Our data for the acid-catalyzed equilibration of the $\Delta^{1,9}$- and $\Delta^{9,10}$- octalin mixture suggests that the apparent enrichment in the latter is more likely the result of removal of the former by polymerization side-reactions. Thus, while the ratio of $\Delta^{9,10}$-isomer to $\Delta^{1,9}$-isomer increases with time of exposure to phosphoric acid, the undistillable residue shows a corresponding increase (see Experimental).

This explanation is supported by the composition of the equilibrated system when a carbanion catalyst[3] is used. In contrast to strong protic acid catalysts, such carbanion catalysts cannot effect polymerization. A mixture composed of 72% $\Delta^{9,10}$-octalin, 26% $\Delta^{1,9}$-octalin and 2% *trans*-decalin after 42, 48, and 65 hours at reflux over a "benzylsodium" catalyst[3] had the constant composition 70% $\Delta^{9,10}$-, 20% $\Delta^{1,9}$-, 4% *trans*-$\Delta^{1,2}$-, 4% *trans*-$\Delta^{2,3}$-, and 2% *trans*-decalin. Thus the equilibrium ratio of $\Delta^{9,10}$- to $\Delta^{1,9}$-octalin is considerably smaller (7/2) than can be realized by the acid catalyzed "isomerization". The latter is really an enrichment of the unpolymerized octalin mixture by a preferential polymerization of the $\Delta^{1,9}$-isomer.

Our experience with the lithium-ethylamine reduction of tetralin or naphthalene by Benkeser's procedure[4] has been essentially that reported by Dauben.[1]

EXPERIMENTAL

Dehydration of 2-decalol. A mixture of 2-decalol isomers obtained from the hydrogenation of 2-naphthol over nickel-kieselguhr was added to three times its weight of 100% phosphoric acid with stirring and the system was rapidly raised to 150°. A slight vacuum was applied to the system and water was added dropwise while maintaining the temperature at 150°. After all of the steam-volatile product had distilled, considerable (*ca.* 20%) of the reaction product remained as nonvolatile residue. The volatile product was analyzed by vapor partition chromatography through a 1000 plate tri-*m*-cresyl phosphate-on-fire-brick column and was found to consist of 80% $\Delta^{9,10}$-octalin, 20% $\Delta^{1,9}$-octalin, yield 75–80%.

$\Delta^{9,10}$-*Octalin nitroso chloride.* Equimolar amounts of isoamyl nitrite and iced hydrochloric acid were mixed at −10° with 0.5 mole of the octalin mixture. After 1.5 hr. the blue precipitate was filtered and washed with ice cold ethanol; yield, 75%. Recrystallization from acetone-ether gave 55–65% of blue prisms, m.p. 91–92°.[5]

Regeneration of $\Delta^{9,10}$-*octalin.* The blue nitroso chloride, 19.0 g. (0.094 mole), and 30 ml. of *N,N*-dimethylaniline in a 100 ml. flask with a reflux condenser were slowly warmed to 70° when gas evolution began. (Caution! If the temperature is raised too rapidly to this point, gas evolution becomes violent.) The temperature was gradually raised to 85° and maintained there for 2.5 hr. at which time gas evolution was complete. Dilution with water, extraction with pentane, and washing of the pentane extracts with dilute hydrochloric acid served to isolate the product. This distilled at 77.5° at 14 mm., n_D^{20} 1.4990: yield 11–12 g. (85–95%). This product exhibited a single peak when analyzed on the tri-*m*-cresyl phosphate column.

Isomerization studies. A. *Over phosphorus pentoxide.* A 22.0-g. sample having the composition 53% $\Delta^{9,10}$-octalin, 9% $\Delta^{1,9}$-octalin and 38% *trans*-decalin was heated on the steam bath for 2 hr. over 10 g. of phosphorus pentoxide. It was then extracted with ether and distilled. The undistillable residue amounts to 5 g. The volatile product had the composition 47% of $\Delta^{9,10}$-, 7% $\Delta^{1,9}$-, and 46% *trans*-decalin. A second 2-hr. treatment of the mixture left 5.2 g. of polymeric residue. The volatile material had the composition 32% $\Delta^{9,10}$-, 4% $\Delta^{1,9}$-, and 64% *trans*-decalin.

B. Over "benzylsodium" catalyst.[3] A sample of mixed octalins having the composition 72% $\Delta^{9,10}$-, 26% $\Delta^{1,9}$, and 2% *trans*-decalin was refluxed with "benzylsodium" catalyst.[3] A sample was removed periodically for analysis on the 1000 plate tri-*m*-cresyl phosphate column. After 42 hr., the composition was constant at 70% $\Delta^{9,10}$-, 20% $\Delta^{1,9}$-, 4% *trans*-$\Delta^{1,2}$-, 4% *trans*-$\Delta^{2,3}$-, and 2% *trans*-decalin. Additional samples removed at 48 hr. and at 65 hr. had the same composition.

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Are Organic Group Influences Additive in All Reactions of Aromatic Compounds?

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The consensus of opinion is that group influences are additive. Jaffé states in summary that the effect of multiple substitution in the reactivity of a functional group can be expressed in the Hammett equation by the sum of the substituent constants[3]: $\log K/K_0 = \rho\Sigma\sigma$. Since the publication of this work, Benkeser and co-workers[4] have shown that the sigma constants of 3,5-dialkyl groups, including the bulky *tert*-butyl group, are additive in the loss of a trimethylsilane group from an aromatic ring. The predicted dissociation constant of 3,5-di-*tert*-butylbenzoic acid, calculated in this laboratory from published data,[5] does not substantiate Benkeser's conclusions. As the data of Ref. 5 are less extensive and our calculation dependent on two different sources of information,

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(1) In partial fulfillment of the requirements for the Ph.D. degree, Vanderbilt University, 1959. Dissertation Abstracts, 20(4), 1196 (1959), University Microfilms Inc., Ann Arbor, Mich.

(2) To whom correspondence should be sent.

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(5) Data from E. E. Betts and L. R. C. Barclay, *Can. J. Chem.*, **33**, 1768 (1955). Assuming that rho, the slope, is 1.24 in 50% aqueous methanol,[6] we calculate the dissociation constant of 3,5-di-*tert*-butylbenzoic acid to be 3×10^{-6}. Betts and Barclay report 1.66×10^{-6}. Thus, the *meta-tert*-butyl groups appear to be too strong as electron donors in this reaction.

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we place more confidence in the data of Benkeser. Crocker and Jones[7] claim that group influences are additive, except for groups adjacent to the methoxyl group, in the quaternization of dimethylanilines with allyl bromide. The abnormality of the methoxyl group under these conditions may be attributed to steric inhibition of resonance. Brown states that the prediction of relative rates in aromatic substitution of polyalkylbenzenes is "moderately satisfactory."[8] Such predictions are based inherently on additivity of the influences of the groups attached. Keefer and Andrews,[9] however, found that iodination of polyalkylbenzenes, compared to bromination, showed a retardation in rates, *i.e.*, the alkyl group influences were not additive. They attributed the retardation to a direct steric influence. Recently[10] we found a most striking deviation from the additivity of 3,4,5-trialkyl groups in the Beckmann rearrangement of substituted acetophenone oximes. The 3,4,5-trimethylacetophenone oxime rearranged at a rate 18% slower than predicted,[11] and the 3,4,5-triethyl oxime at a rate 30% slower than predicted.[10] As few trisubstituted derivatives have been studied in the conception of the idea of additivity,[12] we thought that nonadditivity of group effects might have escaped detection in other reactions. We therefore determined the dissociation constants of the trisubstituted benzoic acids by potentiometric titration.[13] The difficulties of determining dissociation constants in aqueous ethanol solution have been pointed out by Grunwald[6] and Kilpi.[14] But since the absolute dissociation constants for benzoic acid are now available for various aqueous ethanol solutions,[6] we made the assumption that all values determined in this paper could be corrected by application of the ratio 1.2/1.86 (Grunwald's value for benzoic acid in 57.6% ethanol divided by our value in the same solvent). Some doubt may be raised about the absolute values reported using this assumption, but very little doubt can be raised about the relative values.[6] In addition precaution was taken to minimize changes in activities of ions or in liquid junction potentials by using 57.6% ethanol for every solution including the standard alkali and the potassium chloride salt bridge.

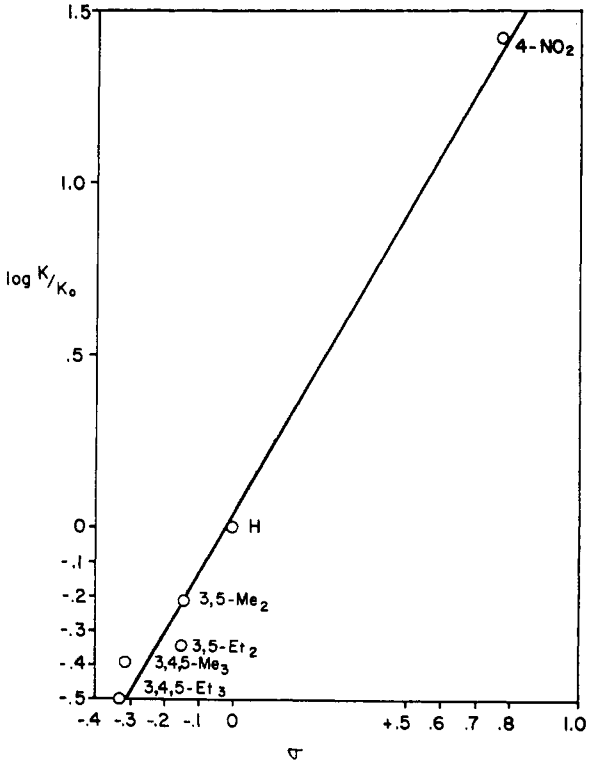

Fig. 1. Plot of log K/K_0 of substituted benzoic acids in 57.6% aqueous ethanol *vs.* sigma. The slope, rho, = 1.73; *s*, the standard deviation, = 0.078; *r*, the standard correlation coefficient, = 0.97.[17] Sigma for 4-ethyl = −0.16; σ for 4-methyl = −0.17; σ for 3-methyl and -ethyl = −0.07; σ for trimethyl = −0.31

The results are given in Table I and illustrated in Fig. 1. As can be noted, correlation of the dissociation constants with sigma is only moderately satisfactory—the 3,4,5-triethyl point falls on the line but the 3,4,5-trimethyl point falls above the line. At least we can say that no trend is established here where the points deviate further from the line as the groups become bulkier. Thus we arrive at the conclusion from our work and from the work summarized earlier that group influences are additive in predicting dissociation constants of acids having up to and including three adjacent ethyl groups. On the other hand, we have concluded previously[10] that in the Beckmann rearrangement, an electrophilic reaction,[15] group influences are not additive with three adjacent alkyl groups. A very definite trend was detected, *i.e.*, triethyl deviated more than trimethyl. This behavior may be general for all electrophilic reactions. Perhaps anions or molecules with free pairs of electrons which are necessary to solvate the transition complex of an electrophilic reaction are bulkier than the hydronium ions, protons, or Lewis acids necessary to stabilize the transition complexes of nucleophilic

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(13) Leading references are included in E. A. Braude and F. C. Nachod, *Determination of Organic Structures by Physical Methods*, Academic Press, Inc., New York, N. Y., pp. 570 and 572.

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(15) Basing our definition on the Hammett equation, we define an electrophilic reaction as one with a significantly negative slope (rho), a nucleophilic reaction as one with a positive slope.

reactions. Thus, the former may be more sensitive to bulk effect of substituents. On the other hand, the explanation may be as simple as stating that the canonical forms with positive charges in the ring are more important in the transition complex hybrid of electrophilic reactions than the corresponding negative charges in nucleophilic reactions. If either or both of these explanations are true, they focus attention on the importance of solvation forces in attempts to study influences of groups remote from the reaction center.[10]

TABLE I

DISSOCIATION CONSTANTS OF SUBSTITUTED BENZOIC ACIDS[a]

Benzoic Acid	$K' \times 10^5$ (Uncorrected)	$K \times 10^5$ (Corrected) ($K' \times 1.20/1.86$)
Unsubstituted	1.86	1.20
3,5-$(CH_3)_2$	1.15	0.741
3,5-$(C_2H_5)_2$	0.851	0.588
3,4,5-$(CH_3)_3$	0.759	0.490
3,4,5-$(C_2H_5)_3$	0.589	0.380
4-Nitro	49.0	31.6

[a] In 57.6% aqueous ethanol at 25°.

EXPERIMENTAL

Materials. Baker and Adamson benzoic acid was twice recrystallized from water. The alkyl substituted benzoic acids were prepared by hypobromite oxidation of the corresponding ketones,[10] the melting points of the purified acids being as follows: 3,5-diethyl, 129–129.5°; 3,5-dimethyl, 171.5–172.5°; 3,4,5-trimethyl, 220.5–221.5°; 3,4,5-triethyl, 142–143°; 4-nitro, 242°. The water and ethanol each were refluxed and distilled, and the distillates stored under a nitrogen atmosphere.

The standard sodium hydroxide was prepared by dilution of 3.6 ml. of saturated sodium hydroxide solution with 330 ml. of carbonate-free water and 570 ml. of 95% ethanol. The solution was approximately 0.1*N* in 57.6% (by weight) of alcohol. It was tested daily for carbonate by adding 5 drops of 0.5*N* barium chloride solution to a 10-ml. aliquot.

Apparatus. Titrations were followed with a Leeds and Northrup *p*H meter, Model 7663-Al, using glass and calomel electrodes. The saturated potassium chloride bridge was made from 57.6% aqueous alcohol, and the glass electrode stored in aqueous alcohol of the same concentration. The *p*H meter was calibrated by means of the known *p*K of benzoic acid in 57.6% aqueous ethanol,[6] and the correction applied to all the other acids as shown in the procedure.

The titration system consisted of storage delivery bottles for water, ethanol, and sodium hydroxide solution, titration jar, and a nitrogen inlet, all in a closed system under about 2.5 lb./sq. in. pressure. The solution was stirred with a magnetic stirrer at a temperature maintained at 25° ± 0.5°.

Procedure. The amount of acid added was always sufficient to make the concentration of the acid one tenth that of the strength of the base.[16] The *p*H meter was checked by buffers at *p*H 7 and 4, and the base added to the 10 ml. buret under nitrogen pressure. After the acid was dissolved in 22 ml. of ethanol, 13 ml. of water was added to make the solution 57.6% aqueous ethanol. The jar was sealed with a rubber stopper containing electrodes, burette tip, and pressure line while the system was swept with nitrogen. The system was then maintained under about 2.5 lbs. of nitrogen pressure.

The *p*H of solution was recorded at 0.1-ml. intervals in the 40–60% neutralization range. Endpoints were also obtained to check the neutral equivalent of each acid. At two points on either side of the half-neutralization point and at the half-neutralization point itself, the five points averaging 0.1 ml. apart from each other, the *p*K was calculated from the formula

$$pK = pH - \log \frac{C_B + a_H{}^+}{C_A - a_H{}^+} + \frac{166\sqrt{\mu}}{1 + 1.65}$$

where C_B is concentration of base added, C_A is concentration of unneutralized acid, and $\alpha_H{}^+$ is the hydrogen ion activity. The formula was used in lieu of extrapolation of the acid dissociation constant to zero concentration.[13] The five values of *p*K were averaged, and the average value shown in Table I as K' (uncorrected). As the value of *K* for benzoic acid in 57.6% aqueous alcohol is 1.2×10^{-5} as reported,[6] the correction factor, 1.20/1.86, was applied to all the other uncorrected dissociation constants. These values are given in the column for K (corrected). As a further check, the *p*K values were determined about a month after the initial values were obtained using new solutions and new electrodes. No difference in K was noted for any acid except *p*-nitrobenzoic acid. The new value was used in the table. Standard deviations and correlation coefficients were calculated by regular procedures.[17]

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2-Ethyl-3-methylhexanamide

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Two different melting points are reported in the literature for 2-ethyl-3-methylhexanamide. Volwiler and Tabern[1] found 97–98° while Maynert and Washburn[2] gave a melting point of 91–93°. This compound was also synthesized in these laboratories by the sequence of reactions formulated below. Although the "purified" end-product (VI) gave the correct analytical values it melted at 95–109°. Since 2-ethyl-3-methylhexanamide has two asymetric carbon atoms, it is likely that compound VI consisted of a mixture of racemates. The separation of the mixture into two racemic pairs was accomplished by chromatography on an aluminum oxide column. Two products were isolated, one melting at 89–90.5° and another at 123–124°. These melting points are uncorrected, and therefore, one may assume that the melting point of the lower melting product is in agreement with that reported by Maynert and Washburn.[2] The analytical

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