182. *Mechanism of Substitution at a Saturated Carbon Atom. Part XVII. Polar Effects in Alkyl Groups, as illustrated by Solvolytic Substitutions of* p-*Alkylbenzhydryl Chlorides.*

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The expected consequences of electron release according to the sequence $\text{Me}<\text{Et}<\text{Pr}^{\beta}<\text{Bu}^{\gamma}$ required for the inductive effect is often disturbed, and Baker and Nathan have suggested that this is due to the tautomeric displacement of the electrons of non-ionising CH-groups toward attached unsaturated carbon. This factor of electron release should work in the order $\text{Me}>\text{Et}>\text{Pr}^{\beta}>\text{Bu}^{\gamma}$. The difficulty hitherto experienced in attempts to demonstrate this is that the differential effects of the co-existing inductive and tautomeric displacements are opposed, and that the significant quantity is the further difference of their combined influence either on initial and transition states, or on initial and final states, according as reaction rates or equilibria are under observation. Only by making an appropriate one of the four terms of this sum-difference combination much bigger than all the others can the new effect be isolated sufficiently to be demonstrated by the undisturbed exhibition of its special consequences.

The unimolecular substitution of *p*-alkylbenzhydryl halides has afforded an opportunity to effect such an isolation: the transition state is the determinative state, because a carbon atom which was saturated has become unsaturated; and the tautomeric electron displacements, for which the system provides a mechanism, will be dominating, because the large electron-demand created in ionisation is not compensated by an electron-transfer from a reagent as in bimolecular substitution. Employing both the hydrolysis and the alcoholysis of benzhydryl chloride and its *p*-alkyl derivatives, complete series of rates and activation energies have been established in accordance with the electron-release sequence $\text{H}<\{\text{Me}>\text{Et}>\text{Pr}^{\beta}>\text{Bu}^{\gamma}\}$. This is the first definite demonstration of the reality of the tautomeric electron displacements of the electrons of non-ionising CH-groups. The absence of CH-ionisation has been confirmed by an isotopic indicator test.

(1) *Electron Displacement in Alkyl Groups.*

It has been shown in many previous papers (*e.g.*, this vol., p. 925) that the effect of alkyl groups R in promoting the ionisation of alkyl halides RX is in the order to be expected for a reaction facilitated by electron release from the alkyl groups through the operation of the general inductive effect:

$$\text{Electron release by R:—Me}<\text{Et}<\text{Pr}^{\beta}<\text{Bu}^{\gamma} \quad . \quad . \quad . \quad . \quad \text{(I)}$$

If the general inductive effect were the only operative mechanism for electron displacement in alkyl groups, this order should apply universally to reactions requiring electron accession to the reaction-zone (reactions of Ingold and Rothstein's " Class A "). Baker and Nathan have pointed out (J., 1935, 1844), however, that this order is sometimes subject to disturbance, and that the simplest, though up to the present largely hypothetical, epitomisation of the known disturbances is expressed in the statement that, for reactions of the same general category (" class A "), subject to a certain structural condition, there is a factor of electron release amongst alkyl groups which works in the order

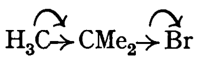
$$\text{Electron release by R:—Me}>\text{Et}>\text{Pr}^{\beta}>\text{Bu}^{\gamma} \quad . \quad . \quad . \quad . \quad \text{(II)}$$

The structural condition for the incursion of this factor (superposed on the usual effect arising from general inductive electron displacement) is that the alkyl group must be directly attached to an unsaturated atom, *i.e.*, an atom that either is unsaturated or becomes unsaturated in the course of reaction. Baker and Nathan's interpretation was that the electrons of CH-bonds are capable of partial conjugation with an attached unsaturated atom, thus permitting tautomeric electron displacement, $\text{H}\overset{\curvearrowright}{—}\text{C}\overset{\curvearrowright}{—}\text{C}{=}$, much as if the electrons were unshared as in chlorine. From the standpoint of ordinary organic chemical theory, this may seem a rather drastic assumption; but, as one of us pointed out

(*Chem. and Ind.*, 1936, 55, 962), a similar assumption has to be made for BH-bonds in order to explain the existence of the diborane, etc., $\mathrm{H}\overset{\curvearrowright}{—\mathrm{B}}\ \mathrm{B}$; and, as the organic chemical facts have also to be accounted for, Baker and Nathan's hypothesis may be accepted provisionally as expressing a general property of all HX-bonds—even those that do not ionise.

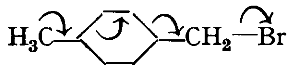
The importance of conjugation in producing conditions wherein the tautomeric electron displacement can create disturbances which are distinctive enough to have some chance of being detectable may be illustrated by a simplified example, related closely to the experimental evidence presented later. Consider comparatively the effect of tautomeric electron displacement from the alkyl groups in promoting the ionisation of simple alkyl and *p*-alkylbenzyl halides. For these reactions it is so obvious that the electron demand of the loosening halogen ion will be much greater in the course of reaction than it was originally that we need not go into further detail regarding existence and development of unsaturation in these systems. Evidently in the simple alkyl series tautomeric electron displacement (*T*) reinforces the general inductive electron displacement (*I*), both absolutely and differentially as between one alkyl group and another; whilst in the alkylbenzyl series the tautomeric displacement reinforces the general inductive absolutely, but opposes it differentially as between one group and another. The two extremes of the alkyl series Me . . . Bu^{γ} are represented:

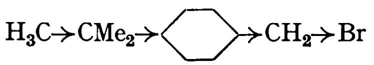
$H_3C—Br$



$\overset{\curvearrowright}{H_3C\rightarrow}CMe_2\overset{\curvearrowright}{\rightarrow Br}$

[*I* (→) leads to sequence (I) whilst *T* (↷) leads also to (I)]





[*I* (→) leads to sequence (I) whilst *T* (↷) leads to sequence (II)]

Accordingly in the simple series we shall obtain sequence (I), whether the assumed tautomeric effect is really present or not. As to the benzyl series, we cannot say in advance whether the differential tautomeric effect will or will not dominate the differential inductive, but if it does we shall obtain sequence (II), thereby detecting the tautomeric effect. Because the two modes of electron displacement always reinforce each other in an absolute sense, the complete order in this case, including the unsubstituted benzyl compound, should be $H<\{Me>Et>Pr^{\beta}>Bu^{\gamma}\}$.

In practice, chemical evidence can come from studies of either reaction equilibria or reaction rate. In the former case we have to consider differentially the initial and the final state of the system: each will be subject to general inductive, and each to tautomeric electron displacement. In the case of reaction rate we have to treat the initial and the transition state in a differential manner: and each of these will be subject both to a general inductive and to a tautomeric electron displacement. Thus in either case our result depends on a sum-and-difference combination of four effects, two relating to the initial state and two to the final or to the transition state. In problems of reaction rate, in contrast to those of chemical equilibrium, it is important to distinguish between polarisation and polarisability effects. For instance, the unsaturation permitting alkyl conjugation may be present in the initial state of the system, when the consequential electron displacement (↷) is classifiable as a polarisation, *viz.*, the mesomeric effect; or it may be present only, or may be enhanced, in the transition state, when the displacement, or the part of it due to the enhancement of unsaturation in the transition state, will be a polarisability, *viz.*, the electromeric effect. In like manner the general inductive electron displacement (→) in the initial state is a polarisation, the inductive effect, whilst its enhancement in the transition state is a polarisability, the inductomeric effect.

In view of the inevitable complexity of the circumstances outlined in the previous paragraph it is not surprising to find that, although there are numerous indications of a disturbance which might be the postulated alkyl conjugation, considerable difficulty has hitherto been experienced in producing unequivocal evidence that this is so, such as, *e.g.*, a well-spaced, regular and complete sequence (II) of rate or equilibrium constants, backed by corresponding and analogously regular activation or reaction heats. Probably the best previous example is Baker and Nathan's original one of the rates of combination of *p*-alkylbenzyl bromides with pyridine. They obtained a rate series $H<\{Me>Et>Pr^{\beta}=Bu^{\gamma}\}$ which is nearly of the desired type for electron-demanding reactions, but the extreme range of rate (H : Me) was only 1 : 1·65, and, for well-known reasons, it is impossible to be confident that so closely spaced a rate series means what it may appear to mean. Not unnaturally the gaps were irregular and the Arrhenius critical energies, far from being confirmatory, gave only a "muddled" series. Evidently no clear result should have been expected because the reaction is a bimolecular nucleophilic substitution, which, on account of the mutually accommodating electron-transfers, has only a small electron-demand, as the internal evidence of the rates confirms: the small electron-demand means that there must be a large amount of mutual cancellation in the four-term combination of effects on which each of the rates depends. Subsequent investigations on the rates of electron-demanding reactions are subject to the same comments to the same or a greater degree, *viz.*, Brynmor Jones' chlorination of *p*-alkylbenzyloxyphenols (J., 1938, 1414), which produced the series $H<\{Me=Et<Pr^{\beta}>Bu^{\gamma}\}$, and W. C. Davies' methylation of *p*-alkyldimethylanilines (J., 1938, 1865), which gave $H<\{Me>Et<Pr^{\beta}>Bu^{\gamma}\}$. Work on equilibria has also produced only muddled series hitherto, the difference between the electron-demand in the initial and the final state being insufficient to prevent an approximate mutual cancellation of the component effects. These investigations are T. T. Davies and Hammick's addition of tetranitromethane to alkylbenzenes (J., 1938, 763), which led to $H<\{Me<Et>Pr^{\beta}<Bu^{\gamma}\}$, W. C. Davies' proton-addition to *p*-alkyldimethylanilines, which gave $H<\{Me>Et<Pr^{\beta}>Bu^{\gamma}\}$, and Baker, Dippy, and Page's proton-addition to *p*-alkylbenzoate ions, which gave $H<\{Me>Et=Pr^{\beta}<Bu^{\gamma}\}$. Other investigations, including one* on the rate of a reaction requiring the withdrawal of electrons (Ingold and Rothstein's "Class B"), have so far yielded only incomplete series, which, though indicating the presence of a disturbance, are still less satisfactory than the above complete researches as evidence of the nature of the disturbance (Baker, Nathan, and Shoppee, J., 1935, 1847; Baker and Nathan, J., 1936, 236; Burkhardt *et al.*, J., 1936, 17, 25, 1649, 1654).

What we need in order to get over the difficulty revealed in all this work is a device for making *one* of the four contributing factors (and it must be one of the two which involve alkyl conjugation) much greater than all the others; and this can be done. We decide to study reaction rate in a ***strongly*** electron-demanding reaction, and there can hardly be any reaction more suitable than a ***unimolecular*** nucleophilic substitution, where there is only a single electron-transfer involving carbon in the rate-affecting stage. We must provide that form of conjugative connexion between the alkyl group and the reaction site which will favour in an absolute sense tautomeric electron displacements originating in the alkyl groups, but will lead to general inductive and tautomeric electron displacements which oppose each other differentially as between one alkyl group and another. Then, if alkyl conjugation is real, the general inductive effects in the initial and the transition state and the tautomeric effect in the initial state may all be unimportant in comparison with the tautomeric effect compensating the electron transfer in the transition state, and alkyl conjugation will determine a distinctive and diagnostic series of rates and activation energies, such as we seek to establish.

(2) *Hydrolysis of* p-*Alkylbenzhydryl Chlorides.*†

All the necessary conditions are fulfilled for the hydrolysis of the *p*-alkylbenzhydryl chlorides. These have the right type of conjugation;‡ and as it was known (section 3) that

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* This is being discussed in some detail in a contemporaneous paper by Dr. J. W. Baker. [Added 20/1/40: The paper has now appeared (J., 1939, 1150).]

† Hughes and Ingold promised (J., 1935, 247) to investigate the *p*-alkylphenylethyl halides in this connection, but afterwards decided to change to *p*-alkylbenzhydryl halides in order to avoid the possible complication of olefin formation.

‡ It was to be expected that the double conjugation of *p*-alkyl with $-C_6H_4-$ and of the latter with ionising C . . . Cl would produce a substantial "extra resonance energy" (excess over the additive contributions) in the transition state; or, in other words, that the presence of the *p*-C_6H_4-system

the alcoholysis of benzhydryl chloride is unimolecular, it was certain in advance that the hydrolysis of this halide, as well as of its *p*-alkyl derivatives, would be unimolecular also. Using " 80% " aqueous acetone as solvent, we have confirmed this, and have obtained the " ideal " rate sequence

$$H < \{Me > Et > Pr^{\beta} > Bu^{\gamma}\}$$

with a rate-range (H : Me) of 1 : 30, regular spacing amongst the alkyl groups, and a qualitatively supporting series of Arrhenius critical energies. Table I illustrates these points (the first-order rate constants, k_1, and likewise the non-exponential rate factors B, are in sec.$^{-1}$, and the apparent energies of activation, E, are in kg.-cals.). Note that for each alkyl group the rate is greater by almost exactly one-third than the rate for the next higher homologue. Further rate data will be found in the experimental section.

TABLE I.

First-order Rate Constants at 0° and Arrhenius Parameters for the Hydrolysis of Benzhydryl Chloride and its p-*Alkyl Derivatives in " 80% " Aqueous Acetone.*

(Initial [Halide] about 0·015M throughout.)

p-Substituent	H	Me	Et	Pr^{β}	Bu^{γ}
$10^6 k_1$ (0·0°)	2·82	83·5	62·6	46·95	35·9
$10^{-11}B$	1·91	1·23	2·19	3·47	4·07
E	21·0	18·9	19·4	19·8	20·05

We regard this as the first satisfactory *evidence* of the reality of alkyl conjugation as envisaged by Baker and Nathan.

The suggestion (Robinson, *Chem. and Ind.*, 1936, **55**, 962) that the phenomena which point in this direction are due to the actual loss of a proton from the methyl, ethyl or *iso*propyl group during the course of reaction, possibly under the influence of the strongly basic reagents, which had been employed in most of the older work, at least does not apply to our case. We employ no strongly basic (or acidic) reagents, for our reactions are of first order and are not accelerated by bases and acids. We can directly show, moreover, that no loss of proton occurs at any intermediate stage of our reactions; for if such loss occurred, then on carrying out the hydrolysis of, say, *p*-methylbenzhydryl chloride in aqueous acetone containing deuterium water in place of ordinary water we should find deuterium in the methyl group of the resulting *p*-methylbenzhydrol. We have done this experiment with the result that the *p*-methylbenzhydrol, after isotopic normalisation of its hydroxyl hydrogen by exchange with cold alcohol, was found to be completely free from excess of deuterium. The experimental method would certainly have detected a proton-loss equivalent to one hydrogen atom in every 250 molecules.

(3) *Ethyl Alcoholysis of* p-*Alkylbenzhydryl Chlorides.*

On commencing the work of the previous section, our theoretical conviction that the method should succeed was a little shaken by a previous inconsistent observation on the ethyl alcoholysis of *p*-alkylbenzhydryl halides. Ward established the unimolecular and irreversible character of the ethyl alcoholysis of benzhydryl chloride (J., 1927, 2285). Norris and his collaborators concluded that the reactions were measurably reversible, and for *p*-alkyl derivatives obtained the rate series H<Me<Et (relative rates 1 : 16·2 : 20·9) (*J. Amer. Chem. Soc.*, 1928, **50**, 1795, 1804, 1811). Kny-Jones and Ward reinvestigated the parent halide, and conclusively proved that its alcoholysis is not measurably reversible (*ibid.*, 1935, **57**, 2394); and Farinacci and Hammett closely confirmed Ward's absolute

would enhance the conjugative effects due to alkyl substitution, thus increasing our chances of securing a clear supremacy of the differential conjugative effect over the differential inductive effect. For this reason it was considered important to retain the C_6H_4-system, which had been present also in all the reactions studied by previous investigators (*locc. cit.*), rather than pass over to purely aliphatic examples, such as the unimolecular reactions of $R_3C{\cdot}CMe_2{\cdot}Hal$, $R_3C{\cdot}C(\overline{CO_2})_2{\cdot}Hal$, etc. (R = H or Me). Such systems will in later publications be used to illustrate the scope and limitation of the effects established in this paper.

value for the rate constant (*ibid.*, 1937, **59**, 2542), from which Norris's value differed appreciably. Apart from these criticisms of Norris's conclusions, we noticed that those parts of his calculations that could be checked contained a high proportion of serious arithmetical errors ; and therefore, when it subsequently became clear that hydrolysis was yielding the sequence $H<\{Me>Et>Pr^{\beta}>Bu^{\gamma}\}$, we thought it desirable to repeat Norris's determinations on the H-, Me-, and Et-compounds, and extend the work to the Pr^{β}- and Bu^{γ}-homologues, which he did not examine.

On completing this programme we obtained the constants, shown in Table II, which again give the sequence $H<\{Me<Et>Pr^{\beta}>Bu^{\gamma}\}$. The constants k_1 are in sec.$^{-1}$.

TABLE II.

First-order Rate Constants at 25° for the Alcoholysis of Benzhydryl Chloride and its p-*Alkyl Derivatives in Dry Ethyl Alcohol.*

(A : $[\text{Halide}]_{t=0}$ ~0·013M. B : $[\text{Halide})_{t=0}$ ~0·084M.)

p-Substituent		H	Me	Et	Pr^{β}	Bu^{γ}
$10^5 k_1$ (25·0°)	A	5·30	123	120	106	98·7
	B	—	125	120	—	—
Relative rates		1·0	23·4	22·6	20·0	18·6
,, ,, for hydrolysis (at 25°)		1·0	21·4	17·3	13·8	10·9

We add a few detailed comments. (1) The constant for benzhydryl chloride is a little lower than that obtained by Ward and by Farinacci and Hammett ($10^5 k_1 = 5{\cdot}73$); but these authors used ordinary lime-dried alcohol, whilst our solvent was further purified by the Lund–Bjerrum method : 0·2% of water in the lime-dried material would account for the difference. (2) The rate constants of series A apply to solutions of about the dilution used in our study of hydrolysis, whilst the rate constants B relate to more concentrated solutions such as Norris used. For reasons explained in following papers (this vol., p. 960, *et seq.*), it is important, in order to obtain first-order constants for some unimolecular reactions, to maintain quite low concentrations; but the disturbances which in principle may enter in more concentrated solutions are evidently not the cause of the discrepancy between Norris's results and our own. One contributory cause may be that his *p*-ethyl-compound was impure, since ours melted 10° higher; and, as we have noted, his measurements and calculations as a whole do not seem to be very accurate. (3) It will be observed, on comparing the last two lines of Table II, that the spacing of the rates amongst the alkyl compounds is appreciably closer than for hydrolysis. The meaning of this in terms of electron displacement must be that, in the transition state, the electron-demand on the alkyl group due to the ionising link is less for alcoholysis than for hydrolysis, or, in other words, that the developing positive charge on carbon is more compensated by solvation in alcoholysis than in hydrolysis; which, perhaps, is natural in view of the known solubility relations of hydrocarbons with alcoholic and aqueous solvents.

EXPERIMENTAL.

Materials.—The *p*-alkylbenzhydryl chlorides were all prepared according to the scheme : $R{\cdot}C_6H_5+C_6H_5{\cdot}COCl \longrightarrow R{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_5 \longrightarrow R{\cdot}C_6H_4{\cdot}CH(OH){\cdot}C_6H_5 \longrightarrow R{\cdot}C_6H_4{\cdot}CHCl{\cdot}C_6H_5$. The ketones, carbinols, and chlorides of the *iso*propyl and *tert.*-butyl series are new. The original hydrocarbons were carefully purified, the *iso*propylbenzene and *tert.*-butylbenzene having been prepared by ourselves from *iso*propyl and *tert.*-butyl chlorides, benzene, and aluminium chloride; yields 70 and 55%, b. p.'s 152·8—153·1°/765 mm. and 169°/764 mm. respectively.

p-*Alkylbenzophenones.* The method of Montagne (*Rec. Trav. chim.*, 1908, **27**, 357) was made the basis of these preparations, which are illustrated with respect to the *tert.*-butyl compound. A mixture of benzoyl chloride (190 g.), aluminium chloride (145 g.), and carbon disulphide (1000 c.c.) was heated on the steam-bath under reflux for 2 hours and cooled. After the addition of *tert.*-butylbenzene (210 g.), heating was continued for 4 hours, and the product was then cooled and added to ice-water. The filtered carbon disulphide solution was washed successively with dilute hydrochloric acid, water, saturated aqueous sodium hydrogen carbonate, and water, and was dried and distilled. The four homologous ketones were obtained all in about

55% yield. In order (methyl- to *tert.*-butyl-) they had: b. p. 185°/17 mm., m. p. 54—55°; b. p. 186°/11 mm. (Found: C, 86·2; H, 6·9. Calc.: C, 85·7; H, 6·7%); b. p. 197°/16 mm.; b. p. 205°/15 mm. They are probably not free (except the crystalline methyl compound) from *o*- and *m*-isomerides, but the elimination of these is effected in the carbinols. The ethyl compound was analysed because of the discrepancy between the m. p. of its carbinol and that of Norris's preparation.

p-*Alkylbenzhydrols.* We used a modification of Marvel and Hansen's method of reduction ("Organic Syntheses," **8**, 24). They employed zinc and a solution of sodium hydroxide in ethyl alcohol containing 5% of water for the reduction of benzophenone, and they state that the water is not harmful, though the use of absolute alcohol as solvent is recommended in previous literature. We found that the presence of water, in even larger proportion than Marvel and Hansen employed, is not only not harmful, but is positively necessary for complete reduction. We illustrate with respect to *p*-*tert.*-butylbenzhydrol. The ketone (80 g.) and sodium hydroxide (110 g.) were dissolved in a mixture of ethyl alcohol (720 c.c.) and water (80 c.c.). After the solution had been heated under reflux with mechanical stirring, zinc powder (140 g.) was added and the heating and stirring were continued for 2 hours. The filtered solution, combined with alcoholic washings, was added to a large volume of ice-water and neutralised with hydrochloric acid (*d* 1·19). The precipitated crude carbinol was dried, crystallised once from ether, and three times from light petroleum. The yield of fully purified carbinol was 75%, and for all the carbinols it was in the range 62—80%. The m. p.'s of the four carbinols in order (methyl- to *tert.*-butyl-) are 52—53° (Norris, 51·5—53°), 43·5° (Norris 33°) (Found: C, 84·8; H, 7·6. Calc.: C, 84·9; H, 7·6%), 60° (Found: C, 85·2; H, 7·8. $C_{16}H_{18}O$ requires C, 85·0; H, 8·0%), and 82° (Found: C, 85·1; H, 8·5. $C_{17}H_{20}O$ requires C, 85·0; H, 8·3%).

p-*Alkylbenzhydryl chlorides.* The following is illustrative. *p*-*tert.*-Butylbenzhydrol (30 g.) was treated with a stream of dry hydrogen chloride in ether (200 c.c.) solution for 2 hours, and the solution was dried with calcium chloride, decanted therefrom, and treated with a further quantity of hydrogen chloride in the presence of fresh anhydrous calcium chloride. The ethereal solution was concentrated, shaken with anhydrous sodium carbonate, and finally distilled (oil-bath). Yield of chloride, 50%. The b. p.'s of the four halides in order (methyl- to *tert.*-butyl-) are 136°/0·4 mm. (Found: Cl, 16·4. Calc.: Cl, 16·4%), 148°/1·0 mm. (Found: C, 78·2; H, 6·7; Cl, 15·2. Calc.: C, 78·1; H, 6·5; Cl, 15·4%), 155°/0·3 mm. (Found: C, 78·4; H, 6·9; Cl, 14·6. $C_{16}H_{17}Cl$ requires C, 78·5; H, 7·0; Cl, 14·5%), and 158—160°/1·5 mm. (Found: C, 79·1; H, 7·4; Cl, 13·3. $C_{17}H_{19}Cl$ requires C, 78·9; H, 7·4; Cl, 13·7%). The unsubstituted benzhydryl chloride had m. p. 18°.

Solvents. Acetone was purified by Conant and Kirner's method (*J. Amer. Chem. Soc.*, 1924, **46**, 245) and ethyl alcohol by Lund and Bjerrum's (*Ber.*, 1931, **64**, 210). The "80%" aqueous acetone used in the rate measurements was a mixture of 8 vols. of dry acetone with 2 vols. of water, the volumes being measured at room temperature. A large quantity of this solvent was prepared, and in all comparative kinetic measurements the solvent was taken from the same stock.

Kinetic Measurements.—The experiments were carried out either at 0·0° or at 25·0° (±0·05°) by the ordinary sampling method, the samples being run into a large volume of cold acetone in order to stop the reaction, and titrated with sodium hydroxide with lacmoid as indicator.

Hydrolysis of chlorides in 80% *aqueous acetone.* Table III illustrates one of the runs of this series. Benzhydryl chloride was initially in 0·01652M-solution. Its concentration, $a - x$, at time t, in seconds, is expressed in c.c. of 0·00980N-sodium hydroxide per 10 c.c. sample. Table IV contains the complete duplicate sets of determined mean constants, from which the data of Table I were computed. All first-order constants are in sec.$^{-1}$.

TABLE III.

Hydrolysis of Benzhydryl Chloride at 25·0° *in* 80% *Aqueous Acetone.*

t.	$a - x$.	10^6k_1.	t.	$a - x$.	10^6k_1.	t.	$a - x$.	10^6k_1.
0	16·85	—	5,161	11·50	73·9	12,420	6·75	73·6
1078	15·58	72·7	6,713	10·30	73·3	14,820	5·75	72·5
2280	14·30	71·9	8,520	9·10	72·2	17,850	4·60	72·6
3658	12·90	72·9	10,330	7·90	73·2	21,720	3·50	72·2

Mean $10^6k_1 = 72·8$.

Alcoholysis of chlorides in anhydrous ethyl alcohol. These experiments are reported fully in Table V in view of the disagreement with Norris's results. The rate constants are summarised

TABLE IV.

Summary of Mean Rate Constants for Hydrolysis of Benzhydryl Chloride and its p-*Alkyl Derivatives at* 0·0° *and* 25·0° *in* 80% *Aqueous Acetone. Duplicate Series "a" and "b." Initial Concentrations of Halide between* 0·013 *and* 0·018M.

p-Substituent		H	Me	Et	Pr$^\beta$	Bu$^\gamma$
10^6k_1 (0·0°)	(a)	2·81	83·1	62·8	46·9	36·0
	(b)	2·83	83·9	62·4	47·0	35·8
10^5k_1 (25·0°)	(a)	7·28	157	127	102·0	79·5
	(b)	7·28	155	125	99·2	79·7

in Table II (p. 953). In the experiments of series A, *a* — *x* is expressed in c.c. of 0·01036N-sodium hydroxide per 10 c.c. sample, and in those of series B, *a* — *x* is given in c.c. of 0·02012N-alkali per 2 c.c. sample. Other units are as before.

TABLE V.

Alcoholysis of Benzhydryl Chloride and its p-*Alkyl Derivatives in Anhydrous Ethyl Alcohol at* 25·0°. *Series A (more dilute) and B (more concentrated solutions).*

(A) *p*-Substituent = H.
$[\text{Halide}]_{t=0}$ = 0·01160M.

t.	*a* — *x*.	10^5k_1.
0	11·10	—
1,140	10·45	5·29
2,527	9·70	5·33
3,965	9·00	5·28
5,740	8·20	5·27
8,163	7·20	5·30
12,320	5·75	5·33
15,980	4·75	5·30
20,570	3·70	5·33
26,160	2·80	5·26

(A) *p*-Substituent = Me.
$[\text{Halide}]_{t=0}$ = 0·01437M.

t.	*a* — *x*.	10^5k_1.
0	13·95	—
110	12·15	126
243	10·40	121
374	8·80	123
532	7·30	122
725	5·65	125
950	4·39	122
1255	3·05	121
1560	2·10	121

(B) *p*-Substituent = Me.
$[\text{Halide}]_{t=0}$ = 0·0865M.

t.	*a* — *x*.	10^5k_1.
0	8·60	—
110	7·50	124
241	6·40	123
368	5·45	125
548	4·35	124
740	3·35	127
975	2·50	125
1375	1·50	127
1718	1·08	121

(A) *p*-Substituent = Et.
$[\text{Halide}]_{t=0}$ = 0·01326M.

t.	*a* — *x*.	10^5k_1.
0	12·80	—
103	11·35	117
230	9·70	120
348	8·45	119
523	6·80	121
702	5·50	120
957	4·00	121
1240	2·90	120
1670	1·70	121
3483	0·20	119

(B) *p*-Substituent = Et.
$[\text{Halide}]_{t=0}$ = 0·0820M.

t.	*a* — *x*.	10^5k_1.
0	8·15	—
134	6·95	119
278	5·85	119
400	5·05	120
588	4·05	119
762	3·25	121
985	2·45	122
1273	1·75	121
1680	1·08	120
2225	0·60	117

(A) *p*-Substituent = Pr$^\beta$.
$[\text{Halide}]_{t=0}$ = 0·01450M.

t.	*a* — *x*.	10^5k_1.
0	14·00	—
125	12·30	103
236	10·90	106
375	9·40	106
545	7·80	107
735	6·40	106
975	4·90	108
1351	3·40	105
1769	2·18	105

(A) *p*-Substituent = Bu$^\gamma$. $[\text{Halide}]_{t=0}$ = 0·01336M.

t.	*a* — *x*.	10^5k_1.	*t*.	*a* — *x*.	10^5k_1.	*t*.	*a* — *x*.	10^5k_1.
0	12·90	—	522	7·60	101·0	1675	2·45	99·0
120	11·45	99·3	705	6·40	99·3	2260	1·50	95·1
234	10·15	98·6	952	4·90	102·0	3432	0·50	94·6
364	9·00	98·8	1243	3·75	99·3			

Products.—Products in ordinary aqueous acetone. Benzhydryl chloride (16·5 g.) was dissolved in "80%" aqueous acetone (1 l.), the solution, after being kept for 48 hours at 25°, was made faintly alkaline with ammonia, and most of the acetone was pumped off at about this temperature. The concentrate was poured into ice-water, and the precipitated product was collected, washed with water, and dried. It weighed 14·58 g. (theoretical yield of benzhydrol = 15·0 g.), and had m. p. 67—68° (mixed m. p. with benzhydrol, the same). Extraction of the residues with ether failed to yield any further substance.

The corresponding experiment with *p*-methylbenzhydryl chloride was carried out with a rather more concentrated solution for reasons of economy, because the parallel experiment described below had to be carried out with a deuterium-containing solvent. A solution of the chloride (5·44 g.) in the "80%" aqueous acetone (100 c.c.) was kept at 25° for 48 hours. In order to make sure that in this rather concentrated solution (*ca.* 0·2M) the hydrolysis goes to completion (*i.e.*, that the reaction is not measurably reversible), a 5 c.c. sample was withdrawn for titration; this showed hydrolysis to be quantitative. The remaining material, worked up as described above, gave 4·36 g. of product (theoretical yield of *p*-methylbenzhydrol = 4·73 g., allowing for the analysis sample), which had m. p. 52—53° (mixed m. p. with *p*-methylbenzhydrol, the same). No further substance was obtained by extraction of the residue with ether.

Product in deuterated aqueous acetone. The preceding experiment with *p*-methylbenzhydryl chloride was repeated with aqueous acetone made from heavy water (5 c.c., containing 99·6 atoms % of deuterium), ordinary water (15 c.c.), and acetone (80 c.c.). The precipitated *p*-methylbenzhydrol was washed well with water, and the alcoholic hydrogen was then isotopically normalised by several times dissolving the substance in cold ethyl alcohol and reprecipitating it with water. Combustion of the dried product gave water of the same density as ordinary water to 1 in 10^6, which is the error of measurement. We are indebted to Dr. E. de Salas for this combustion and pyknometric density determination.

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[*Received, April* 18*th*, 1940.]