as the number of deuterium atoms increases. The previously proposed conformational dependence of the β -deuterium isotope effect quantitatively predicts just such a trend. The retardations caused by complete deuteration of 1, 2 and 3 methyl groups are more nearly cumulative.

The unusually small isotope effect observed in the solvolysis of 2,4,4-trimethyl-2-chloropentane (I) was originally attributed to a conformational dependence



of the isotope effect together with a sterically controlled transition state conformation, related to Ia, in which the deuterium atoms are situated *gauche* to the leaving group.⁴ It was suggested that the larger isotope effects caused by β -deuterium substitution in related systems⁵ were characteristic of a deuterium situated *trans* to the solvolytic leaving group in the transition state. This

conformational dependence of the β -deuterium secondary isotope effect in carbonium ion reactions was further confirmed by the observation of an insignificantly small isotope effect in the solvolysis of the bridgehead deuterated bicyclooctane derivative II,⁶ where the C–D bond is oriented perpendicular to the developing vacant orbital at the adjacent solvolysis center.



This strong conformational dependence of the isotope effect leads to the prediction that the rate retardations caused by successive replacements of the hydrogens of a methyl group adjacent to a solvolyzing center will not be precisely cumulative. For example, if the solvolysis rate with a deuterium *trans* to the leaving group is relatively slower, then the transition state with an

(1) (a) Taken in part from the thesis submitted by B. L. Murr to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree. (b) Supported in part by Grants G 5062 and G 16831 from the National Science Foundation, Washington, D. C.

(2) Alfred P. Sloan Research Fellow, 1957–1961.

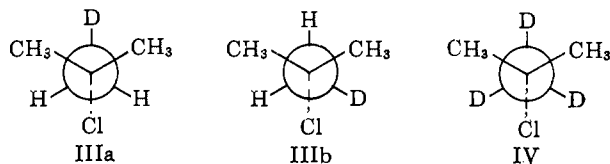
(3) Dow Fellow, 1958–1959.

(4) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **78**, 2653 (1956); **83**, 240 (1961).

(5) For a review see V. J. Shiner, Jr., *Tetrahedron*, **5**, 243 (1959).

(6) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **82**, 2655 (1960).

adjacent $-\text{CH}_2\text{D}$ group oriented with the D *gauche* will have a slightly lower energy than the one with it *trans*. Because of this, the compound will solvolyze slightly faster than if the two conformations had the same energy. The magnitude of this effect can readily be calculated using a few simplifying assumptions. There should be two different conformations possible for the transition state for the solvolysis of *t*-butyl- d_1 chloride, IIIa and IIIb, with IIIb having a statistical weight of two compared to one for IIIa.



If k_H represents the solvolysis rate of undeuterated *t*-butyl chloride, k_D , that of *t*-butyl- d_1 chloride, a is the isotope effect for a D atom in the *trans* position (*i.e.*, $a = k_H/3k_{\text{IIIa}}$) and b is the isotope effect for the D atom in the *gauche* position (*i.e.*, $b = k_H/3k_{\text{IIIb}}$), then the observed isotope effect will be

$$k_H/k_{D_1} = \frac{k_H}{k_H/3a + 2k_H/3b} = 3ab/(b + 2a) \quad (1)$$

Further, if it is assumed that in the solvolysis of *t*-butyl- d_3 chloride (IV) the isotope effect of the *trans*-D is the same as that in IIIa and the isotope effects of each of the *gauche*-D's are the same as that in IIIb, then its rate is

$$k_{D_3} = k_H/ab^2 \quad (2)$$

Using eq. 2, the observed k_H/k_{D_3} , and making various assumptions about the relative size of a and b , one can calculate the expected k_H/k_D , from eq. 1. A similar treatment allows the calculation of k_H/k_{D_2} from eq. 3

$$k_H/k_{D_2} = 3ab^2/(a + 2b) \quad (3)$$

where k_{D_2} is the solvolysis rate of *t*-butyl chloride with two D atoms in one methyl group.

The replacement of three β -hydrogens in a methyl group is known to slow the solvolysis rate of a tertiary chloride by factor around 1.30. Application of the above equations then shows that if the conformational effect were a maximum, *i.e.*, $a = 1.30$ and $b = 1.00$, the observed k_H/k_D , would be almost 1% lower (about 1.09) than it would be if there were no conformational effect (about 1.10). This means that one would have to measure the rate ratios and therefore the rates with a precision of 0.1% or better to have a reasonable chance of observing such a conformational dependence in this system. Murr and Shiner⁷ reported the development of the conductance method of rate measurements to give, under favorable circumstances, limits of reproducibility as small as 0.03%. Thus it became reasonable to use this technique to measure effects of the size expected from the conformational influences discussed above. Of course, there are other influences which may operate to make isotope effects caused by cumulative isotope substitution at equivalent sites not themselves cumulative. For example, the total zero point energy of water does not change by successively equal amounts as the hydrogens are successively replaced.⁸ Due to coupling of vibrations the decrease of zero point energy caused by replacing one H by D is more than one-half that caused by replacement of two hydrogens by deuterium. In addition, it would be empirically useful in comparing and compiling secondary isotope effect information to know how nearly cumulative such

effects are or, to put it another way, if there are important "isotope effects" on isotope effects.

Therefore we have synthesized and measured the solvolysis rates of $(\text{CH}_3)_2\text{CClCH}_3$, $(\text{CH}_3)_2\text{CClCH}_2\text{D}$, $(\text{CH}_3)_2\text{CClCHD}_2$, $(\text{CH}_3)_2\text{CClCD}_3$, $\text{CH}_3\text{CCl}(\text{CD}_3)_2$ and $(\text{CD}_3)_3\text{CCl}$. The rate constants are reported in Table I. These are believed to be accurate to within less than

TABLE I
SOLVOLYSIS RATES IN "60%" AQUEOUS ETHANOL AT 25°

Compound	$10^4 k$, sec. ⁻¹	k_H/k_D	k_H/k_D per D
$(\text{CH}_3)_2\text{CClCH}_3$	12.496		
	12.498		
$(\text{CH}_3)_2\text{CClCH}_2\text{D}$	11.443	1.0922	1.092
$(\text{CH}_3)_2\text{CClCHD}_2$	10.400	1.2016	1.096
	10.390	1.2028	1.097
$(\text{CH}_3)_2\text{CClCD}_3$	9.3934	1.3304	1.100
	9.3936	1.3303	
$\text{CH}_3\text{CCl}(\text{CD}_3)_2$	6.9796	1.7095	1.102
$(\text{CD}_3)_3\text{CCl}$	5.3701	2.3271	1.098 (1.103) ^a

^a Corrected to 100% deuteration.

0.1%; double entries refer to duplicate rate determinations. Standard deviations are all about 0.01%. Probably the largest source of error lies in the possibility of incomplete deuteration or, in other words, in the presence of isotopic impurities. The mono- and di-deuterated compounds were made from lithium aluminum deuteride of >99.5% isotopic purity by methods which our experience has shown to give negligible isotopic dilution. In addition, these compounds on combustion analysis for deuterium showed $99 \pm 1\%$ deuteration of the specified positions. The d_3 -, d_6 - and d_9 - compounds were made through exchange methods. Combustion analysis showed the d_3 - and d_6 - compounds to be $99 \pm 1\%$ deuterated in the specified positions; n.m.r. integration analysis by comparison with standard samples in substitute tubes showed the d_6 - compound to be essentially 100% deuterated and the d_9 - compound to be about 95.3% deuterated. This last analysis on the d_9 - compound is the most accurate because it is essentially a trace analysis for a very small amount of hydrogen. The figure in the last column of Table I for this compound has been entered twice; 1.098 uncorrected and 1.103 corrected for incomplete deuteration. The deuterium analyses for the other compounds are, within the limits of the accuracy of analysis, essentially 100%, so they are not corrected. The d_3 - and d_6 - materials could be as much as 1 or 2% less than 100% deuterated, but it is very unlikely that the d_1 - and d_2 - compounds would be. If the deuteration is 1% lower the last digit in the entries given in the last column would be about 1 unit higher. Thus the deuterium analytical uncertainty, and not the rate measurement, determines the limit of the accuracy. These results, then, show that the isotope effect *per deuterium atom* increases as the extent of deuteration of the methyl group increases. They further show that as 1, 2 or 3 methyl groups are deuterated, the isotope effect per D atom is, almost within the limits of error of deuterium analysis, constant. These two results are just what is predicted from the conformational effect previously postulated. Further, the equations derived above can be used to calculate, assuming that the variation is due to conformational effects alone, just what the conformational dependence is. In Table II are given values for k_H/k_{D_1} , and k_H/k_{D_2} (per D) calculated from eq. 1 and 3, respectively, using the k_H/k_D , value observed (see Table I) and various assumptions covering the range of possible conformational influences which are reflected in the values of a and b , the isotope effects in the *trans* and *gauche* positions. The first four entries represent calculations based on increasingly

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

(8) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. 2, D. Van Nostrand, Inc., New York, N. Y., p. 282.

strong conformational dependence from *a* and *b*, *a* being the maximum and *b* being the minimum. It is obvious that the results of Table I require a very strong conformational dependence, nearly but not quite the maximum represented by the fourth entry in Table II.

TABLE II

ISOTOPE EFFECTS CALCULATED FOR MONO- AND DIDEUTERATED *t*-BUTYL CHLORIDE^a

Assumption	<i>a</i>	<i>b</i>	Calcd. k_H/k_{D_1}	Calcd. k_H/k_{D_2}
$a = b$	1.0998	1.0998	1.0998	1.0998
$a = b^2$	1.1535	1.0740	1.0992	1.0995
$a = b^4$	1.2097	1.0487	1.0974	1.0986
$b = 1.000$	1.3304	1.0000	1.0903	1.0947

^a From eq. 1 and 3 using the observed value 1.3304 for k_H/k_{D_3} , and various assumptions about conformational dependence embodied in the relative values of *a* and *b*, the isotope effect in *trans* and *gauche* positions, respectively.

The observed k_H/k_{D_1} can be used to determine the conformational dependence required, as expressed in the values of *a* and *b*. These calculate to be 1.3016 and 1.0110, respectively. These values can then be used to calculate k_H/k_{D_2} (per D) as a check: 1.0958, calculated, compared to 1.096, observed.

Thus we believe that the comparison between the mono- and trideuterated compounds "calibrates" the conformational dependence, and the observations on the dideuterated material confirm it. Additional evidence that the isotope effects are cumulative in the absence of conformational influences is afforded by the observations in the hexa- and nonadeuterated derivatives. Although it is difficult to conclude that the conformational influences on this system, predicted before these experiments were done, are now proved, the fact that all of these results can be correlated quantitatively with this hypothesis certainly seems to represent strong presumptive evidence.

Since it is well known that the vibrations of hydrogens attached to the same carbon atom are strongly coupled, it must be considered somewhat surprising if this phenomenon does not contribute appreciably to the non-cumulative nature of isotope effects caused by cumulative deuterium substitution at a given atom. A complete vibration analysis on a model system should be capable of giving an at least semiquantitative estimation of the magnitude of this effect. Although we have not done this, a simple intuitive argument suggests that this influence would be in the direction *opposite* to what is observed. Coupling effects usually lead to the *largest* change in zero-point energy for the first isotopic substitution on a given center.⁸ If we conclude further that the *difference* in zero-point energy changes caused by one and two isotopic substitutions will be larger for the state in which the total zero-point energy is largest, then it is concluded, since the zero point energy of the transition state is smaller than that of the initial state, that the largest isotope effect ought to be caused by the *first* deuterium substitution. Since the opposite result is observed, it seems that coupling effects have a negligible influence in these comparisons and must largely cancel out between initial and transition states.

Experimental

Acetone-*d*₆ was prepared using the method previously described⁹ except that larger samples of deuterium oxide, obtained from the U. S. Atomic Energy Commission, and acetone were equilibrated.

Methyl-*d*₃ iodide was prepared using the exchange method described by Cotton, Fassnacht, Horrocks and Nelson.¹⁰

Deuterium analyses were done using the combustion method described earlier⁹ or by integration of the proton magnetic resonance signal from a Varian DP-60 nuclear magnetic resonance spectrometer and comparison with similar integrations of standard samples run at the same time. With extreme care the combustion method gives results accurate to $\pm 1\%$ of the quantity determined. The n.m.r. integrations give a similar accuracy except for the sample of *t*-butyl-*d*₃ chloride in which the determination of the trace amount of hydrogen allowed, by subtraction, a somewhat better estimate of the deuterium content.

Kinetic Method.—The kinetic apparatus and procedure was identical to that described by Murr and Shiner.⁷

Methyl-*d*₂ Alcohol.—To a slurry of 7.4 g. (0.177 mole) of lithium aluminum deuteride in 200 ml. of dry ether was added a solution of 40 g. (0.39 mole) of freshly distilled *n*-butyl formate in 100 ml. of ether. The mixture was hydrolyzed by addition of about 200 ml. of 4 *N* sodium hydroxide solution and the mixture separated by fractional distillation. The fraction boiling between 45 and 50° was redistilled. Methyl-*d*₂ alcohol (7.5 g., 0.22 mole) was collected from 63–65°, yield 62% based on lithium aluminum deuteride.

Methyl-*d*₂ Iodide.—To a stirred solution of 37 g. (0.194 mole) of *p*-toluenesulfonyl chloride in 175 ml. of dry pyridine at 0° was added 6 g. (0.176 mole) of methyl- α -*d*₂ alcohol dissolved in 25 ml. of pyridine. The addition required 10 min. and stirring was continued for 4 hr. while the solution was kept at 0°. The reaction mixture was then diluted with 600 ml. of water and extracted 10 times with ether. The ethereal extract was washed 2 times with dilute aqueous sodium hydroxide, 2 times with dilute aqueous sulfuric acid and once with water. After drying over anhydrous sodium sulfate, the ether was removed by distillation and the residue distilled under reduced pressure through a spinning band column, giving 22 g. (0.118 mole) of methyl-*d*₂ toluenesulfonate, b.p. 97° (0.3 mm.), yield 67%. This ester was dissolved in 50 ml. of acetone and added to a solution of 36 g. (0.24 mole) of sodium iodide in 200 ml. of acetone. The mixture was allowed to stand for 2 hr.; the precipitated sodium toluenesulfonate was removed by filtration and the methyl- α -*d*₂ iodide, b.p. 41–42°, was recovered by distillation through a small glass helix-packed column; yield 15 g. (0.105 mole), 90% based on the toluenesulfonate ester.

2-Methyl-2-propanol-1-*d*₁.—A slurry of 5 g. (0.119 mole) of lithium aluminum deuteride in 500 ml. of anhydrous ether was prepared in a 1-l. three-necked round-bottomed flask fitted with a mechanical stirrer, reflux condenser and a dropping funnel; 32 g. of redistilled isobutylene oxide in an equal volume of ether was added dropwise to the slurry. The solution was refluxed for 2 hr. after complete addition. The mixture was hydrolyzed with dilute hydrochloric acid and the ether layer was separated. The aqueous layer was extracted with ether. The combined ether extract was washed with 5% aqueous sodium bicarbonate and with water. The ether solution was dried with potassium carbonate. Fractional distillation afforded 22.4 g. (61%) of 2-methyl-2-propanol-1-*d*₁ (b.p. 81–82°). The chloride from this alcohol was purified by gas chromatography. Deuterium analysis indicated that the chloride contained 0.972 atom of deuterium per molecule. A blank determination on a known mixture of water-deuterium oxide of the same composition as the *t*-butyl alcohol-*d*₁ showed that the alcohol analysis should be corrected to 0.992 atom of deuterium per molecule. By the method of synthesis the alcohol should have the same isotopic purity (*ca.* 99.5%) as the lithium aluminum deuteride.

2-Methyl-2-propanol-1,1-*d*₂.—A solution of 15 g. (0.105 mole) of methyl-*d*₂ iodide in 100 ml. of dry ether was added dropwise to a stirred suspension of 2.75 g. (0.115 mole) of magnesium in 30 ml. of dry ether. The solution was refluxed for 15 min., then cooled and stirred while 6 g. (0.104 mole) of acetone in 50 ml. of ether was added. The solution was refluxed for 10 min., cooled and hydrolyzed with aqueous ammonium chloride. The ether layer was combined with 10 ether extracts of the water layer and dried over sodium sulfate. Most of the ether was removed by distillation through a glass helix-packed column. The residue was distilled through a spinning band column and 3.5 g. (0.046 mole, 44% yield) of 2-methyl-2-propanol-1,1-*d*₂, b.p. 80–82°, was obtained.

2-Methyl-2-propanol-1,1,1-*d*₃. was made *via* a Grignard reaction similar to that described above, but starting with methyl-*d*₃ iodide.

2-Methyl-2-propanol-1,1,1,3,3,3-*d*₆ was made *via* a Grignard reaction using acetone-*d*₆ and methyl iodide.

2-Methyl-*d*₃-2-propanol-1,1,1,3,3,3-*d*₆ was prepared *via* a Grignard reaction using acetone-*d*₆ and methyl-*d*₃ iodide.

Preparation of Chlorides.—Commercial hydrogen chloride was bubbled into a 1–2-g. sample of alcohol in a 5-ml. centrifuge tube cooled in an ice-bath. When water ceased to separate (*ca.* 2 hr.) the sample was allowed to warm to room temperature. The chloride was separated after centrifugation and dried over 40-mesh C.P. anhydrous calcium chloride. The dried alkyl

(9) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **74**, 5285 (1952);

(10) J. A. Cotton, J. H. Fassnacht, W. D. Horrocks, Jr., and N. A. Nelson, *J. Chem. Soc.*, 4138 (1959).

chloride was introduced into a vacuum line. Hydrogen chloride was removed by degassing, after which two vacuum transfers were made leaving a small residue each time. Commercial *t*-

butyl chloride was distilled from potassium carbonate through a 100 × 2 cm. glass helix-packed column. A center cut gave the same kinetic results as a sample prepared as described above.

[CONTRIBUTION NO. 1118 FROM THE DEPARTMENT OF CHEMISTRY OF INDIANA UNIVERSITY, BLOOMINGTON, IND.]

The Effects of Deuterium Substitution on the Rates of Organic Reactions. IX. Bridgehead β -Deuterium in a Carbonium Ion Solvolysis¹

By V. J. SHINER, JR.,² AND J. S. HUMPHREY, JR.

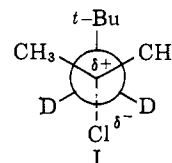
RECEIVED DECEMBER 27, 1962

The bicyclic tertiary chloride 11-methyl-11-chloro-9,10-dihydro-9,10-ethanoanthracene (IIa) and its -12,12-*d*₂ (IIb) and -9,10-*d*₂ (IIc) analogs have been synthesized and their solvolysis rates measured in 60% aqueous ethanol at 45°. While IIb shows a typical β -deuterium isotope effect for a carbonium ion solvolysis ($k_H/k_D = 1.14$), the bridgehead deuterated analog IIc exhibits an isotope effect, $k_H/k_D = 0.986$, not appreciably different from unity. It is concluded that the β -deuterium isotope effect is strongly dependent on the spatial orientation of the isotopic bond. This is consistent with the earlier suggestion that hyperconjugative intramolecular transmission of electronic charge is an essential factor in causing β -deuterium-substituted compounds to give slower carbonium ion type reactions than their protium analogs. Inductive interactions seem to cause a much smaller effect, possibly in the opposite direction.

Introduction

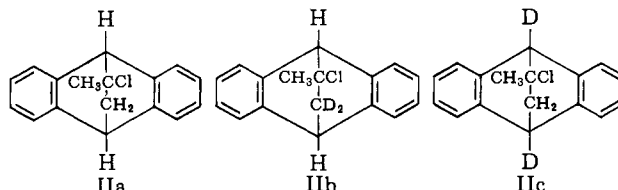
Since their first observation, β -deuterium isotope effects in carbonium ion reactions have generally been interpreted in terms of hyperconjugative interactions between the carbonium ion center and the site of isotopic substitution.³ One of the special properties which should be exhibited by a phenomenon dependent on hyperconjugative interaction between a single bond and an adjacent p-orbital, is that of angular dependence. Although the original theoretical picture of Mulliken, Rieke and Brown,⁴ further developed by Lofthus⁵ and Mulliken⁶ (which considers two or three single bonds from a carbon atom to two or three hydrogen atoms as a quasi-multiple bond), does not predict any steric requirements for the hyperconjugation of the group as a whole,⁵ it seems apparent that the contribution of any single bond of the group would be subject to a steric or orientational influence. It is this influence on the isotopically substituted bond itself that influences the isotope rate effect. The " α -hydrogen bonding" interaction suggested by Kreevoy and Eyring⁷ and related to Winstein's neighboring hydrogen participation⁸ probably gives a clearer picture of the role of each hyperconjugating hydrogen and of the influence of steric factors. In the present paper both the effect originally suggested by Mulliken, Rieke and Brown and the α -hydrogen bonding effect will be included in the term "hyperconjugation" as both have to do with delocalization of the C-H σ -bonding electrons in a "hyperconjugating position" into the neighboring (partially) vacant orbital. The distinction between the two effects would seem to be significant principally in the theoretical interpretation and particularly not in the experiments of this work. Thus in theory hyperconjugation, like conjugation, should be subject to steric hindrance. While the experimental evidence which confirms the steric requirements of conjugation is extensive,⁹ corresponding information about hyperconjugation is sparse.

Arnold and Truett¹⁰ and Baddeley and Gordon¹¹ first claimed observation of experimental consequences of steric inhibition of hyperconjugation, particularly in the solvolysis rates of some cycloalkenobenzhydryl chlorides. The abnormally low isotope effect in the solvolysis of 2,4,4-trimethyl-2-chloropentane-3,3-*d*₂ was suggested to be caused by steric inhibition of hyperconjugation.¹² Thus, if the conformation of the transition state in this solvolysis were controlled by the



bulk of the *t*-butyl group to be as depicted in I, the C-D bonds would be forced into positions relatively unfavorable for hyperconjugation. If hyperconjugative transmission of electron density from these bonds to the solvolysing center were essential for the isotope effect, it is reasonable that this solvolysis would show a relatively small retardation by deuterium substitution in the 3-position. Although the argument is reasonable and seems the only satisfactory way of accounting for the results, it suffers from the lack of independent evidence that the conformation of the transition state is actually as depicted in I.

We therefore sought to determine the β -deuterium isotope effect in the solvolysis reaction of a compound in which the C-D bond axis would be fixed in a direction perpendicular to the axis of the developing vacant p-orbital. The compounds chosen for this purpose were IIa, b and c.



The Diels-Alder adduct of anthracene and vinyl acetate¹³ was hydrolyzed to the secondary alcohol,

(1) A preliminary report of this work has appeared: V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **82**, 2655 (1960).

(2) National Science Foundation Senior Postdoctoral Fellow and Alfred P. Sloan Research Fellow.

(3) For a review of these results see V. J. Shiner, Jr., *Tetrahedron*, **5**, 243 (1959).

(4) R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

(5) A. Lofthus, *ibid.*, **79**, 24 (1957).

(6) R. S. Mulliken, *Tetrahedron*, **5**, 253 (1959).

(7) M. M. Kreevoy and H. Eyring, *J. Am. Chem. Soc.*, **79**, 5121 (1957).

(8) S. Winstein and J. Takahashi, *Tetrahedron*, **2**, 316 (1958).

(9) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 367, and others.

(10) R. T. Arnold and W. L. Truett, *J. Am. Chem. Soc.*, **73**, 5508 (1951).

(11) G. Baddeley and M. Gordon, *J. Chem. Soc.*, 2190 (1952). However, G. Baddeley, S. Varma and M. Gordon, *ibid.*, 3171 (1958), concluded that in these instances "hyperconjugation of a primary alkyl group is unaffected by torsional rotation of the group about the bond attaching it . . ."

(12) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **78**, 2653 (1956); **83**, 240 (1961).

(13) K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1939).