TABLE II

MELTING POINTS OF BENZOPHENONES AND BENZHYDROLS

	Mp, °C			
	Benzophenone		Benzhydrol	
Substituent	Obsd	Found	Obsd	Found
m,m-$(CH_3)_2$	...	...	50–51	50–51[a]
m,m'-$(CH_3)_2$	...	...	Liq[b]	...
m,p'-$(CH_3)_2$	71–72	71,[c] 72[d]	Liq[b]	...
p,p'-$(CH_3)_2$	95	95[e]	71	71[f]
p-Cl-p'-CH_3	127–128.3	128[g]	74–74.2[b]	67.5[h]
p,p'-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.

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.

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).

Results

The rates of solvolysis of several polysubstituted benzhydryl chlorides are determined at 25.0° in methanol, in ethanol, and in 2-propanol; the results are summarized in Table I. Arrhenius parameters for several chlorides are also determined and compared with those of monosubstituted derivatives (Table II).

TABLE I

SUMMARY OF RATE DATA AND EXAMINATION OF ADDITIVITY RELATIONSHIP

Substituent	10^5k_1 at 25.0°, sec^{-1}	k/k_H Obsd	k/k_H Calcd[a]	k/k_H Obsd/Calcd
	Methanolysis			
H	82.8[b]	1.00	...	...
m-Cl-*p'*-CH_3	78.4	0.947	0.573	1.65
m,*p'*-Cl_2	0.821	0.00992	0.00880	1.13
m,*m*-Cl_2	0.0866	0.001046	0.000600	1.74
m,*m*-Cl_2-*p'*-CH_3	4.51	0.0545	0.0140	3.89
m,*m*,*p'*-Cl_3	0.0422	0.000510	0.000215	2.37
	Ethanolysis			
H	5.34[b]	1.00	...	...
m-Cl-*p'*-CH_3O	3700[c]	693	145	4.78
m-Cl-*p'*-CH_3	4.27	0.800	0.538	1.49
m,*p'*-Cl_2	0.0503	0.00942	0.00903	1.04
m,*m*-Cl_2	0.00533	0.000998	0.000548	1.82
m,*m*-Cl_2-*p'*-CH_3O	373	69.9	3.40	20.6
m,*m*-Cl_2-*p'*-CH_3	0.222	0.0416	0.0126	3.30
m,*m*,*p'*-Cl_3	0.00278[d]	0.000521	0.000212	2.46
	2-Propanolysis			
H	0.606[b]	1.00	...	...
m-Cl-*p'*-CH_3O	236	389	107.6	3.62
m-Cl-*p'*-CH_3	0.431	0.711	0.485	1.47
m,*m*-Cl_2-*p'*-CH_3O	22.7	37.5	2.57	14.6
m,*m*-Cl_2-*p'*-CH_3	0.0211	0.0348	0.0116	3.00

[a] $k_{XY}/k_H = (k_X/k_H)(k_Y/k_H)$. [b] Part I of the present series, S. Nishida, *J. Org. Chem.*, **32**, 2692 (1967). [c] Extrapolated from the rate constant at lower temperature by assuming log *PZ* = 11.07;[1] the rate constant at 0.10° was 2.72×10^{-3} sec^{-1}. [d] Extrapolated from the rate constants at higher temperatures (see Table II).

TABLE II

ARRHENIUS PARAMETERS FOR THE ETHANOLYSIS OF SOME BENZHYDRYL CHLORIDES

Substituent	Temp, °C	10^5k_1, sec^{-1}	Log *PZ*	E_a, kcal/mole
m,*m*-Cl_2-*p'*-CH_3O	25.00	373	11.13	18.50
	0.04	21.5		
m,*m*-Cl_2	75.00	2.03	10.73	24.53
	50.07	0.150		
	25.00	0.00553		
m,*m*,*p'*-Cl_3	75.00	1.15	10.64	24.81
	60.00	0.222		
	50.05	0.0724		
H[a]	...	...	11.07	21.4
m-Cl[b]	...	...	11.17	23.32
m-Br[b]	...	...	11.24	23.38
m-NO_2[c]	...	...	10.10[d]	23.26[d]
p-CN[c]	...	...	10.69	24.14
p-NO_2[c]	...	...	10.51	24.39

[a] Calculated from a value reported by S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Am. Chem. Soc.*, **79**, 4146 (1957): $\Delta H^{\ddagger} = 20.84$ kcal $mole^{-1}$ and $\Delta S^{\ddagger} = -7.9$ eu. [b] J. Packer, J. Vaughan, and A. F. Wilson, *J. Org. Chem.*, **23**, 1215 (1958). [c] See footnote *b* of Table I. [d] Lit. log *PZ* = 10.00; E_a = 23.20 kcal $mole^{-1}$ (footnote *b*).

It is apparent that log *PZ* values are constant throughout mono- and polysubstituted benzhydryl chlorides; thus the change in the reactivities can be safely discussed in terms of the change in the energies of activation.

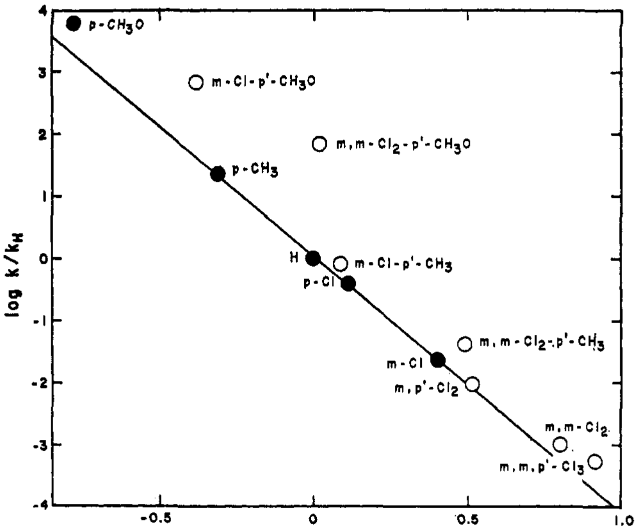

Figure 1.—Hammett plot for the ethanolysis of multisubstituted benzhydryl chlorides at 25.0°; the regression line drawn is for monosubstituted derivatives (footnote *b*, Table I); some points are shown by closed circles.

A plot of relative reactivities *vs.* $\Sigma\sigma^+$ is shown in Figure 1; most of the points for polysubstituted derivatives deviate badly from the regression line for monosubstituted derivatives. Thus, the additivities of the effect of substituents may not be good in the compounds examined and that is certainly seen when the relative rates observed are compared with calculated ones, which are obtained by the multiplication of relative rates of corresponding monosubstituted derivatives (the last column of Table I).

Discussion

In compounds which contain substituted benzene rings symmetrically located with respect to the reaction site (*e.g.*, Ar_1Ar_2YZ), the Hammett equation has been applied in the form[7]

$$\log (k/k_0) = \rho(\sigma_1 + \sigma_2) \qquad (1)$$

where σ_1 and σ_2 are substituent constants for groups Ar_1 and Ar_2, respectively. Equation 1 is valid only if the presence of a substituent in one ring has no effect on the reaction constant for a substituent in the other ring.[7] When substituents are multiplied on one benzene ring, the effect of multiple substitution on the reactivity can be expressed in the form[6,7]

$$\log (k/k_0) = \rho\Sigma\sigma \qquad (2)$$

where the reaction constant is considered to be the same as that of monosubstituted derivatives,[6,7] because the side chain ($C_6H_5\overset{|}{Y}Z$) is common to both monosubstituted and polysubstituted systems. The validity of eq 1 and 2 has been argued in certain typical side-chain reactions,[3-8] such as the ionization of benzoic acids, the reaction of phenyl isothiocyanates with ethanol, and the dissociation of $Ar_1Ar_2SeBr_2$.

If eq 1 and 2 are also valid for the solvolysis of benzhydryl chlorides, a clear Hammett plot is expected; all points of polysubstituted derivatives should lie on the same regression line for monosubstituted benzhydryl chlorides. However, it is definitely found that points of polysubstituted chlorides deviate seriously from a predicted line, as shown in Figure 1. The compound substituted only in one benzene ring, *m,m*-dichlorobenzhydryl chloride, also shows a deviation; thus it is concluded that neither eq 1 nor 2 is applicable to the present results.

The deviations are more clearly seen when the additivity of the effect of substituents is examined; as shown in the last column of Table I, serious deviations are observed in *m,m*-dichloro-*p'*-methoxy, *m,m*-dichloro-*p'*-methyl, and *m*-chloro-*p'*-methoxy derivatives. *m,m*-Dichloro-*p'*-methoxybenzhydryl chloride, for example, solvolyzed at a rate 20.6 times greater than that predicted from the reactivities of *m*-chloro- and *p*-methoxybenzhydryl chloride in ethanol. The relative reactivity for *m,m*-dichlorobenzhydryl chloride, in which two chloro groups are multiplied on one benzene ring, was 1.82 times greater than that predicted; the figure is absolutely out of the experimental uncertainty because the accuracy in the rate constant is within 3%.[1] Thus, it is apparent that the additivity relationship is not held in the electrophilic side-chain reaction even if the substituents are placed at the *m,m*, *m,p'*, or *m,m,p'* position.

Fox and Kohnstam[10] have studied the solvolysis of various *p,p'*-disubstituted benzhydryl chlorides in 85% acetone at 0° and they have concluded that the existing linear free-energy relationship will not be successful in the accurate prediction of rates when polarizable substituents are conjugated to an electron-demanding reaction center. In the present case, however, substituents are multiplied not on the *p,p'* position but on the *m,m*, *m,p'*, and *m,m,p'* positions, where such a conjugating interaction can not be considered to be an important factor; nevertheless, the deviations are still serious in all derivatives investigated. Accordingly, the deviation from a predicted reactivity cannot merely be due to the conjugating interaction of two substituents in the electron-deficient transition state. Moreover, clear additivities observed in *p*-chloro-*p'*-methyl and *p,p'*-dichloro derivatives,[1] where such an interaction must be present, also support this conclusion.

From Table I and Figure 1, it is suggested that the discrepancy in the additivity relationship of multiple substitutions is most serious when the first substituent is strongly electron releasing, such as *p*-methoxy, or strongly electron attracting, such as *m,m*-dichloro. It turns out that a powerful first substituent will change the reaction constant for a second substituent and, therefore, the second substituent will influence the reactivity in the different magnitude from that of the first substituent. In this respect, the observed relative rates are plotted against calculated ones (Figures 2–4).[11,12] It is clearly seen that the compounds examined in this series of investigations[1,12] can be divided into seven groups, namely, *p*-methoxy, *p*-methyl, *m*-methyl, hydrogen, *p*-chloro, *m*-chloro, and *m,m*-dichloro; each of these groups shows good linearity as seen in the figures. These results lead us to a conclusion that the Hammett equation for the multiple substitution in the electrophilic side-chain reaction must be represented in the form

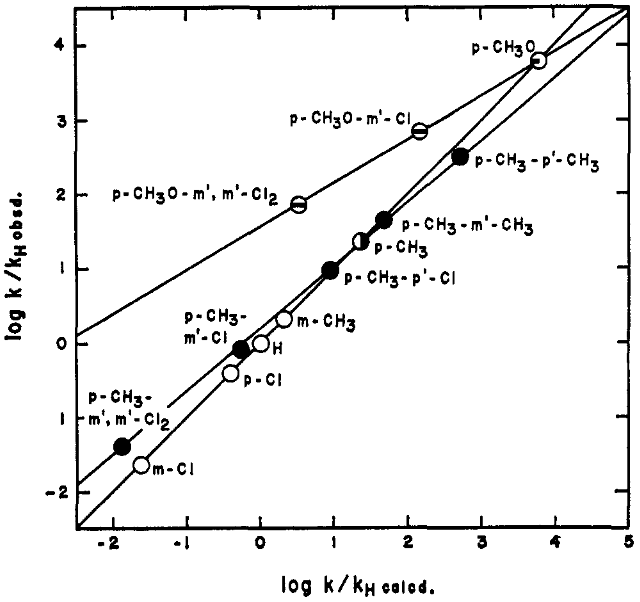

Figure 2.—Plots of log $'k/k_H$ (obsd) *vs.* log k/k_H (calcd); ⊖, $p\text{-}CH_3OC_6H_4CHClC_6H_4X$; ●, $p\text{-}CH_3C_6H_4CHClC_6H_4X$; ○, $C_6H_5CHClC_6H_4X$.

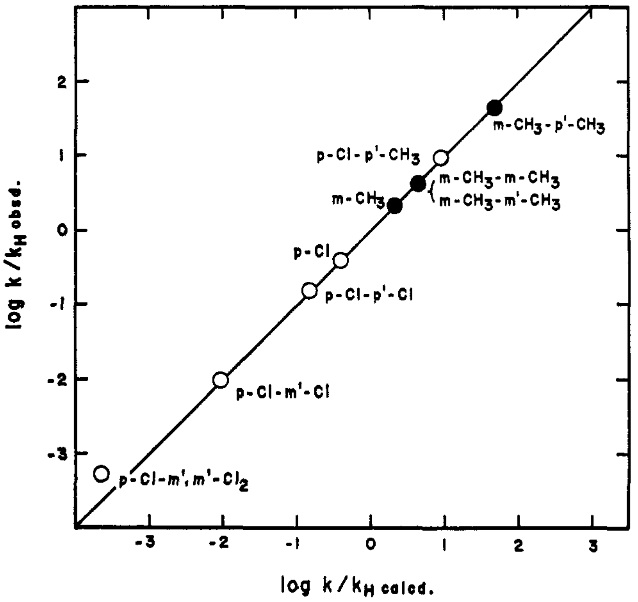

Figure 3.—Plots of log k/k_H (obsd) *vs.* log k/k_H (calcd); ●, $m\text{-}CH_3C_6H_4CHClC_6H_4X$; ○, $p\text{-}ClC_6H_4CHClC_6H_4X$.

$$\log (k/k_0) = \alpha\rho\Sigma\sigma^+ + \beta \qquad (3)$$

where α and β are the constants characteristic for the principal substituent; the values for the present study are given in Table III. Equation 3 indicates that ρ values for polysubstituted derivatives are not generally constant; thus the necessary condition to validate eq 1,[7] *e.g.*, the constancy in ρ throughout, is lost in the solvolysis of benzhydryl chlorides. For *m*-methyl and *p*-chloro series, slopes (α) are found to be close to unity and intercepts (β) are almost zero, so that eq 3 becomes identical with eq 1 and 2. In other words, the additivity of the effect of substituents can be antici-

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(11) Since a point for *p*-methoxybenzhydryl chloride deviated from the regression line in the monosubstituted derivatives,[12] the Hammett plot is not suitable for an accurate evaluation of the effects of multiple substitution. Therefore, a plot between observed and calculated relative rates is employed.

(12) See *footnote b* of Table I.

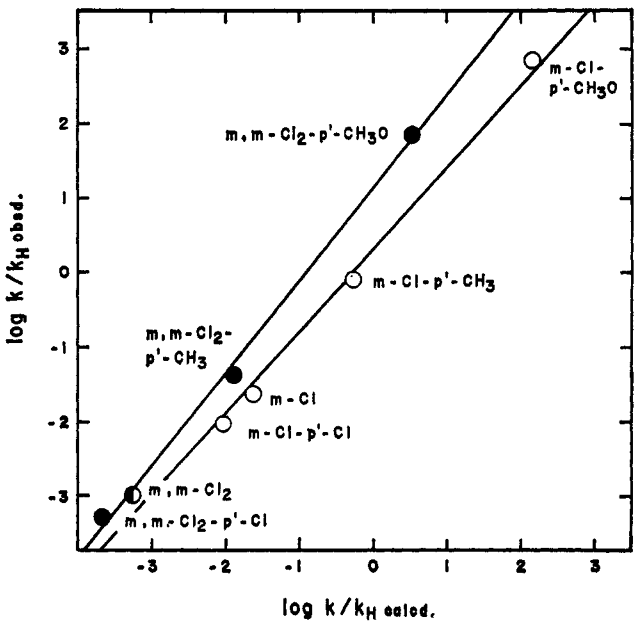

Figure 4.—Plots of log k/k_H (obsd) *vs.* log k/k_H (calcd): ○, m-$ClC_6H_4CHClC_6H_4X$; ●, m,m-$Cl_2C_6H_3CHClC_6H_4X$.

TABLE III

SLOPES AND INTERCEPTS OF THE PLOT OF LOG $k/k_{H\text{obsd}}$ *vs.* LOG $k/k_{H\text{calcd}}$

Group	n^a	Slope, α	Intercept, β	r^b
p-CH_3O^c	3	0.597	1.536	1.000
p-CH_3^d	6	0.848	0.191	1.000
m-CH_3^e	4	0.976	−0.001	1.000
H	...	1.000	0.000	...
p-Cl^f	4	1.001	0.012	0.999
m-Cl^g	5	1.098	0.325	0.997
m,m-Cl_2^h	4	1.239	1.117	0.998

[a] Numbers of the compounds included in a group. [b] Correlation coefficient. [c] Including p-CH_3O, p-CH_3O-m'-Cl, and p-CH_3O-m',m'-Cl_2. [d] Including p,p'-$(CH_3)_2$, p,m'-$(CH_3)_2$, p-CH_3, p-CH_3-p'-Cl, p-CH_3-m'-Cl, and p-CH_3-m',m'-Cl_2. [e] Including m,p'-$(CH_3)_2$, m,m-$(CH_3)_2$, m,m'-$(CH_3)_2$, and m-CH_3. [f] Including p-Cl-p'-CH_3, p-Cl, p,p'-Cl_2, and p,m'-Cl_2. [g] Including m-Cl-p'-CH_3O, m-Cl-p'-CH_3, m-Cl, m,p'-Cl_2, and m,m-Cl_2. [h] Including m,m-Cl_2-p'-CH_3O, m,m-Cl_2-p'-CH_3, m,m-Cl_2, and m,m,p'-Cl_3.

pated in m-methyl and p-chloro series unless the second substituent is not so powerful.[1]

The slope is most steep in the m,m-dichloro series and least in p-methoxy. It suggests that the transition state substituted by a strongly electron-withdrawing group is more electron deficient than it is in the unsubstituted (hydrogen) series, so that the electron demand in such a transition state (for example, m,m-$Cl_2C_6H_3$-$C_6H_5CH^+$) must be more than that in the parent system ($(C_6H_5)_2CH^+$). Consequently, the second substituent in the m,m-dichloro series influences the reactivity more strongly than it does in the hydrogen series; namely, a ρ value for the m,m-dichloro series is bigger than that for the hydrogen series. On the other hand, when the first substituent is strongly electron releasing, such as p-methoxy, then a smaller ρ results for the series. From these arguments, it is apparent that a change of electron deficiency in the transition state must be a function of the electron-releasing or -withdrawing power of the first substituent. Although a plot of α *vs.* σ^+ of the first substituent gives a folded line (Figure 5), it is clearly seen that α depends on the magnitude of the σ^+ of the first substituent.

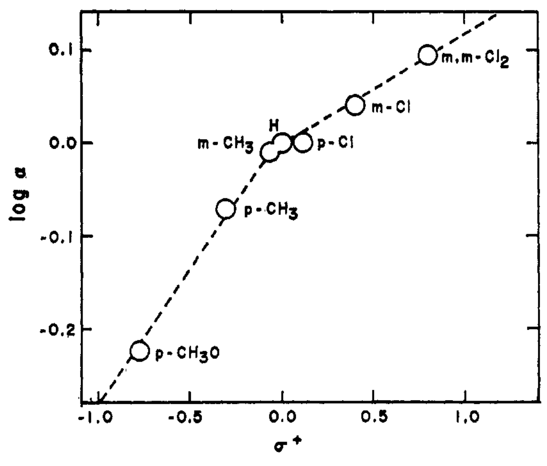

Figure 5.—A plot of log α *vs.* σ^+.

When three substituents are multiplied on a compound, the combined effect is found to be more complicated than that of disubstituted derivatives. m,m-Dichloro derivatives can be considered to be members of the m-chloro group, but they constitute apparently a separate group, as seen in Figure 4; thus an additional correction term must be introduced in the additivity treatment of these derivatives.

In conclusion, it is shown that the effect of the multiple substitution on the reactivity in the electrophilic side chain reaction may not be additive regardless of whether the multiplication of substituents is on one benzene ring or two. Deviations are observed not only in p,p'-disubstituted derivatives but also in m,m-, m,p'-, and m,m,p'-polysubstituted derivatives. An examination of all compounds reveals that the ρ value for polysubstituted derivatives is not the same as that for monosubstituted series and the correlation of the reactivity in the polysubstituted system can be achieved by eq 3. A four-parameter equation proposed by Fox and Kohnstam,[10] in which a σ value for the second substituent is also influenced by the first one, is not necessary in the present case.

Experimental Section[13]

Materials.—The methods used for preparing materials were essentially the same as those reported.[12] Melting points of benzophenones are given in Table IV; boiling points, refractive indexes, and melting points of benzhydrols are shown in Table V.

m,m-Dichlorobenzoyl chloride, mp 28.0–28.3° (lit.[14] liquid), was prepared from p-aminobenzoic acid according to Elion's procedure.[15] Most of benzhydryl chlorides were prepared by the reaction of carbinol with dry hydrogen chloride,[12] but m,m-dichloro, m,p'-dichloro, and m,m,p'-trichloro derivatives were prepared by the reaction of the carbinol with thionyl chloride.[12] Physical properties of these chlorides were as follows: m,p'-dichloro, bp 174–175° (3.8 mm), $n^{20}D$ 1.6107; m,m-dichloro, bp 156–156.5° (2 mm), $n^{20}D$ 1.6104; m,m,p'-trichloro, bp 152.5–153° (1 mm), $n^{20}D$ 1.6185.

Solvent and Rate Measurements.—The purification of the solvent and the technique of rate measurements were the same as those described previously.[12]

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

(14) G. H. Stempel, Jr., C. Green, R. Rongone, B. Sobel, and R. Odioso, *J. Am. Chem. Soc.*, **73**, 455 (1951); J. B. Cohen and H. C. Briggs, *J. Chem. Soc.*, **83**, 1213 (1903).

(15) L. Elion, *Rec. Trav. Chim.*, **42**, 145 (1923).

TABLE IV

MELTING POINTS OF POLYSUBSTITUTED BENZOPHENONES

Substituents	Mp, °C Obsd	Mp, °C Found
m-Cl-*p*′-CH_3O[a]	72.0–72.5	. . .
m-Cl-*p*′-CH_3	97.0–98.0	97–98[b]
m,*p*′-Cl_2	112.5–113.5	113[c]
m,*m*-Cl_2-*p*′-CH_3O[d]	117.0–118.0	. . .
m,*m*-Cl_2-*p*′-CH_3[e]	49.5–50.0	. . .
m,*m*-Cl_2	66.5–67.5	65[f]
m,*m*,*p*′-Cl_3[g]	80.5–81.3	. . .

[a] *Anal.* Calcd for $C_{14}H_{11}O_2Cl$: C, 68.16; H, 4.50; Cl, 14.37. Found: C, 68.38; H, 4.51; Cl, 14.25. [b] W. E. Bachman and J. W. Ferguson, *J. Am. Chem. Soc.*, **56**, 2081 (1934). [c] H. L. Haller, P. D. Bartlett, N. L. Drake, M. S. Newman, S. J. Cristol, C. M. Eaker, R. A. Hayes, G. W. Kilmer, B. Magerlein, G. P. Mueller, A. Schneider, and W. Wheatley, *ibid.*, **67**, 1591 (1945). [d] *Anal.* Calcd for $C_{14}H_{10}O_2Cl_2$: C, 59.81; H, 3.59; Cl, 25.22. Found: C, 59.58; H, 3.46; Cl, 25.49. [e] Analyzed on benzhydrol; see Table V. [f] W. A. Waters, *J. Chem. Soc.*, 2106 (1929). [g] *Anal.* Calcd for $C_{13}H_7OCl_3$: C, 54.68; H, 2.47; Cl, 37.25. Found: C, 54.76; H, 2.31; Cl, 37.01.

TABLE V

PHYSICAL CONSTANTS OF POLYSUBSTITUTED BENZHYDROLS

Substituents	Mp, °C	Bp (mm), °C	$n^{20}D$
m-Cl-*p*′-CH_3O[a]	. . .	154–155 (0.6)	1.5991
m-Cl-*p*′-CH_3[b]	. . .	157–158 (1.1)	1.5933
m,*p*′-Cl_2[c]	. . .	147 (0.5)	1.6078
m,*m*-Cl_2-*p*′-CH_3O[d]	. . .	184–184.5 (1)	1.6064
m,*m*-Cl_2-*p*′-CH_3[e]	88.5–89.0	. . .	. . .
m,*m*-Cl_2[f]	45.5–46.0	149 (1.7)	. . .
m,*m*,*p*′-Cl_3[g]	103.5–104.0	. . .	. . .

[a] *Anal.* Calcd for $C_{14}H_{13}O_2Cl$: C, 67.61; H, 5.27; Cl, 14.26. Found: C, 67.60; H, 5.47; Cl, 14.40. [b] *Anal.* Calcd for $C_{14}H_{13}OCl$: C, 72.26; H, 5.63; Cl, 15.24. Found: C, 72.07; H, 5.66; Cl, 15.50. [c] *Anal.* Calcd for $C_{13}H_{10}OCl_2$: C, 61.68; H, 3.98; Cl, 28.01. Found: C, 61.73; H, 3.68; Cl, 28.20. [d] *Anal.* Calcd for $C_{14}H_{12}O_2Cl_2$: C, 59.38; H, 4.27; Cl, 25.04. Found: C, 59.46; H, 4.04; Cl, 25.25. [e] *Anal.* Calcd for $C_{14}H_{12}OCl_2$: C, 62.94; H, 4.53; Cl, 26.54. Found: C, 63.09; H, 4.75; Cl, 26.49. [f] Since the purification of this carbinol was troublesome, it was purified and analyzed on chloride. *Anal.* Calcd for $C_{13}H_9Cl_3$: C, 57.49; H, 3.34; Cl, 39.17. Found: C, 57.25; H, 3.14; Cl, 39.01. [g] *Anal.* Calcd for $C_{13}H_9OCl_3$: C, 54.29; H, 3.15; Cl, 36.99. Found: C, 54.25; H, 2.86; Cl, 37.01.

Registry No.—Benzhydryl chloride, 90-99-3; *m*-chloro-*p*′-methyl benzhydryl chloride, 13389-44-1; *m*,-*p*′-dichlorobenzhydryl chloride, 13389-45-2; *m*,*m*-dichlorobenzhydryl chloride, 13389-46-3; *m*,*m*-dichloro-*p*′-methylbenzhydryl chloride, 13389-47-4; *m*,*m*,*p*′-trichlorobenzhydryl chloride, 13389-48-5; *m*-chloro-*p*′-methoxybenzhydryl chloride, 13389-49-6; *m*,*m*-dichloro-*p*′-methoxybenzhydryl chloride, 13389-50-9; *m*-chloro-*p*′-methoxybenzophenone, 13389-51-0; *m*-chloro-*p*′-methylbenzophenone, 13395-60-3; *m*,*p*′-dichlorobenzophenone, 7498-66-0; *m*,*m*-dichloro-*p*′-methoxybenzophenone, 13395-62-5; *m*,*m*-dichloro-*p*′-methylbenzophenone, 13395-63-6; *m*,*m*-dichlorobenzophenone, 13395-64-7; *m*,*m*,*p*′-trichlorobenzophenone, 13395-65-8; *m*-chloro-*p*′-methoxybenzhydrol, 13395-66-9; *m*-chloro-*p*′-methylbenzhydrol, 13395-67-1; *m*,*p*′-dichlorobenzhydrol, 13421-95-9; *m*,*m*-dichloro-*p*′-methoxybenzhydrol, 13395-68-1; *m*,*m*-dichloro-*p*′-methylbenzhydrol, 13395-69-2; *m*,*m*-dichlorobenzhydrol, 13395-70-5; *m*,*m*,*p*′-trichlorobenzhydrol, 13421-96-0.

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Reactions of *o*-Halophenylazo Phenyl Sulfones and of (*o*-Chlorophenyl)triphenylphosphonium Iodide with Sodium Methoxide in Methanol[1]

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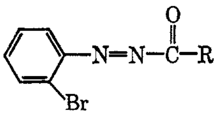
The reactions of *o*-halophenylazo phenyl sulfones with $NaOCH_3$ are essentially reactions of diazonium ions formed by ionic dissociation. In very dilute $NaOCH_3$, halobenzenes are produced by a radical mechanism; ordinary chlorobenzene (C_6H_5Cl) is formed in CH_3OD solution. In concentrated (2 *M*) $NaOCH_3$, halobenzenes arise *via* *o*-halophenyl anion intermediates; chlorobenzene-2-*d* is produced in CH_3OD solution. The action of $NaOCH_3$ on (*o*-chlorophenyl)triphenylphosphonium iodide affords chlorobenzene *via* the *o*-chlorophenyl anion intermediate, as shown by the formation of *o*-C_6H_4DCl in CH_3OD.

With the objective of finding new ways to generate *o*-halophenyl anions in methanol, we carried out the investigations now reported. New ways to generate these reactive intermediates were indeed found, but some of the phenomena encountered did not match our original expectations.

Reactions of *o*-Halophenylazo Phenyl Sulfones.[3]—Hoffmann[4] has reported that *o*-halophenylazo ketones (1) are cleaved by sodium ethoxide, forming esters ($RCOOC_2H_5$) and products which indicate the intermediacy of *o*-bromophenyl anions. Desiring a convenient source of *o*-bromoaryl anions,[5] and having found compounds of type 1 somewhat inconvenient to prepare, we investigated the action of methanolic sodium



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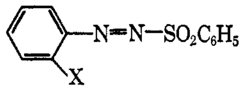

2a, X = Cl
b, X = Br

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(3) Preliminary communication: J. F. Bunnett, D. A. R. Happer, and H. Takayama, *Chem. Commun.*, 367 (1966).

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