Electrophilic Aromatic Substitution. Part 30.[1] The Effects of the *p*-Bicyclo[2.2.2]octan-1-yl, Adamantan-1-yl, *exo*- and *endo*-Norbornan-2-yl, and Neopentyl Substituents in Detritiation. Steric Acceleration of Hyperconjugation

By **William J. Archer, Morteza A. Hossaini,** and **Roger Taylor,*** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex

Rate coefficients have been measured for detritiation of the compounds [*p*-^{3}H]C_6H_4R by anhydrous trifluroacetic acid at 70 °C, and lead to the following partial rate factors (R=): bicyclo[2.2.2]octan-1-yl, 2 650; adamantan-1-yl, 2 000; *exo*-norbornan-2-yl, 1 750; *endo*-norbornan-2-yl, 1 340; and neopentyl, 472. The corresponding σ^+ values are −0.391, −0.377, −0.371, −0.358, and −0.306. These bulky substituents are much more electron releasing than they are in reactions carried out in highly solvating media where steric hindrance to solvation masks their true electronic effect; in trifluoroacetic acid, solvation is very poor, and steric hindrance to solvation therefore largely absent. Among alkyl groups, bicyclo[2.2.2]octan-1-yl is second only to cyclopropyl in its electron-releasing ability which probably derives in part from *steric acceleration of hyperconjugation*. The neopentyl substituent is more electron releasing than methyl due to the greater importance of C–C over C–H hyperconjugation. The concept of ' secondary hyperconjugation ' proposed to account for the low activation by neopentyl in molecular bromination is disproved, the phenomenon arising simply from steric hindrance to solvation. Detritiation of *endo*-norbornan-2-ylbenzene is accompanied by protiodealkylation, which is sterically accelerated by the interaction between the aryl-ring *ortho*-hydrogen, and the *endo*-hydrogen on C-6.

THE electronic effects of large alkyl groups such as t-butyl, cyclohexyl, and trimethylsilyl were recently shown to be very dependent upon the reaction under study.[2] In general, the electron-releasing ability appears to increase as the solvating power of the medium decreases. This is due to steric hindrance to solvation [3] of the respective transition states preventing the true electron-releasing power of the substituent being observed in the highly solvating media. Thus only in the gas phase is the true electron-releasing ability of the substituent observed. Moreover, the effect of steric hindrance to solvation was shown to be even more significant for *meta*-substituents so that as the solvent is made less solvating, their increase in electron-releasing ability is greater than for their *para*-counterparts.

These results have two important consequences. First, they render very unsatisfactory the use of the solvolysis of 1-aryl-1-methylethyl chlorides in aqueous acetone as a standard reaction [4] for determining σ^+ values of bulky groups (insofar as these values are to give a real indication of the electronic effects of substituents) because this medium is just about the most solvating of any used in kinetic studies. Secondly, by observing that under poorly solvating conditions *p*-t-butyl is always more electron releasing than *p*-methyl, it followed that C–C hyperconjugation is more important than C–H hyperconjugation. Thus the Baker–Nathan order of electron release for alkyl groups [5] arises from the effect of steric hindrance to solvation superimposed upon an electron-releasing order which is the exact *reverse* of that which led Baker and Nathan to propose the concept of hyperconjugation in the first place.†

† It is even more remarkable that for 40 years the notion that C–H hyperconjugation should be greater than C–C hyperconjugation has persisted despite the fact that the original paper by Baker and Nathan gave no meaningful mechanistic reason for this supposition. Its acceptance in view of the greater C–H *versus* C–C bond energy is even more curious.

The probe reactions used in these studies were hydrogen exchange in anhydrous trifluoroacetic acid, a poor solvating medium [reaction (1)], and gas-phase pyrolysis of 1-arylethyl acetates in which there is of course no solvent at all [reaction (2)]. In the present paper we describe results for some very bulky alkyl substituents,

$$ArT + CF_3COOH \rightleftharpoons ArH + CF_3COOT \quad (1)$$

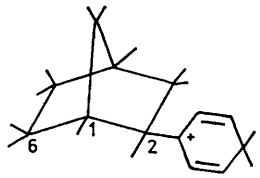
$$ArCH(OAc)CH_3 \longrightarrow ArCH{=}CH_2 + HOAc \quad (2)$$

viz. *p*-bicyclo[2.2.2]octan-1-yl, *p*-adamantan-1-yl, *p*-*exo*- and *endo*-norbornan-2-yl, and *p*-neopentyl in reaction (1) and in the accompanying paper we describe results for some of these substituents in reaction (2).

The results for the former two substituents are of interest not only because they are very bulky which might magnify the effects previously noted, but also because they are very poorly activating in solvolysis (in aqueous acetone, giving σ_p^+ −0.27 and −0.25, respectively) with steric hindrance to solvation suspected as the cause.[6] One of us has tentatively suggested that both substituents should be strongly electron releasing as a result of carbon–carbon hyperconjugation,[2] and spectroscopic evidence [6] indicates that *p*-adamantan-1-yl should be almost as electron releasing as *p*-cyclopropyl, for which σ^+ is −0.473.[7] In the gas phase the adamantan-1-yl cation is more stable than the t-butyl cation,[8] so as *para*-substituents the former group should be more electron releasing than the latter [which gives σ_p^+ −0.312 in reaction (1) and −0.365 in reaction (2)].

The results for the *exo*- and *endo*-norbornan-2-yl substituents have an indirect bearing on the question of σ-bond participation in solvolysis *etc.* of 2-norbornyl compounds [there can of course be no non-classical conjugation between the electrons of the 1,6-bond and the ring cation in (I)]. If the *exo*-substituent turned out to be substantially more activating than the *endo*-isomer, then it would appear that the former is inherently better

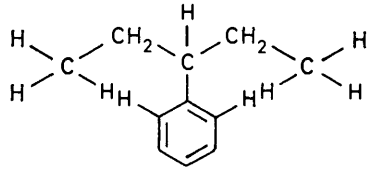
able to release electrons by some mechanism, non-classical or otherwise;[9] this argument assumes that steric effects would be precluded. Jensen and Smart[10] did indeed find the *exo*-norbornan-2-yl substituent to be more electron releasing than the *endo*-substituent in



(I)

benzoylation (σ_p^+ −0.357 and −0.336, respectively). However, Brown has suggested that this result *could be affected by steric hindrance*[9] (though this view of steric hindrance to *para*-substitution is both unique and extraordinary). He therefore proposed solvolysis of 1-aryl-1-methylethyl chlorides in aqueous acetone as a more meaningful reaction. This however gave the same relative reactivities, but with substantially reduced σ^+ values[11] (as expected in view of steric hindrance to solvation which in fact renders this reaction unsatisfactory). Thus examination of these substituents in the present reactions will resolve this question unambiguously.

These substituents are also of interest in connection with sterically accelerated protiodealkylation. Detritiation of 1-methyl- and 1-ethyl-butylbenzenes gave log f_o : log f_p values slightly lower than the standard value of 0.87 which applies to other substituents including t-butyl.[12] This indicated some steric hindrance which would arise from the conformations, *e.g.* (II), in which the substituent and *ortho*-hydrogen distance is smaller than in t-butylbenzene. As a consequence, the



(II)

ring–substituent C–C bond is lengthened and weakened so that *acid-catalysed protiodealkylation* accompanies the reaction to a significant (albeit small) extent, leading to a fall-off in rate coefficient with time; kinetic evidence showed that this process is catalysed by Lewis acid sites on the glass surface of the ampoules used in the runs, since the decrease in rate coefficient with time was greater the smaller the quantity of aromatic used in the run. A similar close approach of substituent and *ortho*-hydrogens is possible in *endo*-norbornan-2-ylbenzene, but not in the *exo*-isomer. It was therefore of interest to see if the kinetics with the former would indicate dealkylation.

* We thank Professor P. B. D. de la Mare for drawing attention to the need for re-examining this substituent effect.

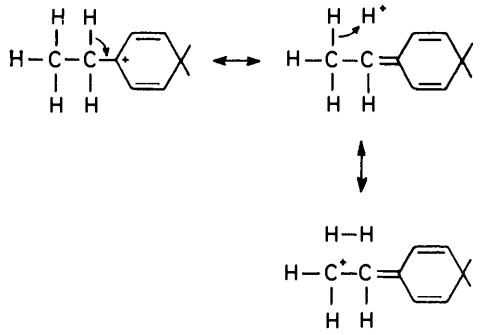
Neopentylbenzene was studied * to ascertain the validity of the concept of ' second-order hyperconjugation '[13] (III) which was proposed to account for the low reactivity of neopentylbenzene in molecular bromination (Table 1). This theory was based on the assumption

TABLE 1

Relative rates of molecular bromination of PhR

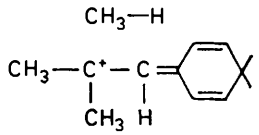
R	CH_3CH_2	$MeCH_2CH_2$	Me_2CHCH_2	Me_3CCH_2
$k_{rel.}$	1.0	0.80	0.53	0.30

that C–H hyperconjugation would be more important than C–C hyperconjugation *i.e.* the analogous canonical



(III)

form (IV) would be less favourable. Since this hyperconjugation order is now known to be wrong, it was relevant to check the effect of the neopentyl substituent under poor and non-solvating conditions.



(IV)

RESULTS AND DISCUSSION

The rate coefficients for detritiation in anhydrous trifluoroacetic acid at 70 °C are given in Table 2, and

TABLE 2

Detritiation of [*p*-^{3}H]C_6H_4R in CF_3COOH at 70 °C

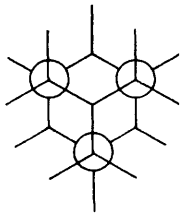
R	10^7k/s^{-1}	f	σ^+
Me	36.5	450	−0.303
Bicyclo[2.2.2]octan-1-yl	216	2 660	−0.391
Adamantan-1-yl	163	2 010	−0.377
exo-Norbornan-2-yl	143	1 760	−0.371
endo-Norbornan-2-yl	109	1 340	−0.358
Neopentyl	38.5	475	−0.306

partial rate factors are calculated from the rate coefficient and standard partial rate factor for toluene (see Experimental section). The main discussion of these results is deferred to the accompanying paper, in which gas-phase results are presented. The main features to be noted here are as follows.

(i) The bicyclo[2.2.2]octan-1-yl and adamantan-1-yl substituents are much more electron-releasing than in

the solvolysis, so much so that if the σ^+ values from that reaction were used to calculate the exchange rate coefficients, these latter would be in error by more than an order of magnitude! Interestingly, however, the former substituent is the more reactive by almost the same amount in each reaction and this also shows the reactivity in the solvolysis to be lowered by steric hindrance to solvation since this should produce a constant effect for substituents of the same bulk. (This they are in the vicinity of the aryl ring.)

We propose that since the high electron release by both these substituents must be due to C–C hyperconjugation (it cannot be simply inductive because the σ values are only −0.25 and −0.24, respectively [6]), the higher activation by the bicyclo[2.2.2]octan-1-yl substituent must be due to *steric acceleration of hyperconjugation*. Thus whereas the adamantan-1-yl substituent has a staggered



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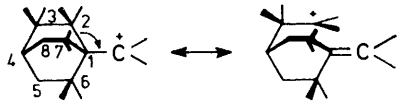
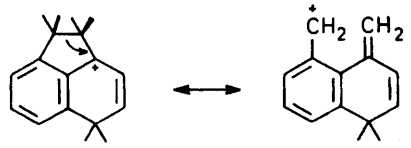


(VII)

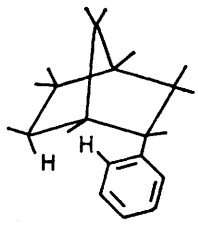
conformation (V), that in bicyclo[2.2.2]octan-1-yl is essentially eclipsed (VI). Carbon–carbon hyperconjugation as in (VII) will relieve this eclipsing through formation of sp^2-hybridised carbon at C-2 (and equivalent atoms). There may also be some relief of hindrance between the hydrogens on C-6 and -7 as the ring angle at C-1 is increased to 120°. One of us first proposed this concept to account for the higher electron release by the cyclopentyl substituent compared to cyclobutyl and cyclohexyl, and for the higher reactivity of acenaphthene; [12] in each example, eclipsing is accompanied by enhanced reactivity.*

(ii) Both the *exo*- and *endo*-norbornan-2-yl substituents turn out to be more electron releasing than in either solvolysis or benzoylation, as was predicted.[2] Once again the *exo*-isomer is the more activating and a reason



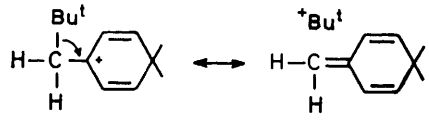
(VIII)

for this is proposed in the accompanying paper. Relevant to that explanation is the fact that the *endo*-isomer did undergo some protiodealkylation and this was catalysed by the surface of the glass ampoules in exactly the same way as for the previous examples noted in the Introduction. There can be little doubt therefore that conformation (IX) is sterically hindered.

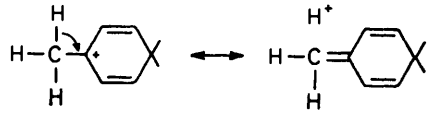


(IX)

(iii) The neopentyl substituent is more electron releasing than the methyl substituent which again shows the greater importance of C–C hyperconjugation (X) over C–H hyperconjugation (XI). The poor activation by



(X)



(XI)

this substituent in molecular bromination must simply derive from steric hindrance to solvation, and the concept of secondary hyperconjugation is disproved.

Three other determinations of the effect of the *p*-neopentyl substituent are available. In solvolysis (in 80% aqueous acetone) of *para*-substituted diphenylmethyl chlorides ArCHPhCl, Shiner and Verbanic [14] found *p*-neopentyl to be less activating than *p*-methyl. This and other results (they also found the *m*-alkyl activation order to be more solvent dependent than the *p*-alkyl activation order, *cf.* ref. 2) they interpreted in terms of solvent assistance of C–H hyperconjugation, though this interpretation is of course no longer necessary or valid. The ρ factor for the reaction can be estimated as −4.88, so that σ^+ for *p*-neopentyl was only −0.24. In protiodesilylation in aqueous methanol,

* The identification of C–C hyperconjugation as the most important mode of electron release by alkyl groups [2] provides an additional explanation for the very high reactivity of acenaphthene (VIII). The C–C bond between the methylenes in the substituent is very stretched and thereby weakened. Breakage of the bond will therefore be easy and the accompanying release of electrons by C–C hyperconjugation will therefore be strong. (The comparative weakness of C–Si, C–Hg *etc.* bonds is of course a reason for the very strong C–Si *etc.* hyperconjugation.) This is thus a further example of steric acceleration of hyperconjugation though of a different type from the examples noted above.

p-neopentyl was by contrast only slightly less activating than *p*-methyl,[15] whilst in ionisation of substituted trityl chlorides in liquid sulphur dioxide (for which ρ may be calculated as −3.87) *p*-neopentyl was more activating than *p*-methyl.[16] From this last reaction, σ^+ for *p*-neopentyl may be calculated as −0.317, almost exactly the same as in detritiation. The similar results for the two reactions are also shown by the σ^+ values for *m*-Me and *m*-Bu^t which are −0.094 and −0.133, respectively, for the ionisation, and −0.090 and −0.175 for detritiation.[2] [The value for *m*-Me in the ionisation provides yet further evidence that the value from solvolysis (−0.66) is wholly unrepresentative of its effect in other reactions and equilibria.[17]]

EXPERIMENTAL

[4-^{3}H]*Neopentylbenzene*.—1-*Bromo*-4-*neopentylbenzene*. The literature method [18] gave neopentylbenzene (38%), b.p. 44—48 °C at 6 mmHg, n_D^{20} 1.4870 (lit.,[13] b.p. 185.1—185.9 °C at 755 mmHg, n_D^{20} 1.4875). Bromine (12 g, 0.15 mol) in trifluoroacetic acid (60 ml) was added dropwise to a stirred solution of neopentylbenzene (10 g, 0.07 mol) in trifluoroacetic acid (40 ml) during 4 h and the mixture allowed to stand during a further 16 h. (This method gives the maximum yield of the *para*-isomer due to the high selectivity.[19]) The acid was recovered for reuse by distillation, and the residue was worked up in the usual way to give 1-bromo-4-neopentylbenzene (8 g, 50%), b.p. 62 °C at 1 mmHg, n_D^{20} 1.5255 (lit.,[16] b.p. 96—98 °C at 3 mmHg, n_D^{25} 1.5240).

The Grignard reagent formed from 1-bromo-4-neopentylbenzene was hydrolysed with tritiated water to give [4-^{3}H]*neopentylbenzene* (83%), b.p. 46—48 °C at 6 mmHg, n_D^{20} 1.4870.

endo-2-([4-^{3}H]*Phenyl*)*norbornane*.—2-*Phenylnorbornene* This was prepared by a modification of the method of Brown *et al.*[11] which both increased the yield and reduced the number of steps. Bromobenzene (60 g, 0.38 mol) was treated with magnesium (14 g, 0.58 mol, a considerable excess to reduce biphenyl formation) in dry ether. Norcamphor (25 g, 0.24 mol) in ether (50 ml) was added to the Grignard reagent, and the mixture heated under reflux during 4 h. Preliminary experiments showed that the reaction was reluctant to go to completion, hence the need for a large excess of Grignard reagent. Normal work-up was followed by fractional distillation at 0.7 mmHg, during which dehydration occurred, the water produced forming an azeotrope with the benzene by-product arising from the use of excess of bromobenzene. Hence in one step we were able to collect 2-phenylnorborn-2-ene (36 g, 94%), b.p. 80 °C at 0.7 mmHg, n_D^{20} 1.5818 (lit.,[11] b.p. 128 °C at 17 mmHg, n_D^{20} 1.5810). This product did not appear to contain any phenylnortricyclene in contrast to that obtained by dehydration with potassium hydrogen sulphate.[11]

endo-2-*Phenylnorbornane*. 2-Phenylnorborn-2-ene (36 g, 0.225 mol) was reduced with hydrogen and Adam's catalyst to give, after fractional distillation, *endo*-2-phenylnorbornane (36 g, 98.7%), b.p. 78 °C at 0.8 mmHg, n_D^{20} 1.5488 (lit.,[11] b.p. 71 °C at 0.6 mmHg, n_D^{20} 1.5481).

endo-2-(4-*Bromophenyl*)*norbornane*. *endo*-2-Phenylnorbornane (3.44 g, 0.02 mol) was brominated with bromine (3.2 g, 0.02 mol) in trifluoroacetic acid (15 ml) at 50 °C during 60 h. G.l.c. analysis of the crude product showed it to contain only small amounts of the *ortho*- and *meta*-isomers. Fractional distillation removed all of the former and most of the latter to give endo-2-(4-*bromophenyl*)-*norbornane* (0.6 g, 12%), b.p. 116 °C at 0.2 mmHg, n_D^{20} 1.5805 (Found: C, 62.0; H, 6.0. $C_{13}H_{15}Br$ requires C, 62.2; H, 6.0%). Hydrolysis of the Grignard reagent prepared from this bromo-compound with tritiated water followed by normal work-up gave endo-2-([4-^{3}H]*phenyl*)*norbornane*, b.p. 58 °C at 0.3 mmHg, n_D^{20} 1.5486.

exo-2-([4-^{3}H]*Phenyl*)*norbornane*.—exo-2-*Phenylnorbornane*. This was prepared as described in the literature,[11] and had the reported physical properties.

exo-2-(4-*Bromophenyl*)*norbornane*. *exo*-2-Phenylnorbornane (26 g, 0.15 mol) was brominated in trifluoroacetic acid as described above and work-up as for the *endo*-isomer gave exo-2-(4-*bromophenyl*)*norbornane* (21 g, 53%), b.p. 115 °C at 0.15 mmHg, n_D^{20} 1.5785 (Found: C, 62.1; H, 6.0%).

Hydrolysis of the Grignard reagent prepared from *exo*-2-(4-bromophenyl)norbornane with tritiated water followed by normal work-up gave exo-2-([4-^{3}H]*phenyl*)*norbornane*, b.p. 77 °C at 0.8 mmHg, n_D^{20} 1.5455.

1-[4-^{3}H]*Phenyladamantane*.—The general routes used above cannot be employed to prepare 1-(4-bromophenyl)-adamantane because the adamantyl group apparently substitutes into more than one benzene ring; [20] one would also expect that more than one adamantyl group would substitute into each benzene ring, this being the usual observation for alkylation; these problems of polysubstitution can now be avoided by the use of iron(III) chloride as catalyst.[21] Topsom and his co-workers [6] used the alternative low-temperature (this we find is critical) adamantylation of bromobenzene using aluminium chloride as catalyst. By this route we obtained 1-(4-bromophenyl)adamantane (61%), m.p. 97—100 °C (lit.,[6] 94.5—95 °C); there were, however, substantial by-products, the main one of which we judge by its g.l.c. retention time to be 1,4-diadamantylbenzene, produced by alkyldehalogenation, a hitherto unobserved electrophilic substitution. We hope to examine this side reaction [which could almost certainly be suppressed by using iron(III) chloride as catalyst] at a future date.

Hydrolysis of the Grignard reagent formed in dry tetrahydrofuran from 1-(4-bromophenyl)adamantane with tritiated water and work-up followed by recrystallisation from I.M.S.* gave 1-([4-^{3}H]*phenyl*)*adamantane* (86%), m.p. 79.5—80.5 °C (lit.,[6] 78—80 °C). We found that different batches of 1-(4-bromophenyl)adamantane with only slight differences in m.p. showed a wide variation in reactivity in the Grignard reaction, the reason for this being unknown; 'unreactive' batches did however react with n-butyllithium.

1-([4-^{3}H]*Phenyl*)*bicyclo*[2.2.2]*octane*.—The Grignard reagent formed in tetrahydrofuran from 1-(4-bromophenyl)-bicyclo[2.2.2]octane † was hydrolysed with tritiated water to give, after normal work up followed by recrystallisation from I.M.S., 1-([4-^{3}H]*phenyl*)*bicyclo*[2.2.2]*octane*, m.p. 80 °C (lit.,[19] 78—80 °C).

Kinetic Studies.—These were carried out as previously described [22] with the modification for the bicyclo[2.2.2]-octyl and adamantyl compounds, that the initial solution of aromatic compound in trifluoroacetic acid was filtered through Celite before dividing and sealing in ampoules.

* Industrial Methylated Spirits.

† Kindly donated by Dr. K. J. Toyne, Hull University.

This is because these compounds are very slow to dissolve, and preliminary runs showed the presence of individual particles of aromatic compound which could not be dissolved without very extensive shaking times being used.

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