# Electrophilic Aromatic Reactivities *via* Pyrolysis of Esters. Part 20.[1] The Electronic Effect of Large Alkyl Groups in the Gas Phase

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The compounds *p*-$RC_6H_4CH(OAc)CH_3$, where R = adamantan-1-yl, neopentyl, *endo*-norbornan-2-yl, and *exo*-norbornan-2-yl, have been prepared and pyrolysed over a temperature range of at least 50° for each compound, between 617 and 678 K. The data give the corresponding *p*-R $\sigma^+$ values as —0.425, —0.35, —0.39, and —0.42, which show that these bulky substituents are all substantially more activating than in solution reactions in highly solvating media, where their effect is masked by steric hindrance to solvation. Each substituent is more activating than in detritiation of [*p*-$^3$H]PhR in trifluoroacetic acid (which is relatively poorly solvating), but the differential effect is smaller than the difference in effects between detritiation and solvolyses of 1-aryl-1-methylpropyl chlorides in aqueous acetone (which is highly solvating). This result exactly parallels that noted previously for other bulky groups, *viz.* t-butyl, cyclohexyl, trimethylsilyl, and phenyl. The data confirm that *p-exo*-norbornan-2-yl is unambiguously more electron releasing than *p-endo*-norbornan-2-yl and this is interpreted as a conformational effect. These alkyl groups release electrons mainly *via* C–C hyperconjugation, but in the *endo*-compound the aryl *p*-orbitals are prevented from becoming coplanar with the 2,3-bond because of steric interaction between the aryl *ortho*-hydrogen and the *endo*-6-hydrogen in the substituent; this interaction is the same as that which facilitates protiodealkylation of *endo*-norbornan-2-ylbenzene.

THE background to the present study is given in the preceding paper.[2] This study describes results for pyrolysis of 1-arylethyl acetates (1), a reaction which proceeds *via* the partial formation of a carbocation at C-1,

$$p\text{-}RC_6H_4\underset{\underset{OAc}{|}}{C}HCH_3 \xrightarrow{\Delta} p\text{-}RC_6H_4CH{=}CH_2 + HOAc \quad (1)$$

R = neopentyl, adamantan-1-yl, *exo*-norbornan-2-yl, *endo*-norbornan-2-yl

and this provides a gas-phase measure of the electrophilic reactivity of the aromatic. The reaction data normally give an excellent correlation with $\sigma^+$ values, significant departures being observed only with compounds containing bulky alkyl (and similar) substituents, and these are all more activating than in solution; in the gas phase the absence of steric hindrance to solvation permits the true electron-releasing ability of the substituent to be observed. For the substituents in the present study, the $\sigma^+$ values should therefore be larger (more negative) than found for detritiation.[2] Owing to preparative difficulties it was not possible to study the effect of the *p*-bicyclo[2.2.2]octan-1-yl substituent in the gas phase, but an estimate of its probable $\sigma^+$ value is made based on the effects of the other substituents.

## RESULTS AND DISCUSSION

The kinetic data are given in Table 1, and from the log $k/k_0$ values and the $\rho$ factor for the reaction at 625 K (—0.63) the $\sigma^+$ values were obtained as given in Table 2. Included in the latter for comparative purposes are the data previously obtained.[3] The main features of the results are as follows.

(i) The $\sigma^+$ values obtained for each substituent are larger than those obtained under any other condition, as predicted. The gas-phase values thus represent the true electron-releasing abilities of these substituents. It is interesting to note therefore that i.r. studies (poorly solvating conditions) indicated [4] that the *p*-adamantan-1-yl substituent should be almost as electron releasing as the *p*-cyclopropyl substituent (for which $\sigma^+$ is —0.473),[5] and the gas-phase results confirm that this is so.

(ii) The differences between the gas-phase and solvolysis $\sigma^+$ values increase approximately with size, as expected,† and thus the difference is biggest for the *p*-adamantan-1-yl substituent.

(iii) The differences between the gas-phase and detritiation $\sigma^+$ values are smaller than those between the detritiation and solvolysis values. This exactly parallels our previous observations for the other substituents and follows from trifluoroacetic acid being a poor solvating medium. Hence of all electrophilic aromatic substitutions, those carried out in trifluoroacetic acid will give results which most accurately represent the true electron-releasing abilities of large alkyl groups.

(iv) The results for the *p-exo*- and *endo*-norbornan-2-yl substituents confirm that the former is the more electron releasing under all conditions. The results of Jensen and Smart (who obtained corresponding $\sigma^+$ values of —0.357 and —0.336 in benzoylation) [6] do therefore represent the *relative* electron-releasing abilities of these substituents (*cf.* ref. 7). Jensen and Smart suggested that since the high activation by these substituents could only arise from carbon–carbon hyperconjugation, and because this concept was not widely accepted at that time, then this mode of electron release would be especially enhanced by strain in the norbornanyl substituent. It is now clear that carbon–carbon hyperconjugation is the main mode of electron release of all large alkyl groups,[3] but nevertheless

† The *decrease* in the value for *p*-methyl probably reflects either small errors in the reaction $\rho$ factors, or different resonance demands of each reaction. Correction of the *p*-Me value for this would make $\Delta\sigma^+$ for the other substituents slightly greater than given in Table 2.

TABLE 1

Pyrolysis of the compounds $p$-$RC_6H_4CH(OAc)Me$

| R | $T$/K | $10^3k$/s$^{-1}$ | log($A$/s$^{-1}$) | $E$/kJmol$^{-1}$ | log $k/k_0$ at 625 K | Correlation coefficient |
|---|---|---|---|---|---|---|
| H | 677.4 | 38.9 | 12.405 | 179.4 | 0 | 0.999 68 |
| | 677.0 | 36.1 | | | | |
| | 672.0 | 28.65 | | | | |
| | 667.7 | 24.3 | | | | |
| | 666.1 | 21.9 | | | | |
| | 663.1 | 18.5 | | | | |
| | 662.9 | 18.2 | | | | |
| | 651.9 | 10.9 | | | | |
| | 649.7 | 9.57 | | | | |
| | 639.4 | 5.73 | | | | |
| | 639.2 | 5.66 | | | | |
| | 638.1 | 5.37 | | | | |
| | 636.4 | 4.86 | | | | |
| | 620.5 | 1.935 | | | | |
| Neopentyl | 677.4 | 59.8 | 12.414 | 176.8 | 0.222 | 0.999 91 |
| | 667.7 | 38.0 | | | | |
| | 651.9 | 17.5 | | | | |
| | 639.1 | 9.24 | | | | |
| | 638.1 | 8.82 | | | | |
| | 617.1 | 2.73 | | | | |
| Adamantan-1-yl | 677.4 | 66.5 | 12.380 | 175.85 | 0.268 | 0.999 82 |
| | 672.0 | 49.7 | | | | |
| | 666.4 | 39.0 | | | | |
| | 649.7 | 17.9 | | | | |
| | 638.1 | 9.37 | | | | |
| | 617.1 | 3.10 | | | | |
| *endo*-Norbornan-2-yl | 677.0 | 62.1 | 12.341 | 175.65 | 0.246 | 0.999 83 |
| | 672.0 | 49.5 | | | | |
| | 667.7 | 38.55 | | | | |
| | 666.4 | 36.95 | | | | |
| | 666.1 | 36.3 | | | | |
| | 651.9 | 18.4 | | | | |
| | 649.7 | 16.8 | | | | |
| | 636.4 | 8.22 | | | | |
| | 620.5 | 3.60 | | | | |
| *exo*-Norbornan-2-yl | 677.4 | 64.4 | 12.384 | 175.95 | 0.265 | 0.999 94 |
| | 667.6 | 41.4 | | | | |
| | 651.9 | 19.6 | | | | |
| | 638.1 | 9.53 | | | | |
| | 617.6 | 3.14 | | | | |

TABLE 2

Values of $\sigma^+$ derived from various reactions

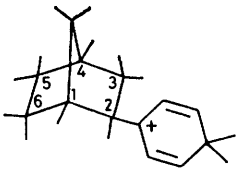
| Substituent | Solvolysis in aqueous acetone | Detritiation in $CF_3CO_2H$ | Pyrolysis in gas phase | $\sigma^+_{solv.} - \sigma^+_{pyrolysis}$ |
|---|---|---|---|---|
| $p$-Me | −0.311 | −0.303 | −0.290 | −0.021 |
| $m$-Me | −0.066 | −0.090 | −0.098 | 0.032 |
| $p$-Bu$^t$ | −0.256 | −0.312 | −0.365 | 0.109 |
| $m$-Bu$^t$ | −0.059 | −0.175 | −0.190 | 0.131 |
| $p$-$SiMe_3$ | 0.020 | | −0.090 | 0.110 |
| $m$-$SiMe_3$ | 0.010 | | −0.160 | 0.170 |
| $p$-Cyclohexyl | −0.285 | −0.338 | −0.380 | 0.095 |
| $p$-Neopentyl | −0.240 | −0.306 | −0.350 | 0.110 |
| $p$-Adamantan-1-yl | −0.250 | −0.377 | −0.425 | 0.175 |
| $p$-Bicyclo[2.2.2]octan-1-yl | −0.270 | −0.391 | (*ca.* −0.44) [a] | |
| $p$-*endo*-Norbornan-2-yl | −0.295 | −0.358 | −0.390 | 0.095 |
| $p$-*exo*-Norbornan-2-yl | −0.309 | −0.371 | −0.420 | 0.111 |

[a] Estimated value based on the results for the other substituents.

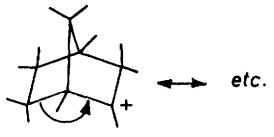
there may be some strain enhancement of this (compare the $\sigma^+$ values for $p$-cyclohexyl and $p$-*exo*-norbornan-2-yl).

The greater electron release by the *exo*-substituent probably has nothing to do with σ-bond participation because there can be no direct conjugation between the electrons of the 1,6-bond and the *para*-positive charge in the transition state (I); only a secondary relay effect might operate. This contrasts of course with solvolysis of norbornan-2-yl derivatives where the positive charge is developed within the substituent (II). We believe that a conformational effect is responsible for the difference in electron release. For carbon–carbon hyperconjugation to occur the aryl $p$-orbitals must be able to be coplanar with the 1,2- and 2,3-bonds. In the *exo*-compound there is no inhibition of this, but in the *endo*-compound conformation (III) involves a steric interaction between the aryl-ring *ortho*-hydrogen and the *endo*-hydrogen at the 6-position. This is precisely the conformation which appears to cause *endo*-norbornan-2-

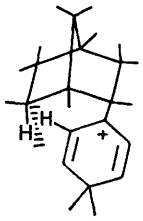
ylbenzene to undergo protiodealkylation in the presence of acids.[2]



(I)



(II)



(III)

EXPERIMENTAL

1-(4-*Neopentylphenyl*)*ethyl Acetate*.—1-*Acetyl*-4-*neopentylbenzene*. Aluminium chloride (13 g, 0.16 mol) was added during 4 h to neopentylbenzene (15 g, 0.1 mol), 1,2-dichloroethane (150 ml), and acetyl chloride (13 g, 0.17 mol) contained in a 250 ml three-necked flask fitted with a stirrer, condenser, and hydrogen chloride trap. The mixture was heated under reflux during a further 4 h, then cooled, hydrolysed with 2N-hydrochloric acid, and worked up as normal to give, after fractional distillation, 1-*acetyl*-4-*neopentylbenzene* (11 g, 60%), b.p. 60—62 °C at 0.2 mmHg, $n_D^{20}$ 1.5162 (Found: C, 82.1; H, 9.5. $C_{13}H_{18}O$ requires C, 82.1; H, 9.5%).

1-(4-*Neopentylphenyl*)*ethanol*. 1-Acetyl-4-neopentylbenzene (11 g, 0.0058 mol) was reduced with sodium borohydride in the usual way, followed by normal work-up to give, after fractional distillation and recrystallisation from light petroleum, 1-(4-*neopentylphenyl*)*ethanol* (10 g, 90%), b.p. 64 °C at 0.1 mmHg, m.p. 64 °C (Found: C, 80.9; H, 10.4. $C_{13}H_{20}O$ requires C, 81.2; H, 10.5%).

Acetylation of the alcohol with pyridine and acetic anhydride with heating during 2 h, followed by normal work-up gave, after fractional distillation, 1-(4-*neopentylphenyl*)*ethyl acetate* (7 g, 60%), b.p. 83 °C at 0.1 mmHg, $n_D^{20}$ 1.4902, τ($CCl_4$) 9.12 (9 H, s, $CH_3$), 8.55 (3 H, d, $CH_3$), 8.06 (3 H, s, $COCH_3$), 7.6 (2 H, s, $CH_2$), 4.25 (s, CH), and 2.95 (4 H, q, ArH) (Found: C, 76.7; H, 9.4. $C_{15}H_{22}O_2$ requires C, 76.9; H, 9.5%).

1-[4-(exo-*Norbornan*-2-*yl*)*phenyl*]*ethyl Acetate*.—exo-2-(4-*Acetylphenyl*)*norbornane*. This was prepared according to the literature method [7] and was obtained in 80% yield, b.p. 164 °C at 1.6 mmHg, $n_D^{20}$ 1.5625 (lit.,[7] 1.5685). 1-[4-(exo-*Norbornan*-2-*yl*)*phenyl*]*ethanol*. exo-2-(4-Acetylphenyl)-norbornane was reduced with sodium borohydride in the usual way. Normal work-up followed by sublimation at 60 °C at 0.1 mmHg gave 1-[4-(exo-*norbornan*-2-*yl*)*phenyl*]-*ethanol* (75%), m.p. 73—74 °C (Found: C, 84.2; H, 8.8. $C_{15}H_{18}O$ requires C, 84.1; H, 8.5%).

Acetylation of the alcohol as above followed by fractional distillation gave 1-[4-(exo-*norbornan*-2-*yl*)*phenyl*]*ethyl acetate* (83%) b.p. 84 °C at 0.1 mmHg, $n_D^{20}$ 1.5274 (Found: C, 79.2; H, 8.4. $C_{17}H_{20}O_2$ requires C, 79.0; H, 8.5%).

1-[4-(endo-*Norbornan*-2-*yl*)*phenyl*]*ethyl Acetate*.—endo-2-(4-*Acetylphenyl*)*norbornane*. *endo*-2-Phenylnorbornane [2] (25 g, 0.145 mol) was dissolved in chloroform (200 ml) in a flask equipped with stirrer, dropping funnel, and hydrogen chloride trap. Aluminium chloride (19.3 g) was added, the temperature lowered to 0 °C, and acetyl chloride (11.4 g, 0.145 mol) added slowly with rapid stirring at 0 °C during 2 h. The temperature was then allowed to rise to ambient and the mixture was hydrolysed and worked up in the usual way to give, after fractional distillation, *endo*-2-(4-acetylphenyl)norbornane (7.5 g, 24%), b.p. 126 °C at 0.2 mmHg, $n_D^{20}$ 1.5652 (lit.,[7] $n_D^{20}$ 1.5476; this is wrong as the *exo*- and *endo*-compounds must have fairly similar values). The low yield in this preparation indicated that the acetylation temperature was higher than optimal.

1-[4-(endo-*Norbornan*-2-*yl*)*phenyl*]*ethanol*. *endo*-2-(4-Acetylphenyl)norbornane (7.5 g, 0.035 mol) was reduced with sodium borohydride in the usual way followed by normal work-up to give the crude alcohol. This was acetylated directly as above to give, after work-up and fractional distillation, 1-[4-(endo-*norbornan*-2-*yl*)*phenyl*]*ethyl acetate* (7.5 g, 83%), b.p. 120 °C at 0.25 mmHg, $n_D^{20}$ 1.5336 (Found: C, 79.3; H, 8.6%).

1-(4-*Adamantan*-1-*ylphenyl*)*ethyl Acetate*.—1-(4-*Acetylphenyl*)*adamantane*. This was prepared in 40% yield by the literature method [4] and had the quoted m.p. A higher yield could probably be obtained if iron(III) chloride was used as the catalyst instead of aluminium chloride. Side reactions are due to the high electrophilic reactivity of 1-phenyladamantane as deduced in this paper.

1-(4-*Adamantan*-1-*ylphenyl*)*ethanol*. Reduction of the above ketone with sodium borohydride, followed by normal work-up and recrystallisation from I.M.S.,* gave 1-(4-*adamantan*-1-*ylphenyl*)*ethanol* (95 %), m.p. 154—155 °C, τ($CDCl_3$) 8.52 (3 H, d, $CH_3$), 8.18 (6 H, d, $CH_2$), 8.18 (6 H, d, $CH_2$), 7.92 (3 H, m, CH), 6.32 (q, CH), and 2.65 (4 H, s, ArH) (Found: C, 81.6; H, 9.4. $C_{18}H_{24}O$ requires C, 81.5, H, 9.45%).

Acetylation of the alcohol as above and work-up followed by recrystallisation from I.M.S. gave 1-(4-*adamantan*-1-*ylphenyl*)*ethyl acetate* (80 %), m.p. 48 °C, τ($CDCl_3$) 8.48 (3 H, d, $CH_3$), 8.16 (6 H, d, $CH_2$), 8.16 (6 H, d, $CH_2$), 7.97 (3 H, s, $COCH_3$), 7.97 (3 H, m, CH), 4.10 (q, CH), and 2.66 (4 H, s, ArH).

*Kinetic Studies*.—The kinetic method has been described [8] and the data are given in Table 1; as is customary for solid esters 1-(4-adamantan-1-ylphenyl)ethyl acetate was injected into the reactor as a solution in chlorobenzene since this has no effect on the reaction rates and is stable under the reaction conditions.[9]

It should be noted that the rate data for the unsubstituted ester do not correspond precisely with those reported previously.[10] This is unimportant with regard to the conclusions which we draw because these are based upon relative rates measured under the same conditions. There are two reasons for the differences in the data.

(i) New stainless steel immersion heaters for the furnace were used in this study, and the temperature gradient within

* Industrial Methylated Spirits

the heaters was not the same as in those used previously. A different, and we believe more representative, point within the furnace was chosen to measure the temperature of the reactions.

(ii) The thermocouples were recalibrated using a new standard N.P.L. thermocouple calibrated to a higher accuracy (± 0.25 °C) than the standard used previously.

The result of these differences is that the present rate coefficients are slightly smaller for a given temperature than those reported previously and the magnitude of the change is such as to produce a small difference (in the second decimal place) of the log ($A/s^{-1}$) value. We believe that the absolute temperatures recorded in this and subsequent papers are more accurate than those given hitherto.

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