Steric effects in the ionic hydrogenation of aryldi(1-adamantyl)-methanols to the corresponding methanes by trifluoroacetic acid and hydrosilanes or sodium borohydride

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The stereoselectivity of the hydrosilane reduction of substituted di(1-adamantyl)benzyl cations obtained by the protonation of aryldi(1-adamantyl)methanols by trifluoroacetic acid (TFA) in dichloromethane depends on both the hydrosilane and the substituent. Hydrosilanes react with *meta*-substituted (Me, Bu^t or CF_3) phenyldi(1-adamantyl)methanols to give variable amounts of the *anti* and *syn* hydrocarbons, the variations being rather more pronounced for Bu^t (*anti*:*syn* = 0.7–23) than for Me (0.32–3.8) and CF_3 (0.41–5.4). Almost all *o*-tolyldiadamantylmethanes give the *anti* isomer exclusively, as established by NMR spectroscopy and a single crystal X-ray diffraction study of the *p*-fluoro derivative. In the case of the [2-methyl-5-(*tert*-butyl)phenyl]diadamantylmethyl cation, however, the stereoselectivity and the rate of hydride transfer depend on the hydrosilane, the most encumbered giving hydrocarbon very slowly. Replacing the hydrosilane by sodium borohydride in these reactions results in untypical stereoselectivities. In particular, small yields of *anti*-(2-ethylphenyl)diadamantylmethane result from reduction of the corresponding alcohol, whereas normally only products with the *syn* conformation are obtained from this material.

Stable silylium ions (R_3Si^+),[1] the silicon counterparts of carbenium ions, have proved to be elusive species, and there is considerable debate as to whether they can exist in the condensed phase. Claims by Lambert *et al.* to have established by NMR, conductimetric and cryoscopic studies the formation of nearly free silylium ions in condensed media[2] have been widely criticized on theoretical and experimental grounds.[3,4] Even solids isolated by associating a silylium ion with a weakly coordinating anion prove to be at the most 50–70% ionic.[2g–i,5] A sterically protected trimesitylsilylium cation, apparently stable in aromatic solvents,[6] and an intramolecularly π-stabilized silanorbornyl cation[7] were recently reported, but no doubt the degree of silylium ion character in these and other species will remain controversial.

On the other hand, it seems to be accepted, albeit on rather slender evidence,[8] that silylium ions can occur as transient intermediates in reactions involving, for example, hydride transfer from hydrosilanes to other species, particularly carbenium ions. There is no proof, however, that the intermediate silylium ions are free and that there is not a loosely coordinated fourth or even fifth ligand (solvent or anion), as NMR studies and *ab initio* calculations suggest.[4] Single electron transfer [SET, eqn. (1)] and synchronous hydride transfer [SHT, eqn. (2)]

$$R_3SiH + {}^+CR'_3 \rightleftharpoons \underset{\text{encounter complex}}{[R_3SiH\ {}^+CR'_3]} \longrightarrow \underset{\text{free radical pair}}{\{R_3Si^+H\cdot\cdot CR'_3\}} \longrightarrow R_3Si^+ + HCR'_3 \quad (1)$$

$$R_3SiH + {}^+CR'_3 \longrightarrow \underset{\text{transition state}}{[R_3Si\cdots H\cdots CR'_3]^+} \longrightarrow R_3Si^+ + HCR'_3 \quad (2)$$

mechanisms have been proposed for such hydride transfers. Arguments in favour of the SET mechanism were advanced by Chojnowski *et al.*[9] Curiously, despite the fact that tri(*tert*-butyl)silane reacted too slowly with the triphenylmethyl cation for its rate to be measured accurately, the similarity of the rate constants for a series of tri-*n*-alkylsilanes was considered to show that steric effects were small, and to support the SET mechanism. Recent work on isotope effects[10] and *ab initio* calculations,[11] however, strongly support the SHT process; theory indicates an early, linear transition state for the reaction of CH_3^+ with SiH_4. The rates of hydride transfer from a large number of hydrosilanes to *para*-substituted diarylcarbenium ions have been interpreted[10] in terms of the stabilization of the silylium ions formed in the rate-determining step (see Table 1).

Reactions in which hydrosilanes function as selective reducing agents have considerable synthetic interest.[12] Conversion of an alcohol to a carbenium ion by means of trifluoroacetic acid (TFA) in chloroform or dichloromethane and reduction of this ion by means of a hydride donor, generally a hydrosilane[12] (though other reducing agents have been used[13]), is known as 'ionic hydrogenation'. In previous work we have considered two ways of reducing tertiary alcohols, in particular aryldi(1-adamantyl)methanols, to the corresponding alkanes.[14,15] In the first, conversion to the bromide by reaction with oxalyl bromide is followed by free radical reduction of the bromide by tri-*n*-butyltin hydride.[16] When applied to *meta*-substituted aryldi(1-adamantyl)methanols, where the alcohols, **1** and **2** and the methanes, **3** and **4**, can exist in two rotameric forms, this route gives mixtures of the *anti* and *syn* isomers in ratios not very different from those of the thermodynamically equilibrated mixtures.[14]

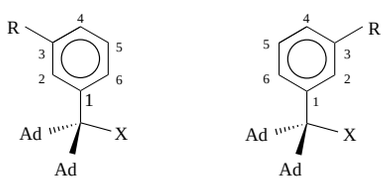
However, *anti*-*o*-tolyldi(1-adamantyl)methanol, **5a**, is converted to *syn*-*o*-tolyldiadamantylmethane, **7a**, by the radical route[14] but to the much less stable *anti* isomer, **6a**, by ionic hydrogenation.[15] A possible reason for this difference, involving intramolecular hydrogen transfer from methyl, has been proposed.[17]

We report here results on the ionic hydrogenation of *meta*-substituted aryldi(1-adamantyl)methanols, **1** or **2** and **5**, which show that the steric bulk of the hydrosilane and the substituent

Table 1 Reduction of *meta*-substituted phenyldi(1-adamantyl)methanols, **1** or **2** and [2-methyl-5-(*tert*-butyl)phenyl]di(1-adamantyl)methanol, **5b**, to the corresponding methanes by TFA–hydrosilane or sodium borohydride: *anti*:*syn* ratios and rate constants for reaction of hydrosilanes with *p*-anisylphenylcarbenium ion[10]

	Alcohol (**a**: R = Me; **b**: Bu^t; **c**: CF_3)				
Hydrosilane	**1** (or **2**)**a** (**3a**:**4a**)	**1**(or **2**)**b** (**3b**:**4b**)	**2c** (**3c**:**4c**)	**5d** (**6d**:**7d**)	k_2/dm^3 mol^{-1} s^{-1}[a]
n-$HexSiH_3$ (NHS)	0.83	0.74	0.52	2.9	0.048
Ph_2SiH_2 (DPS)	0.58	1.3	0.52	5.8	1.2
Ph_3SiH (TPS)	0.32	2.5	0.49	1.6[c]	8.27
$(Pr^i)_3SiH$ (TIPS)	0.72	21	0.60[b]	—[d]	36.7
Et_3SiH (TES)	0.68	3.4	0.41	6.2	124
Me_2PhSiH (DMPS)	0.66	4.1	0.39	2.5	149
$(Me_3Si)_3SiH$ (TTMSS)	3.8	23	5.4	1.2[b]	457
$NaBH_4$	0.66	0.80	0.59	12.0	—

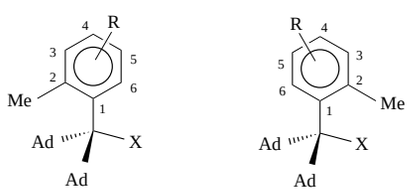
[a] Second-order rate constant for reaction with *p*-anisylphenylcarbenium ion at −70 °C (ref. 10). [b] 6 d. [c] 15 d. [d] No reaction in 30 d.



1: X = OH **2**: X = OH

3: X = H **4**: X = H

a: R = Me; **b**: Bu^t; **c**: CF_3



5: X = OH

6: X = H **7**: X = H

a: R = H; **b**: 4-Me; **c**: 5-Me; **d**: 5-Bu^t; **e**: 4-Cl

f: 5-Cl; **g**: 4-F; **h**: 5-F; **i**: 4-OMe; **j**: 3,4,5-Me_3

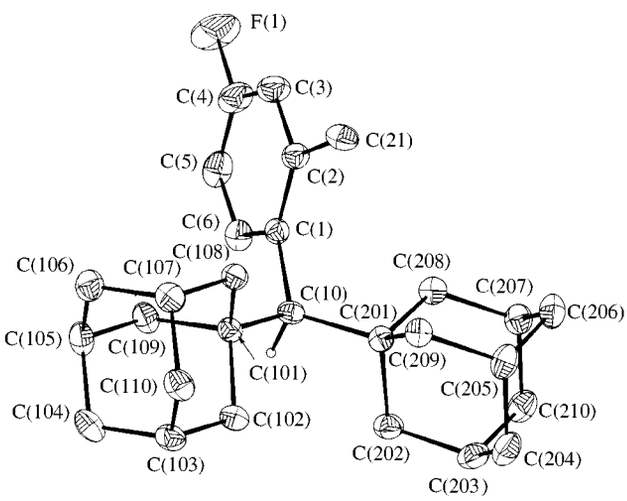


Fig. 1 CAMERON diagram of *anti*-(2-methyl-4-fluorophenyl)di-(1-adamantyl)methane, **6g**

can have important effects on the stereochemistry of hydride transfer. Qualitative experiments suggest that the kinetics of this process also depend on the hydrosilane. Sodium borohydride, a reagent often used with TFA for the reduction of ketones and alcohols,[13] has also been examined.

Reduction of *meta*-substituted aryldiadamantylmethanols

Though not separated, the *anti* and *syn* isomers of *m*-tolyl- and [*m*-(*tert*-butyl)phenyl]diadamantylmethanes, (**3a**,**b** and **4a**,**b**) have been identified and characterized by ^{13}C and ^1H NMR spectroscopy.[14] The methyl derivatives, **3a** and **4a**, are readily distinguished by the methyl proton signals at 2.37 and 2.30 ppm, respectively, while the *tert*-butyl protons in **3b** and **4b** appear at 1.34 and 1.30 ppm, respectively. The *m*-trifluoromethyl derivatives, **1c** and **2c**, have not been previously reported. The most readily obtained was the *syn* isomer, **2c**, though the *anti* isomer, **1c**, was also isolated and characterized. In the present work *meta*-substituted phenyldiadamantylmethanols, **1** or **2**, were subjected to ionic hydrogenation with a variety of hydrosilanes. The methyl derivative gives approximately the same mixture of *anti* and *syn* methanes, **3a** and **4a**, (*anti*:*syn* = 0.6–0.8) regardless of the silane, except when tris(trimethylsilyl)silane (TTMSS) and triphenylsilane (TPS) are used; in the former case the *anti*:*syn* ratio increases from the equilibrium value of about 0.8 to approximately 4 (Table 1), while for the latter it falls to 0.32. The use of sodium borohydride as hydride ion source gives a value insignificantly different from those obtained with typical hydrosilanes. The range of values is slightly greater for the trifluoromethyl substituent (0.41–5.4; equilibrium value = 0.90). With the analogous *tert*-butyl derivative the *anti*:*syn* ratio, **3b**:**4b**, depends markedly on the nature of the hydrosilane, going from 0.7 to 0.8 (below the equilibrium value of 1.2) for *n*-hexylsilane (NHS) and sodium borohydride, respectively, to over 20 for triisopropylsilane (TIPS) and TTMSS. TPS, which might be considered to be akin to TIPS in its steric requirements, gives a remarkably low value of 2.5.

Reduction of *o*-tolyldiadamantylmethanols, 5

The *anti* and *syn* isomers of *o*-tolyldiadamantylmethane, **6a** and **7a**, are readily distinguished by the NMR shifts of the hydrogen and carbon of the benzylic CH and 2-Me groups. Whereas in the *anti* isomer, **6a**, the benzyl group and methyl proton NMR signals are at 2.31 and 2.53 ppm, respectively,[15] they are almost exactly reversed, at 2.49 and 2.32 ppm, respectively, in the *syn* isomer, **7a**.[14] Again, in the ^{13}C NMR spectrum the methyl carbon is at 25.6 and 22.2 ppm in the *anti* and *syn* isomers, respectively, while the benzylic carbon is at 74.4 and 60.7 ppm, respectively.[14,15]

Complete reaction of substituted *anti*-*o*-tolyldiadamantylmethanols, **5**, with TFA–TES under the conditions given in the Experimental section requires about 3 h, except for **5d** and **5j** which are notably less reactive (*ca*. 24 h). The product is in

Table 2 X-Ray crystallographic data for *anti*-(2-methyl-4-fluorophenyl)di(1-adamantyl)methane, **6g**

Bond lengths/Å	
C(1)–C(10)	1.554(4)
C(10)–C(101)	1.581(4)
C(10)–C(201)	1.599(4)
C_{ar}–C_{ar} (mean)	1.384
Bond angles (°)	
C(2)–C(1)–C(10)	128.6(3)
C(6)–C(1)–C(10)	114.3(3)
C(1)–C(2)–C(21)	126.4(3)
C(3)–C(2)–C(21)	114.2(3)
C(1)–C(10)–C(101)	112.6(2)
C(1)–C(10)–C(201)	115.7(2)
C(101)–C(10)–C(201)	120.7(2)
Torsion angles (°)	
C(2)–C(1)–C(10)–C(101)	76.5(4)
C(2)–C(1)–C(10)–C(201)	−68.0(5)
C(2)–C(1)–C(10)–H(101)	−177.2
C(6)–C(1)–C(10)–H(101)	4.7
C(1)–C(10)–C(101)–C(102)	167.8(3)
C(1)–C(10)–C(101)–C(108)	−66.8(4)
C(1)–C(10)–C(101)–C(109)	52.4(3)
C(1)–C(10)–C(201)–C(202)	−133.2(3)
C(1)–C(10)–C(201)–C(208)	−18.9(4)
C(1)–C(10)–C(201)–C(209)	104.6(3)

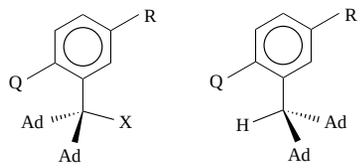
almost all cases the methane with a benzylic carbon shift close to 74 ppm, the 2-Me at about 25 ppm and the corresponding hydrogens at roughly 2.3 and 2.5 (except **6j**) ppm, respectively, indicating formation of the *anti* isomer, **6**. A single-crystal X-ray diffraction study of the *p*-fluoro derivative, **6g**, confirmed that it was indeed the *anti* isomer (Fig. 1). It shows the familiar features of aryldiadamantylmethanes and the corresponding alcohols,[17,18] with long bonds to the benzylic carbon, an in-plane deformed benzene ring and a very large Ad–C–Ad bond angle (Table 2).

In the case of the *m*-(*tert*-butyl) derivative, **5d**, the *tert*-butyl group being *para* to the *ortho* methyl, a small amount of the *syn* isomer, **7d**, is also formed; this was completely characterized by comparing the spectra of the pure *anti* isomer with those of the mother liquors from its crystallization. Variations in the *anti*:*syn* isomer ratio, **6d**:**7d**, are observed when other hydride donors are used (Table 1). In the presence of TTMSS and TPS the red colour of the carbenium ion persists for several days, complete reaction with these hydrosilanes requiring approximately 6 and 15 d, respectively; with TIPS there was no reaction after 30 d. Overall, borohydride is the most stereoselective reagent and TTMSS the least. Refluxing the prehnityl derivative, **5j**, with TTMSS gave a mixture of **6j** and the *syn* isomer, **7j**, together with other, unidentified materials.

Reduction of other *o*-alkyldiadamantylmethanols

ortho Substituents other than methyl are difficult to introduce into aryldiadamantylmethanols, the only success to date being with ethyl and isopropyl groups, giving **8a** and **8b**.[17]

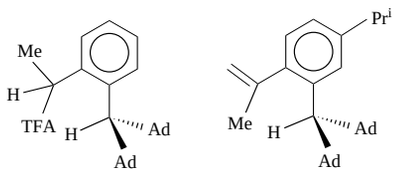
Attempts to reduce these derivatives with TFA–TES result only in products, **11** and **12**, respectively, with the *syn* structure, *i.e.* with the two adamantyl groups remote from the *ortho* substituent, whatever it is.[17] This unusual stereochemistry is attributed to an intramolecular hydride shift from the ethyl or isopropyl group to the carbenium ion centre, this reaction being faster than intermolecular reaction with a hydride donor. However, given that sodium borohydride is much more reactive than hydrosilanes, it seemed possible that the competition between internal and external hydride transfer would not be completely one-sided. Preliminary experiments on *anti*-(2-ethylphenyl)di-(1-adamantyl)methanol, **8a**, indicated that initially a mixture of the *syn* hydrocarbon, **10a**, the trifluoroacetate derivative, **11**, and another hydrocarbon is formed. If the mixture is left for



8: X = OH

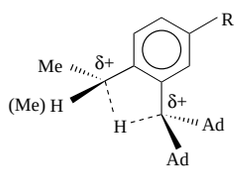
9: X = H **10**

a: Q = Et; R = H; **b**: Q = R = Pr^i



11 **12**

about 72 h the trifluoroacetate is reduced to the *syn* hydrocarbon, the yield of the other being unchanged. The procedure given in the Experimental section gives some 27% of the second hydrocarbon, the NMR and MS spectra of which are consistent with its being the *anti* isomer, **9a**. Various attempts to improve the yield of this isomer, by increasing the amount of borohydride, reducing the amount of TFA or changing the solvent, were unsuccessful.



Similar treatment of *anti*-(2,5-diisopropylphenyl)di(1-adamantyl)methanol, **8b**, results in a mixture of the known hydrocarbon, **10b**, and the styrene derivative, **12**, both with the *syn* conformation.[17] Very small peaks, possibly characteristic of the *anti* isomer, **9b**, indicate that at the most about 2% of this material is formed.

Discussion

Kinetics and mechanism

The *ortho*-substituted derivatives, **5**, are completely ionized in 10% TFA in dichloromethane giving deep red solutions, the broad absorption bands having extinction coefficients of about 6000 $dm^3\ mol^{-1}\ cm^{-1}$ at a maximum near 355 nm.[15,19] The colouration disappears slowly during the reaction of the carbenium ion with a hydrosilane. In contrast, alcohols **1** or **2** are partially or insignificantly ionized in TFA–CH_2Cl_2 and give light yellow or colourless solutions, depending on the substituent (extinction coefficient *ca.* 100 $dm^3\ mol^{-1}\ cm^{-1}$ at 350 nm for alkyl substituents, less than 3 $dm^3\ mol^{-1}\ cm^{-1}$ for trifluoromethyl). When **1a**,**b** or **2a**,**b** are reduced by the more reactive hydrosilanes (DMPS, DPS, NHS and TES), added before the TFA, there is no colouration, whereas with TIPS, TPS or TTMSS one observes the same light yellow colouration as in the absence of hydrosilane. With TIPS this colour is persistent, while with the other two hydrosilanes it fades over a period of minutes.

Mayr's scheme[10] requires slight modification in order to accommodate these results. In the general case (alcohols **1** or **2**) the carbenium ion, Z^+, is not preformed but is produced by reversible protonation/dehydration of the alcohol, ZOH, by reaction with an acid, LH^+, and then reacts with hydrosilane in a step which is not necessarily rate–determining [eqns. (3) and (4)].

$$ZOH + LH^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Z^+ + H_2O + L \quad (3)$$

$$Z^+ + R_3SiH \xrightarrow{k_2} ZH + R_3Si^+ \quad (4)$$

Our qualitative observations and preliminary kinetic studies[20] suggest that with small, reactive silanes carbenium ion formation (k_1) is rate-determining, whereas with the bulky silanes hydride transfer (k_2) is the slow step. Paradoxically, these bulky silanes are associated with the formation of stabilized silylium ions and, therefore, high reactivity in Mayr's work.[10]

Ab initio calculations on very simple models of the reaction[11] indicate that the preferred mechanism is synchronous hydride transfer (rather than SET) and that the transition state in solution is early. For the reaction of CH_3^+ with SiH_4 in dichloromethane the carbon bears an almost complete unit charge (+0.96), the silicon +0.38 and the transferred hydrogen −0.34. Clearly, in real systems with non-hydrogen substituents at the carbon and silicon atoms, the charges would be less than indicated here. Insofar as the rate-limiting step in the SET mechanism is single-electron transfer followed by the migration of a hydrogen, steric effects should be small. At first sight, therefore, our results would appear to argue against this mechanism. However, there is no obvious reason why the pre-equilibrium formation of the encounter complex should not be sterically controlled. It is not clear, then, why the alleged absence of steric effects was taken as a criterion for the SET mechanism,[9] and our data must be considered to be equivocal as regards the mechanism.

Steric and electronic effects

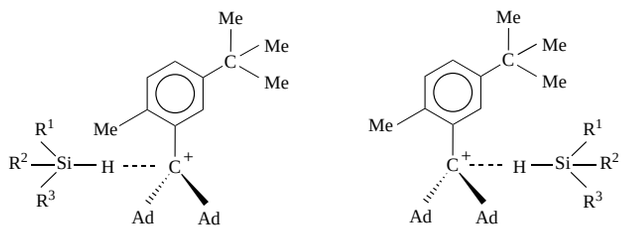
In principle, we could compare the geometries of the various hydrosilanes by, for example, molecular mechanics calculations. However, this would not enlighten us as to their steric requirements in the context of hydride transfer to a carbenium ion, since there is little information, apart from the *ab initio* calculations, concerning the transition state of this reaction upon which to base a model.

Nevertheless, though it is not possible to compare the steric requirements of compounds such as TES, DPS, NHS and DMPS, it seems fairly obvious that both TTMSS and TIPS will be more space-demanding than TES and NHS, and TPS more than DPS. The polar effects of the various substituents to the silicon atom are, according to Mayr's work,[10] very different. Silylium ion stabilization increases by a factor of 10 000 on going from NHS to TTMSS (Table 1), trisubstituted hydrosilanes being more reactive than di- and mono-substituted derivatives, in that order. Phenyl substituents, despite their potential for conjugative charge delocalization, stabilize silylium ions less than alkyl groups. It is noteworthy that TIPS is less effective, by a factor of up to 10, than tri-*n*-alkylsilanes, which suggests that its reactivity even with diarylcarbenium ions is partly controlled by steric effects. Giering's QALE approach,[21] which expresses reactivity in terms of steric, electronic and aryl parameters, gives a reasonably good correlation ($r^2 = 0.961$) of Mayr's data, indicating, in particular, a small inhibitory steric effect.

Crystallographic studies on silylium ion-like species obtained from trialkylsilanes and a large, weakly coordinating halogenated carborane ligand suggest that the triisopropyl derivative most nearly approaches the ideal planar structure [more than tri(*tert*-butyl)], this geometry favouring C–H hyperconjugative stabilization,[4] though this factor is less important in silylium ions than in carbocations.[8,22] The very low reactivity of TIPS with diadamantylbenzyl cations would appear to indicate that in this highly congested system steric repulsion outweighs inductive and hyperconjugative stabilization of the incipient triisopropylsilylium ion. TIPS is reported to react about 100 times more slowly with Ag^+ than does TES.[23]

The results on *meta*- or *para*-substituted *o*-tolyldi(1-adamantyl)methanols reported here indicate, not surprisingly, that the stereochemistry of carbenium ion reduction is indifferent to the electron-donating or -attracting nature of the substituent, hydride donor approach *anti* to the *ortho* methyl being the rule. On the other hand, a *tert*-butyl group in the *meta* position has an obviously steric effect upon the approach of the hydrosilane, this effect being comparable in magnitude to that of the *ortho* methyl substituent. This is reflected not only in the fact that significant amounts of the *syn* isomer are formed (though the donor dependence of the stereoselectivity follows no obvious pattern) but also, qualitatively, in the lower reaction rate with TES. Low reactivity is a feature shared by the methyl-buttressed prehnityl derivative. The *syn* isomer, **7j**, was obtained when the precursor, TTMSS, of the most stable silylium ion (but the most bulky) reacted with the corresponding carbenium ion.

Steric effects upon the reduction of the various diadamantylbenzyl cations can be qualitatively appreciated by considering the following scheme for the reaction of the [2-methyl-5-(*tert*-butyl)]-substituted system.



We assume that the hydrosilane approaches the cation with the Si–H distance substantially shorter than H–C^+, that the incipient bond is roughly orthogonal to the plane of the carbocation which in this early transition state is little pyramidalized, and that the Si, H and C^+ atoms are roughly colinear. It should not be assumed, however, that the silicon atom is in the plane of the aromatic ring. In the example shown, the stereoselectivity is determined by the interaction between the substituents to silicon and the 2-methyl or the *tert*-butyl group methyls. When the *tert*-butyl group is replaced by hydrogen or a small substituent, attack is *anti* to the remaining 2-methyl group in **5**; when the 2-methyl is replaced by hydrogen (alcohol **1b** or **2b**) the product is predominantly *anti*, with the bulky substituent remote from the incoming hydride donor; its proportion is higher than the thermodynamic value (*anti*:*syn* = 1.2) for TPS, TES and DMPS. While it is reasonable that the ratio should be higher for TPS than DPS, it is less clear why the replacement of two phenyls by two small methyl groups (DMPS) should result in a further increase. For both TIPS and TTMSS the very high *anti*:*syn* ratios are consistent with steric control.

The stereoselectivity of the reduction of carbenium ions where there is a smaller *meta* substituent depends very much on the nature of the hydride donor. For *meta* methyl the variations with small hydrosilanes are minor and random, the *anti*:*syn* ratio being generally not far from the thermodynamic value. The behaviour of TPS is anomalous in that it gives a very low *anti*:*syn* ratio, lower than for DPS which should be less sterically demanding. Only TTMSS manifests a clear steric effect with the methyl group, the *anti*:*syn* ratio rising to almost 4. The trifluoromethyl substituent greatly resembles the methyl group, the *anti*:*syn* ratio being small for all except TTMSS. What is surprising, however, is that there is a marked and very regular preference for formation of the *syn* isomer, suggestive of an electrostatic interaction between the electronegative substituent and the incoming hydride donor.

Sodium borohydride proves to be a very efficient hydride transfer agent, being sufficiently reactive for intermolecular hydride transfer to compete with intramolecular transfer in the particular case of *o*-(ethylphenyl)diadamantylmethyl cation.

While it is very unselective in its reactions with *meta*-substituted cations, it unexpectedly shows very high selectivity with the [2-methyl-5-(*tert*-butyl)phenyl]diadamantylmethyl cation, attack *anti* to the methyl group being much preferred.

Conclusions

When it is possible to distinguish the two faces of a carbenium ion by means of an unsymmetrical substituent which, moreover, is capable of exerting a steric effect, be it an *ortho* or, less obviously, a *meta*-substituted benzene ring, the stereoselectivity of hydride transfer to the charged centre depends on the nature of the hydride donor. Although it is not possible to quantify the steric requirements of the various hydrosilanes studied in this work, there does seem to be a tendency for product stereochemistry to be correlated with intuitive ideas of steric bulk, especially when a *meta tert*-butyl substituent is involved. When there are both *ortho* methyl and *meta tert*-butyl substituents hydride transfer to the face remote from *ortho* methyl prevails with, however, significant but unpredictable amounts of the other isomer being formed. UV–VIS spectroscopic observations emphasize the dichotomy between small and bulky hydrosilanes, there being an evident difference in the rate-determining step of the reaction for the two classes. Further work will be devoted to the kinetics of this reaction.

Experimental

General methods

NMR measurements were made on a Bruker AS 200 FT instrument operating at 200 MHz (proton) or 50 MHz (carbon). Unless stated otherwise all measurements were made in $CDCl_3$ and are referenced to internal TMS ($\delta = 0.00$ ppm for ^1H) or to the solvent ($\delta = 77.0$ ppm for ^{13}C); J in Hz. The ^{13}C NMR spectra were assigned on the basis of JMOD experiments and the additivity principle,[24] and the proton signals in some cases were located and identified by two-dimensional heteronuclear correlation experiments. Aromatic carbon and hydrogen shifts are listed in numerical order: C1, C2, C3, *etc.* The spectra of *syn*-[2-methyl-5-(*tert*-butyl)phenyl]di(1-adamantyl)-methane, **7d**, *syn*-(2,3,4,5-tetramethylphenyl)di(1-adamantyl)-methane, **7j**, and *anti*-(2-ethylphenyl)diadamantylmethane, **9a**, were derived from mixtures with the other isomers. GC–MS measurements were performed on a CP-Sil 5 capillary column coupled to a Finnigan MAT ITD 800B Ion Trap Detector with chemical ionization (isobutane).

[3-(Trifluoromethyl)phenyl]di(1-adamantyl)methanols, 1c and 2c. 3-Bromo(trifluoromethyl)benzene (6.3 mmol) in sodium–dry diethyl ether (20 cm^3) under argon at room temp. was treated with *tert*-butyllithium (1.5 mol dm^{-3} in pentanes, 3.5 cm^3, 5.3 mmol). After stirring for 15 min a solution of di(1-adamantyl) ketone (0.5 g, 1.7 mmol) in diethyl ether (40 cm^3) was added in 15–30 min. The reaction mixture was stirred for 2 h, and then worked up as usual. The alcohol was isolated by chromatography on alumina in light petroleum–diethyl ether mixtures to give a 1.6:1 mixture of the *syn* and *anti* isomers (0.71 g, 95%). Crystallization from *n*-hexane gave the *syn* isomer, **2c** (0.35 g, 47%): mp 218 °C; δ_C 145.0 (C1), 124.7 (C2, $J_{C\text{-}F}$ 3.8), 129.8 (C3, 31.3), 122.7 (C4, 3.8), 125.6 (C5), 131.4 (C6), 124.7 (CF_3, 272), 83.1 (COH), 44.6 (2 C_q), 39.4 (6 CH_2), 36.8 (6 CH_2) and 29.1 (6 CH); δ_H 7.96 (H2), 7.48 (H4), 7.37 (H5), 7.75 (H6), 2.09 (s, 1H) and 1.50–2.00 (2 Ad) (Found: C, 75.8; H, 8.0; F, 12.9. $C_{28}H_{35}OF_3$ requires C, 75.65; H, 7.94; F, 12.82%). From the mother liquors by fractional crystallization was obtained the *anti* isomer, **1c** (62 mg, 8%): mp 218–219 °C; δ_C 144.7 (C1), 124.8 (C2, $J_{C\text{-}F}$ 3.8), 127.6 (C3, 31.3), 122.6 (C4, 3.8), 127.7 (C5), 131.5 (C6), 124.6 (CF_3, 272), 83.2 (COH), 44.7 (2 C_q), 39.4 (6 CH_2), 36.8 (6 CH_2) and 29.1 (6 CH); δ_H 7.81 (H2), 7.47 (H4), 7.41 (H5), 7.84 (H6) and 1.50–2.00 (2 Ad).

[3-(Trifluoromethyl)phenyl]di(1-adamantyl)methanes, 3c and 4c. Alcohol **2c** (100 mg, 0.23 mmol) was dissolved in dichloromethane (10 cm^3) containing triethylsilane (0.1 cm^3, 0.63 mmol). The solution was stirred at room temp. and TFA (0.5 cm^3) was added. Stirring was continued for 24 h. The reaction mixture was diluted with light petroleum, washed with water and dried ($MgSO_4$). Evaporation of the solvent and chromatography on alumina in light petroleum gave a mixture of isomeric methanes (0.094 g, 97%): *anti*:*syn* = 0.41; mp 158 °C (Found: C, 78.7; H, 8.1; F, 13.0. $C_{28}H_{35}F_3$ requires C, 78.47; H, 8.23; F, 13.30%). *anti*, **3c**: δ_C 143.2 (C1), 125.8 (C2, $J_{C\text{-}F}$ 3.8), 128.6 (C3, 32.1), 122.2 (C4, 3.8), 127.4 (C5), 136.8 (C6), 124.6 (CF_3, 272), 69.3 (CH), 43.3 (6 CH_2), 38.7 (2 C_q), 36.9 (6 CH_2) and 29.1 (6 CH); δ_H 7.60 (H2), 7.44 (H4), 7.29 (H5), 7.10 (H6), 2.05 (s, 1H) and 1.5–2.0 (2 Ad). *syn*, **4c**: δ_C 143.3 (C1), 129.7 (C2, $J_{C\text{-}F}$ 3.8), 129.4 (C3, 31.2), 122.2 (C4, 3.8), 126.6 (C5), 132.7 (C6), 124.5 (CF_3, 272), 69.6 (CH), 43.3 (6 CH_2), 38.7 (2 C_q), 36.9 (6 CH_2) and 29.1 (6 CH); δ_H 7.17 (H2), 7.44 (H4), 7.36 (H5), 7.55 (H6), 2.04 (s, 1H) and 1.5–2.0 (2 Ad).

Thermal equilibration of 3-(trifluoromethyl) derivatives, 2c and 3c/4c. Samples of alcohol **2c** or the methane mixture **3c/4c** (20–25 mg) with $CDCl_3$ (0.5 cm^3) were sealed under vacuum in pyrex tubes. After 2 h at 120 °C the ^{13}C NMR spectra were recorded in order to determine the *anti*:*syn* ratios: **1c**:**2c** = 0.81; **3c**:**4c** = 0.90.

Determination of *anti*:*syn* ratio for reduction of (3-alkylphenyl)di(1-adamantyl)methanols, 1(or 2)a, 1(or 2)b, 2c. Samples of the 3-substituted phenyldi(1-adamantyl)methanols, **1**(or **2**)**a**, **1**(or **2**)**b** (either isomer can be used) and **2c** (20 mg, *ca.* 0.05 mmol) were dissolved in dichloromethane (5 cm^3). With magnetic stirring hydrosilane (0.15–0.3 cm^3, 1 mmol) or sodium borohydride (40 mg, 1 mmol) was added at room temp., followed by TFA (0.5 cm^3). For the alkyl-substituted alcohols with TPS and TTMSS a light yellow colouration (λ_{max} 350 nm, ε_{max} *ca.* 100 $dm^3\ mol^{-1}\ cm^{-1}$) persisted for several minutes, and with TIPS for several hours. The same absorption was found in the absence of hydride donor. There was no colouration when other hydrosilanes or sodium borohydride were used, nor for **2c** ($\varepsilon_{max} < 3$ $dm^3\ mol^{-1}\ cm^{-1}$). After 20 h (hydrosilanes) or 1 h ($NaBH_4$) no alcohol remained; the mixture was quenched with water and the products extracted with dichloromethane, washed with water, dried ($MgSO_4$) and the solvent evaporated. After column chromatography on alumina in light petroleum the residue (*ca.* 20 mg) was taken up in $CDCl_3$ (0.5 cm^3). For the alkyl-substituted compounds the *anti*:*syn* ratios (**3a**:**4a** and **3b**:**4b**) were determined from the ^1H and ^{13}C NMR spectra (Me or Bu^t proton signals, aromatic and benzylic CH carbon signals) by height comparison and integration, the differences on the percentage of either isomer being generally less than 2% (Table 1). For the trifluoromethyl derivatives only the aromatic and benzylic carbon signals could be used. All determinations were run at least in duplicate. The ^{13}C and ^1H NMR characteristics of **3a**,**b** and **4a**,**b** are given in ref. 14; those of **3c** and **4c** are given above.

Reduction of *anti*-2-tolyldi(1-adamantyl)methanols, 5. Substituted *anti*-2-tolyldi(1-adamantyl)methanols, **5** (100 mg, 0.22–0.26 mmol) were dissolved in dichloromethane (10 cm^3) containing triethylsilane (0.1 cm^3, 0.63 mmol). The solution was stirred at room temp. and TFA (0.5 cm^3) added. Stirring was continued until the initial deep red colouration was completely discharged; this required about 3 h for all except the 5-(*tert*-butyl) (**5d**) and 3,4,5-trimethyl (**5j**) derivatives which needed about 24 h. The reaction mixture was diluted with light petroleum, washed with water and dried ($MgSO_4$). Evaporation of the solvent and chromatography on alumina in light petroleum gave the corresponding methanes almost quantitatively (crystallization yields are given). NMR analysis showed the chromatographically purified products to be the *anti* isomers, **6**, except in the case of **5d** where the *anti* isomer was obtained from a mixture of *anti* and *syn* methanes by crystallization from *n*-hexane. Details on **6a** are given in ref. 15.

***anti*-(2,4-Dimethylphenyl)di(1-adamantyl)methane, 6b.** (76 mg, 79%); mp 237 °C; δ_C 138.6 (C1), 135.9 (C2), 132.5 (C3), 134.8 (C4), 125.1 (C5), 137.5 (C6), 73.8 (CH), 44.0 (6 CH_2), 39.1 (2 C_q), 37.0 (6 CH_2), 29.4 (6 CH), 25.5 (2-Me) and 20.7 (4-Me); δ_H 6.94 (H3), 6.80 (H5), 6.81 (H6), 2.50 (2-Me), 2.28 (4-Me), 2.28 (CH) and 1.5–2.0 (2 Ad) (Found: C, 89.7; H, 10.5. $C_{29}H_{40}$ requires C, 89.63; H, 10.37%).

***anti*-(2,5-Dimethylphenyl)di(1-adamantyl)methane, 6c.** (71 mg, 74%); mp 163 °C; δ_C 141.5 (C1), 133.2 (C2), 131.6 (C3), 126.3 (C4), 133.1 (C5), 138.2 (C6), 74.3 (CH), 44.0 (6 CH_2), 39.1 (2 C_q), 37.0 (6 CH_2), 29.4 (6 CH), 25.2 (2-Me) and 20.9 (5-Me); δ_H 7.01 (*J* 7.6, H3), 6.91 (*J* 1.4 and 7.6, H4), 6.74 (*J* 1.4, H6), 2.49 (2-Me), 2.27 (5-Me), 2.27 (CH) and 1.6–2.0 (2 Ad) (Found: C, 89.3; H, 10.3. $C_{29}H_{40}$ requires C, 89.63; H, 10.37%).

***anti*-[2-Methyl-5-(*tert*-butyl)phenyl]di(1-adamantyl)methane, 6d.** (55 mg, 57%); mp 273 °C; δ_C 141.1 (C1), 133.1 (C2), 131.2 (C3), 122.1 (C4), 146.6 (C5), 134.9 (C6), 74.9 (CH), 44.0 (6 CH_2), 39.1 (2 C_q), 37.0 (6 CH_2), 29.5 (6 CH), 25.2 (2-Me) and 31.4, 33.9 (Bu^t); δ_H 7.03 (*J* 8.0, H3), 7.11 (*J* 1.9 and 8.0, H4), 6.90 (*J* 1.9, H6), 2.49 (2-Me), 2.28 (CH), 1.5–2.0 (2 Ad) and 1.29 (Bu^t); *m*/*z* (ITD) 429, 373, 295, 294, 293, 237, 136, 135 (100%), 107, 93, 79 (Found: C, 89.4; H, 10.9. $C_{32}H_{46}$ requires C, 89.24; H, 10.76%).

***syn*-[2-Methyl-5-(*tert*-butyl)phenyl]di(1-adamantyl)methane, 7d.** δ_C 140.6 (C1), 134.8 (C2), 129.3 (C3), 121.2 (C4), 146.2 (C5), 127.95 (C6), 61.0 (CH), 43.2 (6 CH_2), 39.7 (2 C_q), 37.1 (6 CH_2), 29.3 (6 CH), 21.4 (2-Me) and 31.4, 34.1 (Bu^t); δ_H 7.03 (*J* 8.0, H3), 7.09 (*J* 1.7 and 8.0, H4), 7.35 (*J* 1.7, H6), 2.27 (2-Me), 2.46 (CH), 1.5–2.0 (2 Ad) and 1.33 (Bu^t); *m*/*z* (ITD) 429, 373, 295, 294, 293, 237, 136, 135 (100%), 107, 93, 79.

***anti*-(2-Methyl-4-chlorophenyl)di(1-adamantyl)methane, 6e.** (90 mg, 94%); mp 252 °C; δ_C 140.3 (C1), 138.2 (C2), 131.3 (C3), 130.9 (C4), 124.4 (C5), 138.5 (C6), 73.7 (CH), 44.0 (6 CH_2), 39.2 (2 C_q), 36.9 (6 CH_2), 29.4 (6 CH) and 25.5 (2-Me); δ_H 7.11 (*J* 2.3, H3), 6.96 (*J* 2.3 and 8.3, H5), 6.85 (*J* 8.3, H6), 2.51 (2-Me), 2.29 (CH) and 1.5–2.0 (2 Ad) (Found: C, 81.9; H, 9.0; Cl, 8.6. $C_{28}H_{37}Cl$ requires C, 82.22; H, 9.12, Cl, 8.67%).

***anti*-(2-Methyl-5-chlorophenyl)di(1-adamantyl)methane, 6f.** (80 mg, 83%); mp 186 °C; δ_C 143.9 (C1), 134.9 (C2), 133.0 (C3), 125.4 (C4), 129.7 (C5), 136.3 (C6), 74.2 (CH), 44.0 (6 CH_2), 39.2 (2 C_q), 36.9 (6 CH_2), 29.4 (6 CH) and 25.0 (2-Me); δ_H 7.05 (H3), 7.05 (H4), 6.94 (H6), 2.50 (2-Me), 2.24 (CH) and 1.5–2.0 (2 Ad) (Found: C, 81.9; H, 9.1; Cl, 8.6. $C_{28}H_{37}Cl$ requires C, 82.22; H, 9.12, Cl, 8.67%).

***anti*-(2-Methyl-4-fluorophenyl)di(1-adamantyl)methane, 6g.** (63 mg, 66%); mp 148 °C; δ_C 137.4 (*J* 3.4, C1), 138.2 (*J* 7.0, C2), 117.7 (*J* 19.9, C3), 160.8 (*J* 243.7, C4), 111.1 (*J* 19.6, C5), 138.5 (*J* 7.3, C6), 73.4 (CH), 44.0 (6 CH_2), 39.2 (2 C_q), 36.9 (6 CH_2), 29.4 (6 CH) and 25.7 (2-Me); δ_H 6.82 (*J* 2.9 and 10.0, H3), 6.69 (*J* 2.9, 8.2 and 8.2, H5), 6.87 (H6), 2.53 (Me), 2.31 (CH) and 1.6–2.0 (2 Ad) (Found: C, 85.5; H, 9.4; F, 4.8. $C_{28}H_{37}F$ requires C, 85.66; H, 9.50; F, 4.84%).

***anti*-(2-Methyl-5-fluorophenyl)di(1-adamantyl)methane, 6h.** (74 mg, 77%); mp 149 °C; δ_C 144.1 (*J* 6.0, C1), 131.9 (*J* 2.7, C2), 132.8 (*J* 7.7, C3), 112.2 (*J* 20.2, C4), 159.8 (*J* 242.0, C5), 123.1 (*J* 19.8, C6), 74.5 (CH), 44.0 (6 CH_2), 39.3 (2 C_q), 36.9 (6 CH_2), 29.4 (6 CH) and 24.8 (2-Me); δ_H 7.05 (*J* 6.6 and 8.2, H3), 6.79 (*J* 2.7, 8.0 and 8.2, H4), 6.66 (*J* 2.7 and 11.0, H6), 2.50 (2-Me), 2.24 (CH) and 1.6–2.0 (2 Ad) (Found: C, 85.4; H, 9.4; F, 4.7. $C_{28}H_{37}F$ requires C, 85.66; H, 9.50; F, 4.84%).

***anti*-(2-Methyl-4-methoxyphenyl)di(1-adamantyl)methane, 6i.** (68 mg, 71%); mp 221 °C; δ_C 134.1 (C1), 137.3 (C2), 116.6 (C3), 157.2 (C4), 109.5 (C5), 138.3 (C6), 73.4 (CH), 44.0 (6 CH_2), 39.2 (2 C_q), 37.0 (6 CH_2), 29.4 (6 CH) and 25.8 (2-Me); δ_H 6.67 (*J* 8.4, H3), 6.56 (*J* 2.8, H5), 6.83 (*J* 2.8 and 8.4, H6), 3.78 (4-OMe), 2.53 (2-Me), 2.26 (CH) and 1.6–2.0 (2 Ad) (Found: C, 86.0; H, 10.1. $C_{29}H_{40}O$ requires C, 86.08; H, 9.96%).

***anti*-(2,3,4,5-Tetramethylphenyl)di(1-adamantyl)methane, 6j.** (82 mg, 85%); mp 221 °C; δ_C 139.1 (C_q), 135.6 (C_q), 132.2 (C_q), 132.0 (C_q), 131.8 (C_q), 136.4 (C6), 74.4 (CH), 44.2 (6 CH_2), 39.2 (2 C_q), 37.0 (6 CH_2), 29.5 (6 CH) and 23.7, 20.8, 16.6, 16.0 (4 Me); δ_H 6.59 (H6), 2.27 (CH), 2.33, 2.23, 2.19, 2.19 (4 Me) and 1.5–2.0 (2 Ad) (Found: C, 89.2; H, 10.7. $C_{31}H_{44}$ requires C, 89.36; H, 10.64%). Refluxing **5j** (100 mg, mmol) with TTMSS (0.2 cm^3, mmol) in dichloromethane (10 cm^3) for 35 h (almost complete decolouration) gave a non-polar fraction (eluted from alumina with light petroleum, 95 mg) containing **6j**, **7j**, a chlorine-containing compound and an unidentified hydrocarbon in a GC ratio of approximately 1:0.52:0.35:0.08, together with silicon-containing impurities. Crystallization from pentane gave a silicon-free sample (45 mg; **6j**:**7j** = *ca*. 1.3) the ^{13}C NMR spectrum of which included all signals associated with **6j**, peaks at 60.6 (CH), 39.3 (CH_2), 37.1 (C_q), 36.7 (CH_2) and 29.4 (CH) ppm corresponding to **7j**, and several smaller unattributed signals. The aromatic and methyl carbon signals for **7j** were located from the spectrum of a mixture of **6j** and **7j** obtained by treating **6j** in a sealed tube at 310 °C for 14 h, followed by chromatography on alumina: 137.6 (C_q), 134.0 (C_q), 133.7 (C_q), 131.1 (C_q), 130.6 (C_q), 129.6 (CH), 21.4 (Me), 17.6 (Me), 17.3 (Me) and 16.1 (Me); δ_H 6.98 (H6), 2.57 (CH), 2.29, 2.24, 2.21, 2.21 (4 Me) and 1.5–2.0 (2 Ad). GC–MS(ITD) investigation gave virtually the same spectrum for **6j** and **7j**; *m*/*z* (ITD) 416, 415, 282, 281, 280, 279, 223, 147, 136, 135 (100%), 107, 93, 79. The chlorine-containing compound had: *m*/*z* 453, 452, 451 (100%), 450, 449, 416, 318, 317, 281, 223, 209, 207, 136, 135, 79 and the unidentified hydrocarbon: *m*/*z* 417, 416, 415 (100%), 393, 355, 341, 281, 279, 223, 135, 91, 79.

Determination of *anti*:*syn* ratio for reduction of *anti*-[2-methyl-5-(*tert*-butyl)phenyl]di(1-adamantyl)methanol, 5d. *anti*-[2-Methyl-5-(*tert*-butyl)phenyl]di(1-adamantyl)methanol, **5d** (10 mg, 0.022 mmol) was dissolved in dichloromethane (2.5 cm^3). With magnetic stirring hydrosilane (0.075–0.15 cm^3, 0.5 mmol) or sodium borohydride (20 mg, 0.53 mmol) was added at room temp., followed by TFA (0.25 cm^3). After 24 h (hydrosilanes, unless stated otherwise) or 1 h ($NaBH_4$) the mixture was treated as above. The residue (8–10 mg) was taken up in a mixture of $CDCl_3$ (0.5 cm^3) and C_6D_6 (0.1 cm^3). TTMSS and TPS required 6 and 15 d, respectively, for complete reaction. No hydrocarbon products were obtained with TIPS after 30 d. The *anti*:*syn* ratios (**6d**:**7d**) were determined from the ^1H (Bu^t and Me signals) and the ^{13}C (Ad α-CH_2 and β-CH signals) NMR spectra (Table 1).

Sodium borohydride reduction of *anti*-(2-ethylphenyl)di-(1-adamantyl)methanol, 8a. To the alcohol (100 mg, 0.24 mmol) and sodium borohydride (200 mg, 2.6 mmol) magnetically stirred in dichloromethane (10 cm^3) at room temp. was added rapidly TFA (0.6 cm^3). The flask was stoppered and the contents shaken and stirred until the initial deep red colouration was discharged (*ca*. 5 min). Stopping the reaction at this point gave a mixture consisting of the known *syn* hydrocarbon, **10a**,[17] trifluoroacetate, **11**,[17] and a new hydrocarbon in a ratio of approximately 1.6:1.1:1 (as estimated from the ^1H NMR signals of the benzylic protons and the ^{13}C NMR signals of the aromatic carbons). When the reaction was allowed to continue for a further 72 h before quenching, chromatography on alumina in light petroleum gave a 73:27 mixture of the two hydrocarbons (97 mg, 98%), the major component being **10a**, the other being identified as the *anti* isomer, **9a**, on the basis of its NMR and MS (ITD) spectra.

***anti*-(2-Ethylphenyl)di(1-adamantyl)methane, 9a.** δ_C 141.3 (C1), 142.5 (C2), 129.1 (C3), 125.8 (C4), 124.3 (C5), 137.3 (C6), 75.0 (CH), 44.2 (6 CH_2), 39.0 (2 C_q), 37.0 (6 CH_2), 29.4 (6 CH_2), 28.9 (CH_2) and 15.7 (CH_3); δ_H 7.28 (m, 1H), 7.16 (m, 1H), 6.99 (m, 1H), 6.90 (m, 1H), 2.83 (q, *J* 7.4, 2H), 1.5–2.0 (2 Ad) and 1.33 (tr, *J* 7.4, 3H); *m*/*z* (ITD) 388, 281, 252, 136, 135 (100%), 107, 93, 79.

Sodium borohydride reduction of *anti*-(2,5-diisopropylphenyl)-di(1-adamantyl)methanol, 8b. By the same procedure as for **8a**, the reaction being quenched after 10 min, was obtained a mixture of *syn* hydrocarbon, **10b**,[17] and styrene, **12**[17] in a ratio

of about 1:0.6. Very small signals in the ^{13}C NMR spectrum (20 000 scans) at 44.2, 123.8, 126.7, 136.3, 140.6 and 144.9 ppm, possibly corresponding to the *anti* hydrocarbon, **9b**, indicate that this isomer is formed to the extent of less than 2%, if at all.

X-Ray crystallography

Crystal data for *anti*-(2-methyl-4-fluorophenyl)di(1-adamantyl)methane, 6g. $C_{28}H_{37}F$, $M = 392.6$. Monoclinic, $a = 12.206(2)$, $b = 11.440(3)$, $c = 16.340(4)$ Å, $\beta = 108.21(8)°$, $V = 2167(1)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\ 69$ Å), space group $P2_1/a$, $Z = 4$, $D_c = 1.20$ g cm^{-3}. Colourless prismatic crystals, μ(Mo-Kα) = 0.68 cm^{-1}.

Data collection and processing. Enraf-Nonius MACH3 diffractometer, $\omega/2\theta$ mode with ω scan width = 0.8 + 0.345 tan θ, graphite-monochromated Mo-Kα radiation. 11% decay for two standard reflections. 4232 reflections measured ($1 \leqslant \theta \leqslant 25°$), 3818 unique (merging $R = 0.046$), giving 2103 with $I > 3\sigma(I)$.

Structure analysis and refinement. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic; hydrogens located from Fourier difference map with one, overall, refined isotropic thermal parameter (264 refinable parameters). No absorption correction. Final R and R_w (unit weights) values are 0.045 and 0.044. Program used is the PC version of CRYSTALS[25] for refinements and CAMERON[26] for views.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/97.

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