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Diastereofacial selectivity in some 4-substituted (X) 2-adamantyl derivatives: electronic *versus* steric effects

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π-Facial selectivity data for the reduction and methylation of some 4^{ax}-substituted (X) 2-adamantanones (3, Y = O) as well as the nucleophilic trapping of secondary and tertiary 4^{ax}-substituted (X)-2-adamantyl cations (4; R = H and CH_3, respectively) and the 4-methylene-2-adamantyl radical (8) are presented. The pronounced *anti*-face selectivities observed for (3, Y = O and 4, R = CH_3) emphasize the importance of the steric factor as expected for systems with a strong steric bias. However, the dominant *syn*-face capture of 4 (R = H) was completely unexpected and highlights a subtle interplay between steric and electronic effects. Finally, the very high *anti*-face stereoselectivity for the trapping of (8) with the trimethylstannyl anion (Me_3Sn^-) is rationalized in terms of an electrostatic effect overwhelming the steric factor. Copyright © 2007 John Wiley & Sons, Ltd.

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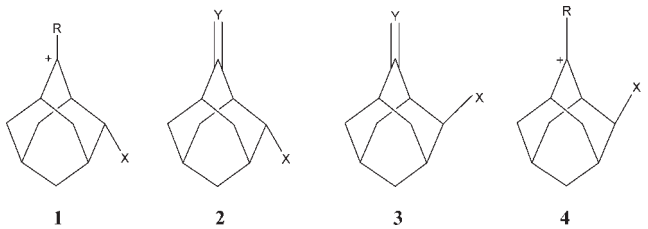
Keywords: adamantane; diastereofacial selectivity; substituent effects; steric effects; electronic effects

INTRODUCTION

By the use of rigid model systems in which steric and conformational effects can be effectively segregated, electronic effects have been shown unambiguously to be a significant factor governing diastereofacial selectivity of additions to trigonal carbon centres.[1] However, in most general situations where all factors are at play in determining π-face selectivity steric effects, which are well recognized and reasonably predictable, generally predominate. The number of examples where the electronic factor overwhelms steric effects are relatively rare,[2] consequently, it was of considerable interest when we discovered unexpectedly several examples which emerged from our recent study of face selection in the nucleophilic capture of secondary (R = H) and tertiary (R = CH_3) 4^{eq}-substituted (X) 2-adamantyl cations (**1**).[3] The synthesis of the precursor 4^{eq}-substituted (X)-2-adamantanones (**2**, Y = O, X = F, Cl, Br, I and $Sn(CH_3)_3$) for this study also provided the corresponding 4^{ax}-substituted



1 **2** **3** **4**

ketones (**3**, Y = O). Essentially for the sake of completion, we subjected these latter compounds to the same reactions we performed on **2** (Y = O), namely, hydride reduction, methylation and olefination followed by fluorination and hydrochlorination of the alcohols and alkenes (**3**, Y = CH_2), respectively. Herein, we report the facial selectivity results of this apparently extraneous study of nucleophilic trapping of 4^{ax}-substituted (X)-2-adamantyl cations (**4**) in which it would be expected that the *axial* disposed group obviously exerts a pronounced steric bias. In addition, we also report on the stereochemical outcome of the trimethylstannylation of the bromo-alkenes (**2** and **3**, Y = CH_2 and X = Br) which was deployed for the synthesis of the tin-alkenes (**2** and **3**, Y = CH_2 and X = $Sn(CH_3)_3$).

EXPERIMENTAL SECTION

Synthesis of compounds

The ketones (**3**, Y = O) were available from another investigation.[3] The halo-alkenes (**3**, Y = CH_2) were prepared from the corresponding ketones in the same manner as previously described for the preparation of 1-bromo-4-methyleneadamantane from 5-bromoadamantan-2-one[4] and were obtained as colourless oils after kugelrohr distillation. ^{13}C NMR data for the aforementioned ketones and alkenes (**3**; Y = O and CH_2, respectively) together with calculated chemical shifts are listed in the Supplementary Material. Spectral assignments were made from additivity and APT methodology as well as chemical shift considerations and, in the main, are in accord with literature values.[5]

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General procedures for reduction ($NaBH_4$), methylation (MeLi) and hydrochlorination (HCl)

The procedures were all identical to those recently reported for **2** (Y = O and CH_2).[3] All the epimeric product mixtures were unambiguously characterized by ^{13}C NMR and analysed by VPC, GC-MS and ^{1}H NMR. The ^{13}C NMR chemical shifts of the various alcohols and chlorides are given in the Supplementary Material together with the calculated chemical shifts. The shifts are mainly in accord with available literature values although some minor discrepancies exist.

Fluorination of alcohol mixtures

Fluorination of the alcohols was performed utilizing DAST as the reagent in the same manner as recently described.[3] The fluoride mixtures were analysed by ^{13}C and ^{19}F NMR, VPC and GC-MS. The ^{13}C NMR chemical shifts of the fluorides are listed in the Supplementary Material together with the calculated shifts. The data are in accord with available literature values.[5e]

The relative selectivity data listed in the various Tables below are the average of determinations by several methods (^{13}C, ^{1}H and ^{19}F NMR, VPC-MS and VPC) and are accurate to ±3%.

Computational methods

The cation and radical calculations reported below were carried out at the B3LYP/6-31G* level of theory utilizing the GAUSSIAN 98 program package.[6] Analytical frequency calculations were performed on the minima and transition states of the density functional theory (DFT) optimized cation structures to determine zero-point vibrational energies (ZPVE) and, as well, to ensure $N_{imag} = 0$ and 1 for the minima and transition states. Other calculations were performed at the B3LYP/6-31 + G* level of theory. The NBO approach is described in detail by Weinhold *et al.*[7] and no detailed account is necessary here. Suffice to state that it is useful methodology for estimating quantitatively the energy of hyperconjugative effects by treating the delocalizing interactions by a standard second-order perturbation approach to provide so-called $E^{(2)}$ energies.

RESULTS AND DISCUSSION

Stereoselectivity of reduction and methylation of ketones (3, Y = O), hydrochlorination of alkenes (3, Y = CH_2) and fluorination of alcohols (5, R = H and CH_3)

The results of hydride reduction ($NaBH_4$) and methylation (CH_3Li) of 4-substituted (X^{ax})-2-adamantanones (**3**, Y = O; X = F, Cl, Br and I) are listed in Table 1 together with those recently reported.[8] It can be seen that 4^{ax}-substituted (X)-2^{ax}-adamantanols (**5**, R = H) and 4^{ax}-substituted (X) 2^{eq}-methyl-2^{ax}-adamantanols (**5**,

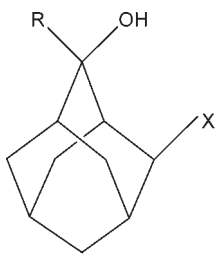

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Table 1. Product distributions for the reduction and methylation of some 4-substituted (X^{ax})-2-adamantanones (**3**, Y = O; X = F, Cl, Br and I)

	Reduction[a]		Methylation[b]	
X	%*E*	%*Z*	%*E*	%*Z*
F	2 (0)[c]	98 (100)[c]	1	99
Cl	0	100	0	100
Br	0 (0)[c]	100 (100)[c]	0	100
I	0	100	0	100
$Sn(CH_3)_3$	0	100	—	—

[a] $NaBH_4/CH_3OH/0\ ^\circ C$.
[b] $CH_3Li/Et_2O/0\ ^\circ C$.
[c] Reference [8].

R = CH_3) are almost the exclusive products. Clearly, the results highlight the dominant role of steric effects in controlling π-face selection during nucleophilic addition to the carbonyl group. This is well recognized and predictable. Thus, it can be seen (Table 1) that the steric factor (this includes electrostatic repulsion between the nucleophile and halogen unshared electrons in this factor)[8] of the 4-X^{ax} substituents dominates the electronic one and directs the reagent ($NaBH_4$ and CH_3Li) almost exclusively to the remote *anti*-face of the ketone (**3**,Y = O). It is worth noting that a simple visualization technique based on the electrostatic potential mapped onto the LUMO with an isosurface proximal to the reactive electrophilic site accurately predicts the *anti* and *syn* face attack by nucleophiles on **3** (Y = O, X = F; Table 1), respectively.[9] Although *a priori*, it is not possible to discriminate between the aforementioned two explanations for the *anti*-face preference of the fluoro-ketone (**3**, Y = O, X = F), we favour the former because through-space electrostatic repulsion between the approaching nucleophile and the substituent as a dominant influence governing diastereoselectivity appears to be an established phenomenon.[10]

The fluoride product mixtures obtained on the treatment of the *syn* (or *Z*) alcohols (**5**, R = H and CH_3; Table 1) with the DAST reagent are set out in Table 2. It should be noted that these substitution reactions proceed via an S_N1 mechanism with 2-adamantyl substrates.[11] A cursory examination of the data

Table 2. Product distributions for the fluorination[a] of some 4-substituted (X^{ax})-adamantan-2-ols (**5**, R = H and CH_3; as in Table 1)

	5 (R = H)		**5** (R = CH_3)	
X	%*E*	%*Z*	%*E*	%*Z*
F	15	85	90	10
Cl	11	89	93	7
Br	16	84	94	6
I	19	81	94	6

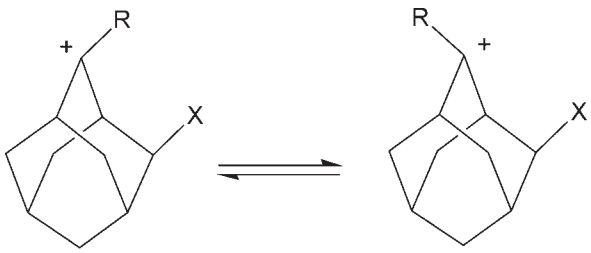
[a] $DAST/CH_2Cl_2$.

Table 3. Product distributions for the hydrochlorination[a] of some 4-substituted (X^{ax})-2-methyleneadamantanes (**3**, Y = CH_2; X = F, Cl, Br and I)

X	%*E*	%*Z*
F	94	6
Cl	100	0
Br	100	0
I	100	0

[a] HCl/CH_2Cl_2.

clearly reveals, quite unexpectedly, that the diastereoselectivities for the capture of the secondary and tertiary cations (**4**, H and CH_3, respectively) are diametrically opposed (*syn* and *anti*-face capture, respectively). Noteworthy is the fact that the product distributions for the hydrochlorination of some 4-substituted (X^{ax})-2-methyleneadamantanes (**3**, Y = CH_2; Table 3), being mediated by the tertiary ions (**4**, R = CH_3), also display pronounced *anti*-face selectivities. Within the framework of the picture presented for **1**[3], namely, that π-facial selectivity is essentially controlled by the relative stability of rapidly equilibrating solvated pyramidalized *syn* and *anti*-epimeric ions prior to capture by the nucleophile, it seems reasonable to assume that the initial formation of the pyramidalized *syn* (or *Z*)-cation readily undergoes interconversion to the epimeric *anti* (or *E*)-cation (**6** ⇌ **7**) prior to nucleophilic capture. A consideration of orbital and steric effects on the relative stability of these ions suggests that the latter ions (**7**) should predominate at equilibrium (*Z* > *E*). Consequently, the observed predominant



6 **7**

anti-face selectivity for both fluoride and chloride ion capture of the tertiary ion **4** (R = CH_3) can be reconciled in terms of **6** (R = CH_3) being captured much more rapidly than **7** (R = CH_3) as a result of steric factors (this includes electrostatic repulsion between the nucleophile and halogen unshared electrons) impeding the *syn* approach of the nucleophile in the latter ion. However, the unexpected stereochemical outcome of capture of the secondary cations (**4**, R = H) by the fluoride anion (Table 2), namely, dominant *syn*-face capture, appears to be a relatively rare situation where the trajectory is not governed by steric effects but by the electronic configuration of the initially formed cationic substrate. Apparently, the rate of conversion of **7** (R = H) to **6** (R = H) is slow with respect to fluoride ion capture which is surprising given the very low barrier between the two in the gas phase (as in Table 19, Supplementary Material). Significantly, this phenomenon has provided a means for the successful synthesis of an interesting model system, namely, *syn*-2,4-difluoroadamantane.[12]

It should be noted that the above proposals concerning the stereoselectivity of capture of the cations (**4**, R = H and CH_3) must remain equivocal until confirmed by the study of the diastereoselectivity of fluorination of the corresponding *E*-epimers of **5** (R = H and CH_3). Unfortunately, these alcohols pose a significant synthetic challenge.

Theoretical calculations

The B3LYP/6-31G*- computed critical structures of the ions (**4**, R = H and CH_3; X = F and Cl) are given in Table 19 of the Supporting Material. After ZPVE corrections, only a single zero-order critical structure has been identified on the potential energy surfaces (PES) of the tertiary ions of **4** (R = CH_3). Except for **4** (R = CH_3 and X = F), which surprisingly gave only the *anti* (or *E*) ion (**6**, R = CH_3), the favoured invertomer of the remaining tertiary ions is *syn* (or *Z*) **7** R = CH_3). In contrast, two zero-order critical structures have been found for the secondary ions (**4**, R = H). The *syn* (or *Z*) ion is favoured in all cases (**7**, R = H). Relevant aspects of their geometries are displayed in Table 20 of the Supporting Material. A pertinent feature is that the electron-deficient centre (C2) is pyramidalized to varying degrees, dependent on electron demand. Although the calculations are for isolated molecules in the gas phase, the finding that only one structural minimum exists on the PES for the tertiary ions raises the possibility that the relative reactivity of the two faces of a single solvated ion may determine the stereoselectivity of these systems in solution. This is not the case for the secondary ions where two minima have been located.

The unexpected calculated result that the *anti* (or *E*) invertomer is the favoured ion of the 4^{ax}-fluoro substituted 3° species (**4**, R = CH_3, X = F; Table 19 of the Supporting Material) is of particular interest since it is counter-intuitive to predictions based on qualitative considerations of differential hyperconjugative and steric effects. Noteworthy is the fact that the H—F distance in this ion (**7**; R = CH_3, X = F) is 2.59 Å which is just inside the sum of the van der Waals radii of hydrogen (1.20 Å) and fluorine (1.47 Å).[13] We believe this unexpected result highlights the importance of a *reversed* electrostatic field effect (a dipolar substituent effect can be modified by its geometrical orientation to be 'normal', diminished, absent or even 'reversed')[14] between the C—F dipole and the positive charge delocalized on the methyl group as a significant contributing factor determining the preferred conformation of the ion. In an attempt to provide support for this conclusion, we have chosen the reaction energy (Δ*E*) of an isodesmic reaction (Eqn (1)) as a measure of the through-space electrostatic field interaction between groups X and Y in the adamantane ring system (Ad). Hence, the effect of orientation (angle and distance) on the electrostatic interaction between

$$\text{X-Ad-H} + \text{Y-Ad-H} \rightarrow \text{X-Ad-Y} + \text{H-Ad-H} \qquad (1)$$

the C-F dipole and positive charge on the methyl group in the various dispositions of the epimeric ions can be readily mimicked in a relative sense by calculating Δ*E* for Eqn (1) where X = F and Y = NH_3^+. The Δ*E* values for the appropriate orientations are listed in Table 4. It can be seen that the electrostatic interaction energy varies widely with orientation and, moreover, is significantly destabilizing (normal effect) for all orientations except for $4X^{ax},2Y^{ax}$ where the interaction is clearly stabilizing (reverse effect).[14] Since this orientation approximates the geometry of

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Table 4. Isodesmic reaction energies (ΔE, kcal/mol) of Eqn (1)

Orientation	X	Y	ΔE
$4X^{eq},2Y^{eq}$	F	NH_3^+	4.99
$4X^{eq},2Y^{ax}$	F	NH_3^+	5.69
$4X^{ax},2Y^{eq}$	F	NH_3^+	2.59
$4X^{ax},2Y^{ax}$	F	NH_3^+	−3.82
$5X,2Y^{eq}$	F	NH_3^+	5.29
$5X,2Y^{ax}$	F	NH_3^+	4.50

[a]Determined from B3LYP/6-31 + G*calculated energies listed in Table 21 of the Supplementary Material.

the 3° epimeric ion (**6**; R = CH_3, X = F) of **4** (R = CH_3), the explanation for the finding above that the *anti* (or *E*) ion and not the expected *syn* (or *Z*) epimer exists on the PES of **4** (R = CH_3) appears validated. The relative magnitude of the destabilizing interaction energies for the orientations of the other dispositions (*syn* > *anti* (4,2) and *anti* > *syn* (5,2)) are of interest in connection with the conclusion that differential electrostatic effects appear to govern the relative stability of the epimeric ions in **1** but not in the 5,2-disposition. Note that in the case of the 4,2 disposition the *syn* orientation ($4X^{eq},2Y^{ax}$) is considerably larger than the *anti* ($4X^{eq},2Y^{eq}$) whereas, in contrast, the reverse situation prevails in the 5,2-disposition. Consequently, extrapolating this pattern to the epimeric tertiary ions of these two dispositions implies that the relative magnitude of the two destabilizing components of the electrostatic field interaction in the *syn* (or *E*) cation of the 4,2 disposition are in unison but opposed in the corresponding ion of the 5,2 disposition.

A useful way of quantitatively describing electron delocalization interactions is by the energies of the second-order perturbation analysis of the Fock matrix elements in the NBO basis ($E^{(2)}$).[7] Consequently, we carried out an NBO analysis of the secondary and tertiary ions of **4** (*Z* and *E*, R = H and Me, respectively) in order to obtain $E^{(2)}$ values for the hyperconjugative interactions between the flanking C—C bonds and the electron-deficient centre (C2). These parameters are set out in Table 5.

One of the more significant aspects of these results is that the decreased donor capacity of the C3—C4 bond by the σ-inductive effect in the *E*-cations of system **4** (R = H) is accompanied by a concominant increased donor effect from the C1—C9 bond as a result of enhanced electron demand at the reaction centre (C2). The low symmetry of the 4-X ions (**4**) is exemplified by the fact that the donor effects of the four flanking C—C bonds in this system are all different. Finally, a further pertinent observation is the considerable reduction in the energy of hyperconjugative interactions on reducing electron demand (*cf.* corresponding interactions of 2° and 3° ions (R = H and CH_3, respectively).

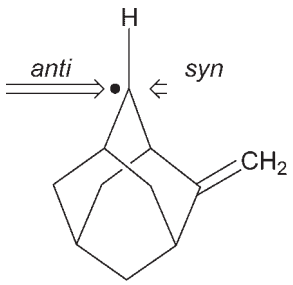
Table 5. Selected NBO $E^{(2)}$ energies (kcal/mol)[a,b] of hyperconjugative interactions (C–C → $C2^+$) in **4**

System	C1–C8	C1–C9	C3–C4	C3–C10
4 (*Z*;R = H, X = F)	34.98	0.92	1.24	18.92
4 (*E*;R = H, X = F)	0.66	39.53	16.98	1.45
4 (*Z*;R = H, X = Cl)	36.76	0.69	0.82	19.60
4 (*E*;R = H, X = Cl)	<[c]	55.91	12.12	1.17
4 (*E*;R = Me, X = F)	3.91	15.95	12.48	4.01
4 (*Z*;R = Me, X = Cl)	17.82	3.14	2.51	14.51

[a,b] Only energies > 0.5 kcal/mol shown.
[f] Parent ions (X = H, R = H): 27.03, 1.02, 1.02, 27.03 (X = H, R = Me): 18.18, 2.54, 2.54, 18.18.
[c] <0.5 kcal/mol.

Stereochemical result for the stannylation of 4-bromo$^{eq/ax}$-2-methylene-adamantanes

Previously,[3] we had occasion to treat 4-bromo^{eq} -and/or 4-bromo^{ax}-2-methyleneadamantane (**2** and **3**, Y = CH_2 and X = Br, Br, respectively) with trimethyltin lithium in THF in order to prepare 4-trimethylstannyl^{eq}-2-methyleneadamantane (**2**, Y = CH_2 and X = $Sn(CH_3)_3$), obtained almost exclusively (>95%) from both bromo isomers. The strikingly high stereoselectivity of this reaction was reported by Duddeck and Islam[5h] more than 20 years ago but no satisfactory explanation was proffered. Mechanistic studies of the trimethylstannylation reaction in recent years[15] have clearly established that nucleophilic tin substitution of bromine in substituted 2-bromoadamantanes occurs exclusively by an $S_{RN}1$-type mechanism (free-radical chain process) in which the first step involves dissociative electron-transfer to form the correspondingly substituted 2-adamantyl radical. The next step involves the capture of this radical with the Me_3Sn^- ion to form a radical tin anion which subsequently loses an electron to form the tin substitution product. Hence, the aforementioned stereoselectivity has its origin in the discrimination of the two faces of a common intermediate by the attacking Me_3Sn^- anion, namely, preferential *anti*-attack on the 4-methylene-2-adamantyl radical (**8**). Noteworthy, is that the preferred direction of attack is diametrically opposite to



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predictions (*syn*) based on the Cieplak model[1a] or steric accessibility (*anti*-approach is sterically more encumbered than *syn* because the nucleophile encounters two *axial* hydrogens for the former *versus* one for the latter). Moreover, it is the most conspicuous example of a distal substituent influencing the stereochemical outcome of trapping of a remotely substituted 2-adamantyl radical (XAd•).[16] In an attempt to provide some insight into the origins of this high stereoselectivity, we have carried out calculations at the B3LYP/6-31G* level of theory on **8** (Table 22, as in the Supplementary Material). Two minima are located on the PES with significant distortions at the carbon bearing the unpaired electron (C2): one (*E* or *anti*) in which the dihedral angle (θ) between the C1—C2—C3 plane and the C2—H

bond is 150.12° and another (*Z* or *syn*) where the corresponding angle is 159.43°.The energy difference between the two isomers is small (0.30 kcal/mol), *E* being slightly more stable than *Z*. The relative stability is in accord with crude expectations based on hyperconjugative effects. An attempt to locate a TS on the PES appeared successful ($N_{imag} = 1$, $\upsilon = -75.5\ cm^{-1}$; C2—H bond bent away from the substituent ($\theta = 167°$)) but after ZPVE correction the energy was found to be lower than the more stable *E* species! The situation highlights that defining such stationary points on a very flat PES is highly problematical. Interestingly, calculations at the B3LYP/DZP++ level of theory found the ground state of 2-Ad$^{\bullet}$ in C_s symmetry ($\theta = 159.7°$) with only a 0.23 kJ/mol energy difference on a very flat PES between the Cs and $C_{2\upsilon}$ structures.[17] Even if **8** exists in solution (THF) as two rapidly equilibrating discrete species (*E* and *Z* epimers), the observed high stereoselectivity in the reaction with Me_3Sn^- cannot be reconciled in terms of their relative populations based on an energy difference of 0.30 kcal/mol (as described above). Although by default it could be ascribed to orbital interactions (Ahn model),[1a,18] there is no precedent in the literature that we are aware of where such interactions lead to such profound stereochemical consequences. Consequently, we calculated the minimum electrostatic potential ($V_{S,min}$, kcal/mol) on the molecular surface of **8** (AM1 geometry, $\theta = 180°$) defined by the 0.002 electron bohr^{-3} contour of the electron density. The $V_{S,min}$ values reveal that the trajectory of the incoming nucleophile on the *syn*-face encounters a much higher 'barrier' of negative potential (i.e. higher electron density) than on the opposing *anti*-face ($V_{S,min}(syn) = -24$ *versus* $V_{S,min}(anti) = -14$). This suggests that the high stereoselectivity of trapping of **8** has its origins in electrostatic effects,[10] namely, the relative magnitude of destabilizing repulsive interactions from approach of the trimethylstannyl anion to the respective faces prior to bond formation (*syn* > *anti*). This is an interesting example where remote electronic effects clearly overwhelm steric effects.[2]

Acknowledgements

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