(6) The pedagogic potential is considerable. A student who is asked to translate mechanisms into symbols and *vice versa* is forced to blend structural change with electron movement. Memorization is discouraged and logical deduction is required. The system also should adapt well to computer-assisted instructional programs and automated examination grading.

(7) The system should be adaptable to information retrieval and would be easily computer coded.

(8) The basic framework provides possibilities for modernization. If, for example, a simple coding system for molecular orbitals were to become available, the atom-designating subscripts could be replaced by molecular orbital designations and possibly allow the incorporation of stereochemical information.

Acknowledgment. The author would like to thank Dr. J. F. Bunnett and Dr. J. W. Wilson for helpful comments and constructive criticism.

References and Notes

(1) J. Mathieu, A. Allis, and J. Valls, *Angew. Chem.*, **72,** 71 (1960). We learned of this paper only after the first draft of our paper was completed. This is mentioned because it points out two important facts: (1) that a system based on the designation of each bond-making and bond-breaking step will be the logical outcome of any serious consideration of mechanistic nomenclature and (2) that chemists are extremely reluctant to accept new nomenclature systems regardless of their advantages.

(2) Common usage seems to be inorganic attacks organic and where both reagents are organic, charged attacks uncharged, but there are many exceptions and examples for which rules are not available.

(3) The terms nucleofugal and electrofugal have also been used: H. Zollinger, *Accounts Chem. Res.*, **6,** 335 (1973), and ref 1.

(4) (a) R. A. Rossi and J. F. Bunnett, *J. Amer. Chem. Soc.*, **94,** 683 (1972); (b) *ibid.*, **96,** 112 (1974).

The Nature of the Ortho Effect. XI. Reaction Rates of Carboxylic Acids with Diazodiphenylmethane

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Rate constants for the reaction of diphenyldiazomethane with eight sets of ortho-substituted benzoic acids, six sets of phenylacetic acids, and seven sets of other acids were correlated with the equations

$$Q_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + \psi\nu_X + h$$
$$Q_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + h$$

to detect the presence of steric effects. All of the benzoic acids clearly showed the presence of a steric effect. This is the first time that a steric effect has been definitively demonstrated in sets of ortho-substituted benzene derivatives. The results obtained show that the electrical effect is definitely predominant, in good agreement with previous findings. Of the eight sets of benzoic acids studied, seven show steric acceleration of the rate; the eighth shows steric deceleration of the rate. Of the six phenylacetic acid sets studied, three showed steric effects. One these was rate accelerating; the other two were rate decelerating. Again, the electrical effect was predominant in these sets. Of the seven sets of other carboxylic acids studied, only the *cis*-α-phenylcinnamic acids showed a steric effect. Again, the electrical effect was predominant in this set. The composition of the electrical effect varied sufficiently to make impossible the use of a single set of ortho-substituent constants for the correlation of all sets studied. The values of α and β obtained in the correlations are linear in the $E_T(30)$ solvent parameters. New values of $E_T(30)$ have been calculated for *i*-BuOH and Me_2EtCOH. The possibility of hydrogen bonding in the case of hydroxyl substituents is evaluated. Hydrogen bonding definitely occurs in the case of salicylic acid; it may possibly occur in the case of 2-hydroxyphenylacetic acid.

In this paper we extend our previous work[1–5] on the nature of the ortho effect by a study of the rates of reaction of ortho-substituted carboxylic acids with diphenyldiazomethane by means of linear free energy relationships. The major objectives of this investigation are to detect the presence or absence of steric effects and to determine the composition of the electrical effect. The method which was employed in the study of steric effects is based on the correlation of the rate constants with linear free energy relationships. In order to carry out the analysis of the data it is necessary to examine four possible cases. 1. The steric effect may be represented by a steric parameter. Then the data will follow the equation

$$Q_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + \psi\nu_X + h \qquad (1)$$

where σ_I and σ_R represent the localized (field) and delocalized (resonance) electrical effects and υ is a steric parameter defined as[6]

$$\upsilon_X = r_{VX} - r_{VH} = r_{VX} - 1.20 \qquad (2)$$

In eq 2, r_{VX} and r_{VH} are the van der Waals radii of the X group and the hydrogen atom, respectively. We have chosen υ as a steric parameter in preference to the Taft E_S steric parameters[7] because we have previously demonstrated a linear relationship between E_S and the van der Waals radii.[1] 2. The steric effect cannot be represented by some steric parameter, and therefore the data do not obey a linear free energy relationship. In this case, the electrical effect of the X substituent remains a function of σ_{IX} and σ_{RX}. Whatever part of the rate constant is not represented by the electrical effect is dependent on the steric effect S_X. Then for the rate constant of the compound bearing the X substituent we may write

$$Q_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + S_X + h \qquad (3)$$

3. The steric effect is constant. Then υ_X is constant, and therefore $\psi\upsilon_X$ is constant. From eq 1

$$Q_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + h' \qquad (4)$$

where

$$h' = h + \psi\nu_X \qquad (5)$$

Table I: Results of Correlations[r]

Set	α	β	ψ	h	R[a]	F[b]	r_{12}[c]	r_{13}[c]	r_{23}[c]	s_{est}[d]	s_{α}[d]	s_{β}[d]	s_{ψ}[d]	s_h[d]	n[e]
1A	1.55	1.04	0.556	−0.467	0.988	66.38[f]	0.730[l]	0.183	0.086	0.0691	0.137[f]	0.277[i]	0.0723[f]	0.0595[f]	9
1B	1.37	0.888		−0.130	0.828	6.562[k]	0.730[k]			0.226	0.441[k]	0.901[o]		0.987[o]	9
2A	1.45	0.820	0.522	−0.0701	0.993	154.1[f]	0.323	0.171	0.302	0.0554	0.0776[f]	0.0836[f]	0.0567[f]	0.0461[n]	11
2B	1.39	1.02		0.277	0.897	16.49[g]	0.323			0.188	0.262[f]	0.273[h]		0.0900[i]	11
3A	2.68	2.58	0.752	0.360	0.998	168.2[h]	0.920[l]	0.414	0.073	0.0205	0.220[h]	0.294[i]	0.0468[h]	0.0203[h]	6
3B	−0.448	−1.49		0.316	0.698	1.424[m]	0.920[k]			0.191	0.948[p]	1.39[o]		0.187[n]	6
4A	2.10	1.18	0.564	−1.45	0.996	196.9[f]	0.730[l]	0.183	0.086	0.0535	0.106[f]	0.214[h]	0.0560[f]	0.0461[f]	9
4B	1.91	1.03		−1.11	0.906	13.77[h]	0.730[k]			0.225	0.440[h]	0.900[o]		0.131[f]	9
5A	2.48	1.85	0.498	−0.938	0.994	137.8[f]	0.730[l]	0.183	0.086	0.0702	0.139[f]	0.281[h]	0.0735[h]	0.0605[f]	9
5B	2.32	1.72		−0.635	0.937	21.63[g]	0.730[k]			0.205	0.400[h]	0.817[l]		0.119[h]	9
6A	1.67	1.25	0.394	−0.278	0.984	50.50[f]	0.730[l]	0.183	0.086	0.0787	0.156[f]	0.315[i]	0.0824[h]	0.0679[h]	9
6B	1.54	1.14		−0.387	0.907	13.86[h]	0.730[k]			0.170	0.331[h]	0.677[n]		0.0988[p]	9
7A	2.15	2.09	−0.118	−1.31	0.999	839.8[f]	0.730[l]	0.183	0.086	0.0239	0.0475[f]	0.0957[f]	0.0250[h]	0.0206[f]	9
7B	2.19	2.12		−1.38	0.995	276.9[f]	0.730[k]			0.0508	0.0992[h]	0.203[h]		0.0296[h]	9
8A	1.94	1.50	0.222	−1.26	0.996	190.2[f]	0.730[l]	0.183	0.086	0.0460	0.0913[f]	0.184[f]	0.0481[h]	0.0396[f]	9
8B	1.87	1.44		−1.13	0.977	62.55[f]	0.730[k]			0.0964	0.188[f]	0.385[h]		0.0561[f]	9
9A	0.377	0.308	0.0384	0.414	0.992	122.3[f]	0.203	0.273	0.062	0.0170	0.0204[f]	0.0391[f]	0.0178[l]	0.0136[f]	10
9B	0.364	0.297		0.437	0.986	118.6[f]	0.203			0.0210	0.0241[f]	0.0480[f]		0.0103[f]	10
10A	0.437	0.347	0.00969	0.0605	0.993	147.4[f]	0.203	0.273	0.062	0.0183	0.0220[f]	0.0422[f]	0.0191[p]	0.0147[h]	10
10B	0.434	0.344		0.0664	0.993	247.2[f]	0.203			0.0173	0.0199[f]	0.0396[f]		0.00847[f]	10
11A	0.520	0.436	0.0190	0.287	0.996	230.6[f]	0.203	0.273	0.062	0.0174	0.0209[f]	0.0401[f]	0.0182[o]	0.0139[f]	10
11B	0.514	0.431		0.299	0.995	341.1[f]	0.203			0.0175	0.0202[f]	0.0401[f]		0.00857[f]	10
12A	0.509	0.422	−0.230	−0.0776	0.994	153.4[f]	0.203	0.273	0.062	0.0214	0.0258[f]	0.0494[f]	0.0224[o]	0.0172[h]	10
12B	0.517	0.428		−0.0916	0.992	227.9[f]	0.203			0.0215	0.0248[f]	0.0492[f]		0.0105[f]	10
13A	0.603	0.514	−0.101	−0.448	0.997	290.1[f]	0.203	0.273	0.062	0.0195	0.0235[f]	0.0450[f]	0.0204[h]	0.0157[f]	10
13B	0.637	0.542		−0.510	0.982	96.56[f]	0.203			0.0408	0.0471[f]	0.0935[h]		0.0200[f]	10
14A	0.672	0.601	−0.0996	−0.703	0.997	343.4[f]	0.203	0.273	0.062	0.0199	0.0240[f]	0.0459[f]	0.0208[h]	0.0159[f]	10
14B	0.705	0.628		−0.764	0.986	121.9[f]	0.203			0.0404	0.0466[f]	0.0925[f]		0.0198[f]	10
15A	0.228	0.270	0.0253	−0.143	0.940	7.567[l]	0.062	0.285	0.130	0.0440	0.0683[k]	0.0801[k]	0.0870[p]	0.0399[k]	7
15B	0.234	0.267		−0.136	0.938	14.66[j]	0.062			0.0387	0.0576[i]	0.0698[i]		0.0275[h]	7
16A	0.330	0.184	−0.0237	0.775	0.994	86.31[g]	0.062	0.285	0.130	0.0147	0.0228[f]	0.0267[h]	0.0290[o]	0.0133[f]	7
16B	0.325	0.186		0.768	0.993	140.9[f]	0.062			0.0141	0.0209[f]	0.0254[h]		0.00999[f]	7
17A	0.257	0.314	0.0726	0.0109	0.925	5.920[l]	0.062	0.285	0.130	0.0582	0.0903[l]	0.106[l]	0.115[p]	0.0528[q]	7
17B	0.273	0.306		0.0316	0.914	10.22[k]	0.062			0.0536	0.0799[k]	0.0969[k]		0.0381[o]	7
18A	0.325	0.311	0.177	0.00577	0.916	5.186[m]	0.062	0.285	0.130	0.0757	0.118[l]	0.138[n]	0.150[o]	0.0687[q]	7
18B	0.364	0.292		0.0561	0.874	6.446[l]	0.062			0.0794	0.118[k]	0.143[n]		0.0564[o]	7
19A$_1$	0.153	0.0987	−0.00955	0.940	0.606	0.579[m]	0.062	0.285	0.130	0.0853	0.132[o]	0.155[p]	0.169[q]	0.0774[h]	7
19A$_2$	0.429	0.420	−0.0988	0.994	0.993	44.39[j]	0.601	0.386	0.116	0.0159	0.0389[h]	0.0454[i]	0.0329[l]	0.0156[f]	6
19B$_1$	0.151	0.0997		0.937	0.605	1.155[m]	0.062			0.0739	0.110[o]	0.134[o]		0.0526[f]	7
19B$_2$	0.383	0.399		0.963	0.958	16.93[j]	0.601			0.0305	0.0684[i]	0.0859[i]		0.0224[f]	6
20A	0.220	0.112	0.0820	1.29	0.958	3.468[m]	0.131	0.435	0.260	0.0480	0.110[o]	0.104[o]	0.0839[p]	0.0480[k]	5
20B	0.272	0.148		1.30	0.910	4.838[m]	0.131			0.0474	0.0944[n]	0.0961[o]		0.0447[h]	5
21A	0.742	0.281	−0.0463	0.505	0.9994	284.3[k]	0.131	0.435	0.260	0.0126	0.0288[k]	0.0273[l]	0.0221[o]	0.0126[i]	5
21B	0.713	0.260		0.496	0.997	157.1[h]	0.131			0.0207	0.0413[h]	0.0420[k]		0.0195[h]	5

[a] Multiple correlation coefficient. [b] F test for significance of regression. Superscripts indicate confidence levels. [c] Partial correlation coefficients of σ_I on σ_R, σ_I on υ, σ_R on υ. [d] Standard errors of the estimate, α, β, ψ, and h. Superscripts indicate confidence level of "Student t" test. [e] Number of points in the set. [f] 99.9% confidence level (CL). [g] 99.5% CL. [h] 99.0% CL. [i] 98.0% CL. [j] 97.5% CL. [k] 95.0% CL. [l] 90.0% CL. [m] <90.0% CL. [n] 80.0% CL. [o] 50.0% CL. [p] 20.0% CL. [q] <20.0% CL. [r] The confidence level of the partial correlation coefficients is less than 90% unless otherwise indicated.

4. The steric effect is negligible or nonexistent. Then $\psi = 0$, and from eq 1

$$Q_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + h \qquad (6)$$

which is simply the entended Hammett equation. Equations 4 and 6 are equivalent.

There is a fifth case which may also be considered. It is possible that in some sets[8] no steric effect occurs until a certain limiting substituent size is reached, while substituents whose size is greater than the limiting value will show a steric effect. Such a set consists of the combination of two subsets, one of which obeys eq 6 (shows no steric effect) whereas the other obeys eq 1 or 3.

The analysis of the data may now be carried out as follows.

I. The set to be studied is correlated with eq 1. The correlation is tested for significance by means of the F test, for which a confidence level greater than or equal to 90% is considered meaningful. If the correlation is significant then, the set may belong to case 1, case 3, or case 4. Case 1 is distinguished from cases 3 and 4 by a "student t" test of ψ. A confidence level greater than or equal to 90.0% indicates that the set is an example of case 1. If the confidence level of the t test is less than 90.0% then the set belongs to case 3 or case 4. If the correlation with eq 1 is not meaningful (that is, if the confidence level of the F test is less than 90.0%), then the set may be an example of case 2, case 3, or case 4, or it may be an example of case 1 with the wrong choice of steric parameter. It is also necessary to consider the confidence levels of the partial correlation coefficients r_{13} and r_{23} which measure the extent of correlation between σ_I and υ and between σ_R and υ, respectively. If either of these partial correlation coefficients has a confidence level greater than or equal 90.0% then it is impossible to separate the steric and electrical effects in the set being studied.

II. The data set being studied is correlated with eq 6. The measure of a successful correlation is again the confidence level of the F test. If the correlation is meaningful, then the set is an example of case 3 or case 4. That this must be true is shown by the following argument. If the set belongs to case 1 or case 2 then a steric effect is present. Since eq 6 does not account for this steric effect it cannot successfully correlate a set which belongs to case 1 or case 2. Case 3 may be distinguished from case 4 by a "student t" test for the significance of the difference between the experimentally observed value for h (this is the data point for the unsubstituted member of the set) and the value of h obtained from the correlation. If $h_{\text{obsd}} \neq h$, then the set belongs to case 3. If $h_{\text{obsd}} = h$, then the set is an example of case 4. Should the correlations with both eq 1 and 6 be unsuccessful, the set is either an example of case 2, or it belongs to case 1 and the choice of a steric parameter and incorrect. Unfortunately, it is not possible at the present time to distinguish between these possibilities. It might be argued that case 5 is also a possibility. Case 5 can be discerned by plotting the data against appropriate substituent constants. Those members of the set which do not shown a steric effect will give a linear plot, from which the larger groups will deviate.

Twenty sets of reaction rates of ortho-substituted carboxylic acids with diphenyldiazomethane have been subjected to the analysis described above. For the data used in these correlations, see the paragraph at the end of this paper regarding supplementary material. The σ_I constants required were taken from our compilation[9] when possible. The σ_R constants were obtained from the equation

$$\sigma_R = \sigma_p - \sigma_I \qquad (7)$$

using the σ_p constants of McDaniel and Brown[10] when available. In the case of the nitro group, the value of σ_I is taken from previous work.[11] Values of υ are generally taken from our collection.[6] Exceptions are the υ values for i-Pr and Et for which values of 0.76 and 0.56 respectively were used. These values were obtained by a method which will be described in a future publication. The value of the rate constant for the hydroxyl group was excluded from all sets in which it occurs (sets 2, 15, 16, and 17) due to the possibility of hydrogen bonding.

Table II
Values of ψ and P_S

Set	Solvent	T	ψ	P_S	Solvent parameter $[E_T(30)]^a$
1	EtOH	20	0.556	18	51.9
2	EtOH	30	0.522	19	51.9
3	EtOH	40	0.752	13	51.9
4	Dioxane	30	0.564	15	36.0
5	EtOAc	30	0.498	10	38.1
6	$MeOCH_2CH_2OH$	30	0.394	12	52.3
7	Me_2NCHO	30	−0.118	2.7	43.8
8	Me_2SO	30	0.222	6.0	45.0
9	MeOH	30	0.0384	5.3	55.5
13	t-BuOH	30	−0.101	8.3	43.9
14	Me_2EtCOH	30	−0.0996	7.3	$(40.6)^b$
19	EtOH	30	−0.0988	10	51.9

[a] K. Dimroth, C. Reichardt, J. Siepmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963). [b] Calculated in this work.

Results

Results of the correlations with eq 1 and 6 are set forth in Table I. Correlations labeled A and B are with eq 1 and 6, respectively. Results for correlation of set 19 with eq 1 and 6 were greatly improved by the exclusion of the value for the nitro group (sets $19A_2$ and $19B_2$).

Discussion

Steric Effect. Of the eight sets of benzoic acids in various solvents, three gave a confidence level of 99.9% and five a CL of 99.0% for the "student t" test for the significance of ψ. It is clear, then, that sets 1–8 belong to case 1. This is the most certain, clear-cut steric effect we have ever observed for any physical or chemical data for ortho-substituted benzenes.[1-5] To describe the magnitude of the steric effect we have defined the quantity P_S, the percent of steric effect, by means of the equation

$$P_S = \frac{|\psi| 100}{|\alpha| + |\beta| + |\psi|} \qquad (8)$$

Values of P_S are set forth in Table II. The values of P_S for the benzoic acid sets range from 2.7 to 19. Thus, although the steric effect is unquestionably present, in all sets it is subordinate to the electrical effect. This is in agreement with our previous results. We have so far observed no set of data, chemical or physical, in which the steric effect was predominant.[1-5] It is interesting to observe that seven of the eight benzoic acids gave positive values of ψ indicating steric acceleration of the rate while the set in dimethylformamide gave a negative value of ψ, indicating steric retardation of the rate. While the magnitude of the steric effect as measured by both ψ and P_S varies with solvent, inspection of Table II shows no relationship of either ψ or P_S with the $E_T(30)$ solvent parameters. As most solvent parameters are very approximately linearly related to each other we

Table III
"Student t" Tests for the Significance of the Difference between h and h_{obsd}

Set	h_{obsd}	h[a]	[b]	s_h[a]	t	n[c]
10	0.0570	0.0664	0.0094	0.00847	1.110[d]	10
11	0.290	0.299	0.009	0.00857	1.050[d]	10
12	−0.0926	−0.0916	0.0010	0.0105	0.095[e]	10
15	−0.145	−0.136	0.009	0.0275	0.327[f]	7
16	0.780	0.768	0.012	0.00999	1.201[d]	7
17	0.0170	0.0316	0.0146	0.0381	0.383[f]	7
18	−0.00131	0.0561	0.0574	0.0564	1.018[d]	7
21	0.505	0.496	0.009	0.0195	0.462[f]	5

[a] From Table I. [b] $h_{obs} - h$. [c] Number of points in the set. [d] 50% CL. [e] 20% CL. [f] 20% CL.

Table IV
Values of P_R

Set	Solvent	T	Side chain	$E_T(30)$[a]	P_R[b]
1	EtOH	20		51.9	40
2	EtOH	30		51.9	36
3	EtOH	40		51.9	49
4	Dioxane	30		36.0	36
5	EtOAc	30		38.1	43
6	$MeOCH_2CH_2OH$	30		52.3	43
7	Me_2NCHO	30		43.8	49
8	Me_2SO	30		45.0	44
9	MeOH	30	CH_2	55.5	45
10	EtOH	30	CH_2	51.9	44
11	*i*-BuOH	30	CH_2	(48.5)[c]	46
12	*i*-PrOH	30	CH_2	48.6	45
13	*t*-BuOH	30	CH_2	43.9	46
14	Me_2EtCOH	30	CH_2	(40.6)[c]	47
15	EtOH	30	CH_2CH_2	51.9	53
16	EtOH	30	CH_2O	51.9	36
17	EtOH	30	*T*-CH═CH	51.9	53
18	EtOH	30	*T*-CH═CPh	51.9	*d*
19	EtOH	30	*C*-CH═CPh	51.9	49
20	EtOH	30	C≡C	51.9	*e*
21	Dioxane	30	C≡C	36.0	27

[a] Footnote *a*, Table II. [b] P_R values for case 1 sets were calculated from correlations with eq 1; P_R values for case 4 sets were calculated from correlations with eq 6. [c] Calculated in this work. [d] β was not significant for this set. [e] Correlation was not significant for this set.

may conclude that neither ψ nor P_S is related to any other solvent parameter.

Of the six sets of phenylacetic acids correlated with eq 1, two gave very good confidence levels for the "student t" test of 99.0%, one gave a poor confidence level of 90.0%, and the other three did not give significant confidence levels. Sets 10, 11, and 12 must belong to case 3 or case 4 as they all gave excellent correlations with eq 6. To differentiate between these possibilities, we must determine whether $h = h_{obsd}$. Values of the "student t" test for the significance of the difference between h and h_{obsd}, together with their confidence levels, are set forth in Table III. Inspection of these values for sets 10, 11 and 12 shows that there is no significant difference between h and h_{obsd} for these sets. It therefore follows that these sets are members of case 4 and are free of any steric effect.

Inspection of the ψ values for the sets which belong to case 1 shows that set 9 has a small accelerating steric effect on the rate whereas sets 13 and 14 show larger decelerating effects on the rate. It is perhaps significant that sets 13 and 14 were studied in t-BuOH and Me_2EtCOH, respectively. These are the largest and bulkiest of the solvents in which the phenylacetic acids were studied. It is of interest to note that the P_S values of sets 9, 13, and 14 again clearly show the predominance of the electrical effect, in agreement with our previous results.[1-5]

Of the seven sets of acids with side chains intervening between the carboxyl group and the ring which were correlated with eq 1, only one set gave a meaningful "student t" test for the significance of ψ, a confidence level of 90% was obtained indicating poor results. This is probably due to the small size of the set ($19A_2$) which had only six points. This set is probably an example of case 1. Of the remaining six sets, five (sets 15–18 and 21) gave significant correlations with eq 6. These sets belong to case 3 or case 4. The sixth set, set 20, did not give significant correlation with either eq 1 or 6. This is probably due to the small number of points in the set, five. Examination of the values of the "student t" test for the significance of the difference between h and h_{obsd} for sets 15–18 and 21 given in Table III shows that for all five of these sets h is equal to h_{obsd} and therefore these sets are examples of case 4; that is, they are free of steric interactions. The steric effect observed for sets $19A_2$ is one of rate deceleration. Again, the P_S value shows that electrical effects are predominant in this set.

Composition of the Electrical Effect. Previously[1] we have described the composition of the electrical effect by means of the parameter where

$$\epsilon = \beta/\alpha \qquad (9)$$

We believe that a better description of the composition of the electrical effect is the parameter P_R, given by

$$P_R = \beta 100/(\alpha + \beta) \qquad (10)$$

The P_R values have the advantage that their range is 0–100 while ϵ has a range from 0 to infinity. Values of P_R are reported in Table IV.

The P_R and ϵ values are related to each other by the expression

$$P_R = \epsilon 100/(\epsilon + 1) \qquad (11)$$

Values of P_R obtained range from 27 to 53. Obviously then no one ortho substituent constant will be applicable to all sets of data involving the reaction of carboxylic acids with diphenyldiazomethane. These results agree with our previous findings.[1-5]

The values of P_R for the benzoic acids seem somewhat dependent on solvent. Inspection of $E_T(30)$ values given in Table IV indicates no dependence of P_R on $E_T(30)$. There seems to be a dependence of P_R on temperature. Values of P_R for the benzoic acid sets range from 36 to 49. It should be noted that r_{12}, the partial correlation coefficient of σ_I on σ_R, was significant at the 90% CL for sets 1, and 3–8. This suggests that there may be some uncertainty in the P_R values for the benzoic acid sets. The values of P_R for the phenylacetic acids are essentially constant and are independent of the solvent. The sets show an average P_R value of 46.

We may now consider the variation of the P_R value with side chain. Considering only sets in EtOH at 30°, we may compare sets 2, 10, 15–17, and 19. In so doing, we observe that with the exception of set 16, there is an increase from $P_R = 36$ for no side chain to $P_R = 44$ for a CH_2 side chain to $P_R = 49$ to 53 for a two carbon-atom side chain. This result is in agreement with our previous observations on the variation of the composition of the electrical effect with side chain in proton transfer reactions.[5]

Variation of the Reaction Parameters with Solvents. Values of α and β for the phenylacetic acid sets (for sets 9,

Table V
Results of Correlations with Equations 12 and 13

Set	m	c	r[a]	F[b]	s_{est}[c]	s_m[c]	s_c[c]	n[d]
A_1	−0.0466	4.04	0.862	11.59[e]	0.207	0.0137[e]	0.615[f]	6
A_2	−0.0654	4.96	0.969	46.34[f]	0.115	0.00960[f]	0.447[f]	5
B_1	−0.0301	2.79	0.438	0.952[g]	0.467	0.0309[h]	1.39[i]	6
B_2	−0.0677	4.63	0.810	5.739[j]	0.338	0.0283[j]	1.32[e]	5
C	−0.0199	1.48	0.997	332.7[k]	0.00934	0.00109[f]	0.0548[f]	4
D	−0.0184	1.32	0.990	95.60[l]	0.0161	0.00189[m]	0.0946[f]	4

[a] Correlation coefficient. [b] F test for significance of regression. [c] Standard errors of the estimate, m, and c. [d] Number of points in the set. [e] 95.0% CL. [f] 99.0% CL. [g] <90% CL. [h] 50% CL. [i] 80% CL. [j] 90% CL. [k] 99.95% CL. [l] 97.5% CL. [m] 98.0% CL.

Table VI
Variation of the Reaction Parameter with Side Chain

Set	Side chain	α	β	Set	Side chain	α	β
2		1.45	0.820	17	*trans*-CH=CH	0.273	0.306
10	CH_2	0.434	0.344	18	*trans*-CH=CPh	0.364	[a]
15	CH_2CH_2	0.234	0.267	19	*cis*-CH=CPh	0.429	0.420
16	CH_2O	0.325	0.186				

[a] β was not significant for this set.

13, and 14 values of α and β are from correlations with eq 1; for sets 10, 11, and 12 values of α and β are taken from correlations with eq 6) were correlated with the $E_T(30)$ solvent parameters[12] by the equations

$$\alpha = mE_T + c \qquad (12)$$

$$\beta = mE_T + c \qquad (13)$$

Results of the correlations are given in Table V. Best results for the correlation of α and β of substituted benzoic acids are obtained on exclusion of the values for dioxane (sets A_2 and B_2, respectively). Set A_2 gave very good correlation and set B_2 gave poor but significant correlation. Correlation of α (set C) and β (set D) for phenylacetic acids gave excellent and good results, respectively. The correlation of α values seems to be superior to that of β values.

The results obtained for the correlation of α for phenylacetic acids (set 6) are good enough to permit their use in the calculation of new E_T values. Values of $E_T(30)$ were calculated for *i*-BuOH and Me_2EtCOH and the values obtained are 48.5 and 40.6, respectively.

Variation of Reaction Parameters with Side Chain. We may now consider the effect of the side chain on values of α and β. Appropriate values of α and β are reported in Table VI. All data are in EtOH at 30°.

Values of α and β for sets 2, 10, and 19 are from correlations with eq 1; values of α and β for sets 15–18 are from correlations with eq 6. With the exception of the α and β values for the *cis*-CH=CPh side chain, the magnitude of α and β falls off with increasing size of the side chain as is expected. The values obtained for the methylene side chain seem too small, however.

Hydrogen Bonding in the Case of Hydroxyl Substituent. The rate constants for X=OH were excluded from the correlations of sets 2, 15, 16, and 17 due to the possibility of hydrogen bonding. To determine whether hydrogen bonding occurs, values of the rate constant for the hydroxyl group were calculated as were values of the quantity $K_{OH,obsd}/k_{OH,calcd}$. These values are set forth in Table VII. The $k_{OH,calcd}$ values were calculated from the correlations with eq 1 in the case of set 2, the $k_{OH,calcd}$ values for sets 15, 16, 17 were calculated from correlations with eq 6. The value of $k_{OH,obsd}/k_{OH,calcd}$ for set 2 suggests a large hydrogen-bonding effect. The value of this ratio for set 16 indicates the possibility of a very small hydrogen bonding effect, if any exists at all. The values of $k_{OH,obsd}/k_{OH,calcd}$ for sets 15 and 17 show no hydrogen-bonding effect.

Table VII
Values of $k_{OH,calcd}$, $k_{CH,obsd}$, and $k_{OH,obsd}/k_{OH,calcd}$

Set	$k_{OH,calcd}$	$k_{OH,obsd}$	$k_{OH,obsd}/k_{OH,calcd}$
2	0.209	7.55	36
15	0.571	0.670	1.2
16	5.42	12.1	2.2
17	0.813	0.594	0.73

Registry No.—Diazodiphenylmethane, 883-40-9.

Supplementary Material Available. The data used in the correlations carried out in this paper will appear following this article in the microfilm edition of this journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-75-407.

References and Notes

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(8) A data set, usually simply referred to as a set, consists of chemical (rate constants, equilibrium constants) or physical (spectral parameters, dipole moments, ionization potentials) properties for a group of compounds XGY in which X, the substituent, is varied; Y, the reaction site, and G, the skeletal group to which X and Y are bonded, are held constant. Also held constant are the reaction conditions such as medium and temperature.
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