1,4-Hydride shifts in *ortho*-alkyl-substituted di(1-adamantyl)benzyl cations: an NMR spectroscopic and X-ray crystallographic study

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When carbocations are formed from *ortho*-alkyl-substituted phenyldi(1-adamantyl)-methanols in the *anti* conformation, the alkyl group being isopropyl or ethyl, rapid 1,4-hydride transfer from the alkyl group to the charged carbon occurs, giving either styrene (*o*-isopropyl) or secondary (*o*-ethyl) derivatives. ^{13}C and ^{1}H NMR spectroscopy and, in one case, single crystal X-ray crystallography show that all products are the *syn* rotamers, with the benzylic hydrogen of the diadamantylmethyl group oriented towards the *ortho* substituent. Even in the presence of triethylsilane no *anti* isomer is formed; instead, the rearranged carbocation is wholly or partially reduced by hydride transfer from the silane.

Introduction

In previous work we have generated extremely stable benzylic cations, with unusually high ^{13}C NMR shifts for the charged carbon, by reacting aryldi(1-adamantyl)methanols in a superacidic medium [1] or, more simply, with trifluoroacetic acid (TFA) in dichloromethane or chloroform.[2] In the latter case, subsequent reaction of the carbocation with an organosilane,[3] usually triethylsilane (TES), leads to the corresponding methanes. This procedure is easier to apply and generally gives better yields than the alternative which consists of first converting the alcohol to the bromide and then reducing this by tributyltin hydride in a radical process.[4] In one notable case, the reduction of *anti*-*o*-tolyldiadamantylmethanol, **1c**, these procedures give the opposite stereochemical result, the cation and radical reactions giving the isomeric *anti* and *syn* methanes, respectively.†[,2,4]

The very high ^{13}C NMR shift of the charged carbon in the carbocations is being attributed to virtually complete loss of resonance interaction with the neighbouring aryl group, we were interested in generating cations with larger *ortho* substituents to see whether it was possible to accentuate this phenomenon. We wish to report now results of attempts to replace the *o*-methyl group with other alkyl groups. The corresponding carbocations have only a brief existence, in contrast to the long-lived *o*-tolyldiadamantylmethyl cations, and intramolecular 1,4-hydride transfer leads to products in which the *ortho*-alkyl has been transformed.

Results and discussion

Alcohol synthesis

The *o*-ethyl and *o*-isopropyl derivatives of phenyldi(1-adamantyl)methanol, **1a** and **1b**, respectively, were prepared by reaction of the appropriate alkylphenyl lithium compounds with di(1-adamantyl) ketone. For the sake of convenience 1,4-di(isopropyl)benzene was used as starting material for the isopropyl derivative, which, therefore, contains an easily identifiable second isopropyl group *meta* to the diadamantylmethyl moiety. This also facilitates the interpretation of the NMR spectra.

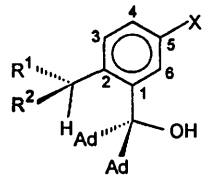
The NMR spectra of the alcohols isolated indicate that in both cases the major product is the *anti* isomer. In particular, the signal for the *ortho* proton, at 7.88 and 7.99 ppm in **1a** and **1b**, respectively, is to be compared with the values of 7.50 and 8.03 ppm for the same proton in *syn* and *anti*-*o*-tolyldi(1-adamantyl)methanol, respectively. Analysis of the aromatic carbon signals in the ^{13}C NMR spectra leads to the same conclusion. Taking the spectra of the *anti*- and *syn*-*o*-tolyldiadamantylmethanols as starting points and allowing for the different substituent effects, assumed to be additive,[5,6] of methyl, ethyl and isopropyl groups (taken directly from data tabulated in the literature [6]), we can calculate the shifts for the aromatic carbons in alcohols **1a** and **1b**. The calculated values are matched as well as possible with those observed, and the root mean square (rms) value is taken as a criterion of goodness of fit. If it is assumed that **1a** and **1b** are the *anti* rotamers then the rms values are 1.1 and 0.8 ppm, respectively, whereas for the *syn* isomers they are substantially worse, 2.1 and 1.4 ppm. The obvious conclusion, that the isolated products are the *anti* isomers, is in agreement with previous work on **1c**[4] and substituted *o*-tolyldi(*tert*-butyl)methanols,[7] where the *anti* isomer constitutes about 90% of the crude alcohol, despite the fact that the *syn* rotamer is some 6–7 kcal mol^{-1} (1 cal = 4.184 J) more stable than the *anti*.

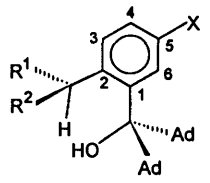
The conversion of **1c** to the *syn* isomer by rotation about the sp^2–sp^3 bond is a remarkably slow process.[8] Treatment of **1a** and **1b** for several hours in toluene at 240 °C gave, however, the corresponding *syn* alcohols, **2a** and **2b**, in good yield. These were readily distinguished from the previously isolated alcohols by their NMR spectra. The *ortho* hydrogen now has a shift of 7.37 and 7.51 ppm in **2a** and **2b**, respectively, comparable to the value of 7.50 ppm for **2c**, while the aromatic ^{13}C shifts calculated for the *syn* isomers by application of the additivity principle agree reasonably well with the experimental data, the rms values being 1.5 and 0.4 ppm for **2a** and **2b**, respectively.

It should also be mentioned that the IR spectra support these assignments, the *anti* isomers being associated with two OH stretching frequencies whereas there is only one for the *syn* isomers.[7]

For the sake of clarity, the results concerning the reactions of the *anti* alcohols, **1a** and **1b**, will be presented as though the geometry of the products were self-evident; this is only established by the NMR analysis related in a following section.

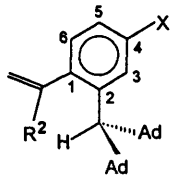
† *syn* and *anti* refer to the orientation of the least bulky substituent (H or OH) of the diadamantylmethyl group: *syn* when this is oriented towards the *ortho* substituent and *anti* when it is oriented away from this substituent.

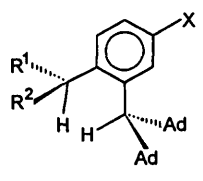




1a–c **2a–c**

a: R^1 = Me; R^2 = Me; X = Pr^i
b: R^1 = Me; R^2 = H; X = H
c: R^1 = R^2 = X = H

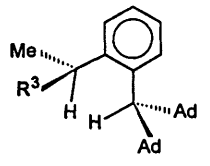


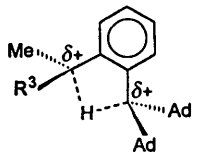


3a–b **4a–b**

a: R^2 = Me; X = Pr^i
b: R^2 = H; X = H

a: R^1 = Me; R^2 = Me; X = Pr^i
b: R^1 = Me; R^2 = H; X = H





5a–c **6**

a: R^3 = CH_3COO
b: R^3 = CF_3COO
c: R^3 = OH

Acid-catalysed dehydration of *anti*-2,5-di(isopropyl)phenyldi(1-adamantyl)methanol, 1a

When TFA is added to a solution of **1a** in chloroform or dichloromethane at room temperature there is a short-lived red colouration (λ_{max} about 360 nm), probably due to the transient formation of the corresponding carbocation. After a few minutes the reaction mixture is colourless and the reaction is complete. The sole product is *syn*-α-methyl-4-isopropyl-2-[di(1-adamantyl)methyl]styrene, **3a**. Reduction of this styrene by palladium/charcoal-catalysed hydrogenation gives the corresponding di(isopropyl) derivative, *syn*-2,5-di(isopropyl)phenyldi(1-adamantyl)methane, **4a**. When the reaction of alcohol **1a** is run in the presence of a large excess of TES **4a** is obtained as the sole product.

Acid-catalysed reactions of *anti*-2-ethylphenyldi(1-adamantyl)-methanol, 1b

Acetic acid/sulfuric acid. When alcohol **1b** is treated with acetic acid in the presence of a small amount of sulfuric acid as catalyst a secondary acetate, **5a**, is obtained. Refluxing this in toluene with toluene-*p*-sulfonic acid for a short time provides *syn*-2-[di(1-adamantyl)methyl]styrene, **3b**, catalytic hydrogenation of which gives *syn*-2-ethylphenyldi(1-adamantyl)methane, **4b**.

Trifluoroacetic acid. The product of the reaction of **1b** with TFA in dichloromethane or chloroform is the corresponding trifluoroacetate, **5b**. Again, a short-lived red colouration is observed. An attempt to purify this material by alumina chromatography led to the alcohol, **5c**. When alcohol **1b** is treated with TFA in the presence of a large excess of TES it gives an approximately 5:3 mixture of **5b** and **4b**, the former being isolated as **5c** by chromatography.

^{13}C and ^1H NMR analysis of reaction products

In previous work on *o*-tolyldi(1-adamantyl)methane rotamers, it was possible to isolate both the *syn* and *anti* isomers, the former by reduction of the corresponding bromomethane and the latter by TES reduction of the carbocation generated from the *anti* alcohol, **1c**, by reaction with TFA.[2] The *anti* isomer is converted to the more stable, *syn* isomer by a very slow rotation about the appropriate sp^2–sp^3 bond.[2] The two isomers are readily distinguished by NMR spectroscopy.[2,4] Whereas in the *anti* isomer the methyl group and the benzylic proton NMR signals are at 2.53 and 2.31 ppm, respectively, they are almost exactly reversed, at 2.32 and 2.49 ppm, respectively, in the *syn* isomer. 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.

The fact that the *ortho*-methyl group has been replaced by ethyl or isopropyl and the lack of appropriate reference structures make it difficult to use the alkyl group proton or carbon shifts to determine the geometry of the various products obtained from **1a** and **1b**, but inspection of the signals associated with the benzylic CH of the diadamantylmethyl group, present in all the products, reveals a remarkably consistent pattern. The ^1H NMR shift of the benzylic proton is at 2.61 (**3a**), 2.59 (**3b**), 2.60 (**4a**), 2.55 (**4b**), 2.53 (**5a**), 2.47 (**5b**) and 2.55 ppm (**5c**), while the corresponding carbon NMR shifts are: 60.6, 60.5, 59.6, 59.7, 59.7, 60.3 and 59.5 ppm. The similarity of these values and those for the benzyl group in *syn*-*o*-tolyldiadamantylmethane indicates very clearly that all the products obtained in the acid-catalysed reactions of **1a** and **1b**, as well as in the subsequent transformations, have the CH hydrogen of the di(1-adamantyl)methyl group oriented towards the *ortho* substituent.[2,4]

As in the *anti* and *syn* alcohols, the shifts of the *ortho* protons in the corresponding methanes are indicative of the rotamer type; the *ortho* proton signal appears at 7.32 and 6.91 ppm in *syn*- and *anti*-*o*-tolyldiadamantylmethane, respectively,[4,9] while the shifts are 7.15 and 7.31 ppm for **4a** and **4b**, respectively. Whereas the first value lies, unfortunately, midway between the two previous values, that for **4b** is clearly in favour of its being the *syn* rotamer. The NMR shift of the corresponding carbon is a rather better indicator of the geometry; this has values of 130.2 and 137.5 ppm in the *syn* and *anti* rotamers, respectively.[4,9] Inspection of the spectra of the various reaction products reveals no CH carbon shift close to the latter value, except in the styrene **3b**, where the signal at 137.9 ppm is attributable to the olefinic CH (at 135.8 ppm in styrene itself[6]). On the other hand, all the spectra include one CH signal close to 130 ppm (lowest 128.5 in **4a**; highest 130.8 ppm in **5a** and **5b**).

Using again the additivity principle, taking the carbon NMR spectrum of *syn*-*o*-tolyldiadamantylmethane as our starting point and allowing for the different substituent effects of methyl, ethyl, isopropyl, vinyl and methylvinyl groups,[6] we can calculate the shifts for the aromatic carbons in the styrenes **3a** and **3b**, and in the hydrogenation products **4a** and **4b**. Overall, the agreement between the calculated and experimental values is, with one exception, remarkably good. The rms values are 3.2 and 1.3 ppm for **3a** and **3b**, and 1.3 and 0.8 ppm for **4a** and **4b**, the styrenes being predicted less accurately than the hydrogenation products and the isopropyl derivatives less well than the ethyl derivatives. In the styrenes, the greatest errors are associated with the adjacent substituted carbons, likely to be the most perturbed by steric strain and for which the chemical shifts are all more than calculated. This effect is much greater in **3a** (5.3 and 5.3 ppm) than in **3b** (2.1 and 2.3 ppm). In **3a** even the neighbouring carbon atoms are significantly further downfield

Table 1 Comparison of X-ray crystallographic data and values calculated by molecular mechanics for *syn*-2-ethylphenyldi(1-adamantyl)methane, **4b**

	X-Ray	MM2 (85)	MM3 (89)
Bond lengths/Å			
C(1)–C(10)	1.536(5)	1.535	1.531
C(2)–C(20)	1.520(6)	1.519	1.517
C(10)–C(101)	1.590(5)	1.578	1.589
C(10)–C(201)	1.598(5)	1.583	1.594
C_{ar}–C_{ar} (mean)	1.384	1.400	1.399
Bond angles (°)			
C(2)–C(1)–C(10)	122.9(3)	123.9	122.3
C(6)–C(1)–C(10)	119.9(3)	118.5	119.8
C(1)–C(2)–C(20)	124.4(4)	124.9	125.2
C(3)–C(2)–C(20)	116.0(4)	115.8	115.5
C(1)–C(10)–C(101)	110.0(3)	111.6	110.0
C(1)–C(10)–C(201)	113.3(3)	112.9	112.0
C(101)–C(10)–C(201)	120.3(3)	122.8	121.3
Torsion angles (°)			
C(1)–C(2)–C(20)–C(21)	96	95	90
C(2)–C(1)–C(10)–C(101)	100	103	106
C(2)–C(1)–C(10)–C(201)	−122	−114	−116
C(2)–C(1)–C(10)–H	−11	−6	−5
C(1)–C(10)–C(101)–C(102)	−177	−172	−175
C(1)–C(10)–C(101)–C(108)	58	63	61
C(1)–C(10)–C(101)–C(109)	−60	−55	−58
C(1)–C(10)–C(201)–C(202)	145	140	146
C(1)–C(10)–C(201)–C(208)	30	24	31
C(1)–C(10)–C(201)–C(209)	−92	−97	−91

than expected (1.3 and 1.8 ppm). That the errors are much greater in the styrenes than in the hydrogenation products **4a** and **4b** may be related to the coplanarity (or lack) of the olefinic double bond and the aryl system.

X-Ray crystallographic characterization of *syn*-2-ethylphenyldi(1-adamantyl)methane, 4b

A first attempt to determine the structure of the trifluoroacetate, **5b**, by X-ray diffraction was only partially successful. The crystals were of poor quality and the diffraction weak. Though it was possible to establish that the two adamantyl groups were remote from the *ortho* substituent, indicating the *syn* rotamer, the trifluoroacetate chain was badly defined and the structure failed to converge to an acceptable *R* value.[10] Better results were obtained with **4b** for which a single-crystal X-ray diffraction study confirmed that it was the *syn* isomer and provided detailed information concerning its geometry.

Recent work on *anti* and *syn*-*m*-(*tert*-butyl)phenyldi(1-adamantyl)methanols[11] has shown the C–OH bond to be virtually in the plane of the benzene ring, in contrast to previous work on analogous aryldi(*tert*-butyl)methanols,[12] where the angle was about 12°. In this respect the new structure is closer to the latter, the angle between the benzylic CH bond and the benzene ring being about 11°. Other features are typical of this sort of structure: long C–Ad bonds; high Ad–C–Ad bond angle; the adamantyl group furthest from the benzene plane (in terms of its torsion angle) nicely staggered and the other at 30° to the normal staggered position; in-plane deformations of the benzene ring and the bond angles to the substituents. The distance between the secondary carbon of the ethyl group and the benzylic hydrogen is notably short, 2.59 Å. On the whole there is good agreement with the results of MM2[13] or MM3[14] calculations. Details are listed in Table 1 and a CAMERON diagram is given in Fig. 1.

Mechanism of the reactions of *o*-alkylphenyldi(1-adamantyl)-methanols

Though brief, the red colouration observed when alcohols **1a** and **1b** are treated with TFA in chlorohydrocarbon solvents

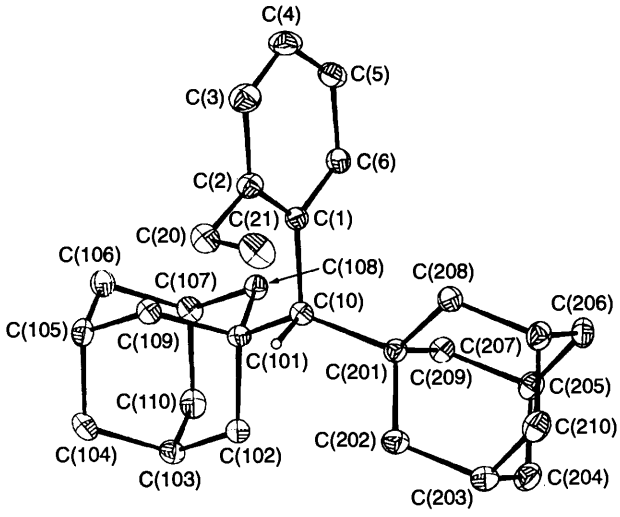


Fig. 1 CAMERON diagram of *syn*-2-ethylphenyldi(1-adamantyl)-methane, **4b**

indicates that the first step of the reaction is, not surprisingly, the formation of a carbocation. However, unlike that derived from the previously studied *o*-tolyldiadamantylmethanol, **1c**, these carbocations are short-lived and are not reduced by hydrosilanes to give the corresponding methane with the *anti* conformation. Instead, various products with the *syn* conformation are obtained, these products involving a transformation of the neighbouring *ortho* substituent. It is, therefore, clear that these reactions can be best understood in terms of 1,4-hydride transfer[15] from the alkyl substituent to the charged carbon of the diadamantylbenzyl cation, as depicted in **6**.

Subsequently, either nucleophilic attack or proton elimination completes the reaction. In the case of the isopropyl substituent, nucleophilic attack would require the formation of a highly unstable tertiary trifluoroacetate, but for *ortho* ethyl both the secondary trifluoroacetate and acetate are stable. Nevertheless, elimination from the acetate is readily accomplished, leading to the styrene derivative analogous to the product obtained directly from **1a**. On slightly moist alumina the trifluoroacetate is hydrolysed to an alcohol, **5c**, which is isomeric with the starting alcohol, **1b**. The MM2-calculated[13] steric energies of **1b** and **5c** are 70.9 and 50.5 kcal mol^{-1}, respectively. The MM3[14] force field gives virtually the same difference, the corresponding values being 86.6 and 66.6 kcal mol^{-1}.

Even in the presence of excess TES no intermolecular reaction with the initial carbocation is observed. Instead, the 1,4-hydride shifted carbocation reacts wholly or partially with the silane to give hydrocarbons **4a** and **4b** with the *syn* conformation. In the case of **1b** nucleophilic attack by trifluoroacetate ion competes with reduction of the carbocation by the hydrosilane.

An idea of the geometry of the intermediate carbocation and the distance between the two carbon centres can be obtained from molecular mechanics calculations (MM2)[13] on **4a**. The CH hydrogen of the isopropyl group is 2.75 Å from the carbon of the diadamantylmethyl group, but this distance is no doubt slightly exaggerated by the repulsion between the two groups. An *ad hoc* force field for the carbocation, based on Müller's UNICAT4 parametrization,[16] suggests a value of *ca.* 2.56 Å. Both these values are of the same order of magnitude as distances calculated for hydride transfers in other systems.[17] While the distance depends little on the angle between the plane of the cation and that of the benzene ring, it is obvious that if the two are orthogonal then the neighbouring alkyl hydrogen (which is close to the aryl plane) will be ideally positioned with respect to the empty orbital of the cation for transfer to occur.

There are surprisingly few reports of similar hydride transfers in aromatic systems, but 1,5-hydride shifts have been reported in 1,8-disubstituted naphthalenes[18] and in an *ortho*-substituted triphenylmethyl chloride.[19] Why an analogous reaction does not occur when the *ortho* substituent is methyl, *i.e.* in **1c**, is clearly related to the fact that it is much more difficult to form a primary carbocation than a secondary or tertiary. In this case intermolecular hydride transfer from the silane prevails, giving the opposite geometry. These results incidentally suggest an explanation for the difference between the cation and radical reactions mentioned above.[2,4] Formation of a primary radical by hydrogen atom transfer from a methyl group to a neighbouring diadamantylbenzyl radical must be much easier than the corresponding cation reaction; consequently, in the radical reaction the hydrogen of the diadamantylmethyl group is oriented towards the group which delivered it, the *ortho* $CH_2^{\bullet}$ radical having been subsequently reduced by the organotin reagent, in the same way as the 1,4-shifted carbocations react with TES.

Conclusion

The acid-catalysed reactions of *ortho*-alkyl-substituted phenyldi(1-adamantyl)methanols, where the alkyl group is other than methyl, lead to products resulting from a fast 1,4-hydride shift from the alkyl group to the charged carbon of the diadamantylbenzyl cation. Though we have only examined two cases, those where the alkyl group is ethyl or isopropyl, it is clear that other alkyl derivatives will behave in the same way. It is interesting to speculate as to what would happen if the alkyl group were di(1-adamantyl)methyl; in this case the hydride transfer would be degenerate and we would have a stable carbocation (since elimination and nucleophilic attack are prohibited) with a hydrogen oscillating between, or shared between, two carbon centres. More generally, the present and previous results indicate that a hydrogen atom 2.5–2.7 Å from a positively charged carbon may be transferred to that carbon, provided no other reaction is substantially easier, such as elimination or nucleophilic attack. This suggests that charge could be transferred from one end of a suitably constructed chain to the other by a series of hydride shifts.

Experimental

General methods

NMR measurements were made on a Bruker AS 200 FT instrument operating at 200 MHz (proton) or 50 MHz (carbon). All measurements were made in $CDCl_3$ and are referenced to internal $SiMe_4$ (δ_H = 0.00 ppm for ^1H) or to the solvent (δ_C = 77.0 ppm for ^{13}C). *J* values are given in Hz. Melting points were determined in capillary glass tubes on a Mettler FP5 instrument with a heating rate of 3 °C min^{-1}. IR spectra were recorded on a Perkin-Elmer 781 instrument. Gas chromatography was performed on a packed SE30 column (10%, 30 cm). Preparative chromatography was carried out on standardized (Brockmann activity II–III) alumina (Merck).

***anti*-2,5-Di(isopropyl)phenyldi(1-adamantyl)methanol, 1a.** Reaction of 2,5-di(isopropyl)bromobenzene (1.25 g, 5.2 mmol) in diethyl ether (25 cm^3) with *tert*-butyllithium (1.6 M solution in pentanes, 3 cm^3, 4.8 mmol) at room temp. under argon, followed by addition of di(1-adamantyl) ketone (0.5 g, 1.7 mmol) in diethyl ether (30 cm^3) and stirring overnight before work-up (washing with water and dilute acid, drying over $MgSO_4$, evaporation of solvent) gave the crude product which was treated with lithium aluminium hydride in diethyl ether to reduce residual ketone, then purified by chromatography on alumina in light petroleum–diethyl ether mixtures (0.185 g, 24%): mp 230–231 °C (acetone); δ_C 24.1 (2 CH_3), 26.3 (2 CH_3), 29.5 (6 CH), 31.8 (CH), 34.0 (CH), 37.0 (6 CH_2), 39.7 (6 CH_2), 45.7 (2 quaternary C, C_q), 88.3 (C–OH), 123.7 (CH), 127.5 (CH), 128.9 (CH), 142.8 (C_q), 144.2 (C_q) and 144.9 (C_q); δ_H 1.25 (d, *J* 6.9, 6 H), 1.36 (d, *J* 6.5, 6 H), 1.61 (br s, 12 H), 1.8–2.1 (br m, 18 H), 2.09 (s, 1 H), 2.87 (sept, *J* 6.9, 1 H), 3.56 (sept, *J* 6.5, 1 H), 7.09 (br d, *J ca.* 1 and 7.9, 1 H), 7.31 (d, *J* 7.9, 1 H) and 7.88 (d, *J ca.* 1, 1 H); ν_{max}/cm^{-1} (CCl_4) 3606 and 3640 (Found: C, 86.0; H, 10.5. $C_{33}H_{48}O$ requires C, 86.03; H, 10.50%).

***syn*-2,5-Di(isopropyl)phenyldi(1-adamantyl)methanol, 2a.** A solution of **1a** (64 mg, 0.14 mmol) in toluene (0.5 cm^3) was sealed under vacuum in a thick-walled glass ampoule and heated for 5 h at 240 °C. After cooling, the ampoule was carefully opened and the solvent evaporated under reduced pressure. Alumina chromatography of the residue gave **2a** (61 mg, 95%): mp 207 °C; δ_C 24.0 (2 CH_3), 25.5 (2 CH_3), 28.9 (CH), 29.4 (6 CH), 33.5 (CH), 37.0 (6 CH_2), 39.6 (6 CH_2), 46.5 (2 C_q), 88.8 (C–OH), 124.1 (CH), 127.1 (CH), 128.0 (CH), 139.4 (C_q), 141.4 (C_q) and 147.6 (C_q); δ_H 1.18 (d, *J* 6.9, 6 H), 1.26 (d, *J* 6.9, 6 H), 1.6 (br s, 12 H), 1.7–2.0 (br m, 18 H), 2.04 (s, 1 H), 2.87 (sept, 6.9 Hz, 1 H), 4.47 (sept, 6.9 Hz, 1 H), 7.03 (dd, *J* 1.5 and 8.1, 1 H), 7.27 (d, *J* 8.1, 1 H) and 7.37 (d, *J* 1.5, 1 H); ν_{max}/cm^{-1} (CCl_4) 3629 (Found: C, 85.8; H, 10.6. $C_{33}H_{48}O$ requires C, 86.03; H, 10.50%).

***anti*-2-Ethylphenyldi(1-adamantyl)methanol, 1b.** Reaction of a solution of 2-ethylbromobenzene (1.2 g, 6.5 mmol) in diethyl ether with *n*-butyllithium (1.6 M solution in hexanes, 3 cm^3, 4.8 mmol) at room temp. under argon gave 2-ethylphenyllithium which was then treated with di(1-adamantyl) ketone (0.75 g, 2.5 mmol) and stirred overnight. The reaction mixture was worked up as for **1a** to give alcohol **1b** (0.69 g, 68%): mp 130–131 °C; δ_C 16.3 (CH_3), 29.5 (6 CH), 30.6 (CH_2), 36.9 (6 CH_2), 38.7 (6 CH_2), 45.7 (2 C_q), 87.6 (C–OH), 124.8 (CH), 125.9 (CH), 130.0 (CH), 130.4 (CH), 141.8 (C_q) and 143.5 (C_q); δ_H 1.36 (tr, *J* 7.3, 3 H), 1.5–2.0 (br m, 30 H), 2.11 (s, 1 H), 3.01 (q, *J* 7.3, 2 H), 7.1–7.4 (br m, 3 H) and 7.99 (dd, *J* 1.5 and 7.8, 1 H); ν_{max}/cm^{-1} (CCl_4) 3608 and 3643 (Found: C, 86.3; H, 10.1. $C_{29}H_{40}O$ requires C, 86.08; H, 9.96%).

***syn*-2-Ethylphenyldi(1-adamantyl)methanol, 2b.** As for **2a**, **1b** (60 mg, 0.15 mmol) was converted to **2b** (53 mg, 88%): mp 190 °C; δ_C 18.3 (CH_3), 29.3 (6 CH), 31.0 (CH_2), 37.0 (6 CH_2), 39.4 (6 CH_2), 46.2 (2 C_q), 87.9 (C–OH), 122.3 (CH), 125.7 (CH), 130.1 (CH), 132.5 (CH), 140.6 (C_q) and 145.3 (C_q); δ_H 1.25 (tr, *J* 7.4, 3 H), 1.59 (br s, 12 H), 1.8–2.1 (br m, 19 H), 3.02 (q, *J* 7.4, 2 H), 7.0–7.1 (br m, 3 H) and 7.51 (d, *J* 7.7, 1 H); ν_{max}/cm^{-1} (CCl_4) 3631 (Found: C, 86.3; H, 9.8. $C_{29}H_{40}O$ requires C, 86.08; H, 9.96%).

Acid-catalysed dehydration of *anti*-2,5-di(isopropyl)-phenyldi(1-adamantyl)methanol. Dropwise addition of TFA (0.5 cm^3) to a stirred solution of **1a** (0.30 g, 0.66 mmol) in dichloromethane (15 cm^3) at room temp. gave a short-lived red colouration (λ_{max} *ca.* 360 nm). After 10 min, the mixture was quenched with water, washed with dilute sodium hydrogen carbonate solution and the organic layer dried. Evaporation of the solvent and purification by chromatography on alumina in light petroleum gave *syn*-α-methyl-4-isopropyl-2-[di(1-adamantyl)methyl]styrene, **3a** (0.285 g, 98%): mp 133 °C; δ_C 24.0 (2 CH_3), 26.6 (CH_3), 29.3 (6 CH), 33.7 (CH), 37.1 (6 CH_2), 39.1 (2 C_q), 43.2 (6 CH_2), 60.6 (CH), 116.4 (CH_2), 122.8 (CH), 128.0 (CH), 129.2 (CH), 138.7 (C_q), 142.7 (C_q), 144.4 (C_q) and 146.5 (C_q); δ_H 1.28 (d, *J* 6.9, 6 H), 1.5–2.0 (br m, 30 H), 2.09 (s, 3 H), 2.61 (s, 1 H), 2.91 (sept, *J* 6.9, 1 H), 4.86 (d, *J* 1.5, 1 H), 5.22 (d, *J* 1.5, 1 H), 7.01 (s, 2 H) and 7.29 (s, 1 H) (Found: C, 89.6; H, 10.6. $C_{33}H_{46}$ requires C, 89.53; H, 10.47%).

Deoxygenation of *anti*-2,5-di(isopropyl)phenyldi(1-adamantyl)methanol by TFA/TES. To a stirred solution of **1a** (0.10 g, 0.22 mmol) and TES (0.2 cm^3, 1.25 mmol) in dichloromethane (5 cm^3) at room temp. was added TFA (0.3 cm^3). After 30 min, the mixture was worked up as usual to give *syn*-2,5-di(isopropyl)phenyldi(1-adamantyl)methane, **4a** (93 mg, 96%): mp 204–205 °C (hexane); δ_C 24.0 (2 CH_3), 24.7 (2 CH_3), 28.1 (CH), 29.3 (6 CH), 33.6 (CH), 37.1 (6 CH_2), 39.3 (2 C_q), 43.4 (6 CH_2), 59.6 (CH), 123.2 (CH), 125.0 (CH), 128.5 (CH), 138.6

(C_q), 142.7 (C_q) and 145.6 (C_q); δ_H 1.19 (d, *J* 6.7, 6 H), 1.25 (d, *J* 6.9, 6 H) 1.5–2.0 (br m, 30 H), 2.60 (s, 1 H), 2.86 (sept, *J* 6.9, 1 H), 3.37 (sept, *J* 6.7, 1 H), 7.02 (dd, *J* 1.5 and 8.1, 1 H), 7.15 (br s, 1 H) and 7.17 (d, *J ca.* 8 Hz, 1 H) (Found: C, 88.9; H, 11.0. $C_{33}H_{48}$ requires C, 89.12; H, 10.88%).

Reduction of *syn*-α-methyl-4-isopropyl-2-[di(1-adamantyl)-methyl]styrene. A stirred solution of **3a** (0.10 g, 0.23 mmol) in absolute ethanol (75 cm^3) in the presence of 10% Pd/C (0.1 g) was held under hydrogen at 3 bar (1 bar = 10^5 Pa) for 15 min. Filtration, extraction into light petroleum, washing with water, drying and evaporation of the solvent gave *syn*-2,5-di(isopropyl)phenyldi(1-adamantyl)methane, **4a**, (95 mg, 95%) identical with the above.

Reaction of *anti*-2-ethylphenyldi(1-adamantyl)methanol with acetic acid/H_2SO_4. To a stirred solution of **1b** (0.2 g, 0.5 mmol) in acetic acid (20 cm^3) at room temp. was added 95% sulfuric acid (0.1 cm^3). After 30 min, the mixture was quenched with water, the products extracted into diethyl ether, washed and dried. Evaporation of the solvent left a product consisting essentially of *syn*-2-(1′-acetoxyethyl)phenyldi(1-adamantyl)-methane, **5a**, which was purified by chromatography on alumina (0.176 g, 80%): mp 174 °C (hexane); δ_C 21.4 (CH_3), 21.5 (CH_3), 29.1 (3 CH), 29.2 (3 CH), 36.8 (6 CH_2), 39.1 (C_q), 39.2 (C_q), 42.8 (3 CH_2), 43.1 (3 CH_2), 59.7 (CH), 68.5 (CH) 125.4 (CH), 125.5 (CH), 126.5 (CH), 130.8 (CH), 139.6 (C_q), 140.2 (C_q) and 170.1 (CO); δ_H 1.5–2.0 (br m), 1.54 (d, *J* 6.5), 2.03 (s, 3 H), 2.53 (s, 1 H), 6.48 (q, *J* 6.5, 1 H), 7.20 (m, 2 H), 7.38 (m, 1 H) and 7.52 (m, 1 H); ν_{max}/cm^{-1} (KBr) 757, 765, 942, 1038, 1231, 1368, 1451, 1732, 2850 and 2900 (Found: C, 83.6; H, 9.6. $C_{31}H_{42}O_2$ requires C, 83.36; H, 9.48%).

Reaction of *anti*-2-ethylphenyldi(1-adamantyl)methanol with TFA. Treatment of **1b** (0.15 g, 0.62 mmol) with TFA (0.5 cm^3) in dichloromethane (10 cm^3) at room temp. gave a light red colouration (λ_{max} *ca.* 360 nm). After 10 min, the reaction was quenched with water and the mixture worked up as for **1a** to give *syn*-2-(1′-trifluoroacetoxyethyl)phenyldi(1-adamantyl)-methane, **5b** (0.171g, 92%): mp (decomp.) 161 °C (hexane); δ_C 21.6 (CH_3), 29.2 (6 CH), 36.80 (3 CH_2), 36.84 (3 CH_2), 39.3 (2 C_q), 43.0 (3 CH_2), 43.3 (3 CH_2), 60.3 (CH), 73.8 (CH), 114.6 (CF_3, $^1J_{C-F}$ 286.0), 125.9 (CH), 126.5 (CH), 126.6 (CH), 130.8 (CH), 138.1 (C_q), 139.9 (C_q) and 156.9 (CO, $^2J_{C-F}$ 41.9); δ_H 1.5–2.0 (br m), 1.69 (d, *J* 6.4), 2.47 (s, 1 H), 6.69 (q, *J* 6.4, 1 H), 7.31 (m, 2 H), 7.43 (m, 1 H) and 7.55 (m, 1 H); ν_{max}/cm^{-1} (KBr) 777, 1152, 1228, 1775, 2848 and 2902 (Found: C, 74.6; H, 8.1; F, 11.3. $C_{31}H_{39}O_2F_3$ requires C, 74.37; H, 7.85; F, 11.38%).

Attempted purification of the trifluoroacetate by chromatography on alumina gave the corresponding alcohol, **5c**: mp 227–228 °C; δ_C 24.7 (CH_3), 29.16 (3 CH), 29.24 (3 CH), 36.9 (6 CH_2), 39.15 (C_q), 39.25 (C_q), 43.0 (3 CH_2), 43.6 (3 CH_2), 59.5 (CH), 65.8 (CH-OH), 125.0 (CH), 125.3 (CH), 125.8 (CH), 130.4 (CH), 138.8 (C_q) and 145.3 (C_q); δ_H 1.50 (d, *J* 6.4, 3 H), 1.5–2.0 (br m, 31 H), 2.55 (s, 1 H), 5.39 (q, *J* 6.4, 1 H), 7.1–7.4 (m, 3 H) and 7.56 (dd, *J* 1.8 and 7.5, 1 H); ν_{max}/cm^{-1} (CCl_4) 3613 (Found: C, 85.7; H, 10.0. $C_{29}H_{40}O$ requires C, 86.08; H, 9.96%).

Reaction of *anti*-2-ethylphenyldi(1-adamantyl)methanol with TFA/TES. To a stirred solution of **1b** (88 mg, 0.22 mmol) and TES (0.2 cm^3, 1.25 mmol) in dichloromethane (5 cm^3) at room temp. was added TFA (0.3 cm^3). After 30 min, the mixture was worked up as usual. ^{13}C and ^1H NMR spectra of the crude material indicated an approximately 5:3 mixture of *syn*-2-(1′-trifluoroacetoxyethyl)phenyldi(1-adamantyl)methane, **5b**, and *syn*-2-ethylphenyldi(1-adamantyl)methane, **4b** (see below). Chromatographic separation on alumina gave **5c** (48 mg, 54%) and **4b** (31 mg, 36%).

***syn*-2-[Di(1-adamantyl)methyl]styrene, 3b.** Refluxing a solution of **5a** (0.35 g, 0.78 mmol) in toluene (35 cm^3) with *p*-toluenesulfonic acid (100 mg) for 2 h gave *syn*-2-[di(1-adamantyl)methyl]styrene (0.277 g, 91%): mp 166 °C (pentane); δ_C 29.2 (6 CH), 37.0 (6 CH_2), 39.7 (2 C_q), 43.1 (6 CH_2), 60.5 (CH), 115.7 (CH_2), 125.3 (CH), 125.6 (CH), 126.6 (CH), 130.2 (CH), 137.9 (CH), 139.8 (C_q) and 140.3 (C_q); δ_H 1.5–2.0 (br m, 30 H), 2.59 (s, 1 H), 5.25 (dd, *J* 1.7 and 10.9, 1 H), 5.47 (dd, *J* 1.7 and 17.2, 1 H), 7.1–7.3 (m, 3 H) and 7.3–7.5 (m, 2 H) (Found: C, 89.8; H, 10.0. $C_{29}H_{38}$ requires C, 90.09; H, 9.91%).

Reduction of *syn*-2-[di(1-adamantyl)methyl]styrene. Styrene **3b** (0.137 g, 0.35 mmol) in absolute ethanol (75 cm^3) in the presence of 10% Pd/C (0.1 g) was held under hydrogen at 3 bar for 15 min and the products worked up as for **1b** to give **4b** (0.115 g, 83%): mp 158 °C; δ_C 14.9 (CH_3), 26.2 (CH_2), 29.3 (6 CH), 37.0 (6 CH_2), 39.4 (2 C_q), 43.1 (6 CH_2), 59.7 (CH), 123.4 (CH), 125.0 (CH), 127.5 (CH), 130.4 (CH), 140.1 (C_q) and 143.2 (C_q); δ_H 1.25 (tr, *J* 7.5, 3 H), 1.5–2.0 (br m, 30 H), 2.55 (s, 1 H), 2.72 (q, *J* 7.5, 2 H), 7.05–7.2 (m, 3 H) and 7.31 (m, 1 H) (Found: C, 89.6; H, 10.7. $C_{29}H_{40}$ requires C, 89.63; H, 10.37%).

X-Ray crystallography

Crystal data for *syn*-2-ethylphenyldi(1-adamantyl)methane, 4b. $C_{29}H_{40}$, M = 388.6. Monoclinic, a = 10.894(1), b = 11.022(3), c = 18.783(3) Å, β = 101.15(1)°, V = 2213(6) $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/n$, Z = 4, D_c = 1.17 g cm^{-3}. Colourless prismatic crystals, μ(Mo-K) = 0.6 cm^{-1}.

Data collection and processing. Enraf-Nonius CAD4 diffractometer, $\omega/2\theta$ mode with ω scan width = 0.8 + 0.345 tan θ, graphite-monochromated Mo-Kα radiation. No decay for two standard reflections. 4342 reflections measured ($1 \leqslant \theta \leqslant 25°$), 3885 unique (merging R = 0.0273), giving 1696 with $I > 3\sigma(I)$.

Structure analysis and refinement. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic, and hydrogens in calculated positions with one, overall, refined isotropic thermal parameter (264 refinable parameters). Absorption correction applied (DIFABS).[20] Final R and R_w (unit weights) values are 0.047 and 0.046. Program used is the PC version of CRYSTALS[21] for refinements and CAMERON[22] 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*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/25.

Molecular mechanics calculations

Steric energies and geometries were calculated with Allinger's MM2(85)[13] or MM3(89)[14] force fields, using block matrix minimization. Parameters for carbocations were taken from Müller's UNICAT4 force-field[16] with the addition of certain *ad hoc* geometric and energy parameters required to handle aromatic systems. C_{ar}–C^+: K(S) = 7.4, R(0) = 1.44; C_{ar}–C_{ar}–C_{ar}–C^+ and H–C_{ar}–C_{ar}–C^+: $V2$ = 10.0, $V1$ = $V3$ = 0; C_{ar}–C^+–C–C: $V1$ = $V2$ = $V3$ = 0. C_{ar}–C_{ar}–C^+ and C_{ar}–C^+–C: KB = 0.5, θ(0) = 120°. The force-field ignores resonance stabilization of the carbocation by the aryl system. This can be simulated by the inclusion of a torsional parameter, $V2$ for C_{ar}–C_{ar}–C^+–C, which would put the carbocation in the same plane as the aryl group if there were no opposing steric effects. Varying this between 2.5 and 10 kcal mol^{-1} had a small effect upon the torsion angle between the aryl ring and the carbocation plane (84.7 and 82.1°, respectively, for *o*-Pr^i:) and even less on the relevant H to C^+ distance (2.568 and 2.558 Å).

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