Diastereofacial Selectivity in Reactions of 5-Substituted (X) Adamant-2-yl Cations: Manifestations of Electron Demand

William Adcock,* Nicholas J. Head, Nigel R. Lokan, and Neil A. Trout

Department of Chemistry, The Flinders University of South Australia, Adelaide, Australia 5001

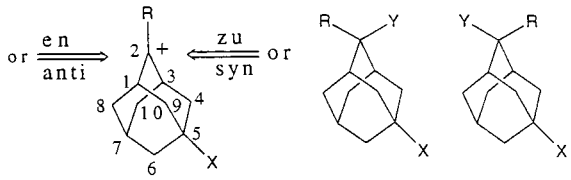
Received April 2, 1997[⊗]

A series of 5-substituted (X) 2,2-dimethoxyadamantanes (**4**, X = F, Cl, Br, $COOCH_3$, OCH_3, CH_3, C_6H_5, *p*-$NO_2C_6H_4$, *p*-BrC_6H_4, $SiMe_3$, and $SnMe_3$) as well as 2-methylene-5-*tert*-butyladamantane (**6**, Y = CH_2; X = $C(CH_3)_3$) have been synthesized and characterized. Reduction of the ketals **4** under ionic conditions with triethylsilane and phenylsilane provide π-facial diastereoselectivities for hydride trapping of 5-substituted (X) 2-methoxyadamant-2-yl cations (**1**, R = OCH_3 ↔ **5**). A comparison of this data with known diastereoselectivities for nucleophilic capture of tertiary and secondary 5-substituted (X) 2-adamantyl cations highlights that stereoselectivity in these systems is a function of electron demand. Diastereoselectivities for the hydrochlorination of **6** (Y = CH_2, X = $C(CH_3)_3$) in CH_2Cl_2 and NO_2CH_3 have been determined and compared with the corresponding data for the silicon analogue (**6**, Y = CH_2; X = $SiMe_3$). Low electron demand coupled with the stereoelectronic requirement of double hyperconjugation appears the most likely explanation, rather than a long-range steric factor, for the total lack of stereoselectivity in the Cl^- capture of the 2-methyl-5-(trimethylsilyl)adamant-2-yl cation (**1**, Y = CH_2; X = $SiMe_3$) in NO_2CH_3 as solvent.

Introduction

5-Substituted (X) 2-adamantyl derivatives have been deployed extensively as stereochemical probe substrates in the assessment of the electronic factor governing π-facial selectivity of additions to trigonal carbon centers.[1,2] These model systems are attractive for essentially two reasons. Firstly, their rigid molecular frameworks ensure that ambiguities associated with conformational uncertainty are precluded. Secondly, substitution at the remote 5-position permits electronic fine tuning of the π-faces at C2 without introducing steric bias into the system.

The most conspicuous examples of diastereoselectivity among the various adamantyl substrates are those involving reactions which are mediated by the formation of secondary (secondary) and tertiary (tertiary)[1a,2,3,4a] 5-substituted (X) adamant-2-yl cations **1**. For example, powerful σ-electron-withdrawing and -donor groups such as X = F and $SnMe_3$, respectively, can lead to nucleophilic capture ratios in excess of 9:1 but with diametrically opposite stereochemistry. Syn (or zu) approach of the nucleophile is favored by the former and anti (or en) by the latter. The stereoselectivity has been rationalized in terms of hyperconjugation.[1a,2−4a] However, the precise nature of the hyperconjugative mode responsible for differentiating the energies of the diastereomeric transition states is significantly different for the two disparate substituent types. In the case of σ-electron-withdrawing groups hyperconjugative charge dispersal within the cation of the transition state (TS) leading to the *Z* isomer (**2**) is less destabilizing than the corresponding interaction leading to the *E* isomer (**3**). This is largely because coulombic forces of repulsion are minimized by delocalizing the positive charge away from the electrostatic field of the substituent.[2b] An additional contributing factor but probably a minor one is that the donor capacity of the proximate carbon−carbon bonds (C1−C9 and C3−C4) is reduced compared to the distal ones (C1−C8 and C3−C10) by the hyperconjugating influence of the substituent ($\sigma_{CC} - \sigma_{CX}$*). On the other hand, σ-electron-donor groups, all of which exert very weak electrostatic field influences ($\sigma_F \sim 0$), preferentially stabilize the cation of the TS leading to the *E* isomer as a result of double hyperconjugation.[2a,4a] The stereoelectronic requirement of this electronic transmission mode, namely, an antiperiplanar relationship of the participant orbitals, is accommodated in the TS leading to the *E* (**3**) but not the *Z* (**2**) product. It is important to note that this variant of hyperconjugation results in charge transfer from the C−X bond to the "vacant" orbital at C2 via the bridging ethano bonds and, in the extreme, can merge into fragmentation.[4]



1 **2** **3**

An interesting question concerning the nucleophilic capture of **1** is the extent to which stereoselectivity is a function of electron demand. Sometime ago le Noble et al.[3b] noted somewhat similar effects for secondary (R = H) and tertiary (R = CH_3, *p*-SC_6H_4, and OCH_3) 5-fluoro-2-adamantyl cations (**1**, X = F) and, therefore, concluded that σ-delocalization-induced stereoselectivity is not sup-

* Corresponding author. Tel: (08) 8201 2134. Fax: (08) 8201 3035. email: chwa@cc.flinders.edu.au.

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1997.

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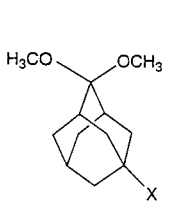
S0022-3263(97)00600-2 CCC: $14.00

pressed by cation-stabilizing groups. Contrary to these observations, Liu et al.[5] have reported kinetic and facial selectivity data for tertiary 5-fluoro-2-adamantyl cations (**1**, X = F; R = *p*-SC_6H_4 where S = H, CF_3, and CH_3) which suggest that the tool of increasing electron demand is applicable.[6] More recently, by use of deuterium as an electronically neutral marker group at C5, Kirmse et al.[7] have shown that the stereoselectivity previously observed[1a] for the parent secondary ion (**1**, X = H(D); R = H), apparently as a result of σ-delocalization, is effectively suppressed in the tertiary species (**1**, X = H(D); R = CH_3 and C_6H_5).

In an attempt to shed further light on the relationship between stereoselectivity and electron demand in the capture of **1** we decided to examine the ionic hydrogenation of a series of 5-substituted (X) 2,2-dimethoxyadamantanes (**4**) which covers a reasonably wide range of



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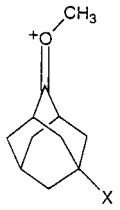

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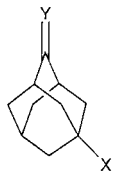

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substituent electronic effects (X = F, Cl, Br, $COOCH_3$, OCH_3, CH_3, C_6H_5, *p*-$NO_2C_6H_4$, *p*-BrC_6H_4, $SiMe_3$, and $SnMe_3$). The reaction leads to the formation of an ether mixture of *E* and *Z* isomers (**2** and **3**, Y = H and R = OCH_3, respectively) by hydride transfer to an intermediate oxonium ion (**1**, R = OCH_3 ↔ **5**). Thus, the cation generated in this circumstance has the powerful π-electron-donating methoxyl group dispersing and, hence, stabilizing the positive charge at the reaction center.[8]

Herein we report the results of this study and, in addition, we also report the synthesis of 2-methylene-5-*tert*-butyladamantane (**6**, Y = CH_2 and X = $C(CH_3)_3$) and its diastereoselectivity with respect to hydrochlorination. The impetus for the latter investigation was a surprising and perplexing result we recently reported[2b] for the hydrochlorination of the silicon analogue (**6**, Y = CH_2 and X = $Si(CH_3)_3$), namely, the failure of $Si(CH_3)_3$ (a relatively good σ-electron donor group) to exert any influence on facial selectively for this reaction in nitromethane as solvent.

Table 1. Product Distributions for the Reduction (Et_3SiH)[a,b] of 2,2-Dimethoxy 5-Substituted (X) Adamantanes (4)

	ethers				ethers		
X	%*E*	%*Z*	analytical methods	X	%*E*	%*Z*	analytical methods
CO_2CH_3	62	38	^{13}C NMR	OCH_3	72	28	^{13}C NMR
CO_2CH_3	63	37	^1H NMR	OCH_3	71	29	^1H NMR
CO_2CH_3	64	36	VPC	OCH_3	74	26	VPC
F	75	25	^{13}C NMR	C_6H_5	47	53	^{13}C NMR
F	74	26	^1H NMR	C_6H_5	47	53	^1H NMR
F	78	22	^{19}F NMR	*p*-$NO_2C_6H_4$	45	55	^{13}C NMR
F	77	23	VPC	*p*-$NO_2C_6H_4$	44	56	^1H NMR
Cl	67	33	^{13}C NMR	*p*-BrC_6H_4	47	53	^{13}C NMR
Cl	69	31	VPC	*p*-BrC_6H_4	46	54	^1H NMR
Br	63	37	^{13}C NMR	$Si(CH_3)_3$	35	65	^{13}C NMR
Br	64	36	^1H NMR	$Si(CH_3)_3$	37	63	^1H NMR
Br	66	34	VPC	$Si(CH_3)_3$	35	65	VPC
CH_3	51	49	^{13}C NMR	$Sn(CH_3)_3$	30	70	^{13}C NMR
CH_3	52	48	^1H NMR	$Sn(CH_3)_3$	33	67	^1H NMR
				$Sn(CH_3)_3$	28	72	VPC

[a] CH_2Cl_2/Et_3SiH/PPHF. PPHF ≡ pyridinium poly(hydrogen fluoride). [b] $CH_2Cl_2/Et_3SiH/CF_3CO_2H/NH_4F$ reducing system gave the following *E*/*Z* ratios: 62/38 (CO_2CH_3, VPC), 69/31 (Br, VPC), 45/55 (C_6H_5, ^1H and ^{13}C NMR).

Results and Discussion

Hydride Reduction of Ketals 4. Our initial strategy was to effect ionic hydrogenation of a solution of the dimethyl ketals **4** in dichloromethane by use of triethylsilane in the presence of trifluoroacetic acid and ammonium fluoride ($Et_3SiH/NH_4F/CF_3CO_2H$).[9] However, very early in the investigation we found that these conditions lead to loss of fluorine from the important fluoro derivative (**4**, X = F). In a previous study[10] we also noted the enhanced nucleofugality of fluorine at bridgehead positions in the adamantane ring system under conditions that provide strong electrophilic assistance. An additional problem with the $Et_3SiH/NH_4F/CF_3CO_2H$ reducing system in acquiring stereoselectivity data under common conditions for the entire ketal series (**4**) is the protolytic instability of the $SnMe_3$ group. Consequently, we turned to a relatively new ionic reduction system (Et_3SiH/PPHF(pyridinium poly(hydrogen fluoride))[9] which is only mildly acidic. Under these conditions, reduction of the ketals to the isomeric mixture of methoxy ethers was very clean and the conversion complete in every case. Most importantly, the fragile $SnMe_3$ group was not affected by the mildly acidic system.

The diastereoselectivities (*Z*/*E*) for the hydride reduction of **4** are presented in Table 1. A cursory examination of the data quickly reveals a glaring anomaly. It can be seen that the very modest selectivities for the phenyl group (*Z* > *E*) are diametrically opposite to expectations (*E* > *Z*; preferential *syn* approach of the reagent to **1**, R = OCH_3) based on their σ-electron-withdrawing electronic character! The possibility of a competing steric factor being responsible emerged from two considerations: (i) The steric environment of a reaction center in the substrate can be important in the stereochemical outcome of Et_3SiH reductions.[11] (ii) Under the conditions of the reaction the fluoride ion serves to nucleophilically activate the Si−H bond for hydride transfer.[9] Thus, the effective steric size of the pentacoordinate silicon species

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Table 2. Product Distributions for the Reduction ($C_6H_5SiH_3$)[a] of 2,2-Dimethoxy-5-Substituted (X) Adamantanes(4)

	ethers				
X	%*E*	%*Z*	analytical methods	% ether formation	% ketone formation
CO_2CH_3[b]	65	35	^{13}C NMR	34	66
F	74	26	^{19}F NMR	32	68
F	76	24	VPC	32	68
Cl	60	40	^{13}C NMR		
Cl	62	38	VPC	16	84
Br	58	42	^{13}C NMR		
Br	58	42	VPC	25	75
OCH_3[b]	71	29	^{13}C NMR	17	83
C_6H_5	58	42	^{13}C NMR	40	60
C_6H_5	59	41	^{1}H NMR		
p-$NO_2C_6H_4$	60	40	^{13}C NMR	25	75
p-BrC_6H_4	59	41	^{13}C NMR	43	57
$Si(CH_3)_3$	41	59	^{13}C NMR		
$Si(CH_3)_3$	42	58	^{1}H NMR		
$Si(CH_3)_3$	41	59	VPC	57	43
$Sn(CH_3)_3$	25	75	^{13}C NMR		
$Sn(CH_3)_3$	26	74	^{1}H NMR		
$Sn(CH_3)_3$	24	76	VPC	100	0

[a] $CH_2Cl_2/C_6H_5SiH_3$/PPHF. PPHF ≡ pyridinium poly(hydrogen fluoride). [b] VPC analysis precluded due to the similar retention times of the *E*/*Z* ethers and the corresponding ketone.

in the transition state of the rate-determining step must be quite large. The main ambiguity arising from a significant steric bias is associated with the results for the σ-electron donor groups ($SiMe_3$ and $SnMe_3$) since here steric and electronic factors would impact synchronously on diastereoselectivity to yield *Z* > *E*. In the case of the σ-electron-withdrawing substituents, because the two factors would influence selectivity in opposite directions, the diastereoselectivities where *E* > *Z* can be safely interpreted as being minimal estimates of the electronic factors role. In an attempt to clarify the situation we decided to repeat the reductions of the ketal series (**4**) utilizing phenylsilane ($C_6H_5SiH_3$) as the hydride source. Compared to Et_3SiH this species is certainly a much less bulky reducing agent but has the disadvantage of being a much poorer hydride ion donor.[12] A slow hydride transfer process permits competing side reactions to appear, and these can become dominant as we shall see below. The diastereoselectivities for the $C_6H_5SiH_3$ reduction of **4** are presented in Table 2. Most importantly, it can be seen that the *Z*/*E* ratios for the phenyl groups are now in accord with expectations (*E* > *Z*) from electronic considerations. This appears to vindicate the idea that a steric factor is indeed overlaid on the corresponding results utilizing Et_3SiH (Table 1). However, it can also be seen (Table 2) that the remaining data (*Z*/*E*) for the other groups is fairly similar to the selectivities observed for Et_3SiH (Table 1). This is particularly pertinent for the metalloidal substituents where the factors may have acted in concert. A major difference between the results for the two reagents is that whereas hydride transfer with Et_3SiH gives the methyl ethers exclusively (Table 1), ketone formation was the dominant reaction pathway for the $C_6H_5SiH_3$ reductions (Table 2) except for the donor groups (X = $Si(CH_3)_3$ and $Sn(CH_3)_3$). Apparently under the latter conditions, hydride transfer to C2 in **1**, R = OCH_3(≡ **5**) cannot compete effectively against nucleophilic attack at methyl (presumably by the fluoride ion) in the oxonium ion **5** when the substituent (X) is a σ-electron withdrawer. The important conclusion to be drawn is that except for the phenyl groups the selectivity data listed in Table 1 can be essentially viewed as manifestations of substituent electronic effects.

On closer scrutiny of the data (Tables 1 and 2) in the above light it is appropriate to consider the two classes of substituents separately since, as pointed out in the introduction, their hyperconjugative modes are basically different. The following points are noteworthy. Firstly, it can be seen that fluorine dominates the selectivity order of the σ-electron-accepting groups. However, the *E*/*Z* ratio (75/25) is somewhat less than that previously observed (83/17) by le Noble et al.[3b] for the borohydride reduction of the same oxonium ion (**1**, R = OCH_3 ↔ **5**; X = F). Given the vastly different reaction conditions for the two reductions (homogeneous/CH_2Cl_2/Et_3SiH *versus* heterogeneous/ether/BH_4^-) it would be futile to place any significance in this apparent discrepancy. Secondly, the selectivity data for the σ-electron withdrawing groups (Tables 1 and 2) are significantly suppressed compared to the corresponding data for chloride ion trapping of **1** (R = CH_3) in CH_2Cl_2 (hydrochlorination of 5-substituted (X) 2-methyleneadamantanes (**6**, Y = CH_2)).[2b] Since the methoxy group is well known to be a much better π-electron donor than methyl, the trend appears understandable in terms of reduced electron demand in **1**, R = OCH_3 ↔ **5** compared to **1**, R = CH_3. The relative extent of σ-delocalization of the available positive charge determines the selectivity response of the system to electrostatic field effects.[2b] Interestingly, the selectivity for the Me_3Si group (Tables 1 and 2), a σ-electron donor which controls selectivity by engaging in a stabilizing double hyperconjugative interaction with the electron deficient reaction center, is only marginally less than that observed for the Cl^- trapping of **1** (R = CH_3) in CH_2Cl_2. Double hyperconjugation is facilitated by pyramidal distortion of the reaction center. The latter effect in 2-adamantyl cations was first proposed on the basis of NMR data,[13] and there is accumulating experimental[2,4a,14] and theoretical[8b,15] evidence to corroborate the idea. Thirdly, the diastereoselectivities for the σ-electron donor groups (Tables 1 and 2) are markedly suppressed compared to the stereochemical outcome of reactions mediated by the corresponding metalloidal substituted secondary 2-adamantyl cations (**1**, R = H).[2a,4a] Furthermore, the marked propensity of the latter tin species (**1**, R = H and X = $SnMe_3$) to undergo fragmentation[2a,4a] is effectively "tamed" by the presence of the methoxy group at C2. The NMR and GC-MS analyses of the product mixtures from the reduction (Et_3SiH or $C_6H_5SiH_3$) of the tin ketal (**4**, X = $SnMe_3$) indicated the absence of characteristic fragmentation products. The appropriate ethers (*E* and *Z*) were obtained in essentially quantitative yields. These results appear to be clear manifestations of reduced electron demand in **1**, R = OCH_3 ↔ **5**.

Finally, in contrast to the trends noted above the stereoselectivities for the hydride reduction of the oxonium ions **5** are, in the main, *enhanced* compared to the corresponding data[1a,2] for the $NaBH_4$ reduction of the

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Table 3. Product Distributions[a,b] for Hydride Reductions of Some 5-Substituted (X) Adamantan-2-ones (6, Y = O)

	$NaBH_4$[c]		$LiAlH_4$		DIBAL-H[d]	
X	%*E*	%*Z*	%*E*	%*Z*	%*E*	%*Z*
F	59	41	60	40	61	39
Br	60	40	60	40	60	40
$Si(CH_3)_3$	50	50	44	56	48	52
$Sn(CH_3)_3$	48	52	38	62	42	58

[a] Capillary VPC analysis. [b] Duplicate results. [c] Taken from ref 2a. [d]Diisobutylaluminum hydride ($(((CH_3)_2CHCH_2)_2AlH$).

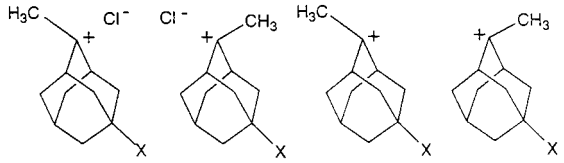
Table 4. Product Distributions[a] for the Hydrochlorination of Some 5-Substituted (X) 2-Methyleneadamantanes (6, Y = CH_2)

	CH_2Cl_2		NO_2CH_3	
X	%*E*	%*Z*	%*E*	%*Z*
$C(CH_3)_3$[b]	45(45)	55(55)	47(48)	53(52)
$Si(CH_3)_3$[c]	65(69)	35(31)	50	50

[a] Ratios determined by ^{13}C NMR (^1H NMR). [b] This study. [c] Taken from ref 2b.

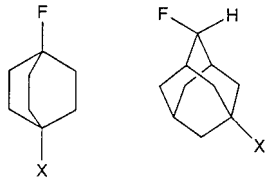
ketones (**6**, Y = O). This is particularly the case for the σ-electron donor groups and, hence, raises the question whether or not facial selectivities for the hydride reduction of the ketones can be enhanced by utilizing reagents which strongly ligate to oxygen prior to rate-determining hydride transfer. We addressed this question by examining the reduction of a limited number of ketones (**6**, Y = O; X = F, Br, $SiMe_3$, and $SnMe_3$) with $LiAlH_4$ (ether) and $((CH_3)_2CHCH_2)_2AlH$ (toluene). Both these reagents are believed to ligate to oxygen to varying degrees prior to hydride transfer.[16] The results of these reductions are listed in Table 3 together with the previously reported $NaBH_4(CH_3OH)$ data.[2a] It can be seen that while the stereoselectivities for the σ-electron withdrawing groups (F and Br) remain largely unaffected there does appear to be a significant general enhancement of selectivities for the σ-electron donors ($SiMe_3$ and $SnMe_3$), particularly for $LiAlH_4$. The results highlight the different nature of the electronic effects associated with these disparate substituent types. Apparently in the case of $SiMe_3$ and $SnMe_3$, the double hyperconjugative interaction mode is particularly sensitive to electron demand as well as to the ease of pyramidal distortion of the reaction center.

Hydrochlorination of 2-Methylene-5-*tert*-butyladamantane (6, Y = CH_2; X = $C(CH_3)_3$). The diastereoselectivity data for the hydrochlorination of **6** (Y = CH_2, X = $C(CH_3)_3$) in CH_2Cl_2 and NO_2CH_3 are listed in Table 4. The previously reported results for the silicon analogue[2b] are also presented in order to facilitate comparisons. Previously[2b] we proposed that the stereoselectivity observed for the Me_3Si group in CH_2Cl_2 (*E* > *Z*; Table 4) is understandable in terms of double hyperconjugation acting as a stereoinductive factor. However, we expressed surprise to find that this group appears electronically benign when the same reaction is carried out in NO_2CH_3 (*E*/*Z* = 50/50; Table 4). Based on the mechanistic distinction for HCl addition in CH_2Cl_2 *versus* NO_2CH_3, namely, the formation of tight ion pairs (**7** and **8**) for the former and free ions (**9** and **10**) for the latter,[17]



7 **8** **9** **10**

we speculated that this anomaly might be explained by invoking a long-range steric interaction by the relatively bulky Me_3Si substituent in the free *E*-cation (**10**, X = Me_3Si) which is transmitted via the axial 4,9-hydrogen atoms. The consequential destabilizing interaction would offset the energy gain as a result of double hyperconjugation. This steric phenomenon is hidden in CH_2Cl_2 because the fairly similar effective steric size of Cl and CH_3 ensures that its contribution to the relative energies of the product-determining TS (ion-pair-like; **7** and **8**) essentially cancels out. We reasoned that if this explanation is valid then the stereoselectivity data for HCl addition to **6** (Y = CH_2, X = $C(CH_3)_3$) should also reveal a similar steric effect but more markedly because of the greater effective steric size of $C(CH_3)_3$ compared to $Si(CH_3)_3$.[18] Although these two substituents are electronically similar in that they both exert negligible long-range (beyond two bonds) electrostatic field effects ($\sigma_F \sim 0$),[19] they differ significantly because their σ-electron effects are diametrically *opposite*. The latter situation is dramatically highlighted in the neutral ground state by the relative signs and magnitude of their respective ^{19}F substituent chemical shifts (SCS, ppm) in 4-substituted (X) bicyclo[2.2.2]oct-1-yl fluorides (**11**; −3.11



11 **12**

($C(CH_3)_3$) and 1.54 ($Si(CH_3)_3$) in c-C_6H_{12})[19b] and (*E*)-5-substituted (X) adamant-2-yl fluorides (**12**; −4.00 ($C(CH_3)_3$)[20] and 0.12 ($Si(CH_3)_3$)[2a] in c-C_6H_{12}). It is not surprising, therefore, that these groups display opposing diastereoselectivities in CH_2Cl_2 (Table 4). Note, however, that the very modest selectivity (*Z* > *E*) induced by the weak σ-electron-accepting influence of $C(CH_3)_3$ in CH_2Cl_2 is slightly reduced rather than being significantly increased in NO_2CH_3! Clearly the trends for $C(CH_3)_3$ do not corroborate the aforementioned steric proposal.

What then is the explanation for $Si(CH_3)_3$ being an ineffectual bystander with respect to Cl^- trapping of **1** (R = CH_3, X = $Si(CH_3)_3$) in NO_2CH_3? The aberrancy of this result is further heightened by the stereochemical results for F^- trapping of secondary 2-adamantyl cations in the fluorination (DAST/CH_2Cl_2) of (*E*)- and (*Z*)-5-(trimethylsilyl)-2-adamantanols (*E*/*Z* = 86/14)[2a] compared to a mixture of (*E*/*Z*)-5-(*tert*-butyl)-2-adamantanols (*E*/*Z* = 51/49).[20] Moreover, the secondary cation mediated solvolysis of (*E*)- and (*Z*)-5-Me_3Si-substituted 2-adaman-

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(17) For expedience, structures **9** and **10** are drawn in an abbreviated form, but it is implicit that any full description of these ions must include the solvent and/or counterion as indicated by Sorensen et al.[13]

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(20) This study.

tyl brosylates also occurs with high stereoselectivity (*E*/*Z* = 91/9 (97% trifluoromethanol/3% water), 95/5 (80% ethanol/20% water) for the *E* isomer and 88/12 (97% trifluoromethanol/3% water or 70% ethanol/30% water) for the *Z* isomer).[4] Perhaps the origin of the anomaly resides in the demanding stereoelectronic requirements of the double hyperconjugative interaction. Thus, in the absence of high electron demand as encountered in the secondary 2-adamantyl cation, the electronic influence of the C−Si bond is only brought into play in situations where the essential marked pyramidalization at the reaction center is enforced by either a counterion or by the lateness of the transition state. This seems to be the case for Cl^- trapping of **1** (R = CH_3, X = $SiMe_3$) in CH_2Cl_2 and H^- transfer to **5**, respectively. However, in the case of the former reaction in NO_2CH_3, the low inversion barrier at C2 in the free tertiary ion **1** (R = CH_3, X = $SiMe_3$; **9** ⇌ **10**, X = $SiMe_3$) as a result of low electron demand ensures that the averaged geometry is trigonal coplanar relative to the rate of Cl^- trapping. Consequently, in the absence of a significant stereoinductive factor there is equal probability of attack from either the *Z* or *E* direction. The situation, therefore, is much like the nucleophilic trapping of tertiary 2-adamantyl cations (**1**, R = CH_3 or C_6H_5; X = D) under solvolytic conditions recently reported by Kirmse et al.[7] However, it is worth noting that if ionic recombinations are diffusion controlled, which is distinctly possible in non-hydrogen bonding solvents, then stereochemistry will be lost irrespective of the electronic character of the substituent.

Experimental Section

General. Melting and boiling points are uncorrected. Liquid samples were purified by distillation on a Kugelrohr apparatus (Büchi, GKR-50). Hence, boiling points quoted pertain to this instrument. All the anhydrous solvents used in this study were dried by standard procedures.

Compounds. Adamantan-2-one was purchased from the Aldrich Chemical Co., Inc. All the 5-substituted (X) adamantan-2-ones (**6**, Y = O; X = F, Cl, Br, $COOCH_3$, OCH_3, CH_3, C_6H_5, *p*-$NO_2C_6H_4$, *p*-BrC_6H_4, $SiMe_3$, and $SnMe_3$) were prepared by literature procedures as previously indicated or described.[2]

Synthesis of 5-Substituted (X) 2,2-Dimethoxyadamantanes (4). Except for the trimethylstannyl derivative (X = $SnMe_3$), which was prepared by trimethylstannylation of the corresponding bromo-ketal (X = Br) in exactly the same manner as previously described for the synthesis of 2-methylene-5-(trimethylstannyl)adamantane (**6**, Y = CH_2; X = $SnMe_3$),[2b] all the ketals (**4**, X = F, Cl, Br, $COOCH_3$, OCH_3, CH_3, C_6H_5, *p*-$NO_2C_6H_4$, *p*-BrC_6H_4, and $SiMe_3$) were prepared from the corresponding ketones (**6**, Y = O) by a standard procedure described below for the bromo derivative (X = Br). Details of the physical properties, NMR, and exact mass data of the ketals (**4**) are contained in the Supporting Information. The spectra were assigned by the additivity of substituent effects on the adamantane ring.[21]

1-Bromo-4,4-dimethoxyadamantane (4, X = Br). A solution of the bromo-ketone (**6**, Y = O; 2.0 g, 8.73 mmol), methanol (50 mL), trimethyl orthoformate (10 mL), and some Dowex (or Amberlite) resin was stirred under reflux for 24 h. The reaction mixture was allowed to cool to room temperature before being filtered onto dry potassium carbonate. After being filtered, the solvent was removed in vacuo to afford a colorless oil which solidified on standing. Sublimation (60 °C/0.05 mm) gave the title compound as a white solid (2.21 g, 92%), mp 40−41 °C; ^{1}H NMR ($CDCl_3$) δ 1.57−2.55 (m, 13H), 3.13 (s, 3H), 3.16 (s, 3H); ^{13}C NMR ($CDCl_3$, relative Me_4Si) δ 36.77 (Cl,3), 100.11 (C2), 44.97 (C4, 9), 64.24 (C5), 48.94 (C6), 31.27 (C7), 31.80 (C8, 10), 46.95 (OCH_3, *syn*), 46.70 (OCH_3, *anti*); HRMS(EI) calcd for $C_{12}H_{19}O_2Br$ 276.0549/274.0569, found 245.0385/243.0399($M^{\bullet+}$ − OCH_3), calcd for ($M^{\bullet+}$ − OCH_3) 245.0365/243.0385.

General Procedures for Reduction of Ketals 4. (a) Using $Et_3SiH/NH_4F/CF_3CO_2H$. By use of a procedure of Olah et al.,[9] CF_3CO_2H (0.14 mL, 1.82 mmol, 5 mol equiv) was added slowly to a well-stirred solution of the ketal (**4**, 0.36 mmol), Et_3SiH (0.087 mL, 0.54 mmol, 1.5 mol equiv), and NH_4F (20 mg, 0.54 mmol, 1.5 mol equiv) in anhydrous dichloromethane (4 mL) maintained at 0 °C. After stirring the reaction mixture for 15 min at 0 °C, it was allowed to warm to room temperature and then stirred overnight. The mixture was then quenched with ice−water and extracted with CH_2Cl_2 (3 × 1). The combined extracts were then washed with a saturated aqueous $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated in vacuo to afford the ether mixture of *Z* and *E* isomers (**2** and **3**, Y = H and R = OCH_3, respectively) in excellent yield (>90%).

(b) Using Et_3SiH or $C_6H_5SiH_3$/PPHF. By use of a modified procedure of Olah et al.,[9] PPHF (0.35 mL) was added slowly to a well-stirred solution of the ketal (**4**, 0.36 mmol) and Et_3SiH or $C_6H_5SiH_3$ (2.6 mol equiv) in anhydrous dichloromethane (2 mL) maintained at 0 °C. The reaction mixture was brought to room temperature and then worked up as described above in a. ^{13}C NMR chemical shift data for the 5-substituted (X) (*E*)- and (*Z*)-2-methoxyadamantanes (**2** and **3**, Y = H and R = OCH_3, respectively), which were readily assigned largely by additivity methodology,[21] are contained in the Supporting Information.

General Procedures for Reduction of Ketones (6, Y = O; X = F, Br, $SiMe_3$, and $SnMe_3$). (a) $LiAlH_4$. To a stirred solution of $LiAlH_4$ (0.39 mmol) in anhydrous diethyl ether (1.5 mL) under nitrogen at 0 °C was added a diethylether solution (1.5 mL) of the ketone (0.37 mmol). After addition was complete, the mixture was brought to room temperature and then stirred for 2 h before being quenched with a saturated aqueous NH_4Cl solution. The mixture was extracted with CH_2Cl_2 which was then dried ($MgSO_4$) and evaporated in vacuo to afford the product mixture.

(b) DIBAL-H. To a well-stirred solution of the ketone (0.320 mmol) in dry toluene (5 mL) maintained at −10 °C under nitrogen was added a solution of DIBAL-H in toluene (0.53 mL, 1.5 M, 2.5 mol equiv). The reaction mixture was allowed to warm to room temperature and then stirred overnight before being quenched with a saturated aqueous NH_4Cl solution. After filtering through Celite, the reaction mixture was extracted with CH_2Cl_2 which was then dried ($MgSO_4$) and evaporated in vacuo to afford the product mixture. It should be noted that the reduction of the fluoro- and bromo-ketones by this procedure led to substantial loss of F and Br, respectively. This side reduction was completely circumvented by utilizing only 1 mol equiv of DIBAL-H.

The mixtures of 5-substituted (X) (*E*)- and (*Z*)-2-adamantanol were then analyzed by VPC and NMR. The ^{13}C NMR chemical shifts of the various alcohols were in accord with published data.[1a,4a]

2-Methylene-5-*tert*-butyladamantane (6, Y = CH_2; X = $C(CH_3)_3$). A mixture of (*E*/*Z*)-methyl 4-methoxyadamantane-1-carboxylate (**2** and **3**, Y = H and R = OCH_3; X = $COOCH_3$, respectively; see above and Supporting Information), prepared from the appropriate ketal (**4**, X = $COOCH_3$; see above and Supporting Information) by ionic reduction with $Et_3SiH/NH_4F/CF_3COOH$ (see above), was converted into a mixture of (*E*/*Z*)-2-methoxy-5-*tert*-butyladamantanes by use of a procedure employed by Adcock et al. for introducing a *tert*-butyl group at the bridgehead position of the bicyclo[2.2.2]octane[22] and adamantane[23] ring systems. The overall conversion utilized relatively common reagents ((i) MeLi/diethyl ether. (ii) HCl/CH_2Cl_2. (iii) Me_3Al/CH_2Cl_2/−80 °C) and was uneventful. A ^{13}C

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NMR, GC-MS, and mass spectral analysis confirmed the composition of the ether mixture.

(*E*)-2-Methoxy-5-*tert*-butyladamantane (2, Y = H and R = OCH_3; X = $C(CH_3)_3$): ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 31.88 (Cl,3), 82.44 (C2), 35.14 (C4, 9), 36.14 (C5), 36.08 (C6), 27.96 (C7), 30.86 (C8, 10), 55.14 (OCH_3), 34.76 (Cq), 24.50 (CH_3); HRMS(EI) calcd for $C_{15}H_{26}O$ 222.1984, found 222.1955.

(*Z*)-2-Methoxy-5-*tert*-butyladamantane (3, Y = H and R = OCH_3; X = $C(CH_3)_3$): ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 31.45 (C1,3), 83.13 (C2), 29.95 (C4, 9), 36.14 (C5), 36.08 (C6), 27.90 (C7), 35.89 (C8, 10), 55.06 (OCH_3), 35.58 (Cq), 24.71 (CH_3); HRMS(EI) calcd for $C_{15}H_{26}O$ 222.1984, found 222.1955. The spectra were assigned by the additivity of substituent effects on chemical shifts of the adamantane ring[21] as well as the relative intensity of the peaks (*E*/*Z* = 57/43). *E*-Isomer (calcd): 31.88 (C1, 3), 82.73 (C2), 34.96 (C4, 9), 36.31 (C5), 36.08 (C6), 28.01 (C7), 30.95 (C8, 10). *Z*-Isomer (calcd): 31.88 (C1, 3), 82.73 (C2), 29.88 (C4, 9), 36.28 (C5), 36.08 (C6), 28.04 (C7), 36.03 (C8, 10).

To a well-stirred solution of a mixture of (*E*/*Z*)-2-methoxy-5-*tert*-butyladamantanes (710 mg, 3.2 mmol) in acetone (10 mL) at 0 °C was added an acetone solution of dimethyldioxirane[24] (90.47 mL, 1.89 mol equiv, 0.0067 M) maintained at −10 °C. The progress of the reaction was monitored by GC-MS. After 2 days ca. 80% of the ether mixture was consumed. Further dioxirane (ca. 2 mol equiv) was added, and the reaction was complete after a further 2 days. Evaporation of the solvent afforded the crude product. Kugelrohr distillation (65 °C/0.03 mm) gave 5-*tert*-butyladamantan-2-one as a white solid (300 mg, 46%): mp 59−62 °C (lit.[25] 57−58 °C); ^1H NMR ($CDCl_3$) δ 0.79 (s, 9H), 1.75−2.10 (m, 11H), 2.46 (bs, 2H); ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 46.36 (C1, 3), 219.29 (C2), 38.32 (C4, 9), 36.40 (C5), 35.17 (C6), 27.92 (C7), 38.71 (C8, 10), 34.60 (Cq), 24.80 (CH_3). These shifts are in accord with the reported values.[25]

A sample of 5-*tert*-butyladamantan-2-one (124 mg, 0.602 mmol) was converted to the title compound in the same manner as recently described for the preparation of 1-bromo-4-methyleneadamantane from 5-bromoadamantan-2-one.[2b] The desired alkene (**6**, Y = CH_2; X = $C(CH_3)_3$) was obtained as a colorless oil (75 mg, 61%) after chromatography on silica gel (pentane as eluent). ^1H NMR ($CDCl_3$) δ 0.83 (s, 9H), 1.6−2.1 (m, 11H), 2.5 (bs, 2H), 4.5 (s, 2H); ^{13}C NMR ($CDCl_3$, relative Me_4Si) δ 39.28 (C1, 3), 158.46 (C2), 38.43 (C4, 9) 36.67 (C5), 35.99 (C6), 28.90 (C7), 39.28 (C8, 10), 100.30 (CH_2), 34.83 (Cq), 24.84 (CH_3); HRMS(EI) calcd for $C_{15}H_{24}$ 204.1878, found 204.1867.

Hydrochlorination of 2-Methylene-5-*tert*-butyladamantane (6, Y = CH_2; X = $C(CH_3)_3$). The procedure was identical with that previously described.[2b] The product distributions of the reaction mixtures from CH_2Cl_2 or NO_2CH_3 were determined by ^{13}C NMR (see Table 4). **(*E*)-2-Chloro-2-methyl-5-*tert*-butyladamantane:** ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 41.22 (Cl,3), 80.77 (C2), 33.80 (C4, 9), 35.98 (C5), 37.56 (C6), 27.52 (C7), 33.93 (C8, 10), 30.61 (C2-CH_3), 34.67 (Cq), 24.72 (C(CH_3)$_3$). **(*Z*)-2-Chloro-2-methyl-5-*tert*-butyladamantane:** ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 41.53 (C1, 3), 80.77 (C2), 33.24 (C4,9), 35.68 (C5), 37.49 (C6), 27.71 (C7), 34.58 (C8, 10), 30.06 (C2-CH_3), 34.82 (Cq), 24.72 (C(CH_3)$_3$). The spectra were assigned by additivity methodology.[21] *E*-Isomer (calcd): 41.61 (C1, 3), 80.47 (C2), 33.56 (C4,9), 36.19 (C5), 37.50 (C6), 27.25 (C7), 33.99 (C8,10). *Z*-Isomer (calcd): 41.61 (C1, 3), 80.47 (C2), 32.92 (C4, 9), 36.02 (C5), 37.50 (C6), 27.92 (C7), 34.63 (C8, 10).

Fluorination of a Mixture of (*E*)- and (*Z*)-5-*tert*-Butyl-2-adamantanols (2 and 3, R = OH and Y = H, respectively). Solid sodium borohydride (160 mg, 4.2 mmol, 9.36 mol equiv) was added portionwise over 2 min to a well-stirred solution of 5-*tert*-butyladamantan-2-one (93 mg, 0.45 mmol) in methanol (5 mL) maintained at 0 °C. The reaction mixture was then allowed to stir overnight before being quenched with dilute hydrochloric acid and then extracted with ether (2 × 1). The combined extracts were dried ($MgSO_4$) and then evaporated in vacuo to afford the mixture of alcohols as a white solid (81.1 mg, 87%). An analysis by ^{13}C NMR indicated a 55/45 mixture of the *E*/*Z* isomers. This was confirmed by VPC. **(*E*)-5-*tert*-Butyl-2-adamantanol:** ^{13}C NMR ($CDCl_3$, relative to Me_4Si) 35.31 (C1, 3), 74.56 (C2), 34.76 (C4, 9), 35.65 (C5), 36.24 (C6), 28.06 (C7), 30.59 (C8, 10), 34.58 (Cq), 24.82 (CH_3). **(*Z*-5-*tert*-Butyl-2-adamantanol:** ^{13}C NMR ($CDCl_3$, relative to Me_4Si) 35.25 (C1,3), 73.79 (C2), 29.59 (C4, 9), 35.89 (C5), 36.20 (C6), 27.60 (C7), 35.99 (C8, 10), 34.90 (Cq), 24.55 (CH_3). These shifts are in accord with literature values.[1a]

A sample of the alcohol mixture (60 mg, 0.27 mmol) was fluorinated employing DAST as the reagent in the same manner described for the preparation of 2-fluoroadamantane.[2a] The fluoride mixture (50 mg) was obtained as a colorless soil after chromatography on basic alumina (pentane as eluent). An analysis by ^{13}C NMR indicated a 51/49 mixture of the *E*/*Z* isomers. This was confirmed by ^{19}F NMR (51/49), VPC (50/50), and GC-MS. **(*E*)-5-*tert*-Butyladamant-2-yl fluoride (2, R = F and Y = H):** ^{13}C NMR ($CDCl_3$, relative to Me_4Si) 33.53, J_{CF} = 16.85 Hz (C1, 3), 95.04, J_{CF} = 177.70 Hz (C2), 34.64, J_{CF} = 9.24 Hz (C4, 9), 35.74 (C5), 35.99, J_{CF} = 3.75 Hz (C6), 27.76 (C7), 31.05 (C8, 10), 34.96 (Cq), 24.88 (CH_3); ^{19}F NMR (relative to internal $FCCl_3$) δ (ppm) −178.51 ($CDCl_3$), −178.52 (c-C_6H_{12}); HRMS(EI) calcd for $C_{14}H_{23}F$ 210.1783, found 210.1791. **(*Z*)-5-*tert*-Butyladamant-2-yl fluoride (3, R = F and Y = H):** ^{13}C NMR ($CDCl_3$, relative to Me_4Si) 33.02, J_{CF} = 17.74 Hz (C1, 3), 95.94, J_{CF} = 177.92 Hz (C2), 30.20 (C4, 9), 35.74 (C5), 35.93, J_{CF} = 3.75 Hz (C6), 27.43, J_{CF} = 1.51 Hz (C7), 35.23, J_{CF} = 8.95 Hz (C8, 10), 34.96 (Cq), 24.60 (CH_3); ^{19}F NMR (relative to internal $FCCl_3$) δ (ppm) −174.39 ($CDCl_3$), −174.38 (c-C_6H_{12}); HRMS(EI) calcd for $C_{14}H_{23}F$ 210.1783, found 210.1791. The ^{13}C NMR spectra were assigned by additivity methodology[21] as well as the characteristic carbon−fluorine coupling constant pattern in 2-fluoroadamantanes.[2a] *E*-Isomer (calcd): 33.52 (C1,3), 95.30 (C2), 34.37 (C4,9), 35.84 (C5), 35.86 (C6), 27.91 (C7), 31.17 (C8,10). *Z*-Isomer (calcd): 33.52 (C1,3), 95.30 (C2), 30.10 (C4,9), 36.18 (C5), 35.86 (C6), 27.57 (C7), 35.44 (C8, 10). The ^{19}F NMR spectra were assigned on the basis of the unambiguously assigned corresponding spectra of the methyl analogues (**2** and **3**, R = F and Y = H; X = CH_3).[2b] *E*-Isomer: δ (ppm, relative to internal $FCCl_3$) −178.76 ($CDCl_3$), −178.95 (c-C_6H_{12}). *Z*-Isomer: δ (ppm, relative to internal $FCCl_3$) −174.41 ($CDCl_3$), −174.52 (c-C_6H_{12}).

Acknowledgment. We are grateful to the Australian Research Council for partial financial support of this work.

Supporting Information Available: Melting (or boiling) points, yields, exact mass data, ^1H and ^{13}C NMR data of the ketals **4** as well as ^{13}C NMR data of (*E*)- and (*Z*)-5-substituted (X) 2-methoxyadamantanes (**2** and **3**, Y = H and R = OCH_3, respectively) (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO970600P

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