[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

The General Applicability of a Fixed Scale of Inductive Effects. II. Inductive Effects of Dipolar Substituents in the Reactivities of *m*- and *p*-Substituted Derivatives of Benzene[1,2]

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Evidence is presented that, to a useful quantitative approximation, the inductive effects of dipolar *m*- and *p*-substituents on the side-chain reactivities of benzene derivatives, obtained quite generally from the quantity, $\frac{1}{1-\alpha}$ [log (k^m/k_0) − α log (k^p/k_0)], follow a $\sigma_I\rho_I$ linear inductive energy relationship which is widely independent of reaction type. This relationship for inductive effects on reactivity applies with acceptable precision to all reaction series for which the Hammett $\sigma\rho$ relationship for the total observed effects of substituents is of comparable precision. In addition, the linear inductive energy relationship applies with equal precision to numerous reactions series for which the Hammett linear free energy relationship is of much poorer precision.

Evidence of a general scale of inductive effects of substituent groups, sufficiently independent of reaction nature and conditions to lead to useful quantitative correlations of the effects of structure on reactivity, recently has been presented.[2,3] The systems treated were those in which the substituent groups are bonded directly to a common functional center or are separated from it by a saturated chain. For reaction series within which resonance and steric effects are essentially constant, the equation log $(k/k_0) = \sigma^* \rho^*$ was found to apply with useful precision, where ρ^* is a reaction series constant and σ^* is Taft's polar substituent constant.

For a variety of reaction series within which there are substantial steric and resonance contributions, evidence has been presented showing that the effects of substituents on the free energy change can be treated to useful quantitative approximation as the sum of inductive, steric and resonance effects.[2-4] The inductive contributions to the free energy change for such reaction series are given by the quantity, $\sigma^*\rho^*$

The reactivities of *m*- and *p*- substituted side-chain derivatives of benzene as a class are characterized as rarely involving steric contributions.[5] Accordingly, the following treatment of these reactivities is expected to apply generally[5,6]

$$\log (k/k_0) = \text{inductive effect} + \text{resonance effect} \quad (1)$$

Recent evidence indicates that the scale of inductive effects found in the aliphatic series applies as well to inductive contributions to the observed polar effects of *m*- and *p*- substituents on the ionization of benzoic acids[7] and on the n.m.r. lines of fluorobenzenes.[8] In the former case, this was demonstrated by the applicability of the equations

$$\log (K^p/K_0) = \sigma_I + \sigma_R \quad (2)$$

$$\log (K^m/K_0) = \sigma_I + {}^1/_3\sigma_R \quad (3)$$

σ_I is the inductive contribution of the substituent to the ionization of *m*- or *p*-substituted benzoic acid. This inductive substituent constant is obtained by adjusting the σ^* value of the substituent to an appropriate scale, *i.e.*, σ_I for the substituent X equals 0.45 σ^* for the substituent XCH_2. That is, σ_I values are based upon *inductive effects from the aliphatic series.*

σ_R is a substituent constant measuring the contribution to the free energy of ionization which results from the existence of π-bond resonance interaction of the substituent with the benzene π-orbitals. A resonance contribution for a *m*-substituent equal to approximately one-third of that for the corresponding *p*-substituent is considered to result from the indirect inductive transmittal of the effect of direct resonance interaction of the *m*-substituent with the positions *ortho* (and *para*) to the carbon atom bearing the side-chain reaction center.[9] It is apparent that both equations 2 and 3 conform to the model equation 1.

Equations 2 and 3 may be combined to eliminate σ_R according to the relationship

$$3/2\ [\log (K^m/K_0) - 1/3 \log (K^p/K_0)] = \sigma_I \quad (4)$$

Figure 1 shows a plot of the quantity, ${}^3/_2$ [log (K^m/K_0) $-{}^1/_3$ log (K^p/K_0)] for the ionization of benzoic acids[10] *vs.* corresponding values of σ_I. The line shown is one of unit slope. This plot, in so far as the authors are aware, represents the first general quantitative correlation of the polar effects of *m*- and *p*-substituents in benzene derivatives with those of the corresponding substituents in aliphatic systems.

This demonstration, in light of the Hammett linear free energy (L.F.E.) relationship, log (k/k_0) = $\sigma\rho$, offers compelling evidence of the general ap-

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(1) This work was supported in part by the Office of Naval Research, Project NRO55-328. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) Paper I, R. W. Taft, Jr., THIS JOURNAL, **75**, 4231 (1953).

(3) *Cf.* also (a) M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapt. 13; (b) R. W. Taft, Jr., *J. Chem. Phys.*, **26**, 93 (1957).

(4) (a) R. W. Taft, Jr., THIS JOURNAL, **75**, 4534 (1953); (b) M. M. Kreevoy and R. W. Taft, Jr., *ibid.*, **77**, 5590 (1955); **79**, 4011, 4016 (1957); (c) W. A. Pavelich and R. W. Taft, Jr., *ibid.*, **79**, 4935 (1957); (d) S. S. Biechler and R. W. Taft, Jr., *ibid.*, **79**, 4927 (1957); (e) R. W. Taft, Jr., *ibid.*, **79**, 5075 (1957).

(5) (a) L. P. Hammett, *Chem. Revs.*, **17**, 125 (1935); (b) "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 184.

(6) (a) Reference 5b, p. 77; (b) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice–Hall, Inc., New York, N. Y., 1941, p. 193.

(7) (a) J. D. Roberts and W. T. Moreland, Jr., THIS JOURNAL, **75**, 2167 (1953); (b) ref. 3a, pp. 578–580, 594–597.

(8) R. W. Taft, Jr., THIS JOURNAL, **79**, 1045 (1957).

(9) (a) C. C. Price and D. C. Lincoln, *ibid.*, **73**, 5841 (1951); (b) ref. 7a; (c) ref. 7b.

(10) All of the ionization constants used are those given in a comprehensive review by D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

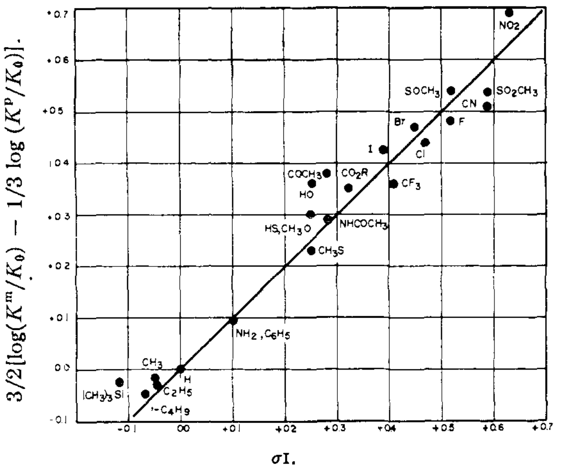

Fig. 1.—Linear inductive energy relationships between inductive contribution, $3/2[\log (K^m/K_0) - 1/3 \log (K^p/K_0)]$, to the ionizations of *m*- and *p*-substituted benzoic acids, water, 25°, and the aliphatic inductive substituent constant, σ_I.

plicability of the σ_I (or σ^*) inductive scale. Hammett has defined σ values according to the equations[5]

$$\log (K^p/K_0) \equiv \sigma_p \qquad (5)\,(a)$$

$$\log (K^m/K_0) \equiv \sigma_m \qquad (b)$$

where K/K_0 values refer to the ionization constants of benzoic acids in water at 25°. Combining equations 4 and 5 gives $\sigma_m - {}^1/_3\,\sigma_p = {}^2/_3\,\sigma_I$ and this, according to the Hammett equation gives

$$\log (k^m/k_0) - 1/3 \log (k^p/k_0) = 2/3\, \sigma_I \rho \qquad (6)$$

Consequently, Fig. 1 provides evidence that the σ_I inductive scale applies generally to the reactivities of *m*- and *p*-substituted side-chain derivatives with a precision which is at least on the order of that of the Hammett equation. Figure 2 gives a typical example of the application of equation 6.

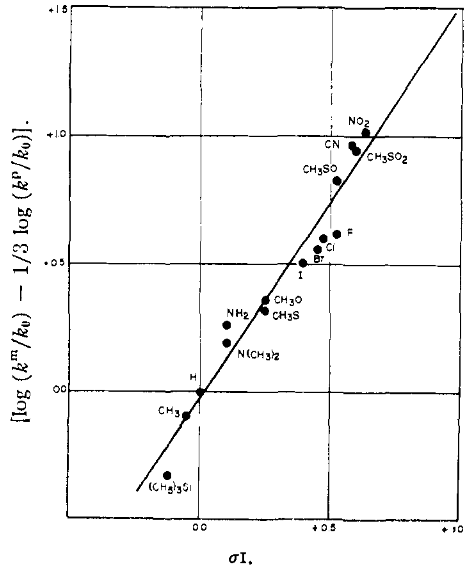

Fig. 2.—Linear inductive energy relationship for the rates of saponification of *m*- and *p*-substituted ethyl benzoates, 60% aq. acetone, 25°, according to equation 6.

It is of interest to determine whether the $\sigma_I \rho_I$ relationship for inductive effects is more independent of reaction type than the Hammett $\sigma\rho$ relationship. It has been recognized that the failure of the Hammett L.F.E. relationship to hold with relatively high precision for certain reaction series results from a specific dependence of the resonance effect of appropriate substituents on the nature of the reaction.[11] Evidence particularly pertinent to this conclusion comes, for example, from recent results of Bordwell *et al.*[12] The effects of *m*- and *p*-substituents on the ionization of phenols, a reaction series included in the original $\sigma\rho$ treatment, do not generally follow a precise L.F.E. relationship with corresponding effects on the ionization of benzoic acids (*cf.* Fig. 3).

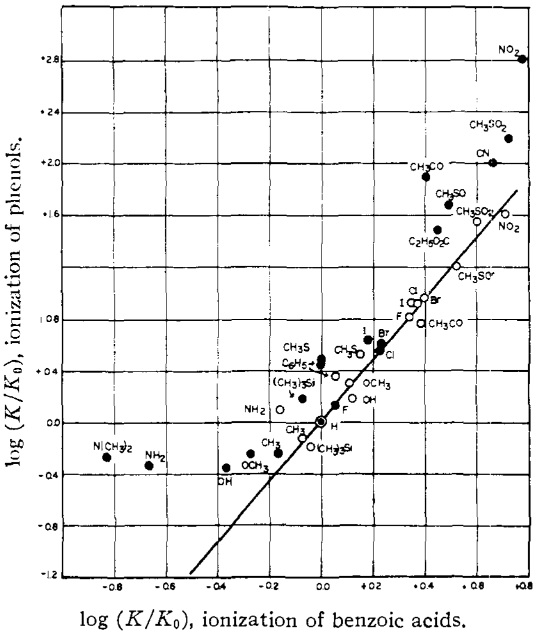

Fig. 3.—Limited linear free energy relationship for ionization of *m*- and *p*-substituted phenols and benzoic acids, water, 25°: ●, *p*-substituents; ○, *m*-substituents.

Para substituents which are electron-withdrawing by resonance interaction (hereafter referred to as +R groups) deviate from the reasonably precise line defined principally by points for *meta* substituents. The effect of the +R *p*-substituent on the ionization of anilinium ions was found by Hammett to give a dual substituent constant (now given[8] the symbol σ^-) which can be applied to the reactivities of derivatives of phenol and aniline. Resonance interaction between the +R *p*-substituent and the electron-rich reaction center is considered to be the cause of the deviations for points such as those for *p*-NO_2, *p*-CN, etc., in Fig. 3.

The more recent data indicate further that *p*-substituents which are electron-releasing by resonance interaction (hereafter referred to as −R groups) also deviate widely from the line defined

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[11] (a) Reference 6h, p. 250; (b) F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058 (1952).

[12] (a) F. G. Bordwell and P. J. Boutan, *ibid.*, **78**, 854 (1956); **79**, 719 (1957); (b) F. G. Bordwell and H. M. Andersen, *ibid.*, **75**, 6019 (1953).

by many (but not all) of the *m*-substituents (*cf.* points for *p*-NH_2, *p*-OCH_3, *p*-SCH_3, etc., Fig. 3).

Similar deviations from Hammett L.F.E. relationships have been widely demonstrated for $-R$ substituents in electrophilic reactions[13] (*cf.* Fig. 4).

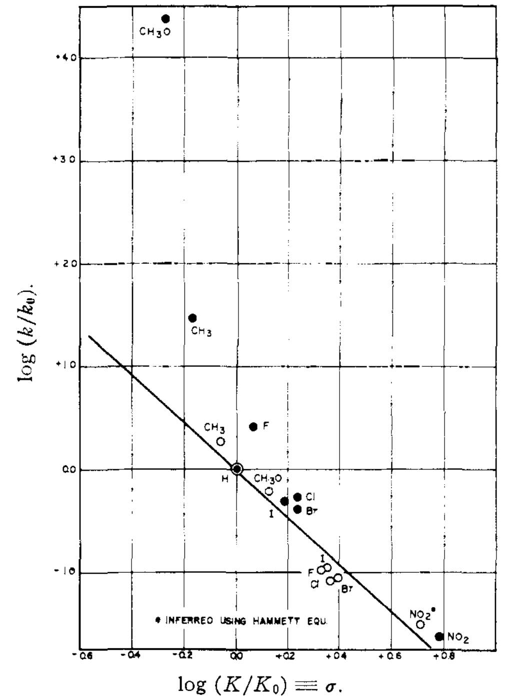

Fig. 4.—Limited linear free energy relationship for rates of solvolysis of benzyl tosylates, 76% aq. acetone, 25°, and ionization of benzoic acids, water, 25°: ●, *p*-substituents; ○, *m*-substituents.

The basic model equation 1 offers a means of determining whether these deviations result from a breakdown in the general applicability of the σ_I inductive scale, of the σ_R resonance scale, or both.

If one assumes that inductive effects are given by $\sigma_I\rho_I$ (where ρ_I is an inductive reaction constant), and that the resonance effect of a *m*-substituent is equal to a constant fraction, α, of the resonance effect for the corresponding para substituent in the same reaction series,[14] equation 1 then leads to the relationships

$$\log (k^m/k_0) = \sigma_I\rho_I{}^m + \alpha \text{ (resonance effect), and}$$

$$\log (k^p/k_0) = \sigma_I\rho_I{}^p + \text{(resonance effect), or}$$

$$\log (k^m/k_0) - \alpha \log (k^p/k_0) = \sigma_I(\rho_I{}^m - \alpha\rho_I{}^p) \quad (7)$$

According to equation 7 a plot of the quantity $[\log (k^m/k_0) - \alpha \log (k^p/k_0)]$ *vs.* σ_I should be linear. It is apparent that equation 7 reduces to equation 6 for $\alpha = {}^1/_3$ and $\rho_I{}^m = \rho_I{}^p = \rho$.

The demonstrated applicability of equation 7 to reaction series which do not follow precise Hammett L.F.E. relations would provide evidence, therefore, that the $\sigma_I\rho_I$ relationship for inductive effects is more independent of reaction type than the Hammett $\sigma\rho$ relationship.

This paper is concerned with the results and conclusions to be drawn from applying equation 7 to a variety of reaction series with emphasis on those series for which the Hammett equation holds to relatively poor approximation.

Results

Equation 7 has some inherent disadvantages. Data for each substituent in a given reaction series must be available for both the *m*- and the *p*-positions. Five points in a plot of the quantity $1/(1 - \alpha)[\log (k^m/k_0) - \alpha \log (k^p/k_0)]$ *vs.* σ_I require, in addition to the five σ_I values, 11 pieces of experimental data from the aromatic series—the constants for five substituents in both the *m*- and the *p*-positions and that for the unsubstituted derivative. Although the Hammett $\sigma\rho$ relationship has been applied to over 3,000 rate and equilibrium constants,[15] there are relatively few reaction series where adequate data are available to suitably meet these requirements. Furthermore, there is the problem of magnification of experimental errors and, perhaps, of small specific effects (such as solvation) in the complex quantity, $(1/1 - \alpha)$ $[\log (k^m/k_0) - \alpha \log (k^p/k_0)]$. No reasonable procedure for treating the error in this quantity is apparent.

In spite of these disadvantages the results of applying equation 7 are striking and provide important new evidence concerning the nature of the polar effects of *m*- and *p*-substituents. Fortunately, there are sufficient data to apply equation 7 to reaction series which appear to be representative of most of the extreme types of systems. The results given in Table I therefore, are probably generally representative of the reactivities of *m*- and *p*-substituted benzene derivatives.

Figures 1, 2 and 5 illustrate the results of applying equation 7 to four different systems taking $\alpha = {}^1/_3$ and $\rho_I{}^m = \rho_I{}^p = \rho_I$. In Fig. 5, plotted *vs.* σ_I are shown the quantities, $\log (K^m/K_0) - {}^1/_3 \log (K^p/K_0)$, for the ionization of phenols in water at 25° (closed circles and full line), and $-[\log (k^m/k_0) - {}^1/_3 \log (k^p/k_0)]$ for the rates of solvolysis of phenyldimethylcarbinyl chlorides in 90% aq. acetone at 25°.

The salient features of the application of equation[7] are the following. The points for most substituents, including those for which the *p*-substituents do not follow the Hammett equation, define lines of reasonable precision (compare, for example, points for $N(CH_3)_2$, OCH_3, SCH_3, in Figs. 3 and 5). There appear to be no trends from linear relationships, deviations from the least squares line being random and of not unreasonable magnitude considering the nature of the function $[\log (k^m/k_0) -$

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[13] (a) D. E. Pearson, J. F. Baxter and C. J. Martin, *J. Org. Chem.*, **17**, 1511 (1952); (b) J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953); (c) P. B. D. de la Mare, *J. Chem. Soc.*, 4450 (1954); (d) N. C. Deno and A. Schriesheim, THIS JOURNAL, **77**, 3051 (1955); (e) H. G. Kuivila and L. E. Benjamin, *ibid.*, **77**, 4834 (1955); (f) C. Eaborn, *J. Chem. Soc.*, 4858 (1956); (g) N. N. Lichtin and M. J. Vignale, THIS JOURNAL, **79**, 579 (1957), and earlier papers; (h) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957); (i) N. C. Deno and W. L. Evans, *ibid.*, **79**, 5667 (1957).

[14] This second assumption, of course, amounts to a special linear resonance energy relationship. The first assumption is one of a linear inductive energy relationship. The success of equation 7 will therefore depend not only upon a completely general linear inductive energy relationship, but upon a linear resonance energy relationship between resonance effects of corresponding *m*- and *p*-substituents *within a given reaction series*. Equation 7 does not demand as does the $\sigma\rho$ relationship, the much more general linear resonance energy relationship between resonance effects of corresponding substituents in *different reaction series*; *cf.* Discussion.

[15] H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

TABLE I

SUMMARY OF APPLICABILITY OF EQUATION 7 ($\rho_I^m = \rho_I^p = \rho_I$)

Reaction	Ref[a]	ρ_I	S	a	R	$\alpha = 1/3$	$\alpha = 1/10$
(1) E-Ionization of benzoic acids, H_2O, 25°	1	+1.00	0.05	0.00		1, 2, 3, 4, 5, 7, 8, 9, 11, 12, 13, 14, 15, 16, 18, 19, 20, 21, 22, 23, 24, 25, 26	
(2) R-Alkaline saponifn. of ethyl benzoates in 60% aq. acetone, 25°	2, 3	+2.33	.09	− .03	0.975	1, 4, 5, 8, 9, 11, 13, 18, 20, 21, 22, 23, 24, 25, 26	
(3) R-Alkaline saponifn. of ethyl benzoates in 88% aq. ethanol, 30°	2, 3	+2.28	.08	+ .01	.987	1, 4, 5, 9, 11, 18, 20, 21, 22, 26	
(4) R-Methanolysis of *l*-menthyl benzoates in methanol, 40°	2	+2.63	.08	+ .01	.989	4, 5, 11, 20, 21, 26	
(5) R-Alkaline saponifn. of ethyl cinnamates in 88% aq. ethanol, 30°	2	+1.29	.03	+ .01	.994	4,[b] 5, 9, 11,[b] 18, 21, 22, 26	
(6) E-Dissocn. of phenylboric acids in 25% aq. ethanol, 25°	2, 17	+2.15	.05	+ .01	.991	4, 5, 9, 11, 15, 16, 18, 20, 21, 22, 26	
(7) R-Coupling of benzene-diazonium ions with 2,6-naphthylaminesulfonic acid, H_2O, 20°	4	+4.48	.08	+ .01	.997	4, 5, 11, 21, 26	
(8) R-Free radical chlorination of substituted toluenes, 70°	5	−0.81	.02	+ .02	.995	4, 5, 7, 21, 24	
(9) R-Solvolysis of benzoyl chlorides in ethanol, 0°	2, 6	+2.00	.04	.00	.995	4, 5, 6, 10, 14, 18, 20, 21, 26	
(10) E-Ionization of phenols, H_2O, 25°	2, 7, 8	+2.30	.07	+ .03	.991	4, 5, 8, 9, 11, 12, 13, 18, 20, 21, 22	1, 7, 14, 23, 25, 26
(11) E-Ionization of phenols in 49% aq. ethanol, 20–22°	2	+2.70	.10	− .01	.984	4, 5, 11, 18, 20, 21	14, 16
(12) E-Ionization of thiophenols in 48% aq. ethanol, 25°	2, 7b, 9	+2.93	.12	− .11	.985	4, 5, 8, 11, 18, 20, 21	14, 16, 25, 26
(13) E-Ionization of anilinium ions, H_2O, 25°	2, 10, 11	+2.83	.15	+ .11	.973	4, 5, 9, 11, 12, 13, 18, 20, 21, 22	1, 14, 16, 19, 25, 26
(14) R-Oxidation of azobenzenes with perbenzoic acid in benzene, 25°	2	−1.29	.03	− .02	.997	4, 5, 11, 20, 21, 22	16, 26
(15) R-Alkaline hydrolysis of trialkylphenoxysilanes in 51% ethanol, 25°	12	+1.70	.06	− .02	.986	4, 5, 11, 21	
(16) R-Solvolysis of benzyl chlorides in 50% aq. acetone, 60°	2	−1.43	.05	− .06	.994	5, 24, 26	4, 18, 20, 21
(17) R-Solvolysis of phenyldimethylcarbinyl chlorides in 90% aq. acetone, 25°	13	−4.19	.13	− .09	.993	5, 16, 19, 24, 26	2, 3, 4, 7, 13, 18, 20, 21
(18) R-Brominolysis of benzene boronic acids in 20% acetic acid, 25°	14	−3.62	.04	+ .01	.998	5, 16	4, 18, 20, 21, 22
(19) R-Solvolysis of benzyl tosylates in 76% aq. acetone, 25°	15	−2.31	.08	− .04	.992	5, 26[b]	4, 11, 18, 20, 21, 22
(20) R-S_N2 reaction of benzyl chlorides with potassium iodide in acetone, 20°	16	+0.72	.08	.00	.936	5. 26	4, 18. 20, 21, 22

[a] Reference numbers refer to the following rather than those cited in the text. [b] *meta* values estimated using the Hammett equation. (1) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958). (2) References to the original literature are given in H. H. Jaffé, *Chem. Revs.*, **53**, 198 (1953). (3) J. D. Roberts and C. M. Regan, THIS JOURNAL, **75**, 4102 (1953). (4) H. Zollinger, *Helv. Chim. Acta*, **36**, 1730 (1953). (5) (a) C. Walling and B. Miller, THIS JOURNAL, **79**, 4181 (1957). (6) Substituent (11) does not fit equation 7 with either of the indicated α-values for this reaction. (7) (a) F. G. Bordwell and P. J. Boutan, THIS JOURNAL, **78**, 854 (1956); (b) **79**, 719 (1957). (8) F. Fieffer and P. Rumpf, *Compt. rend.*, **238**, 360 (1954). (9) F. G. Bordwell and H. M. Andersen, THIS JOURNAL, **75**, 6019 (1953). (10) G. M. Bennett, G. L. Brooks and S. Glasstone, *J. Chem. Soc.*, 1821 (1935). (11) R. A. Benkeser and H. R. Krysiak, THIS JOURNAL, **75**, 2421 (1953). (12) E. Akerman, *Acta Chem. Scand.*, **11**, 373 (1957). (13) (a) H. C. Brown and Y. Okamoto, THIS JOURNAL, **79**, 1913 (1957); (b) H. C. Brown, Y. Okamoto and T. Inukai, *ibid.*, in press. (c) Substituents 1, 11 and 22 do not fit equation 7 with the dual α-values indicated for this reaction. (14) (a) H. G. Kuivila and A. R. Hendrickson, THIS JOURNAL, **74**, 5068 (1952); (b) H. G. Kuivila and L. E. Benjamin, *ibid.*, **77**, 4834 (1955). (15) (a) J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953); (b) F. T. Fang, J. K. Kochi and G. S. Hammond, *ibid.*, **80**, 563 (1958). (16) P. Bivot and J. Fierens, *Bull. soc. chim. Belges*, **65**, 995 (1956). (17) Text reference 6b, p. 256.

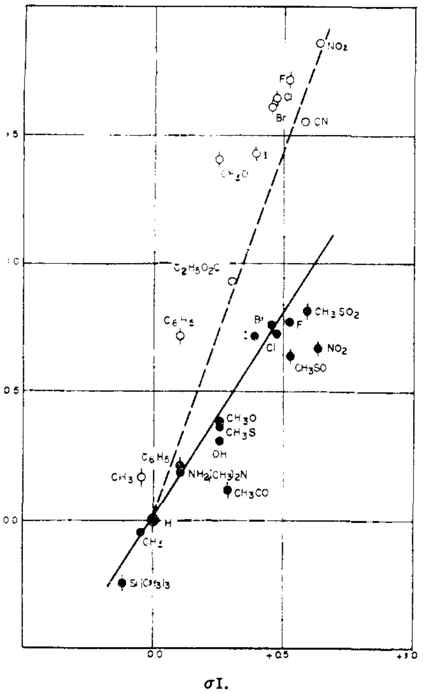

Fig. 5.—[log (K^m/K_0) − $^1/_3$ log (K^p/K_0)] *vs.* σ_I for ionization of phenols, H_2O, 25°, and −[log (k^m/k_0) − $^1/_3$ log (k^p/k_0)] *vs.* σ_I for rates of solvolysis of phenyldimethylcarbinyl chlorides, 90% aq. acetone, 25°. Ordinate, full line and closed circles, ionization of phenols; dashed line and open circles, rates of solvolysis of phenyldimethylcarbinyl chlorides; points with tails are conjugated substituents.

$^1/_3$ log (k^p/k_0)]. Exceptions occur for the same substituents for which dual ($\sigma-$ or $\sigma+$) substituent constants have been proposed. For example, in the ionization of phenols the points for +R substituents (such as NO_2) fall markedly below the line defined by the other points (*cf.* Fig. 5, closed circles with tails). In the solvolysis rates of the phenyldimethylcarbinyl chlorides, the points for −R substituents (such as OCH_3) likewise deviate markedly in the same direction (*cf.* Fig. 5, open circles with tails).

In most instances in which a change in conjugation between *p*-substituent and the reaction center is involved, it has been noted that equation 7 can still be applied if a smaller but constant value of α is used for all such substituents. This does not generally appear to be a question of the necessity of using a variety of α values, for a fixed value of approximately 1/10 appears to suffice for most of the reactivities which we have examined to date (*cf.* further comment in Discussion). For example, the points for NO_2, CH_3SO_2, CH_3SO in the ionization of phenols may be made to satisfactorily fit the line defined by the non-conjugating (−R) substituents if a value of α = 1/10 is taken for the former substituents (*cf.* Fig. 6). That is, all points are fitted by a single line in the plot of $(1/1 - \alpha)$ [log (K^m/K_0) − α log (K^p/K_0)] *vs.* σ_I using $\alpha = {}^1/_3$ for the non-conjugating (−R) substituents (closed circles in Fig. 6 and $\alpha = {}^1/_{10}$ for the conjugating (+R) substituents (open circles in Fig. 6).

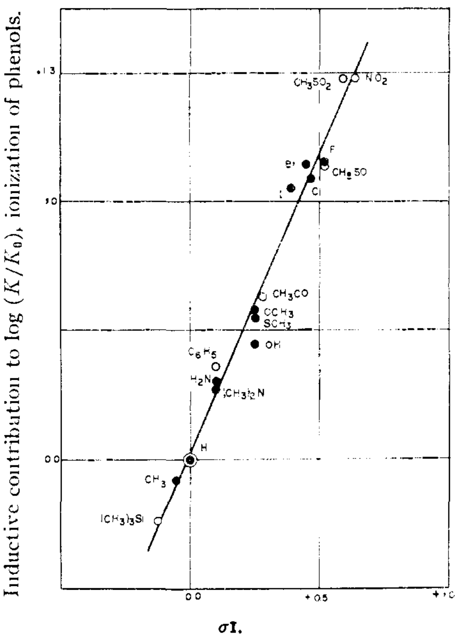

Fig. 6.—Linear inductive energy relationship between inductive contribution, $[1/(1 - \alpha)]$[log (K^m/K_0) − α log (K^p/K_0)], to the ionization of *m*- and *p*-substituted phenols, water, 25°, and the aliphatic inductive substituent constant, σ_I. α = 0.33 for non-conjugating (−R) substituents (closed circles); α = 0.10 for conjugating (+R) substituents (open circles).

Similar results are obtained for most electrophilic reactivities if the reduced α value is used for substituents such as NH_2, OCH_3, halogens, CH_3, etc. Figure 7 gives, as an example, the results of plotting $(1/1 - \alpha)$ [log (K^m/K_0) − α log (K^p/K_0)] *vs.* σ_I for the rates of solvolysis of benzyl tosylates in aq. acetone at 25°, using $\alpha = {}^1/_3$ for the non-conjugating (+R) substituents, closed circles in Fig. 7 and $\alpha = {}^1/_{10}$ for the conjugating (−R) substituents (open circles).

The results of applying equation 7 to twenty different reactions are summarized in Table I. These particular reactions were selected because of: (1) the relatively large number of substituents for which data are available for both the *m*- and *p*-positions; (2) the relatively large substituent effects on reactivity involved in these reactions and (3) the variety of reactivity types. Reaction series number 1–9 in Table I, follow the Hammett $\sigma\rho$ relationship with good precision and with no apparent systematic deviations. All of the other reaction series show at least some type of systematic deviation from the Hammett L.F.E. relationship.

Table I includes a description of the reaction, a designation as to an equilibrium (E) or a rate (R) process, literature reference, ρ_I, S, a and R obtained by standard least squares procedure,[16] where S is the standard error of a single point for the quantity $(1/1 - \alpha)$ [log (k^m/k_0) − α log (k^p/k_0)], a is the residual of the correlation and R is the correlation coefficient. In addition, Table I lists the substituents by number (as given in Table II) which have been included for each reaction, with

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(16) *Cf.*, for example, ref. 15, p. 253.

the appropriate values of α indicated (in each case consistent with the generalizations given above). The substituent designations are given in the last two columns to the right in Table I.

It is apparent from Table I that the general precision of equation 7 is relatively good. The average standard error of a single inductive contribution to the logarithm of the rate or equilibrium constant for the entire table is 0.07, which corresponds to less than 20% in the value of the constant. This figure derives from data which cover a range of inductive contributions of three powers of ten obtained from observed constants covering five powers of ten in reactivity. In only one case is the correlation coefficient less than 0.973. The average value of S/ρ_I for Table I is 0.03. This is somewhat better than the general order of precision obtained from the equation $\log (k/k_0) = \sigma^*\rho^*$ for reactivities in the aliphatic series.[17]

The precision of equation 7 for reactions 1–9 is very similar to that given by Jaffé for Hammett's $\sigma\rho$ relationship.[15] Further, as expected for these reaction series, the ρ_I values are essentially equal in each case to the ρ value given by Jaffé. For reactions 10–20, in cases where comparison is possible, the precision of equation 7 is appreciably improved over that listed by Jaffé for correlation according to the $\sigma\rho$ relationship.[15] The ρ_I values of these reaction series are generally measurably different than ρ values, but in no case has the change been sufficiently severe to alter the sign (in fact, the general magnitude of the difference in ρ_I and ρ is small).

No data known to the authors have been excluded from the results given in Table I. The few apparent exceptions to equation 7 which have been excluded from the reported correlations are indicated by footnotes to Table I. The deviation of the methoxy substituent in reaction 9 is consistent with the change to the SN1 type mechanism for the *p*-methoxybenzoyl chloride suggested by Hughes.[18] For reaction 17, equation 7 is not followed with the usual precision by substituents: 1, 11, and 22. For substituents 11 and 22, the failure of equation 7 apparently is due to a substantial breakdown in the special linear resonance energy relationship between *meta* and *para* resonance effects assumed in deriving equation 7. Other examples of this kind undoubtedly will appear. The failure for substituent 1 in reaction 17 is the only one of its kind encountered for all of the reactivities examined to date and is unexplained.

A complete statistical examination of the reactivities of other *m*- and *p*-substituted benzene derivatives in terms of equation 7 (with α variable) is in progress in collaboration with Professor H. H. Jaffé and these results will be published in the near future.

Table II gives a summary of σ_I values for the substituents involved in Table I.

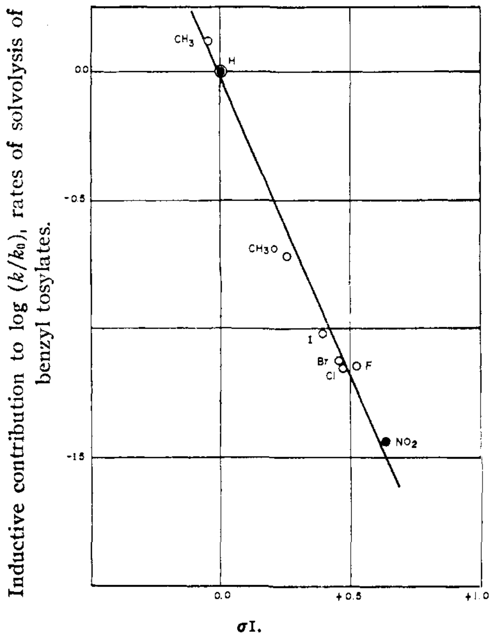

Fig. 7.—Linear inductive relationship between inductive contribution, $[1/(1 - \alpha)][\log (k^m/k_0) - \alpha \log (k^p/k_0)]$, to the rates of solvolysis of *m*- and *p*-substituted benzyl tosylates, 76% aq. acetone, 25°, and the aliphatic inductive substituent constant, σ_I. $\alpha \approx 0.33$ for non-conjugating (+R) substituents (closed circles); $\alpha = 0.10$ for conjugating (−R) substituents (open circles).

Conclusions

The results may be interpreted in summary as providing critical evidence supporting the following conclusions: (a) the $\log (k/k_0)$ values for *m*- and *p*-substituents in the reactivities of most side-chain derivatives of benzene may be treated to useful quantitative approximation as the sum of inductive and resonance effects (model equation 1); (b) the quantity $(1/1 - \alpha)$ $[\log (k^m/k_0) - \alpha \log (k^p/k_0)]$ gives a reasonably quantitative measure of inductive effects; (c) these inductive effects follow with useful precision the aliphatic series σ_I scale of inductive effects (equation 7). The applicability of this $\sigma_I\rho_I$ relationship is approximately independent of reaction type or experimental conditions; (d) failure of precise Hammett L.F.E. relationships in many instances results from a specific dependence of the scale of resonance effects on the nature of the reaction series; (e) the wide generality of equation 7 suggests its failure to hold

TABLE II

SUMMARY OF σ_I VALUES

	Substituent	σ_I		Substituent	σ_I
(1)	$(CH_3)_3Si$	−0.12	(14)	CH_3CO	+ .28
(2)	*t*-C_4H_9	− .07	(15)	CH_3CONH	+ .28
(3)	C_2H_5	− .05	(16)	COOR[a]	+ .30
(4)	CH_3	− .05	(17)	OC_6H_5	+ .38
(5)	H	.00	(18)	I	+ .39
(6)	$C_6H_5CH_2$	+ .04	(19)	CF_3	+ .41
(7)	C_6H_5	+ .10	(20)	Br	+ .45
(8)	$N(CH_3)_2$	+ .10	(21)	Cl	+ .47
(9)	NH_2	+ .10	(22)	F	+ .52
(10)	CH_2Cl	+ .17	(23)	CH_3SO	+ .52
(11)	OCH_3	+ .25	(24)	CN	+ .58
(12)	OH	+ .25	(25)	CH_3SO_2	+ .59
(13)	RS[a]	+ .25	(26)	NO_2	+ .63

[a] R = H or alkyl.

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[17] Reference 3a, p. 621.

[18] E. D. Hughes, *Trans. Faraday Soc.*, **37**, 626 (1941).

to reasonable precision for certain cases of *p*-substituents conjugated with the reaction center (*cf.* for example, reaction 17) results from the failure of the special linear resonance energy relationship: (effect of resonance of *m*-substituent = α (effect of resonance for *p*-substituent in the same reaction series).

Conclusions a-c follow directly from the introductory discussion. Conclusion d requires further comment. Combining the Hammett equation with equation 2 gives for *p*-substituents, for example

$$\log (k^p/k_0) = \rho(\sigma_I + \sigma_R) = \sigma_I\rho + \sigma_R\rho \qquad (8)$$

Although equation 8 is consistent with the basic model, equation 1, it requires in addition that resonance effects in a given reaction series must follow a precise linear resonance energy relationship with the corresponding resonance effects in the ionization of benzoic acids, *i.e.*, resonance effect = $\sigma_R\rho$. This requirement places limitations on the Hammett relationship for two reasons. First, the linear resonance energy relationship may not hold. Second, even though the σ_R scale of resonance effects applies, the log (k/k_0) values may not show the same susceptibility to σ_I and σ_R values, *i.e.*, $\rho \neq \rho_I \neq \rho_R$. This latter situation has been shown to apply to shielding effects on the n.m.r. lines of fluorobenzenes,[8] and for electrophilic reactivities such as the equilibrium constants for arylcarbonium ion formation from arylcarbinols.[19]

The more general applicability of equation 7 apparently results from the fact that neither of these conditions is required. It is apparent that conclusions a-d conform in large part to the discussion of the $\sigma\rho$ relationship by Branch and Calvin.[20] It is likewise apparent that equation 7 cannot be regarded as a substitute for the wide general utility of the Hammett $\sigma\rho$ relationship for approximate prediction and correlations of reactivities. Equation 7 deals only with the approximate correlation and prediction of inductive contributions to reactivities.

The cause of certain reaction series requiring a "dual" reduced α value for substituents which undergo a change in conjugation with the reaction center during the reaction process is readily apparent. These results indicate that the same scale of resonance effects holds for the *p*- as well as the corresponding *m*-substituents in the given reaction series, but that there is an enhanced resonance effect from the conjugating *p*-substituent which necessitates a reduced α value in applying equation 7. The "normal" value of α ($^1/_3$) apparently represents the ratio of *meta* to *para* resonance effects which results from resonance of the substituent with the aromatic system alone, *i.e.*, these are the so-called "resonance polar effects."[21] The reduced α ($^1/_{10}$) signifies a change in resonance interaction of the *p*-substituent with the side-chain reaction center as a consequence of the reaction process. It is significant that in the ionization of benzoic acids and in the rates of saponification of its esters, a normal value ($^1/_3$) of α suffices for all substituents. The use of α values to diagnose the extent of resonance interactions will be considered in detail in later publications.

The precision of the α factor in equations 3 and 7 is worthy of comment. The precision of the correlations given in Table I is not highly sensitive to this figure. In general, "normal" values of α varying from 0.25 to 0.45 may be used without appreciably changing the precision of equation 7. Outside of these limits the linear relationship is generally not of useful precision. A similar statement apparently applies to "dual" α values. The precision of equation 7 can be somewhat improved by making α a variable (a different constant for each reaction series), but at the present time it appears doubtful that the precision is generally sufficiently improved (or significant) to warrant the added complication of the treatment (except in the situations requiring "dual" α values). The general significance of making α a variable quantity is however under further investigation.

We have found a striking example of the application of equation 7 to the rates of decomposition of benzenediazonium chlorides in water at 29°,[22] which requires a value of α markedly different from either $+^1/_3$ or $+^1/_{10}$. This reaction gives no semblance of a Hammett L.F.E. relationship, a log *k vs.* σ plot leading to a wide scattering of points. However, the data follow equation 7 with a precision typical of that indicated in Table I using $\alpha = -0.65$ (for all substituents), as indicated by the following least squares quantities: $S = 0.12$, $a = -0.03$, and $R = 0.983$. The ρ_I value for the reaction is -4.21, determined for the substituents: 4, 5, 7, 11, 21 and 26. Deviations for the OH and CO_2H groups of greater than five times the standard error for the other substituents are obtained (and these substituents have consequently been omitted in obtaining the above results.) However, the deviations for these two substituents can be accommodated readily on the basis that the diazonium ion group markedly increases the normal hydrogen bonding tendencies of these substituents.

The cause of resonance effects for this reaction series having opposite signs in the *m*- and *p*-positions has been discussed qualitatively[23] and will be considered in detail by us in a subsequent paper on resonance effects. In the connection with which the present paper is concerned, the applicability of equation 7, this example affords ample indication that other reaction series will be found for which α is meaningfully different from $^1/_3$ or $^1/_{10}$.

Limitation of the present treatment to dipolar substituents is also worthy of comment. In general, insufficient data for positively or negatively charged substituents, *e.g.*, CO_2^- or $N(CH_3)_3^+$ are available to make an extensive application of equation 7 to this type of substituent. In the instance where the required data are available, points for such substituents frequently deviate seriously from the lines defined by the dipolar substituents

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(19) R. W. Taft, Jr., Abstracts of Fifteenth National Organic Symposium, American Chemical Society, Rochester, N. Y., June 17–20, 1957, p. 52–53.

(20) Reference 6b, pp. 246–257, 416–419.

(21) Reference 3a, p. 570, 578.

(22) M. L. Crossley, R. H. Kienle and C. H. Benbrook, This Journal, **62**, 1400 (1940).

(23) (a) J. F. Bunnett and E. Zahler, *Chem. Revs.*, **49**, 273 (1951); (b) C. K. Ingold, "Structure and Mechanism of Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 800–802.

(although the $N(CH_3)_3^+$ group generally does fit). It is likely, therefore, that charged substituents involve additional complications. The nature of the inductive effects of charged substituents will be considered further in later publications.

TABLE III

VALUES OF ρ_I FOR ACID IONIZATIONS IN WATER, 25°

Acid	ρ_I
1. $C_6H_5NH_3^+$	2.83
2. C_6H_5SH	2.93
3. C_6H_5OH	2.30
4. $C_6H_5B(OH)_2$	2.15
5. C_6H_5COOH	1.00
6. $C_6H_5\overset{\overset{O}{\uparrow}}{P}(OH)_2$	0.76
7. $C_6H_5\underset{\underset{O}{\downarrow}}{\overset{\overset{O—}{\vert}}{P}}—OH$	0.95
8. $C_6H_5\overset{\overset{O}{\uparrow}}{As}(OH)_2$	1.05
9. $C_6H_5\underset{\underset{O}{\downarrow}}{\overset{\overset{O^-}{\vert}}{As}}—OH$	0.87
10. $C_6H_5\overset{\overset{O}{\uparrow}}{Se}—OH$	0.91
11. $C_6H_5CH_2NH_3^+$	0.72
12. $C_6H_5CH_2COOH$	+0.49
13. $C_6H_5CH_2CH_2COOH$	+0.21

Table III lists ρ_I values obtained for a number of acid ionization equilibria in aqueous solution. The values given for acids 6–13 are actually the Hammett ρ values given by Jaffé, since too few data are available in most of these reaction series to apply equation 7. The ρ_I and ρ values for these acids are expected to be quite similar, although when comparison is possible the relationship discussed in the following paragraph is frequently followed more closely by ρ_I values.

The important point illustrated in Table *III* is that to a rough approximation ρ_I depends only upon the position with respect to the benzene ring at which ionization occurs in the side-chain. Acid ionizations (1–3) in which the formal charge on the first atom of the side-chain is decreased by one unit have ρ_I values of 2.3 to 2.9. If the unit decrease in formal charge acts through an additional atom, ρ_I values of 0.72 to 1.05 are obtained (acids 5–11). Acids 12 and 13 provide further examples of the applicability of the equation: $\rho_I \cong (2.8 \pm 0.5)^{1-i}$, where i = the number of saturated atoms between the benzene ring and the atom at which the unit decrease in formal charge takes place. This relationship is followed in a manner roughly independent of the charge type of the acid or the kind of atom involved, and conforms to the Branch and Calvin scheme for treating inductive effects in acid ionization equilibria.[24]

The ρ_I value of phenylboric acid (4) is of special interest. Although the proton leaves from the second atom of the $-B{<}\begin{smallmatrix}OH\\OH\end{smallmatrix}$ group, the conjugate base is probably adequately represented by the major resonance form, $(C_6H_5\text{-}B^{-1}{<}\begin{smallmatrix}O\\OH\end{smallmatrix})^-$, so that the *first* atom loses nearly a unit formal charge on ionization of the acid. Accordingly, the ρ_I value is nearer to that for acids 1–3 than 5–11.

Having used equation 7 to demonstrate the general applicability of the σ_I inductive scale, and to determine the inductive reaction constant, ρ_I, we are now in a position to evaluate the total resonance effect by applying equation 1 in the form

$$\begin{aligned}&\text{total effect of reson.} \equiv \log(k^p/k_0) - \sigma_I\rho_I \text{ for } p\text{-substituent}\\&\text{total effect of reson.} \equiv \log(k^m/k_0) - \sigma_I\rho_I \text{ for } m\text{-substituent}\end{aligned} \tag{9}$$

Equation 9 can be used to examine the general applicability and limitations of the σ_R resonance scale, and to establish the nature of the dependence of resonance effects on reaction type. The next paper in this series will deal with such an examination.

Acknowledgment.—The authors wish to express their appreciation to Professor H. H. Jaffé for the benefit of valuable discussions.

[24] Reference 6b, pp. 193–200. NOTE ADDED IN PROOF.—The ionization of pyridinium ions in H_2O, 25°, with ρ = +5.69, (H. H. Jaffé and G. O. Doak, THIS JOURNAL, **77**, 4441 (1956)) also conforms to this rough scheme. The formal charge of the nitrogen atom of the ring is decreased by one in the ionization, corresponding in the above formulation to $i = -1$.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

Cyclic Benzeneboronate Esters

BY JAMES M. SUGIHARA AND CARLOS M. BOWMAN

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Reaction products of benzeneboronic acid with *cis*- and *trans*-cyclopentane-1,2-diol, *cis*- and *trans*-cyclohexane-1,2-diol, pyrogallol, methyl β-D-glucopyranoside, 2,3-butanediol, 1,3-butanediol, 1,4-butanediol, 3,4-di-*O*-benzoyl-D-mannitol and galactitol are described in addition to the previously prepared tribenzeneboronates of D-mannitol and D-glucitol. Ring structures containing 5-, 6- or 7-members are possible. Polyols tend to form completely substituted benzeneboronates. An explanation, based upon ease of hydrolysis and method of preparation, is offered for the latter observation.

Cyclic boronate esters of the compounds D-mannitol, D-glucitol, pinacol, pentaerythritol, diethyl D-tartrate, *cis*-indane-1,2-diol and catechol are reported.[1] Reaction was effected in aqueous media in all cases. Benzeneboronate esters of pentoses and two 6-deoxyhexoses were prepared[2] by fusing the two reagents. However, knowledge concerning steric requirements for ring formation and preferred ring size is largely lacking. Accordingly, this investigation was initiated in the hope of obtaining some information in this direction.

Cyclic diols were selected as model compounds to study the possibility of formation of cyclic boronate esters, since the relative positions of the hydroxyl groups are essentially fixed. Refluxing of

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[1] H. G. Kuivila, A. H. Keough and E. J. Soboczenski, *J. Org. Chem.*, **19**, 780 (1954).

[2] M. L. Wolfrom and J. Solms, *ibid.*, **21**, 815 (1956).