Acid-catalyzed Hydrolysis.—Unlike the saponification of the esters, the acid-catalyzed hydrolysis of these compounds proceeded as a first-order reaction. This indicates that the liberation of one carboxyl group in the phthalate ester has little influence on the hydrolysis of the remaining carbethoxyl group. Under the conditions of the experiment it was possible to attain equilibrium.

The rate constants for the hydrolysis reaction were calculated by the usual equation. Table V is a presentation of the first-order rate constants and also the percentage hydrolysis at equilibrium. The reaction medium was 85% ethanol by weight.

TABLE V

ACID-CATALYZED HYDROLYSIS OF ETHYL ESTERS

Constituent acid	$k_{100}° \times 10^6$, sec.$^{-1}$	Hydrolysis at equilibrium, %
Benzoic	3.93	18.4
Anisic	2.27	17.8
Phthalic	1.09	13.8
Isophthalic	4.13	19.9
2-Methoxyisophthalic	3.09	18.3
4-Methoxyisophthalic	3.33	20.3
5-Methoxyisophthalic	4.81	19.5
Terephthalic	4.44	19.3
Methoxyterephthalic	5.48	20.5

Ethyl anisate hydrolyzes under these conditions at a rate about one-half that of ethyl benzoate, indicating that the 4-methoxyl group causes a pronounced retardation of hydrolysis. Similarly, it was observed that the diethyl 2- and 4-methoxyisophthalates hydrolyzed at a rate considerably less than that of diethyl isophthalate. In contrast both diethyl 5-methoxyiso- and methoxyterephthalate hydrolyzed at a rate greater than that of the corresponding unsubstituted diethyl phthalates. It again appears that the methoxyl group in the m-position exerts an accelerating effect upon the hydrolysis, and in the o- or p-position the effect is opposite.

Within the series of the unsubstituted phthalate esters, it is of particular interest to note that diethyl phthalate hydrolyzes at a rate only about one-quarter of that of the diethyl iso- and terephthalates.

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SCHENECTADY, N. Y.

Rates of Solvolysis of m-Alkylbenzhydryl Chlorides[1,2]

BY ERNST BERLINER AND MABEL M. CHEN

Rate constants for the solvolysis of four m-alkylbenzhydryl chlorides have been determined at three temperatures in 80% by volume aqueous acetone. The order in which the alkyl groups enhance the rate is m-Me > m-Et > m-i-Pr < m-t-Bu. This order, which is essentially the same as that for p-alkyl groups but more closely spaced, is attributed to carbon–hydrogen hyperconjugation from the m-position. Alternate explanations are discussed.

The iodination of p-alkylphenols and p-alkylanilines in the position meta to the alkyl groups proceeds in the order m-t-Bu > m-i-Pr > m-Et > m-Me, i.e., the alkyl groups affect the rates in accordance with the order of their inductive effects.[3] Two explanations have been advanced. One is that resonance effects are not effectively transmitted through the m-position, and that therefore only the inductive effect can be operative. The other, and preferred, explanation is that the obtainment of the inductive order is not so much a consequence of the position of the alkyl groups on the benzene ring as of the nature of the substituting agent. The substituting agent in aqueous iodination is thought to be a cationic species, H_2OI^+ or I^+,[4] of great electrophilic activity and therefore of low selectivity,[5]

and not sufficiently electron demanding to bring about the operation of the hyperconjugation effect. The situation would be analogous to p-nitration of alkylbenzenes,[6] but unlike p-bromination[7,8] or chlorination.[7] In order to support this latter view, it seemed of importance to study the effect of m-alkyl groups in a reaction which is known to proceed through a highly electron-demanding transition state. In such a reaction a hyperconjugation effect might be expected to be transmitted even through the m-positions.

One of the best documented cases of an electron-demanding reaction which follows a hyperconjugation order of alkyl groups is the solvolysis of p-alkylbenzhydryl chlorides in 80% by volume aqueous acetone.[9] As a test case for the m-alkyl groups, we have chosen therefore the similar SN1 solvolysis of the m-alkylbenzhydryl chlorides in the same solvent. The mechanism of the reaction can

(1) Electronic Effects of Alkyl Groups. IX. This title is now given to a number of previous papers, i.e., Hyperconjugation, I–V: ref. 3, 8, 13, 29.

(2) Taken from a dissertation submitted by Miss M. M. Chen to the Graduate School of Bryn Mawr College in partial fulfillment of the requirements for the Ph.D. degree, June, 1956.

(3) E. Berliner, F. Berliner and I. Nelidow, THIS JOURNAL, **76**, 507 (1954); E. Berliner and F. Berliner, ibid., **76**, 6179 (1954).

(4) E. Berliner, ibid., **72**, 4003 (1950); **73**, 4307 (1951); B. S. Painter and F. G. Soper, J. Chem. Soc., 342 (1947). For further work see E. Grovenstein and D. C. Kilby, THIS JOURNAL, **79**, 2972 (1957).

(5) H. C. Brown and K. L. Nelson, ibid., **75**, 6292 (1953).

(6) H. Cohn, E. D. Hughes, M. H. Jones and M. G. Peeling, Nature **169**, 291 (1952).

(7) P. B. D. de la Mare and P. W. Robertson, J. Chem. Soc., 279 (1943); P. W. Robertson, P. B. D. de la Mare and B. E. Swedlund, ibid., 782 (1953).

(8) E. Berliner and F. Berliner, THIS JOURNAL, **71**, 1195 (1949).

(9) E. D. Hughes, C. K. Ingold and N. A. Taher, J. Chem. Soc., 949 (1940).

TABLE I

RATES OF SOLVOLYSIS OF m-ALKYLBENZHYDRYL CHLORIDES IN 80% AQUEOUS ACETONE

Alkyl group		0°		$k_1 \times 10^5$, sec.$^{-1}$ 15.2°		25.1°	E, kcal.	log A	$\Delta S^{\ddagger}$, e.u.
H		0.279 ± 0.001		2.19 ± 0.01		7.24 ± 0.03	21.1 ± 0.2	11.3 ± 0.1	-8.87
		$.279 \pm .001$		$2.20 \pm .01$		$7.23 \pm .03$			
		$.278 \pm .001$		$2.20 \pm .01$		$7.27 \pm .02$	21.0^a	11.3^a	
	Av.	0.279	Av.	2.20	Av.	7.25	20.9^b	11.2^b	
		$.282^a$				7.28^a			
		$.284^b$				7.23^b			
		$.262^c$							
m-Me		0.478 ± 0.004		3.71 ± 0.01		12.3 ± 0.2	20.9 ± 0.1	11.4 ± 0.1	-8.27
		$.477 \pm .004$		$3.70 \pm .02$		$12.1 \pm .1$			
		$.480 \pm .003$		$3.71 \pm .01$		$12.2 \pm .1$			
	Av.	0.478	Av.	3.71		$12.3 \pm .1$			
		$.468^c$			Av.	12.2			
m-Et		0.428 ± 0.002		3.32 ± 0.01		11.0 ± 0.1	21.0 ± 0.1	11.5 ± 0.1	-8.14
		$.428 \pm .003$		$3.32 \pm .01$		$11.0 \pm .1$			
		$.428 \pm .003$		$3.34 \pm .01$		$11.3 \pm .1$			
	Av.	0.428	Av.	3.33	Av.	11.1			
m-i-Pr		0.393 ± 0.003		3.03 ± 0.02		10.1 ± 0.1	21.0 ± 0.1	11.4 ± 0.1	-8.55
		$.393 \pm .004$		$3.03 \pm .01$		$10.1 \pm .1$			
		$.393 \pm .001$		$3.04 \pm .02$		$10.1 \pm .1$			
	Av.	0.393	Av.	3.03		$10.2 \pm .1$			
					Av.	10.1			
m-t-Bu		0.433 ± 0.003		3.32 ± 0.02		11.0 ± 0.1	21.0 ± 0.1	11.4 ± 0.1	-8.19
		$.419 \pm .004$		$3.28 \pm .03$		$11.0 \pm .1$			
		$.421 \pm .002$		$3.28 \pm .02$		$11.3 \pm .1$			
		$.435 \pm .003$	Av.	3.29		$11.0 \pm .1$			
	Av.	0.427			Av.	11.1			
		$.394^c$							

^{a} Ref. 9. ^{b} R. T. Arnold, K. Murai and R. M. Dodson, THIS JOURNAL, **72**, 4193 (1950). ^{c} Ref. 11.

be considered sufficiently well understood for the present purposes, i.e., it involves a highly solvated transition state with a large degree of carbonium ion character, and the rate is accelerated by electron-donating groups.[9,10] A study of the hydrolysis of m-t-butyl- and m-methylbenzhydryl chloride in various solvents has been reported recently,[11] and rate constants for the solvolysis of p- and m-alkylphenyldimethylcarbinyl chlorides have been published.[12] The results are similar to those reported here and will be referred to below.

Results and Discussion

The results of the kinetic runs, carried out at three temperatures, are listed in Table I. Some literature values are included for comparison. The values for the unsubstituted compound agree well with those reported by previous workers. The relative order m-Me > m-t-Bu accords with the order obtained by Shiner and Verbanic,[11] although the absolute values differ slightly. Because of the small differences in rates, activation energies do not show any appreciable differences among themselves, nor can any conclusions be drawn from activation entropy differences. It is therefore more fruitful to consider only rate differences, which, although small, are well beyond the experimental errors.

At all three temperatures the m-alkyl groups increase the rate of solvolysis over that of the un-

substituted compound, but the increase is considerably less in the m-series ($k_{Me}/k_H = 1.68$ at 25°) than in the p-series ($k_{Me}/k_H = 21.4$ at 25°).[9] Within the alkyl groups there is a small decrease in rate in the order m-Me > m-Et > m-i-Pr. The series is not completely regular, because the m-t-Bu compound reverses itself, so that m-t-Bu > m-i-Pr, but at the extremes the order is m-Me > m-t-Bu, in agreement with the order obtained by Shiner and Verbanic.[11] These authors observed, in addition, that the relative orders depend on the solvent, as had previously been noticed in the alkaline hydrolysis of ethyl p-alkylbenzoates.[13] Important as this observation is, it does not detract from the present conclusion that, under a given set of conditions, alkyl groups in the m-, as well as the p-position, can cause a reaction to follow a hyperconjugation order, provided the reaction proceeds through a highly electron-deficient transition state.[14]

(13) E. Berliner, M. C. Beckett, E. A. Blommers and B. Newman, ibid., **74**, 4940 (1952).

(14) The very interesting observations that no deuterium isotope effect is observed in the solvolysis of m-tolylmethylcarbinyl chloride (E. S. Lewis and R. R. Johnson, Abstract of Papers, 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 16-21, 1956, p. 20-O), while they have been observed with the p-compound (E. S. Lewis and G. M. Coppinger, THIS JOURNAL, **76**, 4495 (1954)) are not considered evidence against this view. If there is "...a connection between the magnitude of the isotope effect and the weakening of the C–H bonds by hyperconjugation . . .," the effect should be much smaller in the m- than in the p-position, and possibly within the experimental errors. The significance of the C–H isotope effects, as far as they pertain to hyperconjugation, is still a matter of debate. See, for instance, C. G. Swain, T. E. C. Knee and A. J. Kresge, ibid., **79**, 505 (1957); V. J. Shiner and S. Cross, ibid., **79**, 3599 (1957); E. A. Halevi, Tetrahedron, **1**, 174 (1957).

(10) S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).

(11) V. J. Shiner and C. J. Verbanic, ibid., **79**, 369 (1957).

(12) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, ibid., **79**, 1897 (1957).

Our results are very similar to those obtained by Brown and co-workers in the m-alkylphenyldimethylcarbinyl chloride system.[12] The similarity includes the reversal of the m-t-Bu compound (m-t-Bu > m-i-Pr) at 0 and 15°. However, at 25°, in the tertiary chloride system, the order has become regular.[15] We agree with the interpretation of these authors that the experimental Baker–Nathan order[16] is due to the hyperconjugation effect. The transmission of the effect through the m-position may occur through direct meta interaction, or, more likely, through conjugation to the position ortho to the reaction center and from there by inductive relay to the side chain.[8,12]

While the results, and the analogous ones in the carbinyl system, are consistent with the view expressed in the Introduction, it is appropriate to consider briefly alternate explanations. In recent years several proposals, in place of hyperconjugation, have been advanced to account for the Baker–Nathan order Me > t-Bu.[17–19] These proposals usually assume that alkyl groups release electrons predominantly, or only,[19] in the inductive order (though not necessarily by the inductive mechanism[18]), and that the inductive order t-Bu > Me may be reversed for steric reasons of one kind or other. In one it is proposed that the decrease in rate of a t-Bu compound may be due to steric hindrance to solvation at the reaction site of a highly polar, and therefore highly solvated, transition state, even by remote p-substituents.[17] This was derived for the special case of alkaline ester hydrolysis, where it may well be of importance. Alternately, it is suggested that the decrease is due to varying degrees of hindrance by the alkyl groups to solvation of electron-deficient centers developing on the ring, at or near the alkyl groups, during the transition state.[18] This suggestion is made on the basis of the different behavior of alkyl groups in spectral and other physical measurements, and in reaction rates. On the other hand, the view has been expressed that C–H hyperconjugation can be accentuated by solvation assistance.[20] This view is based on solvent and isotope effects. Regardless of conflicting interpretations, numerous new examples of the Baker–Nathan order have been reported recently.[21]

The effects by which the Baker–Nathan order

is essentially ascribed to steric hindrance to solvation may well be important contributing factors, but they do not satisfactorily account for all the facts in the present case. They would allow one to predict, as is observed, that m-alkyl groups should enhance the rate relative to hydrogen, and that m-Me > m-t-Bu. But the spacing of rates among the alkyl groups should be larger than found, and larger than in the p-position. Alkyl groups in the m-position are closer to the reaction center, and if the decrease of rate is due to hindrance of solvation of the transition state, the m-alkyl groups should provide more hindrance than the p-alkyl groups. Steric hindrance to solvation of electron-deficient sites near the alkyl groups should be at least as great in the m-alkylbenzhydryl chlorides as in the p-series, and probably greater, because one such site would be flanked by two large groups, unless such solvation is only important, or more important, at the p-position.[22] Actually, the relative order H, Me, Et, i-Pr, t-Bu is 1.00:21.4:17.3:13.8:10.9 in the p-series,[9] but only 1.00:1.68:1.53:1.39:1.53 in the m-series at 25°. Furthermore, if the inductive effect were the only effect of importance, and if, as is often assumed, it is less pronounced from the m- than from the p-position, the reversal to a hyperconjugation order should also be greater for the m-position than for the p-position. If the inductive effects in the two positions were of similar magnitude,[23] the reversal should be about the same, if no additional steric factors operate in the m-alkyl compounds. In addition, while the ethyl and isopropyl groups can assume conformations which should alleviate hindrance to solvation, this is not possible for t-Bu, but this is the one group which falls out of line (t-Bu > i-Pr), whereas it should have reacted the slowest. If one takes the view that the observed order is due to a combination of hyperconjugation and inductive effects, one does not know how much closer the hyperconjugation spacing should be for m-alkyl, as compared to p-alkyl groups, except that it should be closer, because of less efficient transmission, and the over-all effect should be less than in the p-position, as observed. Possible explanations in terms of solvation hindrance for the whole series are that the inductive order is so much more pronounced for m- than for p-alkyl groups, that the solvation effects are not sufficient to reverse the order to the same extent as in the p-series, or that in the m-series the demand for ring solvation is less than in the p-series, or that, contrary to the above views, solvation shielding is more, rather than less, important with p- than with m- groups.[22]

Additional observations, although referring to

(15) The relative solvolysis rates for the m-alkylphenyldimethylcarbinyl chlorides (ref. 12) are in the order H, m-Me, m-Et, m-i-Pr, m-t-Bu: 1.00:2.10:1.90:1.75:1.82 at 0°, and 1.00:2.00:1.94:1.87:1.85 at 25°.

(16) J. W. Baker and W. S. Nathan, J. Chem. Soc., 1840 (1935).

(17) C. C. Price and D. C. Lincoln, THIS JOURNAL, 73, 5836 (1951); C. C. Price and W. J. Belanger, ibid., 76, 2682 (1954).

(18) W. A. Sweeney and W. M. Schubert, ibid., 76, 4625 (1954); W. M. Schubert and W. A. Sweeney, J. Org. Chem., 21, 119 (1956); W. M. Schubert, J. Robins and J. L. Haun, THIS JOURNAL, 79, 910 (1957).

(19) A. Burawoy and E. Spinner, J. Chem. Soc., 3752 (1954); 2085 (1955); E. Spinner, ibid., 1590 (1956).

(20) V. J. Shiner, THIS JOURNAL, 76, 1603 (1954); V. J. Shiner and C. J. Verbanic, ibid., 79, 373 (1957), and ref. 11. See also E. S. Lewis and C. E. Boozer, ibid., 76, 791 (1954); footnote 14.

(21) For instance: C. A. Vernon, J. Chem. Soc., 423 (1954); A. Burawoy and E. Spinner, ref. 19; H. C. Brown and C. W. McGary, THIS JOURNAL, 77, 2310 (1955); M. M. Kreevoy and R. W. Taft, ibid., 77, 5590 (1955); P. B. D. de la Mare and J. T. Harvey, J. Chem. Soc., 36 (1956); 131 (1957); C. Eaborn, ibid., 4858 (1956); H. C. Brown, et al., ref. 12.

(22) This view has, in fact, been expressed by a Referee, who has pointed out that Schubert's interpretation (ref. 18) implies that solvent shielding of the ring position attached directly to R would be more pronounced than shielding in the position ortho to R. Since the positive charge of the carbonium ion can be considered to be distributed over the ortho/para positions, and since in the p-series R is directly attached to a site requiring solvation, steric hindrance to ring solvation should then be more pronounced in the p- than in the m-series. Whether or not such hindrance at R is more important than that ortho to two bulky groups (as it would be in the m-series) is a matter of conjecture, but if it were, the above data would not be in disagreement with Schubert's interpretation.

(23) J. D. Roberts, R. A. Clement and J. J. Drysdale, THIS JOURNAL, 73, 2181 (1951).

different examples, are also pertinent: The propositions based on steric hindrance to solvation endeavor to explain a *decrease* in rate accompanying a replacement of a methyl by a *t*-butyl group in an electron-demanding substitution or displacement reaction. There are now a number of reactions known where, because of a nucleophilic attack, the observed Baker–Nathan order is *t*-Bu > Me. These include activated nucleophilic aromatic displacements,[24] the alkaline hydrolysis of *p*-alkylbenzoates in 85% aqueous ethanol,[18] the methanolysis of menthyl *p*- and *m*-alkylbenzoates in methanol,[25] the neutral hydrolysis of substituted benzoic anhydrides.[26] For those reactions in which *t*-Bu > Me, steric hindrance explanations are not applicable,[25] because by their very nature they have to consider the bulk of the alkyl group and must predict Me > *t*-Bu.[27] This also holds for various electron-demanding reactions which follow the inductive order (*t*-Bu > Me), such as *p*-nitration of alkylbenzenes,[6] nitration of phenol ethers and some reactions involving *m*-alkyl groups,[28] or the bromination of *t*-alkylbenzenes, where the rates increase with the size of the alkyl groups.[29] The aforementioned proposals can therefore only be accommodated with all of the facts if additional hypotheses are made about the state of solvation of the various transition states and their demand for solvation, namely, that in reactions in which a *t*-Bu compound reacts faster than a Me compound, rate-decreasing solvation processes are not decisive. At the present time, such considerations might have to be made *ad hoc*, and it seems reasonable to account for the predominant influence of alkyl groups in terms of the two electronic effects. To be sure, here too one cannot always predict when one or the other of the two effects will predominate, but an encouraging beginning has been made in the attempt to discover the factors that make different reactions subject to one or the other of the two electronic effects, for instance in the case of various aromatic substitution reactions of alkylbenzenes.[3,5,30] It is not implied that solvation

in polar reactions is not important, or that solvation is not subject to steric hindrance,[31] and the complete explanation of the apparent electron-releasing effects of alkyl groups will take these factors into account, but we feel that, at the moment, it is not sufficiently in accord with all the facts to consider solvation factors decisive in determining the effect of remote alkyl groups.

Experimental

Preparation of Materials.—The *m*-alkylbenzhydrols were prepared by a reaction between benzaldehyde and the Grignard reagent of the appropriate *m*-bromoalkylbenzene. The preparation of the *m*-bromoalkylbenzenes followed published procedures in outline (*m*-bromotoluene was a commercial sample)[32]; they were obtained by hypophosphorous deamination[33] of diazotized 2-bromo-4-alkylanilines, which had been purified through the solid acetyl derivatives. Bromination was carried out on the purified, solid *p*-alkylacetanilides, prepared and purified as described before.[3] A typical series of transformations was carried out as follows: 4-ethylacetanilide[34] (0.5 mole) was brominated by a modification of the procedure described for *p*-acetotoluidide.[35] A 68% yield of material, once crystallized from 50% aqueous ethanol, was obtained; the yields in the bromination of *p*-isopropyl- and *p*-*t*-butylacetanilide were 66 and 74%, respectively (the latter was recrystallized from benzene). 2-Bromo-4-ethylacetanilide (40 g.) was hydrolyzed for four hours with a mixture of 120 ml. of 95% ethanol and 120 ml. of concd. hydrochloric acid. The hydrochloride (92%), which precipitated on cooling, was filtered and washed with a small amount of chilled ethanol. It was diazotized (0.1 mole; larger amounts were used in other runs) in a solution of 100 ml. of water and 25 ml. of concd. hydrochloric acid, with 8.0 g. of sodium nitrite. The filtered diazonium solution was treated with 335 g. of precooled 30% hypophosphorous acid, and the solution was allowed to remain in the ice-box for several hours and at room temperature for 24 hours. The solution was worked up in the usual way, and colorless 3-bromoethylbenzene was obtained on vacuum distillation in 92% yield. The yields for the *m*-*i*-Pr and *m*-*t*-Bu compounds were 88.7 and 86%. The Grignard reagent of 3-bromoethylbenzene (0.2 mole) and 5.4 g. of magnesium turnings in 180 ml. of dry ether was treated slowly with 20.2 g. of freshly distilled benzaldehyde in 100 ml. of dry ether in the cold. The reaction mixture, from which an addition complex precipitated, was decomposed with a solution of 45 g. of ammonium chloride in 150 ml. of water. The yield of vacuum distilled 3-ethylbenzhydrol was 54% and similar yields were obtained for the other benzhydrols. The chlorides were obtained by passing a stream of hydrogen chloride[36] into the ethereal solutions of the carbinols, as described.[9] They were purified by vacuum distillation (40–50% yield), albeit with some difficulty and partial decomposition. Because of easy decomposition during the distillation, only *m*-*t*-butylbenzhydryl chloride was obtained in analytically pure form. The *m*-*i*-Pr compound gave a correct chlorine analysis immediately after distillation, but the chlorine content for the *m*-Et compound was lower than calculated (95% Cl). Both compounds had higher than calculated carbon, perhaps because they contained some unchanged benzhydrol. The liquid 3-ethylbenzhydrol was characterized further through its solid benzoate, but attempts to recover the alcohol in bulk by hydrolysis of the benzoate were not successful. The kinetic results are not affected, because infinity titers were

(24) E. Berliner and L. C. Monack, This Journal, **74**, 1574 (1952); C. W. L. Bevan, E. D. Hughes and C. K. Ingold, *Nature*, **171**, 301 (1953).

(25) M. S. Newman and E. K. Easterbrook, This Journal, **77**, 3763 (1955). The results for the *m*-series (*m*-*t*-Bu > *m*-Me) have been explained by relief of steric strain on replacing the large *l*-menthyl group by the smaller methyl group. This is clearly a special case, which can also be accounted for by hyperconjugation from the *m*-position.

(26) E. Berliner and L. H. Altschul, *ibid.*, **74**, 4110 (1952).

(27) The suggestion that the Baker–Nathan order is due to steric resistance to bond contraction (ref. 19) has been made specifically for atoms which acquire a (partial) positive charge. It is therefore not clear what the effect should be in reactions, as those mentioned above, where this is not the case. If the transition state is not electron deficient, the contraction effect should then presumably not be operative, and an inductive effect order should obtain, which is not observed. It has been pointed out (W. M. Schubert, J. Robins and J. L. Haun, ref. 18) that the suggestion of steric hindrance to bond contraction does not take sufficient account of the effect of the solvent on the electron release capacity of alkyl groups.

(28) L. J. Goldsworthy, *J. Chem. Soc.*, 1148 (1936); chlorination: A. E. Bradfield and B. Jones, *Trans. Faraday Soc.*, **37**, 726 (1941); (b) N. N. Lichtin and P. D. Bartlett, This Journal, **73**, 5530 (1951); E. S. Lewis and E. B. Miller, *ibid.*, **75**, 429 (1953); H. C. Brown, D. Gintis and L. Domash, *ibid.*, **78**, 5387 (1956).

(29) E. Berliner and F. Berliner, *ibid.*, **72**, 3417 (1950).

(30) P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 100 (1948); P. B. D. de la Mare, A. D. Ketley and C. A. Vernon, *Research*, **6**, No. 2 (1953); also ref. 7, H. C. Brown and C. W. McGary, ref. 21.

(31) For instance, see P. D. Bartlett, M. Roha and R. M. Stiles, This Journal, **76**, 2349 (1954); E. Berliner and N. Shieb, *ibid.*, **79**, 3849 (1957).

(32) M. Crawford and F. H. C. Stewart, *J. Chem. Soc.*, 4443 (1952); ref. 12, 17, 25.

(33) N. Kornblum, in "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 262.

(34) We are indebted to Dr. W. B. Hardy of the American Cyanamid Co., Calco Chemical Division, Bound Brook, N. J., for a generous sample of *p*-ethylaniline.

(35) J. R. Johnson and L. T. Sandborn, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 111.

(36) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., 1941, p. 393.

TABLE II

PHYSICAL PROPERTIES OF INTERMEDIATES AND NEW COMPOUNDS[a]

R	4-R-2-Bromoacetanilide	3-Bromo-R-benzene M.p.[b] or b.p., °C. (mm.)	3-R-Benzhydrol	3-R-Benzhydryl chloride
H			67–68[c]	115–116 (1); 115–116 (1)[d]
Me		e	52.9–53.5; 52.8[f]	120–121 (1); 117–118 (0.6–0.8)[g]
Et	92.7–93.3; 92[h]	64 (5); 57 (3); 96 (15)[i]	144–145 (1)[k]	124–125 (1)
i-Pr	129.9–130.5; 131[i]; 129[l]	65–66 (3); 90–95[i] (15)	59.0–59.6[m]	131–132 (1)[n]
t-Bu	156.6–157.6; 156–158°; 138.5[i]	71–72 (4); 103–106 (17)[p]	68.2–68.8[q]; 67.5–68[r]	133–134 (1)[s]

[a] All carbon–hydrogen analyses by Geller Laboratories, Hackensack, N. J. [b] All melting points corrected. [c] Commercial sample crystallized from ligroin. [d] W. T. Nauta and D. Mulder, *Rec. trav. chim.*, **58**, 1070 (1939). [e] Commercial sample. [f] J. H. Lamneck and P. H. Wise, THIS JOURNAL, **76**, 1104 (1954). [g] Z. J. Vejdelek and M. Protiva, *Coll. Czech. Chem. Communs.*, **16**, 344 (1951); *C. A.*, **47**, 8068 (1953). [h] H. Kondo and S. Uyeo, *Ber.*, **70**, 1094 (1937). [i] M. Crawford and F. H. C. Stewart, ref. 32. [k] *Anal.* Calcd. for $C_{15}H_{16}O$: C, 84.86; H, 7.60. Found: C, 84.49; H, 7.64. The benzoate, (3-ethylbenzhydryl) benzoate, prepared with benzoyl chloride and pyridine, was crystallized from 95% ethanol and forms colorless needles, m.p. 52.3–53.3°. *Anal.* Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.19; H, 6.45. [l] E. C. Sterling and M. T. Bogert, *J. Org. Chem.*, **4**, 20 (1939). [m] Colorless, cotton-like needles from ligroin. *Anal.* Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.27; H, 8.15. [n] *Anal.* Calcd.: Cl, 14.49. Found: Cl, 14.33 (Volhard method). [o] B. W. Larner and A. T. Peters, *J. Chem. Soc.*, 680 (1952). [p] C. S. Marvel, R. E. Allen and C. G. Overberger, THIS JOURNAL, **68**, 1088 (1946). [q] B.p. 152–153° (2 mm.). Crystallized as colorless, cotton-like needles from ligroin–petroleum ether (1:1). *Anal.* Calcd. for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 84.43; H, 8.33. [r] Ref. 11. [s] *Anal.* Calcd. for $C_{17}H_{19}Cl$: C, 78.90; H, 7.40; Cl, 13.70. Found: C, 79.09; H, 7.61; Cl (Volhard method), 13.72.

taken in all runs and showed between 95 and 99% of ionizable chloride, except for the ethyl compound whose chlorine content was 91–93%. Although fairly large amounts of all benzhydrols were available, only 10-g. lots were converted to the chlorides at any one time. All chlorides were redistilled shortly before each kinetic determination. Physical constants and analyses of new compounds are listed in Table II.

Kinetic Determinations.—Four liters of purified[37] thermostated acetone, contained in two 2-l. volumetric flasks, were mixed with 1 l. of thermostated, carbonate-free distilled water to give the 80% by volume acetone. Another 2.5 l. was similarly prepared, and the two batches were mixed to give the stock solution of solvent which lasted for all kinetic runs. The kinetic determinations were carried out as described for the p-compounds.[9] About 0.002 mole of chloride was accurately weighed in a 100-ml. volumetric flask, which was rapidly filled with the thermostated solvent ($T = \pm 0.05°$), and the time of mixing was taken as zero time. Ten-ml. samples were periodically pipetted into 100 ml. of ice-cold acetone and titrated with standard sodium hydroxide contained in a 5-ml. microburet graduated in hundredths. A 0.1% solution of lacmoid, in 60% ethanol, was used as indicator. One 10-ml. sample was allowed to hydrolyze to completion in order to obtain the infinity titer. The first point in a run was sometimes lower than the average, and was then rejected. Reaction was usually followed to 60–70% completion. Rate constants were calculated from the integrated form of the first-order rate equation. Errors in rate constants (Table I) are average deviations. Energies of activation and log A were obtained from least square cal-

(37) J. B. Conant and W. R. Kirner, THIS JOURNAL, **46**, 232 (1924).

TABLE III

RATES OF SOLVOLYSIS OF m-ALKYLBENZHYDRYL CHLORIDES IN 80% AQUEOUS ACETONE

m-Methylbenzhydryl chloride, 0.01815 M, $T = 25.1°$			m-t-Butylbenzhydryl chloride, 0.02088 M, $T = 15.2°$		
Time, min.	Ml. NaOH 0.04286 N	$k_1 \times 10^4$, sec.$^{-1}$	Time, min.	Ml. NaOH 0.04286 N	$k_1 \times 10^5$, sec.$^{-1}$
20	0.570	1.22	140	1.145	3.33
40	1.070	1.23	211	1.590	3.27
60	1.490	1.22	259	1.890	3.32
85	1.935	1.21	310	2.185	3.37
110	2.310	1.21	331	2.255	3.30
140	2.690	1.22	384	2.520	3.35
170	2.985	1.22	452	2.790	3.33
∞	4.200		∞	4.690	

culations; the errors are probable errors obtained from these calculations, rounded off to the figures shown in Table I. Entropies of activation were calculated[38] from log A for 25.1°. In Table III are listed the results of two kinetic determinations.

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(38) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 417.