infrared ν_{max} 3300 (br), 1625, 1575, 1545, 1440, 1400, 1300, 1265, 1175, 860, 830, 781, and 749 cm^{-1}.

Anal. Calcd for $C_9H_7NO_2$: C, 67.08; H, 4.38; N, 8.69. Found: C, 66.94; H, 4.34; N, 8.78.

Registry No.—**1**, 13388-75-5; **2**, 13388-76-6; **3**, 13388-77-7; **4**, 13388-78-8; **5**, 13388-79-9; **6**, 13388-80-2; **7**, 13388-81-3; **8**, 13388-82-4; **9**, 13388-83-5.

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Diphenylcarbinyl Derivatives. I. Solvolysis of Some Monosubstituted Benzhydryl Chlorides

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Rates of solvolyses of various monosubstituted benzhydryl chlorides, including p-CH_3O, m-CH_3O, p-CH_3, m-CH_3, H, p-F, m-F, p-Cl, m-Cl, p-Br, m-Br, p-CN, m-CN, p-NO_2, and m-NO_2, are studied at 25.0° in methanol, in ethanol, and in 2-propanol. Rate data are correlated linearly with σ^+ values; ρ values are found to be rather constant in the three solvents examined.

The Hammett ρ–σ relationship[2] has been studied extensively in recent years[3] and provides a quantitative approach to the correlation between the structure and reactivity of organic compounds. As a result, it is clearly established that the strongly electron-demanding reactions, termed *electrophilic side chain reaction,*[4] are correlated more nicely with σ^+ values[3,4] than with Hammett σ values.[2,5] The solvolysis of benzhydryl chlorides is such an electrophilic side-chain reaction and has been studied by several workers,[6-23] but varieties of the substituents are rather limited and one sided. It is thus our purpose to investigate the solvolytic reactivities of benzhydryl chlorides substituted by a wide variety of substituents.

Results and Discussion

Most benzhydrols are prepared by the sodium borohydride reduction of corresponding benzophenones; chlorides are prepared by the reaction of carbinols with hydrogen chloride. Dry hydrogen chloride is introduced into a solution of benzhydrol in purified methylene dichloride in the presence of Drierite; after drying the solution by the addition of fresh Drierite, the solvent is removed under the reduced pressure. In this manner, benzhydryl chloride is obtained in a satisfactory purity for the kinetic study; the rate constant obtained by solvolyzing the chloride thus prepared is found to be in excellent agreement with that given by the purified chloride (see Experimental Section). Cyano- and nitrobenzhydryl chloride are prepared by the reaction of carbinol with thionyl chloride; the resulting chloride is purified by distillation under reduced pressure. The rates of solvolysis are mostly determined at 25.0°; in the case of certain chlorides, which are extremely reactive or unreactive, extrapolations are made to obtain the rate constants at 25.0°. The results are summarized in Table I.

A plot of the rate data in ethanol, except p-methoxy, *vs.* the Brown σ^+[3c,4] gives a good straight line with the correlation coefficient 0.998 and the standard deviation 0.099 (Figure 1). The p-methoxy derivative is omitted for the treatment because the point deviates from the regression line; the deviation might be primarily due to the experimental uncertainty caused by numbers of the extrapolations made both in the present study and in the solvolysis of phenyldimethylcarbinyl chloride in 90 vol % acetone, from which the σ^+ values have been evaluated.[3c,4] Another reason for the deviation could be the difference in the reaction system between the present study (secondary system) and the solvolysis of phenyldimethylcarbinyl chlorides (tertiary system).

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(3) As leading references, see (a) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 6; (c) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963); (d) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964); (e) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

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TABLE I

RATE DATA FOR THE SOLVOLYSES OF BENZHYDRYL CHLORIDES AT 25.0°

	Methanolysis		Ethanolysis		2-Propanolysis	
Substituent[a]	10^5k_1, sec^{-1}	k/k_H	10^5k_1, sec^{-1}	k/k_H	10^5k_1, sec^{-1}	k/k_H
p-CH$_3$O	...	...	33000[b]	6200	2700[b]	4500
p-CH$_3$	1940[b]	23.4	123[c]	23.0	12.3	20.3
p-F	138	1.67	9.30	1.74	1.156	1.91
m-CH$_3$	174	2.10	11.15[d]	2.09	1.142	1.88
H	82.8[e]	1.00	5.34[f]	1.00	0.606[g]	1.00
m-CH$_3$O	68.5	0.827	5.10	0.955	0.587	0.969
p-Cl	29.7[h]	0.359	2.06[i]	0.386	0.249[j]	0.411
p-Br	23.9	0.289	1.61[k]	0.302	0.204	0.337
m-F	2.97	0.0359	0.174	0.0326	0.0189	0.0312
m-Cl	2.03[l]	0.0245	0.125[m]	0.0234	0.0145	0.0239
m-Br	2.06	0.0249	0.125[n]	0.0234	0.0143	0.0236
m-CN	0.241	0.00291	0.0160	0.00300	...	...
p-CN	0.125	0.00151	0.00984[o]	0.00184	...	...
m-NO$_2$	0.133	0.00161	0.01113[o]	0.00208	...	...
p-NO$_2$	0.0540	0.000652	0.00424[o]	0.000794	...	...

[a] Compounds are arranged in order of σ^+ values.[3,4] [b] Extrapolated from rate constants at lower temperatures (see Experimental Section). [c] Lit. 124,[7] 123.[13] [d] Lit. 9.23 (given as 5.54×10^{-3} min^{-1}),[6] 13.7.[19] [e] Lit.[15] 81.5 (4.89×10^{-2} min^{-1}). [f] Lit. 5.30,[7] 5.37,[13] and 5.39.[19] [g] Lit.[15] 0.572 (3.43×10^{-4} min^{-1}). [h] Lit.[15] 38.0 (2.28×10^{-2} min^{-1}). [i] Lit.[6] 1.78 (1.07×10^{-3} min^{-1}). [j] Lit.[15] 0.292 (1.75×10^{-4} min^{-1}). [k] Lit.[6] 1.47 (8.83×10^{-4} min^{-1}). [l] Lit.[15] 2.12 (1.27×10^{-3} min^{-1}). [m] Lit.[19] 0.121. [n] Lit.[19] 0.131. [o] Extrapolated from rate data at higher temperatures (see Experimental Section).

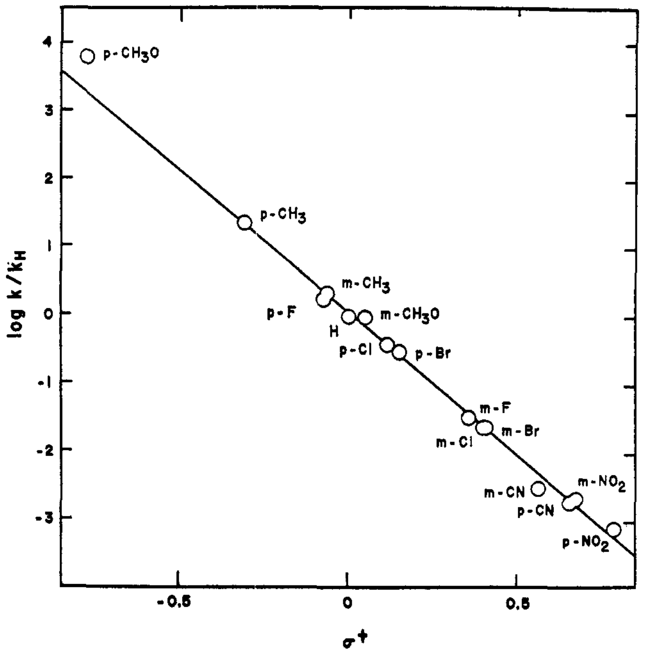

Figure 1.—Hammett plot for the solvolysis of benzhydryl chlorides in ethanol at 25.0°.

Stock and Brown[24] have pointed out that the magnitude of σ^+ for the p-methyl group derived from the study of compounds leading to primary carbonium ions is more than for secondary ions which is more than for tertiary systems. In other words, when the rate data for the secondary system are plotted against σ^+ values which are derived from the reaction leading to tertiary carbonium ions, a point for the p substituent comes above a regression line and it requires a bigger σ^+ to bring the point on a line. Thus the point for p-methoxy could also lie above a point expected from the σ^+ value. The same deviation may exist also in other p-substituted derivatives, but the deviations might be too small to be detected.

Yukawa and Tsuno[25-27] have proposed an equation (eq 1) with which these deviations for p substituents have been examined. When the present results are examined by eq 1, including the data for p-ethyl,[7] p-t-butyl,[7] and β-naphthyl,[19] there is obtained a straight line with a coefficient $r = 1.172$; ρ is found to be -4.13, the correlation coefficient 0.998, and the standard deviation 0.125. Although the point for p-methoxy comes on the regression line by this treatment, other points, such as one for p-fluoro, deviate more badly than those observed in Figure 1; this is also reflected on the standard deviations observed in two treatments—0.099 for the simple Hammett treatment and 0.125 for the treatment by eq 1. Thus the correlation achieved by the simple treatment of rate data with σ^+ values is good enough for the present study.

$$\log (k/k_0) = \rho(\sigma^0 + r\Delta\sigma^+_R) \qquad (1)^{27}$$

Plots of the rate data in methanol and in 2-propanol against σ^+ values give also straight lines. An interesting observation is the constancy of ρ values in the three solvents examined (Table II); although the rate in methanol is more than 100-fold of that in 2-propanol, ρ values are found to be -4.17 ± 0.05 in the three solvents. The dependence of ρ on the change of the solvent has been discussed by several workers,[2,3d,28,29]

TABLE II

REACTION CONSTANTS (ρ), STANDARD DEVIATIONS (s), AND CORRELATION COEFFICIENTS (r) FOR THE SOLVOLYSIS OF BENZHYDRYL CHLORIDES AT 25.0°

Solvent	ρ	s	r
Methanol	-4.22	0.087	0.998
Ethanol[a]	-4.15	0.099	0.998
2-Propanol[a]	-4.13	0.079	0.997

[a] p-Methoxybenzhydryl chloride is not included in the least-square treatment (see text).

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(29) See ref 3b, p 312.

but it is apparent that such a dependence is important only when the solvent change is much more drastic.

In conclusion, the solvolytic reactivities of substituted benzhydryl chlorides can be correlated linearly with σ^+ values, but the *p*-methoxy derivative shows a deviation. The rate of the reaction depends strongly on the change of the solvent, whereas the ρ value does not.

Experimental Section[30]

Benzophenones and Benzhydrols.—Benzophenones were prepared by the Friedel-Crafts reaction of a suitably substituted benzoyl chloride with a benzene derivative in ethylene dichloride. Substituted benzophenone was treated with sodium borohydride in 2-propanol at reflux for 10–15 min and the reaction mixture was poured into a large amount of water containing a trace amount of hydrochloric acid. The resulted carbinol was collected and purified by recrystallization or distillation. Melting points of benzophenones and benzhydrols are given in Table III. *m*-Methoxybenzhydrol was a liquid, bp 147–148° (1.5–2.0 mm), n^{20}_{D} 1.5918.

TABLE III

MELTING POINTS OF BENZOPHENONES AND BENZHYDROLS

	Mp °C			
	Benzophenone		Benzhydrol	
Substituent	Obsd	Found	Obsd	Found
p-CH_3O	60–61	61[a]	67–68	66–68,[b] 68[c]
m-CH_3O	37–38	37,[a] 38[d]	Liq[e]	41,[f] liq[g]
p-CH_3	57–58	55,[h] 59[i]	56–56.5	58,[j] 52–53[h,k]
m-CH_3	...	...	52–53.5	52.9–53.5[l]
H	...	...	67–67.5	67–68[m]
p-F	47–48	48[n]	48.5–49	48[n,o]
m-F	54–55[e]	...	29.5–31	26–27[n,o]
p-Cl	76–76.5	77–78[p]	62–62.5	62[p]
m-Cl	82.5–83.5	82–83[q]	40.5–41	40[o]
p-Br	81.5–82	82[r]	65–66	65[s]
m-Br	76–77	77[o]	44.5–45	43[t]
p-CN	113–113.5	113.5–114.5[u]	70[e]	...
m-CN	90.5–91[e]	...	Liq[e]	...
p-NO_2	137.5–138	138[v]	73–74	74[w]
m-NO_2	95–95.5	95[x]	66–67	68–71,[y] 65.5[z]

[a] F. Ullman and I. Goldberg, *Ber.*, **35**, 2811 (1902). [b] K. E. Hamlin, A. W. Weston, F. E. Fisher, and R. J. Michaels, *J. Am. Chem. Soc.*, **71**, 2731 (1949). [c] D. Y. Curtin and A. Bradley, *ibid.*, **76**, 5777 (1954); R. Adams, W. V. Wirth, and H. E. French, *ibid.*, **40**, 424 (1918). [d] P. Pfeiffer and W. Loewe, *J. Prakt. Chem.*, **147**, 293 (1937). [e] See text. [f] R. Stoermer, *Ber.*, **41**, 321 (1908). [g] M. P. Balfe, E. A. W. Downer, A. A. Evans, J. Kenyon, R. Poplett, C. E. Searle, and A. L. Tarnoky, *J. Chem. Soc.*, 797 (1946). [h] See ref 7. [i] K. V. Auwers and P. Strödter, *Ber.*, **59**, 529 (1926). [j] J. Marshall, *J. Chem. Soc.*, **107**, 509 (1915). [k] R. F. Tietz and W. E. McEven, *J. Am. Chem. Soc.*, **77**, 4007 (1955). [l] See ref 17. [m] See ref 6. [n] W. E. Bachman, R. Hoffman, and F. Whiteland, *J. Org. Chem.*, **8**, 320 (1943). [o] M. S. A. Koopal, *Rec. Trav. Chim.*, **34**, 115 (1915); M. P. J. Montague, *ibid.*, **42**, 499 (1923). [p] M. P. J. Montague, *ibid.*, **26**, 263 (1907). [q] A. Hantsch, *Ber.*, **24**, 31 (1891). [r] A. Schäfer, *Ann. Chem.*, **264**, 152 (1891); C. F. H. Allen and J. Vanaller, *J. Am. Chem. Soc.*, **66**, 7 (1944). [s] M. W. D. Cohen, *Rec. Trav. Chim.*, **38**, 113 (1919). [t] M. P. J. Montague and J. M. van Charante, *ibid.*, **31**, 298 (1912). [u] H. Adkins and C. Scanley, *J. Am. Chem. Soc.*, **73**, 2854 (1951). [v] M. P. Carré, *Ann. Chim. Phys.*, **19**, 206 (1910); G. Schroeter, *Ber.*, **42**, 3356 (1909); A. Basler, *ibid.*, **16**, 2714 (1883). [w] H. Lund, *ibid.*, **B70**, 1520 (1937). [x] M. P. J. Montague, *Rec. Trav. Chim.*, **36**, 258 (1916); R. Geigy and W. Koenig, *Ber.*, **18**, 2400 (1885). [y] M. S. Newman and A. S. Smith, *J. Org. Chem.*, **13**, 592 (1948). [z] See ref 19.

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.37; H, 6.60.

Cyanobenzophenones were prepared from *m*- and *p*-bromobenzophenone by following the procedure for α-naphthonitrile;[31] *m*-cyanobenzophenone, mp 90.5–91°, was ascertained by hydrolyzing it to known *m*-benzoylbenzoic acid, mp 163–164° (lit.[32] mp 161–162°). The sodium borohydride reduction of *m*-cyanobenzophenone gave *m*-cyanobenzhydrol, bp 176° (1.5 mm), n^{20}_{D} 1.5999; the elemental analysis for the *m*-cyano derivative was made on the chloride. *p*-Cyanobenzhydrol, mp 70°, was obtained in the same way. *Anal.* Calcd for $C_{14}H_{11}ON$: C, 80.36; H, 5.30; N, 6.70. Found: C, 80.26; H, 5.33; N, 6.91.

m-Fluorobenzophenone, mp 54–55°, showed the following analytical results. *Anal.* Calcd for $C_{13}H_9OF$: C, 77.99; H, 4.53; F, 9.49. Found: C, 77.89; H, 4.58; F, 9.50.

p-Chlorobenzophenone, *p*-bromobenzophenone, and benzhydrol were commercial products.

Benzhydryl Chlorides.—Dry hydrogen chloride was passed through a solution of carbinol in purified methylene dichloride at 0° in the presence of Drierite. After drying the solution with freshly added Drierite, the solvent was removed completely under reduced pressure and the resulting chloride was used for kinetic measurement without further purification. Cyano and nitro derivatives were prepared by the reaction of carbinols with ten times excess of thionyl chloride; the resulting chloride was distilled under reduced pressure. *m*-Nitrobenzhydryl chloride boiled at 165–166° (2 mm), n^{20}_{D} 1.6117; *p*-nitrobenzhydryl chloride is reported as a solid melting at 63°,[15] but it was a liquid, bp 168° (2 mm), n^{20}_{D} 1.6171, in the present experiment. *Anal.* Calcd for $C_{13}H_{10}NO_2Cl$: C, 63.04; H, 4.07; N, 5.66; Cl, 14.32. Found: C, 62.88; H, 4.00; N, 5.88; Cl, 14.18.

p-Cyanobenzhydryl chloride, bp 162° (2 mm), solidified on standing, mp 58°; *m*-cyanobenzhydryl chloride was a liquid, bp 152° (1 mm), n^{20}_{D} 1.6036. *Anal.* Calcd for $C_{14}H_{10}NCl$: C, 73.85; H, 4.43; N, 6.15; Cl, 15.57. Found: C, 74.09; H, 4.10; N, 6.27; Cl, 15.27.

Solvents.—Ethanol and methanol were dried and purified by Lund-Bjerrum's method;[33] 2-propanol was dried over calcium hydride and distilled over calcium hydride through a 20-in. fractionating column.

Kinetic Measurements.—The method employed was essentially the same as that reported;[34] a 0.02 *M* solution of chloride was thermostated at 25.0° and 5-ml aliquots were taken at appropriate time intervals and quenched by introducing them into 50 ml of dry acetone. The titration was made with standardized 0.02 *N* aqueous sodium hydroxide solution; a mixture of methyl red and bromcresol green was used as an indicator.

The rate constant for the ethanolysis of unsubstituted benzhydryl chloride obtained by undistilled material, which was prepared as described above, was found to be $(5.34 \pm 0.04) \times 10^{-5}$ sec^{-1} in four kinetic runs. This figure was in excellent agreement

TABLE IV

RATE DATA OF SOME BENZHYDRYL CHLORIDES AT VARIOUS TEMPERATURES

Substituent	Solvent	Temp, °C	10^5k_1, sec^{-1}	Log *PZ*	E_a, kcal/mol
p-CH_3O	EtOH	−31.6	67.8		
	2-PrOH	0.02	225		
p-CH_3	MeOH	0.02	112.2		
H	2-PrOH	49.97	9.61	10.32	21.19
		25.00	0.606		
p-CN	EtOH	75.00	3.40	10.69	24.14
		60.00	0.724		
		50.00	0.228		
m-NO_2[a]	EtOH	75.14	3.15	10.10	23.26
		60.17	0.714		
		50.05	0.231		
p-NO_2	EtOH	75.00	1.57	10.51	24.39
		60.00	0.321		
		50.00	0.1026		

[a] Lit.[19] 10^5k_1 (at 75.0°) = 2.78; log PZ = 10.00; E_a = 23.20.

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

(31) M. S. Newman, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 631.

(32) P. Senff, *Ann. Chem.*, **220**, 225 (1883).

(33) A. Weissberger and E. S. Proskauer, "Technique of Organic Chemistry," Vol. VII, Interscience Publishers, Inc., New York, N. Y., 1955, pp 333, 337.

(34) H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Am. Chem. Soc.*, **79**, 1897 (1957).

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$_1$Ar$_2$SeBr$_2$[6] and infrared frequency shifts of the carbonyl stretching vibration in Ar$_1$COAr$_2$.[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$_1$Ar$_2$CHCl) can be represented as eq 1[6]

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

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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