Electronic Effects of Bridgehead Alkyl Substituents: Adamantan-1-yl and Bicyclo[2,2,2]octan-1-yl

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Syntheses are reported for *p*-bicyclo[2,2,2]octan-1-yl- and *p*-adamantan-1-yl-benzoic acids and for the corresponding -2-chloropropanes. Determination of acidities and hydrolysis rates of these compounds gives σ_p values of $-0{\cdot}25$ and $-0{\cdot}24$ and $\sigma_p{}^+$ values of $-0{\cdot}27$ and $-0{\cdot}25$ for the bicyclo-octanyl and adamantanyl substituents. This virtual lack of enhancement of σ values is discussed.

MUCH interest continues to be shown in the effect of alkyl groups on physical properties and reactivities.[1] Recent results show that in the gas phase [2] large alkyl groups such as t-butyl are more polarisable than methyl groups and thus better stabilise either positive or negative charge; this is supported by theoretical calculations.[3,4] The order of either $|\sigma|$ or $|\sigma^+|$ values should thus be $\mathrm{Bu^t > Pr^i > Et > Me > H}$.

Considerable attention has also been given [5,6] to solvation effects on reactions and equilibria in order to explain observed orders. Thus the order of the partial rate factors for the *para*-bromination of toluene and t-butylbenzene can be reversed [6] depending on solvent. Almost all work in solution to date has concerned only the 'big four' [7] alkyl groups above, and in particular σ-values are not available for bridgehead alkyl substituents. The σ-values already available for Me and Bu^t (Table 1) suggest that the latter has a larger σ_p than the former, but the reverse for the $\sigma_p{}^+$ values. The relative $\sigma_p{}^+$ values may arise from a greater steric inhibition of solvation in the $\alpha\alpha$-dimethyl-*p*-t-butylbenzyl chloride hydrolysis compared with that in the *p*-methyl compound. Bridgehead substituents such as adamantan-1-yl or bicyclo[2,2,2]octan-1-yl should greatly enhance

TABLE 1

Hammett σ-values for various alkyl substituents

R	$-\sigma_p$	$-\sigma_p{}^+$	$-\sigma_{\mathrm{R}}{}^0$
Me	0·170 [a]	0·306 [d]	0·099 [f]
Et	0·150 [a]	0·291 [d]	0·103 [f]
Pr^i	0·151 [a]	0·276 [d]	0·115 [f]
Bu^t	0·197 [a]	0·250 [d]	0·125 [f]
Cpr [h]	0·22 [b]	0·46 [e]	0·175 [f]
BCO	0·25 [c]	0·27 [c]	0·169 [g]
Ad [j]	0·24 [c]	0·25 [c]	0·147 [g]

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such an effect. In addition much interest continues to be shown [8] in the adamantane system; its reactivity at the bridgehead position has been the subject of experimental [9] and theoretical studies,[10] and it has been claimed to be a relatively strong electron donor.[11] The bicyclo[2,2,2]octan-1-yl system has been used as a model for the benzene ring in both theoretical [12] and experimental studies.[13]

RESULTS AND DISCUSSION

Table 1 lists the σ_p and σ_p^+ values determined for the adamantanyl (Ad) and bicyclo-octanyl (BCO) substituents together with values for Me, Et, Pr^i, Bu^t, and cyclopropyl groups for comparison. Values for σ_R^0 are also included.

The $|\sigma_p|$ values determined from the dissociation constants of the appropriately substituted benzoic acids are rather greater than those for simple alkyl groups, indicating a greater relative ability for release of electrons. The values of 0·25 and 0·24 are, in fact, greater than the 0·22 obtained for the cyclopropyl substituent. Results listed for σ_R^0 (the interaction with the π-system of a benzene ring in the appropriate alkyl benzene) are consistent with these results and show that the effect is not of an inductive nature. The ring systems of BCO and Ad are fairly rigid but relatively strain free and any effect resulting from a slightly different hybridisation at the bridgehead position compared with, for example, a t-butyl group are likely to be small.[4,14] The BCO and Ad groups clearly are able to interact with the π-system of the benzene ring to a marked degree and one might therefore expect them to be more polarisable than simple alkyl groups. However, their σ_p^+ values (approximately the same as that for a t-butyl group) are virtually unenhanced compared with their σ_p values. This contrasts markedly with the results for a cyclopropyl group. This would appear to be the first example of a moderate or strong electron-releasing substituent having almost identical σ_p and σ_p^+ values. It is unlikely [4,14] that this lack of enhacement with respect to electron demand is related to changes in hybridisation, and we suggest that it results from steric inhibition of solvation of the transition state in the hydrolyses of the 2-aryl-2-chloropropanes, the reaction leading to the σ_p^+ values. This is supported by i.r. results on *p*-substituted phenylbicyclo-octane and phenyladamantane, which indicate [15] that in carbon tetrachloride the Ad and BCO substituents are almost as polarisable as a cyclopropyl group. It is interesting to look at σ_p^+ or related values for alkyl groups derived by other methods less likely to be effected by solvation. Results from measurement of charge-transfer spectra [16] of monosubstituted benzenes with tetracyanoethylene would suggest a higher σ^+ value for the t-butyl than the methyl substituent and i.r. results [17] on *p*-substituted alkylbenzenes would likewise indicate that the t-butyl group was a better donor than methyl in response to electron demand. These results are clearly in accord with those in the gas phase [2] and the theoretical calculations [3] mentioned before.

The charge-transfer results and measurements on the intensity of the ν_{CN} vibration of *p*-substituted benzonitriles [18] would suggest a σ_p^+ value in non-polar media of *ca.* $-0·22$ for methyl, while the former would suggest a value of *ca.* $-0·3$ for t-butyl. It may be that at least part of the effect in the hydrolyses arises from solvent assistance to conjugation between the methyl group and the ring. Such solvent assistance would certainly be at a minimum in Ad and BCO, since approach to the rear of α-carbon of the alkyl substituent is effectively prevented.

EXPERIMENTAL

The identity of all compounds was established by their physical constants, i.r. and n.m.r. spectra, and elemental analyses. Purity was confirmed by g.l.c. on a Hewlett Packard model 5750 research gas chromatograph with a 3 ft × $\frac{1}{8}$ in stainless steel column packed with 10% SE30 on chromosorb WAWDMCS at 150—220°. M.p.s were all uncorrected. I.r. spectra were recorded with a Perkin-Elmer model 257 instrument. N.m.r. spectra were recorded with a Varian T60 spectrometer with tetramethylsilane as internal standard and carbon tetrachloride as solvent.

1-*Phenylbicyclo*[2,2,2]*octane*.—This was prepared as described by Chapman and co-workers,[19] m.p. 78—79° (lit., 78—80°).

p-*Bicyclo*[2,2,2]*octan*-1-*ylacetophenone*.—The product from acetylation of 1-phenylbicyclo[2,2,2]octane with acetyl chloride–aluminium chloride in chloroform at 20 °C was chromatographed on alumina. Elution with light petroleum (b.p. 40—60°) gave starting material, while the product (45%), m.p. 88—90° [from light petroleum (b.p. 40—60°)], was eluted from the column with chloroform (Found: C, 84·0; H, 8·45. Calc. for $C_{16}H_{20}O$: C, 84·2; H, 8·8%).

2-(p-*Bicyclo*[2,2,2]*octan*-1-*ylphenyl*)*propan*-2-*ol*.— Reaction of methylmagnesium iodide with *p*-bicyclo[2,2,2]-octan-1-ylacetophenone in anhydrous ether gave the carbinol (90%), m.p. 116—117° [from light petroleum (b.p.

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40—60°)] (Found: C, 83·7; H, 9·8. Calc. for $C_{17}H_{24}O$: C, 83·6; H, 9·8%).

2-(p-*Bicyclo*[2,2,2]*octan*-1-*ylphenyl*)-2-*chloropropane*.—Treatment of the foregoing alcohol with HCl in benzene[20] gave the substituted cumyl chloride. This product was dried and used in the kinetics without further purification.

p-*Bicyclo*[2,2,2]*octan*-1-*ylbromobenzene*.—Bromination of phenylbicyclo[2,2,2]octane with bromine–pyridine at room temperature[21] gave exclusively the *p*-substituted product in quantitative yield (g.l.c.). This was recrystallised from methanol and then sublimed at 110° at 0·5 mmHg, m.p. 49—51° (Found: C, 63·2; H, 6·55. Calc. for $C_{14}H_{17}Br$: C, 63·4; H, 6·4%).

p-*Bicyclo*[2,2,2]*octan*-1-*ylbenzoic Acid*.—The Grignard reagent from *p*-bicyclo[2,2,2]octan-1-ylbromobenzene was prepared in tetrahydrofuran, which had been distilled directly from sodium wire into the reaction vessel. The mixture was heated at reflux for 3 h, cooled, and poured onto dry ice. After all the dry ice had been consumed the mixture was acidified (dilute HCl), extracted with chloroform, and the extracts were washed (H_2O), dried ($MgSO_4$), and evaporated to dryness. The residue was washed with cold light petroleum (b.p. 40—60°) to remove *p*-bromophenyl- and phenyl-bicyclo[2,2,2]octane, dried, and chromatographed on alumina. The required product, m.p. 258—260°, was eluted with methanol containing 1% conc. HCl (Found: C, 78·2; H, 8·05. Calc. for $C_{15}H_{18}O_2$: C, 78·3; H, 7·8%).

Adamantan-1-*ylbromobenzenes*.—A solution of 1-bromoadamantane (20 g) in bromobenzene (85 ml) was added slowly to a boiling mixture of anhydrous iron(III) chloride (20 g) in bromobenzene (150 ml). The mixture was heated to reflux for 5 h, then cooled and poured onto ice–conc. HCl. The organic layers were combined, dried (Na_2SO_4), and concentrated. Distillation of the residue afforded adamantan-1-ylbromobenzenes (*m*- and *p*-) (16·6 g, 27%), b.p. 170—180° at 1 mmHg. The product was recrystallised from methanol and sublimed (100° at 0·2 mmHg) to assure complete removal of solvent, m.p. 94·5°, $\nu_{max.}$ (Nujol) 859, 775, 695 (*m*-disubstituted benzene), 835, 805, and 719 (*p*-disubstituted benzene) cm^{-1} (Found: C, 65·7; H, 6·4; Br, 27·1. Calc. for $C_{16}H_{19}Br$: C, 66·0; H, 6·6; Br, 27·4%).

p-*Adamantan*-1-*ylbenzoic acid*.—This was prepared from adamantylphenylmagnesium bromide by the method described before for the bicyclo-octyl analogue. The product was sublimed to give a white powder, m.p. 260—270° (decomp.), $\nu_{max.}$ (Nujol) 1685 (C=O), 857, 775, 709 (*p*-disubstituted benzene), 805, 755, and 700 (*m*-disubstituted benzene) cm^{-1} (Found: C, 79·5; H, 7·6. Calc. for $C_{17}H_{20}O_2$: C, 79·65; H, 7·9%).

Esterification of the above acid with methanol–HCl gave a mixture of methyl *p*- and *m*-adamantan-1-ylbenzoates. Recrystallisation from methanol gave a sample of pure methyl *p*-adamantan-1-ylbenzoate, which was sublimed to give white needles, m.p. 143° $\nu_{max.}$ (Nujol) 1725 (C=O), 852, 770, and 707 cm^{-1} (Found: C, 79·8; H, 8·3. Calc. for $C_{18}H_{22}O_2$: C, 80·0; H, 8·2%).

Hydrolysis of the *p*-ester with 10M-sodium hydroxide gave *p*-adamantan-1-ylbenzoic acid, m.p. 316°, $\nu_{max.}$ (Nujol) 1685 (C=O), 857, 775, and 709 cm^{-1}.

1-*Phenyladamantane*.—Treatment of the Grignard reagent from adamantan-1-ylbromobenzene (in tetrahydrofuran) with water afforded 1-phenyladamantane as white crystals, m.p. 78—80° (lit.,[22] 82°) after sublimation at 120° at 0·1 mmHg.

p-*Adamantan*-1-*ylacetophenone*.—Acetylation of 1-phenyladamantane with acetyl chloride–aluminium chloride in chloroform at −20 °C and chromatography of the product (as for the bicyclo-octanyl analogue) gave *p*-adamantan-1-ylacetophenone. The product (40%) was crystallised from light petroleum (b.p. 40—60°) and sublimed at 120° and 0·1 mmHg; m.p. 105—107°, $\nu_{max.}$ (Nujol) 836 and 810 cm^{-1}, δ 7·56 p.p.m. (4H, q) (Found: C, 85·0; H, 8·8. Calc. for $C_{18}H_{22}O$: C, 85·0; H, 8·7%).

2-(p-*Adamantan*-1-*ylphenyl*)*propan*-2-*ol*.—The reaction of methylmagnesium iodide with *p*-adamantan-1-ylacetophenone gave the carbinol (88%), m.p. 113—115° (from pentane) $\nu_{max.}$ (Nujol) 3360 (OH), 840, and 812 cm^{-1}. An identical product was obtained from the reaction of the corresponding ester with 2 mol of methylmagnesium iodide.

2-(p-*Adamantan*-1-*ylphenyl*)-2-*chloropropane*.—Treatment of the preceding carbinol with HCl in benzene gave the chloride. The product was dried and used for kinetics without further purification.

pK_a *Determinations*.—Dissociation constants were measured by the conventional indicator method,[23,24] in methanol–chloroform (4 : 1) with Bromocresol Green as indicator.

Spectrophotometric measurements were made at 620 nm (base form of indicator) using a Unicam SP 500 u.v.-visible spectrophotometer and stoppered 1-cm glass cells at ambient temperatures. Since ρ is not known in this solvent a number of acids were measured to get a measure of ρ. The

TABLE 2

pK_a Values for *p*-substituted benzoic acids relative to Bromocresol Green in methanol–chloroform (4 : 1) at ambient temperature

p-Substituent	$-\Delta$
MeO	0·02
Bu^t	0·18
Me	0·21
H	0·44
Br	0·81
Cl	0·79
Adamantan-1-yl	0·10
Bicyclo[2,2,2]octan-1-yl	0·09

TABLE 3

Kinetic data for the solvolysis of 2-(*p*-substituted phenyl)-2-chloropropanes in 90% acetone–water at 25°

p-Substituent	$10^4k_1/s^{-1}$	$\log k_1^X/k_1^H$
H	1·40	0
Me	37·9; 38·2	1·43[a]
Bu^t	20·3; 19·8	1·16[b]
Adamantan-1-yl	19·6; 19·6; 20·8	1·155
Bicyclo-octan-1-yl	24·2; 24·5	1·24

[a] 1·42 (ref. 19). [b] 1·16 (ref. 19).

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pK_a of Bromocresol Green is not known in this mixture. Instead they are all quoted as Δ values, *i.e.* relative to Bromocresol Green (equation 1). A value of 1·50 for ρ was

$$pK_a - pK_{Ind} = \Delta = \log [HA]/[A] + \log \alpha \qquad (1)$$

obtained under these conditions and this allowed σ_p values of −0·24 (adamantan-1-yl) and −0·25 (bicyclo[2,2,2]-octan-1-yl) to be calculated (see Table 2).

Solvolysis Kinetics.—These were carried out in acetone–water (9 : 1, v/v) at 25° according to the method of Brown.[20] His results [20] for some alkyl substituted cumyl chlorides were duplicated and the ρ value of −4·62 [25] was used therefore to determine σ_p^+ values of −0·25 (adamantan-1-yl) and −0·27 (bicyclo[2,2,2]octan-1-yl) (see Table 3).

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