in place of piperidine and titrating with 0.3 M hydrochloric acid and brom phenol blue. Two blank determinations on the di-n-butylamine solution were made at the beginning of each run and one blank determination on the di-n-butylamine solution for each phenyl isocyanate titration if the interval was more than 2 hr. Two blank determinations were made on the phenyl isocyanate solution at the beginning of each run. A blank on the phenyl isocyanate solution was made during the run if a time was more than 2 hr. from a previous blank.

Materials.—Toluene and xylene were purified by distillation from sodium. Triethylamine and di-n-butylamine were fractionated from sodium hydroxide after standing for several days over solid sodium hydroxide. The three thiols were dried by storage for several days over calcium oxide and distilling from the calcium oxide. Eastman Kodak Co. phenyl isocyanate was fractionated, the fraction b.p. 164.5–165.5° being used. Acetone was dried and purified by storage over and distillation from Linde molecular sieve #4A. All reagents and solvents, except the acetone, were stored in dry glass-stoppered bottles in the dry-box until used.

Preparation of n-Butyl Thiolcarbanilate.[5]—To a solution of 3.2 g. (0.0355 mole) of 1-butanethiol and 0.0084 g. (0.0006 mole per liter) of triethylamine in 70 ml. of dry toluene was added a solution of 4.11 g. (0.0345 mole) of phenyl isocyanate in 70 ml. of dry toluene. This mixture was set aside at approximately 25° for 2 days. After removal of the solvent, the excess thiol and amine, the product crystallized as long needles, yield 7.1 g. (98.5%). On recrystallization from alcohol 6.8 g. (94%) was recovered, m.p. 69°, λ_{max} 249 mμ. *Anal.* Calcd. for $C_{11}H_{15}ONS$: N, 6.70; S, 15.30. Found: N, 6.82; S, 15.41.

Preparation of t-Butyl Thiolcarbanilate.—To a solution of 4.5 g. (0.05 mole) of 2-methylpropane-2-thiol and 0.2 g. (0.02 mole per liter) of triethylamine in 50 ml. of dry toluene was added a solution of 2.9 g. (0.0244 mole) of phenyl isocyanate in 50 ml. of dry toluene. The mixture was allowed to stand at approximately 25° for 7 days, during which period a crystalline precipitate formed. After removal of the solvent and the excess reactants, the product crystallized in long needle crystals; yield 5.1 g. (100%). When recrystallized from benzene, 4.5 g. (88%) was recovered, m.p. 147.5°. There is a marked tendency to sublime at approximately 110°; λ_{max} 254 mμ. *Anal.* Calcd. for $C_{11}H_{15}ONS$: N, 6.70; S, 15.30. Found: N, 6.66; S, 15.28.

Preparation of n-Dodecyl Thiolcarbanilate.—To a solution of 6.7 g. (0.0331 mole) of 1-dodecanethiol and 0.00795 g. (0.0006 mole per liter) of triethylamine in 70 ml. of dry toluene was added a solution of 3.9 g. (0.0328 mole) of phenyl isocyanate in 70 ml. of dry toluene. The mixture was allowed to stand at approximately 25° for 3 days. After removal of the solvent and excess reactants, the product crystallized as plates, yield 10.3 g, (98%). On recrystallizing from ethanol 9.1 g. (87%) was recovered, m.p. 72°, λ_{max} 2.51 mμ. *Anal.* Calcd. for $C_{19}H_{31}ONS$: N, 4.36; S, 9.96. Found: N, 4.14; S, 10.13.

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(5) This compound has been made by a different method by J. W. Batty, H. E. Jackson and F. G. Jeffers, British Patent 599,178, March 5, 1948; m. p. 68°.

[CONTRIBUTION NO. 743 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Solvent Effects on the Rates of Solvolysis of Some Alkylbenzhydryl Chlorides[1]

BY V. J. SHINER, JR., AND C. J. VERBANIC[2]

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The rates of solvolysis of a number of alkylbenzhydryl chlorides were determined conductimetrically in aqueous ethanol and aqueous acetone solutions. The substituent groups studied, in decreasing order of their effectiveness in promoting reactivity, were: p-methyl, p-ethyl, p-n-propyl, p-isopropyl, p-isobutyl, p-neopentyl, p-t-butyl, m-methyl and m-t-butyl. It has been found that the relative rate constants show a marked systematic dependence upon the composition of the aqueous solvent. The order of reactivity of the m-methyl and m-t-butyl compounds can be reversed by proper choice of solvent. The importance of the role of the solvent in kinetic studies of the Baker–Nathan effect is thus emphasized. The rates of solvolysis of the benzhydryl chlorides with the less highly branched substituents in general are more sensitive to solvent variations than their homologs with the more highly branched alkyl substituents. These results may be most readily rationalized in terms of solvation assistance to hyperconjugation and/or of steric hindrance to solvation.

The problem of the mode of electron release of saturated alkyl groups attached to unsaturated centers has been the subject of considerable investigation and discussion recently.[3–6] It is apparent that the concepts of the inductive and the hyperconjugative effects alone do not suffice to explain the pertinent data. Several additional effects have been proposed[7–11] and the importance of hyperconjugation has been questioned.[3] Nevertheless the data presently available do not seem to give a sufficient basis for judging conclusively the merits of the different proposals. The Baker–Nathan effect has probably been most clearly demonstrated by Hughes, Ingold and Taher in their studies on the solvolysis of p-alkylbenzhydryl chlorides.[12] In spite of, and indeed mainly because of, these extensive investigations it seemed that additional studies on this system would be pertinent to the present problem.

The approach has been to synthesize a series of α- and β-branched p-alkylbenzhydryl chlorides and to study their solvolysis rates as a function of solvent composition in "80%," "70%," "66.7%" aqueous acetone and "90%" aqueous alcohol at 0°. The rate measurements were made conductimetrically using a Jones–Joseph type conductance bridge. The mechanism of the solvolysis reactions of these compounds has been the object of considerable investigation by numerous workers.[12] The

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(1) (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.

(2) Hooker Electrochemical Co., Niagara Falls, N. Y.

(3) W. M. Schubert and W. A. Sweeney, *J. Org. Chem.*, **21**, 119 (1956).

(4) A. Burawoy and E. Spinner, *J. Chem. Soc.*, 2085 (1955).

(5) V. J. Shiner, Jr., M. J. Boskin and M. L. Smith, THIS JOURNAL, **77**, 5525 (1955).

(6) V. J. Shiner, Jr., *ibid.*, **78**, 2653 (1956).

(7) E. Berliner and F. Berliner, *ibid.*, **72**, 222 (1950).

(8) P. W. Robertson, J. K. Heyes and B. E. Swedlund, *J. Chem. Soc.*, 1014 (1952).

(9) C. C. Price and W. J. Belanger, THIS JOURNAL, **76**, 2682 (1954).

(10) G. Baddeley and M. Gordon, *J. Chem. Soc.*, 2190 (1952).

(11) R. T. Arnold and W. L. Truett, THIS JOURNAL, **73**, 5508 (1951).

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

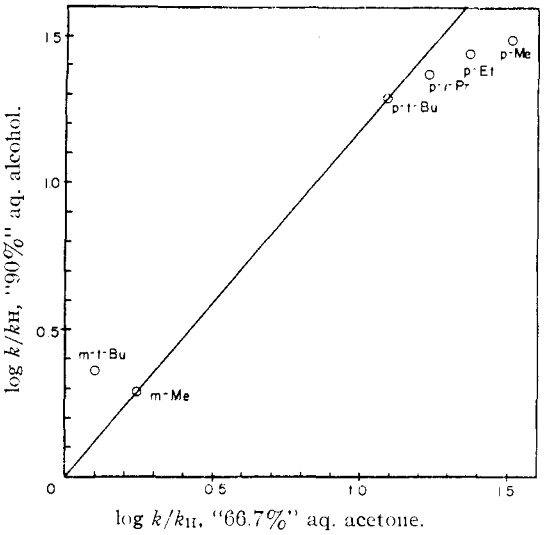

Fig. 1.—Solvolysis of *p*-alkylbenzhydryl chlorides at 0°.

discussion of the details of the mechanism is beyond the scope of this paper, but it seems certain that in the concentration ranges used in this work and in the absence of any dissolved salts the rates being measured without any complications involve the heterolysis of the carbon–chlorine bond to form the solvated chloride anion and benzhydryl cation. Because of the sensitivity of the conductance method it was possible to study the rates in solutions in the concentration range around 0.001 *M*. Thus all salt and mass law effects were minimized. It was shown by independent measurements that in these concentration ranges the conductivity of hydrogen chloride solutions in the solvents used at 0° was directly proportional to the concentration. The first-order rate constants were calculated by the method of least squares and showed standard deviations of around 0.1%. Duplicate runs never differed by more than 0.5%. The rate constants obtained are given in Table I.

TABLE I

RATES OF SOLVOLYSIS OF ALKYLBENZHYDRYL CHLORIDES IN VARIOUS SOLVENTS AT 0°[a]

Alkyl group	"90%" alcohol	"80%" acetone [b]	[c]	"70%" acetone	"66.7%" acetone
p-Methyl	6.326	0.8621	0.835	6.309	12.17
p-Ethyl	5.625	.6516	.626	4.648	8.836
p-*n*-Propyl		.5692		4.085	7.649
p-Isopropyl	4.792	.4976	.4695	3.515	6.507
p-Isobutyl		.5020		3.451	6.298
p-Neopentyl		.4006		2.679	5.017
p-*t*-Butyl	3.967	.3874	.359	2.610	4.699
m-Methyl	0.396	.04680		0.3408	0.6538
m-*t*-Butyl	.470	.03938		.2641	.4774
Benzhydryl	.205	.02618	.0282	.1942	.3792

[a] Units are 10^{-4} sec.$^{-1}$. [b] This investigation. [c] Hughes, Ingold and Taher, *J. Chem. Soc.*, 940 (1940).

Of the kinetic constants reported here, only the *p*-methyl-, *p*-ethyl-, *p*-isopropyl-, *p*-*t*-butyl- and benzhydryl chlorides in "80%" aqueous acetone have been reported previously.[12] These results are given in column 3 of the table and comparison with column 2 shows good agreement between the two investigations. Rate constants for the solvolysis of *p*-*n*-propyl-, *p*-isobutyl-, *p*-neopentyl-, *m*-methyl- and *m*-*t*-butylbenzhydryl chlorides have not been reported previously.

In any of the four solvents one can note the following relationships in the effects of substituents in promoting the solvolysis rate: (1) The order *p*-Me > *p*-Et > *p*-*i*-Pr > *p*-*t*-Bu > *p*-H is essentially the same as that previously observed by Hughes, Ingold and Taher[12] and ascribed to the domination of the hyperconjugative effect over the inductive effect. The reaction is known to be accelerated by electron-releasing groups (compare *p*-Me with *p*-H) so that the electron-releasing abilities of the groups apparently fall in the same order as the rates. The normal inductive order for these groups in *t*-Bu > Et > *i*-Pr > Me. Since the magnitude of hyperconjugation[13] presumably depends mainly on the number of α-C–H bonds the release of electrons by this mechanism is in the order Me > Et > *i*-Pr > *t*-Bu. Both effects are presumably important in facilitating the rate of the benzhydryl chloride solvolyses, but since the order is that corresponding to the hyperconjugative sequence it is presumed that this effect outweighs the inductive effect in this reaction. (2) The sequence *p*-Et > *p*-*n*-Pr > *p*-*i*-Bu > *p*-neo-Pe has not been reported previously for this reaction, but is the same type of sequence that has been observed in the bromination of alkylbenzenes,[7] the bromination of olefins[6] and the elimination reactions of secondary alkyl bromides.[5] Since the number of α-C–H bonds remains constant and the inductive effect should increase in the order given, something in addition to these two electron-release mechanisms must be affecting the rates. This type of result has been ascribed to steric inhibition of solvation,[10] inductive effect on hyperconjugation,[8] second-order hyperconjugation[7] and steric inhibition of hyperconjugation.[10,11] The dependence of the solvolysis rate ratios of the various *p*-alkylbenzhydryl chlorides upon solvent composition emphasizes the importance of the solvent in studies of the Baker–Nathan effect. This is particularly evident in the comparison of the solvolysis rates of the *m*-methyl and *m*-*t*-butyl compounds. The "hyperconjugative" sequence which obtains in the acetone solvents (although it is less marked in the less aqueous ones) is inverted to an "inductive" sequence in 90% ethanol. These results point up again the difference between the physical and chemical evidences for hyperconjugation which has been commented on before.[3,14] The chemical evidence relates almost entirely to rate and equilibrium studies in polar solvents where hyperconjugation is presumably shown up in differences among the apparent electron-releasing abilities of different alkyl groups (see, however, ref. 10 and later comments). Physical evidence refers usually to measurements made in non-polar media or to measurements which are inherently not much affected by solvent interactions. This type of evidence in general either shows up no appreciable differences in electron-releasing abilities among the different alkyl groups or

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(13) J. W. Baker, "Hyperconjugation," Oxford University Press, London, 1952.

(14) V. J. Shiner, Jr., THIS JOURNAL, **76**, 1003 (1954).

shows slight differences falling in an inductive order. Until the reason for this discrepancy and for the important influence of solvent are fully explained the qualitative theory of the electrical effects of alkyl groups must be regarded to be in an unsatisfactory state.

TABLE II

SLOPES OF THE PLOTS OF LOG k *vs.* N_W IN AQUEOUS ACETONE

Chloride	Slope	Chloride	Slope
Benzhydryl	7.195	*p*-Isobutylbenzhydryl	6.871
m-Methylbenzhydryl	7.165	*p*-Neopentylbenzhydryl	6.819
p-Methylbenzhydryl	7.143	*p*-Isopropylbenzhydryl	6.976
p-Ethylbenzhydryl	7.095	*p*-*t*-Butylbenzhydryl	6.789
p-*n*-Propylbenzhydryl	7.041	*m*-*t*-Butylbenzhydryl	6.750

In comparing the rates of solvolysis in the different aqueous acetone solvents it was noticed that for any given benzhydryl chloride the plot of the log of the solvolysis rate constants *vs.* the mole fraction of water in the range studied gave a straight line.[15] The slopes of these lines are given in Table II. It is seen that the slopes of the lines for the different alkyl benzhydryl chlorides fall into a rather interesting series which might allow one to argue that the differential effects of solvent variation are due to differences in steric hindrance to solvation. In general the compounds with the larger alkyl substituents or with the substituent closer to the reaction center show rates which are less sensitive to solvent composition. However, before this can be ascribed to steric hindrance it is necessary to examine the situation more closely: In the following equations the prime values refer to one solvent and the unprimed ones to a second; the subscript zero refers to benzhydryl chloride and the subscript "x" refers to any substituted benzhydryl chloride; k refers to the solvolysis rate constant, N_w to the mole fraction of water and s to the slope of the plot of N_w *vs.* log k

$$s_0 = (N'_w - N_w) \log k_0'/k_0$$

$$s_0 - s_x = (N'_w - N_w)(\log k_0'/k_0 - \log k'_x/k_x)$$

$$s_0 - s_x = (N'_w - N_w)(\log k_x/k_0 - \log k'_x/k_0')$$

If a relationship of the Hammett equation type[16] holds, then

$$\log k_x/k_0 = \rho\sigma_x \text{ and } \log k'_x/k_0' = \rho'\sigma_x$$

then

$$s_0 - s_x = (N'_w - N_w)\sigma_x(\rho - \rho')$$

This shows that even if the compound behaves normally its slope in this type of plot would be expected to be larger the larger the electron releasing ability (σ_x) of the alkyl substituent (x). Thus, differences in such slopes would not be expected to show up differences in steric effects alone but might be due to differences in either electronic or steric effects between the groups.

One way to attempt a correlation of the rates of these reactions in different solvents would be through the use of the Hammett equation.[16] The attempt to do this meets with utter failure. This is probably due either to the inaccuracy of the σ_x values (which seems unlikely), to the variation of σ-values between reactions or to variable steric effects. Another method of correlation which is directly related to the Hammett equation but which avoids the necessity of knowing the σ-values is to plot the function log k/k_0 *vs.* log k'/k_0'. If the relative electron-releasing abilities of the groups concerned remain constant in the two solvents and there are not any differential steric effects the points should fall on a straight line. A plot of this nature is shown in the graph. It is seen that the derivatives with the less highly branched alkyl substituents go relatively faster in the more polar solvent or, conversely, that the ones with the more highly branched alkyl substituents go relatively faster in the less polar solvents. It would seem that this might be due either to solvation enhancement of the electron-releasing abilities of the less highly branched alkyl groups or to steric inhibition of solvation of the transition states in the reactions of the derivatives with the more highly branched substituents.[17] If one knew where the line in this graph would go in the absence of any complicating effects it would be possible to identify which of the above two effects was operative. Two reasonable possibilities suggest themselves. The first assumes that the electron-releasing ability of the m-methyl group remains constant as the solvent changes and that the steric effect of this group is negligible. This is equivalent to drawing the line in the graph through the origin and the point for the m-methyl group. This treatment can be exhibited numerically by calculating σ-values relative to that for m-methyl in each of the solvents by the use of the equation[18]

$$\frac{\log k_x/k_0}{\log k_{m\text{-Me}}/k_0} = \frac{\sigma\rho_x}{\rho\sigma_{m\text{-Me}}} = \frac{\sigma_x}{\sigma_{m\text{-Me}}}$$

The ratios $\sigma_{\text{alkyl}}/\sigma_{m\text{-methyl}}$ calculated in this way are given in Table III.

TABLE III

RATIOS OF $\sigma_{\text{alkyl}}/\sigma_{m\text{-methyl}}$ SOLVOLYSIS OF ALKYLBENZHYDRYL CHLORIDES

Alkyl group	"90%" alcohol	"80%" acetone	"70%" acetone	"66.7%" acetone
p-Methyl	5.21	6.00	6.20	6.35
p-Ethyl	5.02	5.52	5.65	5.79
p-*n*-Propyl		5.28	5.45	5.54
p-Isopropyl	4.79	5.06	5.15	5.23
p-Isobutyl		5.08	5.13	5.17
p-Neopentyl		4.69	4.67	4.75
p-*t*-Butyl	4.50	4.62	4.62	4.64
m-*t*-Butyl	1.26	0.71	0.55	0.42

If the σ-value of the m-methyl group is assumed to remain constant then the σ-values of the other groups in Table III will vary in the same way as the ratios given. It would follow that the σ-constant of the p-methyl group increased in the more polar solvents, that the σ-value of the p-t-butyl group remained about constant and that the σ-constants for other groups increased with increasing solvent po-

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(15) W. H. Cropper, F. Spieth and A. R. Olson, THIS JOURNAL, **76**, 6248 (1954).

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

(17) The deviations from the attempted correlations are probably due to variations in both potential and kinetic energy terms. Since solvation differences would almost certainly be reflected in both kinds of terms the fact that they cannot be considered separately in this treatment should not invalidate the conclusions drawn.

(18) The particular form of this equation was suggested by Prof. H. C. Brown.

larity but not as much as that for the methyl group. This argument would then lead to the conclusion that solvation acted to enhance electron release by the hyperconjugative mechanism. By a reasonable choice of σ'-values the data for the *p*-methyl, *p*-ethyl, *p*-isopropyl and *p*-*t*-butyl compounds can be made to fit a modified Taft–Hammett equation.[19] The "*h*" values increase with increasing polarity of the solvent. The points for *n*-propyl, isobutyl and neopentyl fall off the modified Taft–Hammett plot indicating a progressively lowering value of "*h*" in this series. By this argument this would be most easily ascribed to steric inhibition of hyperconjugation. The only flaw in this treatment is that the data for the *m*-*t*-butyl compound are apparently not explained without another hypothesis. This might be ascribed to the onset of some steric inhibition of solvation in this case.

The second alternative basic assumption which one could make which leads to a different interpretation of the data is to assume that the line in the graph would normally go nearest to the *p*-methyl group and that this group exhibits nearly unchanging electron-releasing and steric properties as the solvent is changed. This can be illustrated numerically by calculating the σ-ratios relative to *p*-methyl. These are given in Table IV.

Table IV

Ratios of $\sigma_{\text{alkyl}}/\sigma_{p\text{-methyl}}$ Solvolysis of Alkylbenzhydryl Chlorides

Alkyl group	"90%" alcohol	"80%" acetone	"70%" acetone	"66.7%" acetone	Column 3 − column 5
p-Methyl	(1)	(1)	(1)	(1)	(1)
m-Methyl	0.192	0.167	0.160	0.157	0.010
p-Ethyl	.963	.920	.912	.908	.012
p-*n*-Propyl		.881	.875	.866	.015
p-Isopropyl	.919	.843	.832	.820	.023
p-Isobutyl		.845	.827	.810	.035
p-Neopentyl		.781	.754	.745	.036
p-*t*-Butyl	.863	.771	.746	.726	.045
m-*t*-Butyl	.242	.117	.0883	.0662	.051

In this argument the fact that the σ-constants for the other alkyl groups change relative to *p*-methyl would be attributed to their larger size and greater steric inhibition of solvation. The figures in the last column represent a measure of the change in apparent relative σ-constant of each alkyl group as the solvent is changed from "80" to "66.7%" aqueous acetone. If this change is attributed to steric inhibition of solvation these numbers represent a relative measure of this effect and show a satisfactory correlation with the structure of the groups and their proximity to the reaction site. It is also noticed that in general the groups that show the largest sensitivity to solvent variations, by this argument, are also the ones whose apparent electron-releasing abilities are the smallest. Because of the varying effect of solvent on the apparent electron-releasing abilities of the groups this argument does not allow one to assess the order of inherent electron-releasing abilities but points up a strong solvent dependent effect which tends to overemphasize the importance of hyperconjugation.

The recent work of Kreevoy and Taft[19] on the correlation of the rates of hydrolysis of acetals and ketals must now be considered to be by far the most important experimental basis for the theory of hyperconjugative effects on reaction rates. A striking result of that work is that they have shown in a quantitative way what Baker perceived earlier, namely, that the replacement of a single α-hydrogen atom by a methyl group will generally produce hyperconjugation and inductive effects on the rates of carbonium type reactions opposite in direction and similar in magnitude.[19] Thus, the actual order of the effectiveness of different alkyl groups in facilitating a reaction such as the one studied here may depend upon other effects which are quantitatively much less significant. The solvent-dependent effect detected here, whether it be solvation enhancement of hyperconjugation or steric inhibition of solvation, falls into this second category. It is of more than passing interest, however, to point out that this secondary effect is probably in the main responsible for the "hyperconjugative orders" of electron-releasing abilities which for many years were considered to be the firmest foundations of hyperconjugation theory. Thus it seems that the best evidence was in a way false, but that the main conclusions derived therefrom were valid.

Secondary deuterium isotope rate effects give promise of providing another important way of measuring and studying hyperconjugation and also indicate that it is an important factor in the type of reaction studied here, at least for some alkyl groups.[20] Whether steric inhibition of hyperconjugation[11] is an important factor in the rate-retarding effects of β-methyl substitution in the *p*-alkyl group is not obvious from these data, but by analogy with some of the isotope rate effects observed in the solvolysis of alkyl chlorides[6] it would seem to be a strong possibility.

Experimental

m-*t*-**Butylbenzoic Acid.**—This compound was prepared as described by Price and Lincoln[21] from commercially obtained *t*-butylbenzene and gave m.p. 125–127°, reported 126–127°.

m-**Alkylbenzophenones.**—*m*-Methyl- and *m*-*t*-butylbenzophenone were prepared from the corresponding alkylbenzoic acids using the procedure of Ador and Rilliet.[22] *m*-Methylbenzophenone was obtained in 67% yield, b.p. 140-143° (1 mm.). *m*-*t*-Butylbenzophenone showed b.p. 191° (6 mm.).

p-**Alkylbenzophenones.**—These materials were prepared in the manner described by Hughes, Ingold and Taher[12] from the corresponding alkylbenzenes and benzoyl chloride. The products were distilled at reduced pressure through a spinning band column: *p*-methylbenzophenone, b.p. 130-138° (1.3 mm.), yield 82%; *p*-ethylbenzophenone, b.p. 148° (1 mm.), yield 68%; *p*-isopropylbenzophenone, b.p. 152° (0.9 mm.), yield 64%; *p*-*n*-propylbenzophenone, b.p. 160° (1.0 mm.), yield 69%; *p*-isobutylbenzophenone, b.p. 160° (0.8 mm.), yield 50%; *p*-*t*-butylbenzophenone, b.p. 158° (0.8 mm.), yield 60%; *p*-neopentylbenzophenone, b.p. 146° (0.4 mm.), yield 55%.

p-**Alkylbenzhydrols.**—These compounds were prepared by the lithium aluminum hydride reduction[23] of the corresponding benzophenones and recrystallized repeatedly from low boiling petroleum ether to constant melting point.

The following alkylbenzhydrols were obtained: *p*-methylbenzhydrol, m.p. 53.4–54.0° (uncor.), reported[12] 53°; *p*-ethyl-

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(19) R. W. Taft and M. M. Kreevoy, This Journal, **77**, 5590 (1955).

(20) V. J. Shiner, Jr., and C. J. Verbanic, *ibid.*, **79**, 373 (1957).

(21) C. C. Price and D. C. Lincoln, *ibid.*, **73**, 5836 (1951).

(22) E. Ador and A. A. Rilliet, *Ber.*, **12**, 2298 (1879).

(23) W. G. Brown in "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 467.

benzhydrol, m.p. 44.0–44.5 (uncor.), reported[12] 43°; *p*-isopropylbenzhydrol, m.p. 59.5–60.6 (uncor.), reported[12] 60°; *p*-*t*-butylbenzhydrol, m.p. 81.5–82 (uncor.), reported[12] 82°; *m*-methylbenzhydrol, m.p. 54–55 (uncor.), reported[12] 53–54°.

p-*n*-Propylbenzhydrol gave m.p. 41–42°. *Anal.* Calcd. for $C_{16}H_{18}O$: 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 $C_{18}H_{22}O$: 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 $C_{17}H_{20}O$: 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 ±0.01° set with an accuracy of ±0.01° 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 × 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%.

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[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 Chlorides[2]

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p-CD_3-, *p*-CH_3CD_2-, *p*-$(CH_3)_2CHCD_2$- and *p*-$(CH_3)_2CD$-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 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

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[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.

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