with that given for purified benzhydryl chloride, mp 18–19° (lit.[7] mp 18°), and also with the literature values[7,13,19] (see Table I). The rates of reactive chlorides, such as *p*-methoxy and *p*-methyl, were followed at lower temperatures (Table IV); the rate constants at 25.0° were calculated by assuming that log *PZ* for ethanolysis was 11.07[35] and for 2-propanolysis was 10.32. The ethanolyses of *p*-cyano, *m*-nitro, and *p*-nitro derivatives were studied at higher temperatures by the sealed-tube technique.[36] The extrapolations were made to obtain rate constants at 25.0°; the data are given in Table IV.

Registry No.—*p*-Methoxybenzhydryl chloride, 6731-11-9; *p*-methylbenzhydryl chloride, 779-14-6; *p*-fluorobenzhydryl chloride, 365-21-9; *m*-methylbenzhydryl chloride, 13391-36-1; benzhydryl chloride, 90-99-3; *m*-methoxybenzhydryl chloride, 13391-37-2; *p*-chlorobenzhydryl chloride, 134-83-8; *p*-bromobenzhydryl chloride, 13391-38-3; *m*-fluorobenzhydryl chloride, 13391-48-5; *m*-chlorobenzylhydryl chloride, 13391-39-4; *m*-bromobenzhydryl chloride, 13391-40-7; *m*-cyanobenzhydryl chloride, 13391-41-8; *p*-cyanobenzhydryl chloride, 13391-42-9; *m*-nitrobenzhydryl chloride, 13391-43-0; *p*-nitrobenzhydryl chloride, 7515-72-2; *m*-methxybenzhydrol, 13391-45-2; *m*-cyanobenzophenone, 6136-62-5; *m*-cyanobenzhydrol, 13428-06-3; *p*-cyanobenzhydrol, 13391-47-4; *m*-fluorobenzophenone, 345-64-7.

Acknowledgment.—The encouragement and support of Professor Herbert C. Brown during the course of the present work carried out in Purdue University are gratefully acknowledged.

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[35] S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Am. Chem. Soc.*, **79**, 4146 (1957); they have given $\Delta H^{\ddagger} = 20.84$ kcal/mole and $\Delta S^{\ddagger} = -7.9$ eu, from which log *PZ* was calculated.

[36] S. Winstein, C. Hanson, and E. Grunwald, *ibid.*, **70**, 812 (1948).

Diphenylcarbinyl Derivatives. II.[1] Solvolysis of Some Disubstituted Benzhydryl Chlorides. An Examination of the Additivity Relationship

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The rates of solvolysis of some disubstituted benzhydryl chlorides, including *m,m*-$(CH_3)_2$, *m,m'*-$(CH_3)_2$, *m,p'*-$(CH_3)_2$, *p,p'*-$(CH_3)_2$, *p*-Cl-*p'*-CH_3, and *p,p'*-Cl_2, are determined at 25.0° in methanol, in ethanol, and in 2-propanol. The additivity of the substituent effects is examined and discussed.

When two or more substituents are introduced into the *m* or *p* position of an aromatic compound, it is usually found that the combined effect of the substituents can be represented by the sum of their individual effects.[3–6] Satisfactory additivites of the effect of substituents have been observed either in the *typical side chain reactions*,[7] such as the saponification of ethyl benzoates,[6] or in the *electrophilic side chain reactions*,[7] including the solvolysis of some *m,p*-dialkylbenzhydryl chlorides[8–11] and the aromatic substitution of polyalkylbenzenes.[12] The additivity relationship has also been applied to the compounds containing more than one benzene ring[6] and its validity has been demonstrated in certain typical side-chain reactions, such as the ionization of $Ar_1Ar_2SeBr_2$[6] and infrared frequency shifts of the carbonyl stretching vibration in Ar_1COAr_2.[6] However, an examination of the solvolytic reactivities of some *m,p'*- and *p,p'*-disubstituted benzhydryl chlorides[13,14] raises the question whether or not the simple additivity relationship can be applied when the substituents are placed at the *m,p'* or *p,p'* position. Thus, in the present study, the alcoholyses of some disubstituted benzhydryl chlorides are investigated and the additivity of the effect of substituents is vigorously tested.

Results and Discussion

The rates of solvolyses of several disubstituted benzhydryl chlorides at 25.0° are determined in methanol, in ethanol, and in 2-propanol; the results are summarized in Table I. When the reactivities of these derivatives are plotted against $\Sigma\sigma^+$, all points lie satisfactorily on the regression line for monosubstituted derivatives[1] (Figure 1). It is apparent, therefore, that the reaction constant of the disubstituted derivatives examined is the same as that of monosubstituted derivatives; thus, the Hammett equation for these compounds (*e.g.*, Ar_1Ar_2CHCl) can be represented as eq 1[6]

$$\log (k/k_0) = \rho(\sigma^+_1 + \sigma^+_2) \qquad (1)$$

where σ^+_1 and σ^+_2 are individual substituent constants of the substituents in groups Ar_1 and Ar_2, respectively.

The validity of eq 1 is also evident from the excellent agreement of observed reactivities with those calculated, as shown in Table I. A simple multiplication of relative rates of corresponding monosubstituted benzhydryl chlorides gave a calculated relative rate for the disubstituted derivative, which is in good agreement with the

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[1] Part I, Solvolysis of Some Monosubstituted Benzhydryl Chlorides: S. Nishida, *J. Org. Chem.*, **32**, 2692 (1967).

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[3] C. K. Ingold and W. S. Nathan, *J. Chem. Soc.*, 222 (1936).

[4] J. Shorter and F. J. Stubbs, *ibid.*, 1180 (1949); F. J. Stubbs and C. Hinshelwood, *ibid.*, S71 (1949).

[5] B. Jones and J. Robinson, *Nature*, **165**, 453 (1950).

[6] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953), and references cited therein.

[7] According to L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 3323 (1959), those reactions correlated with Hammett σ are termed as *typical side chain reaction* and those correlated with σ^+ are *electrophilic side chain reaction*.

[8] G. Baddeley and M. Gordon, *J. Chem. Soc.*, 2190 (1952).

[9] G. Baddeley, S. Varma, and M. Gordon, *ibid.*, 3171 (1958).

[10] A. Altzscher, R. Baltzly, and S. W. Blackman, *J. Am. Chem. Soc.*, **74**, 3649 (1952).

[11] W. R. Moore, E. Marcus, S. E. Fenton, and R. T. Arnold, *Tetrahedron*, **5**, 179 (1959).

[12] L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

[13] J. F. Norris and C. Banta, *J. Am. Chem. Soc.*, **50**, 1804 (1928); J. F. Norris and J. T. Blake, *ibid.*, **50**, 1808 (1928).

[14] J. R. Fox and G. Kohnstam, *Proc. Chem. Soc.*, 115 (1964).

TABLE I

SUMMARY OF RATE DATA AND EXAMINATION OF ADDITIVITY RELATIONSHIP

Substituent	$10^5 k_1$ at 25.0°, sec^{-1}	k/k_H Obsd	Calcd[a]	Obsd/Calcd
		Methanolysis		
m,m-$(CH_3)_2$	387	4.67	4.41	1.06
m,m'-$(CH_3)_2$	367	4.43	4.41	1.00
p-Cl-p'-CH_3	774	9.35	8.40	1.11
p,p'-Cl_2	11.47[b]	0.139	0.129	1.08
H	82.8[c]	1.00	...	...
		Ethanolysis		
m,m-$(CH_3)_2$	22.5	4.21	4.37	0.96
m,m'-$(CH_3)_2$	22.0	4.12	4.37	0.94
m,p'-$(CH_3)_2$	235	44.0	48.1	0.91
p,p'-$(CH_3)_2$	1700[d,e]	320	529	0.60
p-Cl-p'-CH_3	49.6	9.29	8.88	1.05
p,p'-Cl_2	0.807[f]	0.151	0.149	1.01
H	5.34[c]	1.00	...	...
		2-Propanolysis		
m,m-$(CH_3)_2$	2.14	3.53	3.53	1.00
m,m'-$(CH_3)_2$	2.16	3.56	3.53	1.01
m,p'-$(CH_3)_2$	21.1	34.8	38.2	0.91
p,p'-$(CH_3)_2$	156	257	412	0.62
p-Cl-p'-CH_3	5.07[g]	8.37	8.34	1.00
p,p'-Cl_2	0.1060[h]	0.175	0.169	1.04
H	0.606[c]	1.00	...	...

[a] $k_{XY}/k_H = (k_X/k_H)(k_Y/k_H)$. [b] Lit.[10] 10.45 (given as $6.27 \times 10^{-3}\ \text{min}^{-1}$). [c] See ref 1. [d] Calculated from a rate constant at a lower temperature by assuming log $PZ = 11.07$;[1] the rate constant at 0.03° was $1.123 \times 10^{-3}\ \text{sec}^{-1}$. [e] Lit.[13] 1830 ($1.1\ \text{min}^{-1}$). [f] Lit.[13] 0.667 ($4.0 \times 10^{-4}\ \text{min}^{-1}$). [g] Lit.[10] 4.12 ($2.47 \times 10^{-3}\ \text{min}^{-1}$). [h] Lit. 0.095 ($5.7 \times 10^{-5}\ \text{min}^{-1}$),[10] 0.0997 ($5.98 \times 10^{-5}\ \text{min}^{-1}$).[13]

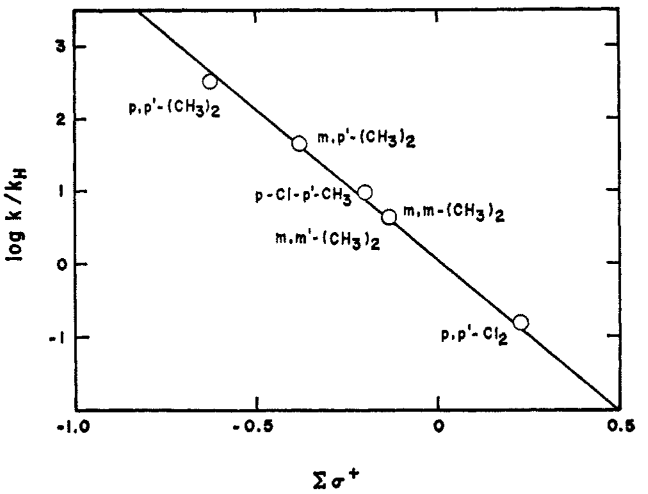

Figure 1.—A plot of log (k/k_H) vs. $\Sigma\sigma^+$ for the ethanolysis of disubstituted benzhydryl chlorides at 25.0°; the regression line drawn is one for monosubstituted derivatives.[1]

observed value to an accuracy of ±10%. An exception was p,p'-dimethylbenzhydryl chloride which solvolyzed slower than expected by a factor of 0.6; because the accuracy of the rate constant is less than 3%, this figure is apparently out of the experimental uncertainty. A similar small deviation in the effect of the multiple p substitution has been known in the equilibrium study of trityl derivatives;[15,16] namely, the additivity relationship is held in the successive m substitution by phenyl,[15] but the effects of second and third p substituents, such as alkyl,[15,16] methoxy,[15] dimethylamino,[15] and phenyl,[16] are found to be no longer additive; the observed K/K_H values are appreciably smaller than those expected. Another example can be seen in the solvolysis of various p,p'-disubstituted benzhydryl chlorides.[14,17] It turns out that the additivity relationship might not hold when two substituents conjugate to a common electron-demanding reaction center, as pointed out by Fox and Kohnstam.[14]

The result obtained for the p,p'-dimethyl derivative seems to support this argument, but the clear additivities were seen in the case of p,p'-dichloro and p-chloro-p'-methylbenzhydryl chloride. Since the resonating abilities of methyl and chloro with the electron-deficient reaction center are in the same order of magnitude,[18] if the deviation observed in the case of p,p'-dimethyl is actually caused by the conjugation of two polarizable substituents to an electron-demanding reaction center, then the same deviations must be observed in the p,p'-dichloro and p-chloro-p'-methyl derivatives, but that was not the case. Consequently, it is necessary to consider another factor which caused a deviation only in the p,p'-dimethyl derivative. A most likely factor is that the $Ar(CH_3C_6H_4)CHCl$ system will have a smaller ρ value than that of the $Ar(C_6H_5)CHCl$ system; thus the second methyl group influences the reactivity less effectively. In this respect, the same deviations must be observed in other systems examined here, but the effect of the first substituent will be too weak to exhibit the deviations in the additivity treatment. This factor will be examined and discussed in the following paper.

In conclusion, the additivity of substituent effects can be held in the derivatives which carry alkyl groups at m,m, m,m', m,p, and m,p' positions; p-halo-m-alkyl, p-halo-m'-alkyl, p-halo-p'-alkyl, and p,p'-dihalo derivatives might also hold the additivity relationship in the electrophilic side-chain reactions.

Experimental Section[19]

Materials.—The methods used in preparing materials were essentially the same as those reported;[1] melting points of benzophenones and benzhydrols are given in Table II.

m,m-Dimethylbenzhydrol, mp 50–51°, was prepared by the Grignard reaction of m,m-dimethylphenylmagnesium bromide with benzaldehyde; m,m'-dimethylbenzhydrol, bp 165.3–166.0° (4 mm), $n^{20}D$ 1.5812, was similarly obtained by the reaction of m-methylphenylmagnesium bromide with m-methylbenzaldehyde. *Anal.* Calcd for $C_{15}H_{16}O$: C, 84.86; H, 7.60. Found: C, 84.80; H, 7.76.

m,p'-Dimethylbenzhydrol was found to be a liquid, bp 166° (3.7 mm), $n^{20}D$ 1.5792. *Anal.* Calcd for $C_{15}H_{16}O$: C, 84.86; H, 7.60. Found: C, 85.00; H, 7.78.

The melting point of p-chloro-p'-methylbenzhydrol was found to be appreciably higher than that reported in a literature (see Table II); the compound was therefore analyzed. *Anal.* Calcd for $C_{14}H_{13}OCl$: C, 72.26; H, 5.63; Cl, 15.24. Found: C, 72.09; H, 5.58; Cl, 15.34.

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(15) N. C. Deno, J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954); N. C. Deno, J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955); N. C. Deno and A. Schriesheim, *ibid.*, **77**, 3051 (1955).

(16) N. N. Lichtin, *Progr. Phys. Org. Chem.*, **1**, 75 (1963), and references cited therein.

(17) A Hammett plot of their data[14] does not give a clear straight line for monosubstituted series; therefore, a strict additivity of the substituent effects may not be evaluated.

(18) For example, $\sigma^+_p - \sigma_p$ are −0.141 for methyl and −0.113 for chloro; see ref 12 and H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

(19) Melting points and boiling points are uncorrected. Elemental analyses were performed by the microanalytical laboratory of Purdue University.

TABLE II

MELTING POINTS OF BENZOPHENONES AND BENZHYDROLS

	Mp, °C			
	Benzophenone		Benzhydrol	
Substituent	Obsd	Found	Obsd	Found
m,m-$(\mathrm{CH_3})_2$	...	...	50–51	50–51[a]
m,m'-$(\mathrm{CH_3})_2$	...	...	Liq[b]	...
m,p'-$(\mathrm{CH_3})_2$	71–72	71,[c] 72[d]	Liq[b]	...
p,p'-$(\mathrm{CH_3})_2$	95	95[e]	71	71[f]
p-Cl-*p'*-$\mathrm{CH_3}$	127–128.3	128[g]	74–74.2[b]	67.5[h]
p,p'-$\mathrm{Cl_2}$	144.5–145	144–145,[i] 144.5[j]	93–93.5	92–94,[f] 94[k]

[a] G. Baddeley, S. Varma, and M. Gordon, *J. Chem. Soc.*, 3171 (1958). [b] See text. [c] P. L. Pickard and D. J. Vaughan, *J. Am. Chem. Soc.*, **72**, 5017 (1950). [d] K. Isimura, *Bull. Chem. Soc. Japan*, **16**, 196, 252 (1941). [e] H. Limpricht, *Ann. Chem.*, **312**, 91 (1900). [f] J. F. Norris and C. Banta, *J. Am. Chem. Soc.*, **50**, 1804 (1928). [g] W. Blakey and H. A. Scarborough, *J. Chem. Soc.*, 2489 (1928). [h] M. W. D. Cohen, *Rec. Trav. Chim.*, **38**, 113 (1919). [i] M. Dittrich, *Ann. Chem.*, **264**, 174 (1891). [j] J. Boeseken and W. D. Cohen, *Chem. Zentr.*, **1915, I**, 1376. [k] M. P. J. Montague and S. A. Koopal, *Rec. Trav. Chim.*, **29**, 136 (1910); M. P. J. Montague and M. Charante, *ibid.*, **31**, 298 (1912).

Some chlorides solidified on standing; melting points were as follows: *p,p'*-dimethyl, 45–46° (lit.[13] mp 45–46°); *p*-chloro-*p'*-methyl, 48–48.5° (lit.[10] solid); *p,p'*-dichloro, 62.5–63.5° (lit.[13] mp 63°).

Solvents and Rate Measurements.—The purification of the solvents and the technique of the rate measurements were the same as those described in a preceding paper.[1]

Registry No.—*m,m*-Dimethylbenzhydryl chloride, 13389-66-7; *m,m'*-dimethylbenzhydryl chloride, 13389-67-8; *p*-chloro-*p'*-methylbenzhydryl, chloride 1698-24-4; *p,p'*-dichlorobenzhydryl chloride, 782-08-1; benzhydryl chloride, 90-99-3; *m,p'*-dimethylbenzhydryl chloride, 13389-69-0; *p,p'*-dimethylbenzhydryl chloride, 13389-70-3; *m,m*-dimethylbenzhydrol, 13389-71-4; *m,m'*-dimethylbenzhydrol, 13389-72-5; *m,p'*-dimethylbenzhydrol, 13389-73-6; *p*-chloro-*p'*-methylbenzhydrol, 13389-74-7.

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Diphenylcarbinyl Derivatives. III.[1] Solvolysis of Polysubstituted Benzhydryl Chlorides. An Examination of the Hammett Relationship in a Multiply Substituted System

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The additivity relationship is examined in several polysubstituted benzhydryl chlorides, including *m,m*-dichloro, *m,p'*-dichloro, *m*-chloro-*p'*-methyl, *m*-chloro-*p'*-methoxy, *m,m*-dichloro-*p'*-methyl, *m,m*-dichloro-*p'*-methoxy, and *m,m,p'*-trichloro derivatives. The additivity was not held in most of these compounds; the biggest discrepancy was observed in *m,m*-dichloro-*p'*-methoxybenzhydryl chloride, which solvolyzed 20.6 times faster than that predicted from reactivities of *m*-chloro- and *p*-methoxybenzhydryl chloride. The results obtained here reveal that a combined effect of two or more substituents is not generally additive; apparently, a first substituent has changed the reaction constant for the second substituent regardless of the multiplication on one benzene ring or two.

From a theoretical point of view, it has been argued that the simple additivity of the effect of substituents is to be expected for those reactions in which the ρ–σ correlation is precisely linear.[3-8] In *typical side chain reactions,*[9] the additivity relationship has been found to be satisfactory in certain instances,[3-8] but, if the magnitude of the mutual interaction of two substituents changes in the reaction, then a deviation will come out in the additivity treatment.[7,8] In *electrophilic side chain reactions,*[9] such a change must be important when two substituents are placed at the *p,p'* position; hence the additivity relationship might not be applied for the solvolysis of *p,p'*-disubstituted benzhydryl chlorides, as has been discussed by Fox and Kohnstam,[10] whereas clear additivities are anticipated for *m,m*-, *m,p*-, *m,m'*-, or *m,p'*-disubstituted derivatives.

In the preceding paper,[1] however, it has been shown that a small discrepancy between the observed and predicted reactivity is observed in the solvolysis of *p,p'*-dimethylbenzhydryl chloride, but clear additivities of the effect of two substituents are demonstrated in *p*-chloro-*p'*-methyl and *p,p'*-dichloro derivatives. Namely, the combined effect of *p,p'* substituents can be additive in some cases, contradicting the above argument. It is of interest, therefore, to investigate further the additivity relationship in the solvolysis of multisubstituted benzhydryl chlorides. The present paper aims to discuss the additivity relationship in those derivatives substituted at the *m,m*, *m,p'*, or *m,m,p'* position.

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(1) Part II, Solvolysis of Some Disubstituted Benzhydryl Chlorides: S. Nishida, *J. Org. Chem.*, **32**, 2695 (1967).

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(3) C. K. Ingold and W. S. Nathan, *J. Chem. Soc.*, 222 (1936).

(4) J. Shorter and F. J. Stubbs, *ibid.*, 1180 (1949); F. J. Stubbs and C. Hinshelwood, *ibid.*, S71 (1949).

(5) B. Jones and J. Robinson, *Nature*, **165**, 453 (1950).

(6) H. H. Jaffé, *Science*, **118**, 246 (1953).

(7) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953), and references cited there.

(8) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 192.

(9) According to L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 3323 (1959), those reactions correlated with Hammett σ are termed as *typical side chain reaction* and those correlated with σ^+ are *electrophilic side chain reaction.*

(10) J. R. Fox and G. Kohnstam, *Proc. Chem. Soc.*, 115 (1964).