Dissociation Constants of Bicyclo[2.2.2]oct-2-ene-1-carboxylic Acids, Dibenzobicyclo[2.2.2]octa-2,5-diene-1-carboxylic Acids, and Cubanecarboxylic Acids[1]

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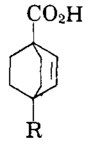
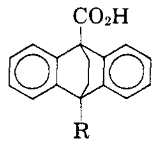
Abstract: Thermodynamic dissociation constants are reported for 4-substituted bicyclo[2.2.2]oct-2-ene-1-carboxylic acids, 4-substituted dibenzobicyclo[2.2.2]octa-2,5-diene-1-carboxylic acids, and cubanedicarboxylic acid in 50% (weight) ethanol-water at 25°. The experimental results indicate that variations in the hybridization of the carbon-carbon bonds between the substituent and the reaction site and a variation in the number of paths between the substituent and the reaction site have a negligible influence on the efficiency of propagation of the polar effect. These observations are compatible with the field effect model and incompatible with the inductive model for the propagation mechanism. The Kirkwood-Westheimer model yields reasonable estimates of the substituent effects. In addition, the origin of the polar effects of the methyl and trifluoromethyl groups are discussed.

Two distinct models, the field effect and the inductive effect, have been considered in recent discussions of the mechanism of propagation of the polar effect.[2-7] In brief, the inductive model presumes that substituent effects are propagated by the successive polarization of the bonds between the substituent and the reaction site. The net polar effect, according to this model, depends on the number and nature of the paths between the substituent and the reaction site. Substituent effects are transmitted through both the σ-bond network (σ-inductive effect) and, when present, the π-bond network (π-inductive effect).[3,7] There is no general agreement concerning either the absolute or relative importance of these contributions to the observed polar effect. However, theoretical considerations require that substituent effects be transmitted more effectively through the more polarizable π bonds than through σ bonds. The transmission efficiency is measured empirically by ϵ, the transmission coefficient, and many values have been proposed for this parameter.[3-8] Bowden's suggestions,[4] ϵ (sp^3 carbon) = 0.48, ϵ (sp^2 carbon) = 0.67, ϵ (aryl carbon) = 0.60, reflect the viewpoint that a large value is necessary for the accommodation of the experimental facts[3-5] and that polar effects are propagated more effectively through π bonds.[3-5,7]

The field effect model presumes that the polar effect originates in bond dipole moments and that the effect is propagated according to the classical laws of electrostatics.[3-7] In the Kirkwood-Westheimer formulation of this theory,[9-11] the molecule is treated as a cavity of low dielectric constant submerged in a solvent continuum. Kirkwood and Westheimer suggested that the cavity dielectric constant was about 2.[9,10] In the absence of a method to assess the constant, subsequent workers have used this value for a variety of compounds. This approach is not unreasonable because, as Ehrenson points out, the contribution of the molecular framework to the effective dielectric constant must be relatively insensitive to the character of the chemical bonds within the cavity.[5] Thus, the two limiting models differ with respect to their predictions concerning the influence of changes in the character of the cavity on the efficiency of propagation. We have examined this point to establish whether, or not, one of the models was more satisfactory. The influences of unsaturation and the number of paths between the substituent and the reaction site are treated in this report.

The importance of unsaturation was studied by the investigation of 4-substituted bicyclo[2.2.2]oct-2-ene-1-carboxylic acids and 4-substituted dibenzobicyclo[2.2.2]octa-2,5-diene-1-carboxylic acids. Substituent effects in these two series of acids may be compared directly with the results for the 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids, examined previously,[12-14] because the distance and number of paths between the substituent and the reaction site remain the same. Accordingly, the results for these acids reflect the relative efficiency of unconjugated, unsaturated π bonds compared to saturated linkages for the propagation of the polar effect. In addition, cubane-1-





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(1) Chemistry of the Bicyclo[2.2.2]octanes. V. This research was supported by a grant, GP4398, from the National Science Foundation.

(2) The term, polar effect, is used to characterize the influence of unconjugated, sterically remote substituents on equilibrium or rate processes. This designation permits the use of the terms, inductive effect and field effect, for the description of the transmission mechanism.

(3) M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3539, 3548 (1962).

(4) K. Bowden, *Can. J. Chem.*, 41, 2781 (1963).

(5) S. Ehrenson, *Progr. Phys. Org. Chem.*, 2, 195 (1964).

(6) C. D. Ritchie and W. F. Sager, *ibid.*, 2, 323 (1964).

(7) J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valence Theory," John Wiley and Sons, Ltd., London, 1965, Chapter 16.

(8) J. C. McGowan, *J. Appl. Chem.* (London), 10, 312 (1960).

(9) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, 6, 506 (1938).

(10) F. H. Westheimer and J. G. Kirkwood, *ibid.*, 6, 513 (1938).

(11) C. Tanford, *J. Am. Chem. Soc.*, 79, 5348 (1957).

(12) J. D. Roberts and W. T. Moreland, *ibid.*, 75, 2167 (1953).

(13) H. D. Holtz and L. M. Stock, *ibid.*, 86, 5188 (1964).

(14) C. F. Wilcox and J. S. McIntyre, *J. Org. Chem.*, 30, 777 (1965).

Table I. Thermodynamic Dissociation Constants for Some Rigid Carboxylic Acids in 50% (weight) Ethanol–Water at 25°

	10^6K			
4-Substituent	Octane acids	Octene acids	Dibenzo acids	Cubane acids
H	0.134 ± 0.015	0.286 ± 0.008	1.78 ± 0.06	1.11 ± 0.01
CH_3		0.314 ± 0.007	1.67 ± 0.09	
OCH_3			3.14 ± 0.05	
F			5.52 ± 0.17	
Cl		1.92 ± 0.11	6.15 ± 0.09	
Br			6.12 ± 0.59	
$CO_2C_2H_5$		0.993 ± 0.006		
$CONH_2$		1.09 ± 0.02		
CF_3	0.568 ± 0.005	1.64 ± 0.01		
CN		3.20 ± 0.06		
NO_2			11.5 ± 0.6	
CO_2H	0.787 ± 0.013	2.09 ± 0.08		7.49 ± 0.05
Stat cor	0.398 ± 0.006	1.05 ± 0.04		3.79 ± 0.03
CO_2^-	0.0337 ± 0.0003	0.097 ± 0.0015		0.298 ± 0.002
Stat cor	0.0674 ± 0.0006	0.194 ± 0.003		0.596 ± 0.004
$N(CH_3)_3^+Cl^-$		14.6 ± 0.4		

Table II. Log (K/K_H) for 4-Substituted Bicyclic Carboxylic Acids in 50% (weight) Ethanol–Water at 25°

	Log (K/K_H)		
4-Substituent	Octane acids[a]	Octene acids[b]	Dibenzo acids[b]
H	0.000	0.000	0.000
CH_3	−0.013 ± 0.032	+0.041 ± 0.015	−0.027 ± 0.039
C_2H_5	−0.020 ± 0.030		
CH_2OH	0.074 ± 0.031		
$CO_2C_2H_5$	0.473 ± 0.035	0.541 ± 0.012	
F			0.491 ± 0.029
Cl	0.739 ± 0.039	0.827 ± 0.028	0.539 ± 0.021
Br	0.736 ± 0.032		0.537 ± 0.054
OH	0.370 ± 0.044		
OCH_3	0.472 ± 0.032		0.246 ± 0.011
CF_3	0.627 ± 0.029[b]	0.758 ± 0.012	
$CONH_2$		0.581 ± 0.015	
CN	0.93[c,d]	1.049 ± 0.015	
NO_2	1.058 ± 0.032		0.810 ± 0.036
CO_2H	0.468 ± 0.030[b,e]	0.565 ± 0.021[e]	
CO_2^-	−0.298 ± 0.026[b,e]	−0.169 ± 0.014[e]	
$N(CH_3)_3^+$	1.50[d,f]	1.707 ± 0.017	

[a] Reference 13. [b] This study. [c] Reference 12. [d] The value reported for 50% (volume) ethanol–water has been extrapolated to 50% (weight) ethanol–water. [e] Statistically corrected. [f] Reference 14.

carboxylic acid and cubane-1,4-dicarboxylic acid[15] were studied to examine the proposition that additional paths between the substituent and the reaction site enhance polar effects. The results for these acids may be compared with the data for bicyclo[2.2.2]octane-1,4-dicarboxylic acid because the C_1C_4 distance differs by only 0.1 A.

Results

The thermodynamic dissociation constants of recrystallized and sublimed samples of the acids[16] were determined by the differential potentiometric method[17] or by potentiometric titration.[18] Independently prepared solutions, different batches of solvent, and different electrodes were used in this work. In addition, the dissociation constant of benzoic acid was frequently determined to ensure the reliability of the data. The pK for benzoic acid measured in this study, 5.74 ± 0.01, is in good agreement with previous determinations, 5.76 ± 0.02[19] and 5.74 ± 0.01.[13] The measured constant of bicyclo[2.2.2]octane-1-carboxylic acid was also in excellent agreement with the earlier result.[13] The results are summarized in Table I. For convenience, the bicyclo[2.2.2]octane-1-carboxylic acids are referred to as the octane acids, the bicyclo[2.2.2]oct-2-ene-1-carboxylic acids as the octene acids, and the dibenzobicyclo[2.2.2]octa-2,5-diene-1-carboxylic acids as the dibenzo acids in Table I and in the subsequent discussion.

Discussion

The dissociation constants for the octane, octene, and dibenzo acids are summarized in Table II.

The results for the three series of acids are correlated by the σ_I constants based on chemical reactivity.[20,21]

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(15) P. E. Eaton and T. W. Cole, *J. Am. Chem. Soc.*, **86**, 962, 3157 (1964). The cubane acids were generously supplied by Professor P. E. Eaton and Dr. Cole.

(16) The methods used for the preparation of the 4-substituted bicyclo[2.2.2]oct-2-ene-1-carboxylic acids are described by F. W. Baker and L. M. Stock, *J. Org. Chem.*, in press. The 4-substituted dibenzobicyclo[2.2.2]octa-2,5-diene-1-carboxylic acids were prepared as described in the Experimental Section.

(17) A. L. Bacarella, E. Grunwald, H. P. Marshall, and E. L. Purlee, *J. Org. Chem.*, **20**, 747 (1955).

(18) J. C. Speakman, *J. Chem. Soc.*, 855 (1940).

(19) E. Grunwald and B. J. Berkowitz, *J. Am. Chem. Soc.*, **73**, 4939 (1951).

(20) (a) R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13; (b) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960); (c) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709, 3146 (1963).

(21) M. Charton, *J. Org. Chem.*, **29**, 1222 (1964).

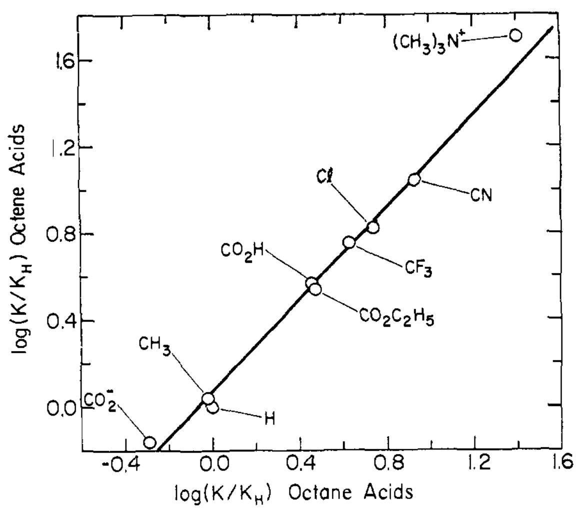

Figure 1. Relationship between log (K/K_H) for octene acids and octane acids.

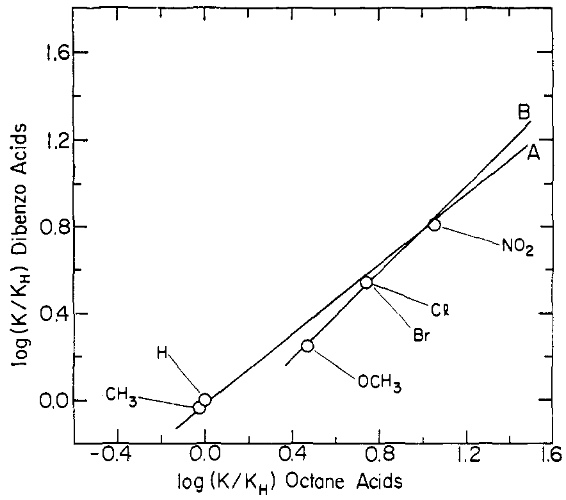

Figure 2. Relationship between log (K/K_H) for dibenzo acids and octane acids.

The correlation equations

$$\log K(\text{octane acids}) = 1.63\sigma_I - 6.88 \qquad (1)$$

$$\log K(\text{octene acids}) = 1.75\sigma_I - 6.49 \qquad (2)$$

$$\log K(\text{dibenzo acids}) = 1.15\sigma_I - 5.75 \qquad (3)$$

are based on least-squares analysis of the available data.[22] The correlations for the octane and octene acids are excellent as judged by Jaffé's criteria[23] confirming the reliability of σ_I as a measure of the polar effect.[24] The results for the dibenzo acids are not correlated with the same precision.[23] The character of these relationships is illustrated in Figures 1 and 2.

The reaction constants for the bicyclic acids may, as noted in the introductory section, be directly compared (without corrections for changes in the distance or the number of paths between the substituent and the reaction site) to assess the influence of unsaturation on the propagation efficiency. The reaction constants (eq 1 and 2) and the slope of the correlation line for the octene acids, Figure 1, each suggest that substituent effects are propagated slightly more effectively (about 1.07-fold) through the octene nucleus. Analysis of the results for the dibenzo series is not so straightforward. The reaction constants (eq 1 and 3) and the conventional least-squares line, A in Figure 2, each suggest that substituent effects are propagated somewhat less effectively (about 0.75-fold) through the dibenzo skeleton. However, these relationships are imprecise and the results may be analyzed in another way. Line B, Figure 2, precisely accommodates the data for the substituents other than the hydrogen atom and the methyl group. The slope of this line is near unity suggesting that substituent effects are propagated with equal efficiency through the dibenzo and octane structures. The fact that hydrogen and alkyl substituents often deviate from linear free energy relationships[6,27] leads us to believe that line B offers a more meaningful estimate of the transmission efficiency. In summary, the experimental results establish that these acids have very similar susceptibilities to polar effects. In closely related work, Grob and his students contrasted the influence of 3-substituents on the dissociation constants of quinuclidine and dehydroquinuclidine.[28] They conclude that resonance contributions alter substituent effects but that very similar reaction constants are applicable for both amines. The observations for the set of bicyclic molecules reveal that isolated π bonds and benzene nuclei have a quite negligible influence on the propagation efficiency of the structure. The data are only compatible with propagation models that do not require an important dependence on bond hybridization. Inductive models of this kind have been suggested.[8] However, strong arguments may be advanced for the greater inductive propagation efficiency of π bonds.[3,5,7] In this sense, the inductive model predicts that the transmission efficiency of the bicyclic compounds should differ. The ϵ values summarized by Bowden[4] are based on this idea. These parameters indicate that ρ should be 1.3- and 1.4-fold greater for the octene and dibenzo acids than ρ for the octane acids and that ρ for dehydroquinuclidine should be twofold greater than ρ for quinuclidine.[29] The observed results are in serious conflict with models of this kind. On the other hand, the field effect model, as noted in the introductory section, does not assign an important role to modest changes in the character of the cavity. The results are, of course, compatible with the model in this form.[30]

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(22) The statistical parameters are $r = 0.994$, $s = 0.030$, $n = 17$ for the octane acids, $r = 0.995$, $s = 0.035$, $n = 10$ for the octene acids, and $r = 0.986$, $s = 0.267$, $n = 7$ for the dibenzo acids.

(23) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(24) The σ_m, Figure 5, and F parameters[3,25] also accommodate the data but significantly less precisely than σ_I. The discrepancies reflect small resonance contributions in σ_m that are retained in F.[3,4,13,26]

(25) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(26) (a) M. J. S. Dewar, "Symposium on Linear Free Energy Relationships," Army Research Office, Durham, N. C., 1964, p 1; (b) M. J. S. Dewar and A. P. Marchand, *J. Am. Chem. Soc.*, **88**, 3318 (1966).

(27) R. W. Taft and I. C. Lewis, unpublished survey cited in ref 20c.

(28) (a) C. A. Grob, A. Kaiser, and E. Renk, *Chem. Ind.* (London), 598 (1957); (b) J. Zergenyi, Inauguraldissertation, Universität Basel, 1963.

(29) These ratios were estimated from the relative values of $\Pi\epsilon_i$ summed over all paths.[4]

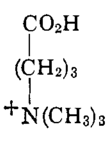
(30) The notion that the cavity has the character of a hydrocarbon is probably incorrect. The cavity contains two quite polar groups and a large free volume in addition to the structural framework of the molecule. Accordingly, the dielectric constant of 2 that is usually assumed is apparently a workable compromise. The introduction of more polarizable matter, such as π electrons, should increase the dielectric constant and decrease the propagation efficiency to a small extent.

The dibasic acids of cubane, bicyclo[2.2.2]octane, and bicyclo[2.2.2]oct-2-ene were examined to assess the influence of the number of paths on the propagation efficiency. These acids provide an excellent test of this point since the C_1C_4 distance is sensibly constant (± 0.01 A) but there are six three-bond paths in cubane compared to three three-bond paths in the bicyclic acids. The observations discussed in the previous paragraph indicate that the differences in hybridization of the intervening carbon–carbon bonds that do exist in these acids are not an important factor. The inductive model predicts that the statistically corrected ratio of the first and second dissociation constants, log $(K_1/4K_2)$, should be twofold greater for cubane than for the bicyclic acids. On the other hand, the field model implies that no differences should be observed. The results, Table III, are within ± 0.05 pK unit.[31] The propagation efficiency is apparently independent of the number of paths available for its transmission.

Table III. Log $(K_1/4K_2)$ for Some Dibasic Acids in 50% (weight) Aqueous Ethanol at 25°

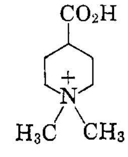
Diacid	Log $(K_1/4K_2)$
Adipic	0.628
1,4-Bicyclo[2.2.2]octane	0.767
1,4-Bicyclo[2.2.2]octene	0.742
1,4-Cubane	0.798

The results of a related investigation led Grob and his associates to conclude that the distance, R, between the reaction site and the substituent, had a greater influence on the propagation efficiency than did the number of bonds between them.[32] This conclusion was based, in part, on the greater acidity of III compared to I and II.

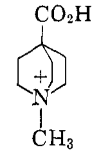


$CO_2H-(CH_2)_3-\overset{+}{N}(CH_3)_3$

I



II



III

In these acids, the number of bonds between the charged nitrogen atom and the carboxyl group remains constant, but R decreases significantly from I to III. Grob pointed out that these results offered evidence for the importance of the field effect. A possible objection to this conclusion that the number of paths for the propagation of the inductive effect also increases from I to III may now be dismissed on the basis of the results for the dibasic acids.

The Kirkwood–Westheimer theory for the polar effect[9,10] has certain well-known practical and theoretical limitations.[9–11,33] Several practical problems may be eliminated when the theory is applied to compounds of rigid structure. The success achieved in the calculation of polar substituent effects in the octane series[13] prompted this further examination of the model. Kirkwood and Westheimer found that very reasonable values of R, the distance between the removable protons, could be calculated for nonrigid dibasic acids from

$$\log (K_1/4K_2) = e^2/2.3kTD_ER \qquad (4)$$

where e is the unit electron charge, k is the Boltzmann constant, T is the absolute temperature, D_E is the effective dielectric constant assessed theoretically, and log $(K_1/4K_2)$ is the statistically corrected ratio of the first and second dissociation constants.[9] Inasmuch as the uncertainty in R is small for the rigid acids examined in this work,[34,35] we calculated log $(K_1/4K_2)$. The spherical cavity model with the volume defined according to Tanford's suggestions was used.[11,36] The calculated values, Table IV, are in good agreement with the experimental results.

Table IV. Calculated and Experimental Log $(K_1/4K_2)$ for Some Dibasic Acids in 50% (weight) Aqueous Ethanol at 25°

1,4-Diacid	R, A	D_E	Log $(K_1/4K_2)$ Calcd	Log $(K_1/4K_2)$ Obsd
Bicyclo[2.2.2]octane	8.57[a]	39.8	0.715	0.768
Bicyclo[2.2.2]octene	8.63[b]	40.0	0.706	0.742
Cubane	8.67[c]	40.1	0.701	0.798

[a] The C_1C_4 distance is 2.59 A, ref 13. [b] The C_1C_4 distance is 2.69 A; see Experimental Section. [c] The C_1C_4 distance is 2.69 A, ref 35.

Dipole substituent effects were calculated from

$$\log (K_X/K_H) = \frac{e}{2.3kT}\left[\left(\frac{\mu \cos \theta}{R^2 D_E}\right)_X - \left(\frac{\mu \cos \theta}{R^2 D_E}\right)_H\right] \qquad (5)$$

where μ is the group or bond moment of the substituent, R is the distance between the midpoint of the dipole vector and the removable proton, and θ is the angle between the dipole vector and the line of length R joining the dipole moment and the reaction site pole and where K_X and K_H are the dissociation constants for the substituted and unsubstituted acids, respectively. The merits of this approach were discussed previously.[13] The values of R and θ used in the calculations are based on the structures for bicyclo[2.2.2]oct-2-ene and dibenzobicyclo[2.2.2]octa-2,5-diene described in the Experimental Section. Two cavity models were examined; an ellipsoid with the volume estimated by Traube's rules[9,10,37] and a sphere with the volume de-

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[31] Although log $(K_1/4K_2)$ is insensitive to the change in structure, the absolute values of the dissociation constants are not. The constants of the monobasic or dibasic cubane acids, Table I, are each about an order of magnitude greater than those of the corresponding bicyclo[2.2.2]octane derivatives. Bicyclo[2.2.2]octane-1-carboxylic acid and pivalic acid, $K = 0.15 \times 10^{-6}$, have similar constants. The enhanced acidity of the cubane acids may be related to the increased s character of the external bond, $J_{C^{13}H}$ is 160 ± 5 cps implying 32% s character,[15] as discussed by J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5030 (1951), and K. B. Wiberg and B. R. Lowry, *ibid.*, **85**, 3188 (1963). This argument holds that the increased s character reflects an increased electronegativity in the exocyclic bonding orbital with an attendant increase in acid strength.

[32] C. A. Grob, E. Renk, and A. Kaiser, *Chem. Ind.* (London), 1222 (1955).

[33] (a) F. H. Westheimer, W. A. Jones, and R. A. Lad, *J. Chem. Phys.*, 10, 478 (1942); (b) F. H. Westheimer and J. G. Kirkwood, *Trans. Faraday Soc.*, **43**, 77 (1947).

[34] The structure of bicyclo[2.2.2]octane has been discussed.[13] The structure of cubane is known.[35] The structure of bicyclo[2.2.2]oct-2-ene is discussed in the Experimental Section.

[35] E. B. Fleischer, *J. Am. Chem. Soc.*, **86**, 3889 (1964).

[36] Tanford proposed that discrete charges be placed 1.0 A below the cavity surface and that the midpoint of a dipole be located 1.5 A below the cavity surface.[11] These suggestions were followed in all calculations involving spherical models.

[37] J. Traube, *Ann.*, **290**, 43 (1896).

fined according to Tanford's suggestion.[11,36] The results for these two models are summarized in Table V. Log (K/K_H) was also calculated for the monobasic acids with charged groups. Equation 4 was used for the trimethylammonium substituent and expressions 4 and 5 were combined to assess the influence of the dipole and charge of the carboxylate group as discussed by Wilcox and McIntyre.[14]

Table V. Calculated and Experimental Values of Log (K_X/K_H) for Monobasic Carboxylic Acids in 50% (weight) Ethanol–Water at 25°

	Ellipsoid model Traube vol.		Spherical model Tanford vol.		Exptl
Group	D_E	Log (K/K_H)	D_E	Log (K/K_H)	Log (K/K_H)
4-Substituted Bicyclo[2.2.2]oct-2-ene-1-carboxylic Acids					
H	7.10	0.00[a,b]	4.42	0.00[a,c]	0.00
CH_3	11.1	−0.04	4.99	−0.04	+0.041
$CO_2C_2H_5$	10.5	0.07	5.16	0.18	0.54
CF_3	9.48	0.19	5.02	0.37	0.76
Cl	7.75	0.31	4.57	0.53	0.83
CN	14.0	0.19	5.16	0.60	1.05
$N(CH_3)_3^+$			20.85	1.52	1.71
CO_2^-			...[d]	−0.44	−0.17
4-Substituted Bicyclo[2.2.2]octane-1-carboxylic Acids					
H			4.38	0.00[a,e]	0.00
$N(CH_3)_3^+$			20.62	1.55	1.50
CO_2^-			...[d]	−0.44	−0.30
4-Substituted Cubane-1-carboxylic Acids					
H			4.42	0.00[a,f]	0.00
CO_2^-			...[d]	−0.43	−0.27
4-Substituted Dibenzobicyclo[2.2.2]octa-2,5-diene-1-carboxylic Acid					
H	4.8	0.00[a,g]	4.3	0.00[a,h]	0.00
CH_3	7.2	−0.06	4.8	−0.05	−0.02
OCH_3	5.4	0.12	4.5	0.15	0.25
F	4.7	0.56	4.4	0.58	0.49
Cl	5.2	0.47	4.4	0.56	0.54
Br	5.2	0.44	4.4	0.53	0.54
NO_2	5.2	0.82	4.5	0.95	0.81

[a] The second term of eq 5 measures the acidity of the 4-hydrogen derivative relative to a hypothetical acid of the same size and shape but without a dipolar group.[13] The values of log (K_H/K_i) are presented in the footnotes. [b] Log (K_H/K_i) = 0.07. [c] Log (K_H/K_i) = 0.12. [d] A single value of D_E cannot be defined, eq 6. [e] Log (K_H/K_i) = 0.12. [f] Log (K_H/K_i) = 0.12. [g] Log (K_H/K_i) = 0.11. [h] Log (K_H/K_i) = 0.13.

The calculated results for the dipolar-substituted octenes exactly parallel those found for the octane acids.[13] In each series, the ellipsoid cavity model with a Traube volume fails seriously. The spherical cavity model with a Tanford volume yields log (K/K_H) values that reproduce the order of acid strength but with a rather large discrepancy between theory and experiment. However, when a reference substituent other than hydrogen is selected, the agreement between theory and experiment is far more satisfactory, Table VI.

The disparity in the calculations of log (K/K_H) and log (K/K_{Cl}) for the octane[13] and octene acids originates in the nonlinear relationship between $\mu \cos \theta/R^2$ and the observed pK, Figure 3. In each series, the hydrogen and alkyl groups deviate significantly from a line that accommodates the data for the other substituents. The effective dielectric constant defined by the slope is 4.3 for the octene acids in good accord with the values calculated for the Tanford model, Table V.

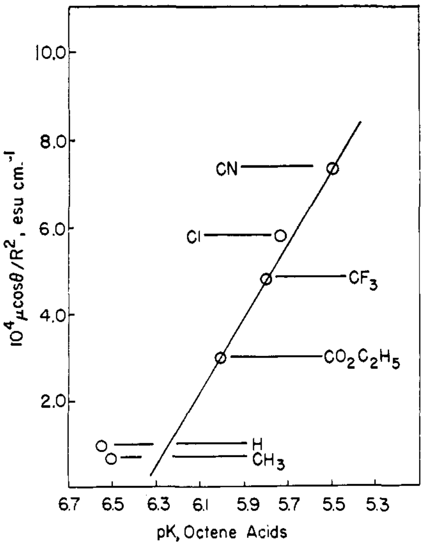

Figure 3. Relationship between $\mu \cos \theta/R^2$ and the observed pK for the octene acids.

In contrast to the results for the octane and octene acids, both cavity models predict similar and reasonable log (K/K_H) values for the dibenzo acids, Table V. The calculation is successful because the relationship between $\mu \cos \theta/R^2$ and the observed pK is virtually linear, Figure 4, with a slope equivalent to an effective dielectric constant of 4.6 in satisfactory agreement with the theoretical values, Table V.

Table VI. Calculated and Experimental Log (K/K_{Cl}) for Bicyclic Acids in 50% (weight) Ethanol–Water at 25°

	Log (K/K_{Cl})			
	Calcd[a]		Exptl	
Substituent	Octane acids[b]	Octene acids	Octane acids[b]	Octene acids
Cl	0.00	0.00	0.00	0.00
NO_2	0.35		0.31	
Br	−0.05		−0.01	
OCH_3	−0.30		−0.27	
OH	−0.34		−0.37	
CN	+0.05	+0.08	+0.19	+0.23
$CO_2C_2H_5$	−0.36	−0.35	−0.27	−0.28
CF_3	−0.14	−0.15	−0.12	−0.07
CH_3	−0.58	−0.57	−0.76	−0.78
H	−0.53	−0.53	−0.74	−0.82
$N(CH_3)_3^+$	1.02	0.99	0.76	0.88
CO_2^-	−0.96	−0.96	−1.04	−1.00

[a] Spherical model, Tanford volume. [b] Reference 13.

Only rather speculative interpretations can be advanced for the curious differences in the relationships between pK and $\mu \cos \theta/R^2$. An attractive explanation centers on the idea that solvent structure in the vicinity of the substrate, and hence the dielectric environment, depends on the substrate structure and on the nature of the substituent groups. According to this view, the solvent structure about the lyophobic hydrogen and alkyl groups differs from that about the other, more polar groups in the octane and octene series.[13] The similar behavior observed for these acids is not unexpected in view of the close structural relationship. The fact that a near-linear relationship is found for the dibenzo acids may also be rationalized on this basis.

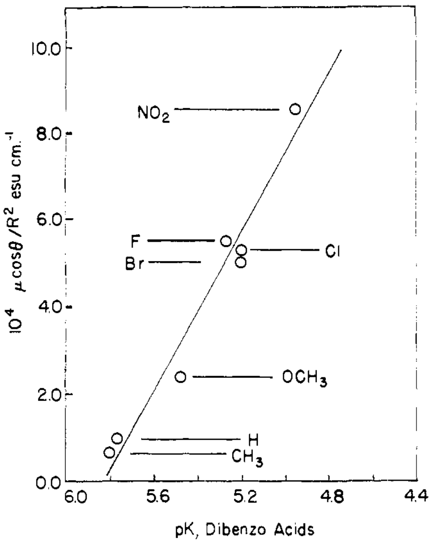

Figure 4. Relationship between μ cos θ/R^2 and the observed pK for dibenzo acids.

Presumably, the benzene nuclei have a major influence on the structure of the surrounding solvent because of their size and hydrogen bonding capacity. In this situation, it is not unlikely that the variations in the properties of the smaller, somewhat screened substituents have a less pronounced effect on the dielectric environment.

In summary, the results reveal that internal cavity perturbations such as the π bond in the bicyclo[2.2.2]-octene nucleus, the fused aryl rings in the dibenzo acids, and the highly strained bonds of the cubane structure have a negligible effect on the propagation of the polar effect. The three additional paths for the transmission of the polar effect in cubane diacid do not increase the influence of a polar substituent. Moreover, the polar effect exhibits an angular dependence.[38] These results are fully consistent with an electrostatic model for the polar effect and are extremely difficult to reconcile with an inductive model. The Kirkwood–Westheimer theory provides reasonable quantitative results for the dibasic acids and for the polar-substituted monobasic acids. There are some doubts concerning the way in which hydrogen and alkyl groups should be treated. Nevertheless, we believe that the merits of their theory have been seriously underestimated.

Polar Effect of the Methyl and Trifluoromethyl Group. Roberts and his associates proposed that the apparently enhanced electron-withdrawing effect of the p-CF_3 group compared to the m-CF_3 group had its origin in carbon–fluorine hyperconjugation.[39–41] Dewar and Exner point out that polar effects are generally propagated more efficiently from the *para* position than from the *meta* position with $\sigma_{p\text{-X}}/\sigma_{m\text{-X}} = 1.2$.[42,43] This ratio is 1.26 ± 0.01 for the trifluoromethyl derivatives of the benzoic acids, anilines, and dimethylanilines.[41] These data support the view that there is nothing unusual about the polar contribution of the trifluoromethyl group. However, a detailed examination of the results of reaction chemistry and F^{19} chemical shifts led Sheppard to suggest that the p electrons on fluorine may interact with the aromatic π system to return significant electron density to the ring-reducing and the electron-withdrawing influence of the group.[41] The data require that this backbonding effect be more important at the *meta* position than at the *para* position.[41]

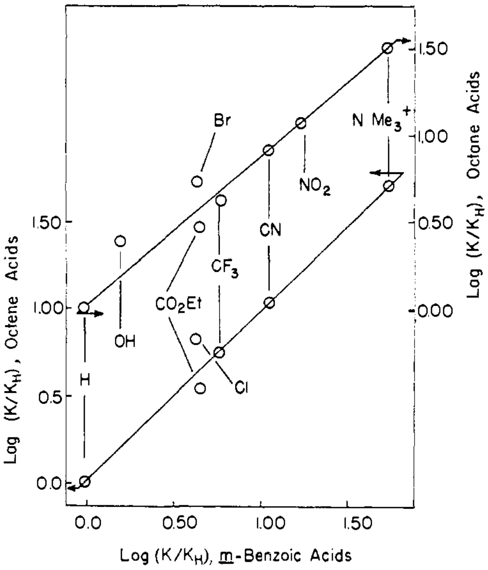

Figure 5. Relationship between log (K/K_H) for the octene (lower line) and octane (upper line) acids and log (K/K_H) for m-benzoic acids under similar conditions.

The dissociation constants of the trifluoromethyl derivatives in the octane and octene acids provide a new basis for an evaluation of these interpretations. Empirically, log (K/K_H) for the bicyclic acids is related to log (K/K_H) for the *meta*-substituted benzoic acids, Figure 5. Substituents capable of acid-weakening donor resonance, *e.g.*, hydroxyl and halogen, exhibit significant positive deviations from the lines defined by the groups incapable of important resonance. Any important acid-weakening p–π backbonding for the trifluoromethyl group would provide a positive deviation. In fact, log (K_{CF_3}/K_H) for the bicyclic acids precisely obeys the correlation. The results indicate that backbonding of the kind suggested by Sheppard does not contribute to the polar influence of this substituent in reaction chemistry. The concept that polar influences are propagated somewhat more effectively from the *para* position relative to the *meta* position offers the most attractive explanation for the results.[44]

The methyl substituent is an electron donor relative to hydrogen when bonded to sp or sp^2 carbon atoms. The finding that a methyl group retards the addition of benzenesulfenyl chloride to cyclohexene and norbornene[45a,b] and slows the solvolysis of bromoadaman-

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[38] (a) P. R. Wells and W. Adcock, *Australian J. Chem.*, **18**, 1365 (1965); (b) R. Golden and L. M. Stock, *J. Am. Chem. Soc.*, **88**, 5928 (1966).

[39] W. F. Hamner and F. A. Matsen, *ibid.*, 70, 2482 (1948).

[40] J. D. Roberts, R. L. Webb, and E. L. McElhill, *ibid.*, 72, 408 (1950).

[41] The pK values for trifluoromethyl derivatives of benzoic acid, aniline, and dimethylaniline were recently redetermined. The new data reveal that log $(K_{p\text{-}CF_3}/K_{m\text{-}CF_3})$ is somewhat less than originally measured: W. A. Sheppard, *ibid.*, 87, 2410 (1965).

[42] M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962, p 159.

[43] O. Exner, *Tetrahedron Letters*, 815 (1963).

[44] M. J. S. Dewar and A. P. Marchand, *J. Am. Chem. Soc.*, **88**, 354 (1966).

[45] (a) H. Kwart and L. J. Miller, *ibid.*, **83**, 4552 (1961); (b) H. Kwart and T. Takeshita, *ibid.*, **86**, 1161 (1964); (c) R. C. Fort and P. von R. Schleyer, *ibid.*, **86**, 4194 (1964).

tane[45c] prompted the suggestions that the polar effect of the methyl group depends on the hybridization of the carbon atom to which it is bonded[45c] and that the methyl group is electron withdrawing when bonded to sp^3 carbon atoms.[45a,b] A recent investigation of the influence of isotopic substitution on the dipole moments of methylacetylene and propane supports the view that the methyl group is slightly electron withdrawing when bonded to sp^3 carbon.[46] These observations are compatible with the suggestion that bonds between carbon atoms of different hybridization are polar.[47] This argument infers that the polar contribution of the methyl group in saturated molecules reflects the moments associated with the H–C$_{sp^3}$ and C$_{sp^3}$–C$_{sp^x}$ bonds (μ_1 and μ_2) of the methyl derivative and the H–C$_{sp^x}$ bond moment (μ_3) of the parent compound. When the methyl group is bonded to an sp^3 carbon atom, μ_2 is near zero and μ_1 is equal to μ_3. Replacement of the hydrogen atom by a methyl group, in this

$$\mathrm{H}\overset{\mu_1}{\text{——}}\mathrm{C}_{sp^3}\overset{\mu_2}{\text{——}}\mathrm{C}_{sp^x}\sim\sim\mathrm{CO_2H} \qquad \mathrm{H}\overset{\mu_3}{\text{——}}\mathrm{C}_{sp^x}\sim\sim\mathrm{CO_2H}$$

case, only lengthens the distance between the dipole (μ_1 = μ_3) and the reaction site. The influence of the methyl group would be electron donation if hydrogen were the negative terminus of the C$_{sp^3}$–H moment and electron withdrawal if carbon were the negative terminus. The direction of this bond moment is not known with certainty.[48] The observations for the acids of rigid structure, Table II, indicate that the polar influence of the methyl group is small when bonded to an sp^3 carbon atom. The reaction constants (eq 1-3) and log ($K_{\mathrm{Me}}/K_{\mathrm{H}}$) define apparent $\sigma_{\mathrm{I}}^{\mathrm{Me}}$ values of -0.008 for the octane series and -0.02 for the dibenzo series. In contrast, $\sigma_{\mathrm{I}}^{\mathrm{Me}}$ is $+0.02$ for the octene series and $+0.01$ for *cis*-3- and *trans*-4-methylcyclohexane-1-carboxylic acid.[49] The dependence on hybridization may be inferred from the large decrease in the substituent effect in these molecules compared to, for example, its influence on the acidity of benzoic acid, $\sigma_{m\text{-Me}} = -0.07$. The data for these acids indicate that the polar contribution of the methyl group bonded to sp^3 carbon is very small. Moreover, significant variations in the sign of the contribution are discernible even though the bridgehead carbon atoms are near sp^3 hybridization. In view of these results, interpretations based exclusively on small differences in small bond moments seem very insecure. In addition, it is well known that hydrogen and methyl substituents often deviate from linear free energy relationships in the aliphatic series.[27] Accordingly, it seems preferable to recognize the near equivalence of the polar influence of the methyl and hydrogen substituents and to acknowledge that subtle ill-defined interactions may be responsible for alkyl substituent effects.

Experimental Section[50]

Materials. Commercially available anthracene (98%), 9,10-dibromoanthracene, 9-nitroanthracene, and 9-anthraldehyde were used without further purification. 9-Anthroic acid (**1**) was recrystallized from ethanol, anthrone was recrystallized from benzene, and 9-methylanthracene was chromatographed on alumina (hexane) prior to use.

10-Methyl-9-anthroic Acid (2). 9-Methylanthracene was converted to 10-methyl-9-bromoanthracene by the method of Barnett and Matthews.[51] Butyllithium exchange and carbonation[52,53] yielded **2** (yellow, mp 221.5–222.5° after recrystallization from ethanol and sublimation).[54]

10-Methoxy-9-anthroic Acid. Acid **3** was prepared *via* the sequence: anthrone → 9-methoxyanthracene (**3a**) → 9-methoxy-10-bromoanthracene (**3b**) → **3**.

Compound **3a**[55] (2.39 g, 11.5 mmoles) was dissolved in carbon disulfide (30 ml) and cooled to −10°. Bromine (1.8 g, 11.5 mmoles) in carbon disulfide was added dropwise (15 min) with the temperature maintained at about −10°. Volatile materials were removed *in vacuo*. The residue was chromatographed on neutral alumina (benzene). Recrystallization of the principal component yielded **3b** (yellow, mp 150–151° after sublimation, 2.33 g, 70%, unstable in air).

Anal. Calcd for $C_{15}H_{11}OBr$: Br, 27.83. Found: Br, 27.78.

Compound **3b** (6.0 g, 20.8 mmoles) was added to *n*-butyllithium (0.1 mole) in ether (60 ml) at 0°. The solution was warmed to 10° and carbonated.[52,53] Compound **3** (yellow, mp 205–205.5° after recrystallization from ethanol, 3.66 g, 73%) was isolated in the usual way. Recrystallization and sublimation raised the melting point to 212–212.5°. Rigaudy and Nédélec report[56] mp 219–221° for **3** and an analysis was obtained.

Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 76.25; H, 5.02.

Acid **3** was converted to the methyl ester for another comparison. The trifluoroacetic anhydride method[57] yielded methyl 10-methoxy-9-anthroate in 97%. Oxidation of **3** gave anthraquinone in good yield securing the identity of 3.

10-Chloro-9-anthroic Acid (4). 9-Anthroic acid (5.0 g, 27.5 mmoles) was dissolved in warm acetic acid (250 ml). After the solution cooled to ambient temperature, chlorine (22.6 mmoles) in acetic acid (25 ml) was added. Acid **4** (yellow, mp 273–274° after recrystallization from ethanol and sublimation, 4.1 g, 70%) precipitated during the reaction.

10-Bromo-9-anthroic Acid (5). 9,10-Dibromoanthracene was converted to **5** by exchange with phenyllithium and carbonation.[52,53] Acid **5** (yellow, mp 278° after sublimation and recrystallization from ethanol) was obtained in 90% yield.

10-Nitro-9-anthroic Acid (6). 9-Anthroic acid was converted to the methyl ester.[57] Nitration by the procedure of Norman and Ralph[58] yielded anthraquinone as the principal product and only minor amounts of the desired nitro derivative. A more practical method was devised. Methyl 9-anthroate (10.0 g, 42.4 mmoles) was dissolved in acetic acid (500 ml)–acetic anhydride (20 ml). An equimolar amount of nitric acid dissolved in 98% sulfuric acid was added to the solution at room temperature with vigorous stirring. A transient green color appeared as the acid mixture was added. After 2 min, the final orange solution was poured into cold water (1 l.). The yellow solid was collected, dried, and chromatographed on alumina (300 g, benzene). Methyl 10-nitro-9-anthroate (yellow, mp 171.5–172.5° after recrystallization from 5:1 ethanol–benzene, 5.6 g, 50%) eluted first.

The methyl ester was converted to the air-unstable acid **6** (yellow, mp 273–275° after recrystallization from 75% ethanol and sublimation) in 20% yield by the method of Norman and Ralph.[58]

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(46) V. W. Laurie and J. S. Muenter, *J. Am. Chem. Soc.*, **88**, 2883 (1966).

(47) (a) A. D. Walsh, *J. Chem. Soc.*, 398 (1948); (b) A. J. Petro, *J. Am. Chem. Soc.*, 80, 4230 (1958); (c) T. L. Brown, *ibid.*, **81**, 3229, 3232 (1959).

(48) The problem is discussed by D. Steele, *Quart. Rev.* (London), **18**, 21 (1964).

(49) J. F. J. Dippy, S. R. C. Hughes, and J. W. Laxton, *J. Chem. Soc.*, 4102 (1954).

(50) Infrared spectra were recorded on a Beckman IR-7. A grant from the National Science Foundation enabled the acquisition of this instrument. Mr. William Saschek performed the microanalyses. Detailed procedures for the preparation of the anthracene derivatives are presented in the dissertation of R. C. Parish, University of Chicago Library, 1965.

(51) E. de B. Barnett and M. A. Matthews, *Chem. Ber.*, **59**, 1429 (1926).

(52) B. M. Mikhailov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 420 (1948).

(53) B. M. Mikhailov and V. P. Bronovitskaya, *Zh. Obshch. Khim.*, 22, 157 (1952).

(54) Sublimation conditions for the compounds described in this report are 140–180° (1 mm).

(55) E. de B. Barnett, J. W. Cook, and M. A. Matthews, *J. Chem. Soc.*, **123**, 1994 (1923).

(56) J. Rigaudy and L. Nédélec, *Compt. Rend.*, **246**, 619 (1958); *Bull. Soc. Chim. France*, 648 (1959).

(57) R. C. Parish and L. M. Stock, *J. Org. Chem.*, **30**, 927 (1965).

(58) R. O. C. Norman and P. D. Ralph, *J. Chem. Soc.*, 2221 (1961).

Table VII. Conditions and Analytical Results in the Preparation of 4-Methyl- (**8**), 4-Methoxy- (**9**), 4-Chloro- (**10**), and 4-Bromodibenzobicyclo[2.2.2]octa-2,5-diene-1-carboxylic Acid (**11**)

Acid	Conditions Pressure,[a] psi	 Temp, °C	 Time, hr	Yield, %	Mp, °C	Found, % C	 H	 X[b]
8[c,d]	1700	140	28	63	238.5–239	81.89	6.23	
9[d,e]	2500	140	24	46	255–256	77.13	5.83	
10[d,f]	3000	150	72	57	233	71.84	4.35	12.21
11[d,g]	2200	140	72	56	257–258	62.21	4.21	24.29

[a] Maximum attained. [b] Chlorine or bromine. [c] Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. [d] Colorless solid. [e] Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. [f] Calcd for $C_{17}H_{13}O_2Cl$: C, 71.71; H, 4.60; Cl, 12.45. [g] Calcd for $C_{17}H_{13}O_2Br$: C, 62.02; H, 3.98; Br, 24.28.

1-Carboxydibenzobicyclo[2.2.2]octa-2,5-diene (7). Acid **7** and several other bicyclic acids were prepared by the additlon of ethylene to the corresponding anthroic acid. Typically, acid **1** (4.0 g, 18 mmoles) was dissolved in pyridine (100 ml) and 2,5-di-*t*-butylhydroquinone (50 mg) added. Ethylene was added at about 1000 psi and the reaction carried out at 150° for 50 hr (maximum pressure about 3000 psi). The yellow solution which resulted was evaporated at reduced pressure to an orange oil. The oil was dissolved in ethylene glycol (30 ml) containing potassium hydroxide (5 g). This solution was extracted with ether (five 10-ml portions) to remove nonacidic contaminants. The glycol layer was acidified, and the acidic components were extracted into ether. Evaporation of the ether provided a light yellow solid which was dissolved in aqueous base and treated with Norit. The product (**7**) was regenerated by acid. Acid **7** (colorless white needles, mp 250° after recrystallization from ethanol and sublimation) was obtained in 45% yield.

4-Methyl- (**8**), 4-methoxy- (**9**), 4-chloro- (**10**), and 4-bromodibenzobicyclo[2.2.2]octa-2,5-diene-1-carboxylic acid (**11**) were prepared and isolated in the same way. The pertinent observations are summarized in Table VII.

4-Fluorodibenzobicyclo[2.2.2]octa-2,5-diene-1-carboxylic Acid (12). 10-Cyano-9-bromoanthracene[58] (3.1 g, 10.9 mmoles) was refluxed with potassium fluoride (9.6 g, 0.17 mole, anhydrous) in dimethylformamide (150 ml) for 36 hr under nitrogen. The reaction mixture was treated in the usual manner. The residual black oil was chromatographed on alumina (benzene) to yield a slightly impure (analytical data for C and N were low) sample of 9-cyano-10-fluoroanthracene (**12a**), mp 218–219.5°, 10% yield. Impure **12a** (1.0 g) was treated with ethylene (3200 psi) for 98 hr at 150° in toluene (150 ml). The solvent was removed *in vacuo*, and the orange oil obtained was chromatographed on neutral alumina (benzene). Concentration of the principal fractions yielded a semisolid from which 1-cyano-4-fluorodibenzobicyclo[2.2.2]octa-2,5-diene (**12b**) (mp 109–110°, 174 mg) was isolated by vpc.

Anal. Calcd for $C_{17}H_{12}FN$: C, 81.91; H, 4.84. Found: C, 82.28; H, 4.91.

Nitrile **12b** (125 mg, 0.51 mmole) and potassium hydroxide (5.0 g) were refluxed in ethanol (22 ml)–water (3 ml) for 93 hr. Acid **12** (mp 235° after sublimation, 97%) was isolated in the usual way.

Anal. Calcd for $C_{17}H_{13}FO_2$: C, 76.11; H, 4.88. Found: C, 76.24, 76.04; H, 4.96, 4.85.

4-Nitrodibenzobicyclo[2.2.2]octa-2,5-diene-1-carboxylic Acid (13). The air instability of 10-nitro-9-anthroic acid (**6**) necessitated the addition of ethylene to the corresponding methyl ester. Methyl 10-nitro-9-anthroate (3.3 g, 11.8 mmoles) and 4-*t*-butylcatechol (50 mg) were dissolved in toluene (150 ml) and treated with ethylene (1900 psi) for 24 hr at 140°. The reaction mixture was treated in the usual way to yield methyl 4-nitrodibenzobicyclo[2.2.2]octa-2,5-diene-1-carboxylate (colorless, mp 173.5–175°, 21%).

Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89. Found: C, 70.15; H, 4.92.

The ester was saponified with sodium hydroxide in 85% aqueous ethanol at reflux for 18 hr. Acid **13** (mp 255–256° after recrystallization from ethanol and sublimation, 95%) was isolated in the usual way.

Anal. Calcd for $C_{17}H_{13}O_4N$: C, 69.14; H, 4.44; N, 4.74. Found: C, 69.40; H, 4.40; N, 4.82.

Dissociation Constants. The thermodynamic dissociation constants of the monobasic acids (except 4-trimethylammonium bicyclo[2.2.2]oct-2-ene-1-carboxylic acid) were determined by the method developed by Grunwald[17] as outlined previously.[13] The results are summarized in Table I.

The dissociation constants of the dibasic acids and some monobasic acids were determined by potentiometric titration as described by Speakman.[18] A saturated calomel electrode, Beckmann No. 39170, and a glass electrode, Beckmann No. 40485, were used with the conventional precautions. The pH meter was standardized with the acetate buffer described by Bates for ethanol–water.[59,60] The reported dissociation constants are based on 12–14 "pH" observations from 25 to 75% neutralization using Speakman's method of analysis.[18] Activity coefficients were calculated from the Debye–Hückel limiting law as described by Grunwald and Berkowitz.[19] The results are presented in Table I.

Kirkwood–Westheimer Calculations. The calculations for the octene acids are based on a model with an untwisted bridge structure with bond distances of $C(sp^3)–C(sp^3) = 1.54$ A, $C(sp^2)–C(sp^2) = 1.33$ A, $C(sp^3)–C(sp^2) = 1.50$ A and bond angles of angle $C(sp^3)C(sp^3)C(sp^2) = 112°$, $\alpha = 110°$, and $\beta = 7°$. The C_1C_4 distance is 2.69 A; angle $C_1C_2C_3$ = angle $C_2C_3C_4 = 117°$, YH = R and angle $C_4YH = \theta$. The group moment, R, and cos θ are summarized in Table VIII. An internal dielectric constant of 2.0 and a solvent dielectric constant of 49.5 were used in all the calculations.

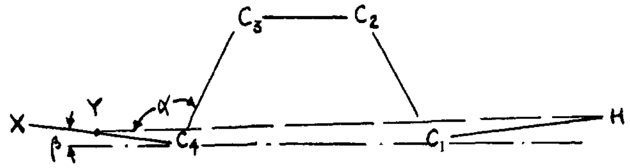

Table VIII. Parameters for Kirkwood–Westheimer Calculations

Group	R, A Octene	 Dibenzo	μ, D.[a]	cos θ, octenes
H	6.20	6.10	0.4	0.986
CH_3	7.37	7.28	0.4	0.990
OCH_3	...	6.64	1.1	...
F	...	6.21	2.4	...
Cl	6.52	6.42	2.5	0.987
Br	...	6.51	2.4	...
CN	7.71	...	4.4	0.991
CF_3	7.43	...	2.7	0.990
$CO_2C_2H_5$	7.71	...	1.8	0.991
NO_2	...	6.55	4.1	...

[a] Vector component projected on C_4–X bond.

The calculation of log (K/K_H) for the dipolar groups was accomplished in the normal way with the volume of the ellipsoidal cavity defined by Traube's rules.[37] Tanford's suggestions[11,36] were followed in the calculations for the spherical models with the center of the sphere taken as the midpoint of R. For the trimethylammonium group, the charge was located on the nitrogen atom with the substituent methyl groups at the periphery. The positive pole is 2.10 A below the surface of the sphere in this approximation. The radius of the sphere is $(1.0 + 2.1 + R)/2$ with its center on R.[11,36] D_E was assessed from eq 9 of ref 9. For the carboxylate

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(59) R. G. Bates, "Determination of pH," John Wiley and Sons, Inc., New York, N. Y., 1964.

(60) R. G. Bates, M. Paabo, and R. A. Robinson, *J. Phys. Chem.*, **67**, 1833 (1963).

$$\log (K_{CO_2^-}/K_i) = \frac{e\mu \cos \theta}{2.3kTR^2D_E} + \frac{e^2}{2.3kTRD_E} \quad (6)$$

group, the calculation is based on eq 6 as outlined by Wilcox and McIntyre[14] with $\mu = 3.50$.

Tanner and Gilman report the dipole moment of dibenzobicyclo[2.2.2]octa-2,5-diene is 0.81 D. and propose that the angle between the planes of the aromatic nuclei is about 110–120° to account for the dipole moment on the basis of two *o*-xylene units.[61] The C_1C_4 distance for this structure is 2.4 A, with the carbon atoms of the ethano bridge separated by 1.5 A. Further, the $H_1C_1C_4H_4$ nuclei are nearly colinear. The only deviation from normal bond angles is the $C_1C_2C_3$ angle of 110°. This structure requiring small angle deformation was adopted for the calculations. The values of *R* and the bond moments are presented in Table VIII. The results of the calculation are summarized in Table V.

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[61] D. D. Tanner and T. S. Gilman, *J. Am. Chem. Soc.*, **85**, 2982 (1963).

Chlorination and Bromination of Isobutyl and *t*-Butyl Chlorides and Bromides[1]

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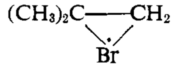
Abstract: Photochlorination of *t*-butyl bromide at room temperature gives only 1-bromo-2-chloro-2-methylpropane probably through a bridged-bromine radical. Chlorination of isobutyl bromide gives 1-bromo-2-chloro-, 1-bromo-3-chloro-, and 1-chloro-2-bromo-2-methylpropane. Photobromination of *t*-butyl chloride at room temperature yields a single organic product, 1,2-dibromo-2-methylpropane; isobutyl chloride under the same conditions gives exclusively 1-chloro-2-bromo-2-methylpropane. Mechanisms of the reactions are discussed.

Neighboring group participation has been proposed in the halogenation of some alkyl halides. When *t*-butyl bromide is chlorinated with *t*-butyl hypochlorite at −78° a 92% yield of 1-bromo-2-chloro-2-methylpropane[3] is obtained; this product could come from an intermediate having a bridged bromine atom. Thaler[4] found that bromocyclohexane and bromocyclopentane gave on photobromination at 60° predominantly the *trans*-1,2-dibromo derivatives, probably *via* a bridged intermediate. Skell[5] found that the bromination (photochemical or with *t*-butyl hypobromite) of (+)-1-bromo-2-methylbutane at 25° gave (−)-1,2-dibromo-2-methylbutane of high optical purity. When (+)-1-chloro-2-methylbutane is photobrominated, (−)-1-chloro-2-bromo-2-methylbutane is the sole dihalide (about 97%). However, reaction of *t*-butyl hypochlorite or chlorine with (+)-1-bromo-2-methylbutane is said to give only inactive products. Conversely Haag and Heiba[6] have shown that photobromination of (+)-1-cyano-2-methylbutane gives (+)-1-cyano-2-bromo-2-methylbutane. Further, when *t*-butyl bromide reacts with *t*-butyl hypochlorite at −78° bromine atoms can be trapped with allene, indicating that elimination of bromine atoms occurs to some extent.[7]

We here report two examples of halogenation reactions that appear to proceed by way of a bridged-bromine radical: the photochlorination of isobutyl bromide and of *t*-butyl bromide with elemental chlorine.

t-Butyl bromide was photochlorinated at 24° in carbon tetrachloride at an initial concentration of 0.3 g/ml with sufficient chlorine to react with 30% of the *t*-butyl bromide. Only one product was shown by gas chromatographic analysis of the reaction mixture; this component was identified as 1-bromo-2-chloro-2-methylpropane. The production of this compound is explained most easily by assuming the formation of an intermediate bridged radical



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This would open preferentially at the tertiary position when attacked by a chlorine atom because of the electron-releasing ability of the methyl groups. Although the $(CH_3)_2CBrCH_2\cdot$ radical could eliminate a bromine atom and form isobutylene, the latter would probably add a molecule of chlorine very quickly. Since no dichloro isomer was obtained, it seems unlikely that the elimination and addition mechanism[7] was operative.

It is interesting to note that Skell[3] found only one product, 1-bromo-2-chloro-2-methylpropane, in the reaction of *t*-butyl hypochlorite with *t*-butyl bromide at −78°. When the reaction was carried out in carbon disulfide solution, Haag and Heiba[7] found both 1-bromo-2-chloro-2-methylpropane and 1-chloro-2-bromo-2-methylpropane; the concentration of the latter compound increased with the proportion of *t*-butyl hypochlorite used.

When isobutyl bromide was subjected to photochlorination at 24° in carbon tetrachloride three products were obtained: 1-bromo-2-chloro-2-methylpropane, 59%; 1-bromo-3-chloro-2-methylpropane, 33%; and 1-chloro-2-bromo-2-methylpropane, 8%. The 1-bromo-3-chloro-2-methylpropane comes from reaction

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