[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Rates of Solvolysis of Phenyldimethylcarbinyl Chlorides Containing Meta Directing Substituents[1,2]

BY Y. OKAMOTO,[3] T. INUKAI[4] AND HERBERT C. BROWN

RECEIVED FEBRUARY 28, 1958

Rates of solvolysis in 90% aqueous acetone have been determined for *m*- and *p*-carboxyl-, *m*- and *p*-carbomethoxy-, *m*- and *p*-carboethoxy-, *m*- and *p*-cyano, and *m*- and *p*-trifluoromethylphenyldimethylcarbinyl chlorides. In each case the *para* derivative solvolyzes at a slower rate than the related *meta* compound, corresponding to the *meta* orientation exhibited by these groups in electrophilic aromatic substitution. The decrease in solvolysis rates, $CO_2H < CO_2Me$, $CO_2Et < CF_3 < CN < NO_2$, likewise agrees with the available data on the effects of these groups on the reactivity of aromatic nuclei toward electrophilic substitution. The solvolysis rates correlate satisfactorily with the Hammett σ-constants in the case of both *meta* and *para* substituents.

The electrophilic substituent constants, σ^+, obtained from the solvolysis of substituted *t*-cumyl chlorides,[5] have exhibited considerable promise in correlating the available data on electrophilic aromatic substitution[6] and electrophilic side-chain reactions.[7] In order to provide a more extensive test of the full utility of these constants, we decided to evaluate such constants for additional substituents. In the present paper, substituent constants are reported for typical *meta* directing groups: $-CO_2H$, $-CO_2Me$, $-CO_2Et$, $-CN$ and $-CF_3$.

Results

m-Carboxyphenyldimethylcarbinol was synthesized by permanganate oxidation of *m*-tolyldimethylcarbinol. The isomeric *para* compound was prepared by controlled oxidation of cumic acid with potassium permanganate. The acids were converted into the corresponding methyl and ethyl esters.

m-Cyanocumene was treated with N-bromosuccinimide to form the tertiary bromide. This was dehydrohalogenated to form the olefin, *m*-cyano-α-methylstyrene. *p*-Cyanocumene was oxidized with potassium permanganate to form the tertiary alcohol.

m- and *p*-trifluoromethylbenzoic acids were synthesized *via* *m*-trifluoromethylaniline. The acids were transformed into the methyl esters and treated with methylmagnesium iodide to form the tertiary alcohols.

The alcohols and olefin were converted into the tertiary chlorides with hydrogen chloride at 25° and the rates of solvolysis of these chlorides were measured in 90% aqueous acetone. Since the rates for some of the compounds were very slow at 25°, the rates in these cases were calculated by extrapolation of data obtained at elevated temperatures. The results are summarized in Table I.

In the case of the carboxyl substituent, we were concerned over the possibility that solvolysis might occur through both the ionized and un-ionized derivative. However, the rate data exhibited no change during the course of the solvolysis, in spite of the increasing acidity of the solution (see Experimental Part). It was therefore concluded that ionization of the carboxylate group was not a significant factor in influencing the solvolysis rate.

In the previous studies the entropies of activation exhibited quite satisfactory constancies. However, in the present cases considerable variation is observed in this quantity. The data in individual studies exhibited satisfactory constancy. Nevertheless, we suspect that the variations are not real but result from the slowness of the reactions, the volatility of the solvent, and the shortness of the temperature range to which this volatility restricted the rate measurements. There is also the possibility that under the influence of the acid formed in the solvolysis, the organic component of the solvent, acetone, may undergo some change in the relatively long reaction times which were necessary for these rate studies. Such minor changes in the composition of the solvent might introduce minor variations in the rate constants, and the latter could result in relatively large variations in the activation parameters.

Fortunately, the extrapolations required to calculate the rate constants at 25° are relatively short, usually no more than 10° and never more than 20°. Consequently, the uncertainty in the temperature coefficient of the rate constants should not introduce a serious error in the extrapolated value of the rate constant and the value of the σ^+-constant calculated therefrom.

It was of interest to determine the σ^+-constant for the carboxylate group, CO_2^-. However, our attempts to ionize the carboxyl group by addition of sodium hydroxide or other bases to solutions of *p*-carboxy-*t*-cumyl chloride in 90% acetone invariably resulted in the formation of two phases. It became apparent that a new solvent system would be required for this particular study.[8]

Discussion

All of the *meta* directing groups examined ($-CO_2H$, $-CO_2Me$, $-CO_2Et$, $-CF_3$, $-CN$, $-NO_2$) markedly reduce the rates of solvolysis of the *t*-cumyl chlorides. Moreover, in each case the group

---

(1) Directive Effects in Aromatic Substitution. XXVII.

(2) This research was supported in part by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

(3) Post-doctorate research assistant on a National Science Foundation Grant (G-2752), 1956–1957.

(4) Research assistant on a grant from the Petroleum Research Fund, 1956–1958.

(5) (a) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, THIS JOURNAL, **79**, 1897 (1957); (b) Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1903 (1957); (c) H. C. Brown, Y. Okamoto and G. Ham, *ibid.*, **79**, 1906 (1957); (d) Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1909 (1957).

(6) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957).

(7) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

(8) Y. Okamoto, T. Inukai and H. C. Brown, THIS JOURNAL, **80**, 4972 (1958).

TABLE I

RATE CONSTANTS AND DERIVED DATA FOR THE SOLVOLYSIS OF *t*-CUMYL CHLORIDES CONTAINING *meta* DIRECTING SUBSTITUENTS

Substituent	Rate constant, k_1, sec.$^{-1}$ × 10^5 25.0°	35.0°	45.0°	55.0°	65.0°	Rate ratio at 25°	E_{act}	log *A*	$\Delta H\ddagger$	$\Delta S\ddagger$
m-Carboxy	0.428		4.58	12.3		0.0345	21.8	10.6	21.2	−11.9
p-Carboxy	.154[a]	0.489	1.26	3.75		.0124	20.5	9.3	19.9	−18.3
m-Carbomethoxy	.263		2.70	8.72		.0212	22.5	10.9	21.7	−11.2
p-Carbomethoxy	.0750[a]	.261	0.817	2.48		.00605	22.7	10.5	22.1	−11.1
m-Carbethoxy	.269		2.77	8.22[b]		.0217	22.0	10.6	21.5	−11.9
p-Carboethoxy	.0806[a]	.286	0.908	2.81		.00650	23.1	10.7	22.4	−11.1
m-Trifluoromethyl	.0550		.572	1.64		.00441	22.0	9.9	21.4	−15.5
p-Trifluoromethyl	.0206		.226	0.644		.00166	22.3	9.7	21.7	−16.3
m-Cyano	.0347[a]		.342	0.925	2.54	.00279	21.5	9.3	20.8	−18.3
p-Cyano	.0126[a]		.161	0.531	1.53	.00102	24.1	10.7	23.4	−11.5
m-Nitro[c]	.0108					.000871				
p-Nitro[c]	.00319					.000257				

[a] Calculated from rate constants at higher temperatures. [b] Rate constant observed for solvolysis of 1 g. of chloride in presence of 0.6 g. of benzoic acid was 8.81 (sec.$^{-1}$ × 10^5). [c] Ref. 5d.

exerts a larger effect upon the solvolysis rate in the *para* than in the *meta* position. This decreased rate of the *para* derivative as compared to the corresponding *meta* isomer parallels the preferred *meta* orientation exhibited by these groups in electrophilic aromatic substitution.

The observed ratio, k_m/k_p, is very nearly constant, 3.1 ± 0.4, in the series: $-CO_2H$, 2.8; $-CO_2Me$, 3.5; $-CO_2Et$, 3.3; $-CF_3$, 2.7; $-CN$, 2.7; $-NO_2$, 3.4. This behavior is very different from that observed with activating groups such as fluoro, methyl and methoxy. Presumably, the difference in behavior arises from the fact that these *meta* directing groups exert their influence predominantly through an inductive mechanism with only minor resonance contributions.[9]

This conclusion is further supported by a plot of log *k* for the hydrolysis of these substituents *versus* the σ-constants. In contrast to the behavior of *ortho–para* directing groups in such a plot, these *meta* directing groups give a reasonably good linear relationship with the σ-constants (Fig. 1). Even the trifluoromethyl groups, which exhibit the largest deviation, fall just within the limits of the estimated uncertainty in the value of the σ-constants.[10]

Utilizing $\rho = -4.54$[11] values of σ_m^+ and σ_p^+ have been calculated with the aid of the expression

$$\sigma = \frac{1}{\rho} \log (k/k_H)$$

The results are listed in Table II together with the values of σ. It is apparent that the deviations fall within the limit of the estimated uncertainties of the σ-values.

It was pointed out that for these six substituents, k_m/k_p was very nearly constant, 0.31 ± 0.4. It follows that for these six substituents, the difference in the *meta* and *para* electrophilic substituent constants, $\sigma_p^+ - \sigma_m^+$, will be very nearly constant, 0.10 unit. If we may generalize on the basis of these six cases, this simple relationship should be quite useful in estimating σ^+ (or σ) constants for *meta* directing substituents in cases where the value of but one of the two constants is known.

The effect of these groups on the solvolysis rates, $-CO_2H < -CO_2Me$, $-CO_2Et < -CF_3 < -CN < -NO_2$, corresponds roughly with the available data on the effect of these groups on decreasing the reactivity of the corresponding aromatics toward electrophilic substitution.[12] The utility of these groups to correlate quantitatively the rates and isomer distributions observed in aromatic substitution will be considered in the final paper of this group.[11]

TABLE II

SUBSTITUENT CONSTANTS FOR *meta* DIRECTING SUBSTITUENTS

Substituent	Substituent constant σ^a	σ^+	Difference $\sigma - \sigma^+$	Estimated uncertainty in σ^a
m-Carboxy	(0.37)[b]	0.322	0.05	0.10
p-Carboxy	(.45)[b]	.421	.03	.10
m-Carbomethoxy	(.37)[b]	.368	.00	.10
p-Carbomethoxy	(.45)[b]	.489	− .04	.10
m-Carboethoxy	.37	.366	.00	.10
p-Carboethoxy	.45	.482	− .03	.10
m-Trifluoromethyl	.42	.520	− .10	.10
p-Trifluoromethyl	.54	.612	− .07	.10
m-Cyano	.56	.562	.00	.05
p-Cyano	.660	.659	.00	.02
m-Nitro	.710	.674	.04	.02
p-Nitro	.778	.790	− .01	.02

[a] Reference 10. [b] Estimated from σ-constants for *m*- and *p*-carboethoxy.

Experimental Part

***m*- and *p*-Carboxyphenyldimethylcarbinol.**—*m*-Tolyldimethylcarbinol[5a] ($n^{20}D$ 1.5180, 60 g.) was placed in a 5-l. 3-necked flask, fitted with stirrer, reflux condenser and dropping funnel. A solution of 140 g. of potassium permanganate in 3.5 l. of water was added in 100-ml. portions, each portion being added only after the color of the previous portion had been largely discharged. The solution was filtered, and acidified to precipitate the product. After re-

---

[9] For a detailed discussion of the inductive and resonance factors in aromatic substitution, see G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 476 ff.

[10] For a summary of the available σ-constants based only on the ionization of benzoic acids together with an estimate of the probable limits of uncertainty, see D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

[11] H. C. Brown and Y. Okamoto, THIS JOURNAL, **80**, 4979 (1958).

[12] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapt. VI.

crystallization from boiling water, the product was obtained in 42% yield, m.p. 124.5–125.5° (lit.[13] 123–124°).

Cumic acid (Hercules Powder Co.) was oxidized by alkaline permanganate to the carbinol in 44% yield, m.p. 154–156° (lit.[14] 155–156°).

m- and *p*-**Carboethoxy-α-methylstyrene.**—*m*-Carboxyphenyldimethylcarbinol was refluxed with ethanol, in the presence of hydrogen chloride as catalyst, for approximately six hours. In the course of the esterification, the carbinol was dehydrated to the olefin. *m*-Carboethoxy-α-methylstyrene, b.p. 89.6–89.8° at 2 mm., n^{20}_{D} 1.5298, was obtained in 59% yield.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.73; H, 7.37.

p-Carboethoxy-α-methylstyrene, m.p. 21.5–22.5°, n^{20}_{D} 1.5400, was obtained from *p*-carboxyphenyldimethylcarbinol in a similar manner in 53% yield.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.92; H, 7.35.

m- and *p*-**Carbomethoxy-α-methylstyrene.**—*p*-Carbomethoxy-α-methylstyrene, m.p. 55.0–56.0° (lit.[15] 53.0°), was obtained in 39% yield by esterification of the acid with methanol.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.99; H, 7.00.

m-Carboxyphenyldimethylcarbinol was esterified by methanol in a similar manner. The product distilled as a mixture of olefin and alcohol, b.p. 123–132° at 10 mm. This mixture was used directly for the preparation of the tertiary chloride.

m-**Cyano-α-methylstyrene.**—*m*-Cyanocumene, b.p. 73–74° at 4 mm., n^{20}_{D} 1.5163, was prepared by the reaction of cuprous cyanide on *m*-bromocumene, b.p. 71–74° at 2.5 mm., n^{20}_{D} 1.5370.[16] The *m*-cyanocumene, 10.0 g., was refluxed with 16.0 g. of N-bromosuccinimide and 1.0 g. of benzoyl peroxide in 35 cc. of carbon tetrachloride. The reaction mixture was filtered, the solvent removed, and 20 cc. each of benzene and 2,6-lutidine were added to the residual material. After standing overnight, the reaction mixture was heated for 30 min. at 70°. The precipitated salt was removed by filtration, and the solution was washed with dilute hydrochloric acid, water, and dried over Drierite. *m*-Cyano-α-methylstyrene, b.p. 77° at 1 mm., n^{20}_{D} 1.5569, was obtained in 66% yield.

Anal. Calcd. for $C_{10}H_9N$: C, 83.87; H, 6.35; N, 9.78. Found: C, 84.20; H, 6.18; N, 9.59.

p-**Cyanophenyldimethylcarbinol.**—*p*-Bromocumene, b.p. 116–118° at 30 mm., n^{20}_{D} 1.5378, was converted into *p*-cyanocumene by the same procedure. The product, b.p. 143–145° at 40 mm., n^{20}_{D} 1.5210, was oxidized with potassium permanganate to form the carbinol. The crude product was obtained in 44% yield. After two recrystallizations from petroleum ether (b.p. 30–60°), the *p*-cyanophenyldimethylcarbinol was obtained in 22% yield, m.p. 49–51° (lit.[17] 51–52°).

m- and *p*-**(α,α,α-Trifluoro)-tolyldimethylcarbinols.**—Originally we prepared *m*- and *p*-bromobenzotrifluoride, converted them to the corresponding Grignard reagents, and synthesized the desired carbinols by reaction with acetone. The reaction kinetics exhibited peculiarities which suggested that the preparations, analytically pure, contained more than a single isomer. Consequently, we decided to proceed through the well characterized solid derivatives, *m*- and *p*-trifluoromethylbenzoic acids.

p-Bromobenzotrifluoride was prepared from *m*-trifluoromethylaniline, b.p. 84° at 16.5 mm., n^{20}_{D} 1.4789, following the procedure of Tarrant and Lilyquist[18] in 20% yield. The bromide, b.p. 157.2–157.7° at 752 mm., n^{20}_{D} 1.4728 (lit.[18] b.p. 154–155°, n^{25}_{D} 1.4705), was converted into the Grignard reagent and carbonated.[19] The acid, recrystallized from 75% aqueous acetic to constant melting point, 219–220° (lit. m.p. 212–213°,[19] 219–220°[20]), was obtained in 58% yield.

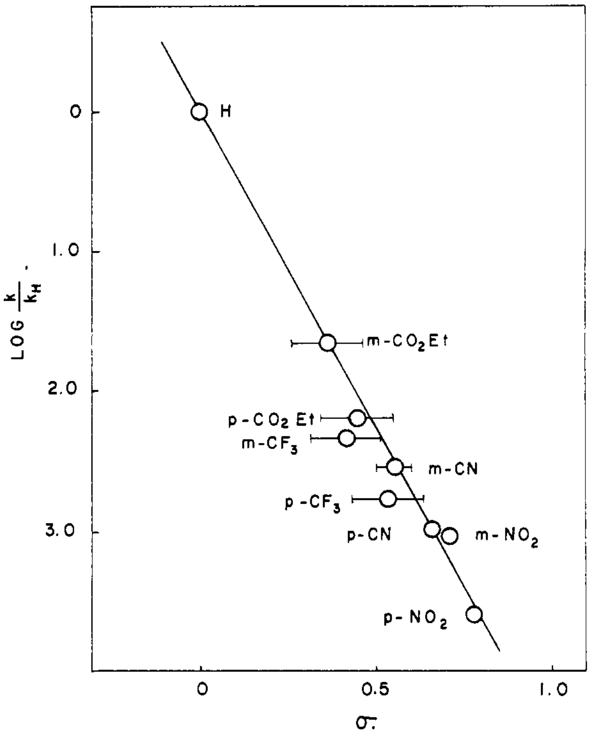

Fig. 1.—Linear free energy relationship between the rates of solvolysis of *t*-cumyl chlorides containing *meta* directing substituents and the Hammett substituent constants. The line shown is based on a least squares treatment of all meta substituents whose sigma constants are based on thermodynamic dissociation constants.

The acid was esterified by methanol in the presence of hydrogen chloride (5% by weight) and the methyl ester, b.p. 94.3–94.8° at 21 mm., m.p. 13.0–14.0°, n^{20}_{D} 1.4517, was obtained in 81% yield.

Anal. Calcd. for $C_9H_7F_3O_2$: C, 52.95; H, 3.46. Found: C, 53.03; H, 3.28.

The ester was treated with methylmagnesium iodide to form the *p*-trifluoromethylphenyldimethylcarbinol, b.p. 73.5–74.9° at 3 mm. After recrystallization from pentane, the carbinol was obtained in 70% yield, m.p. 40.5–41.5°.

Anal. Calcd. for $C_{10}H_{11}F_3O$: C, 58.82; H, 5.43. Found: C, 59.52; H, 5.18.

Methyl *m*-trifluoromethylbenzoate was prepared from *m*-trifluoromethylbenzoic acid,[21] m.p. 101.5–103°. The product, obtained in 73% yield, exhibited b.p. 93.5–94.5° at 20 mm., n^{20}_{D} 1.4524.

Anal. Calcd. for $C_9H_7F_3O_2$: C, 52.95; H, 3.46. Found: C, 53.25; H, 3.49.

The carbinol, b.p. 73–73.5 at 3 mm., m.p. 32.0–32.6°, n^{20}_{D} 1.4590 (lit.[22] b.p. 91.5° at 10 mm., n^{25}_{D} 1.4572) was obtained in 96% yield.

Anal. Calcd. for $C_{10}H_{11}F_3O$: C, 58.82; H, 5.43. Found: C, 58.90; H, 5.19.

Preparation of Tertiary Chlorides.—As in the previous cases, the chlorides were formed from the tertiary carbinols or olefins by treatment with hydrogen chloride at room temperature in methylene chloride solution.[5c] Usually the chlorides were used directly for the rate studies without further purification. In the case of the carboxy derivatives,

---

[13] O. Wallach, *Ann.*, **275**, 159 (1893).

[14] R. Mayer, *Ber.*, **11**, 1284 (1878).

[15] R. Mayer, *Ann.*, **219**, 275 (1883).

[16] The procedure followed was that described for α-naphthonitrile, M. S. Newman, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 631.

[17] M. Fileti and V. Abbona, *Gazz. chim. ital.*, **21**, II, 399 (1901).

[18] P. Tarrant and M. R. Lilyquist, THIS JOURNAL, **75**, 3034 (1953).

[19] R. G. Jones, *ibid.*, **69**, 2346 (1947).

[20] A. Mooradian and C. M. Suter, *ibid.*, **71**, 3507 (1949).

[21] We are indebted to Professor J. D. Park, of the Department of Chemistry, University of Colorado, for a sample.

[22] G. B. Bachman and L. L. Lewis, THIS JOURNAL, **69**, 2022 (1947).

it was observed that the products were crystalline solids: *p*-carboxy-*t*-cumyl chloride, m.p. (dec.) 138°; *m*-carboxy-*t*-cumyl chloride, m.p. (dec.) 114–115°.

Kinetic Measurements.—The procedures were similar to those used for the related compounds previously described.[5] The 90% acetone used as solvent was adjusted to yield a rate of solvolysis identical within the experimental uncertainty of ±3% with that previously observed for *t*-cumyl chloride.[5a] Typical rate data are summarized in Table III.

TABLE III

RATE DATA FOR THE SOLVOLYSIS OF SUBSTITUTED *t*-CUMYL CHLORIDES IN 90% AQUEOUS ACETONE

Time, hr.	x, ml.	$a - x$, ml.	k_1, hr.$^{-1}$
A. *m*-Carboethoxy-*t*-cumyl chloride at 25.0°			
0	0.068	8.357	
2.42	0.262	8.163	0.00974
13.42	1.062	7.363	.00944
20.00	1.525	6.900	.00958
27.67	2.028	6.397	.00966
38.58	2.670	5.755	.00967
43.83	2.990	5.435	.00982
53.25	3.470	4.955	.00982
∞	8.425		
		Average	0.00968 ± 0.000095
B. *p*-Carboxy-*t*-cumyl chloride at 35.0°			
0	4.470	2.940	
2.92	4.640	2.770	0.0204
8.25	4.880	2.530	.0182
21.25	5.360	2.050	.0170
33.75	5.750	1.660	.0169
44.75	6.090	1.320	.0179
57.08	6.300	1.110	.0171
76.75	6.550	0.860	.0160
∞	7.410		
		Average	0.0176 ± 0.00085
C. *m*-Trifluoromethyl-*t*-cumyl chloride at 25.0°			
0	0.112	8.512	
138.7	2.113	6.511	0.00193
138.8	2.154	6.470	.00198
192.0	2.822	5.802	.00200
193.2	2.820	5.804	.00198
211.6	3.306	5.588	.00199
215.6	3.079	5.545	.00198
∞	8.624		
		Average	0.00198 ± 0.00002

LAFAYETTE, IND.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Rates of Solvolysis of Substituted Phenyldimethylcarbinyl Chlorides in Methyl, Ethyl and Isopropyl Alcohols. Influence of the Solvent on the Value of the Electrophilic Substituent Constant[1,2]

BY Y. OKAMOTO,[3] T. INUKAI[4] AND HERBERT C. BROWN

RECEIVED FEBRUARY 28, 1958

Rates of solvolysis at 25.0° have been determined for a number of representative substituted *t*-cumyl chlorides in methyl, ethyl and isopropyl alcohol. With previous data in 90% acetone, the results make available rate data for eighteen different *t*-cumyl chlorides in two to four solvents. Good linear free energy relationships are exhibited between these new rate data and the rate constants obtained previously in 90% acetone. The reaction constant ρ, −4.54 in 90% acetone, is −4.82 in methanol, −4.67 in ethanol and −4.43 in 2-propanol. In the case of some groups, the relative rates, k/k_H, exhibit a significant change with change in solvent. However, k_m/k_p is far more constant. *It is suggested that varying solvation of the substituent in the different solvents are responsible for the relatively minor changes in the* k/k_H ratios. Since the substituent in the *meta* and *para* position will be similarly solvated, the k_m/k_p ratios exhibit relatively little change with solvent. It is concluded that the alcoholic solvents can be utilized to obtain values of the electrophilic substituent constants within the precision with which these constants are normally used.

Electrophilic substituent constants, σ^+, have been derived from the rates of solvolysis of substituted *t*-cumyl chlorides at 25° in 90% aqueous acetone.[5] Considerable promise has been observed in the correlation of aromatic substitution data[6] and electrophilic side reactions[7] with the aid of these constants.

In the course of further work, certain disadvantages of the 90% aqueous acetone solvent have become apparent. The solvent contains one volatile component and relatively frequent testing with the parent compound, *t*-cumyl chloride, and adjusting of the composition are required to obtain good values for the relative rates. Moreover, the volatility of the acetone introduces difficulties in attempting to evaluate relatively inert derivatives by carrying out the solvolysis at higher temperatures.[5f] Finally, in attempting to determine the substituent constant for the carboxylate group, we observed separation into two phases in our attempts to neutralize the carboxyl group in the carboxyl-*t*-cumyl chloride in this solvent.[5f]

For these reasons we decided to undertake a survey of other solvents, restricting our attention to single component systems. Methyl, ethyl and isopropyl alcohol were selected. In addition to their possible utility in the practical aspects of the determination of electrophilic substituent constants, the study made possible a careful examination of the

---

[1] Directive Effects in Aromatic Substitution. XXVIII.

[2] This research was supported in part by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[3] Post-doctorate research assistant on a National Science Foundation Grant (G-2752), 1956–1957.

[4] Research assistant on a grant from the Petroleum Research Fund, 1956–1958.

[5] (a) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, THIS JOURNAL, **79**, 1897 (1957); (b) Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1903 (1957); (c) H. C. Brown, Y. Okamoto and G. Ham, *ibid.*, **79**, 1906 (1957); (d) Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1909 (1957); (e) H. C. Brown, Y. Okamoto and T. Inukai, *ibid.*, **80**, 4964 (1958); (f) Y. Okamoto, T. Inukai and H. C. Brown, *ibid.*, **80**, 4969 (1958).

[6] H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957).

[7] Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).