

benzhydrol, m.p. 44.0–44.5 (uncor.), reported¹² 43°; *p*-isopropylbenzhydrol, m.p. 59.5–60.6 (uncor.), reported¹² 60°; *p*-*t*-butylbenzhydrol, m.p. 81.5–82 (uncor.), reported¹² 82°; *m*-methylbenzhydrol, m.p. 54–55 (uncor.), reported¹² 53–54°.

p-*n*-Propylbenzhydrol gave m.p. 41–42°. *Anal.* Calcd. for C₁₆H₁₈O: C, 84.91; H, 8.02. Found: C, 84.80; H, 8.12. *p*-Isobutylbenzhydrol formed gels on attempts at recrystallization from petroleum ether and could not be satisfactorily recrystallized. The chloride prepared in the manner described below gave good first-order rate constants and was therefore presumably pure enough.

p-Neopentylbenzhydrol gave m.p. 83.5–84.0° and mixed m.p. with *p*-*t*-butylbenzhydrol 70–72°. *Anal.* Calcd. for C₁₈H₂₂O: C, 84.99; H, 8.72. Found: C, 84.61; H, 9.1.

m-*t*-Butylbenzhydrol gave m.p. 67.5–68°. *Anal.* Calcd. for C₁₇H₂₀O: C, 84.95; H, 8.39. Found: C, 84.85; H, 8.48.

Benzhydryl Chlorides.—A portion of the alkylbenzhydrol was placed in a vial and anhydrous hydrogen chloride was passed through until the solid hydrol dissolved. The mixture was taken up in ether, washed rapidly with ice-cold water, and the ether layer after separation was dried with potassium carbonate. The ether was removed on the steam-bath and the last traces were removed under reduced pressure. The chlorides obtained in this way were used without further purification and in all cases gave good first-order solvolysis rate constants when followed to more than 75% reaction. Further, *p*-methylbenzhydryl chloride prepared in separate batches gave essentially the same solvolysis rate constants.

Preparation of Solvents.—The reaction solvents were prepared by mixing the appropriate volumes, measured at 25°, of acetone and water or of ethanol and water. The percentage designations refer to volume per cent., *i.e.*, "80%" aqueous ethanol was made by mixing four volumes of ethanol and one of water. The ethanol was dried by distilling added benzene from commercial absolute alcohol through a packed column. After removing the water benzene–alcohol azeotrope (b.p. 64.9°), the ethanol–benzene azeotrope (b.p. 68.2°) and a generous foreshot of ethyl alcohol (b.p. 78.5°), the material to be used was collected. Eastman Kodak Co. spectro grade acetone was used without additional purification. Infrared analysis based on the water absorption band at about 2.8 μ showed that the acetone contained 0.3% by weight of water. The solvent compositions given are not corrected for this small water content of the acetone. The water used was distilled and subsequently passed through an ion-exchange column. The conductances of the solutions used were always less than 1×10^{-4} ohm⁻¹ at the start of each kinetic experiment.

Kinetic Apparatus.—The solvolysis rate constants could be measured very simply and accurately by a conductance method because the reactions produce hydrogen chloride in

initially non-ionic solutions. The constant temperature bath containing ethylene glycol and water was kept at 0° by continuous refrigeration and intermittent heating. The temperature regulation was $\pm 0.01^\circ$ set with an accuracy of $\pm 0.01^\circ$ by a Beckman thermometer calibrated in an ice-water-bath. The conductivity apparatus consisted of a Leeds and Northrup variable frequency oscillator operated at 2,000 c.p.s., an amplifier and a Jones–Josephs bridge.²⁴ An oscilloscope was used to determine the balance point. A number of conductance cells were made using 10 \times 14 mm. platinum electrodes fixed 5 mm. apart. The electrodes were platinized in a 3% platinum chloride solution. Through the use of standard hydrogen chloride solutions in the respective solvents it was determined that the conductivity was proportional to hydrogen chloride concentration in the range from 5 to 100×10^{-4} ohm⁻¹ for 80% aqueous acetone and from 5 to 75×10^{-4} ohm⁻¹ for 90% aqueous ethanol. Absolute alcohol showed marked deviations from linearity and was not used as a reaction solvent. It was deemed unnecessary to check the linearity relationship in 70 and 66.7% aqueous acetone. The conductivity of these solutions was stable at least for several days.

Kinetic Procedure.—Fifteen to twenty milliliters of the solvent was poured into an 8-inch test-tube and the conductance cell with stopper inserted into the tube. After allowing at least one-half hour for the cell and contents to come to temperature the cell was raised in the tube and one drop of the organic chloride was added from a capillary pipet. The tube and cell was closed and shaken vigorously in the bath for 30 seconds. Since the reactions were all first order, the zero resistance (R_0) was taken at any convenient time (t_0). The reaction was followed for at least two half-lives during which period the resistance of the cell was measured 40 to 80 times. The rate constants for the individual points were calculated from the integrated first-order rate law in the form

$$k = \frac{2.303}{t} \log \frac{1/R_\infty - 1/R_0}{1/R_\infty - 1/R_t}$$

where R_t is the cell resistance at time t and R_∞ is the resistance after 10 to 20 half-lives. The rate constants and standard deviations recorded in Table I were obtained from a least squares treatment of the plot of $\log (1/R_\infty - 1/R_0 / 1/R_\infty - 1/R_t)$ vs. time. Fourteen to twenty points chosen at random were used in the least squares calculations. In a trial calculation on one run the use of 40 instead of 20 points had no appreciable effect on the results. Standard deviations in the rate constants were all of the order of 0.1%. Duplicate runs never differed by more than 0.5%.

(24) P. H. Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

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The Effects of Deuterium Substitution on the Rates of Organic Reactions. IV.¹ Solvolysis of *p*-Deuteroalkyl Benzhydryl Chlorides²

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p-CD₃, *p*-CH₂CD₂, *p*-(CH₃)₂CHCD₂, and *p*-(CH₃)₂CD-benzhydryl chlorides were synthesized and their solvolysis rates compared with those of the corresponding protium analogs in several different solvents. The isotope rate effects (1) are positive and of the order of 6% or less, (2) become progressively smaller in the order listed above and (3) apparently show a marked solvent dependence.

The rather large secondary deuterium isotope rate effects that have been observed in certain organic

(1) Part III, *THIS JOURNAL*, **76**, 1603 (1954).

(2) (a) Abstracted from the thesis submitted by C. J. Verbanic to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree. (b) Presented in part before the Division of Organic Chemistry at the 129th National Meeting of the American Chemical Society, Dallas, Texas, April 12, 1956. (c) Supported in part by the National Science Foundation.

reactions in recent years^{1,3} give promise of providing a very powerful tool for the investigation of mechanisms of organic reactions with particular reference to the nature of the bonding of certain hydrogen atoms (which can be isotopically substituted) in transition states. However, before these secondary

(3) E. S. Lewis and C. E. Boozer, *THIS JOURNAL*, **76**, 791, 794 (1954).

isotope rate effects can be interpreted unambiguously in terms of conventionally recognized modes of intramolecular electronic transmission, more systematic data from presumably well characterized reactions must be obtained and interpreted. Such results, besides serving to clarify our understanding of secondary isotope rate effects, may also cause some revision or refinement of current ideas concerning the reactions studied.

With these aims in mind the authors decided to measure secondary isotope rate effects in the solvolysis of *p*-alkylbenzhydryl chlorides. This class of reactions provides some of the best data for the Baker-Nathan effect that exist in the literature.⁴ In addition, since the solvent has come to be recognized as an important factor in the Baker-Nathan effect,⁵ it was hoped that a study of solvent effects on the isotope rate effect would prove fruitful. At the start of this work it was not known whether a measurable secondary isotope rate effect could be transmitted across a molecule through unsaturated linkages. After this program was well underway a communication by Lewis and Coppinger⁶ confirmed that they had been able to observe such an effect in the solvolysis of methyl-*p*-tolylcarbinyl chloride.

p-Methyl-*d*₃-benzhydryl chloride was obtained via the corresponding benzhydrol from toluene- α -*d*₃ made by the deuteriumolysis of benzyl- α -*d*₂ alcohol over palladium-on-charcoal. The benzyl- α -*d*₂ alcohol was made by lithium aluminum deuteride reduction of ethyl benzoate. The other deuterioalkylbenzhydryl chlorides were made from the corresponding deuterioalkylbenzenes. The other deuterioalkylbenzenes were made by deuteriumolysis of the corresponding α -hydroxy or α -keto benzene derivatives. Combustion deuterium analyses were carried out on all of the deuterated benzhydrols and on several of the other compounds as well. These results are given in Table I.

TABLE I
DEUTERIUM ANALYSES

| Compound | Average atoms D/molecule | Average atoms D per deuterated bond |
|--|--------------------------|-------------------------------------|
| Toluene- α - <i>d</i> ₃ | 2.71 | 0.90 |
| <i>p</i> -Methyl- <i>d</i> ₃ -benzophenone | 2.66 | .886 |
| <i>p</i> -Methyl- <i>d</i> ₃ -benzhydrol | 2.54 | .846 |
| <i>p</i> -Methyl- <i>d</i> ₃ -benzhydryl chloride | 2.46 | .82 |
| <i>p</i> -Ethyl- α - <i>d</i> ₂ -benzhydrol | 1.82 | .91 |
| <i>p</i> -Isopropyl- α - <i>d</i> -benzhydrol | 0.92 | .92 |
| <i>p</i> -Isobutyl- α - <i>d</i> ₂ -benzhydrol | 1.72 | .86 |

The solvolysis rate constants were measured conductimetrically as described in a preceding paper.⁵ The results are given in Table II.

The duplicate values of the rate constants given show that they could be reproduced generally to within 0.5% or better. One run each on the *p*-methyl and *p*-methyl-*d*₃ compounds was done using a different preparation of the alkylbenzhydryl chloride made from a sample of the alkylbenzhydrol which had been recrystallized one additional time.

(4) C. K. Ingold, E. D. Hughes and N. Taher, *J. Chem. Soc.*, 940 (1940).

(5) V. J. Shiner, Jr., and C. J. Verbanic, *THIS JOURNAL*, **79**, 369 (1956).

(6) E. S. Lewis and G. M. Coppinger, *ibid.*, **76**, 4995 (1954).

TABLE II
SOLVOLYSIS RATES OF *p*-ALKYLBENZHYDRYL CHLORIDES AT 0°^a

| <i>p</i> -Alkyl group | Solvents | | | |
|--|--------------------|---------------|---------------|-----------------|
| | "90%" ethanol | "80%" acetone | "70%" acetone | "66.7%" acetone |
| Methyl | 6.323 | 0.8617 | 6.306 | 12.166 |
| | 6.341 | .8625 | 6.312 | 12.183 |
| | 6.315 ^b | | | |
| Methyl- <i>d</i> ₃ | 6.168 | .8146 | 6.093 | 11.924 |
| | 6.195 | .8156 | 6.067 | 11.920 |
| | 6.158 ^b | | | |
| Ethyl | 5.632 | .6512 | 4.661 | 8.836 |
| | 5.613 | .6520 | 4.636 | 8.837 |
| Ethyl- α - <i>d</i> ₂ | 5.567 | .6353 | 4.561 | 8.729 |
| | 5.585 | .6357 | 4.563 | 8.730 |
| Isopropyl | 4.796 | .4973 | | |
| | 4.789 | .4979 | | |
| Isopropyl- α - <i>d</i> | 4.800 | .4941 | | |
| | 4.801 | .4947 | | |
| Isobutyl | | .5011 | | |
| | | .5029 | | |
| Isobutyl- α - <i>d</i> ₂ | | .4929 | | |
| | | .4915 | | |
| Methyl (25°) | | 17.273 | | |
| | | 17.377 | | |
| Methyl- <i>d</i> ₃ (25°) | | 17.00 | | |
| | | 17.13 | | |

^a Units are 10⁻⁴ sec.⁻¹. ^b Separate preparation of the halide from the hydrol.

These constants agreed with the others within the usual limits of error. The data of Table II are further summarized in Table III.

TABLE III
RATE RATIOS FOR THE SOLVOLYSIS OF ALKYL- AND DEUTERO-ALKYLBENZHYDRYL CHLORIDES

| | Solvents | | | |
|---|---------------|---------------|---------------|-----------------|
| | "90%" ethanol | "80%" acetone | "70%" acetone | "66.7%" acetone |
| Dielectric constant ⁷ | 28.1 | 29.6 | 35.7 | 37.5 |
| <i>p</i> -Methyl-/ <i>p</i> -methyl- <i>d</i> ₃ - | 1.025 | 1.058 | 1.038 | 1.021 |
| <i>p</i> -Ethyl-/ <i>p</i> -ethyl- α - <i>d</i> ₂ - | 1.009 | 1.025 | 1.019 | 1.012 |
| <i>p</i> -Isopropyl-/ <i>p</i> -isopropyl- α - <i>d</i> - | 0.998 | 1.006 | | |
| <i>p</i> -Isobutyl-/ <i>p</i> -isobutyl- α - <i>d</i> ₂ - | | 1.020 | | |

It can be seen that the effects, although small, are for the most part positive and beyond the experimental error. Thus α -deuteration of the *p*-alkyl group definitely slows the solvolysis rate. This effect is similar to the effect of β -deuteration in the solvolysis of alkyl chlorides and related compounds observed by Shiner¹ and by Lewis and Boozer³ and also similar to the effect of *p*-alkyl deuteration observed by Lewis and Coppinger⁶ in the acetolysis of methyl-*p*-tolylcarbinyl chloride.

It is of interest that α -deuteration of the isopropyl group does not produce as large an effect as α -deuteration of the *p*-ethyl group which in turn is not as effective in lowering the rate as deuteration of

(7) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," A.C.S. Monograph No. 95, 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

the *p*-methyl group. It has been observed previously that in the solvolysis of alkyl carbinyl chlorides α -deuteration (beta to the chlorine) of either methyl, ethyl or isopropyl groups produced effects of nearly the same magnitude.¹ The effects in the three groups here are apparently not in a 3:2:1 ratio corresponding to the number of α -hydrogens deuterated or available for hyperconjugation. The effects of solvent variation on the isotope rate effects are difficult to interpret. Since the effects themselves are frequently near the limits of error there is unfortunately a good deal of uncertainty regarding the trends apparently shown in the effects as solvent changes. However, the regularity of the trends observed would seem to speak for their reliability.

If there were solvation enhancement of hyperconjugation one would expect that in a solvent of higher dielectric constant the ionic charge would be more highly dispersed and specific solvation at the α -C-H bonds would be looser (if the solvating species remained the same) and the isotope rate effect would be smaller. The observed trends in the aqueous acetone solvents confirm this expectation. However, the demand for specific localized solvation should be proportional to the electron demand at the reaction center which is measurable by ρ .⁸ Examination of the data in the previous paper⁵ shows that the changes in ρ are in the expected direction but are not nearly as large as the changes observed in the isotope rate effects.

It is difficult to explain the large solvent effects on the isotope rate effects without involving the solvent at the site of isotopic substitution, but it is obvious that more information on the whole question of solvent effects on secondary isotope rate effects must be obtained before a satisfactory explanation can be forthcoming. Further work on this point is in progress in these laboratories. The isotope rate effect in the case of the *p*-isobutyl- α - d_2 compound is smaller than that for the *p*-ethyl- α - d_2 compound, suggestive of steric inhibition of hyperconjugation, but this result must be considered to be on the borderline of the limits of experimental error.

The rates of solvolysis of the *p*-methyl- and *p*-methyl- d_3 -benzhydryl chlorides were also measured at 25° in an attempt to determine the temperature coefficient of the isotope rate effect. The free energy of activation for the deuterium compound is 11.6 ± 0.2 calories per C-D bond greater than that of the hydrogen compound at 0° and 3.5 ± 1.5 cal. per C-D bond greater at 25°. This leads to an activation energy of 106 ± 20 calories per C-D bond greater and a log frequency factor of 0.075 ± 0.0015 per C-D bond greater for the deuterium compound. This compares reasonably well with calculations based on the data of Lewis and Copinger⁶ for isotope rate effects in the acetolysis of methyl *p*-tolyl- α - d_3 carbinyl chloride which gives

(8) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapt. VII.

154.5 and 0.084 for the corresponding quantities in that reaction. In these two examples the changes in the two Arrhenius parameters due to deuteration are of about the same relative importance (although both are much smaller) as they are in the solvolysis of 2,3-dimethyl-2-chlorobutane-3- d .¹

Experimental

Benzyl- α - d_2 Alcohol.—Ethyl benzoate, 10.5 g. (0.07 mole), b.p. 210–211°, n_D^{25} 1.5032, was reduced with 1.58 g. (0.0386 mole) of lithium aluminum deuteride using the general procedure of Brown.⁹ The product was distilled through a spinning band column and collected from 203–204°; yield 7.5 g. (0.069 mole), 96%.

Dimethylphenylcarbinol.—This compound was prepared by the conventional Grignard reaction procedure from bromobenzene and acetone. The product was distilled at 62° (1 mm.) from the spinning band column and obtained in 68% yield.

Deuteroalkylbenzenes.—A Parr low-pressure hydrogenation apparatus was modified to eliminate the large gas reservoir and subsequently calibrated in the usual way with a 250-ml. pressure bottle. The α -hydroxy and α -keto benzene derivatives were reduced with hydrogen or deuterium¹⁰ gas in the absence of solvent with an amount of 30% palladium-on-charcoal catalyst equal to about 2 to 10% of the weight of the material to be reduced. After near the theoretical amount of hydrogen or deuterium had been taken up, the products were removed from the bottle at low pressure and caught in a trap surrounded by solid carbon dioxide. After distillation the yields were of the order of 65 to 80%. With the exception of isobutyrophenone, which required a temperature of 50 to 55°, all the reductions were done at room temperature. The rates of the reductions seemed to be independent of (1) the concentration of ketone or carbinol, (2) the pressure of the gas and (3) the isotopic nature of the gas (hydrogen or deuterium).

***p*-Alkyl- d -benzophenones, Benzhydrols and Benzhydryl Chlorides.**—These compounds were prepared using the same methods previously described.⁵

Oxidation of *p*-Methyl- d_3 -benzhydrol.—In a 100-ml. round-bottom flask, 0.200 g. of sodium carbonate, 0.8 g. of potassium permanganate and 0.2 g. of *p*-methyl- d_3 -benzhydrol and 50 ml. of water were refluxed for two hours. The reaction mixture was cooled and acidified with 2 *N* hydrochloric acid. Sodium bisulfite was added to remove the excess permanganate and manganese dioxide. The suspension was filtered and dried. The powder was dissolved in 5% sodium hydroxide, heated, and the manganese dioxide that formed was removed by filtration. The solution was then poured slowly with vigorous stirring into 2 *N* hydrochloric acid to which some sodium bisulfite had been added. In this way 0.09 g. of *p*-benzoylbenzoic acid was obtained which gave a neutralization equivalent of 205; calcd. 214. The acid showed no deuterium bonds in the infrared spectrum and combustion analysis also showed that no deuterium was present. This indicates that in the parent *p*-methylbenzhydrol all of the deuterium was in the methyl group.

Kinetic Apparatus, Procedure, Calculations and Solvents.—The apparatus, techniques and solvents were the same as in the previous paper.⁵

Deuterium Analyses.—Combustion analyses for deuterium using the gradient density tube method were done as described in an earlier paper.¹¹ The analyses are generally reproducible within $\pm 2\%$.

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(9) W. G. Brown in "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., p. 263.

(10) Obtained from the Stuart Oxygen Co., San Francisco, Cal., 99.5% isotopically pure.

(11) J. R. Johnson and V. J. Shiner, Jr., THIS JOURNAL, **75**, 1350 (1953).