catalysts, and therefore an essential precaution in its preparation is avoidance of contact with traces of acidic or alkaline material. A sample of the diol stored in an acid-rinsed soda-lime sample bottle had become liquid in several months. The hydroxyl content of the resulting liquid was found to be 13% after having stood for three years, thus indicating the relatively less sensitive character of the higher members of the series of α,ω-diols toward dehydration catalysts.

Preparation of Tetramethyldisiloxane-1,3-diol.—This second member of the series can be prepared readily by another method. The corresponding alkali salt, 150 g. (0.5 mole) of the composition, $NaO\ (Me_2SiO)_2\ Na\cdot 5H_2O$, was added in powder form in small portions with good stirring to a mixture of 1500 ml. of ethyl ether and 60 g. (1.0 mole) of gl. acetic acid. The added salt disappears and a precipitate of sodium acetate is formed. Tests with Alk-Acid paper were used to follow the course of the reaction to the neutral point. The solids were filtered and the ether filtrate concentrated on the water vacuum. This procedure yielded 54 g. of a mixture of oil and needle-like crystals. The needle-like crystals, freed from oil by washing with petroleum ether, had a melting point of 65–69°. The molecular weight, determined cryoscopically in glacial acetic acid, was 156 (calcd. for $HO(Me_2SiO)_2H$, 166). The density, determined by pycnometer, was 1.095 ± 0.008.

Anal. Found: OH, 20.8; Si, 34.0. Calcd.: OH, 20.5; Si, 33.8.

The solubility in water of the dimerdiol is approximately 11 g./100 g. of H_2O at 25°. Samples stored for approximately three years have become only slightly oily.

Preparation of Tetramethyldisiloxane-1,3-diol Sodium Salt.—To 296 g. (1 mole) of octamethylcyclotetrasiloxane was added 320 g. of 50% aqueous NaOH (4 moles). After adding approximately 100 ml. of methanol the mixture was stirred and gradually heated to boiling. More methanol was added in small amounts during this time until the reaction mixture became homogeneous. After cooling somewhat the water suction was applied to remove the solvent, and any uncombined water. The remaining powdery mass represented essentially a quantitative yield of the hydrate. The product was readily recrystallized from hot acetone giving a neut. equiv. value of 151 (calcd. for $NaO(Me_2SiO)_2Na\cdot 5H_2O$, 150).

Further Physical Measurements for Characterization and Identification. A. X-Ray Diffraction Data.—For rapid identification, powder diffraction data may be used. The following data were obtained by standard procedures on samples prepared by triturating with mineral oil.

TABLE I

PRINCIPAL LINES

Dimethylsilanediol		Tetramethyldisiloxane-1,3-diol			
d	I/I_1	*d*	I/I_1	*d*	I/I_1
11.3	0.534	9.5	0.197	2.03	0.102
8.55	0.647	7.75	1.00	1.98	.094
4.50	1.00	5.00	0.564	1.95	.094
4.26	0.193	4.55	.718	1.81	.077
4.10	.181	4.36	.290	1.74	.077
3.76	.091	3.92	.256		
3.16	.136	3.40	.154		
3.00	.193	3.08	.265		
2.71	.125	2.62	.085		
2.21	.148	2.49	.077		
1.90	.102	2.12	.059		

B. Microscopic Data.—Examination of the dimethylsilanediol at a magnification of 40× showed its characteristic crystal habit to be flat elongated octahedral plates. The tetramethyldisiloxane-1,3-diol at a magnification of 100× was found to be in the form of long needles. Both were entirely homogeneous showing no signs of the presence of one in the other.

The dimeric diol crystals, on crushing, showed a marked cleavage tendency parallel to the long direction and the fragments had a fibrous appearance with curved and distorted ends indicating flexibility.

The following additional microscopic data were obtained. *Monomer:* refractive indices (5893 Å., 25°): $n_1 = 1.454 \pm 0.002$, $n_2 = 1.446 \pm 0.002$; extinction: parallel. *Dimer:* refractive indices (5893 Å., 25°): $n_1 = 1.459 \pm 0.002$, $n_2 = 1.464 \pm 0.002$; extinction: parallel; sign of elongation: positive.

C. Infrared Measurements.—Patterns of solid films of the two compounds formed on sodium chloride plates using a Baird instrument are well defined and unique.

Acknowledgments.—The author gratefully acknowledges the assistance of Mary Purcell Roche, formerly of the Corning Glass Works, and of Mr. Gust Kookootsedes, Mr. Arnold Kolb and Dr. L. Smith of the Dow Corning Corporation in carrying out various phases of this work.

MIDLAND, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Electrical Effects of Substituent Groups in Saturated Systems. Reactivities of 4-Substituted Bicyclo[2.2.2]octane-1-carboxylic Acids[1]

BY JOHN D. ROBERTS AND WALTER T. MORELAND, JR.[2]

RECEIVED SEPTEMBER 2, 1952

The reactivities of a series of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids and esters with X = $-H$, $-OH$, $-CO_2C_2H_5$, $-Br$ and $-C{\equiv}N$ have been determined. The apparent ionization constants of the acids in 50% aqueous ethanol at 25°, the reactivities of the acids toward diphenyldiazomethane in ethanol at 30°, and the saponification rates of the ethyl esters were measured and found to parallel one another throughout the series. The order of reactivities with the various substituents at the 4-position was $-C{\equiv}N > -Br > -CO_2C_2H_5 > -OH > -H$. Although transmission of electrical effects of substituent groups through the bicyclo[2.2.2]octane ring system is not possible by resonance interaction involving conjugated unsaturation, the magnitudes of the substituent influences were found to be comparable to those observed in *m*- and *p*-substituted benzene derivatives. The Kirkwood–Westheimer ellipsoidal cavity model for calculation of electrostatic effects of polar substituent groups on reactivity gives qualitative agreement with the experimental results.

Introduction

One of the important problems in the theoretical treatment of the relation of structure to reactivity of organic compounds is elucidation of the mechanisms of transmission of electrical effects of substituent groups in aromatic systems. Of the so-called "static" or ground-state electrical influences, the resonance (mesomeric), inductive and direct electrostatic (or field) effects appear to be most clearly recognized. The latter two influences have to a great extent resisted disentanglement and are very frequently treated together as a composite effect. In this and succeeding papers, we plan to recognize

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[2] U. S. Atomic Energy Commission Predoctoral Fellow, 1951–1952.

these two effects separately and will use the term *inductive effect* to designate that portion of the electrical influence of a group which is transmitted through a chain of atoms primarily by polarization of the bonding electrons from one atom to the next. The term *field effect* will be reserved for that part of the electrical influence of a polar or dipolar substituent which is primarily transmitted to the reactive group through space (including solvent, if any) in accord with the laws of classical electrostatics.

The inductive effect in substances containing conjugated unsaturation might be considered to travel either through the σ-bonds or the π-electron system. If the π-electrons are importantly involved, there is considerable theoretical justification[3] for the operation of a "non-classical long-range" influence primarily affecting the charge distribution at alternate atoms. It would appear to be a question of taste as to whether such an influence should be designated as an inductive or a resonance effect.

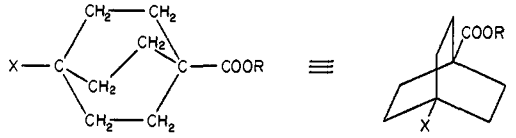
The present situation with regard to theoretical speculation as to the mode of transmission of the inductive effect and the relative importance of the field effect in aromatic systems is fairly described as chaotic. In the elegant early work of Lucas[4] on *p*-substituted benzoic acids, it was assumed that the field effect was negligible and that the inductive effect was relayed from a substituent preferentially to the *p*-position. A similar viewpoint, with the exception that the *o*- and *p*-positions were assumed to be more or less equally affected, was adopted by the English schools of Robinson and Ingold and very lately reiterated both by Taft[5a] and Sutton.[5b] Nonetheless, a number of recent experiments on the electrical effects of substituent groups[6] provide no support for postulation of an alternating transmission of the inductive effect in aromatic systems. Ri and Eyring[7] claim to be able to calculate quite accurately isomer distributions in nitration of benzene derivatives by assuming for each substituent: (1) that the field effect is completely negligible[8] at distances greater than about 2 Å.; (2) that the inductive effect is transmitted *equally* to all of the carbons of the benzene ring; and (3) that the resonance effect can be determined from Sutton's[9] mesomeric moments. Price[10] assumes an inductive effect, transmitted through the σ-bonds of aromatic systems, which falls off smoothly with distance and a concomitant electrostatic polarization of the π-electrons by the substituent group; the polarization being such to influence alternate positions around the ring. A somewhat similar picture of an inductive effect falling off with distance has been employed by Branch and Calvin.[11]

Standing in confutation of the above electrical effect formulations (all of which assume the direct field effect to be negligible) is the demonstration by Westheimer[12] using equations developed by Kirkwood and Westheimer[13] that the electrical effects of *p*-substituted dipolar groups on the acidities of benzoic and phenylacetic acids can be quantitatively correlated by assuming only direct electrostatic action of the substituent on the ionizable proton of the carboxyl group. Westheimer's treatment worked well except for those acids which carried substituents such as $-OH$ and $-OCH_3$ with unshared electron pairs known by other evidence to interact strongly with the benzene ring.

Some of the foregoing postulations of electrical influences are evidently mutually exclusive since we can hardly simultaneously have negligible field and negligible inductive effects as well as important alternating and non-alternating inductive effects. Further experimental work is clearly required. In this paper, we present evidence gained from a study of reactivities of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids and esters which bears on the role of the π-electrons in the transmission of the effects of substituents through aromatic systems.

Experimental Results and Discussion

The preparation of the series of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids and esters (I) has been described previously.[14]



I

The reactivities of the compounds were measured in three rather different processes, each of which has been used before with benzoic acid derivatives. The ionization constants K_A of the acids in 50% ethanol (by volume) at 25.0° and the rates of reaction of the acids with diphenyldiazomethane in absolute ethanol at 30.0° were determined by customary procedures.[15] The rates of hydrolysis of the ethyl esters (I, R = C_2H_5) in 87.83% ethanol at

[3] G. W. Wheland and L. Pauling, This Journal, **57**, 2086 (1935).

[4] H. J. Lucas, *ibid.*, **48**, 1827 (1926); E. P. Valby and H. J. Lucas, *ibid.*, **51**, 2718 (1929).

[5] (a) R. W. Taft, Jr., *ibid.*, **74**, 3120 (1952); (b) K. B. Everard and L. E. Sutton, *J. Chem. Soc.*, 2820 (1951).

[6] (a) J. D. Roberts, R. L. Webb and E. A. McElhill, This Journal, **72**, 408 (1950); (d) J. D. Roberts, R. A. Clement and J. J. Drysdale, *ibid.*, **73**, 2181 (1951).

[7] T. Ri and H. Eyring, *J. Chem. Phys.*, **8**, 433 (1940).

[8] This postulate is also adopted by Eyring in considering the reactivities of short-chain saturated systems; *cf.* R. P. Smith, T. Ree, J. L. Magee and H. Eyring, This Journal, **73**, 2263 (1951); R. P. Smith and H. Eyring, *ibid.*, **74**, 229 (1952).

[9] L. E. Sutton, *Proc. Roy. Soc. (London)*, **133A**, 668 (1931).

[10] (a) C. C. Price, "Mechanisms of Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 946, pp. 28–30; (b) C. C. Price, This Journal, **73**, 5833 (1951); (c) C. Price and D. C. Lincoln, *ibid.*, **73**, 5838 (1951).

[11] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice–Hall, Inc., New York, N. Y., 1941, pp. 240–257, particularly pp. 245–246.

[12] (a) F. H. Westheimer, This Journal, **61**, 1977 (1939). (b) See J. N. Sarmousakis, *J. Chem. Phys.*, **12**, 277 (1944), for a corresponding treatment of *m*-substituted aromatic acids. (c) The conclusion of Westheimer regarding the importance of field effects was anticipated much earlier by W. A. Waters, *J. Chem. Soc.*, 1554 (1933).

[13] (a) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); (b) F. H. Westheimer and J. G. Kirkwood, *ibid.*, **6**, 513 (1938).

[14] J. D. Roberts, W. T. Moreland, Jr., and W. Frazer, This Journal, **75**, 637 (1953).

[15] (a) J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949); (b) J. D. Roberts, W. Watanabe and R. E. McMahon, *ibid.*, **73**, 760 (1951); (c) J. D. Roberts and E. A. McElhill, *ibid.*, **72**, 628 (1950).

30° were determined essentially as described by Kindler.[16] The experimental results are given in Tables I–III.

TABLE I

APPARENT IONIZATION CONSTANTS IN 50% ETHANOL (BY VOLUME) AT 25.0 ± 0.1° OF 4-SUBSTITUTED BICYCLO-[2.2.2]OCTANE-1-CARBOXYLIC ACIDS, X-$C_8H_{12}CO_2H$

X	Half-point[a]	Av. $K_A \times 10^7$ [b]
H	6.74, 6.75	1.80
OH	6.31, 6.35	4.68
$CO_2C_2H_5$	6.32, 6.30	4.90
Br	6.07, 6.09	8.32
CN	5.92, 5.88	12.6

[a] Readings, at point of half-neutralization, on pH scale of Beckman pH meter calibrated against aqueous buffer solutions using glass and saturated potassium chloride–calomel electrodes without correction for liquid junction potentials. [b] Calculated assuming unit activities and pH meter readings equal to logarithm of reciprocal of the hydrogen ion concentration.

TABLE II

REACTIVITIES OF 4-SUBSTITUTED BICYCLO[2.2.2]OCTANE-1-CARBOXYLIC ACIDS, X-$C_8H_{12}CO_2H$, TOWARD DIPHENYLDIAZOMETHANE IN 100% ETHANOL AT 30.0 ± 0.1°

X	Acid concn., M	Half-life, min.	k_2, l. mole^{-1} min.$^{-1}$
H	0.00792	369	0.237
OH	.00860	218	.370
$CO_2C_2H_5$	.00944	195	.376
Br	.00744	186	.501
CN	.00891	131	.592

TABLE III

RATES OF ALKALINE HYDROLYSIS OF 4-SUBSTITUTED ETHYL BICYCLO[2.2.2]OCTANE-1-CARBOXYLATES, X-$C_8H_{12}CO_2C_2H_5$, IN 87.83% ETHANOL AT 30.0 ± 0.01°

X	Concn. of ester, M[a]	$k_2 \times 10^3$, l. mole^{-1} min.$^{-1}$
H	0.02427	1.62
OH	.02411	7.55
$CO_2C_2H_5$	.02467	8.35[b]
Br	.02467	17.3
CN	.02427	31.8

[a] The concentrations of ester and sodium hydroxide were equal in every run. [b] Corrected by dividing the observed rate constant by a statistical factor of two.

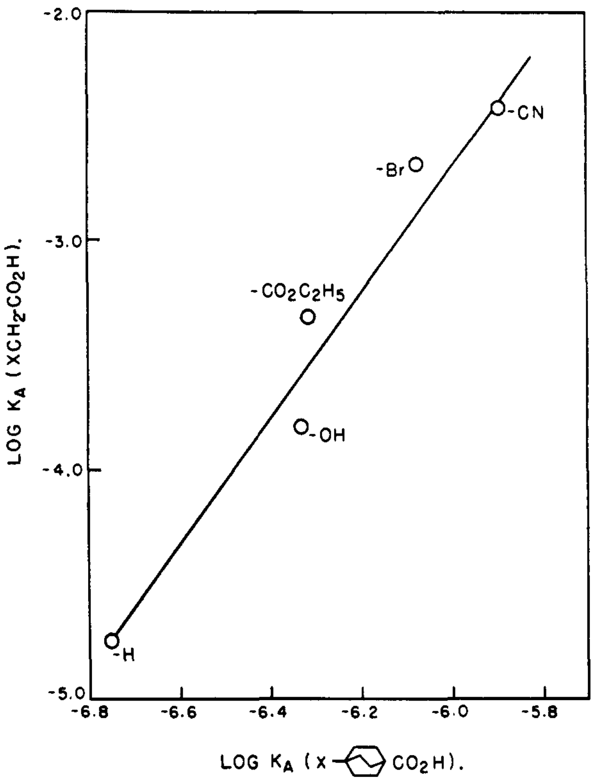


Fig. 1.—Relationship between the ionization constants of substituted acetic acids in water at 25° and the apparent ionization constants of 4-substituted bicyclo[2.2.2]-octane-1-carboxylic acids in 50% ethanol (by volume) at 25°. The constants for the acetic acids were taken from Landolt-Börnstein, "Physikalisch–Chemische Tabellen," Springer Verlag, Berlin, Eg. III, Vol. III, 1936, p. 2109 ff.

Variation of the substituent group X clearly has a substantial influence on the reactivity of compounds of type I. Indeed, substitution of a cyano group for hydrogen increases the rate of ethyl ester hydrolysis by a factor of *twenty*. The order of the various groups in changing the acid strength of the carboxyl group parallels fairly closely the order observed with substituted acetic acids and log K_A for XCH_2COOH is almost linear with log K_A of $XC_8H_{12}COOH$ (Fig. 1). Of particular importance to discussion of the effects of the substituents and the mode of their transmission is the question of whether or not the substituent influences are actually due to potential energy changes rather than kinetic energy changes. We find a linear relationship holds within experimental error between the logarithms and rate or equilibrium constants for the three reactions studied (Figs. 2 and 3). Linear relationships of this type correspond to linear free-energy relationships which strongly imply that the effects of the substituents are exerted through changes of potential energy (ΔE_P)[17] and that steric and entropy terms remain essentially constant through the series. The linear relationships permit a correlation similar to that employed by Hammett[17] for *m*- and *p*-substituted benzene derivatives where experimental reactivities were found to be well-fitted by the equation

$$\log k - \log k^0 = \sigma\rho$$

Here, k^0 and k, respectively, are equilibrium (or rate) constants observed for reactions of unsubstituted and *m*- or *p*-substituted benzene derivatives, ρ is a constant characteristic of the reaction involved and σ is a constant characteristic of the substituent. For our 4-substituted bicyclo[2.2.2]octane-1-carboxylic acid derivatives, we can use the same type of equation and compute reaction and substituent constants which will be designated as ρ' and σ', respectively.

Hammett[17] has arbitrarily taken ρ as +1.000 for the ionization equilibria of benzoic acids in water at 25.0°. Such equilibria with the bicyclo[2.2.2.]octanecarboxylic acids were not studied in the present work because some of the compounds were too water-insoluble. Since it was desirable to have the σ- and σ'-constants on as comparable a basis as

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(16) K. Kindler, *Ann.*, **450**, 1 (1926).

(17) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chaps. III, IV and VII.

TABLE IV

COMPARISON OF σ- AND σ'-VALUES

Substituent	σ'	n^a	r^b	$\sigma_{para}{}^c$	$\sigma_{meta}{}^c$	$\sigma_{para} - \sigma'$	$\sigma_{meta} - \sigma'$
H	0.000	3	...	0.000		.....	.....
OH	+ .283	3	0.015	−0.341[d]	+0.014[d]	−0.624	−0.269
$CO_2C_2H_5$	+ .297	3	.010	+ .402[d]	+ .334[d]	+ .105	+ .037
Br	+ .454	3	.008	+ .232	+ .391	− .222	− .063
CN	+ .579	3	.009	+ .656[e]	+ .608[e]	+ .077	+ .029

[a] Number of reactions for which data are available. [b] Maximum deviation of σ' in all reactions so far run. [c] Data from ref. 17 unless otherwise noted. [d] J. D. Roberts and W. T. Moreland, Jr., THIS JOURNAL, **75**, 2267 (1953). [e] Ref. 15c.

possible, we have set ρ' for the ionization constants of the acids in 50% ethanol (by volume) equal to +1.464, the value previously[14a] obtained for substituted benzoic acids in the same solvent. The σ'- and ρ'-values using this standard are presented in Tables IV and V along with the corresponding values for substituted benzoic acids.

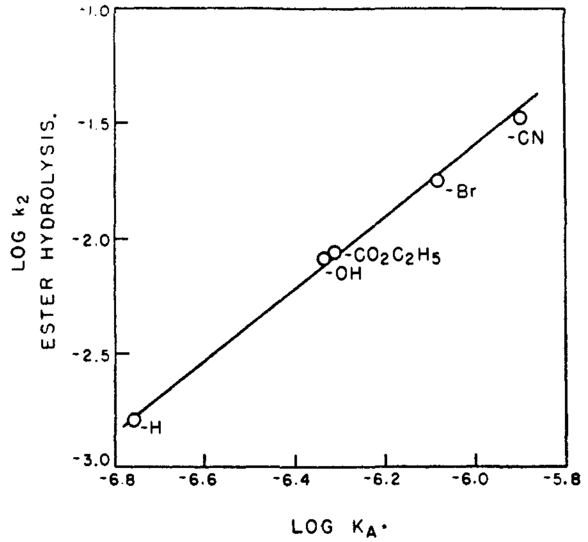


Fig. 2.—Relationship between apparent ionization constants of acids at 25° in 50% aqueous ethanol (by volume) and second-order rate constants for saponification of the esters in 87.83% ethanol at 30°. The point for $-CO_2C_2H_5$ was determined using a statistical factor of two.

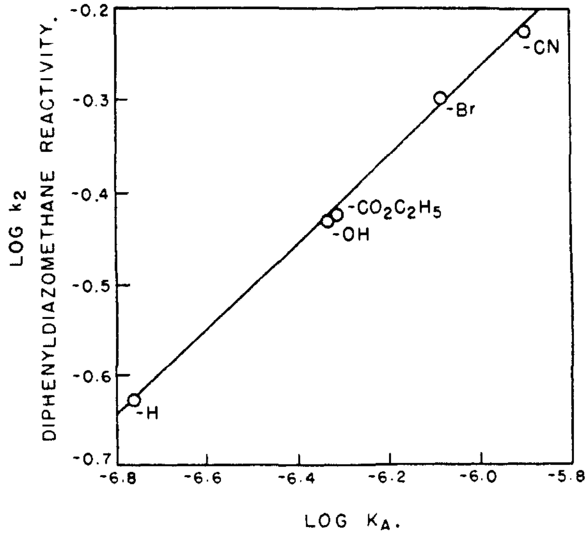


Fig. 3.—Relationship between apparent ionization constants of acids at 25° in 50% aqueous ethanol (by volume) and second-order rate constants for reactivities of the acids toward diphenyldiazomethane in 100% ethanol at 30°.

TABLE V

COMPARISON OF ρ- AND ρ'-VALUES

Reaction	log k^0	ρ'	r^a	n^b	ρ	D^c
Ionization of acids, 50% EtOH (by volume), 25°	−6.745	+1.464[d]	...	5	+1.464[e]	54
Alkaline hydrolysis of ethyl esters, 87.83% EtOH, 30°	−2.791	+2.24	0.074	5	+2.498[f]	28
Acids with diphenyldiazomethane, 100% EtOH, 30°	−0.625	+0.698	.016	5	+0.937[e]	24

[a] Medium deviation of points from the line. [b] Number of substituents for which data are available. [c] Dielectric constant of the solvent; *cf.* J. Wyman, Jr., THIS JOURNAL, **53**, 3292 (1931). [d] Taken as standard. [e] Ref. 14a. [f] Ref. 17.

All of the reactivity data indicate that the effects of substituent groups in determining the reactivities of substituted benzoic and bicyclo[2.2.2.]-octane-1-carboxylic acids are quite comparable even though transmission of electrical effects through the bicyclo[2.2.2]octane ring is not possible by resonance involving conjugated unsaturation. The comparison is vividly shown by plotting the logarithms of the equilibrium (or rate) constants of the two series against one another as in Figs. 4, 5 and 6. In each case, a straight line of unit slope drawn through the point for the unsubstituted compounds reproduces the general trend of the reactivities. The conclusion seems inescapable that the aromatic π-electron systems in substituted benzoic acids do not play a dominant role in the transmission of the electrical effects of dipolar groups to the ionizable carboxyl (excepting the customary resonance or mesomeric effects involving unshared electron pairs or partially filled *p*-orbitals of the substituents, see below). Consequently, the concept of an important π-electron-transmitted alternating inductive effect can now be abandoned.[6]

Comparison of the σ- and σ'-values is very interesting. With the groups which are meta directing in electrophilic aromatic substitution, *i.e.*, $-CO_2C_2H_5$ and −CN, both the σ_{meta}- and σ_{para}-constants are more positive than the σ'-constants. With the ortho-para directing groups, −Br and −OH, the σ'-constants are more positive. The trends are well illustrated by Figs. 4, 5 and 6 where the points for meta directing groups lie above the lines and those for the ortho-para groups lie below the lines. In all cases, the points for *m*-substituents lie closer to the line than for *p*-groups. This fact is good evidence that the σ-constants are influenced by π-

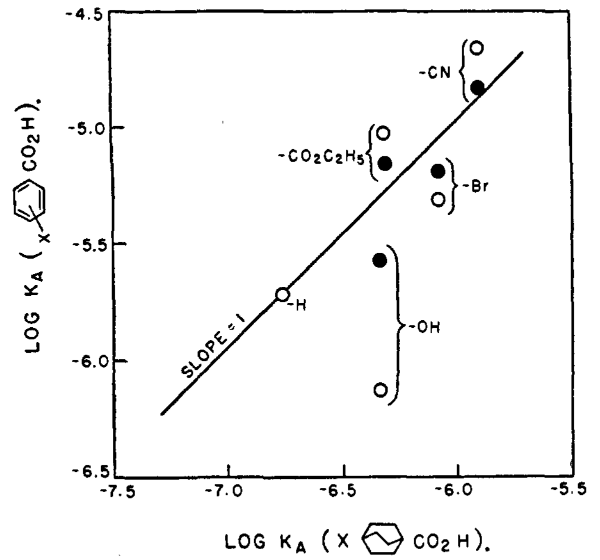


Fig. 4.—Relationship between apparent ionization constants of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids and *m*- and *p*-substituted benzoic acids: ●, *m*-benzene substituent; O, *p*-benzene substituent.

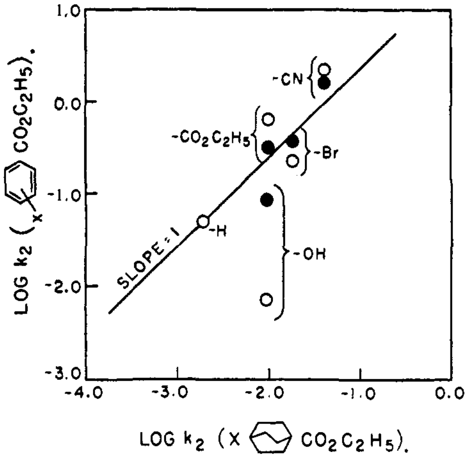
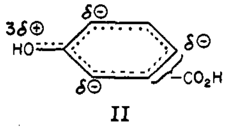
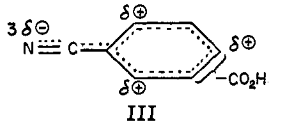


Fig. 5.—Relationship between the second-order rate constants for the saponification of esters of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids and the corresponding values for *m*- and *p*-substituted ethyl benzoates: ●, *m*-benzene substituent; O, *p*-benzene substituent. The points for the *m*, *p*-substituted benzoates, for which no direct experimental data were available, were calculated from the ρ,σ-relationship of Hammett.[17]

electron resonance effects since these should be felt most strongly at the *p*-positions. Indeed, $\sigma - \sigma'$ (see Table IV) should be a reasonable measure of such resonance effects. It should be clear that the resonance effects are not identifiable with inductive effects since they operate in opposition to the dipole field for hydroxyl and bromine. The most satisfactory formulations of the resonance effects seem to be as shown below (II and III) using the hydroxyl and cyano groups as examples.



II



III

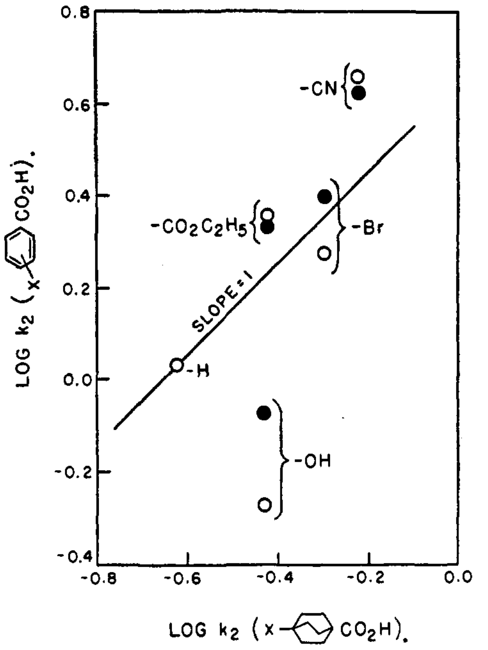


Fig. 6.—Relationship between the second-order rate constants for reactivity toward diphenyldiazomethane of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids and the corresponding values for *m*- and *p*-substituted benzoic acids: ●, *m*-benzene substituent; O, *p*-benzene substituent.

In aromatic systems, both hydroxyl and cyano groups are expected to be acid strengthening by inductive and/or field effects which should be approximately the same at the *m*- and *p*-positions and measured by σ'. Superimposed are conventional interactions between the substituent and the π-electron systems of the benzene rings which preferentially charge the *o*- and *p*-positions. The effects of the charge increments on the ionizable protons are greatest when the carboxyl is para to the substituents and will operate in opposite manners for the hydroxyl and cyano groups. The effects are expected to be smaller when the carboxyl is meta and farther away from the ring charges.[10c] The fact that the ratios $(\sigma_{\text{para}} - \sigma')/(\sigma_{\text{meta}} - \sigma')$ are roughly constant for all of the substituents is in harmony with the above considerations.

The present experiments do not provide a decisive answer to the question about the relative importance of the field and inductive effects, and, indeed, either effect by itself is qualitatively capable of accommodating the results. Unfortunately, most equations for quantitative evaluation of "inductive" effects in saturated systems have parameters which are fixed by experiment[18] and actually employ a composite of inductive and field effects. At present, there seems no very good way to calculate the contribution of the inductive effect alone to the transmission of electrical effects from one end of the bicyclo[2.2.2]octane ring system to the other.[19] On the other hand, field effect calculations[12,13] need not require adjustment of parame-

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(18) See for example, ref. 11, p. 217.

(19) It is possibly significant that the factors computed by Waters[12c] for the damping of the inductive effect in saturated carbon chains from bond polarizabilities make the calculated inductive effect essentially negligible with 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids.

ters by recourse to experiment and, in principle, are reasonably straightforward. Difficulties are encountered in the electrostatic treatment of molecules with which free rotation can make uncertain the distance between a substituent and a reactive center. However, little difficulty would be expected from substances like I or benzoic acids on this score. Indeed, it is difficult to conceive of a series of compounds as ideally suited for a quantitative test of the field effect as the 4-substituted bicyclo[2.2.2]octane-4-carboxylic acids. With these substances, the distances between the dipolar and carboxyl groups can be estimated accurately, the dipoles of substituents such as bromo and cyano lie on the major axis of the ring system, resonance effects involving conjugated unsaturation are absent and, as indicated earlier, the differences in reactivity are likely to be due to potential energy effects alone.

We have applied the Kirkwood–Westheimer[12,13] electrostatic equation (1) to the ionization constants of the unsubstituted, 4-bromo- and 4-cyano-

$$\Delta pK = \frac{e\mu \cos \zeta}{2.303kTR^2D_E} \qquad (1)$$

bicyclo[2.2.2]octane-1-carboxylic and benzoic acids in 50% aqueous ethanol. The particular acids were chosen of those for which data are available because ζ the angle between the dipole and the line joining its center with the ionizable proton is certain to be close to 0°. Equation (1) takes into account only the classical electrostatic interaction between the dipole and the ionizable proton. The difference between (1) and a similar equation derived by Bjerrum[20] is the replacement of D, the dielectric constant of the solvent, by an "effective" dielectric constant D_E which is calculated on the assumption that the molecules are *homogeneous* cavities of low dielectric constant in the solvent. D_E is a function of the shape of the molecule, the positions of the dipolar and carboxyl groups and the respective dielectric constants of the solvent and the cavity. A serious limitation of the treatment is the mathematical necessity for using cavities with rather arbitrarily defined spherical or ellipsoidal shapes.[12,13] In our calculations we have not used the Westheimer[12] formulations for aromatic acids which involve assumptions of identical volumes and distances R between the center of the dipole and the ionizable proton regardless of the nature of the substituent. The results of the calculations in which ΔpK, the difference in pK values for the substituted and unsubstituted acids in each series, was obtained are given in Table VI.

TABLE VI

CALCULATED ΔpK VALUES IN 50% AQUEOUS ETHANOL (BY VOLUME) FOR 4-SUBSTITUTED BENZOIC AND BICYCLO-[2.2.2]OCTANE-1-CARBOXYLIC ACIDS BY KIRKWOOD–WESTHEIMER METHOD

	p-BrC_6H_4-CO_2H	*p*-NCC_6H_4-CO_2H	4-BrC_8H_{12}-CO_2H	4-NC-C_8H_{12}-CO_2H
Vol. per molecule,[a] Å.^{3}	202	209	265	272
R, Å.[b]	6.7	7.9	6.5	7.7
λ_0[c]	1.39	1.27	1.50	1.36
μ[d]	1.7	4.4	2.1	4.1
D_E[e]	11	23	6.9	13
ΔpK (calcd.)[f]	0.20	0.20	0.40	0.30
ΔpK (found)	0.40[g]	1.05[h]	0.67	0.85

[a] Calculated by Traube's rule, *cf*. ref. 12. [b] Distance between center and dipole taken conventionally as the midpoint of the C–Br or C≡N bonds and ionizable proton. The proton was placed following F. H. Westheimer and M. W. Shookhoff, THIS JOURNAL, 61, 555 (1939), 1.45 Å. beyond the carbon of the carboxyl group on the extension of the bond joining the carboxyl to the rings. Other distances were taken from the compilation of L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1940. [c] Equation of prolate ellipsoid. [d] Data from L. G. Wesson, "Tables of Electric Dipole Moments," Technical Report No. II, Laboratory for Insulation Research, Massachusetts Institute of Technology, in Debye units. [e] Obtained by graphical interpolation from the tables of Westheimer, Jones and Lad[21] using D equal to 54 (*cf*. Table V) and D_i equal to 2.00. [f] Calculated to the nearest 0.05 pK unit by the equations of Kirkwood and Westheimer.[13a] [g] Data from ref. 15a. [h] Data from ref. 15c.

While the agreement between the calculated and found values is not good, it must be remembered that the experimental figures represent, not absolute but only, apparent pK values obtained with a glass electrode. Furthermore, a mixed solvent (50% aqueous ethanol) was used in which there might be a tendency for one kind of solvent molecule to cluster preferentially around the ions.[21] Another very important factor in evaluating the degree of success of the electrostatic treatment is the substantial sensitivity of ΔpK (calcd.) to R as a consequence of the prolate ellipsoid cavity model used for mathematical convenience. The difficulties are well illustrated by the fact that the calculated value of ΔpK for the 4-bromobicyclic acid is actually larger than that for the 4-cyano acid even though the cyano dipole is twice as large and but 15% farther away from the carboxyl group. The difference in molecular volume of the 4-bromo and 4-cyano acids is small. Consequently, when the distance R between the substituent and carboxyl groups varies, considerable changes occur in the eccentricity of the ellipsoidal solvent cavity. With large R as assigned to the cyano acid, the ellipsoid becomes more sausage-like and more of the lines of force are considered to travel outside of the cavity thus greatly increasing the effective dielectric constant D_E over the value for the bromo acid. The calculated effect on D_E is not physically realistic since changing the size of a group at the 4-position is not actually expected to alter markedly the shape of the solvent cavity at the center and far end of the molecule in the manner suggested by the mathematical equations.[22]

The large variation of D_E with R puts also a premium on accurate positioning of the substituent dipole if reliable calculated ΔpK values are desired. The cyano group is particularly important in this regard since the conventional centering of the substituent dipole at the midpoint of the C≡N bond ignores induction of positive charge on the

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(20) N. Bjerrum, *Z. physik. Chem.*, **106**, 219 (1923).

(21) F. H. Westheimer, W. A. Jones and R. A. Lad, *J. Chem. Phys.*, **10**, 478 (1942); G. Scatchard, *ibid.*, **9**, 34 (1941).

(22) If one follows the procedure [S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, **70**, 821 (1948)] of assuming constant size and shape of the solvent cavity for structurally similar compounds, *i.e.*, D_E as a disposable parameter, and uses the 4-bromobicyclic acid as a standard, then the calculated ΔpK for the 4-cyanobicyclic acid is 1.10 in fair agreement with the experimental value of 0.85.

carbon to which the cyano group is attached. If induction is of sufficient importance to shorten the distance R between the dipole center and carboxyl group by as little as 0.5 Å., ΔpK (calcd.) is increased by more than 50%.

It is probable that at least part of the general discrepancy between the calculated and found ΔpK values in Table VI is real and reflects the observation[23] that the Kirkwood–Westheimer treatment predicts too small a dependence of ΔpK values on solvent dielectric constant. If the differences between calculated and found figures for ΔpK are real, they indicate either the magnitude of the bond-transmitted inductive effect or the degree of inadequacy of the Kirkwood–Westheimer treatment.[24]

The electrostatic treatment is effective in accounting for the differences in ΔpK for 4-bromobicyclo[2.2.2]octane-1-carboxylic acid and δ-bromovaleric acid which are 0.67 and about 0.12,[25] respectively. The effective dielectric constant for the long, thin δ-bromovaleric acid is expected to be much larger than for the relatively fat bicyclo acid. Furthermore, free rotation in the aliphatic acid can result in orientations of the C–Br dipole which would not enhance the acidity of the carboxyl group. On the basis of the inductive effect, the only difference between the two acids is that in the bicyclic acid there are more chains of carbon atoms for the effect to travel from the substituent to the carboxyl group. At most, the inductive effect alone can account for about half of the difference in ΔpK between the aliphatic and bicyclic acids.

Electrostatic calculations of the effects of substituents on the rates of alkaline hydrolysis of ethyl 4-bromo- and 4-cyanobicyclo[2.2.2]octane-1-carboxylates give results similar to those for the ΔpK values for the corresponding acids. At present, we have no explanation for the difference between ρ and ρ' for the reactions of the acids with diphenyldiazomethane. It may be significant that ρ/ρ' for the reactions so far studied (Table V) bears an inverse relation to the solvent dielectric constant.

Acknowledgment.—We are grateful to Professor F. H. Westheimer for many suggestions and helpful discussions regarding the interpretation of the experimental results.

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(23) J. H. Elliott and M. Kilpatrick, *J. Phys. Chem.*, **45**, 472 (1941); M. Kilpatrick and W. H. Mears, THIS JOURNAL, **62**, 3047, 3051 (1940). See ref. 12b and F. H. Westheimer and J. G. Kirkwood, *Trans. Faraday Soc.*, **43**, 77 (1947), for discussions.

(24) (a) Professor F. H. Westheimer has offered the following comments with respect to the results of the present research. "Roberts' and Moreland's data for the bicycloöctane system clearly show that equations based on our cavity model[12b,13] somewhat underestimate the effect of substituents on ionization constants. It should be noted, however, that whereas our equations underestimate the observed effects by a factor of about 2, the older Bjerrum–Eucken equation underestimates the observed effects by a factor of about 10; the newer approximation is therefore better than the older one by almost an order of magnitude. Furthermore, a logical extension of the electrostatic theory would lead to an approximation closer to the observed value of ΔpK than that obtained from the equations Kirkwood and I developed, since such an approximation might take into account the effect of electrical saturation in the solvent. This effect would necessarily decrease D_E and therefore increase the calculated value of ΔpK. Our equations are also limited by the mathematically convenient but physically unrealistic requirement that all charges or dipoles must lie at the foci of ellipsoidal cavities. Although the best approximation currently available underestimates the influence of dipoles in the bicycloöctane series, it is probable that a large part of the influence of substituents on ΔpK can be ascribed to simple electrostatic effects. It remains an open question whether any electrostatic theory which ignores the detailed structure of the substituted molecule can do better than yield a crude approximation to the observed results." (b) The relatively greater discrepancies between calculated and found ΔpK values for the aromatic acids suggests that a lower internal dielectric constant D should be used for such compounds.

(25) Computed from ΔpK for δ-bromovaleric acid in water at 25° which is 0.07, W. A. Waters, "Physical Aspects of Organic Chemistry," 4th Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1950, p. 243, and the usual approximate proportionality of ΔpK to the reciprocal of the solvent dielectric constant.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, THE OHIO STATE UNIVERSITY, AND THE SCHOOL OF CHEMISTRY, INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

Infrared Spectra of Chlorophyll and Related Compounds[1]

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The infrared spectra of chlorophylls-a and -b, pheophytin-a, bacteriochlorophyll-a and allomerized chlorophyll-a are reported. A partial analysis of these complex spectra has been attempted.

In 1933, Stair and Coblentz[2] published infrared spectra of chlorophyll and certain related compounds, such as ethyl chlorophyllide, phytol and pheophytin. Since that time there has been sufficient progress in the fields of chlorophyll chemistry and infrared spectroscopy to warrant repetition of this work. While the new investigation provides substantially improved data, which permit more detailed interpretation, it also confirms the earlier, remarkably good, results.

Five compounds were examined: chlorophyll-a; chlorophyll-b, which differs in having a formyl, instead of a methyl, group at carbon 3; pheophytin-a, in which the central magnesium atom of the chlorophyll is replaced by two hydrogens; bacteriochlorophyll, in which ring II has been reduced and the vinyl radical at carbon 2 oxidized to an acetyl group; and finally, "allomerized" chlorophyll-a, which, according to Fischer[3] is chlorophyll-a whose

(1) This work was made possible by the support of the Office of Naval Research (NR 051 028, Contract N6ori-212, T.O. I) to which the authors are indebted.

(2) (a) R. Stair and W. W. Coblentz, *J. Research Natl. Bur. Standards*, **11**, 703 (1933). (b) Compare E. I. Rabinowitch, "Photosynthesis," Vol. 2, Interscience Publ., Inc., New York, N. Y., 1951, pp. 610–612.

(3) H. Fischer and M. Strell, "FIAT" Rev. of German Science, Vol. 39 (1947), pp. 141–186; H. Fischer and H. Pfeiffer, *Ann.*, **555**, 94 (1944).