

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.

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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.

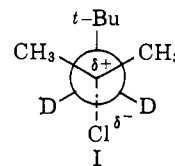
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The bicyclic tertiary chloride 11-methyl-11-chloro-9,10-dihydro-9,10-ethanoanthracene (IIa) and its -12,12-*d*₂ (IIb) and -9,10-*d*₂ (IIc) analogs have been synthesized and their solvolysis rates measured in 60% aqueous ethanol at 45°. While IIb shows 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

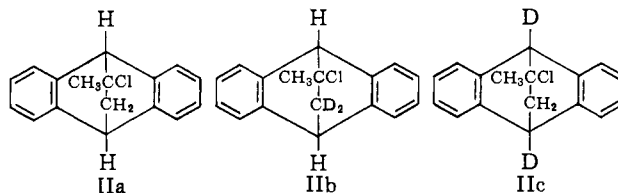
Since their first observation, β -deuterium isotope effects in carbonium ion reactions have generally been interpreted in terms of hyperconjugative interactions between the carbonium ion center and the site of isotopic substitution.³ One of the special properties which should be exhibited by a phenomenon 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).

oxidized to the ketone¹⁴ and converted with methylmagnesium iodide to the tertiary alcohol III. This product on treatment with thionyl chloride gave IIa; IIb was obtained through the use of a sample of the ketone which had first been subjected to several triethylamine-catalyzed exchanges with deuterium oxide in boiling dioxane solution; IIc was made by the same route from anthracene-9,10-*d*₂, made by reduction of anthrone with zinc and sodium deuterioxide in deuterium oxide.¹⁵ Nuclear magnetic resonance spectra of IIa, IIb, IIc, the corresponding alcohols and ketones were entirely consistent with these formulations and showed the deuterium compounds to be *ca.* 90% isotopically pure. This constitutes essentially an independent proof of structure. The solvolysis rate constants given in the table were determined in 60% aqueous ethanol at 45°.

TABLE I

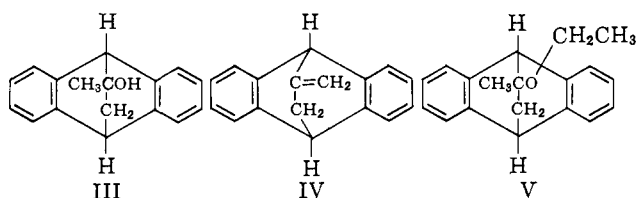
FIRST-ORDER RATE CONSTANTS (10^{-5} SEC.⁻¹) FOR SOLVOLYSIS IN "60%" AQUEOUS ETHANOL AT 45.00°

Each constant given is the average for one experiment of a number of integrated rate constants calculated for points taken over about 3 half-lives. The point by point values drifted downward 1% or less during any run.

Compd.	k				k_H/k_D
IIa	9.05	8.98	8.99 ^a	9.14 ^{a,b}	
IIb	7.80	7.88	7.92 ^a		1.14 ± 0.01
IIc	9.12	9.29 ^{a,b}			0.986 ± 0.01

^a Taken after one additional recrystallization of previously used material. ^b Run in a second solvent batch.

The products and yields were determined from solvolysis of more concentrated solutions of IIa in 60% ethanol by isolation with the aid of chromatography. The unrearranged alcohol III was isolated in about 52% yield while the olefin IV and the ethyl ether V were isolated in approximately 19 and 23% yields, respectively. These products constitute about 94% of the theoretical yield.



Thus it seems that the solvolysis of IIa is fairly normal and is not accompanied by extensive rearrangement. The fact that its rate is about one-sixteenth that expected for *t*-butyl chloride under these conditions is not surprising in view of its strained bicyclic structure. The isotope rate effect caused by deuteration of the methylene group is slightly smaller than normal. However, the bridgehead deuterated material IIc does not show the normal β -deuterium isotope effect. Instead, the effect is close to the experimental error and inverse. Thus the prediction based on the initial suggestion that normal β -deuterium isotope effects in carbonium ion reactions are mainly due to hyperconjugation interactions is borne out. The inductive influence is shown to be relatively small and probably in the opposite direction, as expected.¹⁶

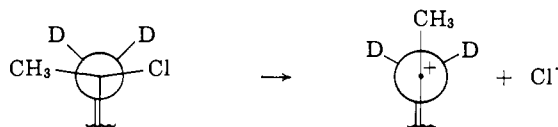
It is now apparent that the earlier treatment of group isotope effects in terms of an average effect per D atom was an oversimplification which led to some partly erroneous conclusions.³ Thus conformation and substituent electrical effects cannot be evaluated separately.

The following analysis of all of the data on tertiary chloride solvolyses indicates that the variations in the β -deuterium isotope effects from group to group and compound to compound are predominantly due to conformational changes and that electrical influences of alkyl groups on isotope effects must be small. Also, the variation in carbonium ion character among the different (tertiary alkyl chloride solvolytic) transition states does not seem to be big enough to produce large variations in the β -deuterium isotope effects. Deuteration of a β -methyl group leads to isotope effects of 1.3308 (*t*-butyl chloride),¹⁷ 1.34 (*t*-amyl chloride), 1.34 (2,4-dimethyl-2-chloropentane) and 1.40 (2,4,4-trimethyl-2-chloropentane). The latter figure may be higher because it refers to a more reactive tertiary halide or perhaps because some initial state non-bonded interactions between the 2- and 4-situated methyl groups¹⁸ are relieved in the transition state.

It has been shown further¹⁹ that the solvolysis rate retardations caused by substitution of one, two and three 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. These results are consistent with a strong conformational dependence of the isotope effect and are quantitatively explained if it is assumed that the isotope effect per deuterium substitution *trans* to the departing chloride in the transition state is about 1.31 while that for deuterium substitution in the *gauche* position is about 1.01.

Deuteration of a methylene group leads to isotope effects of 1.40 (*t*-amyl chloride), 1.34 (2-methyl-2-chloropentane), 1.47 (2,4-dimethyl-2-chloropentane) and 1.08 (2,4,4-trimethyl-2-chloropentane).¹² The latter small figure is apparently due to the conformation of the transition state being such as to prevent either of the 3-hydrogens (or deuteriums) from being *trans* to the leaving chloride or parallel to the developing vacant p-orbital. If we assume that the others all have one 3-hydrogen *trans* and one *gauche* to the leaving chloride ion, then the isotope effect for each type C-H bond must be similar to that for the same type in a methyl group. If they were *exactly* the same, methylene deuteration should give an isotope effect of about 1.32, or slightly less than deuteration of a methyl group, due to the absence of one *gauche* hydrogen. Since the observed effects are larger for methylene deuteration (by 10% or less) some increase due to the electrical influence of the 3-alkyl substituent is indicated. The β -methyl group apparently increases hyperconjugation by stabilizing the partial double bond character in the C₂-C₃ linkage. Since the solvolytic k_H/k_D for 2-chloro-2,3-dimethylpentane-3-*d* is only 1.28¹² (*i.e.*, slightly *smaller* than that believed to be characteristic of a *trans*-hydrogen of a β -methyl group), it might appear that the transition state conformation is such as to prevent the 3-hydrogen from being exactly in the *trans* position.

Deuteration of the β -methylene group in II leads to a solvolytic isotope rate effect of 1.14. The conformation of the initial state and the carbonium ion are represented as



(17) B. L. Murr, Ph.D. Thesis, Indiana University, 1961.

(18) L. S. Bartell, *J. Am. Chem. Soc.*, **83**, 3567 (1961).

(19) V. J. Shiner, Jr., B. L. Murr and G. Heinemann, *ibid.*, **85**, 2418 (1963).

(14) S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953).

(15) V. Gold and F. A. Long, *J. Am. Chem. Soc.*, **75**, 4543 (1953).

(16) V. J. Shiner, Jr., *ibid.*, **75**, 2925 (1953).

The dihedral angles between the two C-D bonds and the C-Cl axis must be near 0° and 120° in the initial state, 30° and 150° in the carbonium ion. If the carbonium ion is considered to have a plane of symmetry the two C-D bonds are equivalent in that structure. In the transition state they would not be exactly equivalent but probably no serious error would be introduced in considering them almost so and assigning the isotope effect for a C-D bond with dihedral angle of 30° as approximately 1.07. The variation of k_H/k_D with conformation seems then to be

Dihedral angle	30°	60°	90°	180°
Isotope effect, k_H/k_D	1.07	1.01	0.99	1.31

Streitwieser, *et al.*,²⁰ reported that *cis*- and *trans*-2-deuteriocyclopentyl toluenesulfonates showed k_H/k_D values for solvolysis in acetic acid at 50° of 1.22 and 1.16, respectively. The stereochemistry should be similar to that for II discussed above and it is reasonable that the *cis* effect would be somewhat larger because to the extent that the transition state differs from the carbonium ion (in being like the initial state) the *cis*-C-D bond would be more nearly parallel to the developing vacant orbital. These isotope effects are both larger than would be expected for a tertiary chloride solvolysis in aqueous ethanol. This seems to be generally true for toluenesulfonate acetolyses,²¹ but unfortunately the data do not seem accurate or extensive enough to allow one to compare quantitatively specific isotope effects in the two systems. The comparison of the *cis*- and *trans*-2-D isotope rate effects in the cyclopentyl tosylate acetolysis does not seem to warrant the conclusion that specific solvation of the β -hydrogen is unimportant in these reactions.²⁰ First, it is invalid to assume that the *isotope effect* caused by such specific solvation would be subject to the *same* stereochemical influences as the *ease* of an E2 elimination process. The former is determined largely by vibrational frequency changes of the isotopically substituted bond on activation while the latter depends on the total free energy of activation. Secondly, it now appears that *cis* (parallel) elimination is more facile than was formerly believed; the difficult eliminations seem to be those where a *parallel* orientation of the orbitals binding the two eliminant fragments is prevented.²² Thirdly, to the extent that the transition state resembles the cyclopentyl cation the *cis*- and *trans*-C-D bonds are equivalent. It is also clear that the similarity of these *cis*- and *trans*-2-D isotope effects does not indicate that there is no conformational influence on the β -deuterium isotope effect in carbonium ion-forming reactions.

It has been suggested that the β -deuterium isotope effect on carbonium ion reaction rates may be due to relief of non-bonded repulsions on activation.¹⁸ It is therefore pertinent to consider whether the larger pattern of substituent influences on such isotope effects here discussed might also be readily explained by variations in these steric interactions. It seems clear that they cannot, and it therefore appears that either such steric influences contribute only in a minor way or that additional steric influences must be postulated to explain these variations. First the isotope effect on the *t*-butyl chloride solvolysis, for which Bartell made his calculation, has now been measured.¹⁷ It is very similar to that observed earlier for *t*-amyl chloride and thus about twice as large as that calculated by the Bartell steric model which even so overestimates the suggested

effect by assuming that the transition state is a planar carbonium ion. Secondly, since more than one-fourth of the steric effect is due to each deuterium substituted *gauche* to the departing chloride ion, the angular dependence of the steric effect would be too small to explain the non-cumulative nature of the isotope effect as 1, 2 and 3 hydrogen atoms of one methyl group in *t*-butyl chloride are replaced by deuterium.^{17,19} Thirdly, the near constant value for the isotope effect whether a β -methyl, methylene or methine group is deuterated cannot be readily accommodated to the simple steric model. Thus the isotope effect caused by the single deuterium atom in 2-chloro-2,3-dimethylbutane-3-*d* is much larger than that calculated for *any single* deuterium atom in the *t*-butyl chloride calculation. If this hydrogen is *trans* to the departing chloride ion in the transition state, the steric model would certainly give a much smaller value than what is observed. Fourthly, it seems apparent that the simple steric model does not provide an explanation for the observation that methylene deuteration has a large effect ($k_H/k_D = 1.40$) on *t*-amyl chloride solvolysis but a small effect on the dimethylneopentylcarbinyl chloride solvolysis ($k_H/k_D = 1.08$). Thus all of these results, which are correlated very nicely by the hyperconjugation postulate and the expected angular dependence, are not predicted or correlated by the simple steric model.

Experimental

N.m.r. spectra were observed using either a Varian DP-60 or A-60 magnetic resonance spectrometer. Spectra were run at 60 Mc. in carbon tetrachloride (or, for ketonic compounds, deuteriochloroform) solutions with tetramethylsilane as the internal reference standard.

11-Acetoxy-9,10-dihydro-9,10-ethanoanthracene was prepared by the method of Alder and Rickert,¹³ recrystallized from benzene and then from methanol; m.p. 98.1–99.0°, lit. 100–101°.

11-Hydroxy-9,10-dihydro-9,10-ethanoanthracene was prepared by hydrolysis of the acetate, recrystallized from ethyl acetate and then from cyclohexane; m.p. 139.0–139.4°, lit. 140–142°.

11-Keto-9,10-dihydro-9,10-ethanoanthracene was prepared by chromic oxide oxidation in glacial acetic acid, by Oppenauer oxidation¹³ and by oxidation with sodium dichromate and sulfuric acid in 50% aqueous acetic acid. These products after recrystallization from absolute alcohol showed identical melting points and mixture melting points; m.p. 151–152°, lit. 152.5–153°. The aliphatic hydrogen region of the n.m.r. spectrum showed: (1) a singlet at 4.76 δ characteristic of the bridgehead hydrogen at position 9; (2) a triplet centered at 4.50 δ with $J = 3$ c.p.s. characteristic of the bridgehead hydrogen at position 10; (3) a doublet at 2.29 δ with $J = 3$ c.p.s. characteristic of the methylene group at position 12.

11-Keto-9,10-dihydro-ethanoanthracene-12,12-*d*₂ was prepared by repeated exchanges of several samples with deuterium oxide in refluxing dioxane using triethylamine as catalyst. A sample of 3.5 g. (0.016 mole) of the ketone was mixed with 5 g. (0.25 mole) of deuterium oxide, 1 ml. of triethylamine and 65 ml. of purified, carefully dried dioxane and refluxed for 68 hr. The solvent was distilled, the residue dried at reduced pressure and analyzed for deuterium by combustion.²³ The material contained only 1.53 atoms of D. Exchange was thus only about 77% complete. Three additional exchange reactions on the same ketone sample but using fresh deuterium oxide were each kept under reflux at least 120 hr. Two additional samples of 6 g. (0.027 mole) each were also put through three such exchanges with 5 ml. (0.25 mole) of deuterium oxide. These preparations were combined to give 12.5 g. (80% recovery) of deuterated ketone. The aliphatic proton region of the n.m.r. spectrum showed: (1) a singlet at 4.82 δ characteristic of the bridgehead hydrogen at position 9; (2) a singlet at 4.54 δ characteristic of the proton at position 10, unsplit because of the absence of hydrogen at position 12; (3) no absorption near 2.3 δ because of the absence of hydrogen at position 12.

Anthracene-9,10-*d*₂ was prepared by a modification of the Martin procedure.^{15,24} To a mixture of 100 ml. (5.0 moles) of deuterium oxide and 150 ml. of toluene was added, in small pieces, 4.5 g. (0.195 mole) of sodium metal. To this was added 10 g. (0.0515 mole) of anthrone and 25 g. (0.38 mole) of powdered zinc. The mixture was refluxed for 5 days. The toluene layer was combined with toluene extracts of the water layer

(20) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

(21) E. S. Lewis and C. E. Boozer, *ibid.*, **76**, 791 (1954).

(22) C. H. DePuy, R. D. Thurn and G. F. Morris, *ibid.*, **84**, 1314 (1962).

(23) V. J. Shiner, Jr., *ibid.*, **74**, 5285 (1952).

(24) E. L. Martin, *ibid.*, **58**, 1438 (1936).

and evaporated to dryness. The residue was purified by dissolving in benzene and passing through grade I alumina; 7 g. (0.038 mole) of anthracene, m.p. 216–217°, was obtained. Combustion analysis showed this material to contain 1.77 atoms of D per molecule.

11-Hydroxy-11-methyl-9,10-dihydro-9,10-ethanoanthracene.—Methylmagnesium iodide was made in the usual way from 1.2 g. (0.05 mole) of magnesium and 7.0 g. (0.049 mole) of methyl iodide in 50 ml. of anhydrous ether. To this was added a solution of 3.5 g. (0.016 mole) of 11-keto-9,10-dihydro-9,10-ethanoanthracene in a mixture of 60 ml. of dry ether and 20 ml. of dry benzene. After standing overnight the mixture was hydrolyzed by the addition of a minimum amount of saturated aqueous ammonium chloride. The organic layer was decanted and combined with two benzene extracts of the residual solids before evaporation. The organic residue was taken up in hot cyclohexane, treated with decolorizing charcoal while hot and recrystallized. The product weighed 2.5 g. (0.011 mole), yield 69%, m.p. 133.5–134°, mixture m.p. with the corresponding secondary alcohol 115–120°. A second crop of 0.5 g., m.p. 129.5–132°, was obtained from the mother liquor. The first crop was crystallized five additional times from cyclohexane; m.p. 134–135°. *Anal.* Calcd. for $C_{17}H_{18}O$: C, 86.40; H, 6.83. Found: C, 86.46; H, 6.84. The aliphatic proton region of the n.m.r. spectrum showed: (1) a singlet at 3.93 δ characteristic of the proton at position 9; (2) an unresolved triplet centered at 4.16 δ characteristic of the proton at position 10; (3) an unresolved group centered at 1.75 δ characteristic of the methylene group at position 12; (4) a singlet at 1.08 δ characteristic of the 11-methyl group.

11-Hydroxy-11-methyl-9,10-dihydro-9,10-ethanoanthracene-12,12- d_2 was prepared using a procedure analogous to that described above for the undeuterated tertiary alcohol but starting with the exchanged ketone prepared as described above. The n.m.r. spectrum was the same as that described for the undeuterated alcohol except that the group at 1.68 δ was missing and the absorption at 4.05 δ appeared as a singlet.

11-Hydroxy-11-methyl-9,10-dihydro-9,10-ethanoanthracene-9,10- d_2 was prepared in a fashion exactly analogous to the preparation described for the undeuterated compound, beginning with anthracene-9,10- d_2 prepared as described above. The n.m.r. spectrum was essentially the same as that for the undeuterated compound except that the singlet at 3.9 δ and the triplet at 4.16 δ were absent.

11-Chloro-11-methyl-9,10-dihydro-9,10-ethanoanthracene.—The chloride was made from the tertiary alcohol and thionyl chloride. Several experiments indicated that a relatively stable chlorosulfite may be formed which is only decomposed by heating to around 80° for 5 to 10 min. Some exocyclic olefin seems to be produced in the same reaction and crystallizes more readily. In addition, chromatography on grade I Woelm alumina caused dehydrohalogenation of tertiary chloride. Therefore the best purification procedure seemed to be passage through grade II alumina column (which apparently does not separate the olefin but removes some other contaminants) followed by recrystallization first from *n*-hexane and then from methanol. A typical preparation follows: 0.100 g. (0.42 mmole) of the tertiary alcohol was mixed with 0.216 g. (1.8 mmoles) of thionyl chloride and heated on a hot-plate for a few minutes to evaporate the excess thionyl chloride, the last traces of which were removed at reduced pressure. The residue weighed 0.109 g. This was chromatographed in hexane on 50 ml. of grade II alumina, 67 mg. being eluted from the fourth to the ninth 15-ml. fractions. This was recrystallized from methanol, from *n*-hexane and from methanol again; m.p. 92.5–93.0°. Another preparation giving no depression in melting point with the sample described above, was used for elemental analysis. *Anal.* Calcd. for $C_{17}H_{16}Cl$: C, 80.14; H, 5.93. Found: C, 80.15; H, 6.27. The aliphatic proton region of the n.m.r. spectrum showed a singlet at 4.23 δ characteristic of the proton at position 9, a triplet centered at 4.00 δ with $J = \sim 2.5$ c.p.s. characteristic of the proton at position 10, a quartet at 2.11 δ with $J = 12$ c.p.s. (further split by the

proton at position 10, $J = 3$ c.p.s.) characteristic of the 12-methylene group and a singlet at 1.40 δ characteristic of the 11-methyl group.

11-Chloro-11-methyl-9,10-dihydro-9,10-ethanoanthracene-12,12- d_2 was prepared from the corresponding tertiary alcohol and thionyl chloride. The n.m.r. spectrum was similar to that for the undeuterated material except that the absorption at 2.11 δ was missing and that at 4.00 δ was an unsplit singlet.

11-Chloro-11-methyl-9,10-dihydro-9,10-ethanoanthracene-9,10- d_2 was prepared from the corresponding tertiary alcohol and thionyl chloride. The n.m.r. spectrum was similar to that of the undeuterated material except that the peaks at 4.23 and 4.00 δ were missing and the absorption at 2.11 δ was a quartet not having the secondary splitting shown by the non-deuterated chloride.

Kinetic Experiments.—Solvolysis rates were measured conductometrically in 60% by volume aqueous ethanol at 45.00°. The cell volume was 50 ml. and the cell constant (at 25°) was 0.2259. The concentration of chloride used was from 0.3 to $1 \times 10^{-3} M$. The reactions were followed for 2 half-lives and infinity readings taken at 10 to 20 half-lives. Point by point constants were calculated using the integrated first-order rate law and assuming that the concentration was proportional to the conductance. Reproducibility in the rate constant was generally of the order of 0.1 to 0.5%.

Solvolysis Products.—A 0.499-g. (1.95 millimoles) sample of the tertiary chloride IIa was stirred for 13 hr. in 350 ml. of 60% (by volume) aqueous ethanol at 45°. The water was removed by azeotropic distillation with 50 ml. of added chloroform using a phase-separating head. Most of the ethanol was then removed by distillation, *n*-hexane added and the last traces of ethanol removed as the azeotrope. The solution was concentrated to 15 ml. and chromatographed on 16.6 g. of Woelm grade II alumina. Elution with 200 ml. of *n*-hexane yielded a first fraction of 0.218 g.; 260 ml. of benzene eluted a second fraction of 0.239 g.; 195 ml. of methanol yielded 0.004 g. of a third fraction.

The first fraction was separated into two components by chromatography on 15 g. of grade II alumina with *n*-hexane. The first component, 0.081 g. (0.371 mmole), yield 19%, m.p. 103.5–104°, showed moderate infrared absorption at 1650 cm^{-1} and strong absorption at 1450, 1460, 869 and 874 cm^{-1} . *Anal.* Calcd. for $C_{17}H_{24}$: C, 93.54; H, 6.76. Found: C, 93.69; H, 6.62. These results and the n.m.r. spectrum (see below) are entirely consistent with the assignment of the exocyclic olefin structure IV to this material. The n.m.r. spectrum showed a large band near 7.50 δ for the aromatic protons, a singlet at 4.63 δ for the terminal methylene protons, a singlet at 5.03 δ characteristic of the proton at position 9, an unresolved triplet centered at 4.22 δ characteristic of the proton at position 10 and a doublet centered at 2.37 δ with $J = 2$ c.p.s. characteristic of the methylene group at position 12.

The second component (0.119 g.) of the first original fraction was an oil which could not be obtained crystalline even after rechromatographing on grade II alumina. It is inferred from the infrared spectrum, which showed strong absorption at 1120 cm^{-1} , and the n.m.r. spectrum that this compound is the ethyl ether V. If this structure assignment is correct, the yield was 0.45 mmole or 23%.

The second fraction, 0.239 g. (1.01 mmoles), yield 52%, of the original chromatographic separation was shown by mixture melting point and infrared spectrum to be identical with the previously synthesized tertiary alcohol III.

The small third fraction of the original chromatographic separation was not identified.

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