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SOME THOUGHTS ON THE BAKER-NATHAN ORDER*†

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Abstract --The present status of the Baker-Nathan order is discussed in terms of current interpretations. On the basis of the large amount of available experimental data, it is suggested that hyperconjugation of carbon-hydrogen bonds provides the most consistent and satisfactory explanation of this effect.

THE least controversial statement that can be made about the Baker-Nathan order[1] is that it is an experimentally observed order of reactivity, which places a series of alkylated benzene derivatives in a sequence which suggests electron release from the alkyl groups to be $Me > Et > Pr^i > Bu^t$, and therefore in a sequence opposite to that of the general inductive effect ($Bu^t > Pr^i > Et > Me$). This means that in a reaction which is favored by electron accession, a *p*-methyl compound will react faster than a *p-tert.*-butyl compound, while in a reaction involving a nucleophilic attack in the rate-determining step, a *p-tert.*-butyl compound will react faster than a *para*-methyl compound. The concept of the greater electron release of a methyl group than that of higher alkyl groups was originally postulated as an hypothesis in order to explain certain experimental facts,[1] and later became part of the hyperconjugation concept. The situation is similar today, except that, irrespective of explanation, a much larger and more consistent body of experimental data has accumulated, showing the Baker-Nathan phenomenon, than was the case over 20 years ago.

When the concept was postulated in 1935, there were actually very few cases known where clear-cut reactivity orders had been observed, orders that placed the four alkylated benzene derivatives in a monotonously changing sequence. Since then, many reactions have been examined where this is the case. However, one must recognize at the outset, and be resigned to it, that, in experiments with alkylated benzene derivatives, rate differences are usually extremely small and therefore the need for exact work is great. Nevertheless, many cases of clear-cut orders have been reported, in which the rate differences are beyond stated experimental errors and are experimentally reliable. Whether or not these small rate differences mean anything in terms of the problem of the relation of structure to reactivity is perhaps another question. For the present discussion this question is answered in the affirmative, because the consistency of the large body of data now available is sufficiently great and striking to justify an explanation. It is also true that, in spite of some very careful experimental work, activation energies and entropies rarely show sufficiently distinctive differences among the various compounds to be of help in interpreting the data, however much desirable a knowledge of these quantities would be, and by necessity,

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* Electronic Effects of Alkyl Groups— X.

† Some of the ideas expressed here have been discussed in a previous publication. See E. Berliner and M. M. Chen, *J. Amer. Chem. Soc.* **80**, 343 (1958).

[1] J. W. Baker and W. S. Nathan, *J. Chem. Soc.* 1844 (1935); J. W. Baker, *Hyperconjugation.* Oxford University Press, Oxford (1952).

one has to rely on rate differences. A justification of this has been given in other cases.[2, 3]

Even though accepted by most chemists, the concept of hyperconjugation as an explanation for the Baker-Nathan order has never been accepted by all. There are probably several reasons for this scepticism. One has perhaps arisen because in the valence bond description—in which the concept was first conceived—hyperconjugation or "no-bond" resonance structures constitute too much of a departure from views based on classical structural organic chemistry. Another reason is undoubtedly the very small experimental rate differences on which the concept is based (although rate differences showing the generally accepted inductive effect are usually not larger). Moreover, some reactions show either order of apparent electron release, depending on conditions, or no clear-cut order at all. And finally, the scepticism is not lessened by the ease with which practically every case of a Baker-Nathan order can be accounted for by other means.

It is therefore not surprising that instead of hyperconjugation other explanations have from time to time been suggested to account for the Baker-Nathan order.[4, 5, 6, 7] These alternate explanations usually endeavor to maintain the inductive effect (or the inductive order[5]) as the only,[6, 7] or the most important, mechanism (or order) by which alkyl groups release electrons, and ascribe the experimentally observed Baker-Nathan order to steric effects of one kind or other, which are assumed to reverse the normal inductive order and lead to the reactivity sequence Me > Bu^t. The present discussion will exclude those auxiliary concepts which have been added to modify the hyperconjugation explanation, but not to replace it, such as, for instance, steric inhibition of hyperconjugation due to lack of proper orbital overlap,[8] or solvent enhancement of hyperconjugation,[9] because these concepts implicitly acknowledge the operation of hyperconjugation effects. Also, various suggestions which have been made for single special cases, such as relief of steric strain in *meta*-alkyl groups,[10] or buttressing effects by *meta*-alkyl groups,[11] will not be considered. Unanswered will also remain the question if, on theoretical grounds, a methyl group, with three α-hydrogen atoms, should be more favorable to hyperconjugation than an ethyl group with only two but with one α-methyl group, and the latter more than a *tert.*-butyl group with no α-hydrogen atoms but with three α-carbon-carbon bonds. This notion, on which the original hypothesis was based, does not appear to have been worked out by the molecular orbital method, in which no distinction was made between hyperconjugation involving carbon-hydrogen or carbon-carbon bonds.[12] There are, however,

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[2] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Chapter 6. Cornell University Press, Ithaca, New York (1953).

[3] M. J. S. Dewar and R. J. Sampson, *J. Chem. Soc.* 2789 (1956).

[4] C. C. Price and D. C. Lincoln, *J. Amer. Chem. Soc.* **73**, 5836 (1951); C. C. Price and W. J. Belanger, *Ibid.* **76**, 2682 (1954).

[5] W. A. Sweeney and W. M. Schubert, *J. Amer. Chem. Soc.* **76**, 4625 (1954); W. M. Schubert and W. A. Sweeney, *J. Org. Chem.* **21**, 119 (1956); W. M. Schubert, J. Robins and J. L. Haun, *J. Amer. Chem. Soc.* **79**, 910 (1957); W. M. Schubert and J. Robins, *Ibid.* **80**, 559 (1958).

[6] A. Burawoy and E. Spinner, *J. Chem. Soc.* 3752 (1954).

[7] A. Burawoy and E. Spinner, *J. Chem. Soc.* 2085 (1955); E. Spinner, *Ibid.* 1590 (1956).

[8] G. Baddeley, J. Chadwick and S. B. Rawlinson, *Nature, Lond.* **164**, 833 (1949); G. Baddeley and M. Gordon, *J. Chem. Soc.* 2190 (1952); R. T. Arnold and W. L. Truett, *J. Amer. Chem. Soc.* **73**, 5508 (1951); V. J. Shiner, Jr., *Ibid.* **78**, 2653 (1956).

[9] V. J. Shiner, Jr., *J. Amer. Chem. Soc.* **76**, 1603 (1954); V. J. Shiner, Jr. and C. J. Verbanic, *Ibid.* **79**, 373 (1957).

[10] M. S. Newman and E. K. Easterbrook, *J. Amer. Chem. Soc.* **77**, 3763 (1955).

[11] R. A. Benkeser, R. A. Hickner and D. I. Hoke, *J. Amer. Chem. Soc.* **80**, 2279 (1958).

[12] R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Amer. Chem. Soc.* **63**, 41 (1941).

various indications, taken from rate and equilibrium data,[13] that a *tert.*-butyl group is capable of a resonance effect, in addition to its inductive effect, and that both carbon–hydrogen and carbon–carbon hyperconjugation play a role, but that the former is more important than the latter, and that their contributions might be in a constant ratio. Quantitative correlations between the structure of alkyl groups and their reactivities have been uncovered on this assumption.[14]

In earlier years certain cases of reactivity were ascribed to the Baker–Nathan effect, where it could easily be shown that the rate differences must actually be due to steric influences. For instance, substitution *ortho* to the methyl group by various electrophilic reagents in *p-tert.*-butyltoluene was ascribed to the greater electron releasing effect of the methyl group alone,[1] but an inspection of the partial rate factors for *ortho* substitution easily reveals that the orientation in these cases is predominantly influenced by the steric hindrance *ortho* to the large *tert.*-butyl group.[2] The more recent alternate explanations for the Baker–Nathan order which deserve the most serious consideration, because they are in themselves reasonable and have analogies in many reactions not pertaining to hyperconjugation, are those that ascribe the observed decrease in rate on going from a methyl to a *tert.*-butyl group to some sort of inhibition of solvation by the larger alkyl groups. One ascribes the decrease in rate on going from methyl to *tert.*-butyl to a "bulk effect" on solvent stabilization of a polar transition state, even by remote alkyl substituents which prevent solvent dipoles from proper orientation.[4] This explanation was used to account for the relative reactivities in the alkaline hydrolysis of ethyl *p*-alkylbenzoates in aqueous acetone, which follows an inductive order (i.e., a methyl compound reacts faster than a *tert.*-butyl compound because of a rate-determining nucleophilic attack) and, as expected for this effect, it was considered significant that the effect was greater for alkyl groups in the *meta* position, which is closer to the reaction site. A similar decrease in rate on increasing the size of substituents was also found in other ester hydrolyses, and the suggested explanation may well be of importance in these cases. (It is indicative of the perplexities one encounters on working with alkylated compounds—although not pertinent to the particular point under discussion that the alkaline hydrolysis of the same ethyl *p*-alkylbenzoates in aqueous ethanol follows a hyperconjugation order.[15]) The other alternate explanation[5] postulates that the decrease in rate of a more highly branched alkylated benzene derivative is due to inhibition of solvation by alkyl groups of electron deficient centers, which develop in the transition state on the aromatic ring, at or near the alkyl groups, for instance in the solvolysis of *p*-alkylbenzhydryl halides.[16] This view was developed on the basis of the spectral behavior of alkylated compounds and various physical measurements on static molecules, where usually the inductive order is observed. Since a *tert.*-butyl group would have a greater "bulk effect" and also inhibit the solvation of the aromatic ring at, or near, the carbon atom to which it is attached more than the smaller methyl group, the observed reactivity order $\mathrm{Me} > \mathrm{Bu}^t$ can be accounted for.

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[13] (a) E. Berliner and F. J. Bondhus, *J. Amer. Chem. Soc.* **70**, 854 (1948); P. D. Bartlett, *J. Chem. Educ.* **30**, 22 (1953); (b) C. A. Vernon, *J. Chem. Soc.* 423 (1954); (c) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *J. Amer. Chem. Soc.* **79**, 1897 (1957).

[14] R. W. Taft, Jr. and I. C. Lewis, in press. I am indebted to Professor Taft for the personal communication prior to publication. See *Tetrahedron* **5**, 210 (1959).

[15] E. Berliner, M. C. Beckett, E. A. Blommers and B. Newman, *J. Amer. Chem. Soc.* **74**, 4940 (1952); C. W. L. Bevan, E. D. Hughes and C. K. Ingold, *Nature, Lond.* **171**, 301 (1953). However, see R. L. Herbst and M. E. Jacox, *J. Amer. Chem. Soc.* **74**, 3004 (1952).

[16] E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.* 949 (1940).

Either explanation is reasonable in itself, and these factors may be important. There is also no single clear-cut experiment by which these explanations can be shown to be either superior or inferior to that based on hyperconjugation. But while such steric factors may be important, it is the present contention that they do not satisfactorily account for all of the facts and are not decisive, and it is only when the large body of accumulated material is considered that a more consistent picture obtains on the hyperconjugation hypothesis. Such data are collected in Table 1. This table is not complete, nor is it meant to be. Some of the older literature data have been omitted, and only illustrative material has been collected which will fit into the three listed categories.

On first sight one is impressed by the consistency of the data, which was not the case when the concept was first formulated. First of all, in all cases of electrophilic substitution in the *para* position for which exact data are available, a Baker–Nathan order is obtained. (Nos. 1–4). The only exception is nitration (No. 21), while rate constants for hydrogen-deuterium exchange in the *para* positions are the same within experimental errors.[17] A Baker–Nathan order is obtained for bromination by molecular bromine or by positive bromine, for benzoylation in nitrobenzene or in benzoyl chloride, as well as in the brominolysis and protonolysis of the trimethylsilyl group (Nos. 6 and 7). It is very likely also true for molecular chlorination,[18] for iodine-catalyzed bromination[19] and for mercuration,[20] although not all the necessary data are available for an exact comparison. It is also the case for various solvolytic reactions of the S_N1 or limiting case (Nos. 8–11), such as the solvolysis of benzyl halides, benzhydryl halides and cuminyl halides in various solvent mixtures, and for some S_N2 reactions on benzyl halides (Nos. 12–14), in which the spread in reactivity is less, as anticipated. Included are also solvolyses of acetylenic and allylic halides (Nos. 15 and 16) which, although not aromatic, constitute systems where an analogous behavior might be expected. Finally, some equilibrium constants which show the Baker–Nathan pattern are also listed (Nos. 19 and 20). It is therefore no longer true that the Baker–Nathan order is sometimes exhibited in electron demanding processes in aromatic systems, but it would be much more justified to say that the Baker–Nathan order is rarely not exhibited in such processes.

Because of the rate sequence p-Me $>$ p-Bu^t, these are the reactions to which the alternate explanations apply. Two further observations are worth noting in this connection. One is that these reactions were conducted in a variety of solvents, but no systematic change in reactivity pattern is discernible. The other is that, while the ratio of methyl to *tert*.-butyl reactivities is not the same in the direct substitution reactions, these ratios are not due to a different behavior of the alkyl groups in the different reactions, but to the different susceptibility of each reaction to the electron demand of the substituting agents, i.e., to different rho values. This conclusion is based on the remarkably constant behavior of the methyl group in a great variety of substitution reactions, as shown by the excellent quantitative correlation of *para* and

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[17] E. L. Mackor, P. J. Smit and J. H. Van Der Waals, *Trans. Faraday Soc.* **53**, 1309 (1957). This seems to be also true for *para* propylation. See F. E. Condon, *J. Amer. Chem. Soc.* **70**, 2265 (1948).

[18] P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.* 279 (1943). According to a private communication from Dr. P. B. D. de la Mare, such data are now available, showing the Baker–Nathan order for *para* and the inductive order for *meta* chlorination. I am indebted to Dr. de la Mare for this information. See also *Tetrahedron* **5**, 107 (1959).

[19] E. Berliner and F. J. Bondhus, *J. Amer. Chem. Soc.* **68**, 2355 (1946); also in ref. 13.

[20] H. C. Brown and C. W. McGary, Jr., *J. Amer. Chem. Soc.* **77**, 2310 (1955).

TABLE 1A. SOME REACTIONS SHOWING THE BAKER–NATHAN ORDER OF ELECTRON RELEASE (Me > Bu^t)

Reference	Reaction No.		H	p-Me	p-Bu^t	m-Me	m-Bu^t
28	1	Bromination of benzenes by Br_2 (HAc)	1	2420	770		
29	2	Benzoylation of benzenes (nitrobenzene)	1	830	615		
21	3	Benzoylation of benzenes (benzoyl chloride)	1	589	430	—	
30	4	Bromination of benzenes by (HOBr) (H^+) (50% aq. dioxan)	1	59	38·5	—	
31	5	Chlorination of RO-2-Br-4-Alkyl-C_6H_3 by Cl_2 (HAc)	—	—	—	1·00	0·49
32	6	Brominolysis of $ArSiMe_3$ by Br_2 (HAc)	1	49	29	—	—
33	7	Protonolysis of $ArSiMe_3$ by $HClO_4$ (aq. methanol)	1	21·1	15·6	—	—
34	8	Solvolysis of $ArCH_2Br$ (wet HCOOH)	1	57·9	28·0		
13c	9	Solvolysis of $ArCMe_2Cl$ (90% aq. acetone)	1	26·0	14·4	2·00	1·85
16, 23	10	Solvolysis of $Ar(C_6H_5)CHCl$ (80% aq. acetone)	1	21·4	10·9	1·68	1·53
35	11	Solvolysis of $Ar(C_6H_5)CHCl$ (90% aq. ethanol)	1	30·8	19·3	—	
1	12	R. of $ArCH_2Br$ with C_5H_5N (acetone)	1	1·66	1·35	—	
34	13	R. of $ArCH_2Br$ with I^- (acetone)	1	1·46	1·36	—	—
34	14	R. of $ArCH_2Cl$ with EtO^- (ethanol)	1	1·57	1·46		—
13b	15	Solvolysis of $RCH{=}CHCH_2Cl$ (wet HCOOH)*	1	3550	2260		
6	16	Solvolysis of $RC\equiv CCMe_2Cl$ (80% aq. ethanol)*	1	2160	1180		
36	17	Acid hydrolysis of Et_3SiOAr (aq. ethanol)	1	1·45	1·32		
37	18	Beckmann rearrangement of $ArCOCH_3$ oximes (H_2SO_4)	1	1·86	1·78	—	
38	19	Ionization of anilinium ions (24·6 wt. % aq. MeOH) pK_a	4·40	4·89	4·76	—	
39	20	Ionization of 2-nitrophenols (24·5 wt. % aq. acetone) pK_a	7·57	7·89	7·76	—	

* R in this reaction means H, Me or Bu^t.

Table 1b. Some reactions showing the inductive order of electron release (Bu^t > Me)

Reference	Reaction No.		H	p-Me	p-Bu^t	m-Me	m-Bu^t
40	21	Nitration of benzenes (HAc)	1	58	75	2·5	4·0
30	22	Bromination of benzenes by (HOBr)(H$^+$)(50% aq. dioxan)*	1	—		2·5	2·6
41	23	Iodination of p-alkylanilines (30% aq. methanol)	≃0·2			1·00	2·09
42	24	Iodination of p-alkylphenols (25% aq. methanol)	—			1·00	1·70
43	25	R. of pyridines with MeI (nitrobenzene)	1	—	—	2·07	2·77
11	26	Protonolysis of ArSiMe$_3$ (aq. HAc)	1	—		2·16	2·81
44	27	Decomposition of ArN$_2^+$ (0·1 N HCl)	—	—	—	1·00	3·60
35	28	Solvolysis of Ar(C$_6$H$_5$)CHCl (90% aq. ethanol)	1	—	—	1·93	2·29
15	29	Alkaline hydrolysis of ethyl benzoates (56% aq. acetone)	1	0·41	0·31	—	—
4	30	Alkaline hydrolysis of ethyl benzoates (56% aq. acetone)	—	1	0·843	1·45	0·826
24	31	Ionization of Ar(C$_6$H$_5$)$_2$CCl (liquid SO$_2$)	1	17·6	18·8	2·28	3·97
45	32	Ionization of pyridinium ions (H$_2$O) pK_a	5·17	—	—	5·68	5·82
46	33	Ionization of phenylacetic acids (H$_2$O) pK_a	4·31	4·37	4·42	—	—

* See ref. 18 for molecular chlorination.

Table 1c. Some reactions involving a nucleophilic attack and showing the order Me > Bu^t of electron release

Reference	Reaction No.		H	p-Me	p-Bu^t	m-Me	m-Bu^t
15	34	Alkaline hydrolysis of ethyl benzoates (85 wt. % ethanol)	1	0·44	0·56	—	—
10	35	Methanolysis of l-menthyl benzoates (methanol)	1	0·420	0·570	0·747	0·838
47	36	Neutral hydrolysis of benzoic anhydrides (75% aq. dioxan)	1	0·352	0·389	—	—
34	37	Ethanolysis of benzoyl chlorides (ethanol)	1	0·569	0·667	—	—
34	38	R. of N-benzylpyridinium ions with EtO$^-$ (ethanol)	1	0·504	0·691		—
48	39	R. of 2-nitrobromobenzenes with piperidine (piperidine)	1	0·146	0·170	—	
34	40	R. of 2, 6-dinitrochlorobenzenes with EtO$^-$ (ethanol)	1	0·176	0·309	—	

meta partial rate factors,[21] and on the good fit of the methyl and *tert.*-butyl groups in the $\rho\sigma^+$ relationship.[22] To put it differently, in reactions in which a large resonance effect of substituents is called for, the two alkyl groups behave just like many other substituents for which the linear free energy relationship holds.

There are some reactions, notably two solvolytic reactions (Nos. 9 and 10), where alkyl groups in the *meta* position also show the Baker–Nathan order. It has been reasoned elsewhere[23] that if this decrease, m-Me > m-Bu^t, were owing to solvation hindrance, a greater spacing between the two groups should be obtained, because they are closer to the reaction center. Actually, the spacing of the two groups is considerably closer than for the same two groups in the *para* position. A Baker-Nathan order from the *meta* position, however, is an exception, and it is of considerable importance that, in practically all cases of electrophilic substitution, *meta*-alkyl groups follow the inductive pattern, i.e., a *m-tert.*-butyl compound reacts faster than a *m*-methyl compound (Table 1B). This is eminently reasonable when the restriction is recalled that resonance effects are transmitted preferentially through the *ortho/para* positions, but as a rule not through the *meta* position, some exceptions not withstanding. The *meta*-alkyl groups therefore affect rates and equilibria mainly through their inductive effects.[24] It is difficult to see how the usually greater reactivity of the *m-tert.*-butyl than the *meta*-methyl compound can be accommodated with the solvation views, because the *meta*-alkyl groups are closer to the reaction sites, and also any solvation of the ring must be more inhibited by the larger alkyl group. This is what the alternate theories demand, yet in almost all cases the *m-tert.*-butyl compound reacts faster. On the solvation view, one could, of course, say that the *meta*-alkyl groups behave quite normally and their effects need no explanation; but that would not do, because specific solvent effects would be expected to have at least the same influence with *meta*- as with *para*-alkyl groups. Practically the only way to get around this difficulty (which does not arise if electronic effects are used as the explanation) is to postulate that, when alkyl groups are attached to the *meta* position, the demand for solvation of the transition state is less.

There is a third category of reactions which is well accounted for on the hyperconjugation hypothesis, but less so by steric factors. These are reactions which follow a Baker–Nathan order of electron release, but which, because of a nucleophilic rate-determining attack, result in the reactivity order H > Bu^t > Me (Table 1C). Here belong various basic hydrolyses of alkylbenzoates, aromatic nucleophilic displacements and some others. In these reactions, too, a *tert.*-butyl compound reacts faster than a methyl compound. Furthermore, the concept of steric resistance to bond contraction, advanced to account specifically for the Baker–Nathan order in reactions going through an electron-deficient transition state,[6, 7] does not seem to offer an explanation for these reactions.

The consistency of the data is persuasive and lends support to hyperconjugation as the explanation of the observed reactivities. With the various steric effects one cannot easily explain why a *tert.*-butyl compound should ever react faster than a methyl compound. These alternate suggestions can be maintained only if additional hypotheses are made about varying solvation demands, which essentially amounts to

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[21] H. C. Brown and F. R. Jensen, *J. Amer. Chem. Soc.* **80**, 2296 (1958).

[22] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.* **79**, 1913 (1957). See also ref. 21.

[23] E. Berliner and M. M. Chen, *J. Amer. Chem. Soc.* **80**, 343 (1958).

[24] See, for instance, N. N. Lichtin and P. D. Bartlett, *J. Amer. Chem. Soc.* **73**, 5530 (1951).

the new hypothesis that, in those reactions in which a *tert.*-butyl compound reacts faster than a methyl compound, rate decreasing solvation factors are not decisive, or that they are only decisive where a Baker–Nathan order is observed. It seems at the moment more satisfactory to account for the behavior of alkyl groups in terms of the two electronic effects, although it is very likely that solvation factors are also of some importance.

There are many things that are not yet fully explained by hyperconjugation as it pertains to the Baker–Nathan order and that need further investigation. Among these are the role of the solvent and solvation,[4, 5] solvation assistance,[9] the stereochemical requirements of hyperconjugation,[8] the significance of the secondary isotope effects,[9, 25] the relation between hyperconjugation and hydrogen participation,[26] the importance of carbon–carbon hyperconjugation,[13, 14] and probably others. The situation is admittedly complex, because alkyl groups affect rates by three different electronic mechanisms, carbon–hydrogen hyperconjugation, carbon–carbon hyperconjugation and the inductive effect, the last two of which reinforce each other. In addition, various solvation and specific solvent effects, as well as steric factors, must play some role. The difficulty is that one does not know quantitatively how important each of these factors is in determining the total behavior of an alkyl group, although encouraging attempts in this direction are being made.[27] In view of this complexity, it is surprising how consistent, on the whole, the over-all picture is, and there is therefore justification in the statement that the predominant effects of alkyl groups on the benzene ring are usually the hyperconjugation and the inductive effects.

[25] V. J. Shiner, Jr., *J. Amer. Chem. Soc.* **75**, 2925 (1953); E. S. Lewis and C. E. Boozer, *Ibid.* **76**, 791 (1954); E. S. Lewis and G. M. Coppinger, *Ibid.* **76**, 4495 (1954); C. G Swain, T. E. C. Knee and A. J. Kresge, *Ibid.* **79**, 505 (1957); A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki *Ibid.* **80**, 2326 (1958).

[26] S. Winstein and J. Takahashi, *Tetrahedron* **2**, 316 (1958).

[27] M. M. Kreevoy and R. W. Taft, Jr., *J. Amer. Chem. Soc.* **77**, 5590 (1955); R. W. Taft, Jr., *Steric Effects in Organic Chemistry* (Ed. M. S. Newman) Chapter 13. Wiley, New York (1956). See also ref. 14.

[28] P. W. Robertson, P. B. D. de la Mare and B. E. Swedlund, *J. Chem. Soc.* 782 (1953); H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.* **79**, 1421 (1957).

[29] H. C. Brown, B. A. Bolto and F. R. Jensen, *J. Org. Chem.* **23**, 414 (1958).

[30] P. B. D. de la Mare and J. T. Harvey, *J Chem. Soc.* 36 (1956); *Ibid.* 131 (1957).

[31] A. E. Bradfield and B. Jones, *Trans. Faraday Soc.* **37**, 726 (1941).

[32] C. Eaborn and D. E. Webster, *J. Chem. Soc.* 4449 (1957).

[33] C. Eaborn, *J. Chem. Soc.* 4858 (1956).

[34] C. W. L. Bevan, E. D. Hughes and C. K. Ingold, *Nature, Lond.* **171**, 301 (1953).

[35] V. J. Shiner, Jr. and C. J. Verbanic, *J. Amer. Chem. Soc.* **79**, 369 (1957).

[36] E. Akerman, *Acta. Chem. Scand.* **11**, 373 (1957).

[37] D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.* **17**, 1511 (1952).

[38] F. Berliner, V. Connor and K. Foley, unpublished results.

[39] F. Berliner and C. Wang, unpublished results.

[40] H. Cohn, E. D. Hughes, M. H. Jones and M. A. Peeling, *Nature, Lond.* **169**, 291 (1952).

[41] E. Berliner and F. Berliner, *J. Amer. Chem. Soc.* **76**, 6179 (1954).

[42] E. Berliner, F. Berliner and I. Nelidow, *J. Amer. Chem. Soc.* **76**, 507 (1954).

[43] H. C. Brown, D. Gintis and L. Domash, *J. Amer. Chem. Soc.* **78**, 5387 (1956).

[44] E. S. Lewis and E. B. Miller, *J. Amer. Chem. Soc.* **75**, 429 (1953).

[45] H. C. Brown and X. R. Mihm, *J. Amer. Chem. Soc.* **77**, 1723 (1955).

[46] J. F. J. Dippy, *Chem. Rev.* **25**, 151 (1939).

[47] E. Berliner and L. H. Altschul, *J. Amer. Chem. Soc.* **74**, 4110 (1952).

[48] E. Berliner and L. C. Monack, *J. Amer. Chem. Soc.* **74**, 1574 (1952).