Electrophilic Aromatic Reactivities *via* Pyrolysis of 1-Arylethyl Esters. Part 13.[1] Carbon–Carbon Hyperconjugation and the Origin of the Baker–Nathan Effect

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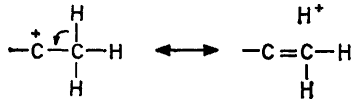
From rates of gas-phase pyrolysis of the appropriate 1-arylethyl acetates, σ^+ values have been determined for the following substituents: *p*-cyclohexyl (−0.380); *p*-t-butyl (−0.365); *m*-t-butyl (−0.19). These values are the highest recorded for these substituents, whereas for analogous reactions carried out in solution, decreasing values of σ^+ are required as the solvent is made more polar. The gas-phase value of $\sigma^+(p\text{-Bu}^t)/\sigma^+(p\text{-Me})$ is 1.26, the highest recorded for a reaction possessing an electron-deficient transition state which may be stabilized by resonance. In solution reactions the value of $\sigma^+(p\text{-Bu}^t)/\sigma^+(p\text{-Me})$ decreases with increasing solvent polarity. The data show conclusively that the Baker–Nathan order of electron release by alkyl groups is a solvation phenomenon, and also that carbon–carbon hyperconjugation is *greater* than carbon–hydrogen hyperconjugation; this latter is confirmed by the greater value of $\sigma_p^+ - \sigma_I$ for t-butyl (0.291) than for methyl (0.244). It is therefore a paradox that Baker and Nathan proposed the important and well established concept of hyperconjugation, but for the wrong reason.

In solution, electrophilic aromatic substitutions carried out in trifluoroacetic acid, *e.g.* hydrogen exchange, give results which most closely parallel those obtained in the gas phase; for hydrogen exchange the required σ^+ values are: *p*-cyclohexyl, −0.338; *p*-t-butyl, −0.320; *m*-t-butyl, −0.175. The solvolysis of αα-dimethylbenzyl chlorides is seen to give exceptionally low σ^+ values for bulky substituents (even more so for *meta*-positions than for *para*-) and this reaction (especially when carried out in aqueous acetone) is therefore exceptionally sensitive to steric hindrance to solvation, *which is more important when the substituent is in the* meta-*position than when it is* para. In this respect therefore, the solvolysis is not a good model for determination of electrophilic substituent constants, and recent conclusions based on this reaction and concerning electron release from the 2-*exo*- and -*endo*-norbornyl substituents may be invalid.

It is just over 40 years since Baker and Nathan published their famous paper describing the fact that *para*-alkyl groups facilitate the reaction of benzyl bromides with pyridine (in acetone) in the order Me > Et > Pr^i > Bu^t.[2] They suggested that the C–H bonds of the methyl group (but not the C–C bonds of the t-butyl group) could conjugate with an adjacent electron deficient centre, as in (1). This process, termed hyperconjugation by Mulliken, was shown to be predicted by quantum-mechanical theory.[3] However, this latter did not indicate that C–H hyperconjugation should be any more effective than C–C hyperconjugation.[4] Carbon–carbon hyperconjugation was first suggested as being important by Berliner and Bondhus, who argued that the high reactivity of t-butylbenzene in molecular bromination could not be due to inductive effects alone.[5] Other authors advanced similar arguments;[6-8] nevertheless the notion that C–H was greater than C–C hyperconjugation persisted, despite the expectation that a methyl group would be able to accommodate a positive charge better than hydrogen. (If this were not the case, the +*I* effect of methyl could not arise.) Until very recently (see Discussion section) only Mulliken and Parr attempted to explain an experimental phenomenon by the assumption that C–C was greater than C–H hyperconjugation.[9]



(1)

There are many references to C–C hyperconjugation,[10-19] yet it has frequently been disposed of as an unknown or unimportant quantity. Only Kreevoy seems to have been sufficiently troubled by the supposed superiority of C–H hyperconjugation to the extent of attempting to suggest a reason for it.[16] The work of Taft and Lewis appeared to indicate that C–C hyperconjugation was 70% as effective as C–H hyperconjugation.[15] However these calculations were based entirely upon the assumption that there were no differential solvation effects on *k*(toluene) : *k*(t-butylbenzene).[18] Nevertheless the majority of discussions of Baker–Nathan electron-releasing orders for alkyl groups have assumed this to arise from the net difference of C–H and C–C hyperconjugation, the latter often being assumed to be relatively insignificant. In more recent years, there has been a wealth of evidence for hyperconjugation from

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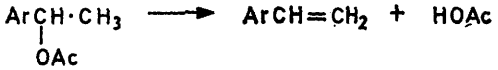
sigma-bonds between carbon and other elements, *e.g.* silicon,[20,21] germanium,[20,21] tin,[22] boron,[23] mercury,[23,24] arsenic,[25] phosphorus,[25] sulphur,[26] fluorine,[27] and the other halogens.[28] Some of these elements provide large rate increases as compared with hydrogen, which emphasizes the need to reconsider carefully the probability and effect of C–C hyperconjugation.

Since the original report by Baker and Nathan, hundreds of papers have appeared relating to the concept of hyperconjugation, with evidence coming from many different areas of chemistry, not merely from kinetic studies. Three pieces of experimental evidence stand out as the most unambiguous. The first was provided by Shiner, who showed that the rate of S_N1 solvolysis of tertiary alkyl chlorides was affected by β-deuterium atoms, but only if these could conjugate with the carbocation.[29] The second demonstrated that carbon–metal hyperconjugation is strongly dependent upon the conformation of the carbon–metal sigma-bond, *i.e.* hyperconjugation electron release is maximal when the sigma-bond and the adjacent *p* orbital are coplanar, as the theory demands. The third is the large difference in $\sigma^+ - \sigma$ for the *p*-methyl substituent, which is considered in more detail below.

Many other theories however were proposed to account for the abnormal electron-releasing order of the alkyl groups. The most relevant of these was that of Schubert,[30] who developed the idea that bulky groups hinder ring solvation [31] and argued that this steric hindrance to solvation of the charge developed and delocalized into the aromatic ring in the transition state could produce the Baker–Nathan order.[30] However his arguments were in part based on differences in activation energies and entropies which were barely outside experimental error; consequently this theory has not attracted the amount of support that it might have done. Moreover, Shiner suggested that hyperconjugation might equally well be solvent-assisted and this would produce the solvent dependence of the Baker–Nathan order.[32] Also the fact that in reactions retarded by electron supply the alkyl groups slow the reaction in the Baker–Nathan order, is difficult to reconcile with the concept of steric hindrance to solvation,[18] even though at least one of these reactions reverts to the inductive order merely on changing the solvent. Some years ago one of us discovered, with Eaborn, the first electrophilic aromatic substitution (hydrogen exchange) in which the order of electron release by the *para*-methyl and -t-butyl groups could also be reversed merely by changing the solvent.[33] We concluded that both solvation effects and hyperconjugation combine to produce the Baker–Nathan order.[34] In the event this prophesy has turned out to be correct, though not in the way that we had intended.

In 1962, one of us showed that the gas-phase pyrolysis of 1-arylethyl acetates (2) proceeded *via* formation of a



$$\underset{\displaystyle\text{OAc}}{\text{ArCH}}\cdot\text{CH}_3 \longrightarrow \text{ArCH}{=}\text{CH}_2 + \text{HOAc}$$

(2)

partial carbocation at the side chain α-carbon atom, and thereby provided a gas-phase model for determining electrophilic substituent effects.[35] In this study we found the *p*-t-butyl group to be both more activating than the *p*-methyl group, and also more activating than required by its literature σ^+ value.[36] Analysis of the relative effects of these two substituents in electrophilic aromatic substitution showed that the tendency to give the Baker–Nathan order was found in those reactions carried out in the most polar media.[37] (This correlation was also noted subsequently by Katritzky and Topsom and their co-workers.[38]) However, in view of the novelty of the gas-phase technique, both with regard to elucidation of the mechanism of ester pyrolysis and its application as a model for electrophilic aromatic substitution, and the lack of sophistication of the apparatus then available, we did not feel justified in making major generalizations based upon the small rate differences obtained; our present data show that these preliminary results were however qualitatively correct.

Our attention has however been refocused upon this earlier work for a number of reasons. Measurements of the ionisation potentials of alkyl free radicals,[39] and of the electron-releasing abilities (measured by ion cyclotron resonance) of *p*-alkyl groups in protonated benzene,[40] and *ab initio* calculations of the stabilities of the ions

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RCH_2^+ [41] and RCO^+,[42] have indicated that the conjugative electron-releasing ability of the t-butyl group is greater than that of the methyl group. *Ab initio* calculations of gas-phase acidities and basicities indicate that t-butyl is more electron-releasing than methyl.[43] That this release is conjugative in origin is indicated by the fact that this is the order of the effect of these groups on i.r. intensities under conditions of high electron demand.[38] (Much earlier, Schubert *et al.*[14] showed that the effect of alkyl substituents upon the energy of the principal electronic transition of a range of compounds in the gas phase was compatible with greater electron release from t-butyl as compared with methyl. However this view was not wholly convincing since it is difficult to evaluate the validity of the extrapolation from electronic transitions to effects upon chemical transitions. The same difficulty was encountered in interpreting the identical effects of the *para*-methyl and -t-butyl substituents upon the position of the charge-transfer band of 1-methylpyridinium iodides in chloroform.[44])

TABLE 1

Pyrolysis of the compounds $RC_6H_4{\cdot}CHMe{\cdot}OAc$

R	t/°C	10^3k/s^{-1}	log A/s^{-1}	E kcal mol^{-1}	$\Delta S^\ddagger$ cal mol^{-1} K^{-1}	log k/k_0 (at 625 K)	Correlation coefficient
H	392.9	28.8	12.8	44.1	−1.4	0	0.999 87
	392.3	27.35					
	373.3	10.75					
	369.2	8.34					
	356.8	4.25					
	354.5	3.67					
	340.8	1.72					
m-Bu^t	393.0	37.4	12.7	43.4	−1.8	0.120	0.999 90
	392.3	34.8					
	373.3	13.7					
	356.8	5.75					
	341.0	2.31					
p-Bu^t	393.2	47.4	12.8	43.4	−1.4	0.230	1.000 00
	368.8	13.8					
	354.5	6.34					
	340.6	2.91					
p-Cyclohexyl	392.3	44.2	12.5	42.3	−3.0	0.240	0.999 97
	373.3	17.5					
	356.8	7.48					
	341.0	3.09					

These reports lead one to the conclusion that the standard solvolysis reaction used for measurement of σ^+ values is *severely affected by steric hindrance to solvation*, since it gives the Baker–Nathan order for both *para*- and *meta*-alkyl groups. This implies that the standard values of σ^+ for all bulky groups are seriously in error. As a final requirement for solution of the origin of the Baker–Nathan effect, it only remains to measure *quantitatively* the effects of the bulky alkyl substituents in a gas-phase *reaction*. In this paper we therefore report an accurate determination of the σ^+ values for the *p*-cyclohexyl and *p*-t-butyl substituents in the gas-phase pyrolysis of 1-arylethyl acetates. To complete our analysis we have also measured the effect of the *meta*-t-butyl substituent in the same reaction, and also in protiodetritiation in trifluoroacetic acid at 70 °C.

RESULTS AND DISCUSSION

Rate coefficients for pyrolysis of the esters (each measured over a 50 K range) are given in Table 1 together with the log k_{rel} values at 625 K; the derived σ^+ values are given in Table 2.

Rates (10^3k/s^{-1}) of protiodetritiation of t-butyl[*m*-^{3}H]benzene at 70 and 100 °C were 3.35 and 37.3, respectively. The rates of exchange of benzene under these conditions are 0.095 and 1.25, respectively,[45] giving corresponding partial rate factors of 35.3 and 29.8. (The decrease in value with increasing temperature arises from the Arrhenius effect.) Since the ρ factor for protiodetritiation in trifluoroacetic acid at 70 °C is −8.8,[46] σ^+ (*m*-Bu^t) is −0.175 in this reaction. The high partial rate factor confirms the high values which one of us obtained in an earlier study using aqueous mineral acids in trifluoroacetic acid as the exchanging medium.[33] At that time the possibility existed that this value could have been produced through dealkylation and transalkylation under the reaction conditions. However, Bancroft subsequently showed that, although these reactions do occur in these media, they contribute an error of no more than 5% to the observed partial rate factor.[47] In the less acidic medium used for the present study, the error in the rate coefficient and hence the partial rate factor would be even less. This is confirmed by the linearity, to 90% of reaction, of the kinetic plots. To produce such linearity, dealkylation and rearrangement would either have to be very fast (in which case the observed rate would be at least

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ten-fold higher), insignificant, or exactly the same as that of the exchange (which would produce no error in the observed rate). It is noteworthy that similarly high partial rate factors were obtained for molecular chlorination in trifluoroacetic acid ($f_m^{\mathrm{Bu^t}} = 33$, $\sigma^+_{m\text{-}\mathrm{Bu^t}} = -0.165$), and Himoe and Stock believed that this reflected an enhanced activity coefficient for t-butylbenzene in trifluoroacetic acid; *i.e.* desolvation of the ground state for t-butylbenzene produces enhanced reactivity.[48] Although this was a reasonable explanation of their results, Stock and Himoe did not have sufficient thermodynamic data for their explanation to be unambiguous,[48] and the data in Table 2 now show it to be incorrect. This Table contains values of σ^+ derived for a number of bulky substituents in solvolysis of αα-dimethylbenzyl chlorides,[49,50] detritiation in trifluoroacetic acid,[51-54] and pyrolysis of 1-arylethyl acetates [35,55] (including the present results).

TABLE 2

Values of σ^+ derived from various reactions

Reaction	Solvent	Substituent							
		p-Me	*m*-Me	*m*-Bu^t	*p*-Bu^t	*p*-Ch *	*m*-SiMe$_3$	*p*-SiMe$_3$	*m*-Ph
Solvolysis	H_2O–Me_2CO †	−0.311	−0.066	−0.059	−0.256	−0.285	0.010	0.020	0.109
Solvolysis	H_2O–EtOH		−0.077	−0.084					0.056
Detritiation	$CF_3{\cdot}CO_2H$	−0.303	−0.090	−0.175	−0.312	−0.338			0.020
Pyrolysis	None	−0.290	−0.098	−0.190	−0.365	−0.380	−0.160	−0.090	0.0
$\sigma^+_{\mathrm{sol.(Me_2CO)}} - \sigma^+_{\mathrm{pyr.}}$		−0.021	0.032	0.131	0.109	0.095	0.170	0.110	0.109

* Cyclohexyl. † Standard condition used for determining σ^+.

Table 2 illustrates a number of important points.

(i) The high negative value of $\sigma^+_{m\text{-}\mathrm{Bu^t}}$ derived from detritiation is confirmed in the gas-phase elimination. Desolvation of the ground state is not therefore the cause of the high *meta* partial rate factors obtained in electrophilic substitutions carried out in trifluoroacetic acid. These values reflect the true electron-releasing ability of the *meta*-t-butyl substituent.

(ii) Whereas the σ^+ values for the *p*-methyl substituent are essentially constant under all three conditions, the σ^+ values for the other substituents show a regular and large increase (*i.e.* become more negative) with decrease in solvating power of the medium. This increase is smallest for *meta*-methyl, larger for the bulky *para*-substituents and larger still for the bulky *meta*-substituents. We believe that this dependence of value upon the medium derives from steric hindrance to solvation, which is severe in the solvolysis reaction, especially in the aqueous acetone medium chosen as the standard for measurement of σ^+ values. Trifluoroacetic acid, being a poor solvating medium, gives data which most closely parallel those obtained in the gas phase. It logically follows that the Baker–Nathan order which is obtained in the solvolysis must arise from steric hindrance to solvation of the transition state. On going to reactions carried out in less polar media, so the ' inductive ' order is more nearly obtained. Examples of this in electrophilic substitution were noted by one of us several years ago,[37] and Schubert and Gurka have also pointed to the fact that $\log f_p^{\mathrm{Bu^t}} : \log f_p^{\mathrm{Me}}$ for molecular bromination increases from 1.006 to 1.044 : 1 as the medium is changed from 73.3 to 100 wt % trifluoroacetic acid.[56] In the gas-phase elimination this value is 1.26, ***the highest obtained in any reaction in which a positive reaction centre can conjugate with the substituent.***

(iii) Given that steric hindrance to solvation causes the Baker–Nathan order, we should expect that the substituent which can best shield the carbon to which it is attached would give the biggest difference in σ^+ values between the solvolysis and the gas-phase reaction. This is the case, the difference being larger for *p*-t-butyl (0.109) than for *p*-cyclohexyl (0.095). The *p*-trimethylsilyl substituent also gives a value of 0.11; although silicon is larger than carbon, the methyl groups are further removed from the ring than are those in t-butyl.

(iv) The fact that the *meta*-substituents show large differences in σ^+ values between the solvolysis and gas-phase reactions than do their *para*-counterparts, reflects, we believe, steric hindrance to solvation being ***greatest for*** meta-***substituents***. By contrast it has been widely assumed that steric hindrance to solvation would be greatest for *para*-substituents. Only Berliner and Chen have suggested that this might not be the case, since in the transition state for the solvolysis of a *meta*-substituted compound, (3)—(5), the positive charge is, in one of the canonical forms (3), delocalized between two bulky groups.[57] However, if the group is bulky enough, differences in its ability to hinder solvation at the *ipso*- and *ortho*-carbon atoms may be very small. Consequently hindrance to solvation of the charge in (4) and (7) will be similar, and because of the remoteness of the substituent this will be true also of (5) and (8). Thus the difficulty in solvating (3) relative to (5) will cause steric

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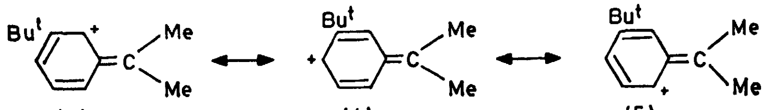
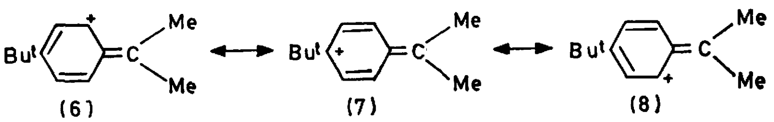
hindrance to solvation to affect adversely *meta*- considerably more than *para*-substituted compounds.

The extent to which this is important may be judged by the fact that even *meta*-methyl, normally regarded as being of no steric consequence, shows a substantial increase in σ^+ value on going from solvolysis (aqueous acetone) to gas-phase elimination (and even on going from solvolysis in aqueous acetone to solvolysis in aqueous ethanol). By contrast the *para*-methyl substituent shows no such increase.* It should also be noted that the much larger increase in the $\sigma_m{}^+$ value for t-butyl between the solvolysis (aqueous acetone) and the gas-phase elimination is also exactly paralleled on going from solvolysis in aqueous acetone to solvolysis in aqueous ethanol. (In fact this latter change causes the Baker–Nathan order to go over to the inductive order.) Likewise the *m*-phenyl substituent shows an exactly parallel series of changes in its σ^+ value.



(3) (4) (5)



(6) (7) (8)

It is clear then that the σ^+ values determined from the solvolysis for the phenyl, methyl, and t-butyl substituents are substantially in error as a measure of the true electron-releasing abilities of the substituents. Previously we showed that the *m*-CF_3 value was wrong,[58] and we shall shortly present evidence to show that the *m*-NO_2 value is wrong as well.

Our conclusion that the Baker–Nathan order is a solvation effect is reinforced by recent measurements of the heats of solution of alkylbenzenes in superacids.[59] The strong protonation of the aromatic compound requires a close approach of the bulky acid anion to the ring in order to solvate the positive charge. Consequently hindrance is high, resulting in the highest Baker–Nathan order on record.

Carbon–Carbon Hyperconjugation.—It must follow from the Baker–Nathan order being a solvation effect, and the $Bu^t > Me$ order of electron release being obtained under conditions of high electron demand, that carbon–carbon hyperconjugation must be *greater* than carbon–hydrogen hyperconjugation. Two other sets of data point to the same conclusion. First, if the variation in the *p*-t-butyl activation order was due to the greater importance of C–H than of C–C hyperconjugation, then the variation in the σ^+ values derived from a range of reactions should be greater for methyl than for t-butyl. In fact the data in Table 3 show that the t-butyl group exhibits twice the variation in σ^+ shown by methyl. While this does not confirm that C–C is greater than C–H hyperconjugation, it proves that the Baker–Nathan effect cannot be due to the converse. Unambiguous support for our hypothesis does however come from consideration of the differences $\sigma_p{}^+ - \sigma_I$, which accurately represent the conjugative electron-releasing power of a substituent. It might be argued that the Taft σ_I values[15] have been determined in solution and may not therefore, in view of the evidence in this paper, reflect the true inductive effects of the substituents in question. However it has recently been shown that the ionization potentials of alkyl and hydrogen halides show an excellent linear dependence on σ_I values[60] (correlation coefficient 0.998), so that we may use the σ_I values with confidence. The values are -0.046 (Me) and -0.074 (Bu^t) so that the $\sigma_p{}^+ - \sigma_I$ values are -0.244 (Me) and -0.29 (Bu^t). Not only do these values confirm the greater importance of C–C over C–H hyperconjugation, they also firmly dispose of the notion that hyperconjugation is unimportant. It is clear that over 80% of the electron-releasing ability of alkyl groups is *conjugative* in origin, so that the inductive component is relatively unimportant.

TABLE 3

Values of σ^+ derived from various reactions [a]

Reaction	$\sigma^+_{p\text{-Me}}$	$\sigma^+_{p\text{-Bu}^t}$
Solvolysis of αα-dimethylbenzyl chlorides	−0.311	−0.256
Protiodesilylation	−0.288	−0.259
Protiodegermylation	−0.294	−0.272
Bromodesilylation	−0.273	−0.236
Mercuration	−0.340	−0.309
Positive bromination	−0.286	−0.256
Hydrogen exchange ($CF_3\cdot CO_2H$)	−0.303	−0.312
Hydrogen exchange ($HOAc-H_2SO_4$)	−0.320	−0.300
Molecular bromination ($H_2O-HOAc$)	−0.280	−0.240
Molecular chlorination (HOAc)	−0.291	−0.260
Acetylation	−0.316	−0.310
Pyrolysis (aryl acetates)	−0.290	−0.365
Overall variation	0.060	0.129

[a] Calculated from data given by R. O. C. Norman and R. Taylor in 'Electrophilic Substitution in Benzenoid Compounds,' Elsevier, 1965.

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* In fact it shows a small *decrease*, which probably reflects small errors in calculating the ρ factors for the reactions. If these were corrected so as to make the *p*-methyl values constant then the increases in the other σ^+ values would be even greater than shown.

[58] R. Taylor, *J. Chem. Soc.* (*B*), 1971, 622.

[59] E. M. Arnett and J. W. Larsen, *J. Amer. Chem. Soc.*, 1969, **91**, 1438; E. M. Arnett and J. M. Abboud, *ibid.*, 1975, **97**, 3865.

[60] L. S. Levitt and B. W. Levitt, *Tetrahedron*, 1973, **29**, 941.

The above conclusions are also indicated by the work of Jensen and Smart, who measured rates of benzoylation of the isomeric phenylnorbornanes in which the 1-phenyl isomer was much more reactive than the others (7-, *endo*-2-, and *exo*-2-). Since each of the substituents is very large, they argued that differential solvation effects arising from steric hindrance would be unimportant.[61] The bicyclic substituents were all more electron-supplying than methyl (as indeed are the monocyclic ring substituents in detritiation),[53] and the 1-norbornyl substituent is sterically best able to supply electrons by C–C hyperconjugation. Jensen and Smart suggest therefore that in these molecules containing strained rings, C–C is at least as important as C–H hyperconjugation. It is now clear however that this is generally true and is not limited to molecules in which steric assistance is provided.

In concluding this part of our discussion we note that Baker and Nathan proposed the concept of hyperconjugation for which there is overwhelming evidence from diverse areas of chemistry. Yet paradoxically, they proposed this concept for the wrong reason. Their result was clearly due to steric hindrance to solvation, and furthermore C–C is greater than C–H hyperconjugation, whereas they believed the former to be insignificant.

The Question of Sigma-bond Participation in the 2-Norbornyl Group.—With but few exceptions (*e.g.* ref. 62), high *exo* : *endo* rate ratios have been obtained in solvolysis of 2-norbornyl derivatives and related compounds, and this has been attributed to sigma-bond participation in the transition state for reaction of the *exo*-isomer,[63] or to steric hindrance to solvolysis of the *endo*-isomer.[64] The differential abilities of the *p*-*endo*- and *p*-*exo*-2-norbornyl substituents to supply electrons is therefore of crucial interest in this connection, since the steric explanation does not apply here. In the benzoylation described above, Jensen and Smart obtained σ^+ values of -0.357 (*p-exo*) and -0.336 (*p-endo*),[61] thereby indicating that the *exo*-isomer is indeed more electron-supplying. However, Brown *et al.*[65] have suggested that the results might be affected by the large steric requirement of benzoylation, and a better indication of the effects of the substituents would be provided from solvolysis of the appropriate $\alpha\alpha$-dimethylbenzyl chlorides, since this latter '*appears to be remarkably free of complications*.' Not only do our results show this to be incorrect, but the σ^+ values obtained in the solvolysis, *viz.* -0.309 (*p-exo*) and -0.295 (*p-endo*) further confirm it. The pattern we have noted is followed precisely here, the solvolysis (which was carried out in aqueous acetone) giving much lower values. The relative effects of the *p*-Me and *p*-t-$\mathrm{Bu^t}$ substituents have not been measured in benzoylation, but acetylation in the same medium (dichloroethylene) gives a slight Baker–Nathan order (Table 3), so steric hindrance to solvation is evidently quite important in this solvent. Consequently the σ^+ values determined for the 2-norbornyl substituent even in benzoylation are likely to be considerably less than would be obtained in hydrogen exchange or the gas-phase elimination. Furthermore, Brown's conclusion that the difference in the *exo*- and *endo*-σ^+ values is not significant, is obviously invalid without further data being obtained under poorly solvating conditions. Certainly the trend (above) in the σ^+ values, albeit small, suggests that, under poorly solvating conditions, the *exo*-substituent will be appreciably more electron-supplying than the *endo* substituent.

One other experiment points to the importance of steric hindrance to solvation in the solvolysis reaction. Topsom and his co-workers found that the σ_p^+ values for the adamantan-1-yl and bicyclo[2.2.2]octan-1-yl substituents were in each case very similar to the σ_p values.[66] They suggest that the apparent lack of conjugative effect is also due to steric hindrance to solvation in the presence of these bulky groups. Although it could be argued that since C–H hyperconjugation is precluded here this is the expected result, under non-solvating conditions these substituents are apparently *strongly* electron-supplying, and C–C hyperconjugation must be solely responsible for this.

Baker–Nathan Orders in Reactions with Electron-rich Transition States.—As noted in the introduction, one of the principal objections to explanation of steric hindrance to solvation was the observation of these orders in reactions with electron-rich transition states. Though it is possible to explain the results in terms of differential solvation effects in the ground state, a more probable explanation lies in the greater polarisability of large alkyl groups than of small ones, such that the larger groups may *accept* electrons more easily than small ones.[43,67] The superimposition of steric hindrance to solvation upon a basic $\mathrm{Bu^t} > \mathrm{Me}$ stabilising order could then produce either Baker–Nathan or inductive deactivation orders, *i.e.* *p*-methyl compounds will be *least* reactive under poorly solvating conditions, and *p*-t-butyl compounds will be least reactive under good solvating conditions.

EXPERIMENTAL

t-Butyl[3-^{3}H]*benzene*.—The sample used was that prepared for an earlier investigation.[33]

1-(4-*Cyclohexylphenyl*)*ethyl Acetate*.—4-*Cyclohexylphenyl methyl ketone*. The literature method,[68] modified in that

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[65] H. C. Brown, B. G. Gnedin, K. Takeuchi, and E. W. Peters, *J. Amer. Chem. Soc.*, 1975, **97**, 610.

[66] T. J. Broxton, G. Capper, L. W. Deady, A. Lenko, and R. D. Topsom, *J.C.S. Perkin II*, 1972, 1237.

[67] J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, 1971, **93**, 3911.

[68] H. A. Mayes and E. E. Turner, *J. Chem. Soc.*, 1929, 500.

dichloroethane was used as a solvent, gave pure 4-cyclohexylphenyl methyl ketone (34%), b.p. 240° at 60 mmHg, m.p. 69° (lit.,[68] 68—69°).

1-(4-*Cyclohexylphenyl*)*ethanol*. Reduction of the above ketone (5 g, 0.025 mol) with sodium borohydride gave a quantitative yield of the alcohol, m.p. 79° (from light petroleum). The n.m.r. spectrum [τ(CCl_4) 2.95 (4 H, m, ArH), 5.39 (q, *J* 6.5 Hz, CH), 7.27 (s, OH), 7.58 (m, CH), 8.40 (m, CH_2), and 8.71 (d, *J* 6.5 Hz, CH_3)] gave the correct integration for the required compound. However, g.l.c. analysis showed more than one peak (with decomposition geometry), which arises from the ease with which this alcohol dehydrates.[69] It is reported that attempts to prepare this alcohol from the bromo-precursor and acetaldehyde *via* a Grignard reagent gave only the corresponding alkene.[70] We initially attempted to make the alcohol in the same way and with the same result, though the reason for this was traced in our case to overheating during fractional distillation of the product. Evidently the alcohol is particularly sensitive to surface-catalysed elimination, which, coupled with its relatively high b.p. for a secondary alcohol, requires the avoidance of high temperatures during work-up.

Acetylation of the alcohol with acetic anhydride–pyridine gave 1-(4-*cyclohexyphenyl*)*ethyl acetate* (70% based on the ketone), b.p. 120° at 0.5 mmHg, n_D^{20} 1.514 5 (Found: C, 78.0; H, 9.0. $C_{10}H_{22}O_2$ requires C, 78.0; H, 9.0%), τ(CCl_4) 2.87 (4 H, m, ArH), 4.20 (q, *J* 6.5 Hz, CH), 7.58 (m, CH), 8.13 (s, $CO{\cdot}CH_3$), 8.42 (m, CH_2), and 8.57 (d, *J* 6.5 Hz, CH_3).

1-(4-*t-Butylphenyl*)*ethyl Acetate*.—The Grignard reagent prepared from 1-bromo-4-t-butylbenzene (10.7 g, 0.05 mol) was treated with an excess of acetaldehyde to give, after normal work-up and fractional distillation, 1-(4-t-butylphenyl)ethanol (4.3 g, 49%), b.p. 96° at 1.4 mmHg. This alcohol (2.0 g, 0.011 mol) was acetylated with pyridine–acetic anhydride to give, after normal work-up and fractional distillation, 1-(4-t-butylphenyl)ethyl acetate (1.9 g 72%), b.p. 105° at 2 mmHg (lit.,[35] 96° at 2.0 mmHg), n_D^{20} 1.493 3, τ(CCl_4) 2.78 (4 H, s, ArH), 4.23 (q, *J* 6.5 Hz, CH), 8.08 (s, $CO{\cdot}CH_3$), 8.56 (s, *J* 6.5 Hz, CH_3), and 8.72 (s, Bu^t).

1-(3-*t-Butylphenyl*)*ethyl Acetate*.—The preparation of this compound proved exceptionally difficult; this we attribute to the steric effect of the t-butyl group. The first attempted preparation was from *m*-t-butyltoluene, prepared by refluxing the Grignard reagent from *m*-bromotoluene with t-butyl bromide. Curiously the product here was accompanied by t-butylbenzene, which suggests that the MgBr substituent promotes alkyl-dealkylation. Oxidation of *m*-t-butyltoluene gave a poor yield of *m*-t-butylbenzoic acid, in contrast to the literature claim.[71] The reason appeared to be the heterogeneous nature of the reaction mixture, arising from the presence of the bulky t-butyl group on the aromatic ring; very efficient stirring is evidently necessary. Esterification of the *m*-t-butylbenzoic acid obtained gave the required ethyl *m*-t-butylbenzoate, but an attempt to convert this into *m*-t-butylacetophenone *via* a Claisen condensation failed completely, even after refluxing for 100 h with ethyl acetate. This is significant for we have been able to obtain satisfactory yields of ketone even at the *peri*-positions of quinoline and isoquinoline [1,72] by this method; the *m*-t-butyl group appears to be able to exert a large long-range steric effect.

A second attempt to obtain the required product utilized 1-chloro-3-t-butylbenzene (prepared from the reaction of t-butyl bromide with the Grignard reagent from 1-bromo-3-chlorobenzene). However, we were unable to bring about the reaction of this with magnesium, or even with n-butyllithium.

1-Bromo-3-t-butylbenzene was prepared by the method given by Brown and Okamoto,[73] and was shown by g.l.c. analysis to be entirely free of the *ortho*- and *para*-isomers. The Grignard reagent prepared from this compound (tetrahydrofuran as solvent) gave on treatment with acetaldehyde and acetylation of the crude alcohol product, the expected ester, together with some of the *para*-isomer, identified by g.l.c. comparison with the authentic sample described above. This is believed to arise from migration of the t-butyl group catalysed by the Lewis acid ($MgBr_2$) produced under the Grignard conditions and aided both by the high temperature of reflux of tetrahydrofuran, and the steric interaction of the secondary and tertiary alkyl groups.

The Grignard reagent prepared from 1-bromo-3-t-butylbenzene (8 g, 0.038 mol) in diethyl ether was treated with acetaldehyde and the crude alcohol acetylated directly to give, after fractional distillation, 1-(3-*t-butylphenyl*)-*ethyl acetate* (3 g, 36%), b.p. 70° at 1.3 mmHg, n_D^{20} 1.490 4, τ(CCl_4) 2.82 (4 H, m, ArH), 4.21 (q, *J* 6.5 Hz, CH), 8.02 (s, $CO{\cdot}CH_3$), 8.51 (d, *J* 6.1 Hz, CH_3), and 8.67 [s, $C(CH_3)_3$]. This compound was shown by g.l.c. and n.m.r. analysis to be entirely free of the *para*-isomer.

Kinetic Studies.—Protiodetritiation of t-butyl[*m*-^{3}H]-benzene was carried out as previously described.[74] This compound gave excellent first-order kinetic plots with linearity beyond 85% of reaction. Bancroft [47] showed that under more strongly acidic conditions, migration of the t-butyl group can occur, but that this would produce not more than 5% error in the derived rate coefficient and partial rate factor. Under our more weakly acidic conditions the error in the rate coefficient would be rather less than 5%, so that it is unnecessary to make any correction to the derived partial rate factor.

Rates of gas-phase elimination of acetic acid from the 1-arylethyl acetates were measured by using the static stainless-steel reactor method previously described.[75] The usual criteria for the absence of surface reactions were applied. This ester gave kinetic plots which were first-order to beyond 95% of reaction. Rates could be duplicated to better than ±1.5% and no significant deviation of individual rate coefficients from the Arrhenius plots were found (this is indicated by the correlation coefficients in Table 1). The absence of surface reactions was also shown by the fact that entropies of activation are essentially constant and within the range -1.8 ± 1.2 cal mol^{-1} K^{-1}, which applies to *ca.* 70 1-arylethyl acetates. (An error of ±1.5% in rate coefficients determined over a 50 K range produces ±1.0 cal mol^{-1} K^{-1} error.) Product analysis showed only the presence of acetic acid and the expected styrene; in the case of the *m*-t-butyl ester the product was also shown by g.l.c.

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to be free of any *p*-t-butylstyrene, *i.e.* no rearrangement occurred during the pyrolysis. This was also evident from the linearity of the kinetic plots; such linearity could only be obtained if rearrangement was very fast as compared with the rate of elimination, but in this case the observed rate of elimination would have to be the same as that of the *para*-isomer, which was not the case.

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